

# **Synthesis and characterization of nanocoatings thin films of TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, and CuO by sputtering deposition**

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## **ABSTRACT**

This work is aiming to synthesis and characterize of nanocoating thin films prepared by sputtering deposition at optimal conditions on various substrates. Magnetron sputtering deposition technique has been used to deposit nanocoating thin films of TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, and CuO on different substrates (stainless steel 316L, commercially pure Ti, Si-Wafer (100), and glass substrates). Surface morphology, crystal structure and size, and films elements deposited have been investigated using SEM, XRF, and XRD characterization technique respectively. From the findings of SEM photographs, the microstructure is uniform and the surface is free of defects or micro-cracks. The deposited thin films have a nanostructure and nanoparticle grain size of 60-90 nm, according to X-ray diffraction patterns. Also, all thin films have a crystal structure aligned in different directions matched to the standard phases peaks. The elements of each film deposit are specific objectives by the XRF peaks that are produced.

## **KEYWORDS**

Nanocoatings, 100nm Thin Films, Sputtering Deposition, TiO<sub>2</sub>, CuO, ZnO, SiO<sub>2</sub>

## **INTRODUCTION**

As a result of unique atom material features relative to bulk materials, nanotechnology applications have increased tremendously. The nanocoatings description is used whether the coated thickness is in nanometre scales or the structure is in nanostructure scales from (1-100nm), which is the ultimate obstacle in materials science nowadays. Nanocoatings have superior properties and characteristics due to the quantum size effect [1]. Nanocoating thin films are formed employing nanocoating facilities such as atomic layer deposition, sputtering deposition, and pulsed laser deposition to build coating layers with varied nano thickness to improve attributes not observed in traditional coating procedures [2, 3]. Masayoshi [4] depended that it is a few thousands of atoms, and the structure and properties gotten are not present in traditional coatings methods. In addition to high corrosion resistance and biocompatibility, nanocoatings of ceramic materials may be synthesized to make the surface bioactive and chemically inert. For that, nanostructured processing is now used in a variety of research and technology materials due to its unique electrical, optical, biological and mechanical properties. Arkadiusz [5] point out that some of the Nanostructure have scattering losses, so they can be used in the plasmonic, biosensor, and functional material applications. The most popular applications of nanomaterials, according [6], are microelectromechanical and nanoelectromechanical structures, bioengineering, biomedical applications, nonlinear optical properties generators, and surface-enhanced Raman scattering instruments.

Kumar [7] reviewed that CuO has an advantageous and exciting material for system biomedical applications due to its nontoxicity and ample abundance of its constituents. It has also been studied extensively for electrical uses, including solar energy conversion, optoelectronics, batteries, sensors, semiconductors, and catalysis. Sawsen et al. [8] study the Properties of TiO<sub>2</sub> thin films deposited by Rf reactive magnetron sputtering on biased substrates. It reviewed that titanium dioxide (TiO<sub>2</sub>) has a powerful transition metal oxide that's useful for catalysis, computing, photonics, sensing, medicine, and controlled drug release, among other things. It has excellent optical

and electrical properties, and ease of mass processing. That was TiO<sub>2</sub> is one of the most commonly used photocatalysts in many areas, including antibacterial applications, water purification, decomposition of different organic compounds, and solar cell applications. Ivan et al. [9] and Joaquim et al. [10] displays that Silicon dioxide (SiO<sub>2</sub>) is a commonly used element in many scientific fields and a variety of applications, such as medicinally because it has excellent chemical and biological compatibility furthermore to an antimicrobial effect, for that its implanted in the brain, food industry and preservation and, microelectronics, and communication. They have been examined in both crystalline and amorphous forms. Wadullah et al. [2] defined the deposition of 25nm and 50nm thin films of Alumina, Titania, and Alumina/Titania multilayer thin films on Co-Cr alloys using the Atomic Layer Deposition (ALD) technique (ASTM F75).

Good thin-film durability, homogeneity, and thin-film properties have been found, as well as no defects or micro cracks. Al<sub>2</sub>O<sub>3</sub> ALD films had lower surface roughness values and greater thin film thickness control than TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/ TiO<sub>2</sub>. Coating the surface of implant alloys improves corrosion resistance while also improving biocompatibility according to Priyadarshini et al. [11]. Wadullah et al. [12] explored platinum (Pt) thin films with thicknesses of 17nm and 34nm deposited by sputtering on Ni-Cr alloy substrates. The findings indicate that a nanostructured and defect-free Pt thin film can be deposited on artificial saliva at 37°C, as well as increased localized electrochemical corrosion resistance. According to Masayoshi et al. [4], metallic nanoparticle synthesis has gotten a lot of attention in recent years due to their ability as green and cost-effective synthesis tools, as well as the biological molecules aimed at them. Vyas S. [13] discuss the wide range of Zinc oxide application which are including robotics, healthcare, food processing, biomedicine, and biosensors as one of the most important parts. ZnO has biocompatible and non-toxic behavior which is the main points for the biological role of the element to be preserved. Electrically, transparent conducting oxides, gas sensors, light-emitting diodes, lasers, and photodetectors are only a few of the ZnO applications.

Several authors [14] have researched in thin film depositions, however, there are only a few experiments that have dealt with the deposition of various thin films by sputtering on various substrates. For that, this work is aiming to prepare nanocoating thin films of TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, and CuO with 100 nm thickness by sputtering deposition on various substrates (stainless steel 316L, commercially pure Ti, Si-100, and glass substrates) at optimal conditions. In addition to analyzing the thickness, roughness, surface morphology, phases, and deposited nanocoatings elements. Where, the paper is a supplement to a Nanoceatings thin film deposition program, which began with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> / TiO<sub>2</sub>, Au., and Pt. films for different applications. The new paper is constructed in the following manner. The experimental setup, as well as the procedure, are described in Section 2. The findings are examined and defined in Section 3. Finally, in Section 4, the new research's findings are addressed.

## EXPERIMENTATION WORK

### Materials and Preparations

In this experiment, the materials used are stainless steel 316L, commercially pure titanium (Ti-6Al- 4V), Si-Wafer(100), and glass specimens with dimensions of 2.5 x 1.9 x 0.1 cm<sup>2</sup> . ASTM D4708 - 12 has been used to prepare the specimens. Plates were cut into samples using a wire cut machine with a slow flow rate and cutting speed, as well as cutting fluid has been used to prevent the cutting from heating up. SiC papers with grits of 400, 600, 800, and 1000 were used to grind samples face. They were then washed with purified water. For Stainless steel 316L and Al alloys, they have been ultrasonically cleaned for 60 minutes with acetone, washed with methanol / de-ionized water to eliminate any organic pollutants, and eventually dried with hot air before being placed in the deposition chamber. For Si-Wafer(100) and glass specimens, before being put have been chemically washed with a diluted 5% HF solution and dried with N<sub>2</sub> gas. The composition of materials has been determined by chemical analysis in the Ministry of Science and Technology, Iraq.

### Deposition Facility and Conditions

Different Targets have been used with high purity in a magnetron sputtering deposition unit according to the type of film needed. After the device was calibrated with different goals and power at Iraq's Ministry of Science and Technology, the calibration graph has been used to guess the power/time needed to deposit a certain thickness of

film which is 100 nm on different substrates selected. The optimal deposition conditions were  $2.8 \times 10^{-7}$  Torr vacuum base pressure, 2nm/min rate, 20 standard cubic centimeter per minute (sscm) Argon steam, and 4 Torr pressure during the deposition. The thin film deposited annealed for 1h in an argon setting for all films used and according to the scheduled temperature related to the type of films.

#### Characterization Facilities and Methods

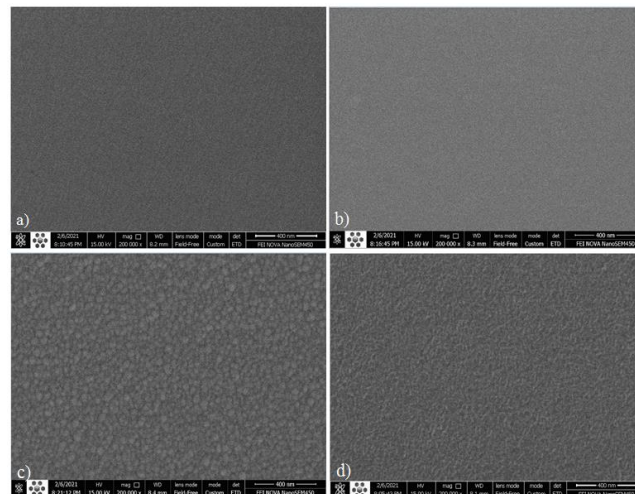
For studying the thin films surface uniformity, SEM (scanning electron microscope) has been used with an imaging system monitored by sophisticated tools. The TFProbe spectroscopic unit has been used in conjunction with algorithms to determine the thickness of films. The Cu-K radiation has been used in an X-ray Diffraction (XRD) from Philips which is used to estimate the average crystallite size. The Debye–Scherrer method has been used to calculate the average crystallite, as follows:

$$(D = \frac{k\gamma}{\beta \cos \theta}) \quad (1)$$

Where :D is the average crystallite size,  $\gamma$  is the X-ray wavelength of the incident radiation (CuK= 0.15406 nm), k is the shape factor with a typical value of 0.89,  $\beta$  is the line broadening full width at half maximum (FWHM) in radians, and  $\theta$  is the Bragg angle. The high-intensity peak (101) has been chosen for the calculation of crystallite size. The non-destructive analytical method XRF (X-ray fluorescence) is used to determine the elemental composition of thin films. By analyzing the fluorescent X-ray released from a sample as it is excited by a primary X-ray light, XRF analyzers can determine the chemistry of a sample. Each element in a sample emits a series of fluorescent X-rays that are unique to it.

#### RESULTS AND DISCUSSION

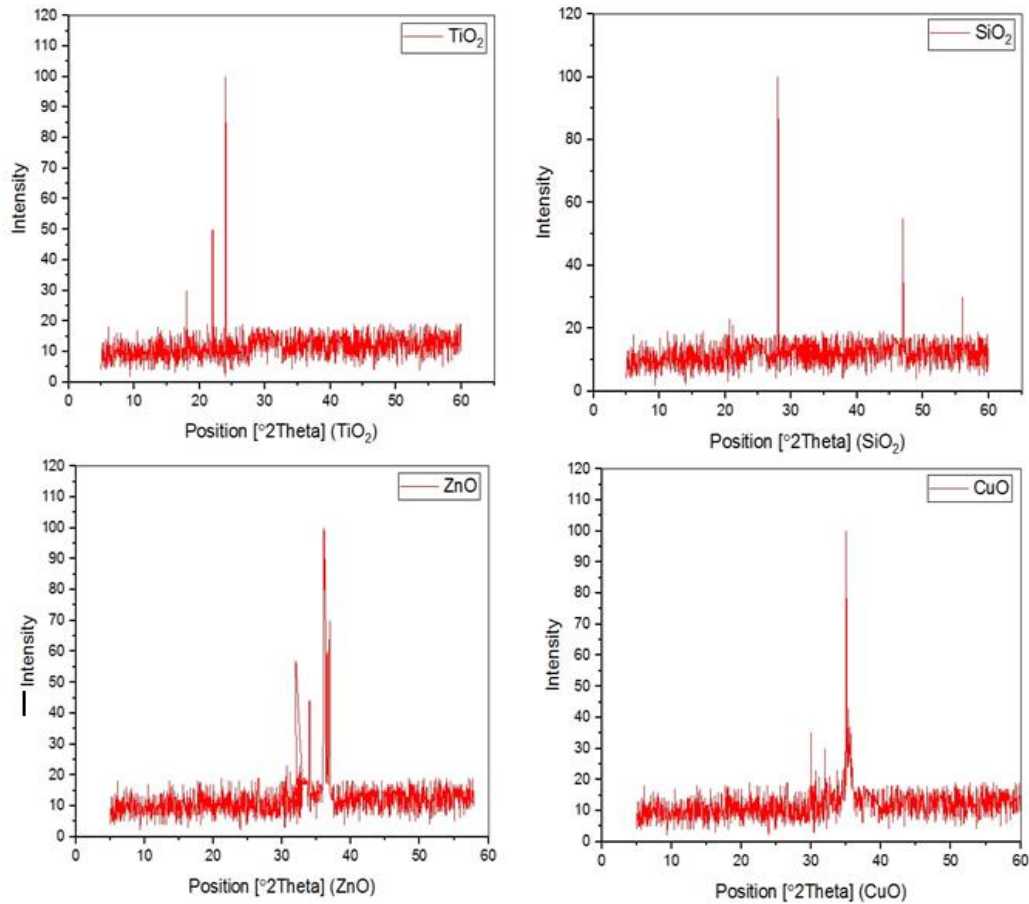
The main challenge of this research is to make uniform and homogeneous thin films nanostructures using magnetron sputtering deposition. To compare the morphology of thin films, different substrates (stainless steel 316L, commercially pure titanium, Si-Wafer (100), and glass) have been used. SEM, XRD, and XRF have been used to analyze the surface morphology, crystal structure, and elements of the deposited films respectively. Figure 1 shows a micrograph of SEM of 100 nm thin film after annealing for 1h in an argon setting, It appears that the films haven't micro-cracks or defect and its homogeneous at 400 nm magnification. Fig. 1a & b shows TiO<sub>2</sub> and SiO<sub>2</sub> thin film, which has a very fine and uniform aggregation as conformed by researchers [15, 16]. Fig. 1 b & c appears ZnO and CuO thin film, which has a different morphology compared with the other films; more coarse grains with larger aggregation, which is matched the findings of the researcher [17].



**Figure 1.** SEM results of thin films deposited; a) TiO<sub>2</sub> thin film, b) SiO<sub>2</sub> thin film, c) ZnO thin film, d) CuO thin film

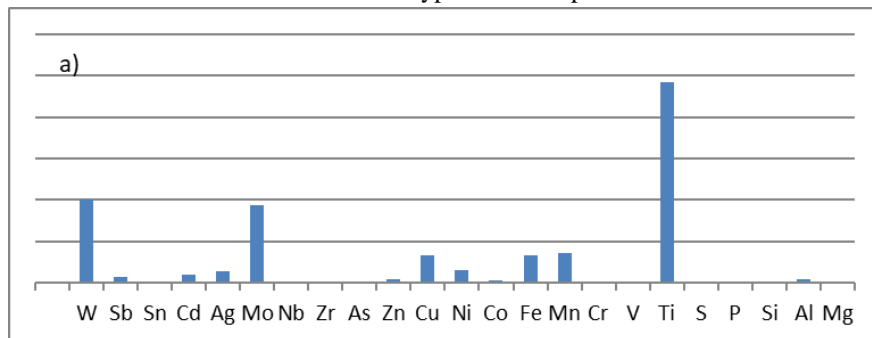
XRD has been used to determine the phase structure of the deposited films. The diffraction patterns of deposited films as seen in Figure 2. In all diffraction patterns of TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, and CuO films, Fig. 2, there is TiO<sub>2</sub>

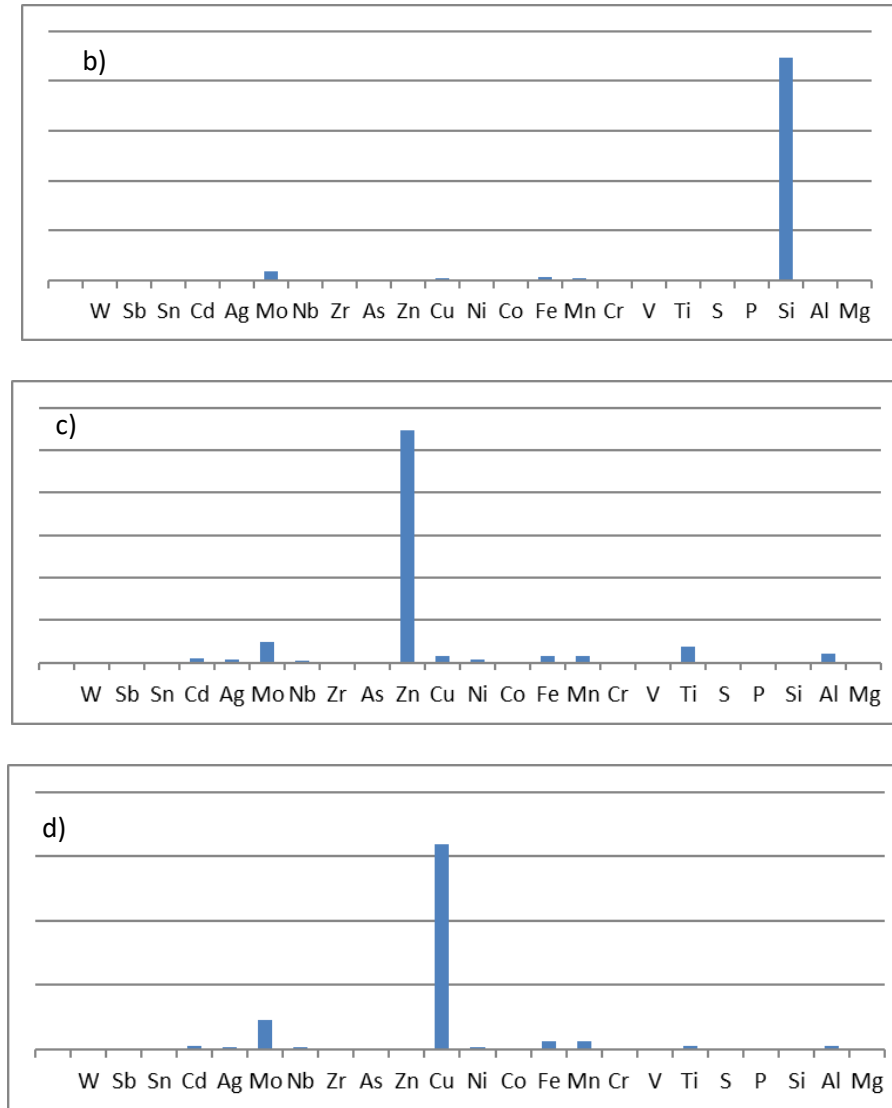
peaks at  $2\theta$  equal to (18 o, 22 o, 23 o) and sharp anatase peak (101) is at  $2\theta = 25^\circ$ . The results are confirmed by the researcher [18]. The sharp peak of  $\text{SiO}_2$  shows at  $2\theta = 37^\circ$ , is formed of (002), and the other peaks at  $2\theta$  equal to (47 o, 56 o).  $\text{ZnO}$  peak at  $2\theta$  equal to (32 o, 34 o, 37 o) and  $\text{CuO}$  peak at  $2\theta$  equal to (30 o, 32 o, 35 o) and sharp anatase peak (111) for  $\text{CuO}$  film is at  $2\theta = 35^\circ$  as confirmed by the researcher [17]. The type of the XRD used in this investigation is more sensitive to the thin films although the thickness was 100 nm. The surface grain size was in the range of 60-90 nm and the size of the crystal are approximately 8, 14, 20, and 35 nm for  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$ , and  $\text{CuO}$  respectively



**Figure 2.** XRD results of thin films deposited; a)  $\text{TiO}_2$  thin film, b)  $\text{SiO}_2$  thin film, c)  $\text{ZnO}$  thin film, d)  $\text{CuO}$  thin film

XRF (X-ray fluorescence) has been used to determine the elemental composition of thin films deposited as seen in Fig 3 a, b, c & d. For the  $\text{TiO}_2$  film, the XRF results appear the max. peak of Ti element compared with other elements. Which is related to the  $\text{TiO}_2$  film deposited on the substrates as verified by the researcher [15]. The XRF of the  $\text{SiO}_2$  film shows max. peak of Si. The max. the peak of  $\text{ZnO}$  film is Zn, and Cu is the max. peak for  $\text{CuO}$  film. All of these results are confirmed with the type of film deposited.





**Figure 3.** XRF results of thin films deposited; a) TiO<sub>2</sub> thin film, b) SiO<sub>2</sub> thin film, c) ZnO thin film, d) CuO thin film

## CONCLUSION

In the current study, nanocoating thin films of TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, and CuO have been deposited on various substrates (stainless steel 316L, commercially pure Ti, Si-Wafer(100), and glass substrates) using a magnetron sputtering deposition process at optimal conditions. The deposition environments have been tailored for various targets during deposition at  $2.8 \times 10^{-7}$  Torr vacuum base pressure, 2nm/min rate, 20 standard cubic centimeter per minute (sccm) Argon steam, and 4 Torr pressure. The SEM, XRD, and XRF have been used for nanocoated substrates. The following findings can be drawn from this research:

1. The thin films deposited haven't micro-cracks or defect with a uniform and homogeneous structure at 400 nm magnification.
2. SEM results indicated that the films have a very fine aggregation for TiO<sub>2</sub> and SiO<sub>2</sub> films compared with more coarse grain and larger aggregation for ZnO and CuO films.
3. Nanostructure and nanoparticle grain size of 60-90 nm with a crystal structure arranged in different directions matched to the standard phases characterized in this study.
4. A unique element of each film deposit identified by XRF peaks as an indication of the films deposited.

## CONFLICTS OF INTEREST

The authors identify and declare that there is no conflict of interest.

## ACKNOWLEDGEMENT

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