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Synthesis and Characterization of Nanocoatings Thin films by Atomic Layer Deposition for Medical Applications

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Abstract. In this work, synthesis and characterization of Al_2O_3, $TiO_2$and Al_2O_3/ TiO_2hyper thin films, with 25 nm and 50 nm,have been investigated by using Atomic layer deposition method (ALD) at high vacuum (0.27 Torr) onto the cobalt chromium alloy (ASTM F75) and si-wafer (100) substrates. The characterizationshave been investigated using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), optical profilometer and ellipsometry spectroscopy. Morphological characterization and thickness evaluation has been obtained by optical profiler and ellipsometry spectroscopy respectively. SEM has been used to find the presence of thin film defects and the particle shape/size of the thin films. EDX has been used to obtain the element analysis of the thin films. The results have shown good quality thin films, homogeneity, without defects or micro-crack and good thin films properties. Small crystalline regions have been found in the TiO_2thin film by selected area diffraction pattern(SADP) image. Al_2O_3ALD film exhibited lower surface roughness values and good thin film thickness control compared with $TiO_2$and Al_2O_3/ TiO_2.

Keywords: Thin Films, Al2O_3, TiO_2 and Al_2O_3/ TiO_2multilayer, ALD, Co-Cr ASTM F75.

1. Introduction

Cobalt Chromium alloys used in biomaterials applications due to their exceptional mechanical properties and good corrosion resistance. For years, Co-Cr-Mo alloys have been used in biomedical implants, due to their good corrosion and wear behavior it used for the metal-on-metal hip resurfacing intersections. For changing the microstructure and improve the mechanical properties, thermal treatments are used on these alloys. However, the effect of that on the corrosion behavior is less well understood. There is a concern that the corrosion process is the cause of in-vivo failures, leading to retrieval actions. The release of metal ions due to corrosion process is thought to have adverse effects on the nearby body tissue and finally leads to failure of the implant [1], [2]. Nanocoating thin films are a synthesis of coatings layers with different nanothickness to improve properties that are typically not found in conventional coating methods by used nanocoating facilities such as atomic layer deposition and sputtering deposition and pulsed laser deposition [3]. Atomic layer deposition (ALD) called formerly atomic layer epitaxy (ALE), is an exclusive method for depositing excellence thin films [4]. ALD method is a chemical vapor deposition (CVD) method appropriate for synthesis inorganic material layers at angstrom depth for each cycle. ALD has the ability to coat exceedingly compound shapes with a conformal material layer with high quality cover. ALD is a film depositing method that is constructed on the successive use of self-terminating gas-solid reactions. The experiments roots of ALD were made in the 1960s and continue until 1970s. The attention of ALD has increased in stage sat the beginning of the 1990s [5], [6]. Titanium dioxide (TiO_2) technologically and scientifically is significant material used in a wide variability of applications. So, it used in such fields as cosmetics, colors, solar cells, photocatalysis, biomaterials, and different sensors. Aluminum oxide has different properties such as high thermal conductivity, high dielectric constant, transparency over a wide range of wavelength, and relatively low refractive index. Since it has outstanding properties, for that can used for many applications [7]. Individual, the high radiation resistance, high chemical stability, low permeability to alkali impurities and high thermal conductivity make it suitable for applications of metal oxide semiconductor (MOS) structures even in conditions of drastic. $Al_2O_3$was usually used as a protecting layer, ion wall layer and as diffusion barriers. Also, it has numerous applications in chemical sensors such as dielectric films and passivation layers [8]. All these applications need films with low surface roughness,good homogeneity and good control thin filmsthickness. Al_2O_3 is one of the finest high-k materials which gratify almost all the strategies for an ideal gate oxide [9], [10], [11]. Aiming of this work is to prepare and deposit of Al_2O_3, $TiO_2$and Al_2O_3/ TiO_2thin film on the Co-Cr alloys and Si-wafer by using ALD method to investigate the homogeneity, morphological and the thin film microstructural characteristics as a preparation steps for the experiment the thin films by biocorrosion tests in vivo and vitro in future works.

2. Experimental Work

2.1. Materials used and samples preparation:
Cobalt Chromium alloy ASTM F75 and Si-wafer (100) were used in this study as a substrate,the samples area was 20×20 mm^2 with surface roughness about 6.33 nm. For cleaning the surfaces, Acetone in the ultrasonic bath for 60 min, ethanol, and deionized water (AMD) was used. The samples surface was dried before placingit in the ALD chamber. But for Si-wafer, 5% HF was used for etching then dried by N_2 gas.

Table 1. Data results by Ellipsometry and optical profiler

Type	Al_2O_3	TiO_2	Al_2O_3/ TiO_2
Theoretically Thickness	50 nm (~1.07 Å / cycle)	50 nm (~0.39Å/ cycle)	50 nm ; (~1.07 Å / cycle) for 25 nm then (~0.39Å/ cycle) for 25 nm
No of Cycle	480	1284	250 Cycle of Al_2O_3 + 700 Cycle of TiO_2
Measured Thickness	47.3nm	43.04 nm	Measured thickness of 25nm Al_2O_3 alone is 26.99 and for25nm TiO_2 alone is 26.45 but together is 49.6 nm
Standard deviation	1.5%	3.5%	0.2 %
Refractive index, n	1.638	2.145	1.98
Reflectivity (R), R= [(n-1)2/(n+1)2]*100	5.85 % of light is reflected	13.25% of light is reflected	10.81 % of light is reflected
Roughness of Co-Cr-MO= 6.33 nm	3. 22 nm	3.68 nm	3.37 nm

ALD Savannah system in high vacuum (0.277 Torr) with constant nitrogen flow at a pressure of about (8.388 * 10^{-2} Torr) was used. Al_2O_3 layer was obtained using trimethyl aluminium (TMA) ($Al(CH_3)_3$) and precursors of water. TiO_2 layer gotten using Tetrakis (dimethylamido) titanium (TDMAT) {Ti $(NMe_2)_4$} and precursors of water.All depositions temperature was high at 250 °C, in order to obtain thecrystalline structure of the layers deposited. Thenumber ofprecursor cycles for each statement was guessed by a growth rate per cycle GRC,which is ~0.39 nm/cycle for TiO_2 and ~1.07 nm/cycle for Al_2O_3, as shown in Table (1).

2.2. Characterization and Evaluation:
Characterization and evaluation tested were by University of Missouri-Columbia, USAinstruments. Scanning Transmission Electron Microscope (STEM) type FEI Tecnai F20 used at high-resolution TEM/STEM model with 200kV field emission gun (FEG). Focused Ion Beam (FIB) method type of Helios-NanoLab 600 FIB was used for TEM lift-out thin film. It is envisioned for high resolution

nondestructive with a simultaneous site-specific FIB cross-sectioning. SEM imaging was used for investigatedthe TEM. Before starting the (FIB), a 200nm Platinum (Pt.) thick layer was deposited with the electron beam at 5kV and a 1.4 nA current. SEM type Hitachi S4700 used with an operating voltage of 3.5-10.00 kV for a scan the thin film surfaces and investigate the existence of deposition defects. The samples were secured onto specimens holders by conductive carbon cement. The imaging process was controlled using smart SEM software. Energy dispersive X-ray spectroscopy (EDX) which is connected to Quanta 600F SEM machine used in order to discover the element analysis of the thin films and substrate by using a 12 mm working distance, 10.0 – 3.5 kV accelerating voltage and 37.3 deg. take off angle. Opticalprofilometer type Veeco model WYKO NT 9100are used for surfaces profile images. The roughness was measured after and before the thin films deposition for Co-Cr-Mo ASTM F75 and Si-wafer (100) substrate. Profillometer gives imaging for X profile, 3-dimension plot, 3-dimensional interactive display and surface data. Spectroscopic Ellipsometry type WVASE32 with software accessible for optical data analyses was used to determine thin layer thickness and/or optical constants for 50 nm of TiO_2, $Al_2O_3$and Al_2O_3/ TiO_2thin films deposited onthe silicon wafer simultaneously with the Co-Cr-Mo alloy substrates. Occurrence and reflected angles were used between 65° to 75°. The Cauchy model was fitted to the data at wavelengths from 2000 to 10000 nm based on the thickness guess and optimization of Cauchy parameters An, Bn, and Cn as shown in the equation (1). The values for refractive index coefficient (n) and reflectivity (k) were determined from the Cauchy model then used as the initial guess for a point-to-pointmodel of the data over the entire wavelength range. Cauchy assumes k=0 for dielectric materials (SiO_2, TiO_2, and Al_2O_3).

$$n = An + \frac{Bn}{d} + \frac{Cn}{2} + \cdots \quad (1)$$

$$R = \left[\frac{(n-1)^2}{(n+1)^2}\right] * 100 \quad (2)$$

Where; n: Refractive index coefficient , and , R: Reflectivity.

3. Results and discussion

Figure (1) shown TEM images were taken at zero tilt angle and with the Si on a zone axis for the other images in addition to both bright field, dark field and the EDX line scans. From TEM of cross-sectional films grown presented shown the that the filmwas really flat and uniform with an average particle size of Titaniaanatase phase is found to be 2.8 ^{0}A (0.28 nm) as shown in the HRTEM. Crystalline area has been found in the TiO_2thin film as clear from SADP image result. The TEM images with the Si-wafer on a zone axis give results with sharper layer boundaries. When looking at the EDX information in the Figure (1), it was observed that there is a smaller overlap in the layers. Also, there is Pt. peak which is associated to 200 nm thick layer of Pt. (sacrificial layer) deposited before starting the thin film lift-out by FIB to keep the involved area from the worst of the ion beam during the thinning process. Furthermore, there is a peak of Tiand O_2 which is correlated to the TiO_2thin film. Also, there is a peak of Si which is correlated to the Si-wafer substrate. Figure (2) shows SEM micrographs of the thin film of Al_2O_3, TiO_2 and Al_2O_3/ TiO_2 on Co-Cr-Mo substrate which can be observed that there is no micro-crack, defect and blistering occurrence on the thin films deposited. So it can be observed that the thin films surface morphologies are apparently different depending on the depositionkind, so the Al_2O_3film consists of nanotubes particle shape with very fine around 10-20 nm spherical particles size between them. But for the $TiO_2$the shape of the particle was like cauliflower with different size around 20-50nm, as reported in the literature [12]. That means the element shape of $Al_2O_3$is different than that of TiO_2 and Al_2O_3/ TiO_2. Furthermore, the element of the Al_2O_3/ TiO_2 has a similar shape and size of the TiO_2 film. These results give a good indication about the conformal of the nanometric size of the thin films deposited in this study. EDX of the thin film at small power of 3.5 Kv was used to find the peaks of the thin film deposited. From Figure (2), it can be noted that the peaks of 50 nm Al_2O_3 were Oxygen with Aluminum, and the peaks of 50 nm TiO_2 were Oxygen and Titanium. But, for 50 Al_2O_3 / TiO_2 there are different peaks which are Titanium for 25 nm TiO_2, Aluminum for 25 nm Al_2O_3 and Oxygen for both of them. In addition, Titanium peak was more clear then Aluminum peak. Also, there is a peak correlated to the Cobalt base substrate. These results of peaks give a good indication about the type of the thin film with the Co-Co-Mo substrate. The

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thickness and refractive index of TiO_2, Al_2O_3 and Al_2O_3 / TiO_2 films on Si-wafer were resolute by Spectroscopic Ellipsometry, as shown in the Table (1). In all cases, the thickness measured was equal to the theoretical thickness calculated. Where the measured thickness was 47 nm for Al_2O_3 at growth per cycle (GRC) ~1.07 Å / cycle with standard diversion about 1.5% from the theoretical thickness. But 3.5% was the diversion between the theoretical thickness and measured thickness for deposited 50 nm of TiO_2. The smaller diversion was 0.2 % for deposition of 50 nm hyper Al_2O_3 / TiO_2. The refractive index was 1.63, 1.98 and 2.145 for Al_2O_3, Al_2O_3 / TiO_2, and TiO_2respectively. While the refractive index for $TiO_2$is higher and around 2.5 as confirmed by [4], [13], [14]. From Figure (3), the roughness results obtained by optical profiler were 3.22 nm for Al_2O_3 thin film, 3.68 nm for TiO_2thin film and 3.37 nm for hyper Al_2O_3 / TiO_2 thin film. There is a difference in the roughness of the thin film although the deposition processes were at the same pressure and temperature. This difference is correlated to the thin film type. Minimum roughness obtained is 3.22 nm for 50 nm Al_2O_3, then 3.37 nm for the hyper 50 nm Al_2O_3 / TiO_2, and 3.68 for TiO_2. Although Al_2O_3 / $TiO_2$was more difficult deposition process because the first deposited was 25nm of Al_2O_3, then in the same condition completed the cycles by changing the precursor No. and the flow rate to deposit TiO_2 at 25 nm in the same vacuum chamber.

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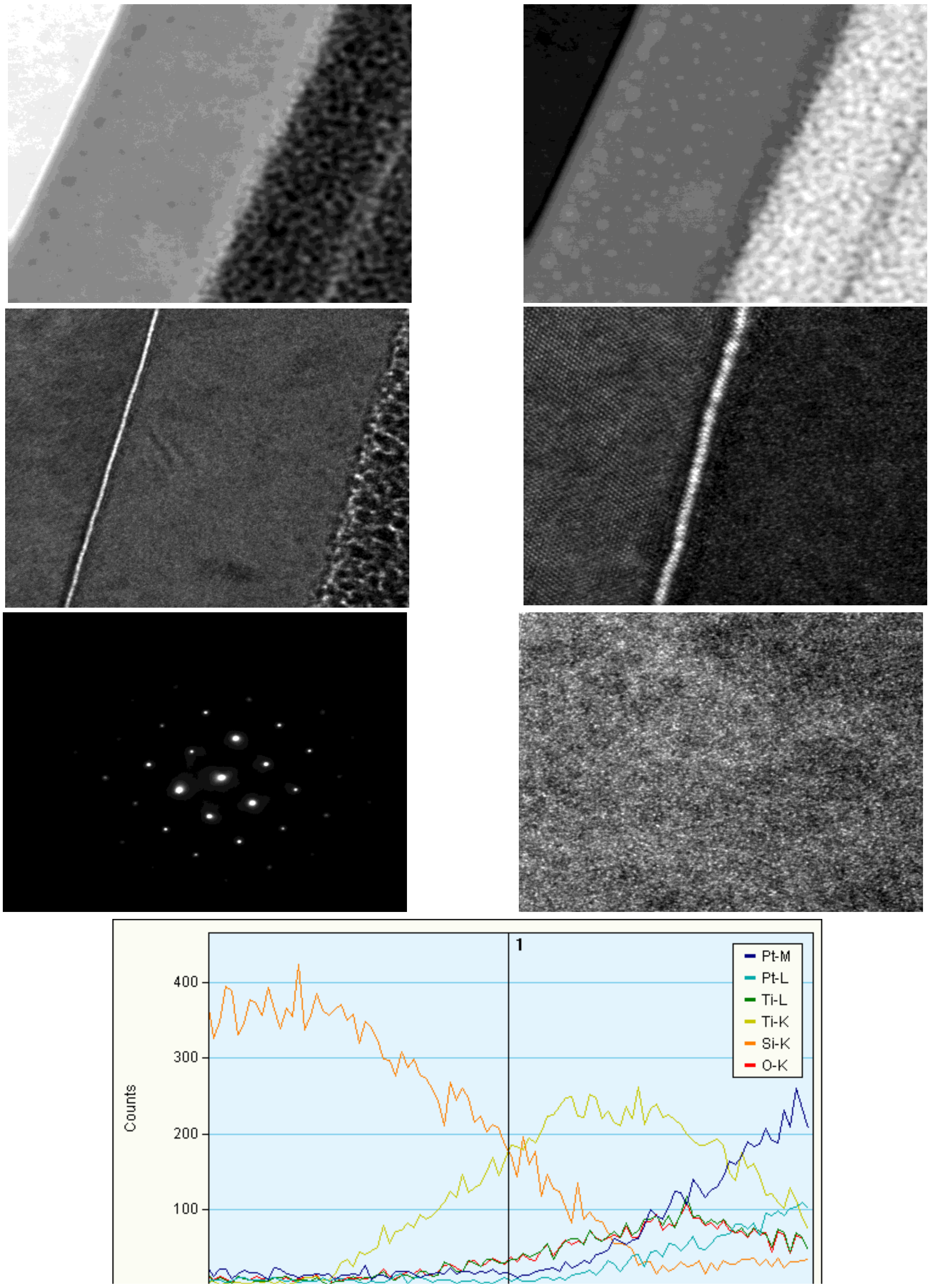

Figure 1. TEM data results of TiO_2 thin film on si-wafer:
a) Bright field (BF) Scanning for STEM, b) Dark Field (DF)Scanning for STEM
c) and d) TEM images e) Selected area diffraction pattern (SADP)
d) HRTEM g) EDS line scans image

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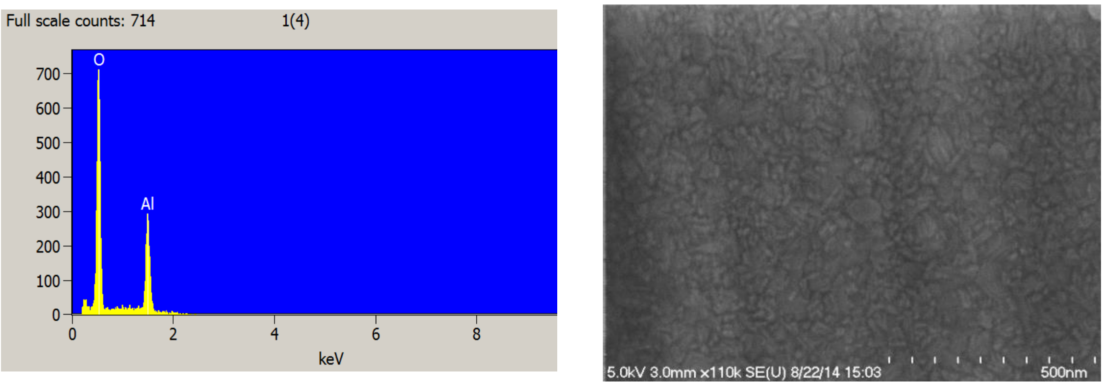
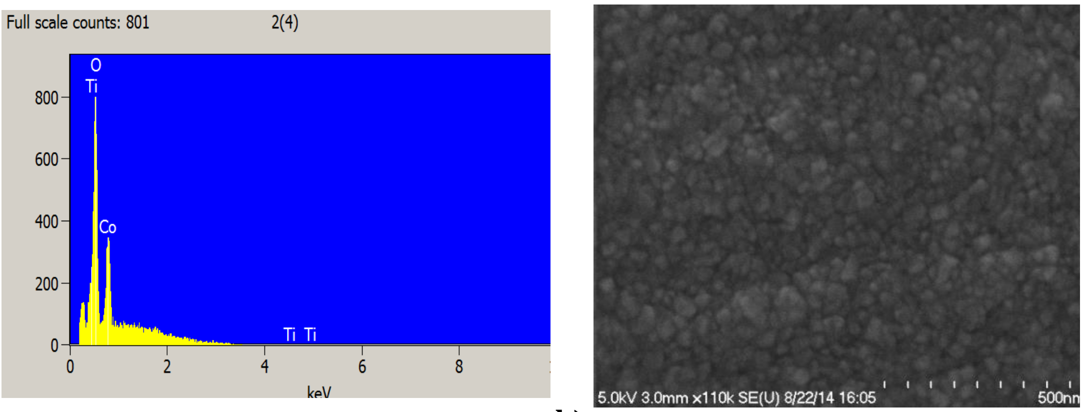


a)



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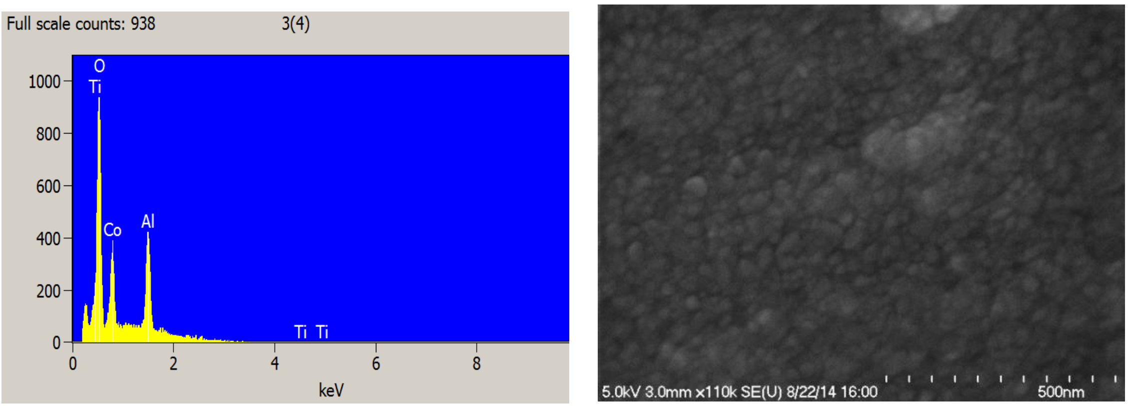

c)

Figure 2. Results of SEM/EDX for deposited thin films; a) 50 nm Al_2O_3 , b) 50 nm TiO_2 , c)50 nm Al_2O_3/ TiO_2

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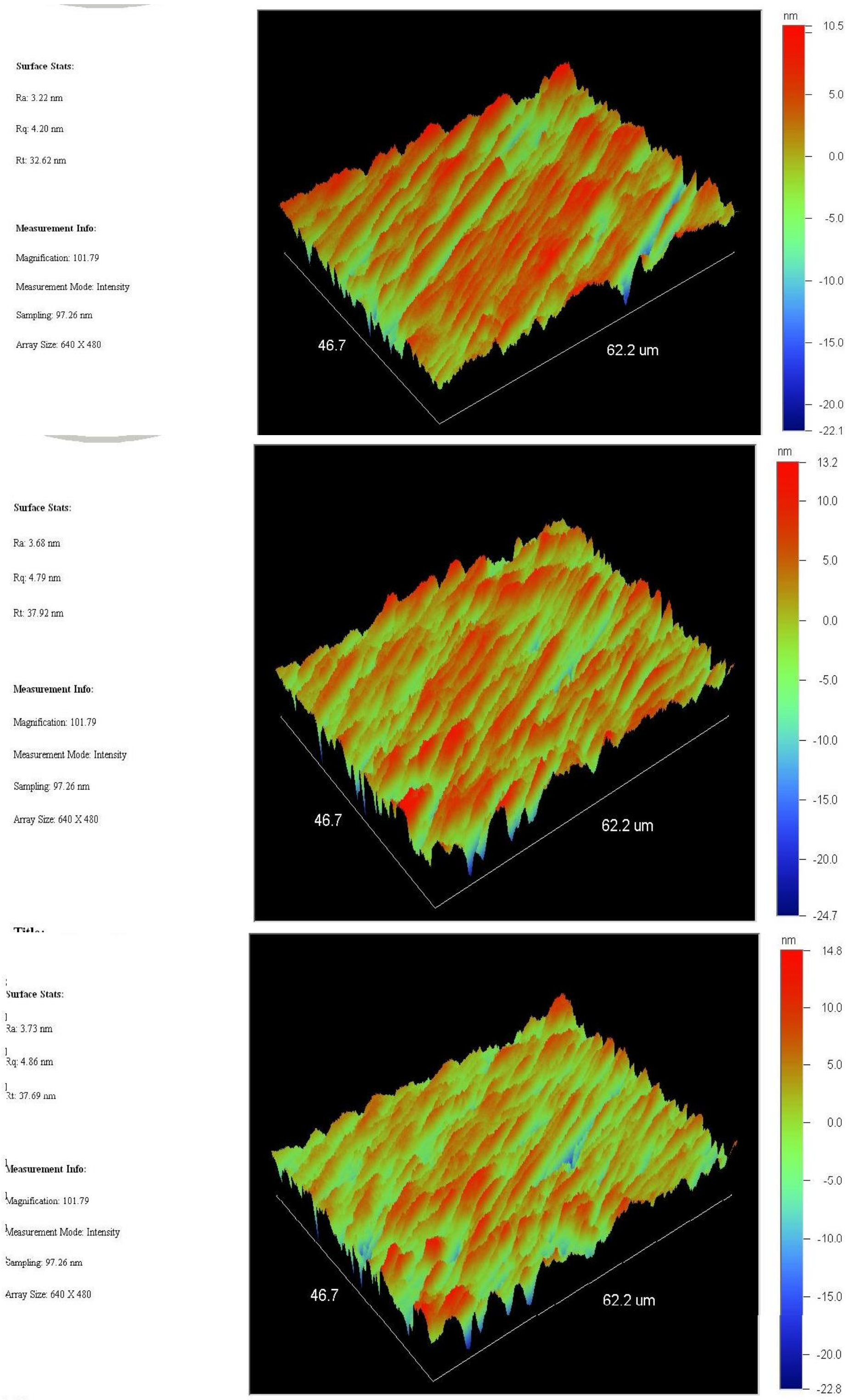

Figure 3. Roughness results of thin films; a) TiO_2 thin film , b) Al_2O_3 thin film , c)Al_2O_3/TiO_2 thin film.

4. Conclusion

Al_2O_3, $TiO_2$and Al_2O_3/ TiO_2 thin films were grown on cobalt-chromium alloys and Si-wafer substrate by Atomic Layer Deposition using TMA precursors for $Al_2O_3$and TDMA precursors for TiO_2. Concluded that the films deposited at 250 ^{0}C by ALD gives good quality films, homogeneity, and with no defects or micro-crack. Also concluded, that the crystalline regions found in the TiO_2 thin film, and the shape/size of the thin film elements depended on the kind of films. Furthermore, the roughness changing depends on the thin films type. The growth per cycle suggested theoretically equal to the thickness of the films measured experimentally by spectroscopic ellipsometry and approved also by TEM.

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