



SATF 2018

Science and Applications of Thin Films, Conference & Exhibition

Proceeding Book

September 17 to 21, 2018

Grand Ontur Hotel

Cesme, Izmir, Turkey

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Preface

On behalf of the Conference Committee, I would like to warmly welcome to everyone participating to the “*Science and Applications of Thin Films, Conference & Exhibition (SATF 2018)*” being held in Grand Ontur Hotel, Cesme, Izmir, Turkey, from September 17 to 21, 2018.

The first series of the conference, SATF 2014, was held at the Altin Yunus Resort & Thermal Hotel, Cesme, Izmir, Turkey, from September 15 to 19, 2014 and the Second series of the conference, SATF 2016 was held in Ilica Hotel Spa & Wellness Thermal Resort, Cesme, Izmir, Turkey, from September 19 to 23, 2016. First two conferences hosted above 700 scientists, and the proceedings were published in Vacuum, Applied Surface Science and Thin Solid Films. The main objective of the SATF conferences is to provide a valuable international platform for individuals to present their research findings, display their work in progress and discuss conceptual advances in many different branches of thin films.

SATF 2018 will focus on various topics related to Thin Films and novel phenomena in Thin Film science and applications. The conference is intended to provide an opportunity to bring prominent scientists together from various countries, with a common objective to exchange information and ideas, to promote stimulus discussions and collaborations among participants and furthermore to foster young scientists. The selected Full-Text Manuscripts of SATF 2018 has evaluated by scientific committee and published in SATF 2018 Proceeding Book. This conference is supported by TUBİTAK 2223B program.

Additionally, Izmir hosts a large number of extremely important architectural and cultural sites. The town is nicknamed as the Pearl of the Aegean and Cesme in İzmir is surrounded by the Aegean Sea in three sides at the very western end of Urla Peninsula and is neighbor of the Sakiz (Chios) Island. My wish is that you will all join us for a symphony of outstanding science and take a little extra time to enjoy the unique beauty of Cesme and its surroundings.

Finally, we want to express our special gratitude to all the participants, and we would also like to thank our colleagues in the Conference Committee, whose commitment enabled us to achieve our goal. In addition, we appreciate our sponsors for their generous support. In the spirit and tradition of Turkish hospitality, we once more welcome you all to SATF 2018, I would like to wish you a nice and enjoyable stay in the Cesme, may you all return home feeling recharged and ready to continue the invaluable explorations.

Best regards,



Lutfi Ozyuzer
Chair

Scope of the SATF 2018 Conference & Exhibition

The SATF 2018 international conference will focus on various topics related to Thin Films and novel phenomena in Thin Film science and applications.

More specifically,

- Science of Thin Films and Quantum Effects
- Theory of Structure, Surface and Interface
- Thin Film Growth & Epitaxy
- Nanostructured Growth
- Optical, Optoelectronic and Dielectric Coatings
- Organic Thin Films
- Thin Films in Biology
- Superconducting Thin Films
- Thin Films in Photovoltaic Cells and Energy
- Metallurgical Coatings
- Applications of Electrochemical and Electroless Depositions
- Advances in Deposition Techniques
- Characterization and Instrumentation
- Large Scale Coating and Industry

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PROCEEDING PAPERS

Friction and wear properties of Nb-V-C-N coatings on AISI 4140 steel by thermo-reactive deposition

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Abstract

Thermo-reactive deposition (TRD) technique is an effective method for obtaining hard coatings that are resistant to wear on the surface of the steel. In this study, Nb-C-N, V-C-N, and Nb-V-C-N based hard coatings were applied on AISI 4140 steel and dry friction and wear properties were investigated. Cylindrical shaped AISI 4140 steel samples were first subjected to nitriding in order to have a nitrogen-rich surface. Subsequently, the TRD coating process was carried out at 1000 °C for 4 hours with pack cementation technique for all compositions. Ball on disc wear tests via alumina ball as a counterpart at atmospheric conditions was realized. From the test results, the friction coefficients were determined according to applied loads. The depths of the traces formed on the surface of the samples were measured by 2D profilometer and the wear rates were calculated. Wear traces were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

Keywords: Wear, Thermo-Reactive Deposition, Niobium Vanadium Carbonitride Coatings.

Introduction

Although many new materials have been developed, today's steel is still widely used in manufacturing many machine parts. Wear on parts made of steel causes a considerable amount of material loss and consequently a significant cost to manufacturers. The studies to prevent the causes of wear and other materials loss have been continuing for many years. Rather than being resistant to abrasion of an entire part, it is often preferred to obtain a wear-resistant layer on the surface of the workpiece for cost reasons. Methods such as physical vapor deposition, thermal spray coatings, chemical vapor deposition, electrolytic coatings, and thermo reactive deposition are now successfully used for coating material surfaces [1]–[5]. Thermo-reactive diffusion (TRD) method is used to obtain hard coating layers which contain carbide, nitride, carbo-nitride and boride phases of reactive transition metals on the surface of steel parts. The TRD method, which has the advantages of low cost, simple equipment and the physical and mechanical properties of the coated part according to other coating methods, has been used industrially for nearly 50 years. In this method, carbon, nitrogen or boron exist in the substrate material reacts with the transition elements such as vanadium, chromium, niobium, and titanium which are consist of the coating bath. In order to form a coating layer by this method, the substrate material selected must contain enough Carbon, boron or nitrogen. If a lower carbon material is used, it is necessary to make the surfaces rich by carbon, nitrogen or boron elements by applying surface modification processes such as carburization, nitriding, boronizing. The coating process can be realized by using molten salt, fluidized bed, and pack cementation media. In the pack cementation process, the

desired piece is applied by placing in a mixture of powdered bath components in steel or graphite crucibles. In this method, coating layers having a thickness of about 25 μm can be obtained between 850°C and 1150 °C, depending on the increasing time [6]–[10].

In the past, researchers have obtained coating layers containing carbide, nitride or boride phases on steel materials by TRD method and their microstructure, wear and corrosion properties have been investigated. Among the mentioned coatings, the carbide, nitride and boride forms of niobium and vanadium have attracted attention with the high hardness, wear and corrosion resistance they provide and the most studied ones have been studied. Recently, the examination of the properties of coating layers containing carbide forms of two different transition metals subject is interesting. However, in the literature, there is no study of coatings containing nitride forms of two transition elements [10] – [12].

In this study, coating layers containing carbide and nitride phases of niobium and vanadium were obtained by TRD method on AISI 4140 steel surface. The microstructure, dry friction, and wear properties of the coatings obtained were compared with those containing Nb-C-N and V-C-N.

Experimental

AISI 4140 steel substrate material is provided in the form of a rod of 20 mm diameter. The spectral analysis of the substrate is given in Table 1. The samples were first cut to a thickness of 5 mm in height, then gradually grounded to 1200 grid emery paper and cleaned with acetone for 5 minutes. After surface preparation, the samples were nitrated to obtain a nitrogen-rich surface. The active nitration time was 6 hours.

Table 1. The chemical composition of AISI 4140 steel that used in this study.

Element	C	Si	Mn	P	S	Cr	Mo
Mass Percentage (wt. %)	0.41	0.20	0.62	0.02	0.02	0.96	0.19

Nb-C-N, V-C-N and Nb-V-C-N coating processes of the samples after the pretreatment were carried out by the pack cementation process. The coating bath used in this process consists a mixture of ferrous niobium and ferrous vanadium, alumina, ammonium chloride and naphthalene powders. Ferrous-alloys powders provide the necessary niobium and vanadium for the desired coating layer. Commercial ferrous alloys were obtained from AVEKS Company and milled to size of $-45 \mu\text{m}$ by using ring mill. Other bath components; as the alumina filler, ammonium chloride activator and naphthalene were added to remove oxygen contained in the crucible. The coating was carried out at 1000 °C for 4 hours using stainless steel crucibles. Compositions of the coating bath of the produced samples are given in Table 2. The coated samples were taken from the bath after the process, and cleaned with boiling water and the hot air was dried.

Table 2. The chemical composition of coating baths that used in this study

	Ferrous Niobium (wt. %)	Ferrous Vanadium (wt. %)	Alumina (wt. %)	NH ₄ Cl (wt. %)	Naphthalene (wt. %)
NbCN	50	-	35	14	1
VCN	-	50	35	14	1
NbVCN	25	25	35	14	1

The microstructural examinations and chemical analyzes of the coated samples were realized using scanning electron microscope (SEM - Model JEOL JSM-6060, FEI Co., Japan) coupled with energy dispersive X-ray spectroscopy (EDS). Preparations for metallographic examination of the samples include cutting, molding, grinding, polishing and etching steps. XRD patterns of the samples in Bragg-Brentano θ -2 θ geometry were realized with the help of a Rigaku diffractometer (Model D/MAX-B/2200/PC, Rigaku Co., Japan) using copper (Cu) K α radiation, continuous scanning with a speed of 2°/min. and scanning angles ranging from 20° to 90°.

A ball-on-disc tribometer which made in accordance with ASTM G133-05 standard was used for the dry sliding wear tests. The tests were conducted at room conditions with an alumina ball in 10 mm diameter the as the counter-body. The sliding speed was selected as 0.1 m/s, 0.3 m/s and 0.5 m/s, and sliding distance was 250 m. The applied loads were, 2.5N, 5 N and 10 N. Mean Hertzian contact pressures calculated for the alumina ball under the applied loads were 389 N/mm², 491 N/mm², and 618 N/mm², respectively. Friction coefficient - distance and wear rate - load graphs were plotted using the SigmaPlot 12.5 program. Wear tracks on the samples were examined using by SEM images and EDS analysis.

Results/Discussion

The cross-sectional images show the NbCN, VCN and NbVCN coated AISI 4140 steel, respectively. It is seen that the NbCN coating layer has a smoother, homogeneous and porosity free structure. For VCN and NbVCN coated samples, a transition layer is formed under the coating layer and there are some porosities in the coated layer. Porosity formation occurred in different studies of vanadium nitride coating by TRD method. Although the NbVCN coated sample includes transition layer between steel matrix and coating layer. It was not so much as the transition layer formed in the interface of the VCN-coated samples. The coating layer thickness for the NbCN coated sample is much higher than that of the VCN and NbVCN coatings.

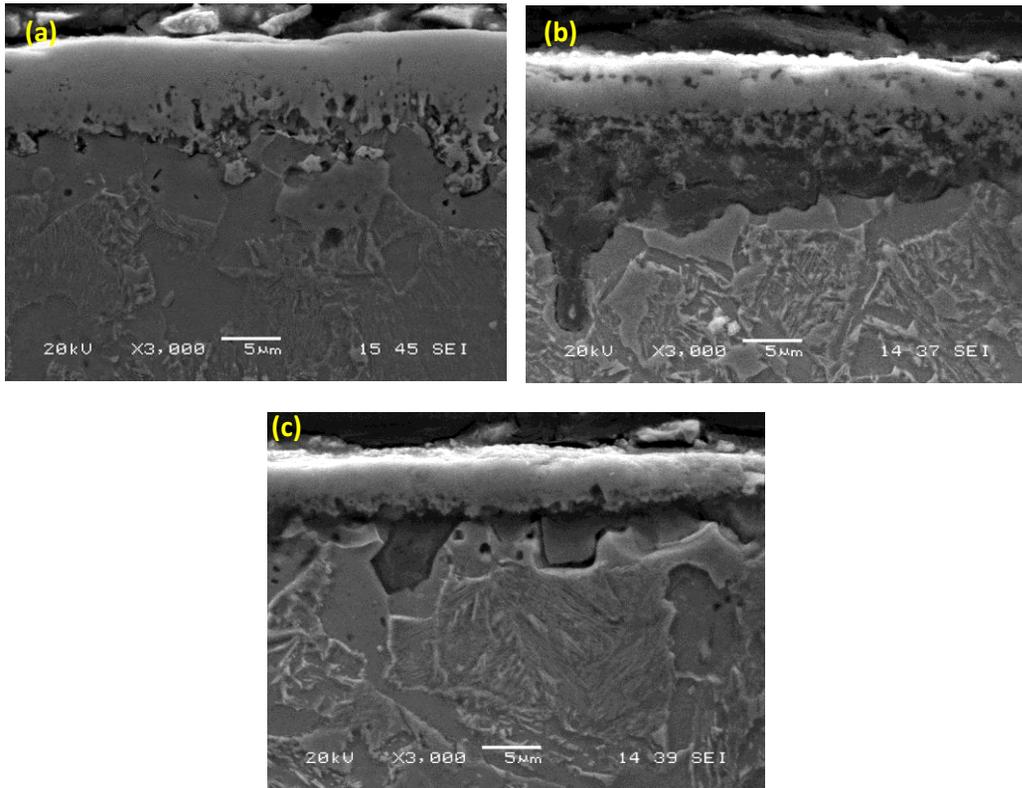


Fig. 1. SEM images of (a) Nb-C-N, (b) V-C-N, and (c) Nb-V-C-N coated samples.

EDS analyzes taken from the section for the NbVCN coated sample are given in the figure 2. The coating layer consists of niobium, and transition zone includes iron and vanadium. In the analysis 3 and 4, the chemical composition of the substrate material was found. Accordingly, for the AISI 4140 steel, a layer formation consisting of carbide, nitride and carbonitride phases formed as a result of the reaction of niobium and vanadium with carbon and nitrogen found in the substrate material. The diffusion of vanadium in the nitrogen and carbon-poor region was realized under the coating and a transition zone containing iron and vanadium phases was formed.

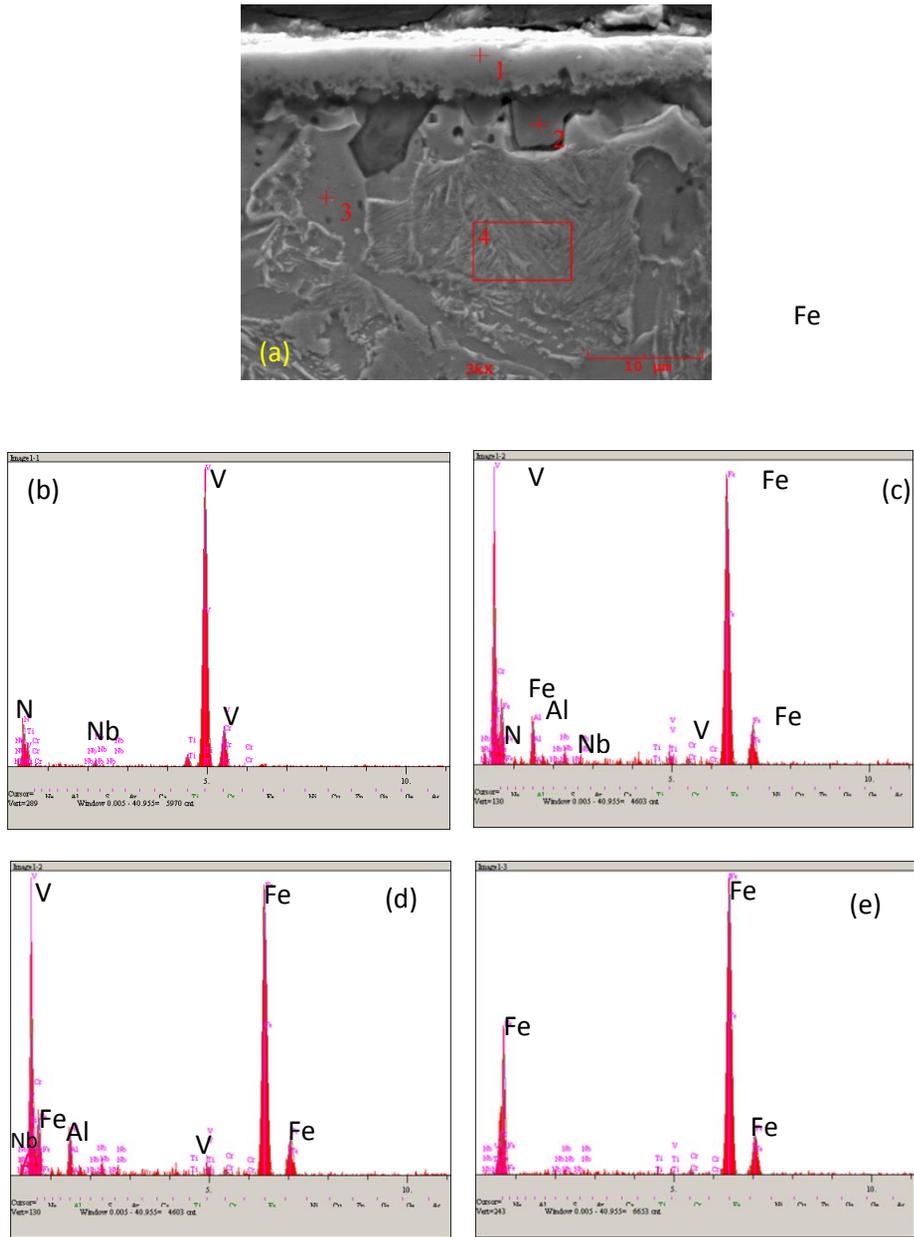


Fig. 2. (a) SEM microstructure from the section of Nb-V-C-N coated sample, (b) - (e) EDS analysis from different regions on the SEM image.

Fig. 3 shows the X-ray diffraction of the coated samples. Nb₂CN, NbN and Fe-Cr phases were found for the NbCN coated sample. Similar phases were found in the structure for the previous study by Kocaman and Sen. When the Gibbs free energies are taken into consideration, it is common for said phases of the niobium

to be present in the structure [14], [15]. V₆C₅ and Fe phases were formed for the VCN coated sample while no nitride based phase was found. In the study conducted by Biesuz and Sglavo, no nitride phase formation was observed in the structure and the situation was thought to be related to carbon diffusion [11]. For the NbVCN coated sample it is seen that the phases in both VCN and NbCN coated samples are formed.

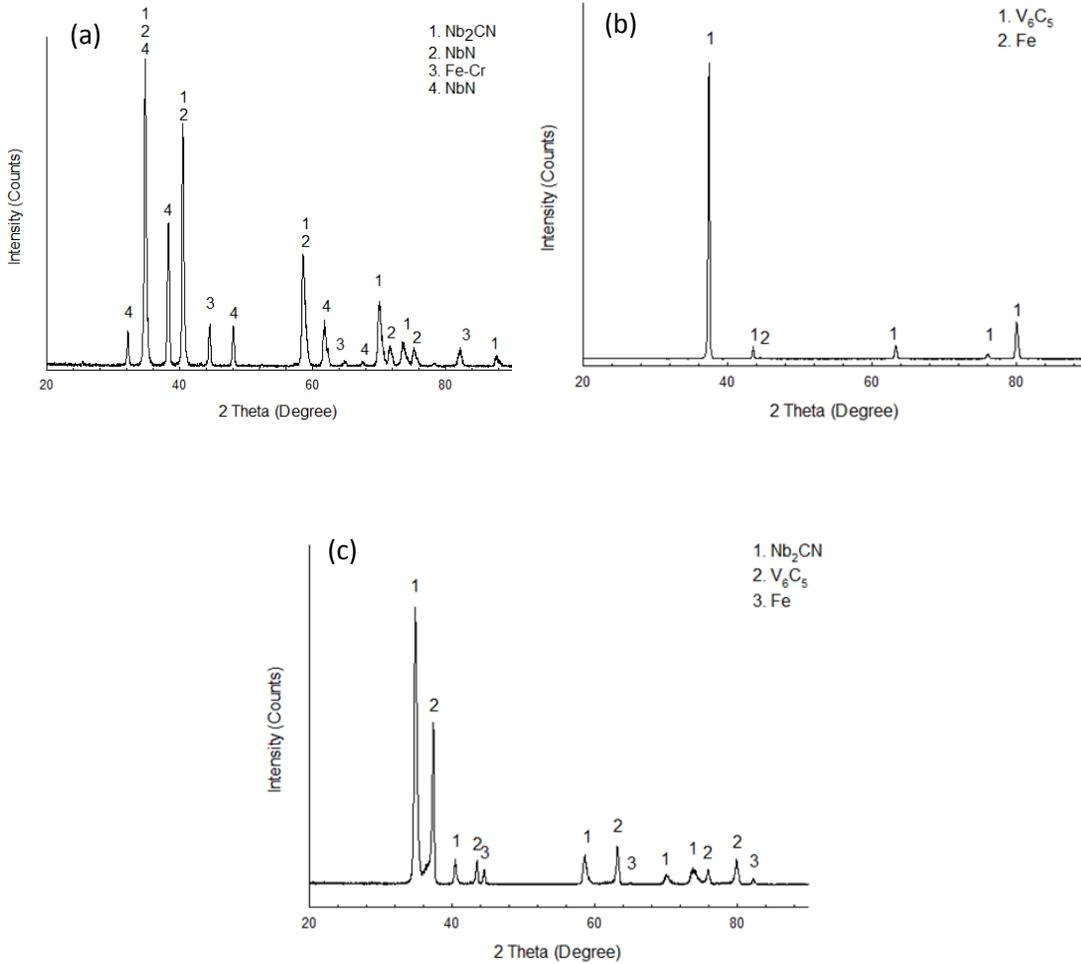


Fig. 3. XRD patterns of (a) Nb-C-N, (b) V-C-N, and (c) Nb-V-C-N coated samples

In the figures 4, friction coefficient-distance graphs are given for loads of 2.5N, 5N and 10N for the samples coated with NbCN, VCN and NbVCN, respectively. The coefficient of friction of NbCN coatings was getting increase up to 10 m and then getting steady state at the sliding conditions of 2.5 N load. The COF was about 0.25+- 0.05. When the applied load increased 5N, the COF was getting increase upto 150m sliding distance and the COF was about 0,48+-0,04. When the applied load was getting increase 10N, the COF was

getting increase up to 50 m sliding distance and then, getting to steady state. The COF value was about 0,48+-0,04. It was similar with the COF measured the loads of 5N. For the VCN coated sample, the coefficient of friction has increased linearly from 0.4 to 0.6 after the running-in distance of approximately 90 m. For the NbVCN coated sample, there was a similar behavior to the VCN-coated sample, but the coefficient of friction showed an increase from 0.2 to 0.4.

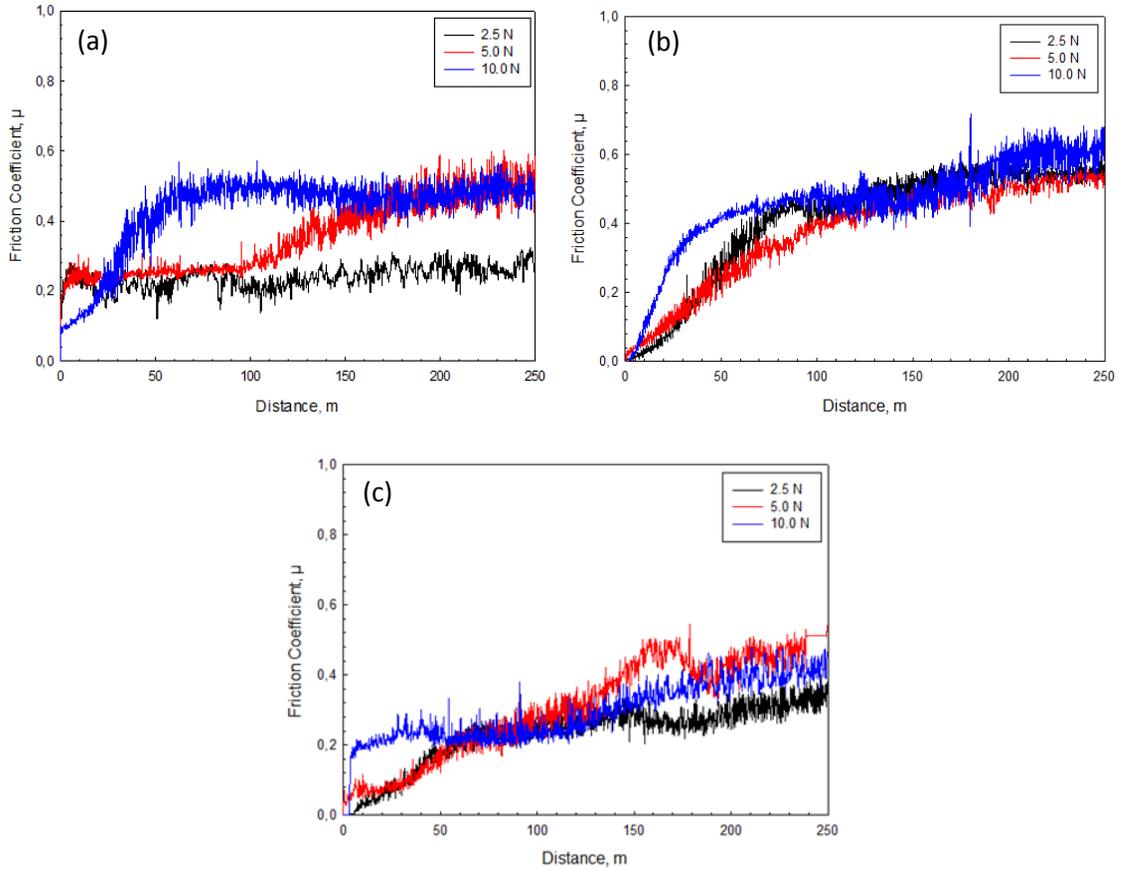


Fig. 4. Friction coefficient – distance graphs of (a) Nb-C-N, (b) V-C-N, and (c) Nb-V-C-N coated samples.

The figure 5 shows the wear rates of the coated samples. There was a linear wear behavior for all coatings. The wear rates of NbVCN coating were much lower than that of the VCN and NbCN coatings. The wear rates of the NbCN, VCN and NbCN coatings were changing between $1.9e^{-4}$ - $2.56e^{-4}$ mm^3/m , $8.59e^{-6}$ - $8.55e^{-5}$ mm^3/m and $1.33e^{-5}$ - $3.57e^{-5}$ mm^3/m , respectively.

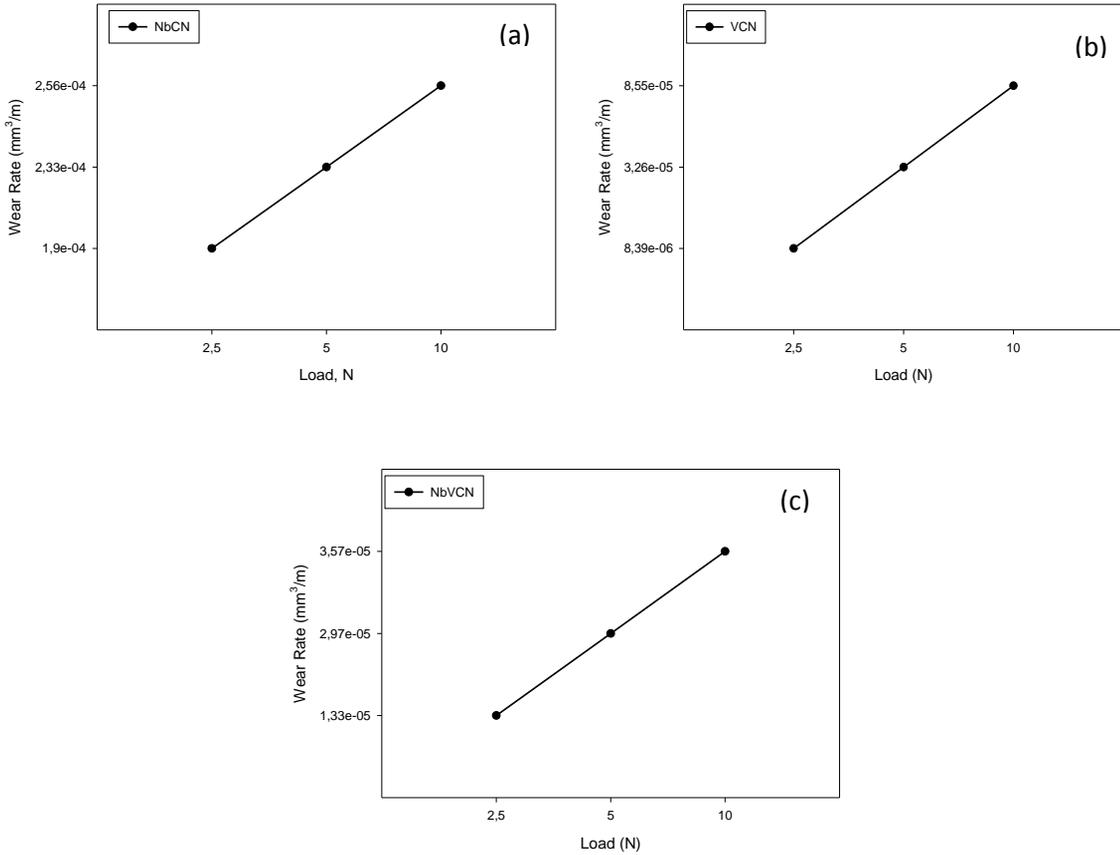


Fig. 5. Wear Rate – load graphs of (a) Nb-C-N, (b) V-C-N, and (c) Nb-V-C-N coated samples.

SEM images of wear tracks formed under 5N load for the coated samples are given in the figure 6. There is no any scratch, cracks or laminations observed on the worn surface of the coated sample with NbCN and it showed only polishing wear. For the VCN coated sample, significant fatigue crack is observed and lamination formation has occurred in some regions on the worn track. NbVCN coated sample showed that polishing wear and some fatigue cracks on the worn track.

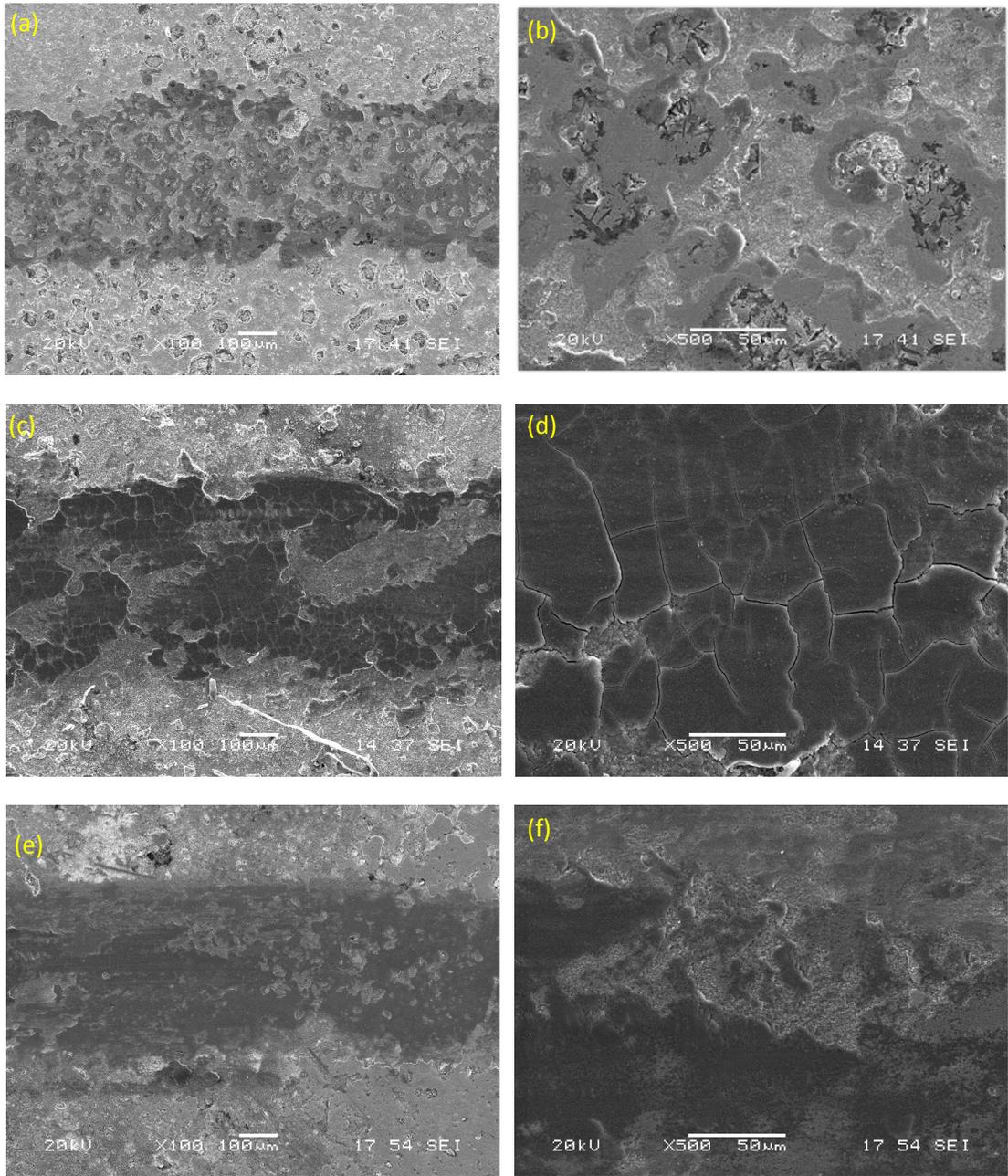


Fig. 6. SEM images of wear tracks for (a)-(b) NbCN, (c)-(d) VCN, and (e)-(f) NbVCN under 5N.

The figure shows the EDS analyzes taken from the wear track formed on the NbVCN coating (for 5N load). In addition to vanadium and niobium, aluminum is also present on the surface. In the presence of aluminum, it can be said that the adhesion of the parts that breaks off the ball during the wear test is effective.

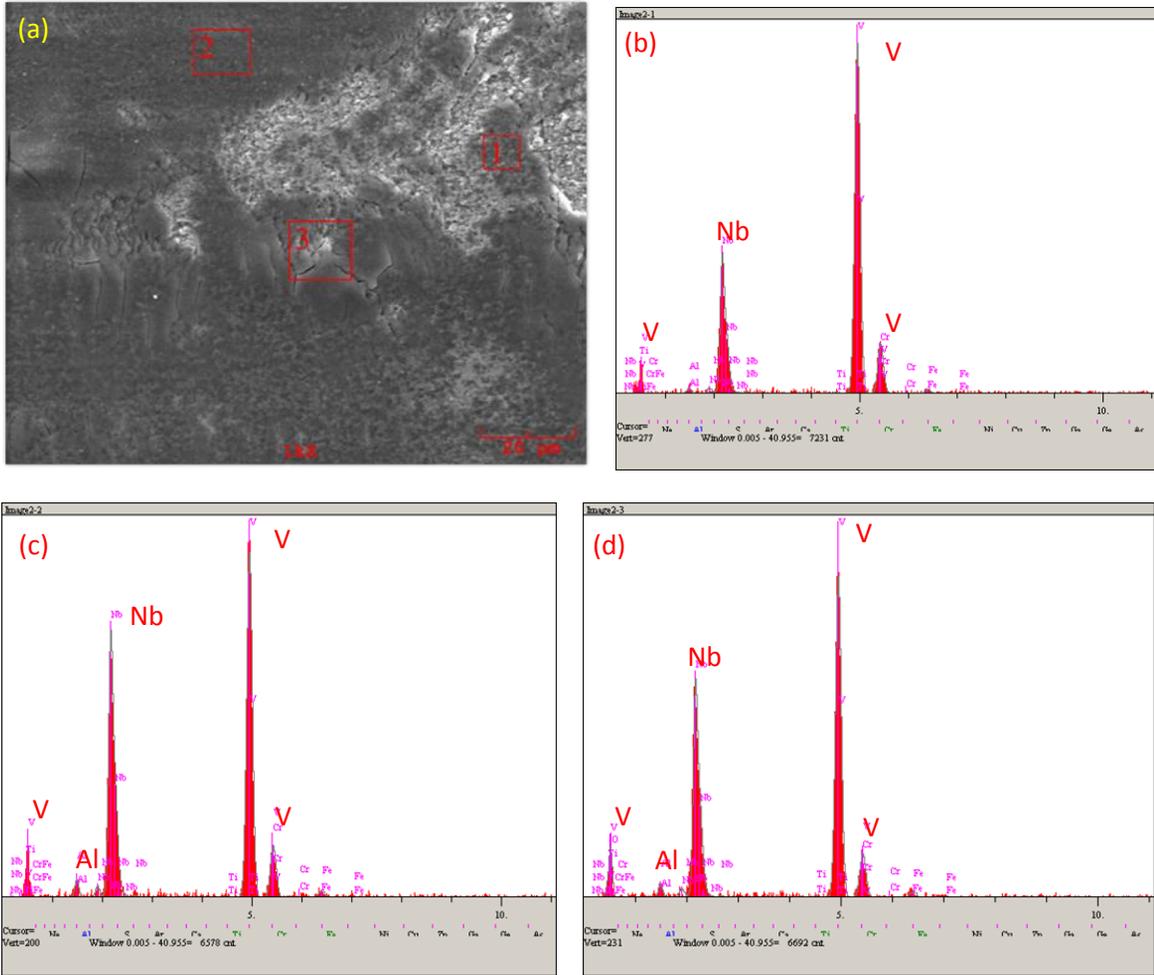


Fig. 7. (a) SEM image and (b)-(d) EDS analyzes of wear tracks for NbVCN coating under 5N.

Conclusion

In this study, NbVCN based coatings were obtained and their properties were compared with NbCN and VCN based coatings. Accordingly, the NbVCN coated sample exhibits similar properties with both NbCN and VCN coated samples. However, it is seen that NbVCN coatings have a high wear resistance compared to NbCN coatings when compared with the wear properties and there is no lamination occurring on the surface of VCN coatings. For the tests carried out under different loads, the friction coefficient was found to be lower for the 5 N and 10 N loads compared to the NbCN and VCN coatings.

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The Effect of Deposition Parameters on The Wear and Scratch Properties of TiAlZrN Coatings

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Abstract

The crucial aim of this study to elevate the scratch and wear resistance of heat treated AISI H13 (X40CrMoV5-1) hot work tool steel which is extensively used in aluminium extrusion process as a mold material. With the intention of increase scratch and wear resistance, prelusively, surface of this steel was nitreded. Thereafter, TiAlZrN coating using Pulsed DC closed field unbalanced magnetron sputtering method with different deposition parameters were coated the surface of this steel. Deposition parameters for this coating technique were designated by using Taguchi experimental design method. The coatings thickness and morphological properties of this coatings were investigated using scanning electron microscopy. The results showed that the TiAlZrN-graded composite coatings have 2-3 μm thickness and a dense and columnar structure. Wear properties were determined by a high temperature ball on disk tribotester. Thereafter, the worn surfaces of this coatings were analyzed by an optical profilometer. Wear resistance tests showed that the highest wear strength was attained at 5 A Zr target content, 90 V bias voltages and 2×10^{-3} Torr working pressure deposition parameters. Besides, this coating exhibited the highest scratch resistance (79N) compare the other coating samples. Hence, in light of this results, this aforementioned coating parameters were obtained optimum deposition parameters.

[keywords] AISI H13, TiAlZrN, Wear resistance

1.Introduction

Hot work tool steels have been extensively used in a wide range of applications such as an extrusion, injection and forging dies, hot working punches, aluminum allow casting, hot cutting tools, etc [1]. The most popular amongst this steels being the AISI H13 steel owing to high toughness and ductility, resistance to softening, high level of machinability and high abrasion properties [2-4]. In recent years, due to advancing technology and manufacturing requirement, there is a need to improve mechanical and wear properties of H13 steels in order to enhance service life and production quality. For this aim, researches hard thin coating films on the steel surface have gained momentum. As a result of this researches, it has been determined that the transition metal nitride coatings are conspicuous for previously mentioned applications due to their

tribological and mechanical properties [5-7]. TiN is the first produced coating amongst the transition metal nitrides. However, their properties are not enough for applications as well [8]. Therefore, some of the transition metal elements can be added to enhance scratch and wear resistance of TiN coatings [9,10]. For example, it has been established that the wear properties of TiN coatings increase with the addition of the Al [11]. On the other hand, the researchers indicated that the wear properties of quaternary transition metal nitrides were more excellent as to turnary transition metal nitrides [12]. Conducted studies showed that adding Si inside the TiAlN increased the wear resistance of coating [13,14]. Other elements were also studied by the researchers. Addition of Zr into TiAlN coatings also showed remarkable oxidation, mechanical and thermal properties [15,16]. However wear properties and scratch resistance properties of TiAlZrN coating was not investigated efficiently.

As a consequence of these observations, in this study, we investigated the chemical, structural, morphological, scratch and wear resistance properties of TiAlZrN coating which was applied on nitreded AISI H13 steel substrate by pulse DC closed field unbalanced magnetron sputtering deposition. Also during this deposition process, we used some variable deposition parameters to determine the effects on the coatings.

2. Experimental Procedure

In this study, AISI H13 hot work tool steel which is commonly used as a mold material, was purchased from the market. The purchased steels were prepared in the specified dimensions (30mm x 4mm). The disk-shaped samples were heat threated in accordance with literature to prepare for the nitriding process. The nitriding process was performed at 525 °C for 8 hours. Before the deposition process, the surfaces of the nitrated samples were grounded with SiC papers with 400, 800, 1000, 1500 and 2000 grit and then polished with diamond suspension. The surface roughness value of the samples were measured as $0,05\mu\text{m}\pm 0,002$.

After this processes, TiAlZrN- graded composite coatings were deposited by using pulse DC closed unbalanced magnetron sputtering technique. Pure Ti, Al, Zr elements was used as a targets, N₂ was used as a reactive gas and argon was used as a sputtering gas for deposition. Ti, Al, Zr target currents, frequency, duty time, deposition duration and Ti target current of interlayer were keep constant, bias voltage and working pressure were selected variable parameters as given in Table 1.

Table 1. Deposition Parameters

Constant Parameters		
Target Currents; Ti / Al / Zr (A)	6 / 2 / 5	
Interlayer Target Current Ti (A)	6	
Deposition Duration (min.)	60	
Duty Time (µs)	2,5	
Frequency (kHz)	100	
Variable Parameters		
Sample Number	Bias Voltage (-V)	Working Pressure (Torr)
R1	50	3×10^{-3}
R2	75	$2,5 \times 10^{-3}$
R3	90	2×10^{-3}

Before deposition, ion cleaning was carried out for 15 minutes to remove contamination on the substrate surface. For the purpose of increasing the adhesion of coatings, oxidation resistance and decreasing the residual stress between coating and substrate, the deposition started with Ti under layer for 5 minutes. After that, in order to decrease the thermal stress due to high temperature, TiN layer was coated for 15 minutes. Lastly, TiAlN/TiAlZrN for each layer was deposited for 20 minutes as shown in Figure 1. During the deposition, glass plate and silicon wafer substrates were coated at the same time for using microstructural and cross sectional analysis.



Figure 1. Design concept of the graded composite of TiAlZrN coating

The surface and cross section morphology of coatings were observed by using scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) were used for elemental analysing. Micro hardness values were measured by Struers Vickers micro hardness tester at 245,3 mN constant load. Adhesion of the TiAlZrN-graded composite films was determined by scratch tester-CSM Revester equipped with a Rockwell C diamond stylus. Worn surfaces were characterized with SEM. The wear properties of coatings were evaluated by using ball-on-disk tribometer. The wear experiment parameters are given in Table 2.

Table 2. Wear experiment parameters

Normal Load (N)	Track Diameter (mm)	Sliding Speed (mm/sn)	Cycle	Counter Body
2	10	60	1600	Al ₂ O ₃

After the wear experiments, wear rates of coatings were measured with optical profilometer and worn surfaces were characterized with SEM.

3. Results and Discussions

3.1. Surface and Cross Section Morphology

The surface morphological SEM photos of coatings are given in Figure 2. The grain size measurements were performed for using SEM photos. The average grain size of coatings are given in Table 3.

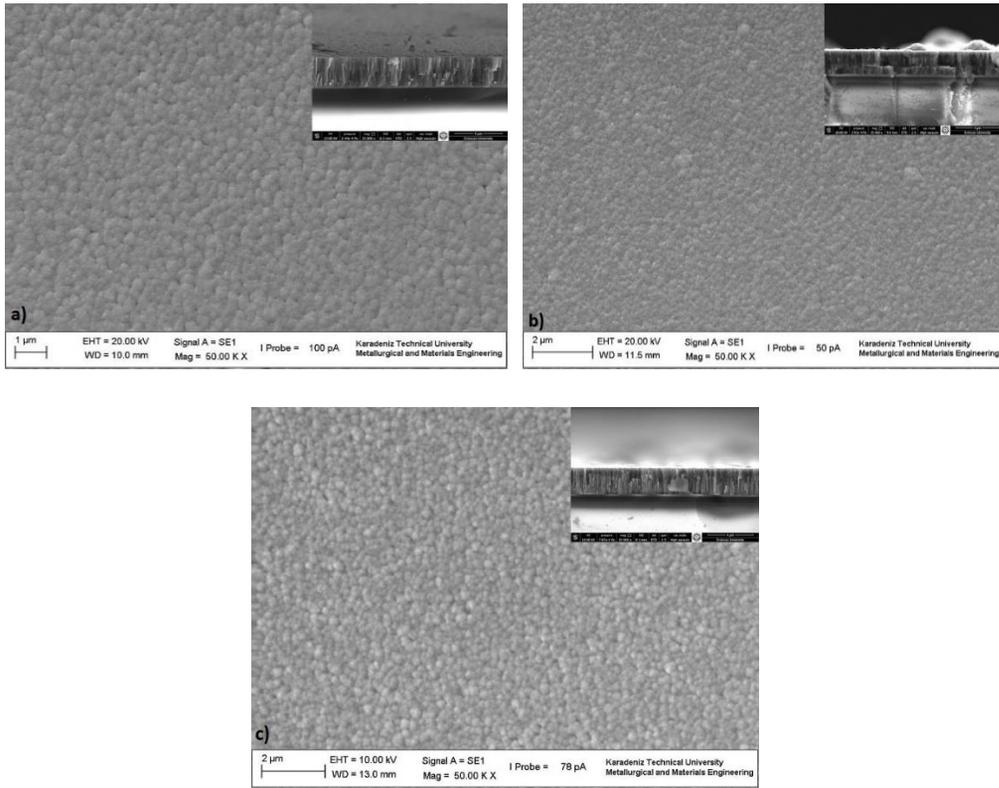


Figure 2. The surface morphology of coatings a) R1 b) R2 c) R3

Table 3. Grain size values of coatings

Sample Number	Grain Size (nm)
R1	430±50
R2	380±50
R3	280±50

All coatings showed granular structure as shown in Figure 2. As Figure 2 and result of the grain size measurements, grain size of R3 coating is relatively smaller than the others and has finer and more compact structure. This can be related with the higher mobility of the adatoms (absorptive atoms) at high bias voltage and low working pressure during deposition process. The results obtained by Yu et al confirmed our finding in this study [17]. Because, of the high bias voltage and low working pressure, the grain size of R3 is smaller than the others due to the sputtered atoms can collide the less amount of gas atoms during their movements to the substrate surface [18].

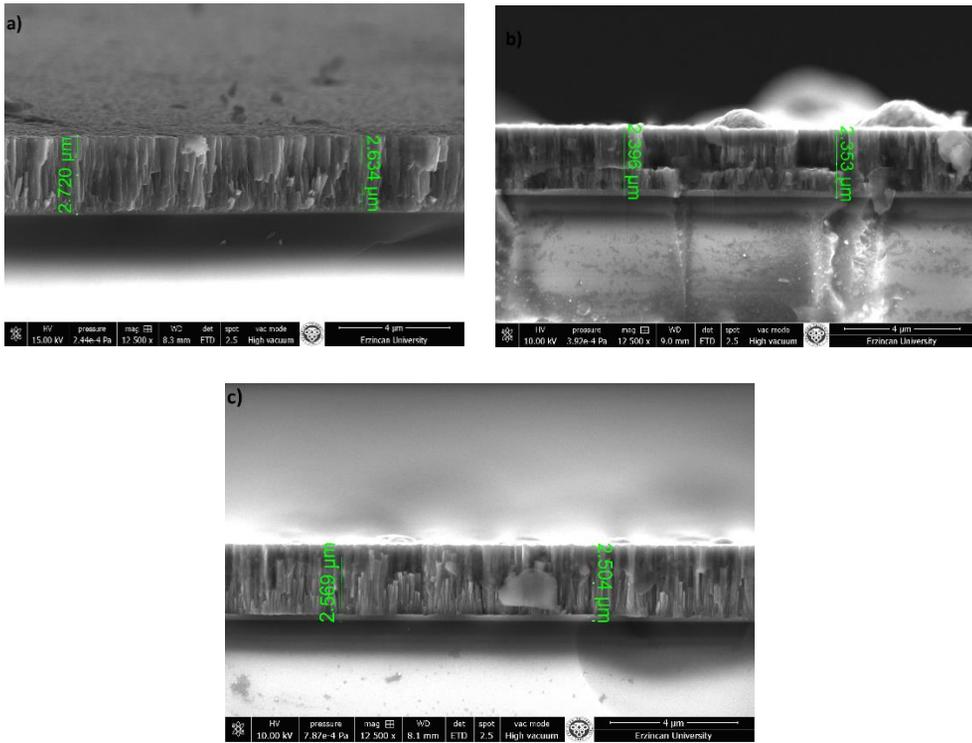


Figure 3. The cross section photos of coatings a) R1 b) R2 c) R3

Table 4. The thicknesses of coatings

Sample Number	Coating Thickness (μm)
R1	2,7
R2	2,3
R3	2,5

Thicknesses of the TiAlZrN coatings were determined using SEM photos of the cross sections obtained by brittle fracture in the radial direction of the films deposited on the glass plates. SEM images of the cross-sectional are shown in Figure 3, and coating thicknesses obtained using SEM images are given in Table 4. The highest coating thickness was measured as 2,7 μm on the R1 sample. The minimum coating thickness was measured as 2.3 μm at R2. It can be seen in Figure 3 that the coatings exhibit a dense and thin columnar structure.

3.2. Elemental Analysis

The chemical composition of coatings are given in Table 5. As seen in Table 5, increasing bias voltage increased the N amounts and decreased the Ti, Zr and Al amounts in the coatings. This may be related with the re-sputtering mechanism. High energetic particles re-sputtered Ti,Al and Zr atoms from coatings at higher bias voltage.

Table 5. Chemical composition of coatings

Sample Number	Chemical composition (% Atomic)			
	Ti	Al	Zr	N
R1	49,92	8,29	11,02	31,01
R2	46,71	8,05	7,37	37,69
R3	45,00	6,10	7,32	41,53

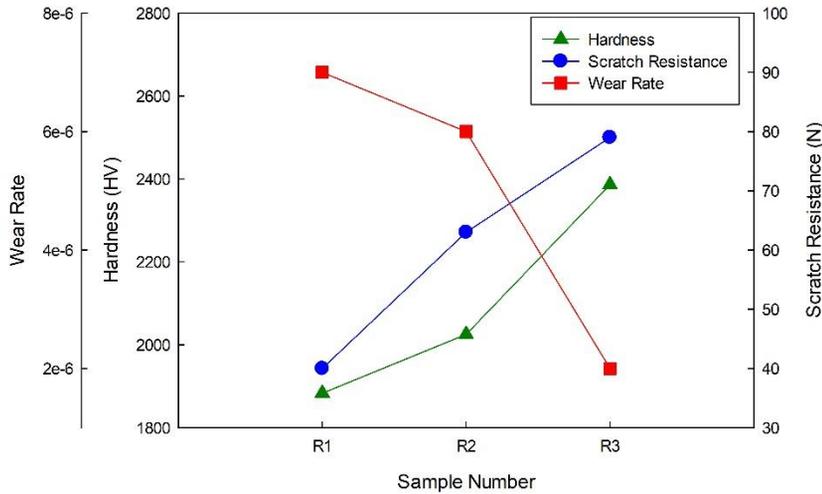


Figure 4. The changes of hardness, scratch resistance and wear rate of the coatings

Hardness Properties

The changes of hardness of coatings are given in Figure 4. As seen in Figure 4, the highest hardness was attained in R3 with highest bias voltage and lowest working pressure. The reason for this is high ion bombardment during coating process as a result of highest bias voltage and lowest working pressure. The same results and interpretations were obtained in studies conducted by some researchers [19]. In a different study on this subject, it was noted that with increasing bias voltage increases the compactness of coatings, hardness by reducing the deterioration of the lattice structure.

Scratch Properties

Residual stresses in the structures of the coatings are due to effects such as lattice parameters of the base material and coating material, thermal expansion coefficients, interatomic voids, and recrystallization. In this study, Ti was coated on the surface of the substrate in order to reduce this difference between the substrate and the coating, and then continued with the transition layer and the TiAlZrN layer was coated on the top.

Scratch resistance change of coatings are seen in Figure 4, also scratch values are seen in Table 6.

Table 6. Scratch resistance values of coatings

Sample Number	Scratch Resistance (N)
R1	40
R2	63
R3	79

The highest scratch resistance was attained from R3 sample, the lowest scratch resistance was attained from R1 sample as given Figure 4 and Table 6. With the increase of the bias voltage, the combination of high energy ions and the energy of ionized atoms enhanced the scratch resistance as a result of implantation in the substrate surface. Besides, as seen in morphological analysis, R3 (higher bias voltage and lower working pressure) has a lower grain size and higher hardness value so has a higher plastic deformation resistance. Hence, scratch resistance improved with increasing plastic deformation resistance.

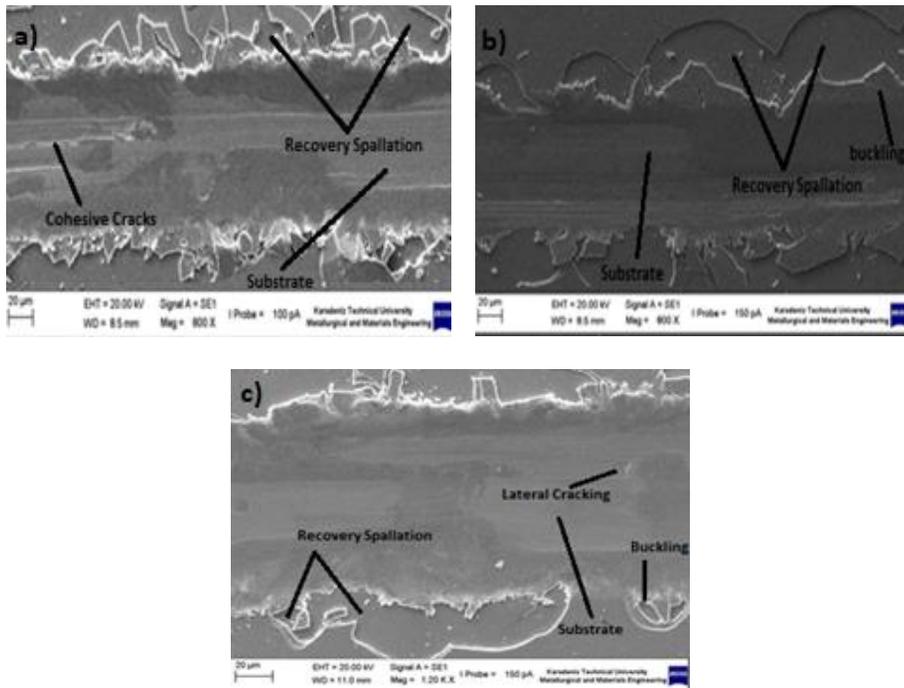


Figure 5. Scratch pattern of coatings a) R1 b) R2 c) R3

The scratch mechanism of samples were obtained by using SEM. Cohesive cracks, buckling and lateral cracking mechanisms were observed for R1, R2, R3 respectively. Additionally, recovery spallation mechanism was observed for all coatings as shown in Figure 5.

Wear Properties

The friction coefficient of coatings are given in Figure 6. The friction coefficient curve of coatings consists of two sections. At early stage of experiments is running in stage (between zero and 500 cycles) and the rest is steady state stage. In addition to, the lowest friction coefficient was obtained from R3 sample which is produced with highest bias voltage and lowest working pressure due to high hardness and scratch resistance.

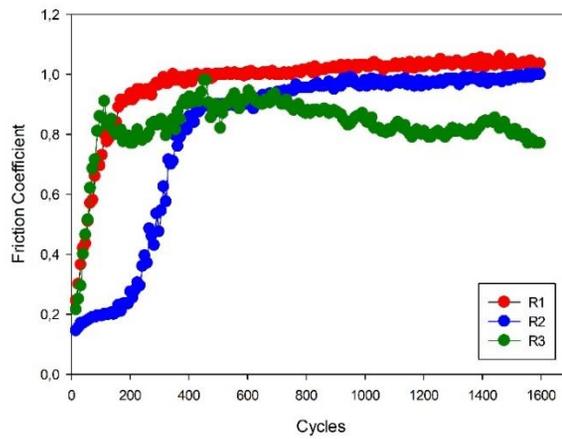


Figure 6. The friction coefficient of coatings

Table 7. The wear rate of coatings and uncoated H13 steel

Samples	Wear Rate (mm ³ /Nm)
R1	7,13x10 ⁻⁶
R2	6,42x10 ⁻⁶
R3	2,24x10 ⁻⁶
Uncoated (Nitreded) H13 steel	2,13x10 ⁻⁴

The wear rates of coatings are shown in Table 7. According to Table 7, all coatings have higher wear resistance than uncoated (nitreded) H13 steel. If the coatings were compared among themselves, it can be seen that, the lowest wear rate was attained from R3 (highest bias voltage and lowest working pressure). Besides, TiAlZrN coatings especially R3 deposition condition increases the wear resistance of nitreded H13 steel approximately 100 times.

4. Conclusions

In this study, The TiAlZrN-graded coatings were successfully deposited on nitred AISI H13 steel by pulsed dc close field unbalanced magnetron sputtering system with the different deposition parameters. And the effect of bias voltage and working pressure on the surface morphology, scratch and wear properties of TiAlZrN coatings were investigated. Following conclusions were obtained;

- The lowest grain size was attained with -90 V bias voltage and 2×10^{-3} working pressure deposition parameter.
- The highest hardness was obtained with highest bias voltage and lowest working pressure
- There is a relation between hardness, scratch and wear resistance. The coating which has highest hardness also showed highest scratch and wear resistance. The coating which has lowest hardness also showed lowest scratch and wear resistance.
- TiAlZrN coatings have been successful in enhancing the wear resistance of nitred H13 steel. The wear resistance of this steel enhanced by 100 times owing to TiAlZrN coatings.

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The Surface-Plasmon - Optical Soliton Photonic Josephson Junction

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Abstract

An evanescently coupled, co-propagating optical soliton and a surface plasmon can exhibit bosonic Josephson junction dynamics similar to that of Bose-Einstein condensates in double-well traps. Moreover, the self-focusing of the soliton generates an inherently intensity (i.e., photon population) dependent coupling, which exhibit unique dynamical features. Here, we review the dynamical properties of this photonic Josephson junction based on a heuristic model and discuss recent extensions involving plasmon-soliton-plasmon double Josephson junctions and Rosen-Zener like transitions generated by spatially modified coupling. With the advancement of photonic materials, realization of this optical system may enable new abilities to control and utilize the propagation of light.

Keywords: Surface-plasmon – soliton; Josephson junction.

1. Introduction

The Josephson junction dynamics arises between two macroscopic quantum states under weak coupling. Originally predicted in a system of two superconductors with a dielectric spacing by Josephson 1962, and named after him, it has been demonstrated shortly after by Anderson, 1963 and kept on revealing itself in various physical systems such as Bose-Einstein condensates of atoms confined in a double-well optical trap, Javanainen 1986, and two superfluids tunneling through a nano aperture, Pereverzev, 1997.

Recently a resonant interaction between optical solitons and surface-plasmons on a planar metal surface through a dielectric spacing has been suggested by Bliokh 2009. As such, the model system has the proper ingredients to constitute a Josephson junction, Eksioglu, 2011, with the unique feature that the coupling inherently depends on the soliton amplitude. In this paper, we review the dynamical features of this Josephson junction based on the semiclassical formulation of the soliton and surface plasmon states that are weakly coupled. In particular, we consider first a dissipationless single Josephson junction consisting of a soliton and a surface-plasmon co-propagating in parallel. This is followed by incorporating several dissipation mechanisms that are adopted from Josephson junctions of Bose-Einstein condensates. A further extension is based on varying the coupling spatially along the propagation to induce Landau-Zener like transitions.

2. Model and Formulation

2.1. Dissipationless single soliton – surface-plasmon Josephson junction

We begin by a brief description of the semiclassical model of this photonic Josephson junction which is derived from the heuristic model introduced by Bliokh, 2009. The model assumes that the soliton propagates in a nonlinear dielectric channel parallel to a metal surface with a linear dielectric spacing. The evanescent lateral extend of the soliton excites and interacts with the surface plasmons on the metal surface, which are assumed to be co-propagating with the soliton. Hence the total electromagnetic field of the weakly coupled soliton – surface-plasmon system can be written by a superposition ansatz as:

$$\Psi(x, z) = c_p(z)\psi_p(x) + c_s(z)\psi_s(x, |c_s|) \quad (1)$$

Here, $c_{s,p}(z)$ denote respectively the soliton and surface plasmon longitudinal amplitudes and $\psi_s(x, |c_s|)$, $\psi_p(x)$ denote their transverse amplitudes. We note that the soliton transverse profile depends on c_s as a result of Kerr nonlinearity of the propagation medium (i.e. self-focusing effect). The system is essentially two-dimensional which is set as the $z-x$ plane in this formulation. Under steady state propagation, the longitudinal amplitudes are governed by coupled nonlinear (soliton) and linear (surface-plasmon) oscillator equations along the propagation axis (z) as follows:

$$\begin{aligned} \frac{\partial^2 c_p}{\partial z^2} + \beta_p^2 c_p &= q(|c_s|)c_s \\ \frac{\partial^2 c_s}{\partial z^2} + \beta_s^2 c_s &= q(|c_s|)c_p \end{aligned} \quad (2)$$

where $\beta_p = \frac{k_p}{k}$ and $\beta_s = \frac{k_s}{k} \cong \varepsilon_K + \frac{\gamma|c_s|^2}{4}$ are wavevector parameters of the surface-plasmon and soliton, ε_K is the linear part of the Kerr dielectric and γ is the nonlinearity parameter. $q(|c_s|)$ is the soliton amplitude dependent coupling function.. Eq(2) is linearized through substitution $c_{s,p} = C_{s,p}(z)e^{iz}$, and by employing slowly varying amplitude approximation for modulation amplitudes $C_{s,p}(z)$:

$$-i \frac{\partial}{\partial z} \begin{bmatrix} C_p \\ C_s \end{bmatrix} = \begin{bmatrix} \beta_p - 1 & -q(|C_s|)/2 \\ -q(|C_s|)/2 & \beta_s - 1 \end{bmatrix} \begin{bmatrix} C_p \\ C_s \end{bmatrix} \quad (3)$$

Finally, introducing phase functions $\phi_{s,p}$ through $C_{s,p}(z) = A_{s,p} \exp(i\phi_{s,p}(z))$, the relative phase $\phi = \phi_s - \phi_p$, and the relative population imbalance variable $Z = (|C_s|^2 - |C_p|^2)/(|C_s|^2 + |C_p|^2)$, the soliton – surface-plasmon Josephson junction (SSPJJ) equations are obtained. Here, we take the total number of photons conserved and normalized i.e. $|C_s|^2 + |C_p|^2 = 1$. Hence, $Z \in [-1, 1]$. The relative phase is defined in the symmetric range $\phi \in [-\pi, \pi]$.

$$\begin{aligned} \frac{\partial Z}{\partial z} &= -q(Z)\sqrt{1-Z^2} \sin \phi \\ \frac{\partial \phi}{\partial z} &= \Delta E + \Lambda Z + q(Z) \frac{Z}{\sqrt{1-Z^2}} \cos \phi \end{aligned} \quad (4)$$

In eq. 4, we further define the parameters $\Delta E = \Lambda - (\beta_p - 1)$ and $\Lambda = \gamma/8$ for the analogy with the Josephson junction formulation of Bose-Einstein condensates in double well traps. Indeed, the dynamic equations of a bosonic Josephson junction (BJJ) in semiclassical formulation are given by Smerzi, 1997, Raghavan 1999 as:

$$\begin{aligned}\frac{\partial Z}{\partial t} &= -q\sqrt{1-Z^2} \sin \phi \\ \frac{\partial \phi}{\partial t} &= \Delta E + Z(t) + q \frac{Z}{\sqrt{1-Z^2}} \cos \phi\end{aligned}\quad (5)$$

The most striking difference is that the coupling is a constant parameter (q) in BJJ whereas it is a function of the soliton amplitude $|C_s|$ in SSPJJ, as the coupling depends on $\psi_s(x, |c_s|)$.

$$q(Z) = \left(\frac{1+Z}{2}\right) e^{-kd\sqrt{2\Lambda(1+Z)}}\quad (6)$$

Here, kd is the wavevector-scaled distance between the center of the soliton channel and the metal surface. This functional form provides the exponential decay in the strong soliton limit ($1-Z \ll 1$) and sublinear enhancement by the soliton intensity ($|C_s|^2$) in the strong surface-plasmon limit ($1+Z \ll 1$).

2.2. Phase space and dynamical features of the dissipationless SSPJJ

Equation set (4) describes the dynamics of the SSPJJ in the $\phi - Z$ phase space. The stationary states are given by $\{\partial_z Z = 0, \partial_z \phi = 0\}$ which occur at $\phi^* = 0, \pi$ and at values Z^* that satisfy

$$\Delta \tilde{E} + Z^* \pm \tilde{q}(Z^*) \frac{Z^*}{\sqrt{1-Z^{*2}}} = 0\quad (7)$$

where the + (-) correspond to $\phi^* = 0, (\pi)$ respectively. $\Delta \tilde{E} = \frac{\Delta E}{\Lambda}$ and $\tilde{q}(Z) = \frac{q(Z)}{\Lambda}$ are scaled parameters. Stable stationary points provide bound orbits with nonzero average value of the population imbalance, which is known as the macroscopic self-trapping in BJJ. Here, we illustrate the phase space for two different sets of $\{\Delta \tilde{E}, kd\}$ values. In Figure 1(a) one $\phi^* = 0$ four $\phi^* = \pi$ stationary points can be observed for $\{\Delta \tilde{E} = 0, kd = 8\}$. With values $\{\Delta \tilde{E} = -0.01, kd = 13\}$, Figure 1(b) shows that $\phi^* = 0$ stationary point shifts upwards (soliton dominant) due to nonzero $\Delta \tilde{E}$. A saddle point at $\phi^* = \pi$ is visible, and there are two more stationary points close to the $Z = \pm 1$ values (not visible in the figure scale, please see Figure 2(b)). Note that the bound states around the stationary points for $\phi^* = \pi$ provide macroscopic self-trapping with soliton-dominant and surface-plasmon dominant average values respectively. The color-coded arrows indicate the gradient distribution in the phase space whose components are given by Eq.4. By increasing kd from 8 to 13 the trajectories are flattened horizontally, indicating the weakened coupling between the soliton and the surface plasmon.

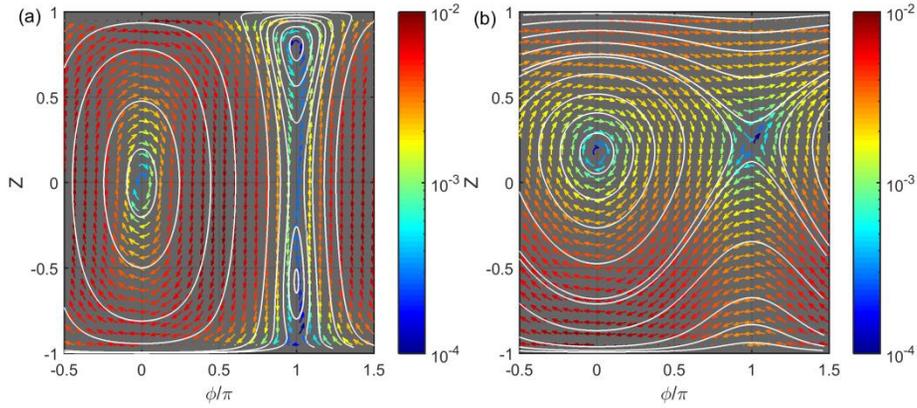


Figure 1: Phase space plot of the SSPJJ for (a) $\{\Delta\tilde{E} = 0, kd = 8\}$ and (b) $\{\Delta\tilde{E} = -0.01, kd = 13\}$. The colored arrows indicate the gradient and the white curves indicate sample trajectories.

The Z -dependence of the coupling renders the phase space asymmetric about the $Z = 0$ axis, even for $\Delta E = 0$ case. This is essentially different than the phase space of the BJJ, which would be symmetric for $\Delta E = 0$, unless the barrier separating the double well is made asymmetric, Smerzi, 1997.

Since the soliton – surface plasmon spacing parameter kd can be controlled trivially, analysing its effect on the phase space is feasible. Figure 2 shows the distribution of (a) $\phi^* = 0$ and (b) $\phi^* = \pi$ stationary points on the Z -axis as a function of $5 < kd < 15$, for $\Delta\tilde{E} = 0$ and $\Delta\tilde{E} = -0.01$, respectively. Note that for $\Delta\tilde{E} = 0$, $Z^* = 0$ is always a critical point as can be inferred from Eq. (6). For nonzero $\Delta\tilde{E}$ values, the stationary point at $\phi^* = 0$ becomes kd dependent as shown in Figure 2. The stationary points at $\phi^* = \pi$ show a nontrivial distribution and up to 4 stationary points can be generated at certain values of $\{\Delta\tilde{E}, kd\}$. The $kd = 8$ and $kd = 13$ correspond to the values used in Figure 1. A detailed analysis of the phase space for SSPJJ system can be found in Eksioğlu, 2011 and Eksioğlu, 2013, albeit with a slightly different coupling function, and in the presence of dissipation. The SSPJJ model including dissipation mechanisms is discussed in section 2.4.

2.3. Dissipative model extensions of the single soliton – surface-plasmon Josephson junction

The analogy to the double-well BJJ can be extended to incorporate similar dissipation mechanisms in the SSPJJ. One dissipation mechanism present in BJJ is about the tunneling between the excited states of two Bose-Einstein condensates in the *same* trap, that populate different hyperfine levels. This generates a damping proportional to the population imbalance in its rate of change. Although an analogous mechanism in the SSPJJ is arguable, it is introduced in an ad hoc manner for comparison:

$$\begin{aligned} \frac{\partial Z}{\partial z} &= -q(Z)\sqrt{1-Z^2} \sin \phi - \zeta Z \\ \frac{\partial \phi}{\partial z} &= \Delta E + \Lambda Z + q(Z) \frac{Z}{\sqrt{1-Z^2}} \cos \phi \end{aligned} \quad (8)$$

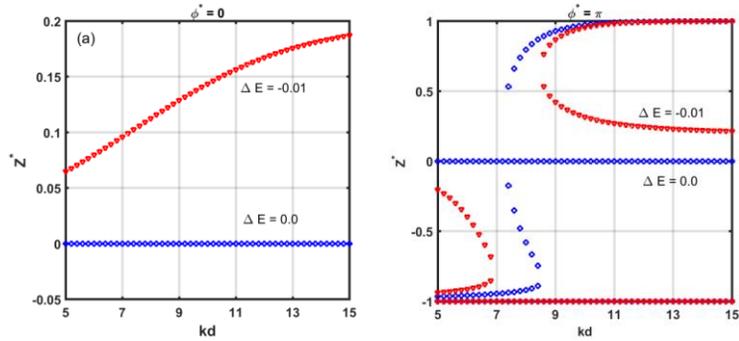


Figure 2: The stationary points as a function of soliton – surface-plasmon spacing for different values of ΔE . (a) $\phi^* = 0$, (b) $\phi^* = \pi$.

A more relevant dissipation is due to the incoherent exchange of photons between the soliton and the surface-plasmon. This is represented by a phase-velocity proportional term in the population imbalance rate, adopted from Marino, 2009:

$$\begin{aligned} \frac{\partial Z}{\partial z} &= -q(Z)\sqrt{1-Z^2} \sin \phi - \eta \frac{\partial \phi}{\partial z} \\ \frac{\partial \phi}{\partial z} &= \Delta E + \Lambda Z + q(Z) \frac{Z}{\sqrt{1-Z^2}} \cos \phi \end{aligned} \quad (9)$$

The first dissipation mechanism generates various bifurcations in the system depending on the model parameters as shown in Figure 3 (a). Here, the $\phi^* = 0, Z^* = 0$ critical point acts as a strong sink and one (upper) critical point near $\phi = \pi$ becomes a source, whereas another (lower) critical point near $\phi = \pi$ becomes a weak sink. For nonzero $\Delta \vec{E}$ values, this dissipation mechanism can generate limit-cycles, thus providing unique macroscopically trapped states, Eksioglu, 2011. The second dissipation mechanism creates the so-called “phase-slip” phenomenon known in BJJ systems, in which the trajectories from $\phi = \pi$ stationary states decay into the $\phi = 0$ stationary state (Figure 3(b)).

We ought to note that the surface-plasmons are inherently dissipative and this can be taken into account by introducing imaginary parts to their propagation constants, $\beta_{s,p} \rightarrow \beta_{s,p} + i\gamma_{s,p}$, Bliokh, 2009. In this case, the total number of photons is not conserved and decays to zero. When the propagation length of surface-plasmon is sufficiently large compared to the relevant length scales in which the aforementioned dynamical features take place, this dissipation may be omitted.

2.4. Soliton – surface-plasmon Josephson junction with spatially modified coupling

Since the coupled soliton – surface-plasmon essentially forms a two-state system, it is natural to exploit some mechanisms that can generate diabatic/adiabatic transition between the two states. Bliokh et al., 2009 investigated resonant transitions induced in the presence of a small damping. In a recent study, Aydindogan, 2017 employed a varying spacing between the soliton and the surface-plasmon to modify the coupling spatially and hence induce population transitions. With a smooth variation of the spacing, the paraxial approximation is applicable and the dynamics of the SSPJJ are still given by equation 4, where the coupling now takes the form

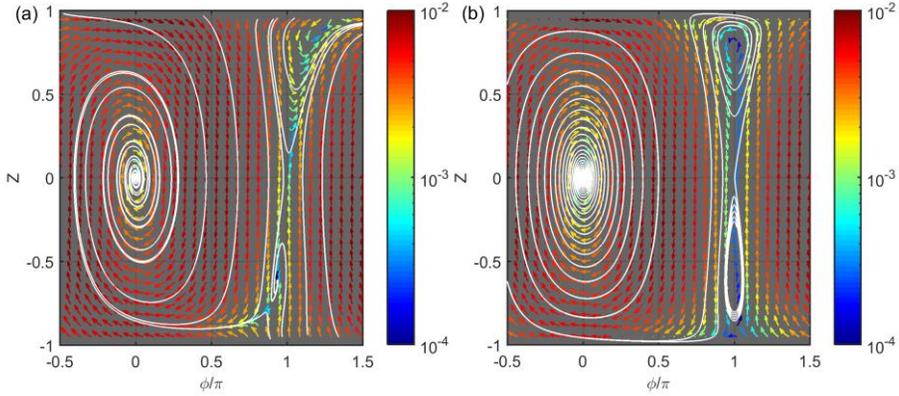


Figure 3: Phase space of the SSPJJ with (a) population imbalance and (b) phase rate dissipation mechanisms.

$$q(z, Z) = \left(\frac{1+Z}{2}\right) e^{-\sqrt{2\lambda(1+Z)}} e^{-k\sqrt{d^2 + \alpha^2 z^2}} \quad (10)$$

That is, the constant spacing, d is now replaced by the hyperbolic spacing $\sqrt{d^2 + \alpha^2 z^2}$, where d is the minimum spacing, z is the propagation axis, and α is the asymptotic slope. By tuning the spatial modulation parameters d, α , full population transfer, population splitting, merging can be generated, as shown in Figure 4. The full population transfer resembles the asymmetric Rosen-Zener adiabatic transitions where the uncoupled soliton and surface-plasmon represent.

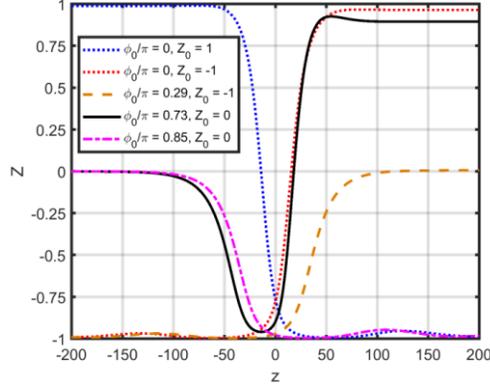


Figure 4: Population transfer between soliton ($Z = 1$), surface-plasmon ($Z = -1$), and equipopulated ($Z = 0$) states.

2.5. Soliton – surface-plasmon double Josephson junction

The soliton channel running along between two parallel metal surfaces forms a double Josephson junction. The single SSPJJ model described in section 2.1 can be extended in a straightforward manner for this case:

$$-i \frac{\partial}{\partial z} \begin{pmatrix} C_{p1} \\ C_s \\ C_{p2} \end{pmatrix} = \begin{pmatrix} \beta_{p1} - 1 & -q_1/2 & 0 \\ -q_1/2 & \beta_s - 1 & -q_2/2 \\ 0 & -q_2/2 & \beta_{p2} - 1 \end{pmatrix} \begin{pmatrix} C_{p1} \\ C_s \\ C_{p2} \end{pmatrix} \quad (11)$$

Here, β_i is the propagation constant for the respective soliton or surface plasmon and $q_{1,2}$ is the coupling between the soliton and the respective surface-plasmon. For a dissipationless system, the sum of intensities is normalized: $|C_s|^2 + |C_{p1}|^2 + |C_{p2}|^2 = 1$. The dynamics become substantially more complicated but also provide features unique to coupling of three states. Notably, the soliton can be in a stationary state while mediating a coupling between the two surface-plasmon states. Evidently, an analogy to that of the BJJ of Bose-Einstein condensates in triple wells, Liu, 2007, Viscondi, 2011 can be drawn here as well. Population transfer among the soliton and surface-plasmon states can be investigated by the three level Landau-Zener formulation, Carroll, 1986. Due to the article length limitations here, we refer the reader to Aydingogun, 2018 for the details of this analysis.

3. Conclusion

The coupling between an optical soliton – surface-plasmon can give rise to new hybridized propagation modes that can be utilized to control surface plasmons via solitons. Within a semiclassical formulation, the dynamics of the coupled system can be cast into that of a Josephson junction with unique features stemming from the nonlinearity of the soliton. The present paper reviewed some of these features involving the onset of macroscopic trapping, dissipation induced population trapping, and asymmetric Rosen-Zener like transitions via spatially varying coupling.

Quite recently, experimental realization of soliton – surface-plasmon coupling in planar waveguides with a geometry very similar to that discussed here has been reported, Kuriakose, 2018. This encourages to pursue the studies to utilize this system in photonic applications.

Acknowledgements

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Sol-gel processed niobium-doped titanium dioxide for transparent conductive coatings

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Abstract

In the present work, the sol-gel method was utilised to fabricate titanium dioxide thin films with doping levels of 3-8% niobium, non-doped TiO₂ films were prepared as reference. The precursors, titanium ethoxide and niobium ethoxide, were dissolved in anhydrous ethanol, acetic acid was used to control reaction kinetics. The films were spun onto glass substrates and subjected to natural hydrolysis while being sintered at 550°C in air.

The prepared films had a blue hue that changed with increasing Nb doping. Electron microscopy and EDX studies showed smooth and homogeneous films with a grainy structure. Grain sizes were found to increase with increasing doping level.

All samples exhibited excellent transparency, with absorption values in the visible range of below 10%. Tauc plots gave band gap values of below 3.6 eV, conductivity was measured with films deposited on platinum interdigitated electrodes and highest for the sample with 8% Nb doping. In all coatings the desired anatase polymorph could be confirmed via XRD.

Indium free; transparent conductive coating; sol-gel; titanium dioxide; NTO

1. Introduction

High integrity transparent conductive coatings (TCCs) play an important role in a huge range of different applications, reaching from antireflective and low-emissivity coatings to using them for protection against electromagnetic interferences as well as in flat-panel screens and PV cells. (Chen, et al., 2011) In fact, the demand for TCCs in the renewable energy and electronics sectors is rapidly growing, as interests in solar cells, thin film LEDs and touch-screen displays are rising. (Sunde, et al., 2012; Stadler, 2012)

The industrial standard for transparent conducting coatings is indium tin oxide (ITO), which accounts for over 90% of the TCC market, due to its excellent electrical conductivity and high light transmission. (Song, et al., 2011; Sunde, 2013) ITO typically consists of up to 90% indium. (J. Liu, 2009; Kwak, et al., 2011) This strong focus on indium-based materials, leaves the industry facing a range of problems. Indium is scarce and found to be a critical technology material, showing a high and volatile price structure with limited export quota. (Furubayashi, et al., 2006; Jariwala, et al., 2015; South American Silver Cooperation, 2012) At the

same time, the production of TCCs is continuously rising, thus increasing the demand for indium. Finding an alternative is therefore highly desired.

In recent years, thin films based on titanium dioxide are generating significant interest, due to their band gap energy lying in the UV wavelength region and the resulting transparency for visible light. When suitably doped with a second metal, such as niobium, TiO₂ demonstrates good electrical conductivity (Bhachu, et al., 2014) and high transparency of up to 90%. Additionally, titanium dioxide is commercially viable because of its relatively low price and non-toxicity (Joshi, et al., 2013; Farooq & Kamran, 2013).

Conventionally, TCCs are deposited by sputter coating and subsequent wet chemical etching with concentrated acids, or by laser ablation. This route has significant limitations in cost and process efficiency, and typically achieves low yields of no more than 50% including recycling. It is therefore highly desirable to replace it with a more cost-effective, non-vacuum deposition process, such as the sol-gel method (Dsy & Ta, 2018; Song, et al., 2011).

The sol-gel method facilitates mixing of substances at a molecular level, with chemical reactions occurring in solution and at relatively low temperature, thus enabling the design of highly homogeneous materials with defined stoichiometry. In reality, different reaction kinetics of the precursors and phase separation during the gelation stage are two big drawbacks of solution-based routes.

Numerous studies have been conducted on titanium isopropoxide (Husain, et al., 2017; Bartic, et al., 2014; Ruiz, et al., 2004), however papers on titanium ethoxide are limited. To further the understanding of the usability of titanium ethoxide as precursors, in the scope of this work, titanium (IV) ethoxide and niobium (V) ethoxide have been studied. Anhydrous ethanol was used as solvent to precisely manage water addition and eliminating the possibility of alcoholysis reactions. Acetic acid is a common additive in titanium-based systems, especially to facilitate the hydrolysis stage of the sol-gel process, as discussed by Cimieri, et al., 2012. In this work acetic acid has been used to address the problem of inhomogeneous reaction speeds of the two precursors, titanium ethoxide and niobium ethoxide. The effect of niobium doping on optical, structural and electrical properties of the titanium dioxide matrix in sol-gel prepared films was evaluated. Spin-coated thin films were prepared to examine the influence of niobium on the anatase crystal structure and grain size.

2. Materials and Methods / Experimental / Theory Calculations

The sol-gel method was selected to prepare the liquid samples for spin coating. All solutions were prepared inside a glovebox with nitrogen atmosphere in order to precisely control the amount of water present in the samples before the coating step, which took place in ambient air. Chemicals were processed as received, with no additional purification.

To prepare the titanium containing sol, in a first step, anhydrous ethanol (Merck, ≥99.5%) was mixed with glacial acetic acid (≥99%, Merck). Then titanium ethoxide (Ti[OCH₂CH₃]₄) (≥99%, VERTEC ET, Alfa Aesar) was added dropwise under vigorous stirring, to form a 0.4 M solution. The molar ratio for acetic acid to titanium ethoxide was 4:1. To produce solutions with 3-8% Nb doping, the samples were stirred for 30 minutes before slowly adding niobium ethoxide (Nb[OCH₂CH₃]₅) (99.95%, Merck).

All samples were then aged for 24 hours in a glovebox prior to being taken out and deposited with an Ossila spin coater at 2000 rpm for 20 seconds in air to allow for natural hydrolysis of the thin films. Glass slides and platinum interdigitated electrodes on glass (DropSens) were used as substrates. To clean the substrates before spin coating, they were first rinsed with deionised water and detergent and then immersed in isopropanol and ultrasonicated for 10 minutes. After a second rinse with deionised water, the substrates were put into acetone and ultrasonicated for 10 minutes again, before being rinsed with deionised water in a last step and were finally blown dry with nitrogen gas. The interdigitated electrodes (IDEs) were taped at the end

that connects to the measurement unit during spin coating, to ensure that no film deposition would take place on this particular part of the IDEs, as illustrated in Fig. 1a. The tape was then removed before drying, which took place on a hot plate at 40°C for 30 minutes. The coated slides were then transferred to a Carbolite furnace and sintered in air as illustrated in Fig. 1b.

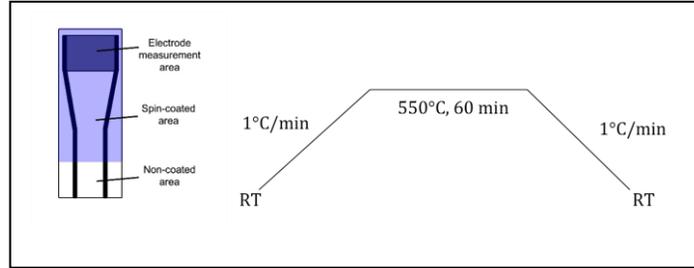


Fig. 1: (a) Illustration of IDE with coated (blue) and non-coated sections, (b) sintering program of spin-coated films

The optical assessment of the sintered films deposited on glass slides was carried out using a VARIAN Cary 50 Scan UV-visible spectrophotometer, while the VARIAN Cary WinUV software was used for data acquisition and analysis. Samples were mounted onto a sample holder and scanned over the wavelength range of 300-1000 nm. Energy bandgaps of the films were calculated using Tauc equation (Tauc, 1974):

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and E_g is the bandgap. For semiconductors with direct allowed transition, the coefficient n takes the value $\frac{1}{2}$.

A Variable Angle Spectroscopic Ellipsometry (J.A Woollam VASE) was utilised to determine the thickness as well as the extinction coefficient “ k ” and refractive index “ n ” of samples spun onto glass slides. The measurement took place over a wavelength range of 350-1700 nm with the angle of incident light set to 70°. Data analysis was undertaken with the CompleteEase 4.92 program where optical constants were calculated from the angles ψ and Δ for the wavelength of 632.8 nm.

Scanning electron microscopy (SEM) images were taken using a Quanta 3D Nano Scanning electron microscope and elemental analysis were carried out using an Oxford Instruments X-MAX EDX detector.

The formation of the desired anatase crystal structure was examined using an EMPYREAN Powder Diffractometer with a cobalt filament as X-ray source. For all measurements, the instrument was set to a voltage of 40 kV and a tube current of 40 mA. The scans were performed over the angle range of 25-70°2 θ .

Current-Voltage measurements were performed on films spun onto IDEs in ambient conditions using a Keithley 4200-SCS over the measurement range of 0-2 V. The electrical conductivity, σ , was then estimated using the following equation:

$$\sigma = \frac{I}{V} \cdot \frac{L}{W \cdot t \cdot n}$$

where the term I/V represents the gradient of the ohmic part of the measured curves, L is the gap between the fingers of the interdigitated electrode ($5\mu\text{m}$), W is the overlapping length (7mm), t is the film thickness (an average of 100 nm) and n stands for the total number of electrode fingers (500).

3. Results /Discussion

3.1 Optical Properties

The visible assessment of the sintered films is demonstrated in **Error! Reference source not found.**Fig. 2. It shows a comparison of the non-doped TiO_2 (TE0Nb) sample and a film with 5% Nb doping (TE5Nb). The blue hue is changing with niobium concentration, this was also found by Bhachu, et al., 2014. The films exhibit a smooth and homogeneous appearance with no visible cracks.

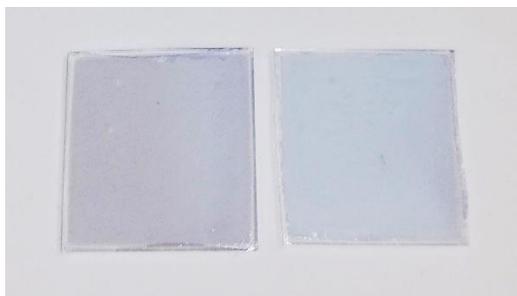


Fig. 2: Sintered films on glass, exhibiting a change in blue colour between TE0Nb (left) and TE5Nb (right)

Fig. 3 shows UV-visible spectra of pure and Nb-doped TiO_2 films. The spectra confirm the low absorption of a maximum of 10% in the visible region and a sharp increase upon reaching the UV region of the measurement range. The non-doped sample also exhibits the lowest absorption at higher wavelengths, however it shows a first absorption onset at a wavelength of around 450 nm before the typical increase in absorption for UV light. The doped films do not demonstrate this behaviour, which could be ascribed to defects in the undoped (TE0Nb) sample. Furthermore, this could be ascribed to a different electronic structure of the films and hence different excitation behaviour. This may be associated with the presence of both the brookite and the anatase phases in the produced TiO_2 as will be confirmed later in the XRD data. The onset of the absorption peak correlates with the optical band gap and thus varies with the concentration of niobium in the sample. Fig. 4 shows a comparison of average and maximum absorption values in the visible region ($400\text{-}700\text{ nm}$) vs. niobium doping level. The higher transparency for undoped films and the sharp increase in absorption is also discussed by Lee, et al., 2014.

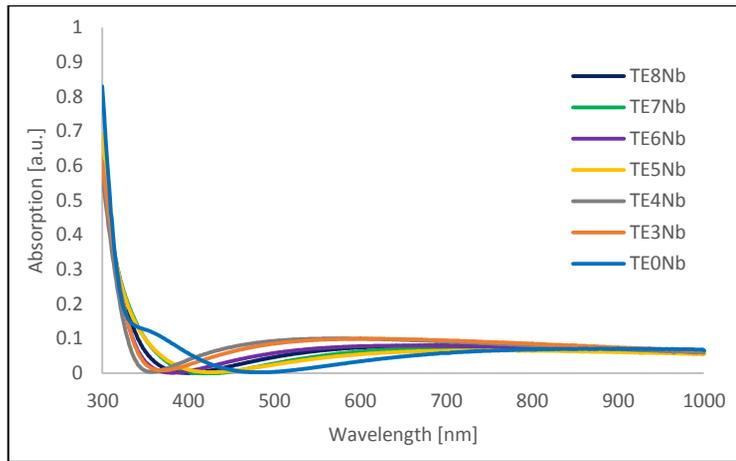


Fig. 3: Absorbance spectra of doped and undoped TiO₂:Nb films

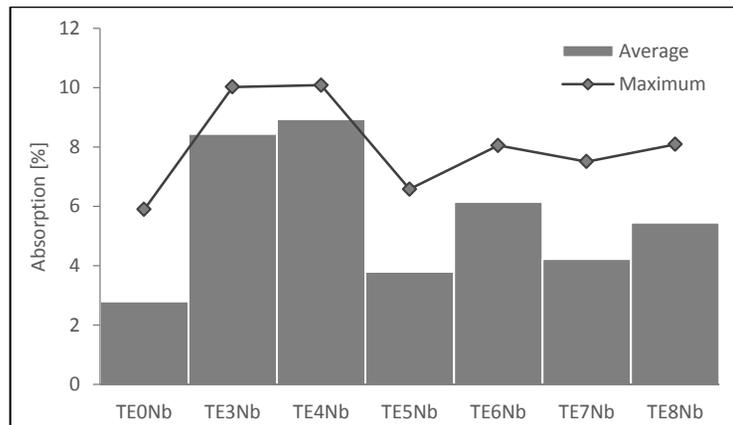


Fig. 4: Correlation of max. (line) and average absorbance (columns) from 400-700 nm with doping level

Energy band gaps of pure and Nb-doped TiO₂ films have been calculated using Tauc equation, as illustrated in Fig. 5 (analysis is shown for 7% Nb-doped TiO₂ as an example), and obtained values are summarised in Table 1. A change in band gap can arise from variations in chemical composition and probably from different grain sizes. Band gaps vary from 3.017 eV for the 5% doped sample (TE5Nb) to 3.616 eV for the undoped TiO₂ film. The values obtained in this study show the lowest band gap for the sample with 5% Nb, followed by the sample with 8% doping. This furthermore is reflected in the conductivity measurements, where those two samples exhibit the best performance. The band gap for anatase is reported to be around 3.4 eV, which is slightly lower than the bandgap obtained for the non-doped titania sample TE0Nb. One reason for this could be the occurrence of two different TiO₂ crystal structures, as can be seen in the XRD graphs. Furthermore, with samples being annealed in air, oxygen defects might play a role in raising the band gap.

Lee & Robertson, 2013 found that in case of annealing TiO₂ in an oxygen rich atmosphere, the donor effect of the dopant can be reduced, which influences the bandgap.

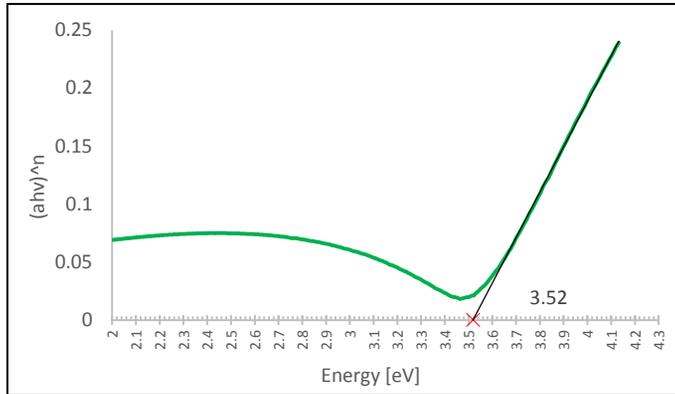


Fig. 5: Tauc plot for 7% doped TiO₂ as an example

Film thickness and optical constants were obtained using spectroscopic ellipsometry. Calculated film thicknesses range from 84.74 for the 3% doped sample to 128.32 nm for the 5% Nb doped TiO₂ film. Variations in thickness are thought to be due to changes in viscosity in the sol with Nb doping level. In Table 1 a summary of absorption values, optical constants and film thickness can be found. The lowest value for the refractive index “n” of 1.816 was found in the case of 8% Nb doped TiO₂, while the highest value of 1.871 was obtained in the sample with 3% doping. All values obtained are lower than typical n values for anatase TiO₂, which are around 2.5. These findings correlate with work undertaken by Manolea, et al., 2013. A falling trend can be observed with the extinction coefficient “k”, where values range from 2.66×10^{-5} to 3.72×10^{-4} , for TE4Nb and TE3Nb respectively. The obtained values for the refractive index and the extinction coefficient “k” are decreasing with increasing doping concentration, as shown in Fig. 6.

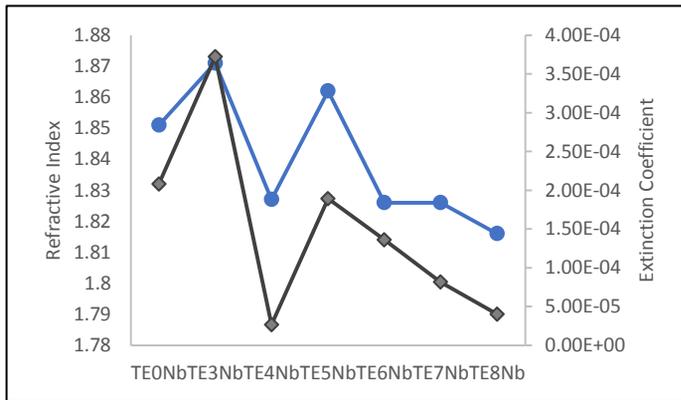


Fig. 6: Variation of refractive index (grey) and extinction coefficient (blue) with increased doping levels

Table 1: Summary of values for absorption, band gap, optical constants and film thickness

Sample	Absorption	Absorption (400-700 nm)		Band gap (eV)	n @632.8 nm	k	Thickness (nm)
	Onset (nm)	AVG (%)	MAX (%)				
TE0Nb	483.977	2.798	5.897	3.616	1.851	2.08E-04	85.02
TE3Nb	368.980	8.441	10.027	3.436	1.871	3.72E-04	84.78
TE4Nb	357.946	8.935	10.089	3.519	1.827	2.66E-05	122.83
TE5Nb	431.967	3.797	6.580	3.017	1.862	1.89E-04	128.32
TE6Nb	382.012	6.151	8.054	3.416	1.826	1.36E-04	110.10
TE7Nb	420.025	4.233	7.511	3.520	1.826	8.16E-05	104.61
TE8Nb	397.029	5.459	8.091	3.285	1.816	4.02E-05	110.06

3.2 Film Formation

Fig. 7 shows a SEM micrograph of the non-doped TiO₂ sintered films as representative example. The formation of clusters, consisting of smaller grains can be seen. Furthermore, the coatings exhibit a very smooth and crack-free structure. The results indicate a change in grain structure with increased doping levels. An estimation of the grain size in TiO₂ films, both pure and Nb-doped, shows values between 30 and 50 nm, which correlates with the data obtained via XRD measurements.

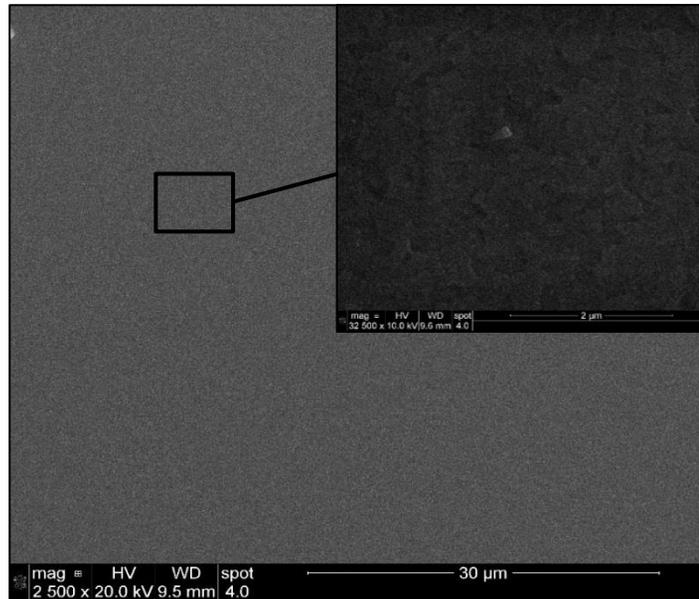


Fig. 7: SEM micrographs showing formation of clusters and grainy structure of TEONb coating

Furthermore, the samples were analysed via EDX to visualise the elemental distribution of titanium and niobium in TiO_2 coatings. Fig. 8 shows a TiO_2 film with 3% niobium doping as a representative result. All coatings demonstrate a homogeneous distribution of both elements.

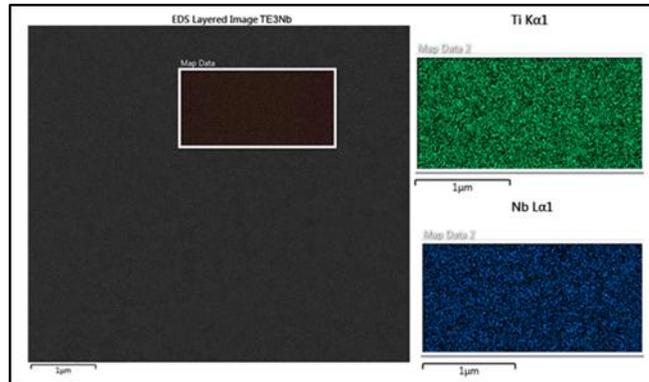


Fig. 8: EDX analysis of sample with 3% Nb concentration, showing homogeneous distribution of elements

3.3 Crystal Structure

XRD measurements were carried out in order to determine the crystalline structure of the TiO_2 films. The data confirms the formation of the desired TiO_2 anatase polymorph in all samples, as can be seen in Fig. 9. In the non-doped films, beside anatase, a second phase, namely brookite, could be detected (ICDD card number: 01-073-1764 and 04-019-9878 for anatase and brookite respectively). Gillispie, et al., 2007 have discussed the destabilisation of the anatase structure and the possible formation of the rutile phase at sintering temperatures of as low as 400°C . However, in this study, no rutile phase was present.

While there was no trend observable for other peaks, the anatase (004) peak in the thin film samples showed a gradual increase with Nb concentration. Peak shifts, as seen for the anatase (100) peak are thought to be due to stresses resulting from the incorporation the slightly larger niobium into the titanium dioxide structure.

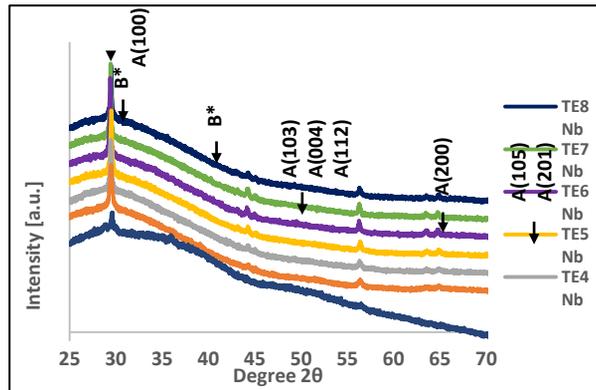


Fig. 9: XRD diffraction patterns, confirming the desired anatase crystal structure (A) and a second brookite structure (B*) occurring in TE0Nb

Hung, et al., 2011; Singh, et al., 2017 and several others have shown the incorporation of Nb into the crystal structure by substituting Ti atoms. This was confirmed by Rietveld analysis carried out in this work, as can be observed in the unit cell parameters displayed in Table 2. The ionic radii of Ti(IV) and Nb(V) are 0.0605 nm and 0.064 nm respectively (Joshi, et al., 2013), hence only a small change in the lattice parameters is seen. For all compositions, except TE7Nb, the lattice parameter a is gradually increasing however no clear trend for c can be observed.

Table 2: Summary of changes in TiO₂ lattice parameters and cell volume with increasing Nb incorporation into the anatase structure

Samples	Unit Cell (Å)		Cell Volume (Å ³)
	a	c	
TE0Nb	3.776(0)	9.486(0)	135.25
TE3Nb	3.790(1)	9.500(3)	136.43
TE4Nb	3.792(3)	9.514(9)	136.79
TE5Nb	3.7925(8)	9.509(3)	136.77
TE6Nb	3.793(1)	9.507(5)	136.78
TE7Nb	3.789(4)	9.501(9)	136.41
TE8Nb	3.795(1)	9.510(3)	136.95

The Debye-Scherrer formula was used to calculate grain sizes in pure and Nb doped TiO₂ films. The non-doped sample exhibits a grain size of 24.52 nm, while calculations show an increase in grain size in the 3, 4, 6 and 7% doped films with values of 31.60 nm, 48.89 nm, 52.68 nm, 54.71 nm respectively. The trend is interrupted by the 5% and 8% samples with particle sizes of 46.79 nm and 42.23 nm.

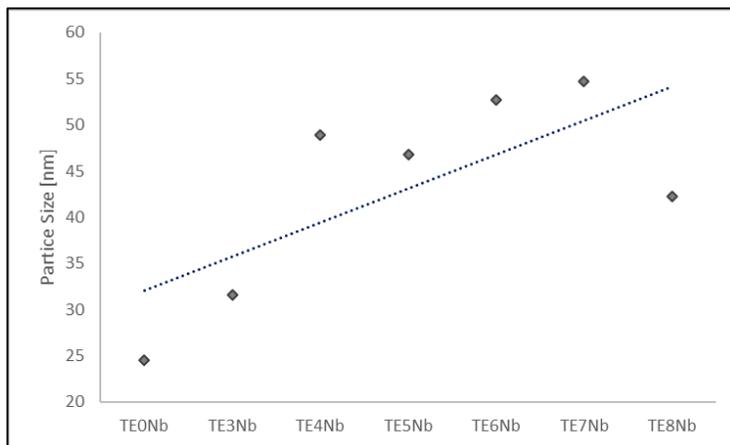


Fig. 10: Particle size distribution with changing doping level

3.4 Conductivity

To calculate the conductivity from I-V curves, a thickness of 100 nm for the coatings was chosen, due to average values obtained from spectroscopic ellipsometry measurements of previous samples deposited on glass slides. The highest calculated value was achieved for the sample with 8% Nb doping, followed by the 5% doped sample. The lowest conductivity was found in the sample with a concentration of 7% niobium, as can be seen in Table 3. Fig. 11 illustrates the change in conductivity with increasing doping level.

Table 3: Summary of conductivity measured for thin films on IDEs

Sample	Conductivity (S/cm)
TE0Nb	1.60×10^{-6}
TE3Nb	1.18×10^{-6}
TE4Nb	1.13×10^{-6}
TE5Nb	5.49×10^{-5}
TE6Nb	1.31×10^{-6}
TE7Nb	2.07×10^{-7}
TE8Nb	1.17×10^{-4}

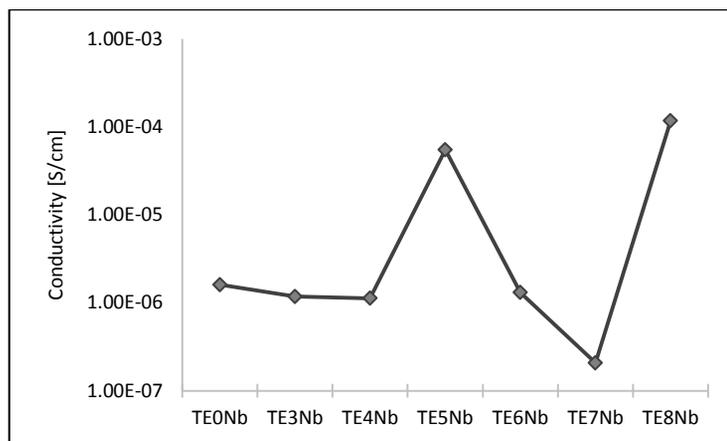


Fig. 11: Variation of conductivity of TiO₂ films with Nb doping concentration

4 Conclusion

Niobium doped titanium dioxide films were successfully prepared with the sol-gel method. All samples exhibited a blue colour that changed with increasing Nb concentration. UV-visible spectroscopy measurements showed low absorption of below 10% for the coatings over the whole measurement range. TiO₂ films exhibited the lowest energy bandgaps for samples with 5 and 8% Nb doping. Spectroscopic Ellipsometry suggests that optical constants, such as refractive index and extinction coefficient, decreased with increasing dopant level and reached a minimum for samples with 4% and 8% Nb respectively. Electron microscopy shows a smooth and crack-free coating with small grains forming clusters. EDX scans reveal a homogeneous distribution of niobium in the titanium dioxide matrix. For all samples the desired anatase crystal structure could be confirmed via XRD analysis, however the un-doped sample also contained brookite phase. The anatase (100) peak showed a slight shift to lower angles with increasing Nb concentration, which is thought to be due to stress caused by the incorporation of niobium into the lattice. Best conductivity was measured for TiO₂ films with 8% Nb doping.

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Crystal structure and surface phase composition of palladium oxides thin films for gas sensors

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Abstract

At detection of ozone and nitrogen dioxide gas sensors based on palladium (II) oxide thin and ultrathin films have shown good sensitivity, signal stability, operation speed, short recovery period, and reproducibility of the sensor response. In this work the influence of oxidation temperature on crystal structure and surface properties of palladium (II) oxide thin films prepared by oxidation at dry oxygen on SiO₂/Si (100) substrates has been studied by X-ray diffraction (XRD), electron probe microanalysis (EPMA), and X-ray photoelectron spectroscopy (XPS). By EPMA EDX it has been established that oxygen atom concentration increased in PdO/SiO₂/Si heterostructures with the rise of oxidation temperature. At oxidation temperature interval $T = 570 - 1020$ K the values of lattice parameters and unit cell volume of PdO film tetragonal crystal structure increased also. Regardless of oxidation temperature by XPS measurements it has been found that palladium

oxide films had three components of each Pd 3d 5/2 peaks which can be attributed to PdO, PdO₂, and Pd(OH)_x. Analysis of peak component contribution has shown that palladium (II) oxide was the dominant surface phase with relatively low value of the pronounced PdO₂ component. The obtained experimental data specify that the deviation from stoichiometry, excess oxygen concentration, and *p*-type conductivity can be caused by interstitial oxygen atoms in PdO films.

Keywords: palladium oxides; gas sensor; ozone; nitrogen dioxide; crystal structure; XPS measurements; surface state

1. Introduction

It is well known that most of the atmospheric ozone (~90%) is located in the stratosphere with a maximum concentration between 17 and 25 km above sea level [1]. However, since 1995 in industrialized countries the ecologists observe an ozone permanent accumulation at the earth's surface that can be very dangerous. World Health Organization (WHO) and United States Environmental Protection Agency (US EPA) declared that three out of six common air pollutants (also called as "criteria pollutants") are the oxidizing gases: sulfur dioxide, nitrogen oxides, and low level ozone (or tropospheric ozone) [2, 3]. The negative impact on human health of noxious oxidizing gases (nitrogen oxides, ozone, sulfur dioxide, and chlorine) formed as the by-product of many modern technologies is very serious. Breathing ozone and nitrogen oxides can trigger a variety of human health problems, particularly for children, the elderly, and people who have lung diseases [2, 3]. On toxicity ozone is comparable to the chemical weapon phosgene. Moreover, interaction of O₃ and NO_x with the volatile hydrocarbons can produce many toxic organic compounds [4].

Unlike many other toxic gases, for example, hydrogen sulphide or ammonia, ozone has no strongly pronounced characteristic smell, therefore it is very difficult to establish its presence in atmospheric air without special apparatuses [1]. The design of the portable individual devices, which are capable to define precisely the ozone and nitrogen dioxide concentration within admissible values, is extremely urgent task. For these reasons, the various types of the binary, ternary and quaternary metal-oxide semiconductors have been widely studied for oxidizing gas detection. In most cases for this purpose the *n*-type semiconductors such as SnO₂ [5–6], ZnO [7–8], WO₃ [9–10], In₂O₃ [11–12], and TiO₂ [13] are traditionally studied.

In recent years, the search for the materials, which could lower the detection limit of oxidizing gases, became more active. With the increasing attention the scientists study *p*-type semiconductors and composites on their basis [14]. For example, the sensor materials based on Cu₂O nanoflowers [15], NiO nanofibers [16], porous NiO microspheres [17], and copper (II) oxide nanostructures [18–19] have been synthesized. For the detection of oxidizing gases the nanocomposites with *p-n*-heterojunction have been used [20–21] as well as the composites based on graphene with *p-n*-heterotransitions are of great interest too [22–23].

In 2016 the experimental results on palladium (II) oxide thin and ultra thin film gas sensor properties were published for the first time [24–25]. The choice of palladium (II) oxide as the material for gas sensors was not incidental. It was done for some reasons. Firstly, a long recovery process and high stability could be referred to the main disadvantages of the SnO₂-based oxidizing gases sensors [26–28]. Secondly, late transition metals, such as Pd, Pt and Au, are widely used as additives to improve gas-sensing performance of tin dioxide, indium oxide and others *n*-type metal oxide semiconductors [29]. Thirdly, there is an opinion that for oxidizing gases detection the metal oxide semiconductors with *p*-type conductivity would be more effective than materials with *n*-type conductivity [14].

The measurement results of Seebeck coefficient and Hall effect verified the fact of *p*-type conductivity of

PdO thin films [30–31], which was known from previous publications [32–33]. Palladium (II) oxide nanostructures demonstrated convincingly that they are the promising candidates for the detection of oxidizing gases in atmospheric air [4, 24–25]. At O₃ and NO₂ detection the gas sensors based on PdO nanostructures such as ultrathin and thin films have shown an excellent sensitivity, signal stability, operation speed, short recovery period, and reproducibility of the sensor response [30–31, 34].

So far there is no exact and definite answer to the question of the nature of the intrinsic point defects which are responsible for the nonstoichiometry and *p*-type conductivity of palladium (II) oxide. In this work one step forward to the solution of this problem has been taken.

The main purpose of this study is to recognize the evolution of chemical composition of surface phase and crystal structure of palladium (II) oxide thin films upon the oxidation temperature in dry oxygen.

2. Experimental

2.1. X-ray diffraction study of PdO films

In detail the two-stage procedure of palladium oxide thin film synthesis was described previously [24–25, 30–31, 34]. Firstly, the initial Pd films (with thickness ~ 35 – 40 nm) were formed by thermal sublimation of palladium foil (purity 99.99 per cent) in a high vacuum chamber evacuated to 6.65×10^{-4} Pa. The condensation of Pd metal vapours was performed on Si (100) substrates with SiO₂ layer (thickness *d* ~ 300 nm). SiO₂/Si (100) substrates were used to prevent the possible interaction of Pd and Si at high temperature. This approach has yielded the positive results (Figure 1).

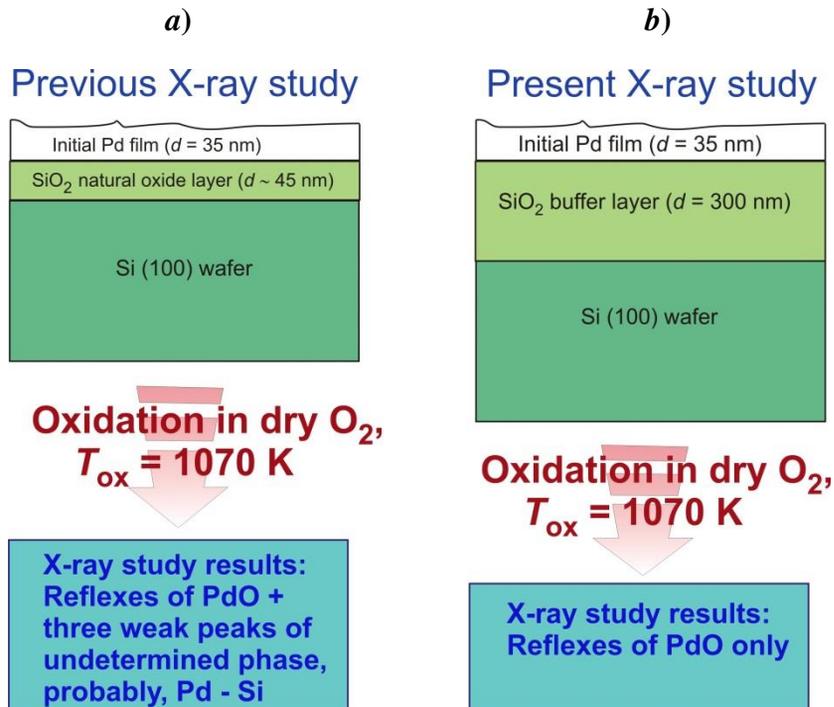


Fig. 1. Illustration of previous (a) and new advanced approach (b) for preparation and research of PdO films on Si substrates.

Initial Pd layers were annealed at dry oxygen atmosphere for 2 hours at temperatures $T_{ox} = 570, 670, 770, 870, 970,$ and 1070 K. According to previous X - ray diffraction (XRD) results [30] the oxidation of initial Pd at temperature range $T_{ox} = 770 - 870$ K led to the formation of homogenous polycrystalline PdO films (space group $P4_2/mmc$). It has been determined that PdO films prepared by oxidation at $T_{ox} = 1070$ K showed three weak peaks of XRD patterns that could not be assigned to palladium (II) oxide [30]. The reflex number did not allow us to determine precisely what phase or phases they belong to. With equal probability and equal inaccuracy these peaks meet $Pd_{3.5}O_4$ phase or one of palladium silicides. As it can be seen in Figure 2 c, PdO films synthesized on Si (100) substrates with SiO_2 layer (thickness $d \sim 300$ nm) are homogenous also.

It should be noted that in this work the data on evolution of palladium (II) oxide film crystal structure depending upon the oxidation temperature are obtained for the first time. Therefore X - ray diffraction (XRD) experiment and quantitative calculations of PdO lattice parameters have been executed with special thoroughness. At the first stage in 2θ region of $20 - 120$ degrees XRD patterns of PdO films were obtained with filtered $CuK\alpha$ -radiation ($\lambda = 0.15405$ nm) on DRON - 4 M diffractometer with 0.02 degree step-by-step movement and sample rotation. These results (Figure 2) have shown that all PdO films prepared by oxidation in dry oxygen at $T_{ox} = 670 - 1070$ K were homogeneous. At the second stage the profiles of PdO film XRD reflexes have been obtained on DRON - 4 M ($CoK\alpha$ -radiation, $\lambda = 0.178897$ nm) and Philips PANanalytical X'Pert ($CuK\alpha$ -radiation, $\lambda = 0.15405$ nm) diffractometers with 0.01 degree step-by-step movement. The single crystal Si (100) substrates were used as internal standards to minimize the random errors. The diffraction angle values were determined as the XRD reflex centroids taking into account the peak asymmetry.

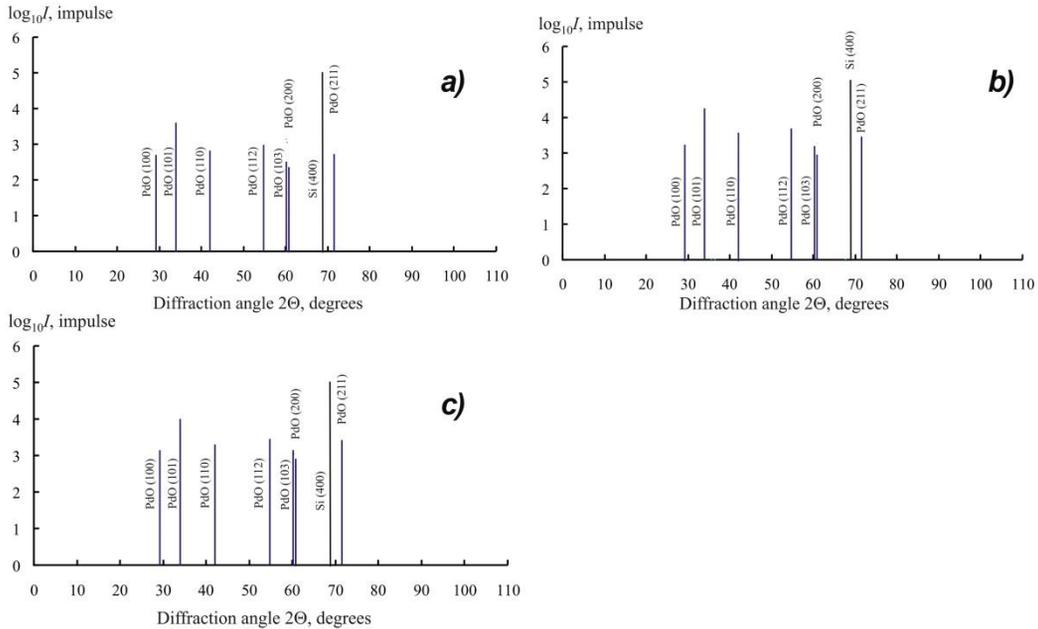


Fig. 2. XRD patterns of palladium (II) oxide films on Si (100) substrates prepared by oxidation in dry oxygen at different temperature: a) $T_{ox} = 670$ K; b) $T_{ox} = 870$ K; c) $T_{ox} = 1070$ K.

The values of lattice constant a and c of palladium (II) oxide tetragonal structure (Figure 3) have been calculated using the special software based on solution algorithm for quadric equation system with two unobvious parameters. Nelson-Riley approximation for $2\Theta = 180$ degrees diffraction angle has been performed for the refinement and more precise determination of a and c lattice constant values.

$$f(\theta) = 0.5 \times \left(\frac{\cos^2 \theta}{\theta} + \frac{\cos^2 \theta}{\sin \theta} \right) \quad , \quad (1)$$

where Θ is diffraction angle (radian).

The target values of a and c lattice constants, for example a_0 , have been calculated by linear approximation of $a = k \times f(\Theta) + a_0$ using the least-squares method.

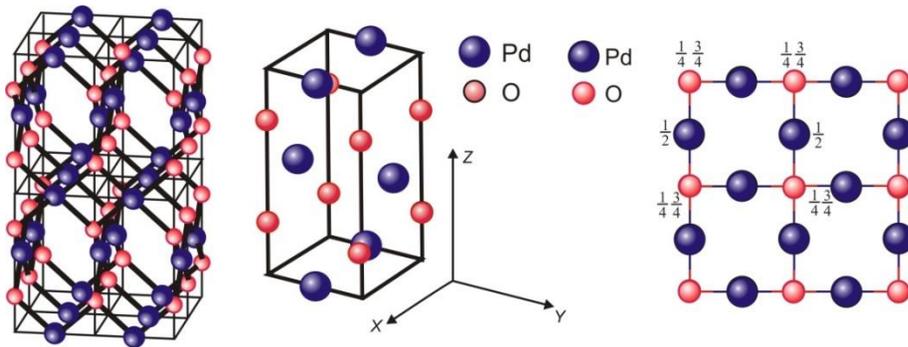
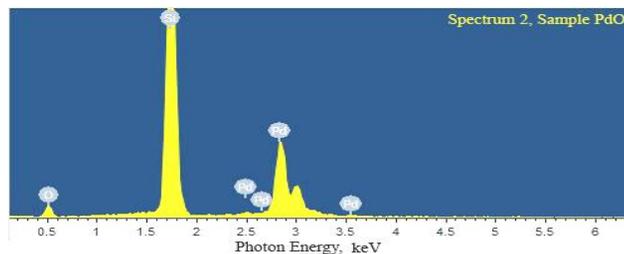


Fig. 3. Tetragonal crystal structure of palladium (II) oxide (a); unit cell of PdO crystal structure (b); projection of four PdO unit cells onto (001) plane – XOY plane (c).

2.2. Analysis of chemical composition of PdO films

The chemical composition of PdO/SiO₂/Si heterostructures was studied by electron probe microanalysis (EPMA) on JEOL JSM 6380 LV equipped with Oxford Instruments INCA X-sight LN2 energy dispersion spectrometer (EDX). In a scanning mode EPMA EDX measurements were performed in five regions of each PdO sample (Figure 4). EDX measurement error was defined by statistical data manipulation and was evaluated as $\Delta x = \pm 0.15$ atomic percent.



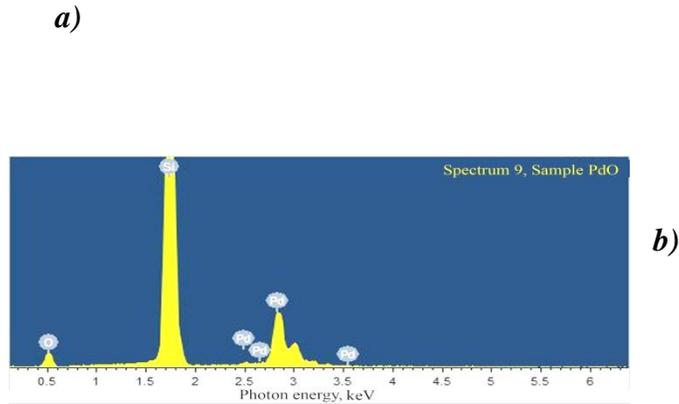


Fig. 4. EDX spectra of PdO/SiO₂/Si heterostructures prepared by oxidation in dry oxygen at different temperature: a) $T_{\text{ox}} = 670$ K; b) $T_{\text{ox}} = 870$ K.

2.3. X-ray photoelectron spectra of PdO films

X-ray photoelectron spectra of palladium (II) oxide films were obtained with the use of highly brilliant synchrotron radiation of Helmholtz Zentrum Berlin (Berlin, Germany) BESSY II storage ring. Russian-German beamline (RGLB) was used together with multitask spectrometer equipped with SPECS PHOIBOS 150 hemispherical electron energy analyzer. Synchrotron photon energy used to excite Pd 3d core level was 800 eV with instrumental broadening ~ 0.1 eV, the highest photon flux of 10^{12} photons/sec, storage ring current of 250 mA in top-up operation mode. The analysis depth was found to be about 1.5 nm [35]. Ultra high vacuum conditions in analytical chamber necessary to conduct high resolution XPS experiment were maintained at 10^{-10} Torr. The calibration and the normalization of the spectra were carried out using a signal of pure gold film and the position of its core 4f level and the Fermi level under the recording conditions identical to those of the studied samples. During the XPS measurements, the registered core level energies were also controlled by the position of the C 1s level of hydrocarbon contamination residuals on the sample surfaces reduced to the known value of 285.0 eV [36–37].

3. Results and Discussion

3.1. Phase characterization of palladium (II) oxide films

XRD patterns of samples prepared by oxidation of initial Pd films in dry oxygen atmosphere at $T_{\text{ox}} = 670, 770, 870, 970,$ and 1070 K are shown in Figure 2. It is necessary to note that owing to a small thickness of the prepared palladium (II) oxide films in Figure 2 the values of XRD reflex intensities are presented in a logarithmic scale since the intensity of Si (400) peak exceeds practically the intensity of PdO peaks by two orders of magnitude. According to XRD results (Figure 2), the oxidation of initial Pd layers on Si (100) wafers with SiO₂ layer (thickness ~ 300 nm) at temperature range $T_{\text{ox}} = 570 - 1070$ K led to the formation of homogenous polycrystalline PdO films. This fact contradicts the data published earlier [30] which were obtained in the study of palladium (II) oxide films on Si substrates with thinner layer of silicon dioxide. In all probability, the SiO₂ layer with 300 nm thickness prevented an interaction of palladium and silicon.

3.2. Chemical composition of PdO/SiO₂/Si heterostructures

Table 1. EDX analysis data of PdO films on SiO₂/Si (100) substrates (oxidation atmosphere - dry oxygen).

Oxidation temperature $T_{ox} = 870$ K			
Element	X-ray spectrum line	Mass fraction $\omega\%$, percent	Mole fraction x , percent
Palladium	<i>L</i> - line	36.64	11.85
Oxygen	<i>K</i> - line	11.34	24.40
Silicon	<i>K</i> - line	52.02	63.75
Total:		100.00	100.00
Composition	$x(\text{Pd}) : x(\text{O}) = 1 : 2.059 \pm 0.004$		
Oxidation temperature $T_{ox} = 1070$ K			
Element	X-ray spectrum line	Mass fraction $\omega\%$, percent	Mole fraction x , percent
Palladium	<i>L</i> - line	36.475	11.78
Oxygen	<i>K</i> - line	11.40	24.47
Silicon	<i>K</i> - line	52.125	63.75
Total:		100	100
Composition	$x(\text{Pd}) : x(\text{O}) = 1 : 2.080 \pm 0.004$		

The quantitative element composition of homogeneous PdO films on SiO₂/Si substrates was studied by EPMA EDX method. In Table 1 the EDX measurement data which have been obtained with the maximum possible measures directed at increasing of the accuracy and reproducibility results are presented.

Undoubtedly, EDX results of the determination of oxygen atom concentration in PdO/SiO₂/Si heterostructures are not exact and ultimate (Table 1, Figure 4). These data testify that the region of the EDX analysis was not limited by PdO film and stretched into SiO₂ layer and silicon substrate. Nevertheless, the presence of systematic procedural bias does not interfere with tracking the tendency of oxygen atom concentration change in PdO/SiO₂/Si heterostructures.

The calculation results of the ratio of oxygen mole fraction and palladium mole fraction

$$\chi = \frac{x_{\text{O}}}{x_{\text{Pd}}} \quad , \quad (2)$$

where x_{O} – mole fraction of oxygen atoms, x_{Pd} – mole fraction of oxygen atoms in PdO/SiO₂/Si heterostructure, are shown in Figure 5.

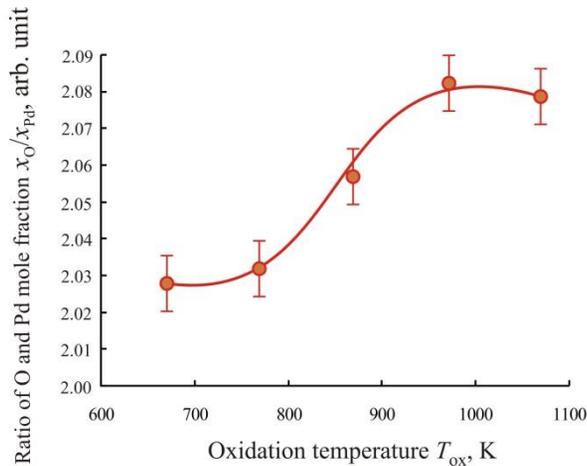


Fig. 5. Dependence of palladium and oxygen mole fraction ratio χ in PdO/SiO₂/Si heterostructures upon the oxidation temperature.

The data in Table 1 and curve $\chi = x_{\text{O}}/x_{\text{Pd}} = f(T_{\text{ox}})$ in Figure 5 show the increase in the oxygen atom concentration with the rise of oxidation temperature up to $T_{\text{ox}} = 970$ K. Valence-saturated and the most stable chemical bond between Si and O atoms causes extremely narrow homogeneity region of silicon dioxide, what it is impossible to expect for palladium (II) oxide. Evidently, the increase in oxygen atom concentration in PdO/SiO₂/Si heterostructures (Figure 5) cannot be explained by interaction of O₂ molecules with SiO₂ layer. Therefore, the increase in the oxygen atom concentration is caused by O₂ interaction with palladium atoms during oxidation process (Figure 4). The conclusion that with the rise of oxidation temperature the oxygen concentration increases due to saturation of palladium (II) oxide is quite reasonable. Some reduction of oxygen atom concentration at $T_{\text{ox}} = 1070$ K is explicable in view of the known facts about palladium (II) oxide thermal decomposition in the temperature range of about $T = 1070 - 1120$ K [38].

3.3. Evolution of crystal structure of palladium (II) oxide films

In Figure 6 the calculation results of a and c lattice constant of palladium (II) oxide film with tetragonal crystal structure (Figure 3) are shown. As it can be seen, the a and c unit cell parameter values increase monotonously with the rise of oxidation temperature up to $T_{\text{ox}} = 970$ K. Incidentally, the lattice values of constant a are higher than ASTM etalon a value for oxidation temperature interval $T_{\text{ox}} = 770 - 1070$ K (Figure 6 a). The interval of oxidation temperature at which c values are above the ones for ASTM etalon, is essentially narrower: from $T_{\text{ox}} = 870$ to $T_{\text{ox}} = 1070$ K only (Figure 6 b).

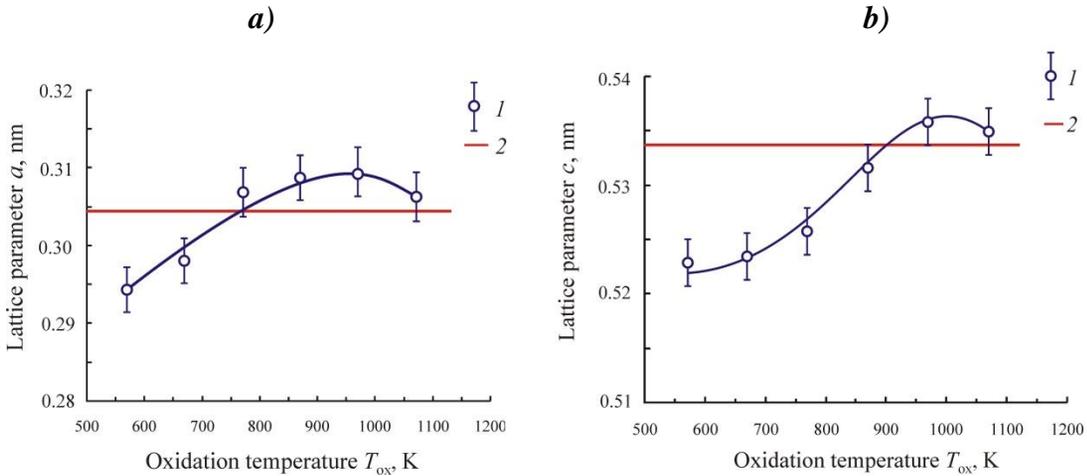


Fig. 6. Dependence of lattice constant a (a) and lattice constant c (b) of PdO film tetragonal crystal structure upon the oxidation temperature: 1 – experimental results; 2 – ASTM etalon data [39].

As it can be seen from the calculation results, the volume V of unit cell of palladium (II) oxide film crystal structure (Figure 7) increases monotonously at oxidation temperature rise from $T_{\text{ox}} = 670$ to $T_{\text{ox}} = 970$ K. The values of V for PdO film unit cell exceed the volume of ASTM etalon unit cell [39] in the temperature range $T = 770 - 1070$ K.

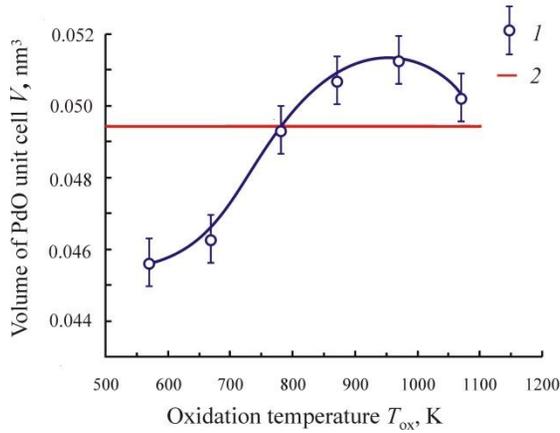


Fig. 7. Dependence of unit cell volume V of PdO films upon the oxidation temperature:

1 – experimental results; 2 – ASTM etalon data [39].

It is also informative to trace the evolution of unit cell parameters ratio c/a of PdO films depending upon the oxidation temperature (Figure 8). At oxidation temperature range $T_{ox} = 570 - 820$ K the decrease in c/a value indicates an anisotropic distortion of PdO film tetragonal crystal lattice mainly by virtue of the parameter a increasing. Therefore, the enlargement of PdO unit cell (Figure 7) is predominantly caused by increase in parameter a values. At further rise of oxidation temperature up to $T_{ox} = 920$ K the continued enlargement of PdO unit cell is accompanied by the decrease in the anisotropic distortion of PdO film tetragonal crystal lattice (Figure 3). At $T_{ox} = 1070$ K the insignificant reduction of the values of PdO film crystal structure a and c parameters (Figure 6) does not contradict the EDX data on the decrease in oxygen atom concentration at this temperature (Figure 5). Probably, the phase diagram of palladium (II) oxide is characterized by the retrograde solidus line.

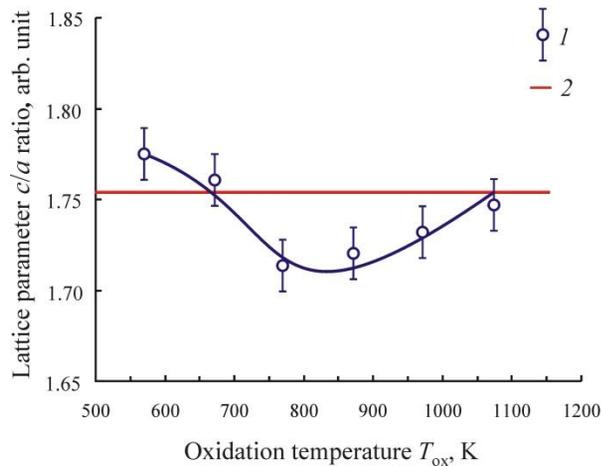


Fig. 8. Dependence of lattice constant c and lattice constant a ratio of PdO film tetragonal crystal structure upon the oxidation temperature: 1 – experimental results; 2 – ASTM etalon data [39].

3.4. XPS study of surface state of palladium (II) oxide films

Figure 9 demonstrates the comparison of XPS surveys recorded for palladium oxide films prepared at $T_{ox} = 870$ and 1070 K. For the comparison of XPS relative intensity distribution features these spectra have been rearranged under one intensity (spectrometer counts) ratio. Core levels peaks of palladium ($3p$, $3d$ and $4d$ states), oxygen ($1s$ states) and carbon ($1s$ states) can be clearly observed for both samples as well as palladium Auger MNN transition feature. Carbon states are usually observed on the surface of samples taken from the ambient and are characteristic of the surface hydrocarbon contaminants. For the sample prepared by oxidation at $T_{ox} = 1070$ K the low-intensity feature of silicon ($2p$ states) is also detected and most likely originates from the substrate used. This observation can be explained

It should be noted that the energy position of $1s$ oxygen states are overlapped with $3p_{3/2}$ states of palladium according to the known core levels binding energy values [35, 37, 40–41]. The relative intensity ratio between $O1s + Pd\ 3p$ peaks and $Pd\ 3d$ doublet is nearly the same, which indicates the similarity of surface chemical state in both studied samples.

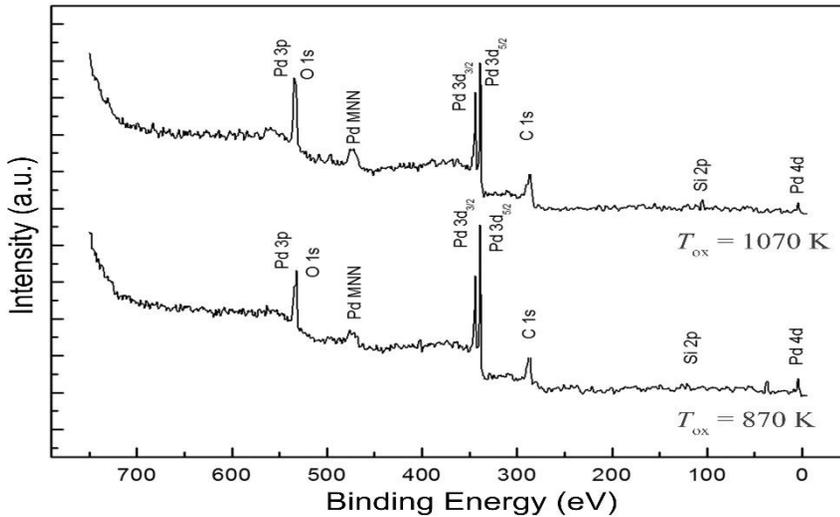


Fig. 9. XPS surveys recorded for palladium oxide films prepared by oxidation at $T_{ox} = 870$ K and 1070 K. Synchrotron quanta excitation energy was 800 eV.

Because of similarity between the $O1s$ and $Pd\ 3p$ binding energies values, we have decided to consider more precisely the most intensive (Figure 9) $3d_{5/2}$ core level of palladium. Figure 10 displays XPS spectra of $Pd\ 3d_{5/2}$ core level taken from the samples oxidized at $T_{ox} = 870$ K and 1070 K. For the component fitting presented in Figure 10 we have used standard Shirley procedure of background removal [42].

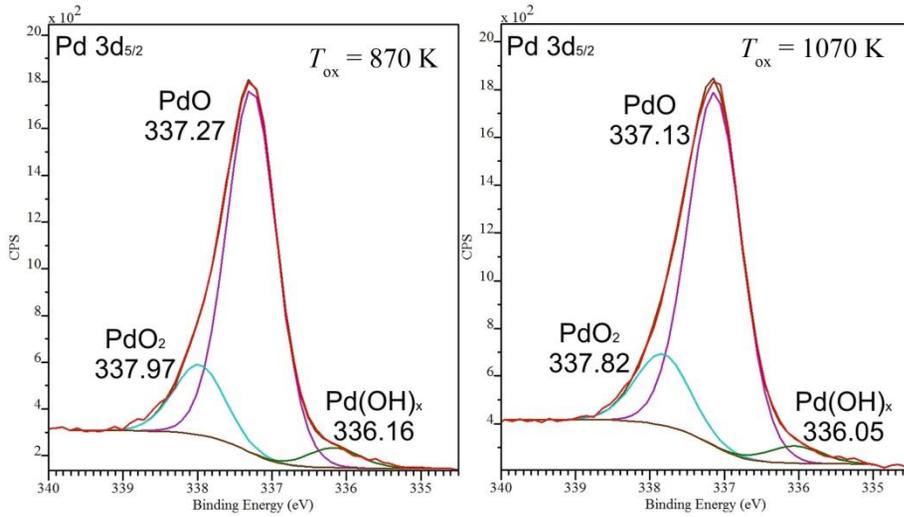


Fig. 10. High resolution XPS Pd 3d_{5/2} core level for palladium oxide films prepared by oxidation at $T_{ox} = 870$ K (a) and 1070 K (b).

Both recorded spectra have three distinct components that are peculiar to palladium oxide PdO [43, 44], PdO₂ [43 – 45], and Pd(OH)_x [43, 44]. Very close relative intensity ratio of three components for both samples indicates the similar palladium oxidation states in the investigated surface layers. These observations of three components simultaneously are in good agreement with the known binding energy values for PdO, Pd(OH)_x, and PdO₂ phases discussed previously [43–44]. Thus, the oxidation of palladium films at $T_{ox} = 870$ and 1070 K does not cause the noticeable changes in the surface composition of palladium oxide films.

3.5. Summarizing of the experimental results

The detection of XPS signal corresponding to palladium dioxide PdO₂ deserves a special consideration (Figure 10). This fact can be interpreted as confirmation of presence on the surface of PdO films of an insignificant quantity of palladium atoms in extra (+4) oxidation state. In other words, on PdO film surface there are the excess oxygen atoms which can oxidize palladium atoms to extra (+4) oxidation state. In PdO films the presence of Pd (+4) atoms assumes the other coordination of palladium atom with oxygen ones, which should differ from Pd – O coordination in PdO crystal structure (Figure 3).

The authors of previous publications maintained that palladium (II) oxide samples were characterized by a small excess of oxygen atoms compared to stoichiometry ratio of the elements [46–47]. Besides, the hypothesis exists that *p*-type conductivity of PdO films with excess concentration of oxygen is caused by the formation of palladium vacancies V_{Pd} [47]. Within the framework of solid state chemistry and Kröger – Vink notation the *p*-type conductivity of undoped PdO can be explained by the formation of intrinsic point defects both of palladium vacancies V_{Pd}^{\times} and oxygen atoms in interstitials O_i^{\times} [48]:

1. The formation of palladium vacancies V_{Pd} during oxidation of initial Pd films:



The neutral Pd vacancies V_{Pd}^{\times} can ionize with the generation of holes:



or



where V_{Pd}' is singly ionized palladium vacancy, V_{Pd}'' is doubly ionized palladium vacancy, h^{\bullet} is hole.

2. The formation of oxygen atoms in interstitials O_i^{\times} during oxidation of initial Pd films:



The neutral oxygen atoms in interstitials O_i^{\times} can ionize with the holes formation



or



where O_i' is singly ionized interstitial oxygen atom, O_i'' – doubly ionized interstitial oxygen atom, h^{\bullet} – hole.

4. Conclusion

The analysis of the experimental data obtained in this work allows us to state the oxidation temperature impact on the oxygen atom concentration and crystal structure distortion of palladium (II) oxide films. In PdO films the rise of oxidation temperature from $T_{ox} = 570$ to $T_{ox} = 970 - 1020$ K leads to the increase in oxygen atom concentration which is accompanied by anisotropic increase in crystal structure unit cell volume mainly due to the increase in a lattice constant value. In total with presence of palladium dioxide PdO₂ established by XPS measurements the obtained experimental data specify that the deviation from stoichiometry, excess oxygen concentration, and p -type conductivity can be caused by interstitial oxygen atoms O_i in the crystal structure of PdO films.

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Nonlinear optical properties of hydrogenated amorphous silicon-chalcogen alloys thin films

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Abstract

Hydrogenated amorphous silicon-chalcogen alloys thin films were grown by capacitively coupled radio frequency glow discharge technique. Chalcogens used in this experiment are mainly sulphur and selenium. Diluted SiH₄, and H₂S or H₂Se gas mixtures were used in the preparation process to reduce potential hazardous outcome. Infrared spectroscopy shows that the material exhibits characteristic vibrational modes of sulphur or selenium in a silicon matrix. Nonlinear properties of the silicon alloys were investigated using z-scan technique. The measurements were carried out at various excitation powers using continuous HeNe laser source at excitation wavelengths of 632.8 nm. For each excitation power, the nonlinear absorption and nonlinear refractive index coefficients were measured. It was found that these films are dominated by a reverse saturation absorption process and a positive refractive index. The origin of nonlinearities was discussed in terms of single photon absorption and reverse saturation absorption. The third order nonlinear optical susceptibility $\chi^{(3)}$ was calculated for given input power. It was shown that a-Si, S:H and a-Si, Se:H alloys exhibit significant optical limiting properties.

Keywords: Thin films; amorphous silicon- sulphur/selenium alloys; z-scan; coefficient of nonlinear absorption; reverse saturable absorption.

1. Introduction

Hydrogenated amorphous silicon-chalcogen alloys have been shown to exhibit attractive optical and electronic properties [Aljishi et. al, 1991; Al Dallal et. al., 1991, 2010; Al Dallal, 2015]. An interesting feature of this material is that has potential applications in a wide range of optical devices. The silicon-chalcogen bond is stronger than the silicon-silicon bond, and therefore, the introduction of chalcogen atoms in the silicon matrix enhances appreciably the stability of this material against aging. Optical nonlinearity is a key process in characterizing materials to probe their potential applications in optical devices. Nonlinear effects include various types of phenomenon, such as third order nonlinear susceptibility, free carrier absorption, reverse saturation absorption (optical limiting), self-focussing, and self-defocusing. The nonlinear optical properties of silicon based materials, such as amorphous silicon, silicon nanocrystal, and porous silicon, have been the subject of intense research work during the past decade [Parkash et. al., 2002; Henari and Blau, 1992; Derkowska et. al., 2004; Banfi et. al., 1994]. Nonlinearities in a-Si are manifested as an intensity dependent absorption, giving rise to optical limiting behaviour via saturation trapping states. Since these states exhibit a slow relaxation time, it should be possible to measure the nonlinear behaviour at low power irradiation.

In this work we report measurements of the nonlinear properties of hydrogenated amorphous silicon-chalcogen alloys thin films using continuous 632.8 nm HeNe laser line. Measurements were carried out using z-scan technique for various laser light powers. Both nonlinear absorption and nonlinear refractive index were measured. However, it was found that at this excitation wavelength the nonlinear absorption was the dominant effect, whereas the nonlinear refractive index is relatively weak. For the nonlinear absorption, an estimation of the excited state cross section has been carried out. We also demonstrate how nonlinear absorption can be used to characterize the optical limiting properties of the material.

2. Experiments

Hydrogenated silicon-chalcogen alloys thin films were prepared by capacitively coupled r.f. glow discharge technique. A controlled flow of gas mixtures of (5% SiH₄ + 95%He) and (2% H₂S or H₂Se +98% He) has been used to deposit thin films of the alloys on 7059 Corning glass substrate. Helium gas was employed for safety purposes. The substrate temperature was held at 250 C^o and the process pressure was maintained at 0.4 Torr. The total plasma power was kept at 30 Watts, and the corresponding power density is 160 mW/cm². The total flow rate was maintained at 40 sccm. Under these conditions the growth rate was about 2Å/s for equal flow rates of silane (SiH₄) and hydrogen sulphide (H₂S) or Hydrogen selenide (H₂Se) mixtures. The deposition rate was found to be a function of the gas volume ratio $R_v = [\text{chalcogen/silane}]$. Linear absorbance of samples were measured using dual beam spectrophotometer.

The nonlinear properties of the samples were characterized using z-scan set up, as illustrated schematically in Fig.(1). The coefficient of refraction has been determined by placing an aperture in front of the detector and

measuring the transmitted light (close aperture configuration). This approach increases the sensitivity of measurement to beam spreading or beam focusing. In this set-up the sample displaying nonlinear refraction will act as a lens that exhibits variable focal length as it transit along the z-axis. For measurements of the nonlinear absorption coefficient the aperture was removed (open aperture configuration). The transmittance versus the sample position is now symmetric around the focus, because the intensity distribution of the laser's Gaussian beam is also symmetric around the focus.

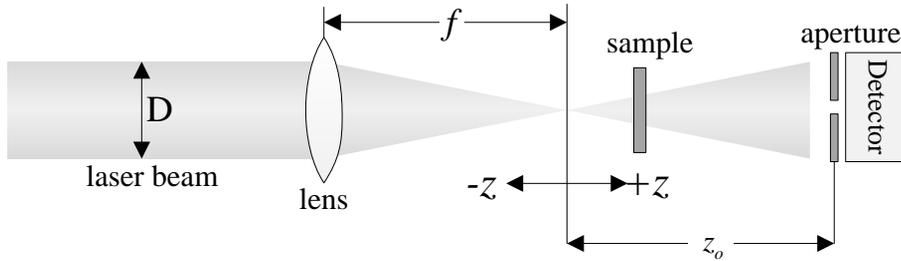


Figure (1): Closed aperture z-scan set up to measure the nonlinear refractive index coefficient.

3. Result and discussion

3.1. Nonlinear absorbance

Figure (2) shows the absorbance of a-Si, S:H and a-Si, Se:H alloys. The absorbance increases rapidly at wavelength below 500 nm. Figure (3) depicts the normalized transmission for z-scan open aperture configuration for typical a-Si, S:H alloy thin film at different excitation powers. Similar variation has been obtained for a-Si, Se:H alloy thin films.

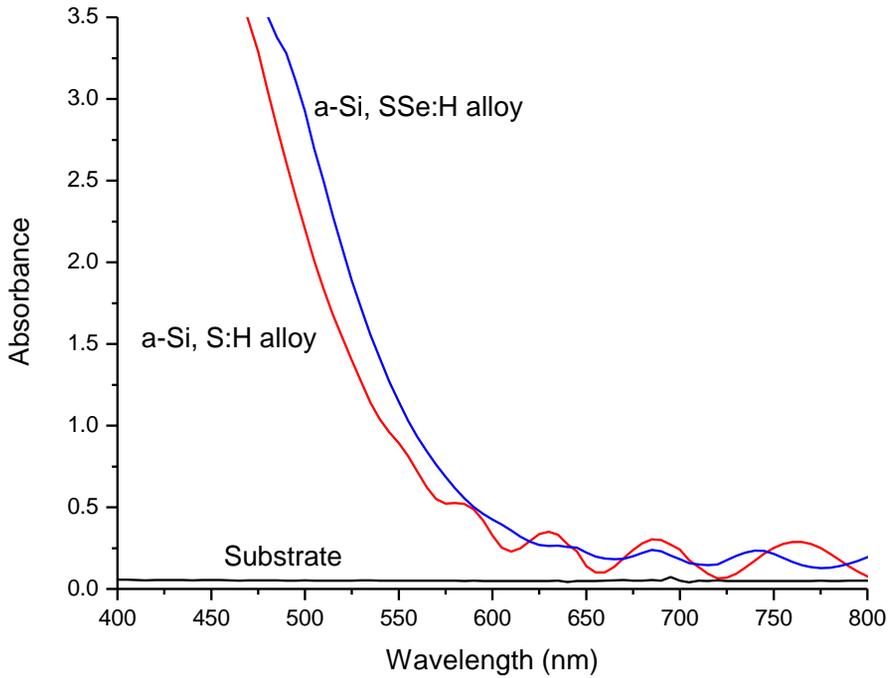


Figure (2). Linear absorbance of typical a-Si, S:H y and a-Si, Se:H alloys deposited on Corning glass substrate.

The normalized transmission for open z-scan is given by [Sheik-Bahaa et. al., 1990]:

$$\Delta T = 1 - \frac{\Delta\varphi}{\left(1 + \frac{z^2}{z_0^2}\right)} \quad (1)$$

Where $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh radius of the Gaussian beam, ω_0 is the beam waist, and $\Delta\varphi$ is the phase distortion. The nonlinear absorption coefficient is given by [Vinitha and Ramalingam, 2008]:

$$\beta = \frac{2\sqrt{2} \Delta\varphi}{I_0 L_{eff}} \quad (2)$$

Where $I_0 = 2P_0/\pi\omega_0^2$, and $\pi\omega_0^2$ is the cross section area of the laser beam waist at the focus. In the above equation L_{eff} is the effective length of the sample, and is given by

$$L_{eff} = [1 - \exp(-\alpha\ell)] / \alpha \quad (3)$$

Where ℓ is the thickness of the sample α is the linear absorption coefficient.

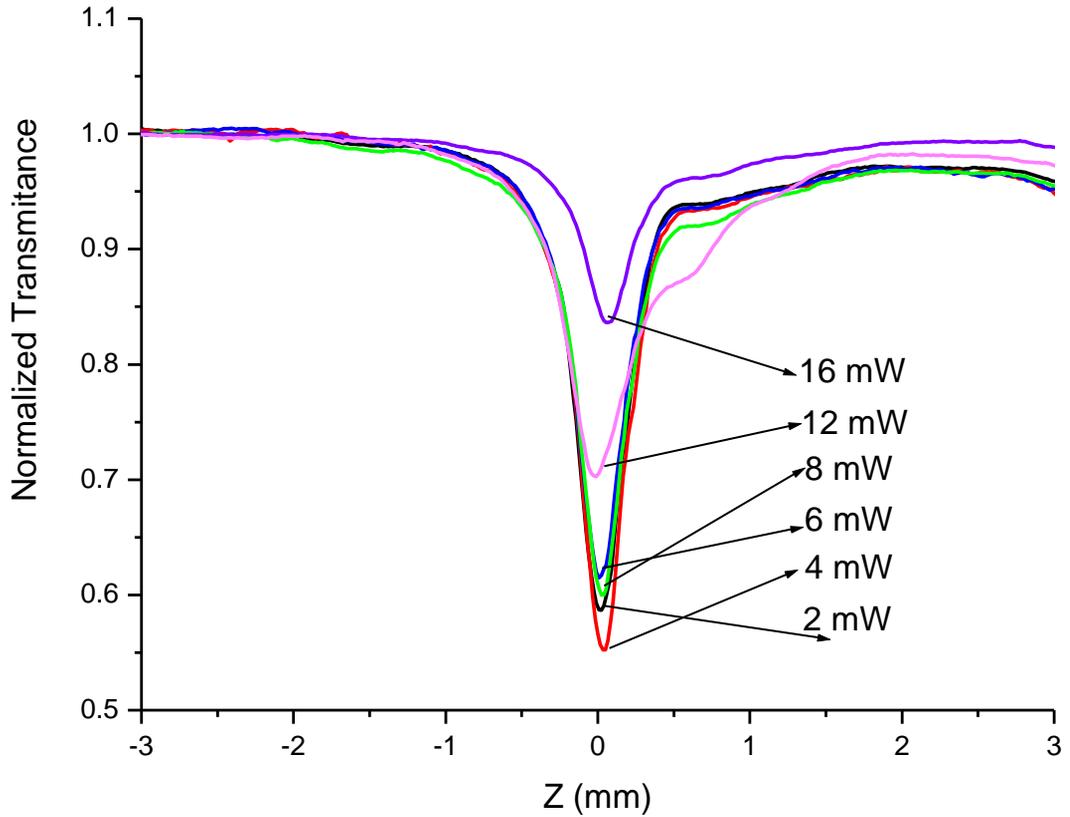


Fig.(3): Normalized transmittance for z-scan open aperture configuration for typical a-Si, S:H alloy at different excitation powers.

Taking $\Delta\varphi = P_1$ as fitting parameter, and $z_0 = \pi\omega_0^2/\lambda = P_2$ as a second fitting parameter, we get $I_0 = 2P_0(\text{mW})/\lambda P_2$, hence:

$$\beta = \frac{\sqrt{2}\lambda P_1 P_2}{P_o(\text{mW})L_{\text{eff}}} \quad (4)$$

From Figure (2) we obtain $\alpha \approx 7.6 \times 10^5 \text{ m}^{-1}$ for both types of alloys. Using $\ell = 1 \mu\text{m}$ in Eq.(3), we obtain $L_{\text{eff}} = 0.699 \mu\text{m}$. For $\lambda = 632.8 \text{ nm}$, Eq.(4) becomes,

$$\beta = \frac{1.28 P_1 P_2}{P_o(\text{mW})} \quad (5)$$

Figures (4) and (5) show typical open-aperture z-scan for a-Si, S:H and a-Si, Se:H alloys at 632.8 nm excitation wavelength respectively. On the same figures are shown the best fit of the data for $P_0 = 8 \text{ mW}$ using Eq.(5). The transmission is symmetric with respect to the focus ($z = 0$), where it reaches its minimum value.

This behaviour is typical of induced absorption such as reverse saturation absorption. Figures (6) and (7) depict the variation of the nonlinear absorption coefficient with excitation power for both types of alloys considered in this work. In these figures we observe a decrease followed by saturation in nonlinear absorption as the excitation power increases.

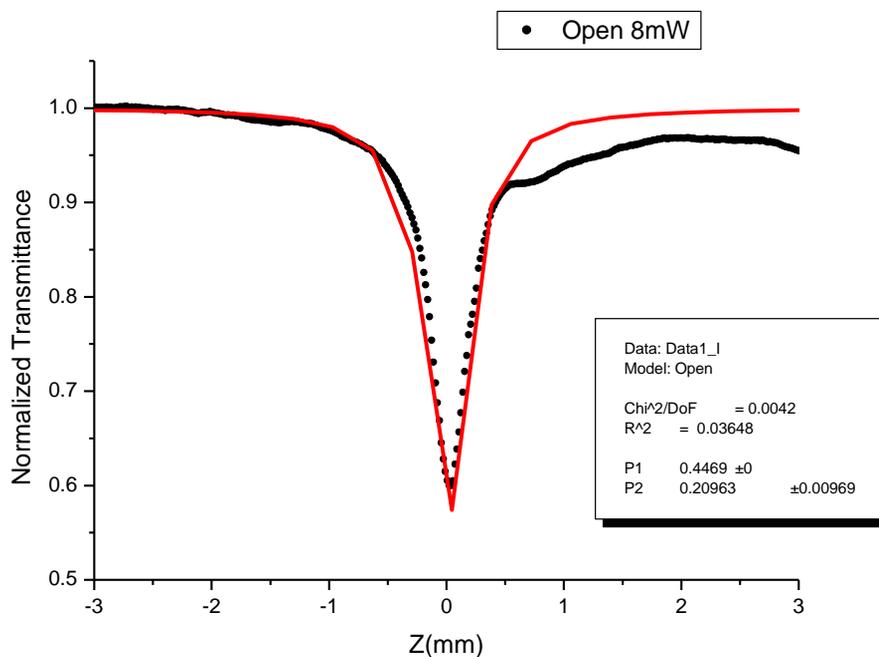


Figure (4): Open aperture z-scan response for a-Si, S:H at 8 mW excitation power. The line corresponds to the best fit of the data.

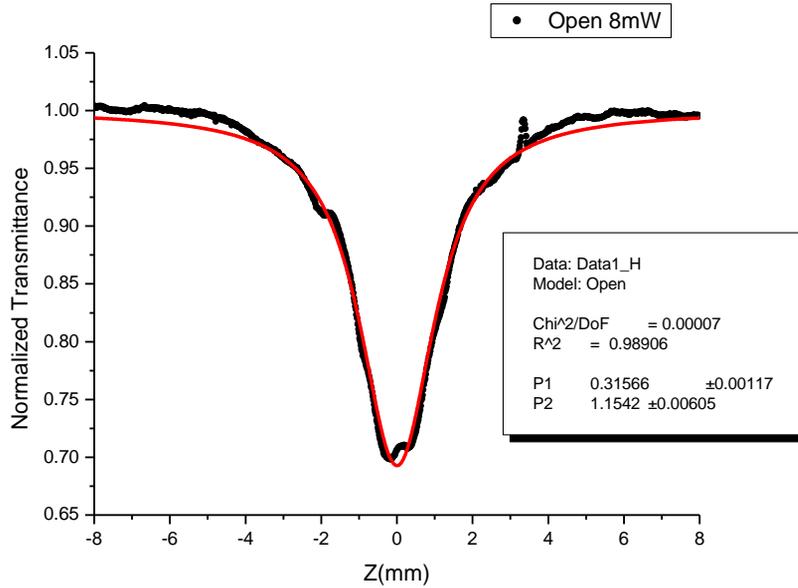


Figure (5): Open aperture z-scan response for a-Si, Se:H at 8 mW excitation power. The line corresponds to the best fit of the data.

The nonlinear absorption coefficient β can also be expressed in terms of the change in absorption cross section $\Delta\sigma$ through the relation [Andrade et. al., 2006]:

$$\beta = \frac{\lambda N_o \Delta\sigma}{4\pi I_s} \quad (6)$$

Where $\Delta\sigma = \sigma_{\text{exc}} - \sigma_{\text{gr}}$ is the difference between the excited state and ground state absorption coefficients, N_o is the concentration of defect states, and I_s is the saturation intensity, and is given by:

$$I_s = hc / \lambda \sigma_{\text{gr}} \tau \quad (7)$$

Here hc/λ is the photon energy, and τ is the response life time, and is taken as equal to 12 ms [Henari, 2008]. N_o depends upon the gas volume ratio (R_v). For $R_v = 0.044$, $N_o \approx 2 \times 10^{20} \text{ cm}^{-3}$ for both a-Si, S:H and a-Si, Se:H alloys [Aljishi et. al, 1991]. $\sigma_{\text{gr}} = \alpha/N_o = 1 \times 10^{-17} \text{ cm}^2$, $hc/\lambda = 1.96 \text{ eV}$, and hence $I_s = 26.17 \text{ kW/m}^2$. Using the above data and Eq.(6), $\Delta\sigma$ can be calculated for both alloys. For a-Si, S:H the change in the absorption coefficient $\Delta\sigma$ decreases from 6.81×10^{-15} to $9.39 \times 10^{-16} \text{ cm}^2$ as the power increases from 2.1 mW to 16.5 mW. The corresponding σ_{exc} obtained for a-Si,S:H alloy ranges between 6.81×10^{-15} and $4.90 \times 10^{-16} \text{ cm}^2$. For a-Si, Se:H $\Delta\sigma$ decreases from 1.628×10^{-14} to $6.70 \times 10^{-15} \text{ cm}^2$ for the same change in excitation power. The corresponding σ_{ex} obtained for a-Si,Se :H alloy ranges between 1.629×10^{-14} and $6.51 \times 10^{-15} \text{ cm}^2$. In all cases σ_{ex} is greater than σ_{gr} , which is typical requirement for reverse saturation absorption. In this process electrons are optically generated by single photons, and are promoted to the higher states of the conduction band. Electrons are then relaxed to trapping levels (defect states). The lack of saturation of these excited states indicates that the relaxation from excited state level into trapping states is very fast, whereas the relaxation

time from these states to the ground state is slow. Excited states absorption would then occur from the trapping states to a higher excited state level within the conduction band.

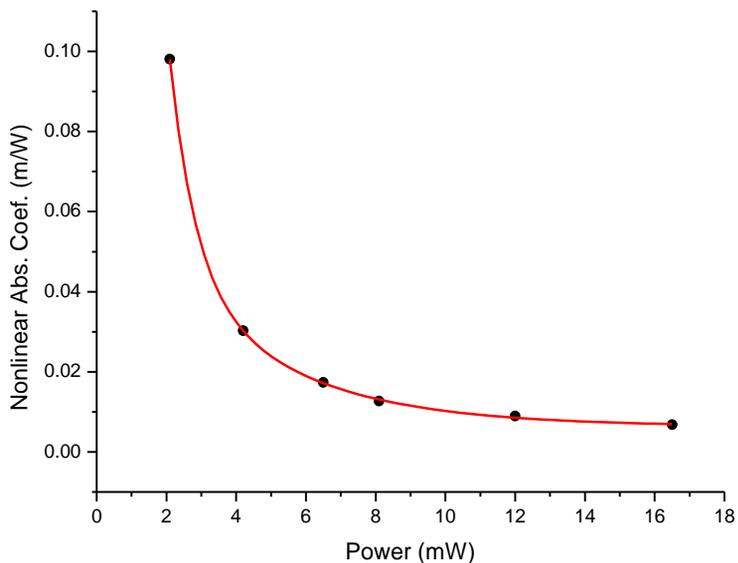


Figure (6): Nonlinear absorption coefficient for a-Si, S:H at different excitation powers.

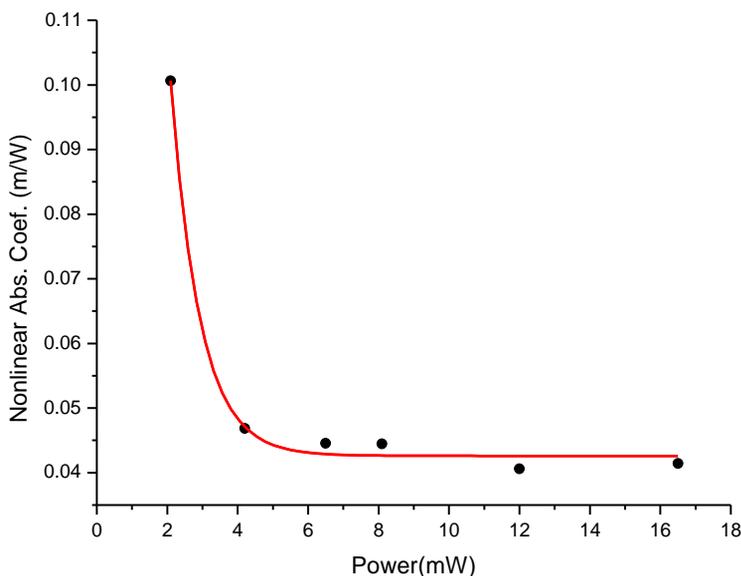


Figure (7): Nonlinear absorption coefficient for a-Si, Se:H at different excitation powers.

3.2. Nonlinear refractive index

The nonlinear refractive index has been determined from closed aperture configuration. Figure (8) shows the normalized transmission for the closed aperture configuration. The normalized transmission is given in this case by [Sheik-Bahaa et. al., 1990; Andrade et. al., 2006]:

$$\Delta T = 1 + 2\Delta\phi \left[\frac{2x}{(1+x^2)(9+x^2)} \right] - 2\Delta\phi \left[\frac{3+x^2}{(1+x^2)(9+x^2)} \right] \quad (8)$$

Where $x = z/z_0$ and,

$$\Delta\phi = \frac{2\pi}{\lambda} I_o \gamma L_{eff} \quad (9)$$

In the above equation γ is the nonlinear refractive index. A fit of Eq.(8) to the experimental data is shown in Figure (8). As it can be seen in this figure, the sample possesses positive nonlinear index of refraction indicating self-focusing action. Substituting the fitting parameter $P_1 = \Delta\phi$ into Eq (9), the value of $\gamma = 2.97 \times 10^{-9} \text{ m}^2/\text{W}$ was obtained.

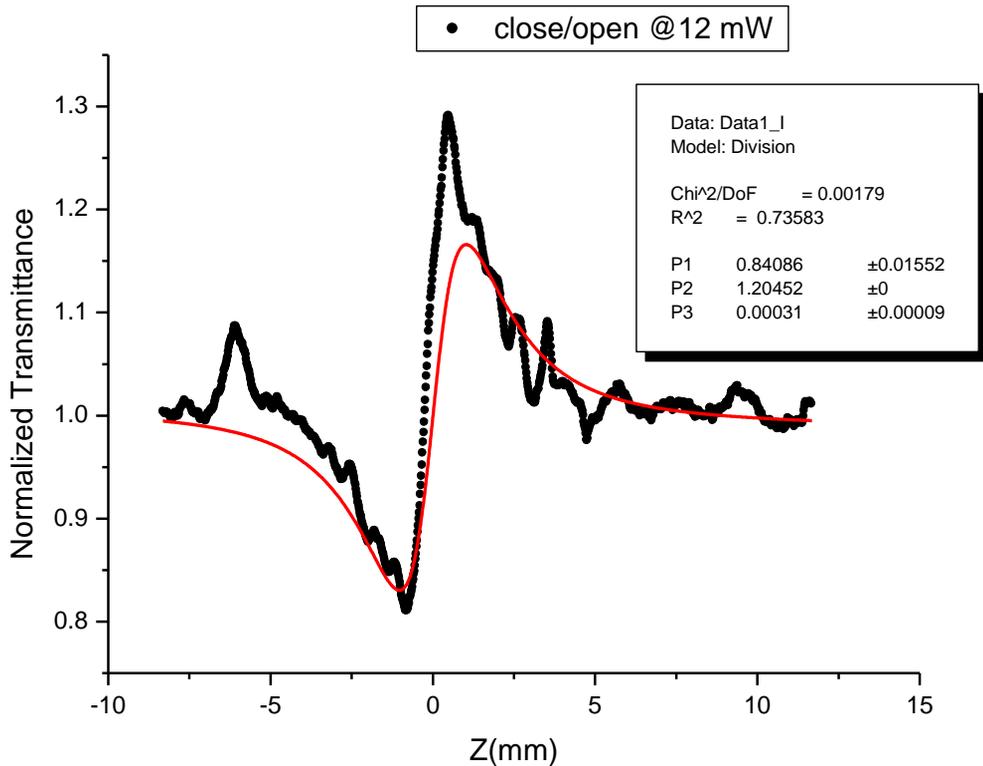


Figure (8): Close aperture z-scan response for a-Si, Se:H at 12.0 mW excitation power. The line corresponds to the best fit of the data.

3.3. Third order susceptibility

The third order nonlinear optical susceptibility $\chi^{(3)}$ can be calculated using the following relations [Rekha et. al., 2009; Sun et. al., 2006]:

$$\text{Re } \chi^{(3)} (\text{esu}) = \left(\frac{\epsilon_0 c^2}{10^4 \pi} \right) n_0^2 n_2 \quad (\text{cm}^2 / \text{W}) \quad (10)$$

$$\text{Im } \chi^{(3)} (\text{esu}) = \left(\frac{\epsilon_0 c^2}{4 \times 10^2 \pi^2} \right) n_0^2 \lambda \beta \quad (\text{cm} / \text{W}) \quad (11)$$

$$|\chi^{(3)}| = \sqrt{(\text{Re } \chi^{(3)})^2 + (\text{Im } \chi^{(3)})^2} \quad (12)$$

Here c is the speed of light in vacuum, and ϵ_0 is the permittivity of free space and $n_0 = 1.51$ is the linear index of the sample. For example at excitation power $P_0 = 12 \text{ mW}$ we have $n_2 = 2.97 \times 10^{-5} \text{ cm}^2/\text{W}$ and $\beta = 4.06 \text{ cm/W}$, thus from equations (10),(11) and (12) we have: $\text{Re } \chi^{(3)} = 1.72 \times 10^{-3} \text{ esu}$, $\text{Im } \chi^{(3)} = 1.18 \times 10^{-3} \text{ esu}$ and $|\chi^{(3)}| = 2.09 \times 10^{-3} \text{ esu}$.

3.4. Optical limiting

Optical limiters exhibit normally low transmittance for sudden increase of light intensity, and thus they are used to protect the human eye as well as optical instruments from potential damage. Our samples are characterized by very low transmittance at short wavelengths, but they are transparent in higher wavelengths. Optical limiting was evaluated by employing fluence-dependent transmission measurements using HeNe laser at 632.8 nm. Figure (9) depicts the optical limiting behaviour of typical a-Si, S:H thin film where the fluence increases linearly and then starts to saturate at higher fluence values.

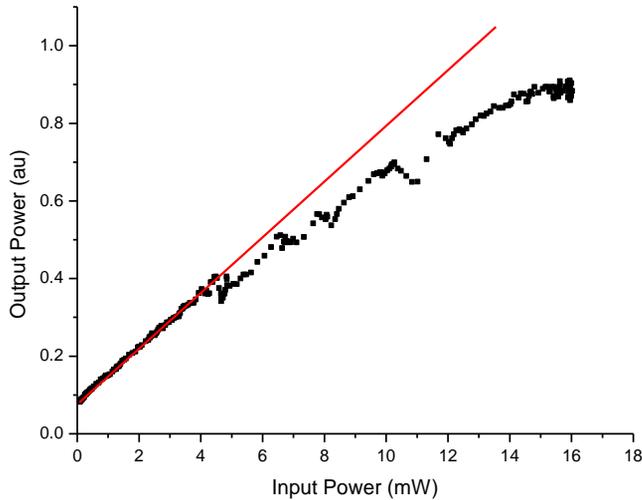


Figure (9): Optical limiting in a-Si, S:H alloy. As the input power increases the output transmitted power saturates at a fixed value.

4. Conclusion

Single beam z-scan technique has been employed to determine the nonlinear refraction index and the nonlinear absorption coefficient as a function excitation power. The measurements were carried out at various excitation powers using continuous HeNe laser source at excitation wavelengths of 632.8 nm. It was shown that the nonlinear absorption coefficient decreases and then reaches a saturation values with increasing excitation power. The nonlinear behaviour was explained in terms of single photon absorption and reverse saturation absorption. The symmetry of the normalized transmittance for z-scan open aperture configuration indicates that reverse saturation absorption is the main mechanism for the observed nonlinearity. This model was confirmed by verifying that the excitation cross section is greater than the ground state cross section. It was found that thin films of this material exhibit positive nonlinear index of refraction indicating self-focusing action. Measurements of fluence-dependent transmittance indicate that these films exhibit optical limiting behaviour.

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The effect of Mg:ZnO films deposit on porous ceramic for the structural, morphological and photocatalytic properties

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Abstract

In the purpose of preparation of purification elements at low cost in our daily life, thin layers of undoped and magnesium doped zinc oxide were deposited on ceramic pellets constituted of cristobalite, mullite and zircon. These substrates are made from abundant local raw materials. The thin films are prepared by dip-coating. The effects of the magnesium doping on the physical and photocatalytic properties have been studied using several techniques such as X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy and UV-visible spectrophotometry. The photocatalytic effectiveness was tested on an aqueous solution of Orange II under UV light. The results obtained show that only porous substrate, consisting essentially of mullite and zircon, gives an important photocatalytic activity. This important effect can be related to the high rate of open porosity in these substrates (due to the consumption of the SiO₂ vitreous phase by zirconia). The presence of the open porosity, able to be filled with ZnO:Mg, makes the specific surface larger and improves the photocatalytic effect.

Keywords: Ceramic substrate; Zirconia; Dip-coating; ZnO:Mg; Degradation rate

Introduction

Membrane filtration is an essential technology for clarification, concentration, purification, salt separation and recycling in the food, pharmaceutical and surface treatment industry [1]. The use of efficient membrane techniques makes it possible to improve water treatment and the production of drinking water [2]. The membrane processes open new possibilities in the exploitation of sources of water, in particular the oceans, which were not easily usable before technical or economic reasons [3]. Moreover, the economical aspect implies the development of processes that consume little reagents and require low-cost and space-saving installations.

Due to specific properties such as refractoriness, chemical stability or mechanical resistance to compression, as well as the wide variety of microstructures, porosities and accessible geometries [4, 5], ceramics are a class of materials that cannot be ignored for many industrial processes currently or in the process of being developed, for the protection of the environment [6]. This article provides an illustration of this by discussing applications for filtration, heterogeneous catalysis, and adsorption or coupled operations, for example in membrane catalytic reactors, based on the multifunctionality of materials [7].

The study have been devoted of thin layers ZnO:Mg to give good results for purification of colorant organic [8, 9]. Many properties of ZnO can thus be modulated by doping Mg [10, 11]. The Mg doping can increase

the band gap and reject the absorption coefficient, which is essential for application in the region of invisible light [12, 13], also to enlarge band gap [14, 15]. The solubility of ZnO in MgO is 40 to 50% of atoms [16]. The objective of this study is to synthesize Mg films doped by ZnO by a dip-coating technique on porous substrates (mullite-zircon) at a deposition temperature of 500 °C and to study the effect of the Mg content in the range on the structural and photocatalysis properties of these films.

Experimental procedure

Preparation of porous substrate

Prepared pellets from clay powders DD3 with 38% zirconium oxide (DD3 + 38 wt% ZrO₂) added using a 13 mm matrix. At the end, an open porosity reaches 33% for a heat treatment at 1300°C for 2 hours with an annealing speed of 5°C / min [4].

Preparation of Mg-doped ZnO nanostructures

Mg doped ZnO thin layers were deposited on ceramic substrates by the sol-gel technique. Zinc acetate dehydrate (Zn (CH₃COO)₂ .2H₂O) was dissolved in absolute ethanol at 70 °C with monoethanolamine (MEA) acting as a stabilizer. Magnesium acetate tetrahydrate (Mg(CH₃COO)₂ .4H₂O) was added to the solution for Mg doping. A serie of samples were prepared by dip coating ceramic substrates, preheating at 200 °C for 3 min in oven, and by repeating the process 50 times. Finally, they were annealed at 500 °C for 2 h to produce Mg doped ZnO thin films [17, 18].

Results and Discussions

Structural analysis

The figure 1.a shows the X-ray diffraction patterns for undoped and Mg-doped ZnO thin layers deposited on a ceramic substrate consisting mainly of millite and zircon (DD3+38 wt% ZrO₂-clays). Mullite, Zircon, Zirconia and cristobalite has essential phases of ceramics. The XRD spectrum (Fig.1.b) indicates that the peak (101) obtained after the deposition of 50 layers of undoped ZnO is polycrystalline with a hexagonal wurtzite structure (JCPDS 03-0891). The insertion effect of 6% of Mg on the crystalline structure of the pellets was observed by a shift towards the highest angles, demonstrating a small crystalline size (Table.1). It is concluded that Mg atoms with a smaller ionic radius ($r_{Mg^{2+}} = 0.65 \text{ \AA}$) replace Zn ($r_{Zn^{2+}} = 0.74 \text{ \AA}$) and Zr ($r_{Zr^{4+}} = 0.72 \text{ \AA}$) atoms in the lattice. The addition of Zn and Mg contributes to the lattice parameter variation which leads to a slight shift of the peaks and occupy interstitial sites. It should be noticed that the calculation of the grain particle size may be determined by the Debye-Scherrer relationship [19]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the wavelength of the anticathode ($\lambda_{Cu} = 1.541 \text{ \AA}$), β is FWHM (half-value width), θ is the diffraction angle and D is the diameter of particle size.

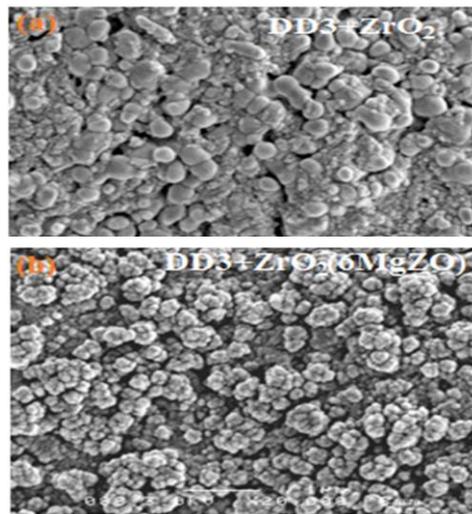


Fig. 2. SEM micrograph of the pellets: a) DD3+38 wt ZrO₂ and b) DD3+38 wt ZrO₂ (6% Mg-doped ZnO).

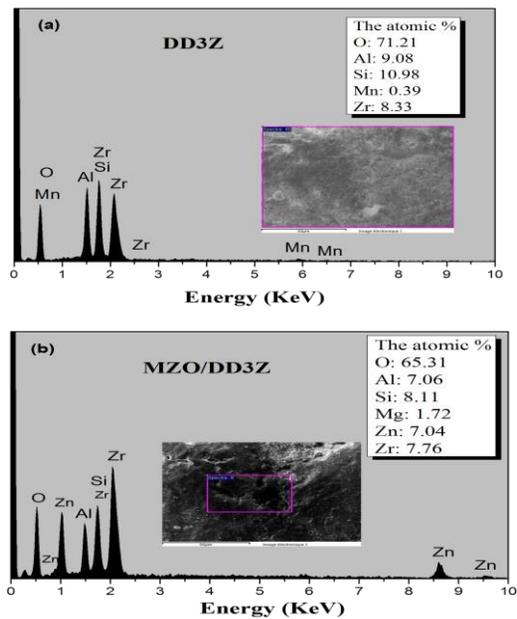


Fig. 3. EDX spectrum of the pellets: a) DD3+38 wt ZrO₂ and b) DD3+38 wt ZrO₂ (6% Mg-doped ZnO).

AFM analyses

The typical cross section view of the samples (Fig. 12) reveals a porous ceramic substrate covered by the thin film and, on top of this, the active Mg: ZnO layer. The texture and morphology of this layer can be observed in Fig. 4. The layer thickness and the grain increases with the amount of deposited thin films. The granular morphology (Fig. 4b) might enhance the photocatalytic activity of the layer, since it increases the exposure area of active particles. According to the AFM results the average particle size is 0.93 μm and the layer roughness is 134 nm. These values are much smaller than the ones without active layers DD3Z (Fig. 4b), Where he was to 0.56 μm and 100 nm for the grain size and roughness (Table.I), respectively. Since the catalytic performance is similar, the actual solution is more interesting from a practical point of view, since it facilitates the surface cleaning by common means.

Table 2: Grain size and the roughness of the samples

Substrates	DD3+38%ZrO ₂ -clays	
Samples	DD3+38%ZrO ₂	MZO-DD3 +38%ZrO ₂
Grain size (μm)	0.56	0.93
Roughness (nm)	100	134

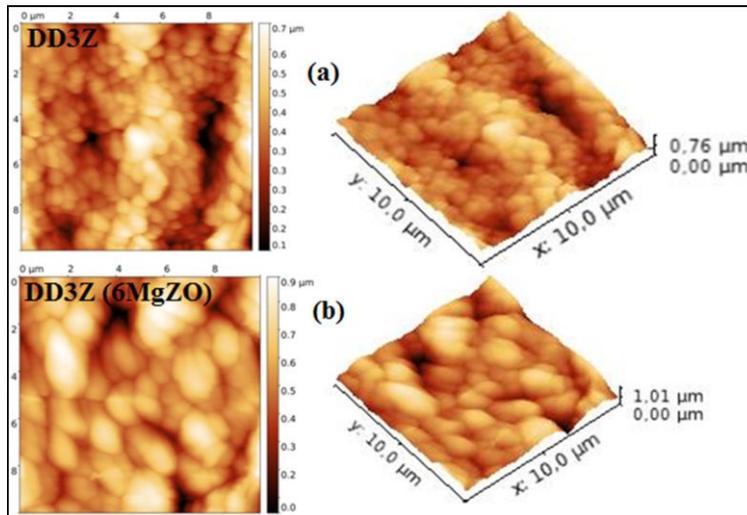


Fig. 4. AFM topography of the pellets: (a) DD3+38 wt ZrO₂ and (b) DD3+38 wt ZrO₂ (6% Mg-doped ZnO).

Confocal spectrum

The confocal spectrum showed the optical properties of the samples. One emission bands could be observed. The broad emission is in the visible region [400- 800 nm]. Fig.5 show that the intensities of the

samples of the porous substrates decrease after the addition of the thin layers of ZnO and Mg: ZnO. Because of the Zn and Mg ions doping this emission band is broadened, it can be speculated that the band width of the ceramic is widened owing to the replacement by the Zn^{2+} and Mg^{2+} [20]. At the same time, it is obvious that the ratio of the intensity of the UV emission decreases to deep level, and this may be caused by the increasing amount of Mg-doping. Also it's can be returned to the degree of electron / hole recombination are clearly decreases with magnesium doping. Hence, it is believed that the prepared MZO/DD3Z thin film with high particle size, high surface area and high surface defects would allow better results on the photocatalytic activity [21]. Pellets with thin layers (MZO) increased the free-charge periphery and has a longer life. As a result, the mobility of the MZO / DD3Z sample increased, while the resistivity was reduced for the Mg-doped sample.

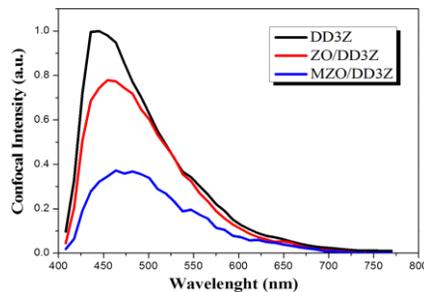


Fig. 5. Confocal spectra of the pellets.

Photocatalytic activity

The photocatalytic activity of Mg-doped ZnO thin layers was investigated by means of the degradation of orange II (OII) in aqueous solution under visible light at room temperature. Blue light lamp 4W (VL-4LC) was used as UV source. The photocatalytic degradation was determined by measuring the absorbance of OII solution every 1 hour using a UV-vis spectrophotometer (V- 630, JASCO) in the wavelength range of 250-650 nm. The degradation efficiency of OII can be calculated by the formula [22]:

$$\text{Degradation \%} = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

The figure 6 shows that the effect of 6 % Mg-doped ZnO, deposition on the porous substrate, on the degradation rate of orange II varies as a function of the time exposition to UV. After 6 hours of UV exposure, 80 % of degradation of the orange II solution was obtained. This result is attributed to the increase of the effective surface leading to a deceleration of the photocatalytic process.

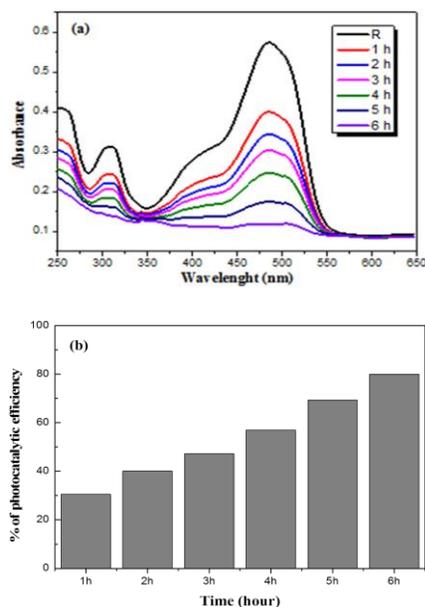


Fig. 6. Degradation rate of Orange II versus UV exposure time for a ZnO:Mg thin film deposited on a porous substrate (DD3+38 wt% ZrO₂- clay)

Conclusion

The project consists in the implementation of processes for the production of composite membranes based on local clay materials such as DD3, for use in the treatment of pollution waters. The syntheses will be carried out by sol-gel processes. All the characterizations demonstrate the properties of the membranes obtained: The substrate and the membranes prepared have been characterized by the structural, morphological, and photocatalytic activity. The X-ray diffraction results show that the samples with thin layers have shifted peaks towards larger angles. The SEM results display that the structure of Mg: ZnO is flower-like. The pores size and the porosity (33%) obtained of the ceramic substrate after deposition will be decelerated in the filtration and purification of orange II solution. A maximum degree of purification of 80% is obtained with an active layer of Mg doped ZnO for an exposure time of 6 hours. The use of this doping process and local materials in the same time lower the cost of the purification operation

Acknowledgements

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Investigation of Bacterial Adhesion to Plasma-Modified Polypropylene Surface

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Abstract

The adhesion of non-pathogenic bacteria *Enterococcus faecalis* on the polypropylene surface is investigated before and after exposure to plasma generated using a capacitively coupled 13.56 MHz radio frequency source. Different gas discharges are generated using oxygen and nitrogen gases. Various studies show that plasma exposure effectively improves the surface properties of the polypropylene without changing its bulk properties. The chemical changes on the surfaces are characterized using a Fourier transform infrared-attenuated total reflection spectroscopy. The plasma exposure leads to form the oxygen-containing and the nitrogen-containing polar groups on the PP surfaces. Moreover, new functional groups formed on the surfaces have a high degree of crosslinking structures. The presence of the crosslinking structures importantly increases the attachment of the bacteria culture to the PP surfaces. Bacterial adhesion is analysed by measuring the cell population attached to the surface. The results showed that oxygen plasma exposure increased the bacterial adhesion to the surface relative to the nitrogen plasma exposure.

Keywords: Surface modification; bacterial adhesion; RF plasma discharge; polypropylene.

Introduction

Discharges generated using a capacitively coupled radio frequency (RF) source are highly preferred to enhance the surface properties of polymers since they do not change the polymer's bulk properties and provide good control over the gas chemistry (Liston et al., 1993, Vesel and Mozetic, 2017, Barton et al., 1999). The plasma discharge effectively improves the poor polymer surface properties by allowing the formation of additional functional groups such as the carbonyl, carboxyl, hydroxyl, and the amine to the polymer surface (Liston et al., 1993, Zille et al., 2015, Grace and Gerenser, 2003). This technique is used for various applications mostly in textile, automotive, packaging, electronic, and biological industries (Zille et al., 2015, Pankaj et al., 2014, Sanchis et al., 2018, Gomathi et al., 2008, Bhat and Upadhyay, 2002). Most importantly, crosslinking structures generated by free radicals provide excellent biocompatibility due to higher concentrations of active molecules on the polymer surface (Gomathi et al., 2008).

Our previous studies show that the RF discharge significantly improves the surface properties of the polypropylene (PP) after the plasma exposure (Mansuroglu and Uzun-Kaymak, 2018, Mansuroglu et al., 2018). PP is a promising material with excellent chemical and mechanical resistance, transparency, and low density (Morent et al., 2008, Bhat et al., 2002). These properties make it very favorable to be utilized in many

fields of the industry (Zille et al., 2015, Pankaj et al., 2014, Sanchis et al., 2018, Carrino et al., 2002). The recent studies show that the PP material can also be used in biomedical areas (Gomathi et al., 2008, Slepíčka et al., 2013, Bhanthumnavin et al., 2016). In this study, we are investigating bacterial adhesion of the modified PP surface. A non-pathogenic bacteria culture, *Enterococcus faecalis* ATCC29212 is used to test the adhesion properties. The plasma discharge is generated using oxygen, and nitrogen gases separately. A capacitively coupled 13.56 MHz RF source generates the gas discharge. Experiments are repeated at similar conditions while parameter scans are performed for the RF input power (50 W, 100 W, and 150 W) and for the plasma exposure time (2 min, 5 min, and 10 min). The surfaces are chemically characterized using a Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy. Bacterial adhesion is analyzed by measuring the cell population attached to the modified surface.

Experimental

RF plasma system

The RF plasma system consists of two parallel aluminum electrodes. 13.56 MHz RF source is used to generate the gas discharge. The pressure of the vacuum chamber initially pumps down to a base pressure of 10^{-3} Torr, and then a gas is filled using an MKS multi-gas controller 647C. All experiments are employed at the gas pressure of 1.2×10^{-1} Torr. The granular PP, $(C_3H_6)_n$, melting at 160 °C, is purchased from PETKIM[®]. A hot-press machine is used to process a flat sheet of PP granules with a thickness of 0.6 mm. Then, the sheet is cut into small samples in sizes of 1×1 cm². All experiments are conducted at the same conditions by varying the RF input power (50 W, 100 W, and 150 W) and the exposure time (2 min, 5 min, and 10 min). O₂ or N₂ gas flow rate is kept constant at 50 sccm. The results are chemically examined using a Thermo Scientific Nicolet iS10 FTIR-ATR spectrometer.

In vitro bacterial adhesion

Non-pathogenic bacteria, *Enterococcus faecalis* ATCC29212, is used in this study. *E. faecalis* stock culture is maintained in a MRS broth, with 25 % (v/v) glycerol at -80 °C. Working culture is prepared from frozen stocks by two sequential transfers in the MRS broth. Incubation is conducted at 37 °C for 18 h. 1 cm² of PP polymers are sterilized in 70 % ethanol for 10 min and rinsed in 0.85% NaCl (w/v). 1 ml of bacterial culture at $\sim 4 \times 10^8$ CFU/ml is added into 24-well plate, and the sterile samples exposed to O₂ or N₂ plasmas or the samples without plasma exposure are placed treated-side down, into the each well. After the plates are incubated at 37°C for 24 h, the samples are placed into a sterile 24-well plate and gently washed with 0.85% NaCl (w/v) to remove loosely adherent bacterial cells. The samples are then placed in 1 ml of 0.85% NaCl (w/v) and vortexed vigorously for 2 min to remove bacteria adhered to the PP surface. A vortexed solution is enumerated by plate count on the MRS agar. Statistical differences of the bacterial adhesion are assessed with the Each Pair Student's Test using JMP version 12 (SAS Institute Inc., Cary, NC) and are presented as the mean \pm SEM. Statistical difference is determined at a P value of 0.05 or less.

Results /Discussion

FTIR-ATR spectroscopy

The chemical changes in the surfaces of PP after the plasma process are investigated using an ATR-FTIR spectrometer for the range of 3500 cm⁻¹ to 500 cm⁻¹. Fig. 1 and Fig. 2 show all spectra of before and after O₂

and N₂ plasma exposures, respectively. C-H stretching vibration bands are observed in the region between 3000 cm⁻¹ and 2780 cm⁻¹: the band at 2950 cm⁻¹ refers to -CH₃ asymmetric stretching, the band at 2916 cm⁻¹ refers to -CH₂ asymmetric stretching, the doublet bands at 2876 cm⁻¹ and 2865 cm⁻¹ refer to -CH₃ symmetric stretching, and the band at 2837 cm⁻¹ refers to -CH₂ symmetric stretching (Morent et al., 2008). Fig. 1 show the intensities of these C-H vibration bands increase with increasing the RF input power after O₂ plasma exposure. Increase in the intensities can be due to the formation of new functional groups on the surfaces (Liston et al., 1993, Bhat et al., 2003). In the spectra, two intense bands observed at 1452 cm⁻¹ referring to an asymmetric C-H deformation and at 1370 cm⁻¹ is due to a symmetric C-H bending vibration of -CH₃ group (Morent et al., 2008). Changes in the intensities of these bands verify the structural modification on the surfaces. The spectra show two broad bands observed at 1748 cm⁻¹ and 1621 cm⁻¹ corresponding to C=O stretching vibration. Moreover, a weak band observed at 1400 cm⁻¹ corresponds to COO- groups (Lehocky' et al., 2003). These bands show the presence of the oxygen-containing polar groups such as -OH, -C=O, and -C-O-O on the surfaces.

Different than O₂ plasma, N₂ plasma first leads to an increase the intensities of C-H vibration bands up to 100 W, and then a decrease is observed at 150 W, as shown in Fig. 2. A decrease in the intensities can be referred as a removal of the surface atoms due to the plasma exposure. The plasma discharge may cause more fragmentations and reactions during the process at high power value. The band observed at 1534 cm⁻¹ refers to -NO₂ stretching vibration and this band broadens after the plasma process. The broadening is observed due to crosslinking and branched structures generated by the plasma exposure. The spectra show that the nitrogen plasma leads to form -NH₂, -NH, and -NO₂ groups on the surfaces. Moreover, both O₂ and N₂ spectra have broadband seen at 1157 cm⁻¹ can refer to C-C asymmetric stretching, CH₃ asymmetric rocking, C-H wagging vibrations (Morent et al., 2008) or C-O stretching vibration (Bhat et al., 2003). They also have weak bands between 980 cm⁻¹ and 650 cm⁻¹. The bending of CH₃ is observed at 893 cm⁻¹, and the alkyl peroxide is observed at 839 cm⁻¹. The band observed at 718 cm⁻¹ refers to the structure of -(CH₂)₄- or -(CH₂)₄O- (Mistry, 2009). The bands observed at the region between 750 cm⁻¹ and 700 cm⁻¹ are assigned to methylene/methylene groups (Mistry, 2009).

The oxygen plasma likely leads to the formation of the carboxylic, carbonyl, hydroxyl and peroxide groups on the PP surfaces while the nitrogen plasma leads to the formation of the amine and imine groups. The presence of these chemical groups generally causes to change and improve the properties of the PP surfaces. Increase in the number density of these groups increases the hydrophilicity of the PP surfaces and improve their adhesion. Another critical factor is the degree of the crosslinking and branched structures occurring due to fragmentation and rearrangement generated during the plasma process. The crosslinking structures can provide excellent biocompatibility by allowing a higher concentration of active molecules on the polymer surface (Gomathi et al., 2008).

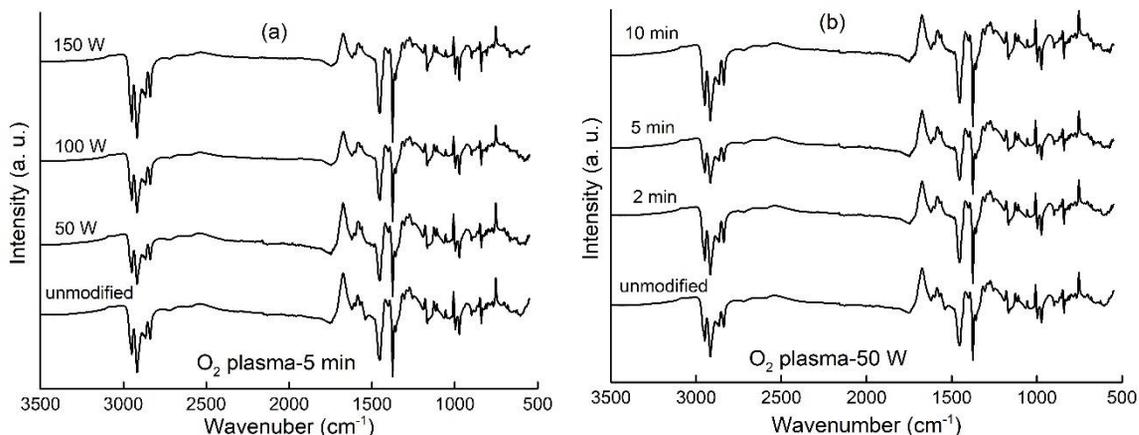


Fig. 1. The FTIR-ATR spectra of the PP surfaces before and after O₂ plasma exposure as a function of (a) the RF input power; (b) the exposure time

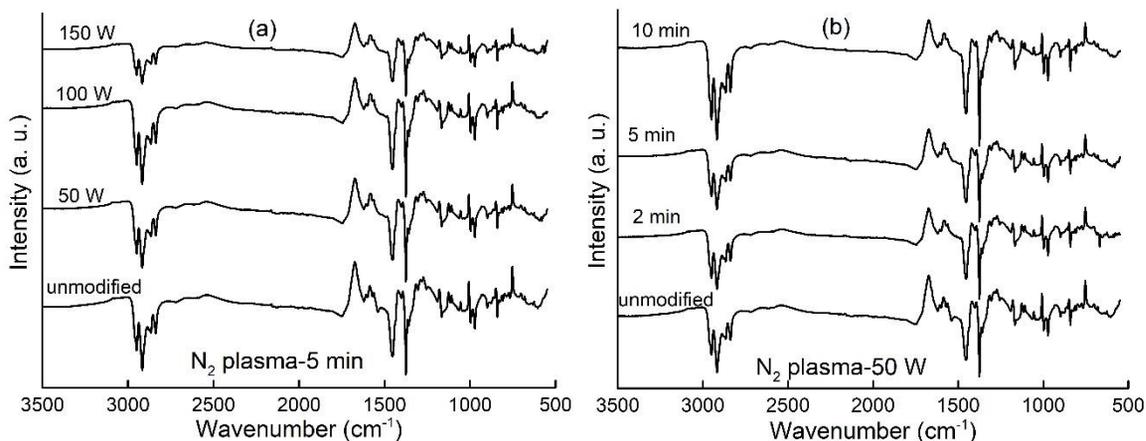


Fig. 2. The FTIR-ATR spectra of the PP surfaces before and after N₂ plasma exposure as a function of (a) the RF input power; (b) the exposure time

Bacterial adhesion

To investigate the bacterial adhesion to the PP surfaces *E. faecalis*, a non-pathogenic bacteria culture, is used. The bacteria is growth on the samples of control (without the plasma exposure) and the plasma exposed as a function of the RF input power and the exposure time. The cell population of the bacteria cultures attached to the surfaces is measured, and the results are shown in Fig. 3. The parameters having a significant difference are marked with a star as a result of the statistical analysis. The results show both O₂ and N₂ plasma exposures increase the adhesion of *E. faecalis* to the PP surfaces. Bacteria adhered to the samples exposed to the oxygen plasma is higher as compared to the nitrogen plasma exposure. This show that the presence of the oxygen-containing polar groups effectively improves the adhesion of *E. faecalis*.

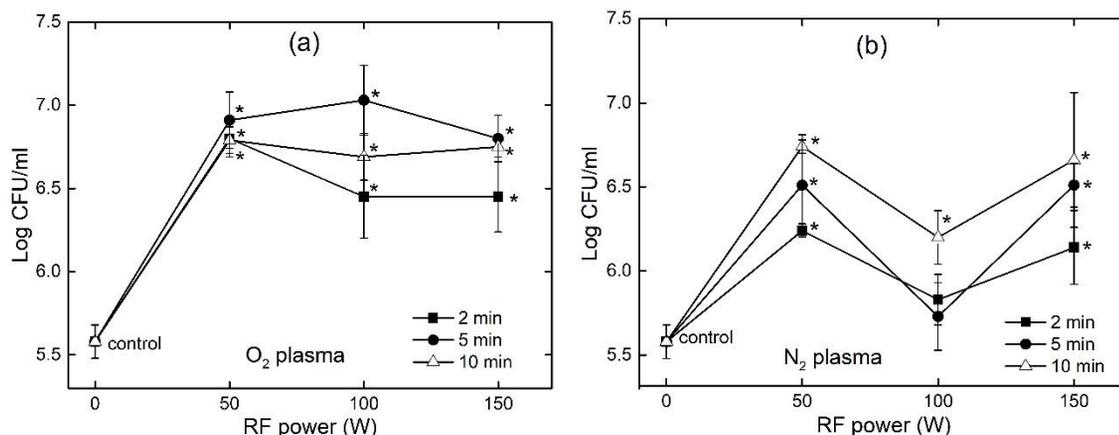


Fig. 3. The adhesion of *Enterococcus faecalis* ATCC29212 on the PP surfaces before and after the plasma exposure (a) for O₂; (b) for N₂ as a function of the RF input power and the exposure time (*p<0.05: significant differences from the control, (n:4/bar))

Fig. 3a shows the highest cell population is obtained at 50 W and 100 W of the RF input power, for 5 min of the exposure time. At 2 min, the highest value is observed at 50 W, and almost the same values are obtained at 10 min, for different power values. It can be seen that all parameters of O₂ plasma exposure have significant differences, which are consistent with the results of the FTIR-ATR spectra. For the samples exposed by N₂ plasma, the cell population of the bacteria increases effectively at 50 W and 150 W, and it increases with increasing the exposure time. Although the samples exposed at 100 W of the RF input power have an increase in the cell population of the growth as compared to the control sample, that is not significantly different at 2 min and 5 min of the exposure time. This can be due to the low number density of the nitrogen-containing groups on the surfaces to connect with the *E. faecalis* bacteria. Consequently, the adhesion of *E. faecalis* to the PP surfaces is generally improve after the oxygen and nitrogen plasma exposures.

Conclusion

The surface properties of PP polymer material are improved using O₂ and N₂ plasma exposures. The presence of the oxygen-containing and the nitrogen-containing polar functional groups are verified by the FTIR-ATR spectra. Also, it is observed that new functional groups have crosslinking structures. These crosslinking functional groups lead to improve the adhesion of PP surfaces. The results of bacterial adhesion show the cell population on the samples significantly increases after the both plasma exposures. Non-pathogenic bacteria *E. faecalis* attach the samples exposed to O₂ plasma with a higher concentration as compared to N₂ plasma.

Acknowledgements

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Plasma Characteristics Aiding the Enhancement of Surface Properties of Polyethylene

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Abstract

Plasma species such as electrons, ions, and free radicals can transfer their energies by interacting with the atoms from the surface of the polymer during the plasma modification process. Although various plasma discharge methods such as microwave, dielectric barrier, or radio frequency(RF) plasma discharges can be used to enhance the surface properties of polymers, in this study a capacitively coupled RF source is preferred due to its unique characteristic to generate weakly ionized cold plasmas. The plasma discharge is generated using a 13.56 MHz source ionizing Argon gas inside a chamber kept nearly around 10^{-1} Torr. The correlation between the changes of the plasma characteristics due to the input power and the changes on the processed surface is investigated. RF input power is scanned for a wide range of power starting at 50 W to 500 W while other plasma parameters such as the gas flow rate, plasma exposure time, and the gas pressure are kept constant. The emission spectrum of the atomic and the molecular lines process are investigated using a broadband optical emission spectrometer. The change in the surface chemistry is characterized using a Fourier transform infrared-attenuated total reflection spectrometer. The results show that new functional groups are generated, and branched structures are formed on the surface. Moreover, the surface energy of the polymer is significantly improved, and this is verified by the increase in the crystallization measured using an X-Ray diffraction spectrometer before and after the plasma exposure.

Keywords: Surface modification; optical emission spectroscopy; RF plasma discharge; polyethylene.

Introduction

Polyethylene (PE) is a widely used material in many applications such as textile (Zille et al., 2015), food packaging (Pankaj et al., 2014), and biomedicine (Slepička et al., 2013) due to its high chemical resistivity, excellent versatility, and relatively low cost (De Geyter et al., 2008). However, it has low surface energy; thus its surface properties should be enhanced to provide the adequate adhesion, printability, wettability, or biocompatibility properties. Various wet- and dry-processing surface modification techniques are used to enhance the surface properties of polymers. They include chemical solvent technique, the flame process, and the plasma discharge (Liston et al., 1993, Grace and Gerenser, 2003, Lee et al., 2009). Among these techniques, the plasma discharge is the most commonly used technique because it is a fast and clean process, and depending on the gas used it can be considered environmentally clean (Liston et al., 1993, Grace and Gerenser, 2003, Morent et al., 2008, Vesel et al., 2008). Plasma discharges can be produced using various discharge techniques including radio frequency (RF), microwave (MW), dielectric barrier (DB), and corona discharges (Morent et al., 2008, Popelka et al., 2018, Gomathi and Neogi, 2009, Vesel and Mozetic, 2017).

Capacitively coupled RF source generates a self-sustained, continuous and stable discharge for a long duration compared to other plasma discharge techniques such as DBDs and plasma torches. Also, it provides a feasible reactivity with an easy control [Liston et al., 1993, Zille et al., 2015, Pankaj et al., 2014, Vesel and Mozetic, 2017]. At low pressure, RF plasma discharge also etches the surface within the depth varying from 1 to 10 nm while the bulk properties of the polymer remain the same (Grace and Gerenser, 2003).

During the plasma surface modification, active plasma species such as electrons, ions, radicals, and excited atoms or molecules interact with the atoms on the upper surface layer of the polymer. As a result of these interactions, volatile products can be produced due to the plasma etching and new functional groups are produced on the surface (Liston et al., 1993, Grace and Gerenser, 2003). Formation of these new products causes changes in the surface energy while improving the surface for bonding, coating, etc. Plasma parameters such as the RF input power, exposure time, gas flow rate, pressure, gas type play an important role by significantly changing the plasma properties. Depending on the plasma parameters even polymers having chemically similar structures may produce different results (Nihlstrand et al., 1997). In this study, the purpose is to understand the effect of plasma on the surface of PE polymer material modified at various values of the RF input power, starting from 50 W to 500 W. The plasma discharge is monitored using a broadband optical emission spectrometer (OES). The chemical changes on the surfaces are examined using a Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectrometer. Moreover, the crystal properties of surfaces are examined using X-ray diffraction (XRD) spectrometer.

Experiment

The experimental set up is a capacitively coupled RF plasma discharge system consisting of two parallel aluminum electrodes. 13.56 MHz RF signal is applied between the electrodes to generate the plasma discharge. First, the pressure of the vacuum chamber is reduced to a base pressure of 10^{-3} Torr, then Argon gas is introduced using an MKS multi-gas controller 647C. All experiments are carried out at the pressure of 1.2×10^{-1} Torr. The granular PE, $(C_2H_4)_n$, melting at 110 °C, is purchased from PETKIM. To prepare polymer samples in sizes of 1×1 cm² and with a thickness of 0.6 mm, a heat press is used. The prepared polymer samples are transferred using a load lock chamber attached to the vacuum vessel.

All surface modifications experiments are conducted at the same parameters except for different RF discharge power varied from 50 W to 500 W with 50 W steps. During these experiments, the plasma exposure time is 10 minutes, and the gas flow rate is fixed at 50 sccm. The plasma emission is measured during the discharge using a broadband Ocean Optics HR2000 spectrometer. The polymer results are chemically examined using a Thermo Scientific Nicolet iS10 FTIR-ATR spectrometer. A Rigaku Ultimate-IV X-ray diffractometer (Cu K_α, $\lambda=1.54$ Å) is used to measure the crystal properties of the polymer surfaces.

Results /Discussion

Optical Emission Spectrometer

OES data are measured in a wavelength range of 300 – 900 nm to investigate the emission of the Ar plasma during the plasma processing. The atomic spectral lines of Ar I observed due to the ionization of the discharge gas while the atomic lines of C I arise from the surface of the polymer. Also, molecular lines of C₂ and CH are detected in the OES data due to the interactions between the species. The wavelength spectra of these atomic and molecular lines are shown in Fig. 1 for the selected data collected at 400 W of RF input power for plasma. Strong and sharp lines observed at the red end of the visible spectrum are mainly due to Ar I atomic emission

lines (NIST atomic database). Due to the wavelength resolution of the Ocean HR2000 spectrometer, some of the observed C I lines may overlap with Ar I lines around 700 nm to 750 nm. Besides these atomic lines, the molecular lines of C₂ and CH are observed in the visible and near the ultraviolet end of the spectrum. C₂ Swan band system ($d^3\Pi_g-a^3\Pi_u$) is observed at bands near 473.7 nm. CH bandhead is observed at regions from 415.9 nm to 428.2 nm and from 431.0 nm to 445.0 nm (Barholm-Hansen et al., 1994).

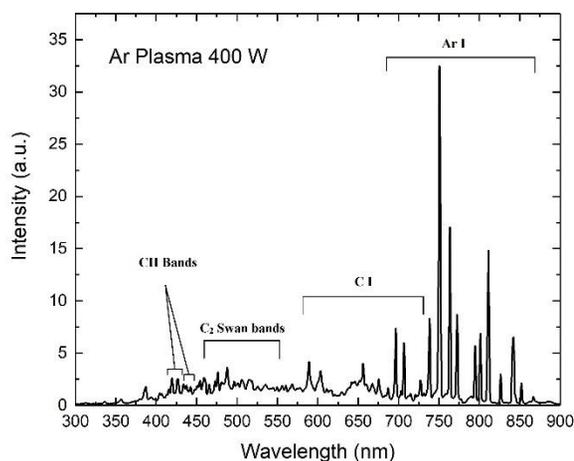


Fig. 1. The OES data for Ar plasma. (Selected for 400 W of the RF input power)

FTIR-ATR Spectrometer

The changes in the chemical structures of the polymer surface are investigated using an FTIR-ATR spectrometer operating in a wavenumber range of 3500 cm^{-1} – 600 cm^{-1} . The band intensities measured at wavenumbers are proportional to the concentration of chemical structures corresponding to these bands (Mistry, 2009). Spectra of the unmodified and the plasma modified surfaces are shown in Fig. 2. Vibrations due to the -CH₂- groups are observed at 2915 cm^{-1} and 2847 cm^{-1} referring to asymmetric and symmetric C-H stretching (De Geyter et al., 2008, Ghosh et al., 2004). Intensities of these main peaks first show a decrease in low RF power settings. This decrease in the C-H stretching bands suggests that the active plasma species dominantly interact with PE surface atoms and generate new chemical structures due to the etching. At 200 W input power, the intensities of the C-H stretching bands are measured roughly about the same as the intensities of measured using the unmodified PE. This can be interpreted as a number density equilibrium between the formation of new functional groups on the surface, and the loses due to the etching of the surface. As the RF input power increases, the intensities of these C-H stretching peaks show a small decrease until they reach a threshold near 400 W. Then, they start to increase at 450 W and at 500 W, which may possibly be due to a substantial increase in the number density of new functional groups on the surface.

In the spectra, the vibration of C-H deformation in $-(\text{CH}_2)_n$ is observed at 1462 cm^{-1} while the vibration of C-C rocking in $-(\text{CH}_2)_n-$ is observed at 719 cm^{-1} (De Geyter et al., 2008). Intensities of these peaks show higher values than those of the unmodified spectra at RF input power values higher than 400 W. The peak seen at 1645 cm^{-1} corresponds to the asymmetric COO- or C=C stretching vibration (De Geyter et al., 2008, Guruvanket et al., 2004). The intensity of this peak significantly increases with increasing RF power after 150 W. Notably its maximum values are observed at 250 W and 500 W. This shows that new functional groups

are formed on the surfaces. Additionally, this peak becomes broader with increasing the RF power due to the existence of crosslinking reactions causing the formed chemical groups to have crosslinking structures (Liston et al., 1993, Grace and Gerenser, 2003, Guruvenket et al., 2004). The hydrogen bonded structures are observed at 3392 cm^{-1} and 3191 cm^{-1} corresponding to -O-H stretching vibration (Ghosh et al., 2004, Guruvenket et al., 2004). The intensities of these peaks increase with increasing input power, and broader peaks are seen due to the crosslinking reactions.

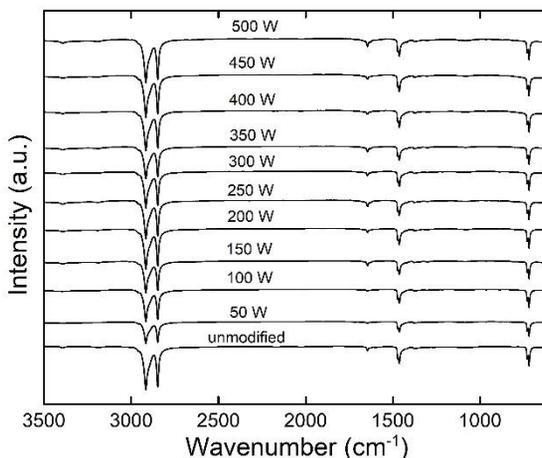


Fig. 2. FTIR-ATR spectra of unmodified and plasma modified PE samples for Argon plasma.

XRD measurements

The XRD patterns are measured between 10° and 60° with 0.02° per 1 s to investigate the structural orders of PE surfaces, as shown in Fig. 3. The pattern peaks are found at 2θ of 21.6° , 24° , 29.9° , 36.3° , and 39.9° . After the plasma exposure, peaks observed at 2θ of 20.5° , 46.8° and 53.1° start to appear more clearly. Intensities of these peaks show a significant increase after the plasma surface modification. It can be considered that Argon plasma leads to improve the surface energy of PE and increase the concentration of the saturated structures on the surface. Due to the relationship between the surface energy and the structural order of the surface, it is observed that the crystal properties of PE surfaces are improved via the plasma exposure (Slepička et al., 2013, Kim et al., 2003). Additionally, the width of these peaks is inversely proportional to the crystallite size, which is observed as decreasing after the plasma exposure. This also verifies that the increase in the crystallinity. It can be suggested that the plasma exposure is effective in improving the crystallinity of PE surfaces, and maximum differences between the unmodified and modified spectra are obtained at 50 W, 150 W and 450 W. As seen in the results, there are no systematic changes with increasing RF input power.

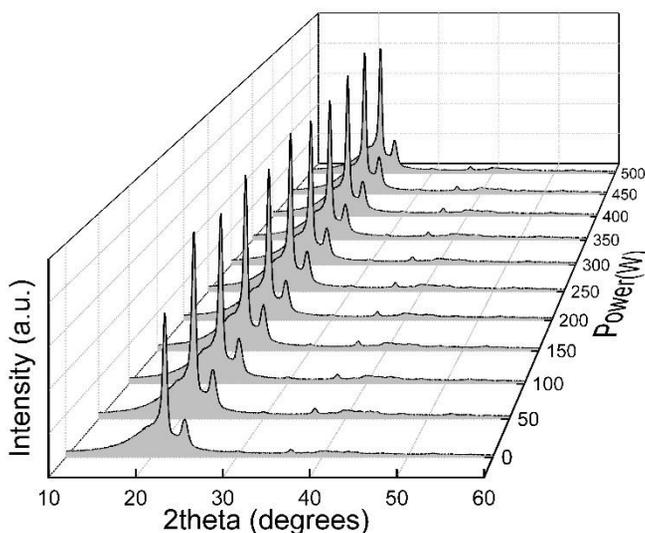


Fig. 3. XRD pattern of unmodified and plasma modified PE samples for Argon plasma.

Conclusion

A capacitively coupled RF plasma system is used to enhance the surface properties of PE polymer material. The results show that Argon plasma provides the formation of new functional groups on surfaces and the activation of the unsaturated structures existing on surfaces to increase the concentration of saturated structures. It is observed that the discharge power plays a significant role in controlling the energy required for the reactions occurring during the process. The OES spectra show the formation of the atomic and the molecular species during the plasma modification and the number density of these species generally have higher values at the high RF input power, but it is not a continuous increase due to the complex interactions. Moreover, the crystallinity of PE surfaces significantly increases with the plasma exposure. This shows that the required energy is transferring from the plasma discharge to improve the low surface energy.

Acknowledgements

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Co-doped ZnO Thin Film Nanocomposites as Model Nanocatalysts

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Abstract

In this work, we report on the deposition of Co-doped ZnO (CZO) thin films on c-sapphire substrate using the relatively novel pulsed electron beam ablation (PEBA) method at different temperatures (450°C, 600°C, 800°C) and under argon pressure of ~3 mTorr. Three main aspects of the films, viz., size of nanoparticles, presence of elemental cobalt and cobalt crystal phase have been assessed using complementary analytical techniques. Scanning electron microscopy (SEM) has revealed that the films consist of cobalt-rich globules dispersed over the surface, which grow out of primitive nanoparticulates with an average size in the range of ~5-16 nm. Film roughness, based on atomic force microscopy (AFM) measurements, increases drastically as the deposition temperature is increased, viz., nearly 5 nm (450°C), 19 nm (600°C), and 18 nm (800°C). X-ray diffraction (XRD) data reveal that the elevated deposition temperatures (600°C-800°C) result in a significant increase in hcp metallic cobalt phase and strong deformation of the hexagonal wurtzite structure of ZnO phase in the films. From crystallographic analysis, the deposition temperature has a strong bearing on ZnO and cobalt crystallite size as well. X-ray photoelectron spectroscopy (XPS) findings point to increasing metallic Co content in the films at high deposition temperature. The potential of the films as nano-catalysts has been evaluated via Fischer-Tropsch synthesis (FTS) in a 3-phase continuously-stirred tank slurry reactor (3-φ-CSTSR) using a Robinson-Mahoney stationary basket (RMSB). The preliminary results are discussed in terms of catalytic activity and selectivity. The reaction liquid product is rich in diesel and wax fractions.

Keywords: Co:ZnO/Al₂O₃ nanocomposites; thin film nanocatalysts; pulsed electron beam ablation; Fischer-Tropsch synthesis.

Introduction

Over the last few decades, oxide-supported metal nanoparticles have triggered increasing interest amongst researchers for their potential applications as bio- and electro-chemical sensors (White et al., 2009), for solar energy harvesting (Chan et al., 2004), in biofuel up gradation (Xu et al., 2012), and as nanocatalysts for the sustainable production of fuels and valuable chemicals (Leshkov et al., 2007; Galvis et al., 2012; Abdollahi et al., 2017). Co supported on ZnO has gained intense interest in many industrially important processes, viz., hydrogen production (Jaramillo et al., 2005), photocatalysis (Poongodi et al., 2015), steam reforming (Martono et al., 2011), and other energy-intensive processes (Pan and Bukur, 2010). Among these energy intensive processes, Fischer-Tropsch synthesis (FTS) is a potentially attractive technology for the production of clean liquid fuels from syngas. FT is a well-established catalytic process in which synthesis gas (a mixture of CO and H₂) is converted into liquid fuels. The most common practical catalysts for FTS are Fe and Co (Aluha and Abatzoglou, 2016; Dalai and Davis, 2008). The water gas shift (undesired) reaction is more

significant on iron catalyst than on Co (Tsakoumis et al., 2010). While the activities of Co and Fe based FT-catalysts are comparable and they display similar chain growth capabilities at relatively low temperature (473-523 K), the productivity at higher conversion is superior using Co based nanocatalysts (Gual et al., 2012). It has been reported that cobalt hexagonal close packed (hcp) phase exhibits higher cobalt sites yield in FT reaction so that cobalt hcp phase seems to be more active than its cobalt face-centered cubic (fcc) phase counterpart (Fischer et al., 2011). Further, cobalt based FTS catalysts are more attractive due to their low water gas shift (WGS) activity and higher productivity of long chain hydrocarbons C_{5+} (Savost'yanov et al., 2017; Jahangiri et al., 2014). Zinc oxide supported Co catalysts have many distinctive features, viz., resistance to oxidation caused by water produced during FTS (Clarkson et al., 2012), tolerance of carbon dioxide (Freide and Hardy, 2009), and, consequently, the catalyst is able to maintain its activity over a long period of time.

In general, the properties of nano-catalysts depend on phase/structure, the presence of the metal in elemental form, and particle size, so that the control of these aspects during film growth, i.e., through the optimization of process parameters, is of primary importance to achieve desirable catalytic features. Since a large portion of atoms in nanoparticles are exposed to the surface, their physico-chemical properties are strongly influenced by the nature of surface species (Gual et al., 2012). On the one hand, the structure of CZO films is significantly affected by the doping level of cobalt in ZnO. For a Co doping level of up to 10-12 wt%, the properties of CZO are practically similar to those of zinc oxide (Juang et al., 2007; Park et al., 2004). Secondary phases, viz., elemental cobalt and cobalt oxides, have been observed in CZO films for higher levels of Co doping. On the other hand, the structure/phase of CZO film is strongly dependent on deposition temperature. Higher deposition temperature is more favourable for the formation of secondary phases in CZO films. Particularly, at 500°C-600°C, secondary phases like Co and CoO are formed in CZO films (Ivill et al., 2008), whereas hcp metallic Co clusters appear in CZO films deposited at 700°C (Kim et al., 2004). Similarly, a secondary phase of metallic Co nano-clusters near the surface has been reported for film deposited at relatively higher temperature (800°C) (Su et al., 2011). The properties of FT nanocatalysts are also size dependent (Gual et al., 2012), so that it is necessary to control their size in order to achieve desired features of a model nanocatalyst. Normally FT reaction takes place on cobalt sites located on the surface of cobalt metallic nanoparticles in the range of 6-30 nm. A catalyst containing metallic cobalt particles smaller than 4-5 nm in size is expected to re-oxidize to CoO during realistic FT reaction conditions, which eventually results in the deactivation of the catalyst (Karaca et al., 2011).

The production of nanoparticulates with well controlled dimensions is a characteristic feature of PEBA, which can be advantageous in the production of nanocatalysts (Mathis and Christen, 2007). Further, many intermediate steps, viz., impregnation, drying, calcination/decomposition and activation/reduction, are involved in the preparation of FT-based catalysts by conventional wet impregnation route, whereas a single step process is possible using PEBA. PEBA is a relatively novel/unexplored technique for the preparation of high quality thin films with superior properties. Preservation of target stoichiometry in the condensing film under optimum deposition condition is another characteristic feature associated with PEBA. High power density leads to rapid heating and evaporation far from thermodynamic equilibrium, making possible solid to vapour transition practically independent from the target material phase diagram and composition (Pattini et al., 2015). Consequently, the congruent sublimation of the target materials results in stoichiometric film condensation.

Recently, we have looked into the effects of Co deposition temperature and discharge voltage on structural and morphological properties of CZO films deposited on Si (100) (Ali et al., 2017). The substrate material, being one of the significant parameters in catalyst synthesis, could affect the structural (Park et al., 2012), optical and electrical properties of the films (Taabouche et al., 2013), and potential lattice mismatch between the film and substrate may result in the development of undesired stresses in the films. The substrate material

may turn out to be a serious limitation for optimum growth of CZO films to carry out a particular catalytic application (Handuja et al., 2010).

In this work, we assess the influence of deposition temperature on morphological, chemical and structural properties of CZO films deposited on c-sapphire substrates. Discussion of the experimental data revolves around three main aspects of CZO thin films viz., presence of elemental cobalt (Co⁰), cobalt crystal phase (hexagonal close-packed structure), and size of nanoparticles. The comparison between the properties of CZO films deposited on c-sapphire and Si (100) has been assessed using complementary analytical techniques. The potential of the films as model nanocatalysts has been examined in the context of FTS.

Materials and Methods

A commercial beam source (PEBS-20, Neocera Inc., USA) has been used to ablate high purity commercial grade CZO target (SINTEF, Norway) containing 20 wt% cobalt to deposit thin films of CZO on c-sapphire substrates (University Wafer, USA). PEBA system is composed of a stainless-steel chamber, which is pumped by a combination of two pumps (rotary and turbo molecular) to achieve a base pressure of 1×10^{-6} Torr. The beam source is composed of a hollow cathode, a trigger and a capillary tube as shown schematically in Fig. 1-a. More ample details on the beam source can be found elsewhere (Ali et al., 2017). Prior to deposition, the substrates and target were cleaned sequentially in an ultra-sonic cleaner (Cole-Parmer 8890, USA) in acetone and methanol at 50°C for 30 minutes, respectively. The target has been pre-ablated before deposition by 3000 electron beam pulses at an accelerating voltage of 10 kV and a pulsed electron beam frequency of 2 Hz in order to remove any surface contamination. The films were deposited at various deposition temperatures (450°C, 600°C, 800°C), whereas beam frequency and accelerating voltage were set to 2 Hz and 16 kV, respectively. During deposition, the substrate to target distance, capillary tube (3 mm in diameter and 18 cm in length) to target distance, beam frequency, and background Ar pressure were set to 50 mm, 2.5 mm, 2 Hz, and 3 mTorr, respectively. The target has been continuously rastered and rotated to allow for smooth ablation. The substrates have been subjected to continuous rotation to enhance film homogeneity.

A 3-phase, continuously-stirred tank slurry reactor, using the Robinson-Mahoney stationary basket (RMSB) configuration, has been used to evaluate CZO thin films for their FTS activity and selectivity. The schematic of the RMSB reactor is presented in Fig. 1-h. About 10 g of Al₂O₃ supported Co-ZnO thin film material containing was loaded into the reactor and reduced in-situ in high purity hydrogen for three hours at a flow rate and temperature of 160 cm³/min and 673 K, respectively. The reactor was cooled down to ambient temperature under a flow of H₂. Subsequently, 150 cm³ of squalane was introduced into the reactor. The catalyst was tested at 267°C and 2 MPa under the flow (280 cm³.min⁻¹) of synthesis gas composed of 60% H₂, 30% CO and 10% Ar (H₂:CO volume ratio = 2) under a stirring speed of 2000 rpm for 120 h. FT gaseous and liquid products were analyzed using two separate off-line gas chromatographs (GCs) by employing the same procedure as described in a previous study (Aluha et al., 2016).

Phase and crystallographic analyses were carried out using a bench top x-ray diffractometer (Rigaku Mini Flex 600, USA). The scan range for 2 θ has been measured from 30° to 80° using theta/2-theta Bragg-Brentano configuration. The system was operated at 15 mA and 40 kV. The diffractograms have been

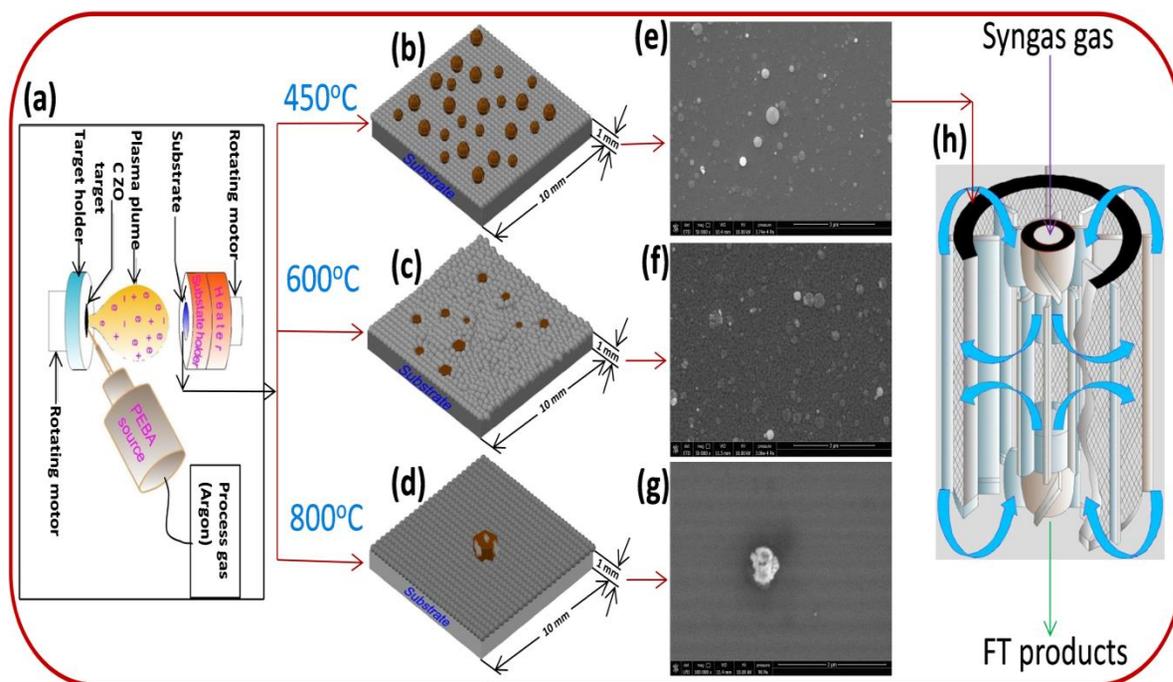


Fig. 1. Fig. 1. Morphological evolution sketch of CZO films deposited on c-sapphire. (a) Schematic pulsed electron beam ablation system. (b, c, d) Schematics of CZO films deposited at 450°C, 600°C and 800°C respectively (e, f, g) SEM images of CZO films deposited at 450°C, 600°C and 800°C respectively. (h) a Robinson-Mahoney stationary basket (RMSB) used to test the activity and selectivity of the deposited films.

generated at a step size of $2\theta = 0.02^\circ$ and a scan speed of $1^\circ/\text{min}$. The morphology of the films has been investigated by two complementary surface characterization techniques, viz., SEM (FEI Quanta FEG 250, USA) and AFM (Anasys Instruments, USA). SEM was operated under high vacuum at 10 kV, whereas AFM was operated with a scan speed of 0.2 Hz–0.5 Hz in contact mode. The elemental composition of the films was characterized by EDX. Film thickness has been measured by visible reflectance spectroscopy (M-Probe Series, Semiconsoft, USA). XPS (Thermo-Fisher Scientific, UK) K-Alpha system has been used to acquire near surface chemical composition of the films. The x-ray source consists of monochromated Al K-alpha x-rays and the measurements were made at an electron take-off of 90° . The samples were analyzed using the largest x-ray spot size ($400 \mu\text{m}$ ellipse) for this instrument.

Results and Discussion

The growth of Co rich globules in CZO films is shown schematically in Fig. 1(e-g). It can be clearly seen that the surface morphology of CZO films is significantly affected as the deposition temperature increases from 450°C to 800°C , and the deposited films follow two different growth modes. The growth of CZO films at 450°C seems to follow the Stranski-Krastanov (S.K.) growth model, i.e., layer plus islands. The first layer (grayish colour) largely consists of ZnO phase on top of which Co-rich globules (whitish colour) are formed and that the latter are uniformly distributed over the film matrix, as shown in Fig. 1(e). It is worth noting that the density of the Co-rich globules, whitish in the corresponding SEM images as shown in Fig. 1(e-f),

decreases as the deposition temperature increases from 450°C to 800°C. In S.K. model, the depositing atoms preferably bond to the substrate rather than to one another. After forming a few layers initially, as a result of a large decrease in Gibbs free energy when the depositing atoms bond to the substrate rather than bonding to one another and provided surface diffusion is fast. Due to lattice mismatch between the films and substrate, the development of strain results in the formation of 3D islands on top of the initial layer to relax the strain. The films grown at 600°C appear to follow the Volmer-Weber (V-W) model, i.e., from 3D islands, which grow side by side. In V-W model, the depositing atoms are more strongly bonded to one another than to the substrate material combined with slow surface diffusion, which results in a pile-up of atoms and subsequent formation of the film out of 3D islands forming a continuous layer. The film corresponding to a deposition temperature of 800°C seems to follow a different growth mode, albeit the main features of S.K. model are obvious therein. In addition, interestingly it is noted that at low deposition temperature (450°C) Co-rich globules are sphere-like in shape, but at higher growth temperatures (600°C and 800°C), Co-rich globules are tapered (faceted). Under similar deposition conditions (450°C-800°C and 16 kV) for CZO films on Si (100), similar growth models have been reported in a previous study (Ali et al., 2017).

Phase analysis of CZO films has been carried out by XRD using theta/2-theta Bragg-Brentano configuration. Fig. 2 shows XRD patterns of the films grown on c-sapphire at different deposition temperatures (450°C, 600°C, 800°C). The diffraction patterns of all films show strong peaks corresponding to the c-sapphire substrate, i.e., the peak at $2\theta \approx 41.68^\circ$ (0001). The characteristic peak of ZnO hexagonal wurtzite structure (002) can be observed at $2\theta \approx 34.43^\circ$ for the film deposited at 450°C, and the film exhibits two additional peaks corresponding to ZnO at $2\theta \approx 36.26^\circ$ (101) and 72.6° (004), as shown in Fig. 2 (bottom). For the film deposited at 600°C, the diffractogram does not show any presence of ZnO peaks corresponding to planes (101) and (004), and only reveals a reflection (relatively less intense compared to the films deposited at 450°C) along the peak corresponding to plane (002), which is likely suggestive of a distortion of ZnO hexagonal wurtzite structure due to enhanced deposition temperature [26]. The sharp and intense diffraction peak (002), for the films deposited at 450°C and 600°C, reveals that the deposited films have a preferential c-axis orientation, see Fig. 2 (bottom, middle). When the deposition temperature is further increased to 800°C, the corresponding diffractogram does not reveal any signals from ZnO phase due to complete distortion of the wurtzite structure. Relatively low intensity or absence of ZnO hexagonal wurtzite structure peak (see Fig. 2- middle, top) corresponding to the plane (002) is most likely due to the low content of ZnO in the films (corroborated by XPS survey scan, see Fig. 3) or may be attributed to a significant distortion of ZnO hexagonal wurtzite structure at higher deposition temperature. Consequently, the diffractogram for the film deposited at 600°C exhibits a less intense peak corresponding to (002) plane, and does not reveal any signals diffracted from ZnO hexagonal wurtzite structure for the film deposited at 800°C. The phase analysis of the film deposited at 450°C reveals two peaks corresponding to $2\theta \approx 64.3^\circ$ (315), 80.2° (600) attributed to hcp metallic Co. While five peaks associated with metallic Co appear at $2\theta \approx 37.6^\circ$ (301), 52.8° (313), 64.3° (315), 71.5° (008) and 80.2° (600) for the films deposited at 600°C, and three peaks appear at $2\theta \approx 37.6^\circ$ (301), 64.3° (315) and 80.2° (600) corresponding to Co_o (PDF card no.: 01-070-2633) for film deposited at 800°C. Overall, a higher intensity of metallic Co can be observed in the film deposited at 600°C and 800°C, which suggests that a high deposition temperature, viz., 600°C and 800°C, is more favorable for the formation of hcp metallic Co in CZO films than 450°C.

Phase analysis of CZO films deposited on Si (100) at 450°C, as reported in a previous study (Ali et al.,

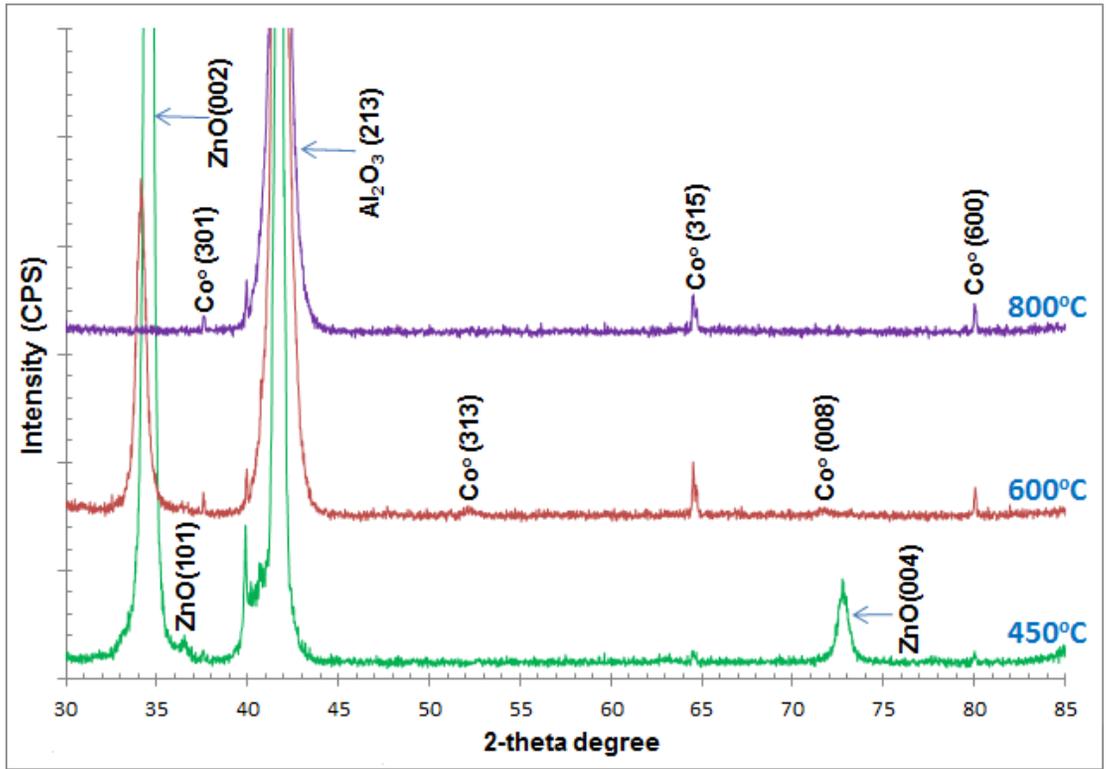


Fig. 2. XRD patterns for CZO thin films deposited on c-sapphire at different temperatures (450°C, 600°C and 800°C) and an accelerating voltage of 16 kV.

2017) reveals two peaks corresponding to hcp metallic Co at $2\theta \approx 42.04^\circ$ (213) and 61.7° (412). The film deposited at 600°C exhibits seven peaks associated with Co° , viz., $2\theta \approx 35.7^\circ$ (203), 41.4° (302), 42.5° (204), 50.1° (205), 51.5° (304), 59.6° (411), and 61.7° (412), whereas the diffractogram of the film deposited at 800°C reveals three peaks of Co° , viz., 42.5° (204), 50.1° (205), and 61.7° (412) [26]. Overall, on the one hand, a higher intensity of hcp Co content can be observed on Si (100) substrate, which suggests that under similar deposition conditions Si (100) substrate is relatively more favorable for the formation of hcp metallic Co in CZO films than c-sapphire substrate material. On the other hand, CZO film deposited on Si (100) shows dismal performance than the film on c-sapphire under similar FT reaction conditions (Ali et al., 2018).

The crystallite size of Co and ZnO can be estimated from the XRD pattern using the Debye Scherer's equation,

$$D = 0.9 \times \lambda / (B \times \cos \Theta) \quad (1)$$

where λ is the X-ray wavelength, Θ is the Bragg diffraction angle, and B is the full-width at half angle maximum (FWHM) of the diffraction peak.

The crystallite size and strain have been calculated for each peak in the diffractogram corresponding to ZnO and Co phase separately, and average values are listed in Table 1. It is noticed that the maximum ZnO crystallite size (22.86 nm) is obtained for the film deposited at lower deposition temperature (450°C), while in Table 1. Average crystallite size and strain of ZnO and Co phases at different temperatures.

Temp. (°C)	ZnO crystallite size (nm)	Stain	Co ^o crystallite size (nm)	Strain
450	22.86	0.0055	78.42	0.0008
600	13.65	0.009	59.63	0.0026
800	0	0	81.81	0.0009

case of metallic Co the maximum crystallite size (81.81 nm) is obtained at higher deposition temperature, i.e., 800°C. Overall, it is also noted that the crystallite size of Co is relatively higher than ZnO counterpart.

The near-surface chemical composition of the films has been investigated by XPS. Fig. 3 shows XPS survey spectra of CZO films deposited at various deposition temperatures, which shows representative peaks of Zn, Co and O for the films deposited at 450°C and 600°C, whereas the film deposited at 800°C exhibits only Co and oxygen peaks. The absence of Zn at the deposition temperature of 800°C is in accordance with XRD results. This can be explained in terms of the boiling point of Zn (907°C) nanoparticles (Viart et al., 2003). When the film is deposited at 800°C close to the boiling point of Zn, most likely Zn would have

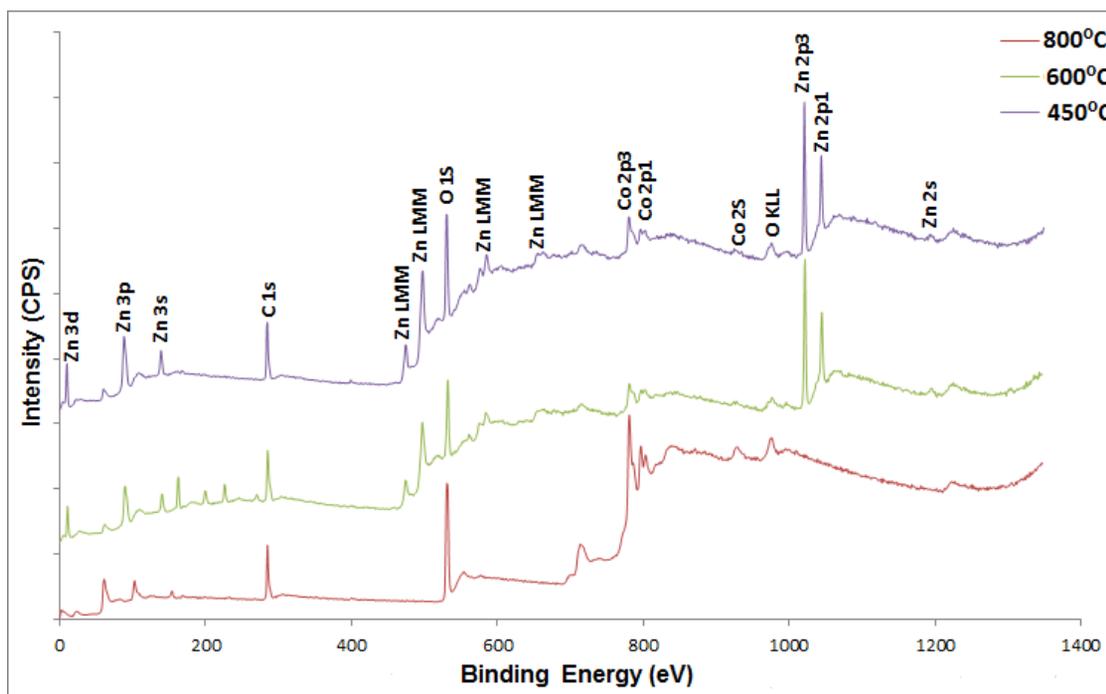


Fig. 3. XPS survey scan spectra of CZO films deposited at different deposition temperatures (shown in the inset).

re-evaporated from the film surface due to its high vapour pressure. This may lead to the elimination of Zn phase in the films and results in Co-phase rich films as can be seen from Fig.3, which is in accordance with XRD measurements.

Fig. 4 depicts spectra of Co $2p_{3/2}$ peaks (and their deconvolutions), and indicates that Co is present in oxidized (Co^{+2} , Co^{+3}) as well as in non-oxidized (Co^0) chemical states in CZO films. The Co $2p_{3/2}$ peak at the binding energy around 780.5 eV is assigned to Co^{+2} oxidation state (Ivill et al., 2008). The energy peak at

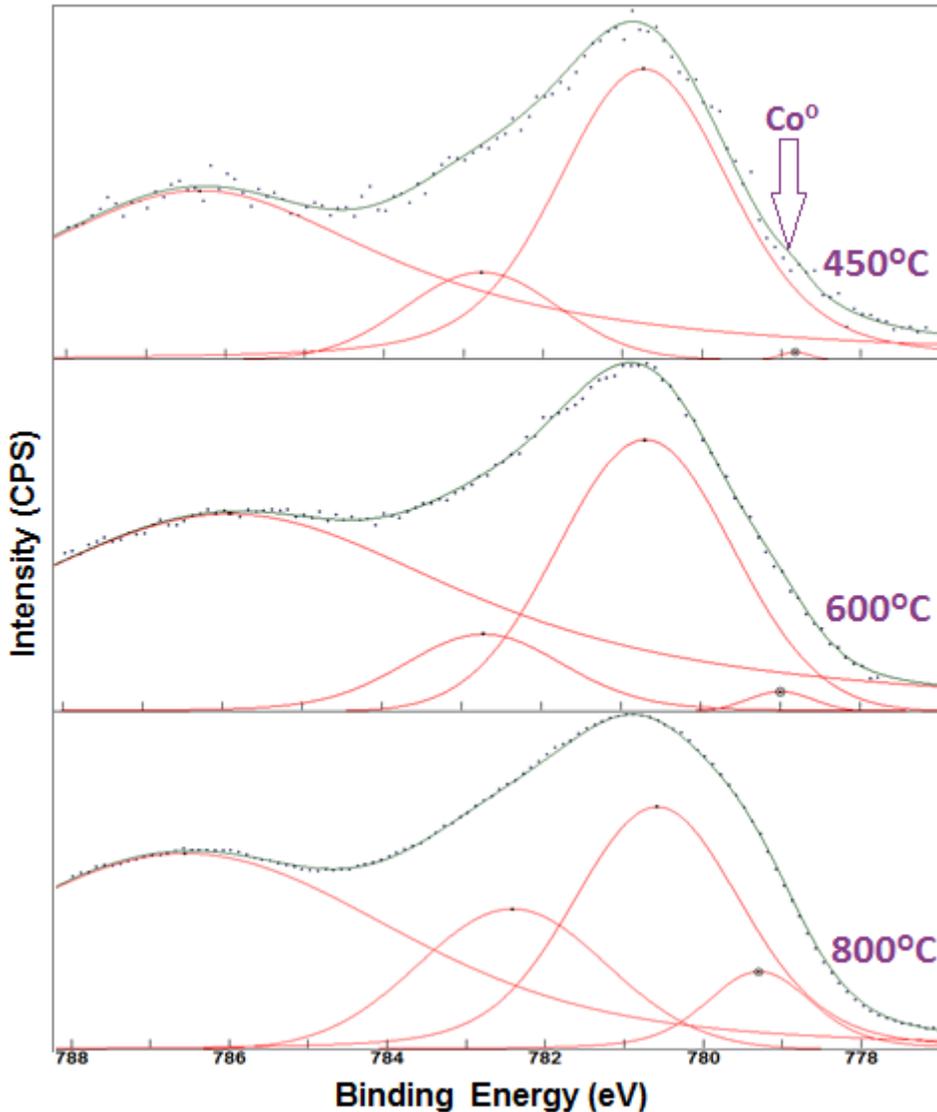


Fig. 4. XPS chemical binding spectra of Co $2p_{3/2}$ peaks (and their deconvolutions) of CZO films grown at different deposition temperatures (450°C–800°C).

around 782.8-783.3 eV is ascribed to Co^{+3} oxidation state (Zhou et al., 2008; Alves et al., 2017). The co-existence of Co^{+2} and Co^{+3} suggests the presence of CoO and Co_2O_3 phases near the surface in CZO films (Vadiyar et al., 2016). The data indicate that a substantial portion of Co atoms are present in the films as Co^{+2} oxidation state, where Co^{+2} substitutes Zn^{+2} lattice sites in ZnO. The intensity ratio of Co^{+2} and Co^{+3} signals in the films changes because of the possibility of oxidation of Co^{+2} to Co^{+3} . The exact nature of the cobalt defect in the structure is not possible to determine unequivocally with XPS measurements (Zhou et al., 2008). The small peak at the low binding energy located at 778 -779 eV is attributed non-oxidized (Co^0) cobalt (Tortosa et al., 2008; Peng et al., 2005). Interestingly, it is to be noted that as the deposition temperature increases, the metallic Co content in the film increases in accordance with XRD measurements. It can be concluded that high deposition temperature (800°C) is more favourable for the formation of metallic Co in the deposited films near the surface. Thus, the deposition temperature plays a key role in controlling metallic Co content in CZO films, and, accordingly, film properties. Based on XRD and XPS analyses, it seems that at lower deposition temperature (450°C) Co ions are largely incorporated into substitutional sites of ZnO structure, whereas for the films deposited at higher deposition temperature (600°C , 800°C) Co ions are located in the interstitial sites of ZnO lattice.

The compositional analysis of the films deposited at relatively high temperature (600°C , 800°C) has been acquired by EDX line scan as shown in Fig. 5, which clearly confirms the presence of Zn, Co and O in CZO films. Line scans provide a quantitative analysis of the elements along the dark green colour line ending with two blue circles. EDX line scan (superimposed on the corresponding SEM image) analysis confirms that the film matrix largely consists of Zn (purple line), while Co (blue line) is mainly to be found in the globules. The more whitish the color of the globule is, the higher the cobalt concentration is relatively to oxygen concentration as shown in Fig. 5(b). The oxygen content (green line) in the film is pretty high mainly due to substrate (c-sapphire) material underneath the film. The data, see Fig. 5(b), confirm that Zn content is remarkably less (1-2 wt.%) in the films deposited at 800°C . This is most likely due to the re-evaporation of Zn from the film surface when the deposition is carried out at 800°C (close to the boiling point of Zn) as

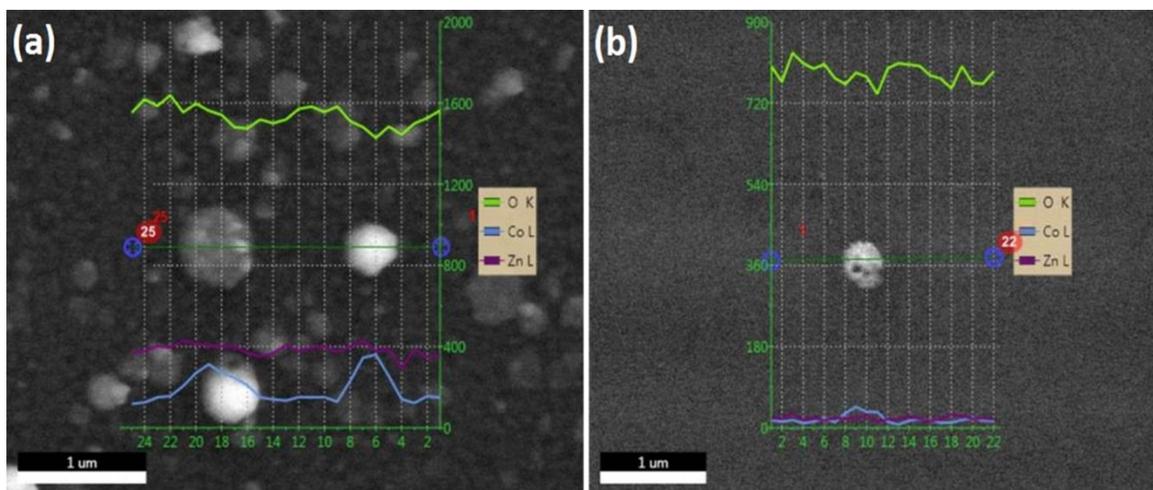


Fig. 5. Typical EDX line scans and their corresponding element profiles of the films deposited at (a) 600°C , (b) 800°C .

explained earlier.

Fig. 6 shows the surface morphology of CZO films grown on c-sapphire at different temperatures as per SEM analysis. Inspection of SEM images indicates that CZO films consist of nano globules, whose size is in the range of $\sim 10\text{-}300$ nm. The films consist of nano globules whose size and density seem to be strongly affected by the deposition temperature when the latter is varied from 450°C to 800°C . It can be seen from Fig. 6(a) that the globules are well isolated for the films deposited at 450°C , while the globules grow side by side forming a continuous layer for the film deposited at 600°C . The globule size decreases and density increases significantly as the temperature is increased from 450°C to 600°C . Cobalt nano particles start to melt at around 600°C (Homma et al., 2003), and, accordingly, the higher globule density and their smaller size at high deposition temperature may be attributed to melting and spreading of Co globules over the film surface. Owing to thermodynamic (the melting process) and kinetic processes, viz., deposition flux, nucleation rate, surface diffusion and re-evaporation, Co particles disperse on the film surface resulting in smaller size and higher density. For the films deposited at 800°C , see Fig. 6(c), and Fig. 5(b), it can be seen that the films consist of a very small number of Co-rich globules on the surface, and the globules exhibit holes (pores). The can be explained in terms of re-evaporation of Zn nano particles from the film surface. The data reveal that

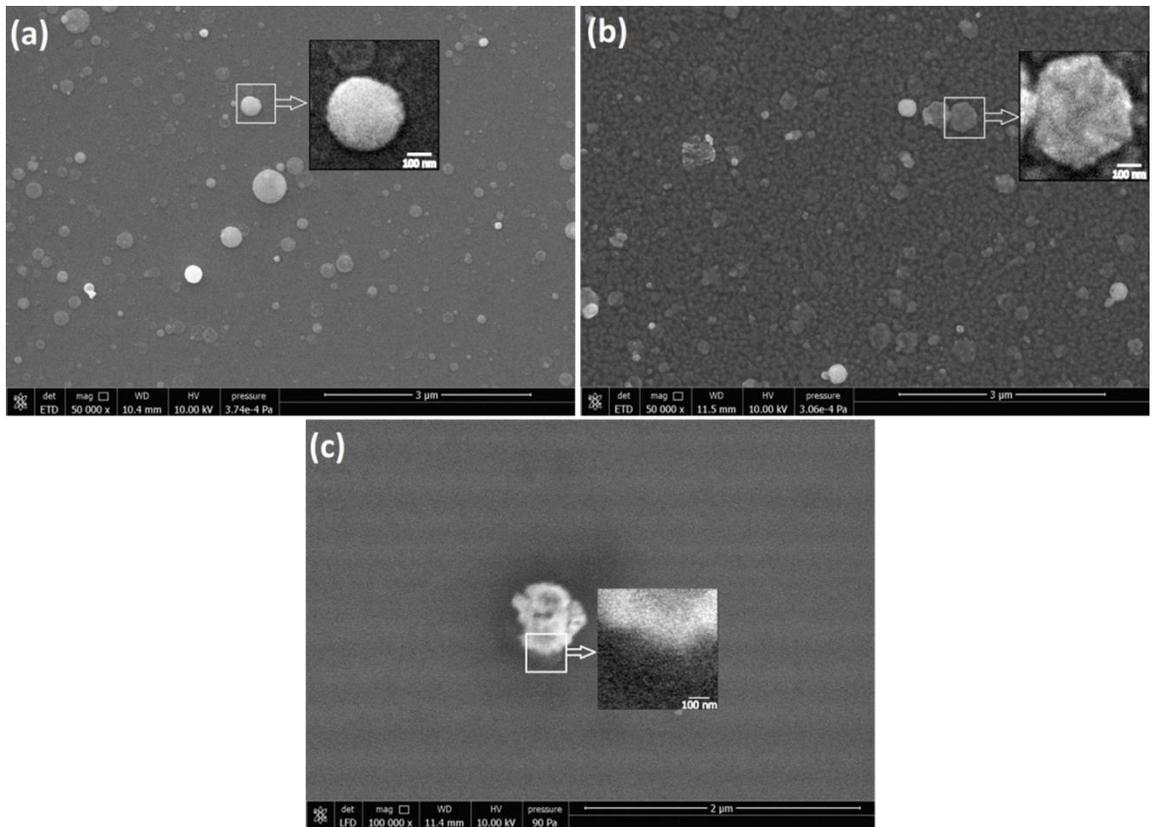


Fig. 6. SEM images of deposited films as a function of temperature at (a) 450°C , (b) 600°C , (c) 800°C . the films deposited at 450°C on c-sapphire has a similar morphology as the film deposited on Si (100) under same process conditions as reported in an earlier study (Ali et al., 2017). Furthermore, the films deposited on Si at 600°C exhibit cracks and voids, while the films on c-sapphire seem to be continuous. The films

deposited on Si at high temperature (800°C) exhibit a higher number of agglomerated secondary particles relatively to the film deposited on c-sapphire at the same temperature, as depicted in Fig. 3(a-c).

A closer inspection of the films (as indicated in the zoomed-in square section of the deposited films) reveals that Co rich globules are dispersed over the film and consist of primitive nano-particles. The particle size distribution of these primitive nano-particles is depicted in Fig. 7. The data reveal that deposition temperature has substantial effect on particle size distribution. The most frequent particle size is in the range of 6 nm–10 nm for the films deposited at 450°C and 600°C, whereas the film deposited at 800°C exhibits a significant number of particles with less than 5 nm in size. The average particle size at 450°C, 600°C and 800°C is nearly 11.4 nm, 16.03 nm, and 5.2 nm, respectively.

From VRS measurements, the thickness of the deposited films is in the range of ~ 70-100 nm. Fig. 8 shows a typical reflectance response of CZO film deposited on c-sapphire at 450°C. Film thickness is indirectly measured by means of a modified Marquardt-Levenberg built-in algorithm. The measured and calculated reflectance profiles are in good agreement, and any discrepancies are most likely due to uncertainties in the film optical properties used as input to the algorithm.

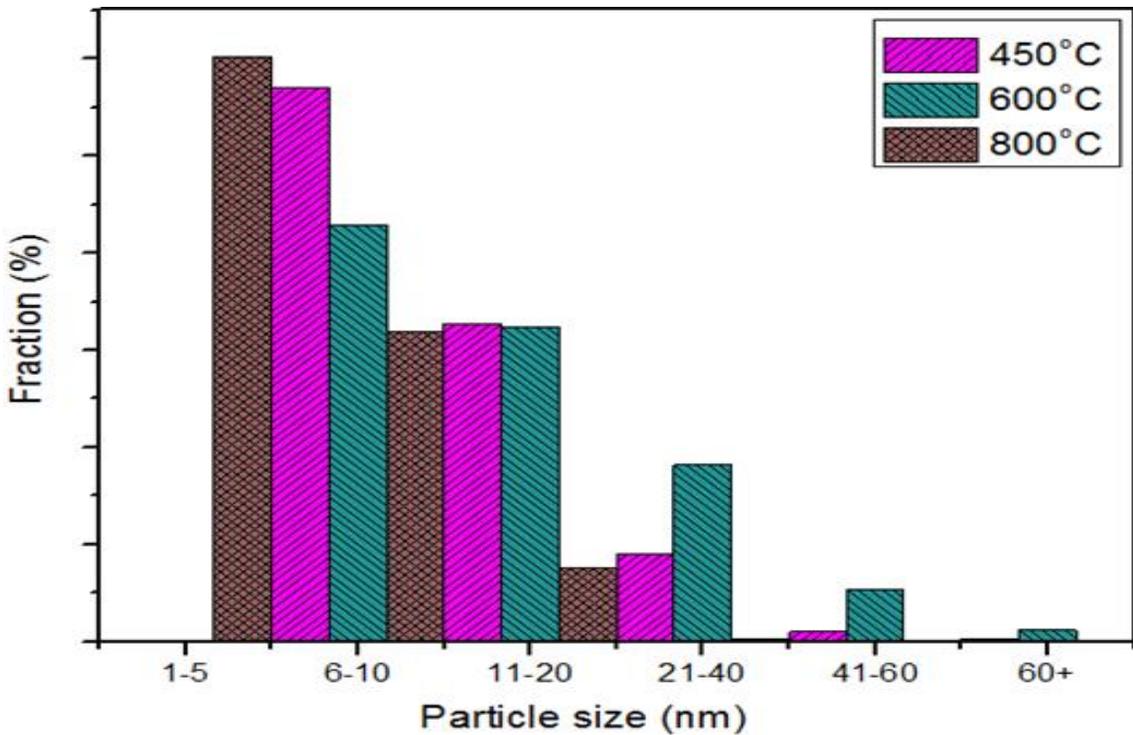


Fig. 7. Particle size distribution in films deposited c-sapphire. The deposition temperature is indicated in the inset.

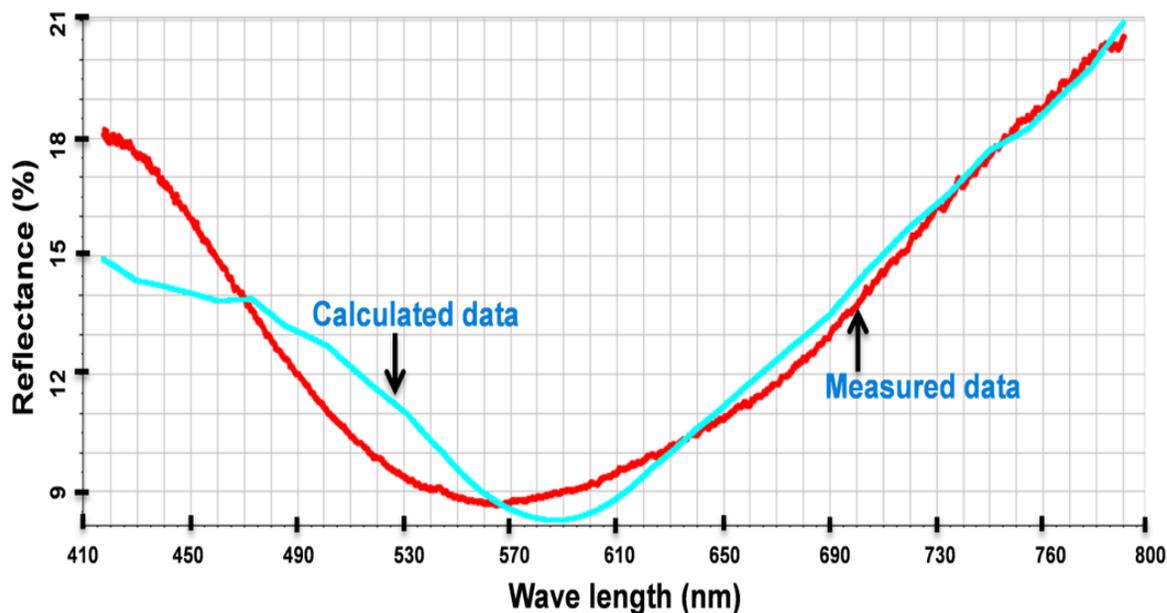


Fig. 8. Typical visible reflectance response of the film deposited at 450°C.

Film surface topography and average arithmetic roughness (Ra) are important properties for catalytic applications as they affect the physico-chemical properties of the films. Fig. 9 shows topographic images (2D, 3D) of CZO films deposited at various temperatures, whereby the findings reveal a drastic variation in film Ra (between ~4.8 nm and 18.2 nm) as the deposition temperature is increased from 450°C to 600°C. There is a marginal difference in Ra, viz., 18.2 nm to 17.6 nm, within the temperature range of 600°C-800°C. The present AFM images are consistent with SEM images reported earlier.

As per AFM data, the film deposited at 450°C consist of well isolated nano-globules, and the latter are uniformly distributed over the film matrix, which largely consists of ZnO, whereby ZnO acts as a support material and keeps the active phase highly dispersed. In the case of exothermic reactions like FTS, this may result in low energy density as ZnO is a semiconductor with a wide band gap, which helps reduce the possibility of sintering of the nano-catalyst. Based on these observations, only the films deposited at 450°C have been selected for the evaluation of FT thin film nano-catalyst activity and selectivity.

To evaluate catalyst activity, Co-ZnO/Al₂O₃ samples have been loaded into RMSBR as schematically shown in Fig. 1(h). This type of reactor has been chosen in order to avoid the stirrer coming into contact with the catalyst samples as this would have damaged the stirrer or CZO thin films. The nano-catalyst activity test procedure has been described elsewhere [31]. Carbon monoxide conversion is nearly 22% with total online time of six hours at 267°C. The catalyst shows higher productivity in the synthesis of long chain hydrocarbons (C₁₃ – C₂₀ and C₂₁₊), i.e., the liquid product is rich in diesel and wax fractions. The nano-catalyst shows a selectivity of ~4%, 31%, and 65% towards gasoline, diesel, and waxes, respectively, at a constant pressure of 2 MPa and a temperature of 267°C in continuous mode for 120 hours.

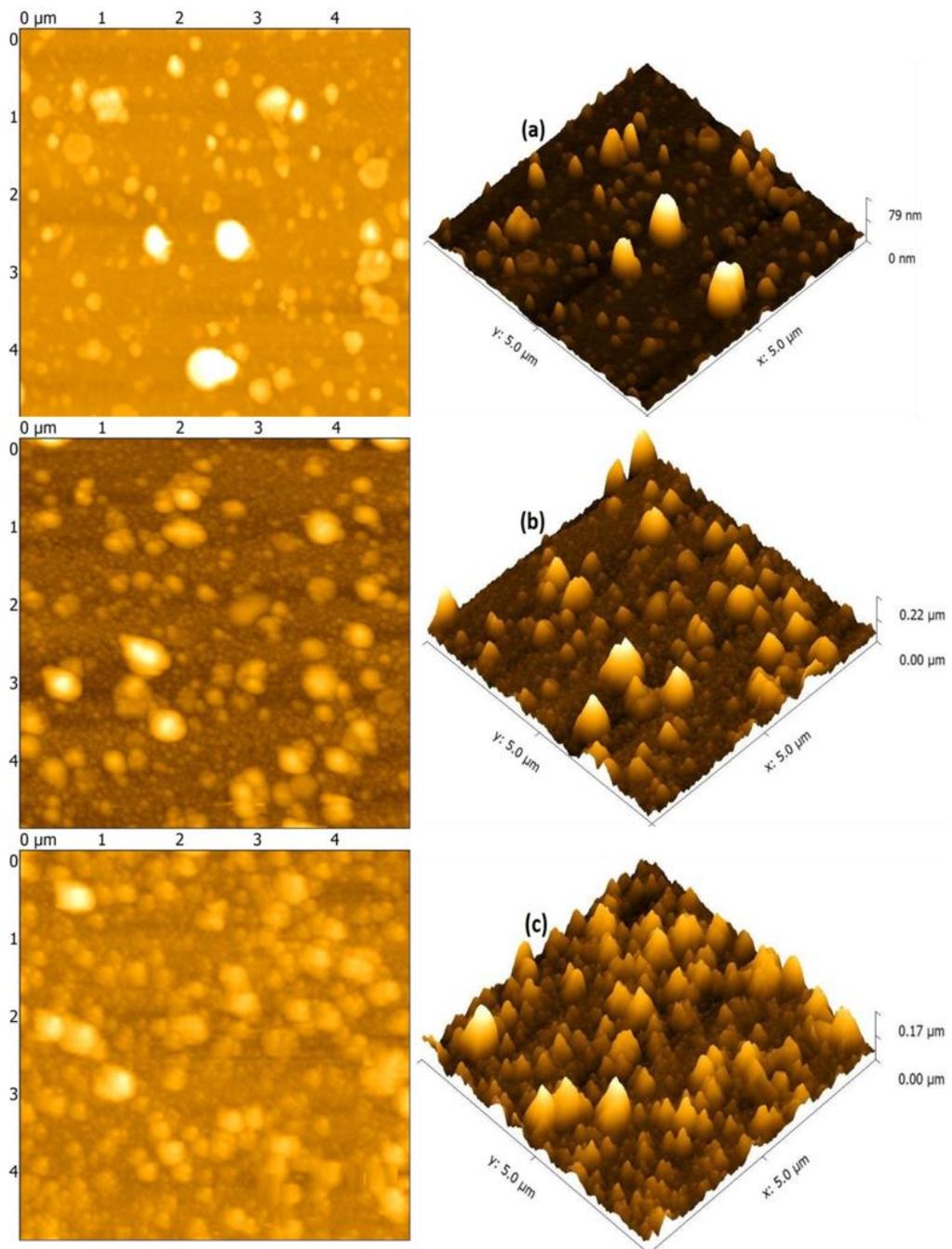


Fig. 9. AFM images (2D, 3D) of films deposited at different temperature (a) 450°C (b) 600°C (c) 800°C.

Conclusion

Co-ZnO thin film nano-composites supported on Al₂O₃ have been deposited in a single step from a single target containing 20 wt. % Co at different deposition temperatures (450°C-800°C) using PEBA technique. Experimental data reveal that the deposited films consist of rich globules, which are either dispersed on the film matrix, viz., films deposited at 450°C and 800°C, or grow side by side viz., films deposited at 600°C, and that the mode of film growth can be described by two models. Both XRD and XPS measurements support the existence of metallic Co nanoparticle in the deposited films and that high deposition temperatures (600°C, 800°C) are more favourable for the formation of metallic Co in CZO films than 450°C. XPS data reveal that all the deposited films exhibit cobalt in three chemical states, viz., oxidized Co (CoO and Co₂O₃), and elemental Co (Co⁰) near the film surface, and that the films deposited at 800°C largely consist of a cobalt phase as corroborated by XRD measurements. Crystallographic analysis reveals that the films deposited at 450°C and 600°C exhibit ZnO hexagonal wurtzite structure, while at 800°C ZnO hexagonal wurtzite structure is completely distorted in CZO films. The average particle size significantly decreases in the films deposited at 800°C (5.2 nm) compared to the films deposited at 450°C (11.4 nm) and 600°C (16.03 nm). The catalyst shows higher productivity in the synthesis of long chain hydrocarbons (C₁₃ – C₂₀ and C₂₁₊). The nano-catalyst shows a selectivity of ~4%, 31%, and 65% towards gasoline, diesel, and waxes, respectively.

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Thin silver film synthesis on polymeric composite surfaces via electroless deposition technique

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Abstract

Highly reflective polymeric surfaces for use in solar collector systems were developed using silver films with electroless deposition method. Vinyl-ester matrix composites reinforced with glass fibers were produced and then used as polymeric substrates. As a first step, catalytically active sites on the polymer surface were generated either by acidic (SnCl₂/HCl) or basic (NaOH) treatments for the subsequent deposition process. Effects of treatment procedure and treatment time were investigated in detail to enhance the adhesion and surface coverage of the resultant silver coatings. Surface atomic composition and roughness profiles of the surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. Tollens' process was then applied to deposit silver layers on the surfaces. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were employed to characterize the resultant films. XRD results proved the growth of silver film on the surface and no impurities were present in the film. Small-sized (~30 nm), and evenly distributed silver crystals with a film thickness of ~100 nm were observed over the surface in SEM images. UV/Vis spectrometer analysis confirmed the high reflectivity of the silver deposited polymeric surfaces (96-97% at 550 nm), indicating their potential applicability in solar collectors.

Keywords: Polymeric composites; Silver thin films; Electroless deposition; Reflective surfaces.

Introduction

Formation of metallic films on polymeric surfaces has attracted great attention recently, since the final product exhibits various optical, electrical, or magnetic properties (Cui et al., 2013). Polymeric substrates have many advantages such as lightweight, flexibility and shock resistance, when compared to inorganic substrates like glass (Southward and Thompson, 2001). Surface-metallized polymeric surfaces have many potential applications including bactericidal coatings, contacts in microelectronics, highly reflective thin film reflectors and concentrators (especially in space environments), lightweight optical mirrors and solar dynamic power generation (Chen et al., 2016). Silver coated polymeric surfaces have been an active area of interest for these application areas, since silver has high electrical conductivity and excellent reflectivity, besides its modest cost (Zaier et al., 2017). Among the various methods developed to deposit silver film on polymeric substrates, electroless plating technique provides a low-cost, solution-based method at atmospheric conditions, and is a promising option for large-scale production (Lili et al., 2011).

Despite plastics' broadening usage, potential for lightweight and at the same time strong materials is increasing for outdoor applications such as solar thermal system reflectors. Here comes into mind the fiber

reinforced polymers/plastics (FRPs), which also resist chemical and corrosive environments thanks to their polymer matrices, which bind together the reinforcing fibers (Masuelli et al., 2013). Polyester, epoxy, polyamide, polypropylene, polyethylene are the most known matrices with polyester being the cheapest and the earliest one in the industry. Vinyl esters, being similar chemically to unsaturated polyesters and epoxies, are somewhere between the two. They combine the crosslinking capability of polyesters with the mechanical and thermal properties of epoxies (Ku and Soares, 2004). Among the reinforcements such as carbon, aramid, boron, etc, glass is the most widespread and historical technical fiber used in polymeric composite production (Sathishkumar et al., 2014).

In light of the literature, an attempt was made in this work to find a functional application area for polymeric composites, which is the development of highly reflective polymeric surfaces for use in solar collector systems by coating silver films via electroless deposition method. Glass fabric reinforcement was preferred due its widespread usage, high strength, and low cost. For the polymer matrix, vinyl ester was used as it is between polyester and epoxy in terms of cost, and close to epoxy when it comes to strength. Besides, it is more durable under atmosphere, seawater, etc conditions (Visco et al., 2011). Therefore, glass/vinyl ester composites were produced and used as polymeric substrates in mirror production. As a first step, catalytically active sites on the polymer surface were generated either by acidic (SnCl_2/HCl) or basic (NaOH) treatments for the subsequent deposition process. Effects of treatment procedure and treatment time were investigated in detail to enhance the adhesion and surface coverage of the resultant silver coatings. Surface atomic composition, roughness profiles and hydrophilicity change of the surfaces before and after treatment were analyzed by X-ray photoelectron spectroscopy (XPS), atomic force microscopy and contact angle measurements, respectively. Tollens' process was then applied to deposit silver layers on the surfaces having different pretreatments. Electron microscopy (SEM), XRD and XPS methods were employed to characterize the resultant films. XRD results proved the growth of silver film on the surface and no impurities were present in the film. Small-sized (~30 nm), and evenly distributed silver crystals with a film thickness of ~100 nm were observed over the surface in SEM images. UV/Vis spectrometer analysis confirmed the high reflectivity of the silver deposited polymeric surfaces (96-97% at 550 nm), indicating their potential applicability in solar collectors.

Experimental

Production of polymeric composite substrates

Vinyl-ester matrix composites reinforced with glass fibers were used as polymeric substrates and produced using vacuum infusion technique. E-glass fabric (300 g/m^2) and vinyl ester resin was used in the synthesis. Resin amount was 1:1 weight of the fibers (10 plies of 30x30 cm fabric weighed 270 g). 2.5 ml accelerator (Cobalt octoat, %1) and 5 ml hardener (MKP-60, metil etil keton peroksit) was mixed in the resin. Open mould was vacuum sealed and release agent was applied on the mould surface. Fabric plies, peel ply, distribution medium, and vacuum bag were placed on the mould. After assembling the resin inlet and outlet connections, the resin was drawn via a tube wetting all the sections uniformly. Then the entire fabric was cured at room temperature for 2 days. Produced composite laminates were cut into 26x76 mm substrates for the experiments.

Pretreatments applied to the substrates

Pretreatments include three steps: (1) Cleaning, (2) Modification, and (3) Activation.

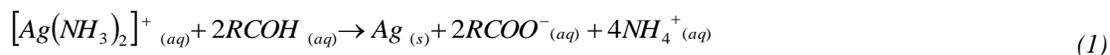
(I) *Cleaning Step*: The substrates were cleaned in dilute detergent solution and isopropyl alcohol, respectively to remove surface impurities (K1). Substrates were rinsed with distilled water thoroughly after each step. The effect of using ultrasonic bath (K2) at each step was also investigated to improve cleaning.

(II) *Modification Step*: Catalytically active sites on the polymer surface were generated either by sensitization treatment (SnCl_2) or etching treatment (NaOH) for the subsequent deposition process. Sensitization of the surfaces was conducted by immersing substrates into 0.05 M SnCl_2 in HCl (37%) solution for 30 min. After that, the substrates were washed with distilled water and then dried at 60°C . In the same manner, etching treatment was carried out in 3 M NaOH solution. Effects of treatment types were investigated in detail to be able to obtain smooth and continuous silver films on the surfaces.

(III) *Activation Step*: The substrates were soaked in $[\text{Ag}(\text{NH}_3)_2]^+$ basic solution for 30 min to activate the surface and to reach adsorption equilibrium between Ag^+ ions and the substrates. $[\text{Ag}(\text{NH}_3)_2]^+$ solution (Tollens' solution) is prepared as: NaOH solution was added to 0.1 M AgNO_3 solution to form brown Ag_2O precipitates. Then ammonia (NH_3 , %28-30) was added dropwise to this solution until all precipitates dissolved, showing the formation of transparent $[\text{Ag}(\text{NH}_3)_2]^+$ solution.

Formation of silver films on the substrates

Tollens' process was applied to deposit silver layers on the surfaces having different pretreatments. The method is based on the adsorption of $[\text{Ag}(\text{NH}_3)_2]^+$ complex ions onto the substrate surface and then their reduction to elemental silver, Ag^0 , with the addition of an reductant. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was chosen as the reductant of this process. The molar ratios of the components were kept constant as $[\text{Glucose}]/[\text{Ag}^+]=2$ and $[\text{OH}^-]/[\text{Ag}^+]=4$ in the coating bath. Silver metal deposition onto the surfaces was started by the addition of glucose solution into $[\text{Ag}(\text{NH}_3)_2]^+$ solution (Eq. 1). Substrates were taken out from the bath after 480 s and then washed with distilled water.



Characterization

The elemental composition of the surfaces before and after pretreatments was identified on an X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha) using monochromatic $\text{Al K}\alpha$ radiation (1486.6 eV) and Fourier transform infrared spectroscopy (Perkin Elmer ATR-FTIR) in the wavelength range of $4000\text{-}600\text{ cm}^{-1}$. In addition, surface roughness profiles of the surfaces were analyzed by atomic force microscopy (AFM, Nanosurf Flex Axiom) in the tapping mode, scanning an area of $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$. The morphology of the silver films were observed by field emission scanning electron microscopy (SEM, FEI, QUANTA-FEG 250). The crystal structure of the films were determined by X-ray diffraction (XRD, Phillips X'Pert Pro), under $\text{CuK}\alpha$ radiation for a 2θ range from 5° to 95° . The reflectance spectras were recorded using a UV/Visible spectrophotometer (Shimadzu, UV-2600-ISR) in the wavelength range of $300\text{-}1100\text{ nm}$. 550 nm , corresponding to wavelength of sunray at maximum radiation, was selected to compare the different results. Reflectance measurements are done at different regions on the same surface to observe the homogeneity of the silver coating.

Results and Discussion

FTIR analyses

Glass/vinyl ester composite FTIR spectra shown in Fig. 1 revealed peaks (1719 and 1180 cm^{-1}) of carbonyl group belonging to the ester in the structure. Ethers, alcohol-end groups, and acryloyl double bonds were observed in the spectra. The peaks present at 2921 cm^{-1} shows the presence of hydroxyl group. Aliphatic hydrocarbon skeleton and the presence of aromatic rings were all found to be typical of vinyl ester polymer. The findings confirmed the epoxy vinyl ester network based on the diglycidyl ether of bisphenol-A.

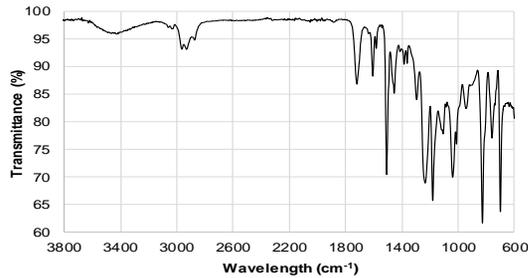


Fig. 1. FTIR spectra of the composite substrate

3.2 XPS analyses

Vinyl ester composite surfaces were found to be composed of carbon and oxygen, approximately 80% and 20%, respectively, which is in agreement with Jiao et al., 2018 and Andrew W. Signor et al., 2003. Surface atomic composition of the substrates is given in Tables 1 and 2 in means of atomic percentages.

Table 1. Wide scan XPS results

Substrate	C1s	O1s	Sn3d	Na1s	O/C
Untreated	79.24	19.41	-	-	0.245
SnCl ₂	66.47	26.24	6.11	-	0.395
NaOH	83.11	16.83	-	0.05	0.203

For SnCl₂ pretreatment, decrease in the C-O and O=C amounts were observed from C1s Scan B and O1s Scan A spectra, respectively (Table 2). O1s Scan B and C values correspond to Sn-O bonds.

Table 2. High resolution XPS spectra results

Substrate	C1s	C1s	C1s	C1s	O1s	O1s	O1s	Sn3d	Sn3d
	Scan A	Scan B	Scan C	Scan D	Scan A	Scan B	Scan C	Scan A	Scan B
Untreated	7.17	2.8	0.22	0.16	2.35	-	-	-	-
SnCl ₂	6.13	1.73	0.28	-	1.49	0.98	0.57	0.45	0.31
NaOH	9.43	2.59	0.10	0.25	2.31	-	-	-	-

For NaOH pretreatment, decrease in the carbonyl content and increase in the carboxylic acid content (O=C-O) was observed from C1s Scan C and C1s Scan D spectra, respectively (Table 2).

3.3 AFM analyses

Surface roughness profiles were analyzed and tabulated as can be seen in Table 3. It was found that the values did not change significantly after SnCl₂ pretreatment. On the other hand, NaOH pretreatment seemed to create nano cavities on the substrate surfaces. These findings correlate with SEM analyses, which can be seen in the related section below.

Table 3. Surface roughness values

Substrate	S _a [nm]	RMS [nm]
Untreated	7.57	9.74
SnCl ₂	8.58	10.94
NaOH	10.70	13.45

3.4 SEM analyses

SEM images confirm the surface roughness values obtained by AFM analyses (Fig. 2). Almost no change in substrate surface was observed after SnCl₂ pretreatment while NaOH treatment created flowerlike patterns on the substrates.

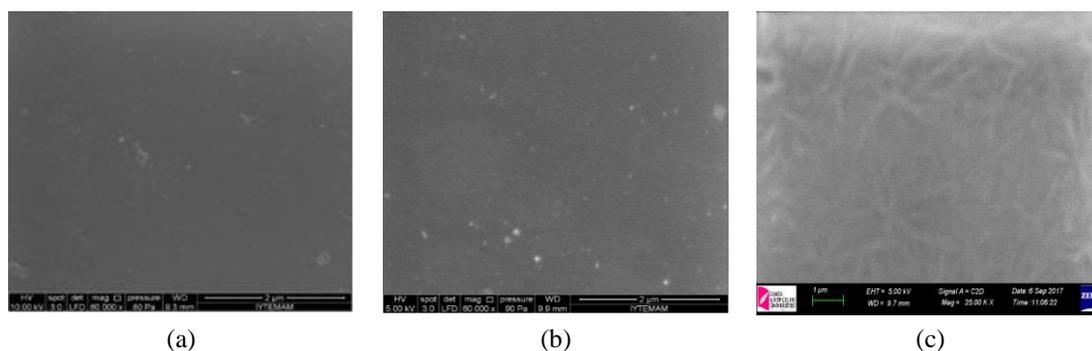


Fig. 2. SEM images of the substrates for the case of (a) Untreated; (b) SnCl₂ treated; (c) NaOH treated

3.5 Effect of the cleaning procedure on the resultant silver film

As can be seen obviously in Fig. 3, regardless of the pretreatment type, ultrasonically cleaned (K2) substrates resulted in silver thin films having higher reflectivity when compared to that of the substrates with no-ultrasonic cleaning step (K1). Therefore, ultrasonic cleaning was preferred throughout the rest of study.

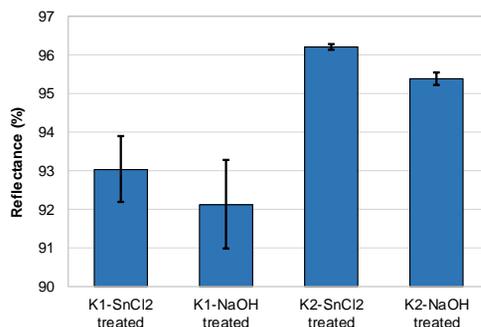


Fig. 3. Reflectance values regarding the cleaning procedure

3.6 Effect of the surface treatment procedure on the resultant silver film

Reflectivity values of silver thin films deposited on substrates having different pretreatments are shown in Fig. 4. The photographs of the silver coatings are also taken and given in Fig. 5(b-c) with the uncoated substrates (Fig. 5(a)). For SnCl₂ pretreated substrates, silver mirror reflectance values were measured as 96.2% and 95.5%, for front and back sides, respectively. NaOH pretreated composite substrates ended up with less reflectivity, that is 95.4% and 92.7% respectively for front and back sides. The difference between front and back sides were minimized for SnCl₂ case. Reflectance of the back sides of the substrates was less than their front sides. This difference must be due to the production technique. The back sides of the substrates seem to be more rough when compared to front sides. When the surfaces are treated with Sn ions, a redox reaction occurs on the surface involving the oxidation of surface Sn²⁺ to Sn⁴⁺ and reduction of Ag⁺ to Ag⁰, with the addition of Ag[NH₃]₂⁺ solution. This results to the formation of tiny silver seeds on the surface. Hence, small-sized and homogeneously distributed silver nanoparticles were obtained with SnCl₂ treatment with the deposition duration, as given in Fig. 5(d). The size of the particles is relatively larger in NaOH treated surfaces, as given in Fig. 5(e). Low reflectivity and larger error margins for NaOH pretreated mirrors confirm this finding.

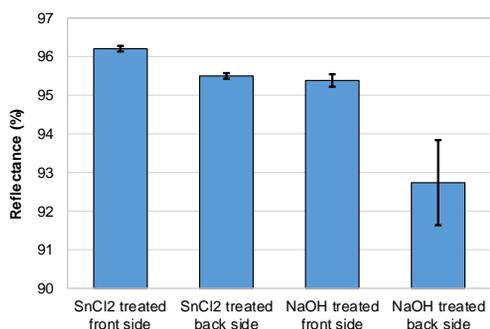


Fig. 4. Reflectivity of silver coated composite substrates

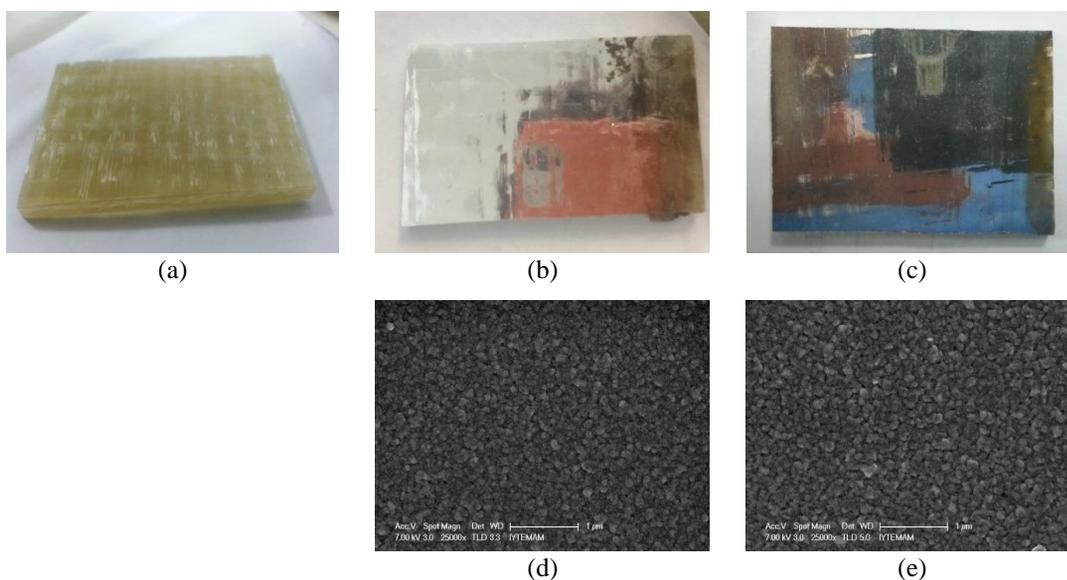


Fig. 5. Photographs and SEM images of the substrates after silver coating for the case of (a) no coating; (b,d) treated with SnCl₂; (c,e) treated with NaOH

Fig. 6 shows the XRD pattern of the silver film. The four peaks seen correspond to the planes of silver crystal matched with the JCPDS card no 65-2871 standard, which show the cubic structure of the metallic silver on polymeric surface. No characteristic peaks are observed for the impurities such as Ag₂O. The crystallinity of the silver particles is higher in SnC₂ treated substrates

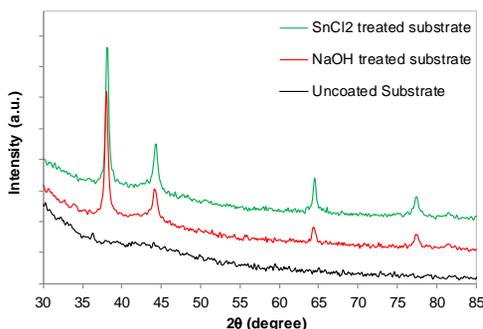


Fig. 6. XRD patterns of the composite substrate

4 Conclusion

Glass fiber reinforced vinyl ester matrix polymeric composite substrates were produced using vacuum infusion technique. Acidic (SnCl_2/HCl) and basic (NaOH) pretreatments were applied on the surfaces. Tollens' process was then applied to deposit silver layers on the substrates and mirrors were produced successfully. XRD results proved the growth of silver film on the surface and no impurities were present in the film. Small-sized (~ 30 nm), and evenly distributed silver crystals with a film thickness of ~ 100 nm were observed over the surface in SEM images. UV/Vis spectrometer analysis confirmed the high reflectivity of the silver deposited polymeric surfaces at 550 nm, indicating their potential applicability in solar collectors. Higher reflectivity was achieved for acidic surface pretreatment (96.2%) when compared to that of the basic pretreatment (95.4%). Besides, the difference between front and back sides were minimized for SnCl_2 case. Moreover, silver nanoparticle size was smaller and distribution was more even for acidic pretreatment.

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Investigation of mechanical and tribological properties of BCN thin films

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Abstract

BCN thin films are one of the most attractive materials in recent years based on their high hardness values, and excellent tribological properties. Having such characteristics, BCN films are becoming crucial for industrial and scientific applications as protective coatings. BCN films are also being used as lubricating coatings for high temperature applications due to good thermal and chemical stabilities. To synthesize BCN films several different deposition techniques have been carried out successfully such as chemical vapor deposition, rf-magnetron sputtering, reactive magnetron sputtering, dc-magnetron sputtering, closed-field unbalanced magnetron sputtering (CFUMBS) and high-power impulse magnetron sputtering (HiPIMS). In this work, BCN films were deposited on 4140 steel substrates by a superimposed closed-field unbalanced and high-power impulse magnetron sputtering system using different deposition parameters. We studied the structural, mechanical and tribological properties of BCN films. To characterize the structural properties of the BCN films SEM techniques were used. Micro-hardness and scratch tester were used to determine mechanical properties of the BCN thin films. Tribological properties such as friction coefficient of the films were calculated by pin-on-disc tribometer in ambient air. The maximum hardness and friction coefficient has obtained as 17.6 GPa and 0.54, respectively. The results showed that the hardness values affected the friction coefficient negatively due to the hard abrasive particles.

Keywords: CFUMBS;HiPIMS;BCN;Friction;Critical load

Introduction

BCN is an attractive coating material that has been worked on intensively in recent years because of its superior mechanical and tribological properties. Compared to other hard coatings (diamond, DLC, CN_x, B₄C and c-BN), BCN films are non-reactive with ferrous materials unlike diamond [1] and exhibit better thermal and chemical stability than DLC and CN_x at high temperature [2,3]. Also, it exhibits better adhesion properties because it has lower internal stresses compared to c-BN and B₄C [4,5]. Having such characteristics, BCN films are widely used as hard, protective and lubricative coatings in industrial and scientific applications. In literature, several different deposition techniques have been carried out successfully to synthesize BCN films such as chemical vapor deposition [6], rf-magnetron sputtering [7], reactive magnetron

sputtering [8], dc-magnetron sputtering [9], closed-field unbalanced magnetron sputtering (CFUMBS) [10] and high-power impulse magnetron sputtering (HiPIMS) [11]. Among these deposition techniques, HiPIMS is the newest and most promising technology. Most importantly, HiPIMS can be used with any type of magnetron sputtering system as a power supply [12]. There is no study that examines the adhesion properties of coatings obtained with HiPIMS in literature.

In this work, BCN films were deposited on 4140 steel substrates by a superimposed closed-field unbalanced and high-power impulse magnetron sputtering system with different deposition parameters. We studied the structural, mechanical and tribological properties of BCN films. To characterize the structural properties of the BCN films SEM techniques were used. Micro-hardness and scratch tester were used to determine mechanical properties of the BCN thin films. Tribological properties such as friction coefficient of the films were calculated by pin-on-disc tribometer in ambient air.

Experimental

To deposited BCN thin films were deposited on 4140 steel (42CrMo4), Si (100) and glass substrates by a superimposed CFUMBS and HiPIMS system. The deposition parameters are presented in Table 1. Prior to coating processes, 4140 substrates were polished to roughness values of $R_a \approx 0.1 \mu\text{m}$. The surface roughness (R_a) determined with a Mitutoyo profilometer. The 4140 substrates were ultrasonically cleaned using ethanol for 15 min and were dried right after mechanical polishing. After that surface of the 4140 substrates were etched in 2% nital solution. BCN thin films were grown by the CFUMBS system produced by Teer Coatings Ltd. This system is shown in Fig. 1.

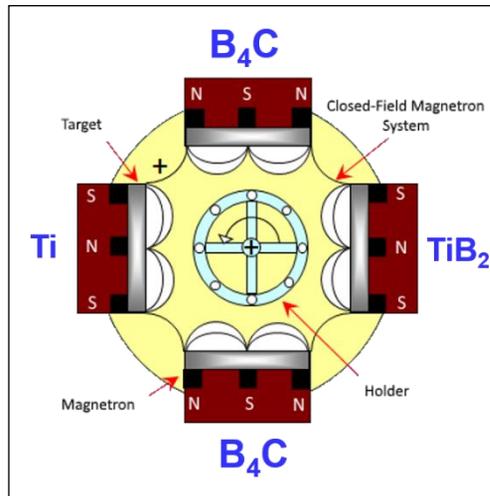


Fig. 1. CFUMBS system for BCN films

BCN films were deposited on 4140 substrate, using two B_4C one Ti and one TiB_2 targets. Ar gas was used in order to generate plasma and sputtering of the targets. The 4140, Si and glass substrates were stabled on a rotating holder. The distance between substrates and targets was fixed to 70 mm. Before deposition, the chamber pressure was set 2.0×10^{-5} Pa and then the surface of substrates was sputter-ion cleaned with Ar^+ at a bias voltage of -800 V under 0.26 Pa pressure for 20 min to eliminate possible contaminants and to obtain

better adhesion between the substrate and film. During the interlayers coating process, the HiPIMS voltage applied to B_4C targets is kept constant at 350 Volts. The target current applied to Ti and TiB_2 targets was varied between 0.1 A and 5 A. The amount of N_2 was set as 10 sccm to create nitride phases for TiN and TiBN interlayers. The working pressure was kept stable at 0.33 Pa through the deposition process. Firstly, Ti and TiN interlayers were deposited for 10 and 15 min respectively to increase adhesion between the substrate and film. Next, TiB_2 and TiBN interlayers were deposited for 15 min to reduce internal stress. Lastly, BCN films were deposited for 60 min. The voltage applied to B_4C targets for R1, R2 and R3 films was changed as 850 V, 750 V and 650 V respectively during the BCN film deposition process. The amount of N_2 was kept constant as 10 sccm. The architecture structure of BCN film is given in Fig 2. The deposition parameters of interlayers are presented in Table 1.

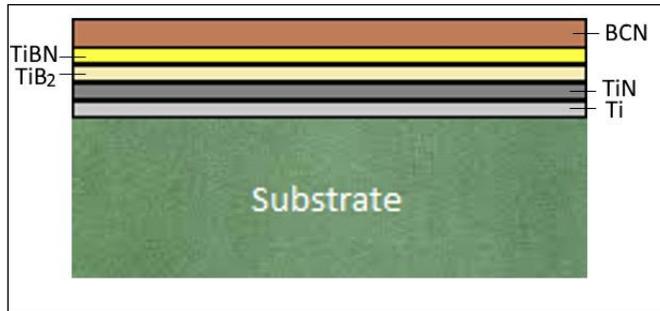


Fig. 2. The architecture structure of BCN films

Table 1. The deposition parameters of BCN films

The variable parameters	R1	R2	R3
B_4C voltage (V)	850	750	650
The constant parameters			
The amount of N_2 (sccm)		4.5	
Duty time (μs)		80	
Frequency (Hz)		500	
Duty cycle (%)		4	
The working pressure (Pa)		0.33	
The time of coated BCN films (min)		60	
Ti interlayer	Ti Target current: 5A	The working pressure: 0.33 Pa	
TiN interlayer	TiB_2 Target current :0.1A	Frequency, duty time:150 kHz, 1.5 μs	
TiB_2 interlayer	Ti Target current : 1A	Interlayer film time: 15 min	
TiBN interlayer	TiB_2 Target current :5A	The rate of Ar/ N_2 (sccm/sccm): 25/10	

The structural properties of the BCN films were characterized by FEI Quanta FEG-450 SEM system. Also, the film thickness was determined by FEI Quanta FEG-450 SEM cross-section images taken from the silicon wafers. To determine the hardness values of the BCN films a Buehler Micromet 2001 microhardness tester (using a Knoop indenter under a load of 10gf load for 15s) was used. One of the most important features of the coating is the adhesion. There are several processes to determine the adhesion between substrate and film.

Many of these are based on calculating the force needed to remove the film from the substrate surface such as tensile test, indentation test, and scratch test. In this work, CSM Instruments scratch tester (using a Rockwell-C diamond indenter with a 200 μm radius hemispherical tip under a load varied from 0 to 100 N with a sliding speed of 10 mm/min at the progressive load mode) was used. The tribological properties were calculated by Teer- POD2 pin-on-disc tribometer (with a load of 2 N at 95 rpm and relative humidity of 45% at room temperature).

Results /Discussion

The elemental analysis, film thickness, hardness values and critical load values of BCN films are presented in Table 2. Microstructural analysis of the BCN films deposited on Si substrates was examined on their cross-sectional SEM micrographs. The microstructure and film thickness values of BCN films are shown in Fig.3. According to Fig. 3., microstructure of all films has dense and non-columnar structure due to coatings by HiPIMS [13,14]. The microstructure is referred to the “Zone 3” region of Thornton’s Structure Zone Models (SZM) [15]. The thickness values of BCN films obtained from cross-sectional SEM micrographs for R1, R2 and R3 are 721.8 nm, 573.7 nm and 532.8 nm, respectively. With increasing the sputtering voltage, the energy of plasma ions increases, which results in an increase in the deposition rate [16]. Therefore, the highest thickness was obtained in the R1 film, which the highest voltage applied. According to the elemental analysis, R1 has the lowest nitrogen content and with the increasing nitrogen content hardness of the films decreases due to the h-BN phase [17].

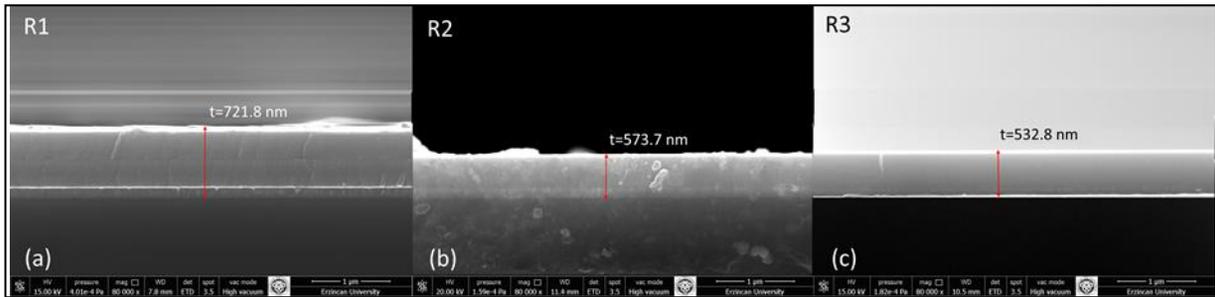


Fig. 3. The SEM images of BCN films for a) R1, b) R2, c) R3

Table 2. The elemental analysis, film thickness, hardness values and critical load values of BCN films

	N K	B K	C K	Ti K	Film Thickness(nm)	Hardness (GPa)	Critical load (N)
R1	27.37	53.73	11.61	7.29	721.8	17.6	55
R2	35.55	47.02	10.03	7.4	573.7	14.2	45
R3	38.46	45.04	9.06	7.44	532.8	8.4	35

In this work, the adhesion properties of BCN films were determined by CSM Instruments scratch tester. The maximum and minimum critical load values are achieved as 55 N and 35 N, respectively. The critical load optical images of scratch scars at 15N, 35N and critical load value are given in Fig. 4. According to results, the critical load value is increased by the increased target voltage value because as the target voltage increases the sputtering rate and the ion bombardment energy of target also increase. Thus, the films can grow more efficiently on the substrate surface [18]. For these reasons, the maximum critical load value is obtained at maximum voltage value (-850V). Furthermore, there is no failure until 15 N. After 20 N, adhesive failures are seen in all films. The volume of adhesive failure is increased by increasing load value.

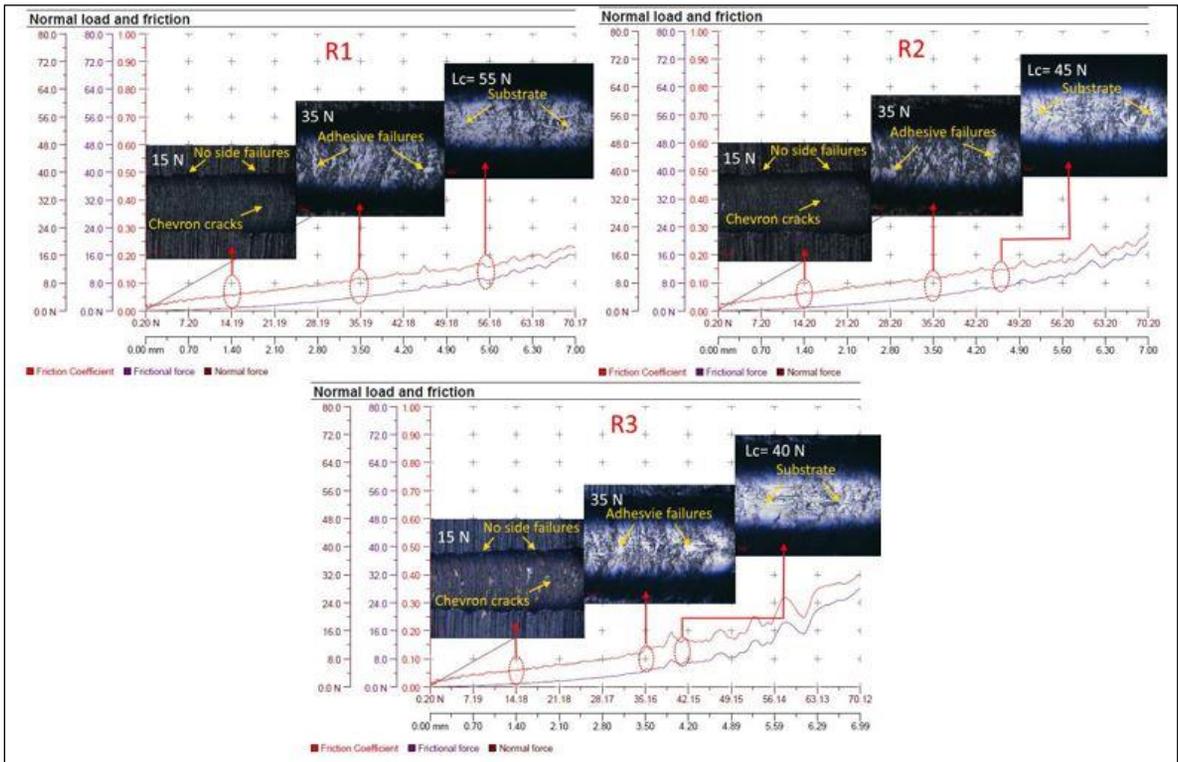


Fig. 4. The critical load values obtained from scratch test for a) R1, b) R2, c) R3

In order to determine the friction coefficient values of BCN films a pin-on-disc tribo-tester was carried out. The friction coefficient to time graphs of BCN films are given in Fig. 5. The friction coefficient values are gained as 0.54, 0.52 and 0.44 for R1, R2 and R3 films, respectively. All films have stable friction coefficient. Still, these friction coefficient values is relatively high compared to literature. This is because, increased hardness value affects the friction coefficient negatively by reason of the hard abrasive particles. Because hard abrasive particles lead to increase contact stress, resulting in increased friction coefficient [19].

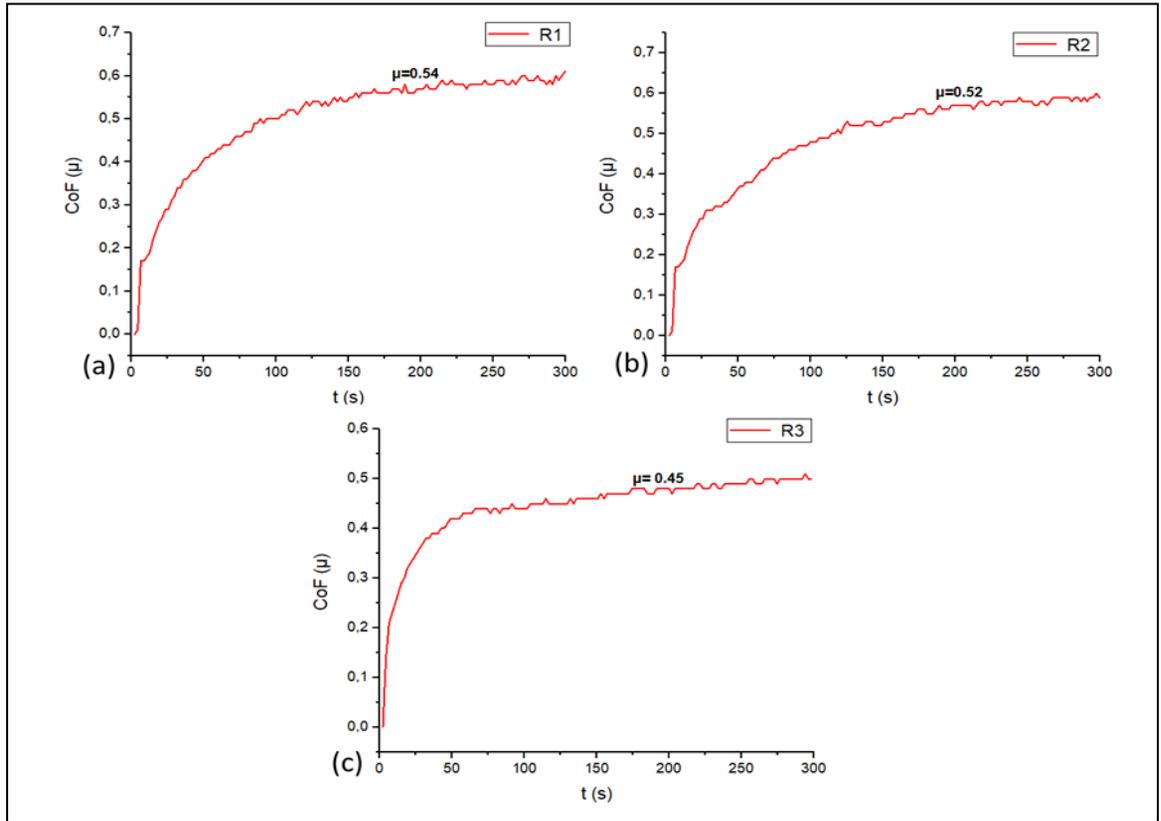


Fig. 5. The friction coefficient to time graph of BCN films for a) R1, b) R2 and, c) R3

Conclusion

In this work, BCN films were successfully deposited by a superimposed CFUMBS and HiPIMS system. Microstructure of all films has dense and non-columnar structure due to coatings by HiPIMS. The maximum hardness value was obtained as 17.6 GPa from R1 film. As a result of the scratch tests, the highest critical load value is obtained as 55 N due to the highest HiPIMS voltage value. The critical load value is increased by the increased target voltage value. Therefore, the highest critical load value was obtained in R1 film applied highest voltage to B_4C targets. All films have stable friction coefficient. The minimum friction coefficient value was obtained as 0.44 due to the hard abrasive particles.

Acknowledgements

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Superconducting Properties of Bi-2212 thin films produced by Pulsed Laser Deposition

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Abstract

In this study, $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ thin films were deposited on MgO (100) substrates by pulsed laser deposition (PLD). The effects of post-annealing temperature and time on the phase formation, the structural and superconducting properties of the films have been investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature dependent resistivity ($R-T$), and DC magnetization measurements. The films deposited at 600°C were post-annealed in an atmosphere of a gas mixture of Ar (%93) and O_2 (%7), at temperature of 860 °C for 30 minutes. All films have demonstrated a mainly single phase of Bi-2212 with a high crystallinity (FWHM $\approx 0.16^\circ$) and c -axis oriented. The critical temperature, T_C , of the films was measured as 82 K and the critical current density, J_C , was calculated as $3,3 \times 10^7 \text{ A/cm}^2$ for the film annealed at 860 °C.

1. Introduction

The high- T_C bismuth-based superconductors have three members described by the general formula of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$, where $n=1, 2$ and 3 [1]. Here, n is related to the number of CuO_2 layers in the crystal structure, producing the Bi-2201, 2212 and 2223 phases with 20, 85, and 110 K critical temperatures, respectively [2-4]. For technological applications, a stable single phase of the superconducting material is highly desirable. Among the three phases of BSCCO superconductor, the Bi-2212 phase has a much better stability compared to other ones. Hence it makes it advantageous for applications. After the discovery of the high temperature superconductors, most of the research groups have focused on the synthesis of these materials in a specific form like a thin film in order to fabricate devices as SQUIDS and Josephson junctions. Several techniques for producing the thin films have been investigated in various laboratories to advance the qualities of thin films for devices. The parameters of the device can be controlled by the preparation techniques. Some of these techniques are involved the molecular beam epitaxy (MBE) [5,6], dc sputtering [7], rf sputtering [8], chemical vapor deposition (CVD) [9,10] and pulsed laser deposition (PLD) techniques [11-14]. Pulsed laser deposition (PLD) technique is a convenient method promising a deposition of smooth surface in nanoscale for mono or multilayer, having a good electrical property, and highly textured thin films with a complex stoichiometry by controlling on all producing parameters such as; target distance, vacuum level, conditions of the ambient gases, mechanical setups, laser parameters, substrate option, and deposition temperature.

In this research, the results on the effects of the post-annealing temperature and time on the Bi-2212 thin films deposited on MgO (100) single crystal substrates by pulsed laser deposition have been summarized.

2. Experimental

$\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ target has been prepared, by using a polymer matrix route described in detail elsewhere [15]. The thin films of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ were deposited onto MgO (100) substrates by pulsed laser deposition (PLD), using an excimer laser (248 nm) focused on the target surface at an angle of 45° . Before deposition (at base pressure 1.0×10^{-6} Torr), substrates were first heated up to 1000°C at a rate of $30^\circ\text{C}/\text{min}$, soaked during 15 min to clean remaining impurities from their surfaces, and then cooled down to 600°C . This helps also to relieve any stresses build up on the substrate. During the deposition, the substrates were kept at 600°C while keeping O_2 gas pressure in the chamber fixed to 250 mTorr. The distance between the substrate and the target was 45 mm. The laser fluence was kept at $\sim 2.39 \text{ J}/\text{cm}^2$ and with a pulse repetition rate of 5 Hz. After deposition, the substrates were cooled down to room temperature at a rate $20^\circ\text{C}/\text{min}$, while maintaining the pressure of O_2 gas at 70 Torr. After deposition, the post-annealing heat treatments were performed in a quartz tube having a mixture of (Ar/ O_2 : 93/7) inside, and the tube was placed inside of a tubular furnace heated at temperatures at the range 860°C during 30 min. Then the samples analyzed via XRD, SEM, resistivity and magnetic measurements.

3. Results and Discussion

In Fig.1, X-ray diffraction pattern of the film is given. As can be seen from the figure all main peaks were situated on (00*l*) reflections of Bi-2212 phase. Additionally, the grown film has a high crystal homogeneity resulting from formation of strongly aligned to the *c*-axis on MgO (00*l*) surface. The lattice parameter *c* and crystal size *L* of film were calculated as 30.9 \AA and 537.1 \AA , respectively. This value is in good agreement with the previous publications for Bi-2212 superconductors [16].

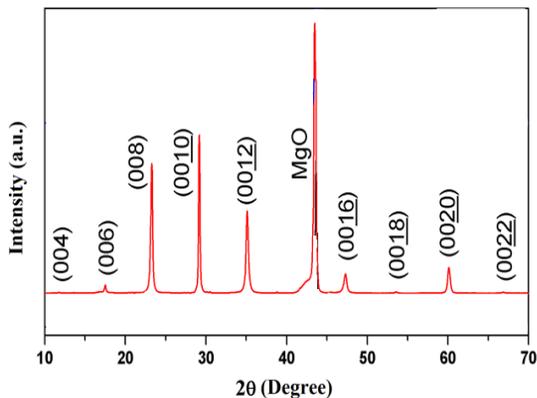


Fig.1. XRD patterns of film

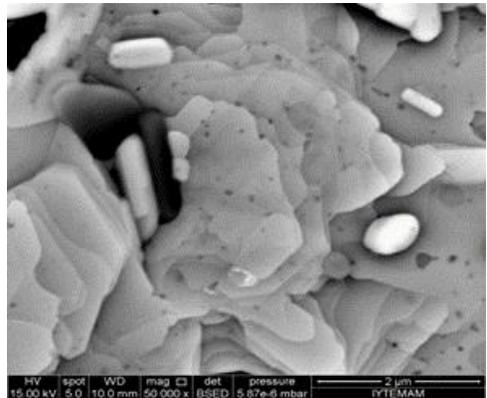


Fig.2. SEM image of the film

SEM image of the thin film annealed at 860°C for 30 minute is exhibited in Fig. 2. As can be seen that a well-stacked and terrace-like typical structures of Bi-2212 grains have formed in the matrix. The appearance of surface morphology of thin film is a cogent that the *a-b* plane of large grains of the Bi-2212 films mostly oriented along *c* axis with layered growth on *a-b* plane of MgO (100) single crystal substrate.

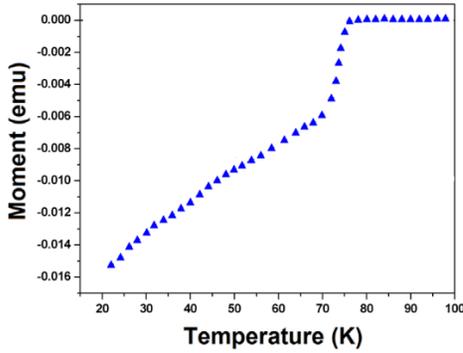


Fig. 3. M-T result of the film

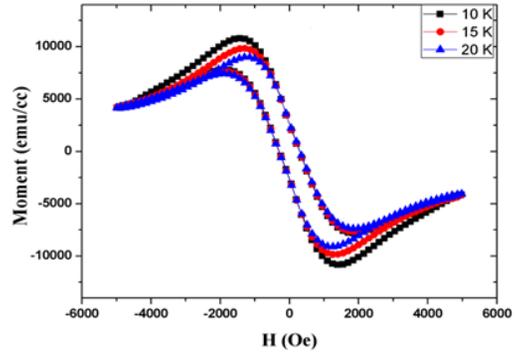


Fig. 4. Hysteresis loops of the film

The DC magnetization measurement of film is given in Fig.3. *M-T* measurement was performed on the samples under a magnetic field of 50 Oe. The field was applied parallel to the *c*-axis of the film surface. The film is exhibited a sharp diamagnetic transition around the critical temperature of 78 K.

Fig. 4 shows the temperature dependence of hysteresis curves of the film annealed at 860°C for 30 minute. The M-H measurement was performed while the applied magnetic field perpendicular to the surface of the film. It is easily seen that, while the temperature decreases, the area of hysteresis loops remarkably becomes larger. It is attributed to the fact that a decrease of the temperature leads to a stronger grain structure, stemming from a better crystallization process taking place.

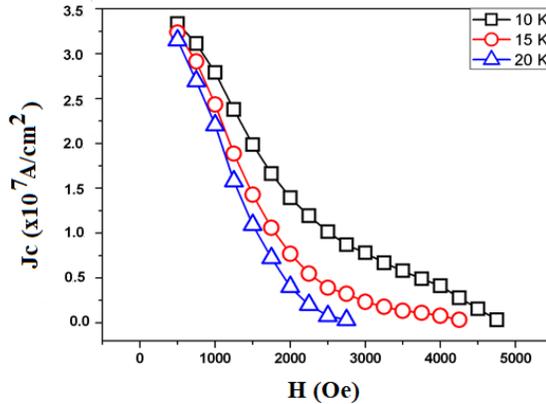


Fig. 5. Critical current densities calculated from M-H loops

The critical current density, J_C , of the film has been calculated by using the Bean model as given in [17]:

$$J_C = \frac{60a|\Delta M|}{b(3a-b)}$$

where a and b are the dimensions of the films and $\Delta M = M_+ - M_-$ is a difference of magnetization values measured in electromagnetic units per cubic. The calculated critical current density of the film as a function of the applied field, at 10, 15, and 20 K is given in Fig.5. The maximum J_C value is calculated as 3.4×10^7 A/cm².

4. Conclusion

In this study, the highly textured and c-axis oriented Bi-2212 thin film was deposited on MgO (100) single crystal substrate by using the pulsed laser deposition (PLD) technique. The film was firstly deposited on the preheated MgO substrate at 600°C. Later on, post-annealing heat treatment has performed at 860°C for 30 minute in argon and oxygen (Ar:93, O₂:7) atmosphere. The lattice parameter *c* and crystal size *L* of film were calculated as 30.9 Å and 537.1 Å, respectively. The critical temperature of the film was obtained as 78 K. The maximum *J_c* value is calculated as 3.4x10⁷ A/cm².

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Study of Thin films of Nickel Oxide (NiO) Deposited by the Spray Pyrolysis Method

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Abstract

In this work, thin films of nickel oxide (NiO) were deposited by a simple and inexpensive technique, which is spray pyrolysis on ordinary glass substrates heated to a fixed temperature of 500 °C, from a solution containing nickel nitrate hexahydrate as a precursor dissolved in water with different values of concentrations. Nickel oxide (NiO) is an interesting material because of its chemical stability [1], it is a p-type conductivity semiconductor [2], energy bandgap value between 3.6 and 4.0 eV[3] and easy to deposit in thin layers many techniques, such as sol-gel and spray pyrolysis. The NiO thin films obtained were characterized to determine the structure with X-ray diffraction technique (XRD), the absorption domain (UV-Visible Spectroscopy), and the surface morphology (SEM). The X-ray diffraction patterns confirm the presence of NiO phase with preferential orientation along the (111) direction. The optical gap (band gap) for nickel oxide calculated from the measurement of optical absorption is 3.6 eV, which is quite comparable to the value of the ratio.

Keywords: NiO; Thin films; Spray Pyrolysis.

Introduction

Advanced Oxidation Processes (AOPs) are among the most recent advances in the treatment of wastewater and industrial effluents that are a major concern today. The latter describes a novel treatment method known as heterogeneous photocatalysis which is a combination of a semiconductor catalyst with a light source. Metallic oxides are catalysts used for the degradation of pollutants existing in water by the heterogeneous photocatalysis process such as ZnO, TiO₂, CuO, NiO. Nickel oxide (NiO) is a binary compound that is an important material because of its large direct optical gap of the order of 3.6-4 eV[1], it is a very resistant to oxidation and has a high chemical stability,[2] a density of 6.72 g / cm³[3]. The work presented in this manuscript is focused on the study of the thin films of nickel oxide developed by the pyrolysis spray technique which presented advantages such as simplicity, inexpensive, efficient and fast with wide surfaces and good uniformity [4,5]. With their characterizations by X-ray diffraction techniques (XRD), UV-Visible Spectroscopy (SEM), with gap calculation.

5 Experimental

The preparation of thin films of NiO are made from a solution of hexa-hydrated nickel nitrate as precursor dissolved in distilled water used to prepare all concentration solutions. The water is used as a reactant to supply the oxygen atoms. The substrates in ordinary glass are well adapted for the optical characterization of our films, these latter are cleaned before use with acetone solution in the ultrasound machine for 10 minutes under 40°C, and in the ultrasound machine for 10 min and rinsed with distilled water, finally dried with a dryer. To obtain the desired molarity (0.05, 0.1, 0.15M), the precursors will be weighed by an electronic scale, where the quantities measured are mixed with a volume of distilled water. The mixture is heated to prevent breaking of the substrates, and ejected onto glass substrates placed in a pyrolysis system. Spray pyrolysis chemical deposition involves causing chemical reactions of a solution to form a solid deposit on a substrate heated between 200 °C and 500 °C.

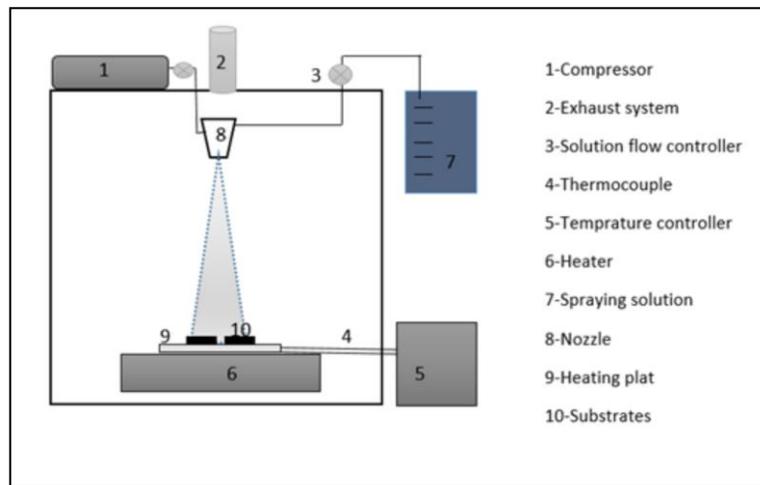


Fig. 1. Schematic the system chemical spray pyrolysis

Results /Discussion

The present chapter contains the results of our work concerning the characterization of thin films nickel oxide (NiO), which are deposited with spray method. Layers obtained were analyzed by different characterization techniques such as X-ray diffraction, scanning electron microscope, optical microscope, spectrophotometer, and so on....).

Structural Characterization

The characterizations with XDR techniques is useful for phase material identification, make it possible to have information on the crystallinity and structure of the prepared thin films.

The spectra of NiO thin films deposited at 500 ° C with a concentration of the fixed solution equal to

0.1M , shown in the figure below.

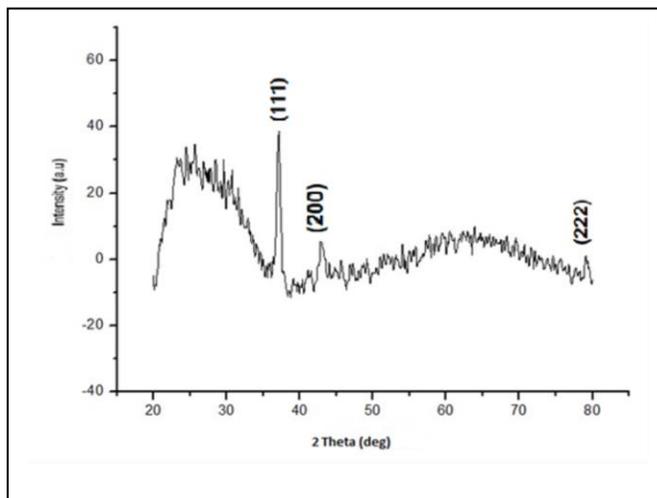


Fig.2. XRD patterns of NiO thin film

From the results of the diffractograms it can be noted that the presence of the peak (111), which confirms the cubic structure of the NiO films with the intensity of the principal peak value of 37 °.

3.2. Morphological characterization

The morphology of the prepared NiO thin films has been investigated using Scanning electron Microscope (SEM). The SEM images showed in the figure below

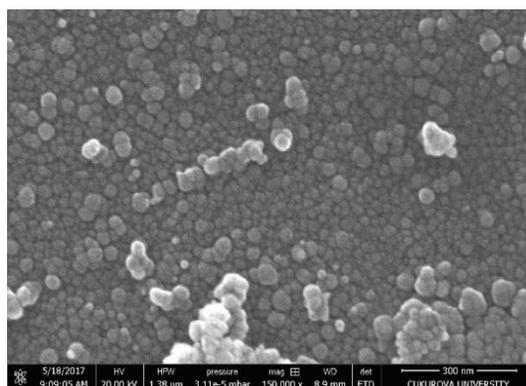


Fig. 3. SEM image of NiO thin films

The investigations obtained by this technique show that the surface of the elaborated layers is covered with material furthermore, the roughness of the surface. The particles of NiO are at the Nano-metric scale.

3.3. Absorption domain

The UV-Visible adsorption spectrum of the NiO films (0.1M) shows that the presence of a maximum adsorption band appears in the ultraviolet range at the value of 34500 cm⁻¹.

The figure 5 shows the UV-Visible transmission spectra of the NiO layers prepared with different concentrations of the precursor dissolved in water (0.05M, 0.1M and 0.15 M).

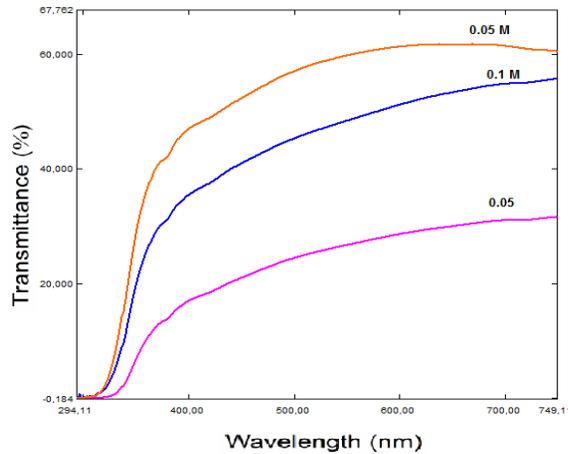


Fig. 5. UV-Visible transmission of NiO thin film with different value of concentration (0.05, 0.1 and 0.15M)

From the figure above, we can note that the concentration has an influence on the transmission of the layers, therefore the optical gap of the NiO will be affected by this variation.

3.4-Determination of the optical gap

Nickel oxide has very interesting optical properties for various applications. For this, the study of optical properties is necessary for the characterization of thin films such as transmittance, energy gap, etc. To determine the width of the optical gap of nickel oxide, we need the model proposed by Tauc where E_g is connected to the absorption coefficient α and the photon energy $h\nu$ by the following equation [6] :

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

Where:

h : Planck's constant $h = 6,6.10^{-34}$

The value of E_g can be obtained experimentally by extrapolating the plot of $(\alpha h\nu)^2 = f(h\nu)$ at $\alpha = 0$.

The latter is calculated in eV by [7] :

$$h\nu = \frac{hc}{\lambda} = \frac{1,24}{\lambda} (eV) \quad (2)$$

λ and c Are the wavelength and speed of light.

The values of the optical gap of NiO thin films deposited with deferent concentration of solution are showed in the figure below:

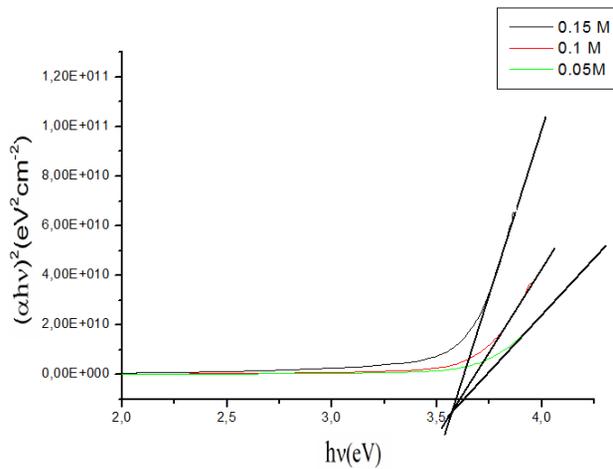


Fig. 6. Determination of the optical gap of NiO thin films (0.05 M, 0.1 M and 0.15M).

Table 1 gives the energy gap values obtained by using the concentration of diposit solutions with different concentrations.

Table.1. Values of E_g (eV) with deferent concentration

Concentration(M)	0.05	0.10	0.15
E_g (eV)	3.63	3.6	3.57

3.5-Raman spectroscopy

Raman spectroscopy (Raman analysis) is an optical spectrometry highlighting the molecular vibrations, allows us to determine the chemical structure of a sample and to identify organic molecules, polymers, biomolecules and inorganic compounds also. The figure below represents the Raman spectrum of the thin film NiO where the band positions expressed in (cm^{-1}) which correspond to the characteristic vibration frequencies of the molecular bonds, as a function of the intensity of these bands is expressed in arbitrary units. (ua).

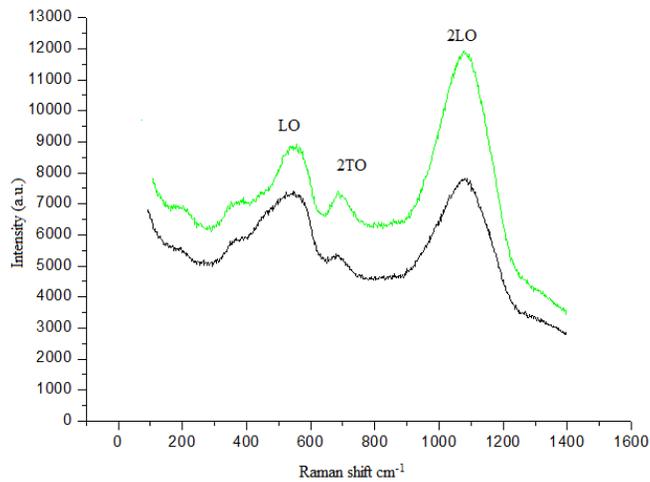


Fig. 7. Raman spectra of nickel oxide thin film (0.1M)

The Raman spectrum of the thin film NiO shows several bands a strong peak at 540 cm^{-1} corresponds to the vibrations of Ni-O [8] (one-phonon TO and LO modes), at $\sim 700 \text{ cm}^{-1}$ two-phonon 2TO modes, The last strongest band at $\sim 1100 \text{ cm}^{-1}$ correspond au 2LO modes.

The phonon related part of the Raman spectra indicate with (LO and 2TO modes in figure above in nanosized NiO thin film is rather similar to that in the single-crystal (u.a.).

4-Conclusion

From the results obtained, we have led to the following observations

- Spray pyrolysis of aqueous Nickel Nitrate solutions is a simple and effective method for preparing NiO thin films at moderate temperatures.
- The formation of the nickel oxide phase by X-ray diffraction analysis, the film crystallites obtained have preferential orientation in the (111) direction.
- The UV-Visible spectra of thin films developed by different concentration values showed that the films show optical transmission in the ultraviolet.
- The observation of the state of the surface of our thin layers by SEM shows that the latter have a uniform distribution and cover the entire surface of the substrate furthermore; there is a roughness of the surface.
- The transmittance of NiO to a good range of transmittance, which is between 30-60%.
- The use of Raman scattering spectroscopy to study the magnetic ordering in nanosized NiO thin film, prepared by the pyrolysis spray method, we observed the appearance of a characteristic band at the longitudinal vibration LO at 540 cm^{-1} corresponds to the vibration Ni-O, as well as band corresponds to 2TO and 2LO modes at (700 and 1100 cm^{-1}).

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