Deposition-rate dependence of optical properties of titanium nanolayers

Haleh Kangarlou and Maryam Motallebi Aghgonbad

Faculty of Science, Urmia Branch, Islamic Azad University, Urmia, Iran,
h.kangarlou@iaurmia.ac.ir, m.motallebi89@gmail.com

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Abstract. Titanium nanolayers with the thickness of 133 nm are deposited on glass substrates at 300 K, using the deposition rates 0.1, 1.0, 1.5 and 2.0 A/s. The layers are produced with a physical vapour deposition method under high-vacuum conditions. The optical reflectance and transmittance of the layers thus produced are measured in the wavelength range of 300–1600 nm. The optical functions are calculated basing on the Kramers–Kronig relation. The relation between the optical properties of the titanium nanolayers and their nanostructure dependent on the deposition rates is investigated.

Keywords: Kramers–Kronig relation, effective medium approximation, titanium, thin films, optical properties, deposition rate.

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UDC: 535.34, 535.312, 539.231, 620.3

1. Introduction

Thin films have many applications in various fields. Because of larger area-to-volume ratio typical for those films, as compared to that of the bulk materials, their physical properties are usually different from the properties inherent to the bulk materials [1]. The most significant parameters of the layered film structures include layer thickness and basic optical properties such as refractive index (n) and extinction coefficient (k) [2]. The basic thin-film properties are well known to depend essentially on its microstructure [3], which can be governed by the methods and quantitative parameters of deposition.

Titanium and its alloys are generally recognised for their low density in comparison with steels, interesting mechanical properties [4], very high strength and excellent resistance to corrosion [5]. They also represent one of the most successful materials widely used in dental and orthopedic fields and for manufacturing biomedical devices [6]. Pure titanium is a highly reactive metal [3]. Its chemical stability results in thin though stable surface oxide films, typically a few nanometres in thickness [5]. The previous studies have indicated that the properties of the titanium films depend on the film thickness, the temperature of substrate [7], and the angle of deposition [8]. Even though titanium thin films are so important in different technologies, their optical properties have only been reported by a few researchers (see the works by Johnson and Christy [9] for the thin samples ~ 30 nm and by Lynch et al [10] for the bulk ones).

In this study we have compared our data to those obtained in the earlier works. It is known that the ratio of the substrate temperature (T_s) to the melting one (T_m) influences both the growth and structure of the films produced under vacuum conditions. A structural zone model comprising three zones has been suggested by Movchan and Demchishin [11] and refined by Thornton [12], in

which an additional zone (a so-called transition zone) appears between the zones I and II [7, 13]. Many researchers have shown that the I-to-II zone boundary changes from $T_s > 0.30T_m$ for thicker films to $T_s > 0.37T_m$ for thinner ones. In this work we have obtained Ti/glass layers with the thickness of 133 nm and the substrate temperature of 300 K, using the same deposition angle (namely, the vertical geometry). The aim of this work is to study the relation between their optical properties, on the one hand, and the deposition rates, on the other hand. It has been proven that the deposition rate represents very important factor that determines the optical constants.

2. Experimental details

Titanium nanolayers were prepared on glass substrates (1×20×20 mm^3) using an ETS160 system with a pressure of 2.9×10^{-5} mbar. The layers were obtained in the conditions of high vacuum, using a vapour deposition method. The deposition rates used by us were 0.1, 1.0, 1.5, and 2.0 A/s. The purity of titanium was 98%. Prior to the deposition process, the substrates were cleaned with an ultrasonic-bath technique. The temperature of the substrates was kept constant (300 K). The thickness of the layers was measured with a quartz crystal method. It turned out to be 133 nm. Optical reflectance and transmittance of the layers were measured in the visible range using a Hitachi u-3310 system. The optical constants of our samples were derived on the basis of standard Kramers–Kronig relations using computer techniques.

3. Results and discussion

It is well-known that the melting temperature T_m for titanium is 1943 K. In this work the ratio of the substrate temperature T_s to the melting temperature T_m is 0.154. So our layers correspond to the zone I. This zone has a porous structure that includes tapered crystallites separated by voids.

The Kramers–Kronig relations are known to link the real and imaginary parts of an analytic function describing some causal-driven physical process [14]:

$$f(x_0) = u(x_0) + v(x_0)\,, \tag{1}$$

$$u(x_0) = \frac{1}{\pi} p \int_{-\infty}^{\infty} \frac{v(x)}{x - x_0} dx\,, \tag{2}$$

$$v(x_0) = -\frac{1}{\pi} p \int_{-\infty}^{\infty} \frac{u(x)}{x - x_0} dx\,, \tag{3}$$

where $u(x_0)$ and $v(x_0)$ are respectively the real and imaginary parts of an analytic function $f(x_0)$ and p denotes the Cauchy principal value. In this work the Kramers–Kronig relations are used to calculate the phase angle $\theta(E)$ [15]:

$$\theta(E) = -\frac{E}{\pi} \int_0^{E_2} \frac{\ln R(E) - \ln R(E_0)}{E^2 - E_0^2} dE + \frac{1}{2\pi} \ln \frac{R(E)}{R(E_2)} \ln \frac{E_2 + E}{|E_2 - E|} + \frac{1}{\pi} \sum_{n=0}^{\infty} \left(4 \left(\frac{E}{E_2} \right)^{2n+1} \right) (2n+1)\,, \tag{4}$$

where E denotes the photon energy, E_2 the asymptotic limitation of the free-electron energy, and $R(E)$ the reflectance. Hence, the $\theta(E)$ function can be calculated provided that the E_2 value (which is about 30 eV for titanium) is known. Then the real and imaginary parts of the refractive index can be calculated, from which the other parameters in need can be derived.

The results for the optical properties are described further on. Fig. 1a shows the reflectance curves for the Ti layers of the same thickness (d = 133 nm) deposited on the glass substrates at 300 K. Here different curves correspond to different deposition rates. The results by Johnson and

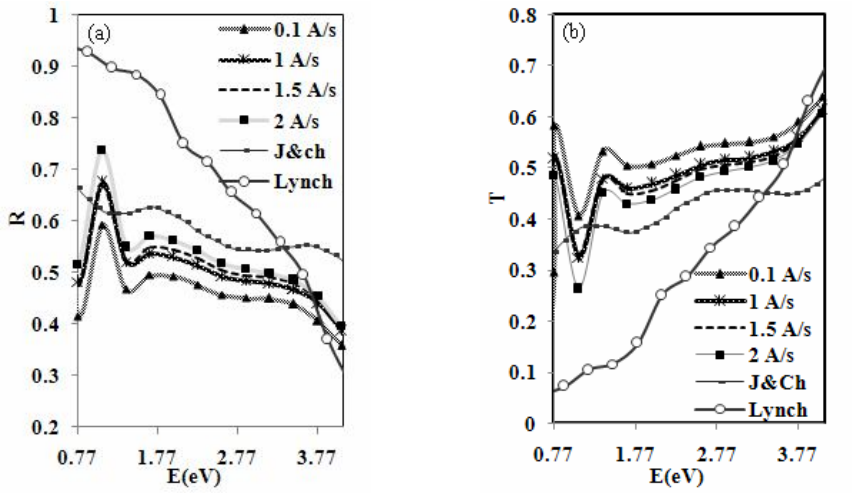

Fig. 1. Optical reflectance (a) and transmittance (b) curves for the titanium layers deposited with different rates. Notations 'J&Ch' and 'Lynch' correspond respectively to the curves obtained by Johnson and Christy [9] for the thin-film sample and by Lynch et al. [10] for the bulk sample.

Christy [9] for the thin Ti films (~ 30 nm) and by Lynch et al. [10] for the bulk Ti samples are included in Fig. 1 and all the further figures for the sake of comparison. It is seen from Fig. 1 that the deposition rate affects notably the reflectance spectra. In particular, the reflectance shows an increasing trend with increasing deposition rate. It is obvious that, due to increasing deposition rate, the layer would get more completed and a surface would fill up with Ti grains, the fraction of voids being decreased. As a consequence, the reflectance should then increase.

The general trend following from our data is similar to that found by Johnson and Christy [9] and Lynch et al. [10]. All of the curves have an extra peak at the energy of 1.2 eV, which depends on the deposition method, the conditions of deposition and the influence of impurities on the layers occurring during the deposition process. When interpreting our results, one has also to consider that Ti is a getter element which absorbs oxygen very easy. Fig. 1b shows the transmittance curves versus the photon energy in the visible region of light wavelengths. The main features seen in our data are again similar to those found earlier by Johnson and Christy [9] and Lynch et al. [10]. A weak peak at 1.2 eV has been observed by in the works [9, 10]. According to our results, this peak is sharper and occurs at 1.3 eV, i.e. an energy shift of about 0.1 eV takes place. The void fraction decreases with increasing deposition rate so that the transmittance decreases, too.

In Fig. 2a we depict the real part of the refractive index n. Here the main peculiarities also correlate with those seen in the data by Johnson and Christy [9] and Lynch et al. [10]. Within the range of deposition rates under test, the refractive index of Ti films in general increases with increasing deposition rate. This is readily understood because, at relatively low temperatures (300 K), the surface gets filled with small grains with increasing deposition rate. As a result, the refractive index would get higher.

Fig. 2b shows the imaginary part k of the refractive index. It increases with increasing deposition rate. The effect may be attributed to decrease in the void fraction and formation of more completed metallic layers. Naturally, the transmittance should decrease and the extinction coefficient increase in the latter case. A dip at the energy of 1.2 eV can be seen in the curves reported by Johnson and Christy [9] and Lynch et al. [10], which in our case is observed at 1.3 eV. Moreover, in all of our curves there occurs a peak at 1.0 eV.

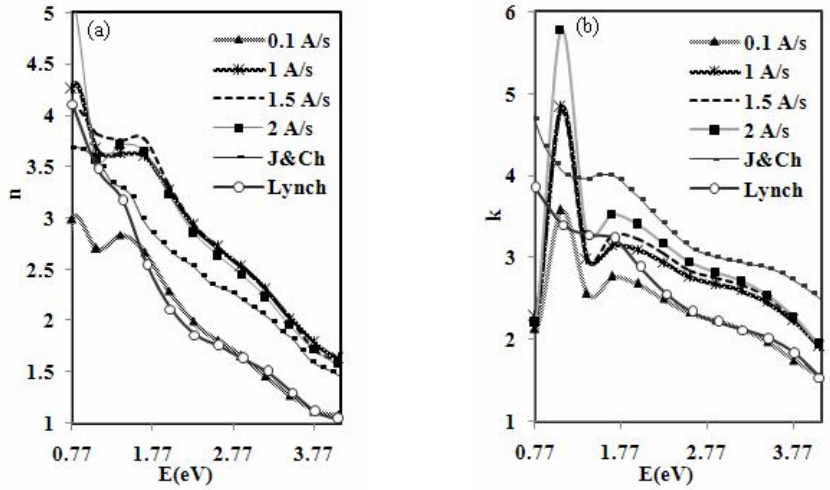

Fig. 2. Real (a) and imaginary (b) parts of refractive index for the titanium layers deposited with different rates. See also the note in caption of Fig. 1.

Fig. 3a displays the real part ε_1 of the dielectric function for the layers produced in this work. Our results are again in good agreement with those reported in Refs. [9, 10], where a wide peak can be seen at the energy of 1.2 eV. The corresponding peak found by us looks sharper and is shifted towards 1.3 eV. It is obvious that the layers get completed with increasing deposition rate, thus giving weakened insulation property and decreased real part of the dielectric function. Besides, one can see an anomaly for the deposition rate of 0.1 A/s.

Fig. 3b shows the imaginary part ε_2 of the dielectric function, which in general agrees well with the results [9, 10]. A peak seen at the energy of 1.5 eV in the curves obtained in the works [9, 10] corresponds to our peak at 1.6 eV. Moreover, we have observed an extra peak at 1.2 eV, which has already been mentioned for the other properties. With increasing deposition rate, the imaginary part of the dielectric function increases.

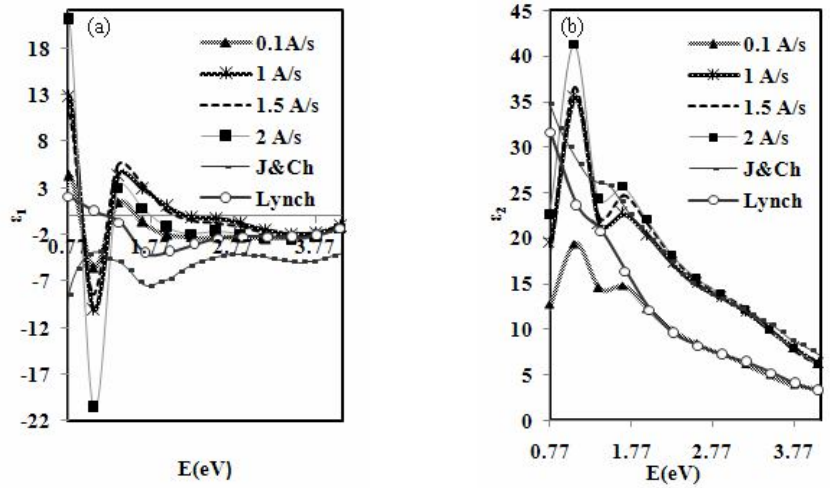

Fig. 3. Real (a) and imaginary (b) parts of dielectric function for the titanium layers deposited with different rates. See also the note in caption of Fig. 1.

Fig. 4a and Fig. 4b display the real and imaginary parts σ_1, σ_2 of the conductivity, which are given by

$$\sigma_1 = \varepsilon_2 \omega / 4\pi \,, \tag{5}$$

$$\sigma_2 = (1 - \varepsilon_1)/4\pi \,, \tag{6}$$

with ω being the angular frequency. As with all the other results, our data are in good agreement with those obtained in the studies [9, 10]. In particular, we have observed two wide peaks at the energies about 1.7 and 3.1 eV, besides the peak at 1.2 eV. Generally, the real part of the conductivity coefficient should increase with increasing deposition rate. This is seen in the experiment, with the only exception observed for the deposition rate 2.0 A/s. It is also evident that a larger number of titanium grains trap more impurities and so the conductivity property should then decrease. This is why there should be a competition between the formation of a complete layer, on the one hand, and the gettering property of titanium atoms, on the other hand.

The dependences of the imaginary part of the conductivity coefficient ($-\sigma_2$) upon the photon energy (see Fig. 4b) obtained in this work conform to those by Johnson and Christy [9] and of Lynch et al. [10]. Here increasing deposition rate generally yields increasing $-\sigma_2$ parameter, except for the curve corresponding to the deposition rate 2.0 A/s. The latter shows the other trend because of the competition mentioned before.

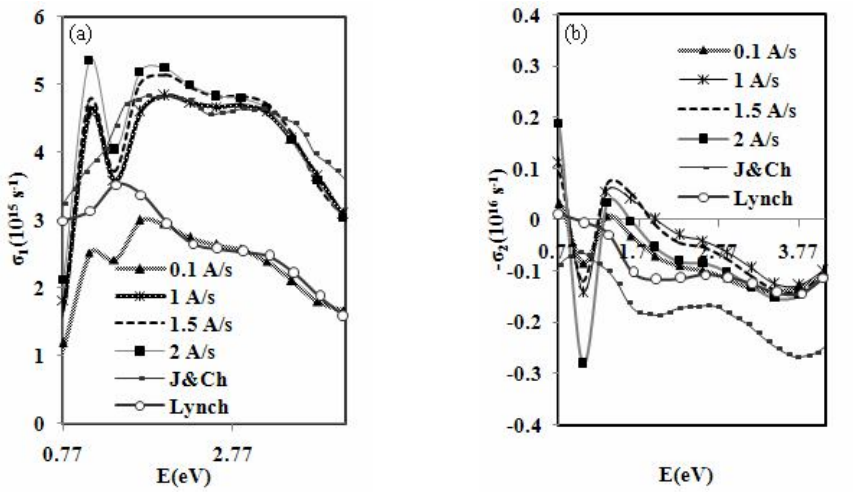

Fig. 4. Real (a) and imaginary (b) parts of conductivity coefficient for the titanium layers deposited with different rates. See also the note in caption of Fig. 1.

Fig. 5a represents the dependence of the absorption coefficient α on the photon energy. Here the absorption is given by

$$\alpha = \frac{2E}{\hbar c} k(E) \,, \tag{7}$$

where c is the free-space velocity. Our results are similar to those obtained in the earlier studies [9, 10], though an extra peak is observed for our samples at the energy of 1.2 eV. The absorption increases with increasing deposition rate. The reason is again that the layers get more completed and the fraction of voids decreases, thus inducing less transmittance and so larger absorption coefficient. Furthermore, there is an anomaly for our layers observed at 1.4 eV.

Fig. 5b illustrates calculations of the optical band gap energy E_g for the layers under test. It has been obtained from the relation

$$\alpha = (h\nu - E_g)^m \,, \tag{8}$$

where ν is the frequency and $m = 2$ is a constant. Due to their substrate materials, all of the thin

layers reveal the properties of semiconductors. Therefore we should deduce a small band gap for them. The optical band gaps calculated for different deposition rates are shown in Table 1. In addition, the value of this band gap is determined by pronounced gettering property of titanium, so that even in the conditions of high vacuum we cannot produce completely pure titanium layers. The band gap decreases with increasing deposition rate. However, the layer becomes completed and becomes a metalloid in case of the deposition rate 2.0 A/s.

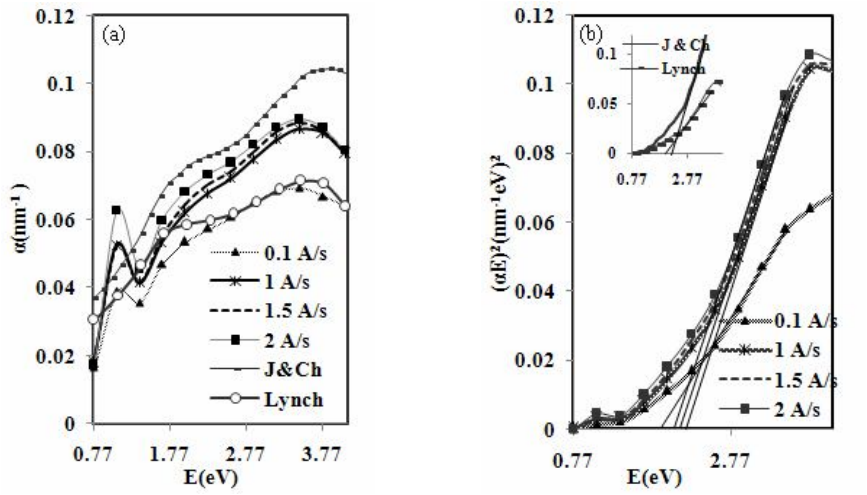

Fig. 5. Absorption coefficient (a) and band-gap estimation (b) for the titanium layers deposited with different rates. See also the note in caption of Fig. 1.

Table 1. Values of band gap energies obtained for our titanium layers.

Ti/glass samples	Deposition rate (A/s)	Band gap energy (eV)
I	0.1	1.96
II	1.0	2.20
III	1.5	2.15
IV	2.0	2.10
V	Johnson and Christy [9]	2.20
VI	Lynch et al. [10]	2.07

Finally, the void fractions of the titanium films calculated for the deposition rates 0.1, 1.0, 1.5 and 2.0 A/s using the known Aspnes' theorem [16] are shown in Fig. 6. All of them correspond to the fixed photon energy of 0.9 eV. It is obvious from Fig. 6 that increasing deposition rate leads to decreasing void fraction.

4. Conclusion

In this work we have deposited thin titanium layers on the glass substrates under the same deposition conditions and different deposition rates. This has been performed in the high-vacuum conditions at 300 K, using the vapour deposition method. The optical constants of our samples have been calculated using the Kramers–Kronig method. We have compared all of our results with those obtained earlier by Johnson and Christy [9] for the thin Ti films (~ 30 nm) and by Lynch et al. [10] for the bulk Ti samples. The general features of our data are quite similar to those found in the works [9, 10]. In particular, increasing deposition rate leads to increasing reflectance and decreasing transmittance. This is because the layers get more completed and their surface becomes

filled up with titanium grains. Both the real and imaginary parts of the refractive index are larger for the layers with higher deposition rates. The reason lies in formation of more completed layers and filling up the voids by titanium grains. Increase in the deposition rate also induces decreasing real part ε_1 and increasing imaginary part ε_2 of the dielectric function. As a matter of fact, completed metallic layers are then formed and so they strongly absorb light.

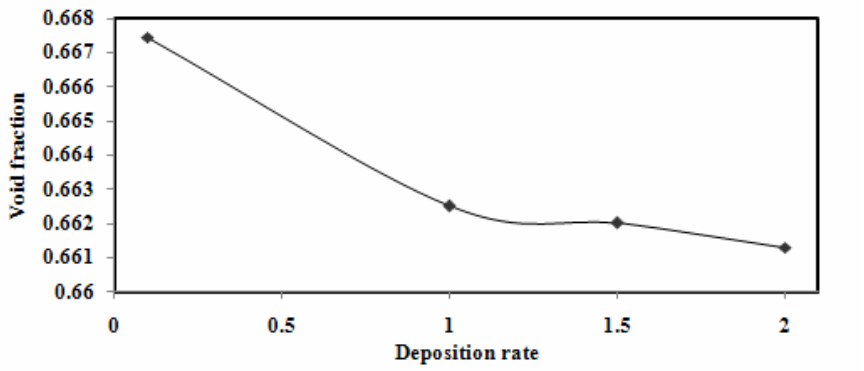

Fig. 6. Dependence of void fraction on deposition rate for the titanium layers (at the energy of 0.9 eV).

The absorption coefficient has been found to increase with increasing deposition rate, since more voids are filled up with metallic grains in that case. For the same reason, the samples prepared under higher deposition rates show larger real and imaginary parts of the conductivity. A particular situation has been shown to occur in case of the deposition rate $R = 2.0$ A/s. Then there is a competition between completing of layers and gettering property of titanium atoms. All of thin layers manifest semiconducting properties, due to a substrate material, so that we have deduced a small enough band gap for them, the average value of which is 2.2 eV. The estimated band gap gets smaller for the layers produced with higher deposition rates. Summarising, the optical properties of the Ti layers are notably influenced by the deposition rate. We have calculated the fraction of voids on the basis of the Aspnes' theorem [16] and it has proven to be lower for higher deposition rates.

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Анотація. *Титанові наношари з товщиною 133 нм нанесені на скляні підкладки при 300 K, з швидкістю осадження 0,1, 1,0, 1,5 та 2,0 A/c. Шари були осаджені у високому вакуумі методом напилення конденсацією з газової фази. Оптичне відбивання виготовлених шарів досліджене в спектральній області 300–1600 нм. Оптичні функції розраховані на основі співвідношення Крамерса-Кронінга. Досліджено співвідношення оптичних властивостей титанових наношарів і їхньої наноструктури в залежності від швидкості нанесення.*