Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Jan 2013.

To cite this article: Elmira Solati & Davoud Dorranian (2013): Investigation of the Structure and Properties of Nanoscale Grain-Size β-Tantalum Thin Films, Molecular Crystals and Liquid Crystals, 571:1, 67-76

To link to this article: http://dx.doi.org/10.1080/15421406.2012.741347

Mol. Cryst. Liq. Cryst., Vol. 571: pp. 67–76, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.741347

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Investigation of the Structure and Properties of Nanoscale Grain-Size β-Tantalum Thin Films

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Nanoscale grain-size tantalum films with tetragonal crystalline structure were prepared on BK7 glass and 304 steel by low power direct current magnetron sputtering at room temperature. Effect of deposition time on structural and electrical properties of tantalum thin films has been investigated. In all cases, highly preferred (330) orientation can be observed in X-ray diffraction measurements. With increasing the thickness of deposited films from 152 to 388 nm, a weak X-ray photon peak is diffracted from (720) planes of β-Ta. The atomic force microscopy micrographs show the grain size of 20–30 and 100–140 nm for films deposited on glass and steel substrates respectively. Deposition rate was approximately constant. The resistivity of samples on glass substrate is decreased with increasing the time of deposition. Transmittance of deposited films on glass substrate is decreased with increasing the thickness of sample.

Keywords Crystal structure; resistivity; tantalum, thin film; magnetron sputtering

Pacs: 81.15.Cd; 61.05.Cp; 68.35.Bd; 81.07.Bc; 68.55.Jd

1. Introduction

Tantalum (Ta), a semiprecious, refractory metal, has properties that make it useful for many applications, from electronics to mechanical and chemical systems [1]. For decades, tantalum thin films have been studied in particular for the fabrication of resistor elements with enhanced long-term stability. Besides this well-established field of application, Ta layers play nowadays an important role in microelectronic devices, predominantly as diffusion barrier between the copper top metallization on the silicon-based substrate, as adhesion promoter for platinum thin films for high-temperature applications and as robust coating of surfaces requiring a high resistance against wear as well as corrosion [2].

However, vapor-deposited tantalum films are often found to contain one or both of two distinct crystalline phases. There are two main phases in the sputtered tantalum film. A stable α-phase Ta (Im3m space group, $a = 3.304$ Å) with a body centered cubic (bcc) crystal lattice structure, is the common phase of the bulk metal. The metastable β-phase Ta (P42/mnm space group, $a = 5.313$ Å, $c = 10.194$ Å) with a tetragonal crystal lattice structure known since 1965 grows during deposition of thin films (International Centre for Diffraction Data (ICDD) cards no. 4–788 and no. 25–1280) [3]. Bulk α-Ta phase with

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low resistivity of 15–60 $\mu\Omega$-cm [4] shows excellent physical and chemical properties such as a high melting point of 2996°C, good ductility, and excellent corrosion resistance in aggressive environments. In contrast to the tough and ductile α-Ta phase, β-Ta phase with higher resistivity of 170–210 $\mu\Omega$-cm [4] is hard and brittle, and its presence compromises the coating integrity under strain [5]. The low resistivity α-phase tantalum is preferred to reduce interconnection resistance and is desirable for thin film interconnection. The high-resistivity β-phase tantalum has good stability and is a good candidate for thin film resistor [4]. Although the physical properties of β-Ta have not been well characterized, it is known to be thermally unstable, and transforms to the bcc phase at temperatures above750°C [6]. Typical Knoop microhardness values for β-Ta are greater than 900 versus Knoop values of 300–400 for α-Ta. These properties make β-Ta more susceptible to crack formation and failure [7]. Therefore, the α phase is preferred in application where coatings are subjected to both chemical attack and wear, such as protecting gun-bore against erosion and β phase is preferred in electronic and microchip devices [5].

The mechanism of the preferential growth of β-phase is not well understood. It is not even clear that this phase has a unique structure as various lattice constants of β-Ta films and a broad range of resistivity has been reported [8]. The nucleation and growth conditions, that is, the impurity levels and the number of defects also influences the phase formation [9].

Beside these two crystalline phases, Ta films can be deposited in amorphous structure. The main difference between these phases is the large difference in their electrical resistivity. In the case of amorphous films resistivity is increased to more than 250 $\mu\Omega$-cm [10].

Previous studies have pointed out that a α-phase tantalum film with giant-grained microstructure was easily formed at a high temperature environment, while a β-phase was easily formed at a room-temperature process [4]. Alami et al. [9] demonstrated the effects of different inclination angles with respect to the sputter source using high power impulse magnetron sputtering, an ionized physical vapor deposition technique. A number of experimental investigations were undertaken to evaluate the effects of sputtering power [2,4] and back pressure [2,11]. In our previous work, the effects of substrate temperature (room temperature -350°C) on the phase composition and crystallization orientation of the tantalum thin film deposited by direct current magnetron sputtering in an extremely low power deposition regime was considered [12]. In this article, we present the results of investigation of the effect of deposition time on the structural and electrical properties of the tantalum thin film deposited by direct current magnetron sputtering on BK7 glass and 304 steel substrates. Differences between effects of steel as a crystalline substrate and BK7 glass as an amorphous substrate on the structure of deposited films are observed and compared. This article is organized as follows. After this introduction the experimental setup is presented in Section 2. Section 3 is devoted to our results and discussion and conclusion can be read in Section 4.

2. Experimental Details

Cylindrical electrodes, direct current sputtering system was employed to deposit tantalum on BK7 glass and 304 steel substrates. The sputtering system was capable of creating an ultimate vacuum of 4×10^{-4} Torr with rotary and diffusion pumps combination. During the sputtering experiment pressure was maintained at 3.5×10^{-2} Torr. A pure tantalum (99.99%), 30 mm diameter and 195 mm in height, was used as the target. The working gas was pure argon (99.999%). The distance between the substrate and the target was 30 mm.

Table 1. Deposition time of samples and the thickness of deposited films on both substrates

Sample	1	2	3	4
Deposition time (min)	10	15	20	25
Film thickness (nm)	152	220	267	388

The discharge current was 200 mA at the voltage difference of about 670 V and deposition time was varied from 10 to 25 min. Uniform magnetic field of 400 Gauss was generated by a solenoid parallel to the axis of cylindrical chamber. Before deposition, substrates were cleaned by ultrasonic waves in alcohol and acetone, and finally dried by blowing air. During deposition, both glass and steel substrates were placed in a same condition respect to sputtered particles and other parameters to deposit similar films on them. In the deposition process, no external heating was provided. The deposition time for different samples is presented in Table 1.

The phase and structure of the deposited tantalum films were identified by X-ray diffraction (XRD) with Cu-K_α radiation ($\lambda = 1.54060$ Å), using the XRD diffractometer from STOE company. The optical reflection and transmission spectra for samples were measured by a Varian Cary-500 spectrophotometer at room temperature. Atomic force microscopy (AFM) micrographs were taken using Auto probe CP from Park Scientific Instrument. Sheet resistance was measured by FPP-5000 Miller Inc. four-point probe at room temperature. The thickness of deposited films was measured by DEKTAK 3 (version 2.13) profilemeter.

3. Results and Discussion

3.1. Structure of Deposited Films

The angular spectrums of the X-ray photons diffracted from samples are presented in Figs 1(a) and (b) for both substrates. In Fig. 1(b), two peaks of steel substrate can be seen at $2\theta = 43.68^\circ$ and 50.76°. The main peak of tantalum with tetragonal crystalline structure is appeared at about $2\theta = 37.1^\circ$ for deposited films on both substrates from (330) planes [13]. There is about 0.16° shift in the place of this peak for different samples. It can be due to several reason one of them is the stress which can be establish in the film during the deposition process. On the other hand, this shift can be due to light impurities such as carbon and oxygen in the sample. Another peak is appeared at about $2\theta = 66.7^\circ$ for samples 3 and 4 on both BK7 glass and 304 steel substrates due to (720) planes of β-Ta [13]. Comparing with similar works [8,14,15], the XRD patterns of samples in this experiment confirm a single-phase structure film of sample 1 and 2 on both substrates. Same effect was observed in our previous work [12]. The XRD pattern is an effective tool for assessing structure and has been extensively applied on β-Ta. However, disagreements exist in the indexing results, which are mainly caused by differing relative intensities in diffraction patterns resulting from texture effects [15]. Thin films often exhibit a surprising degree of texture, even when deposited on an amorphous substrate. The texture observed is, in general, the result of growth competition between different crystallographic directions. In this case, with the increasing of the film thickness the (720) peak of the β-Ta phase becomes more and more evident.

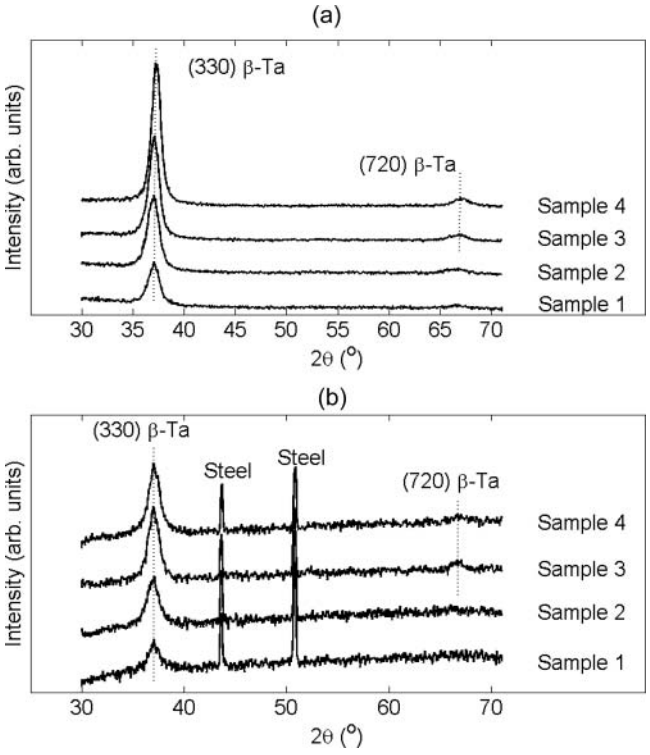

Figure 1. X-ray diffraction spectrums of deposited films on (a) glass and (b) steel substrates.

The intensity of diffracted X-ray photons is increased with increasing the deposition time for both substrates. The intensity of XRD peaks of deposited films on glass substrate is larger than that for steel substrate that is presented in Fig. 2. This is because of the heat conductivity of substrates. The heat conductivity of steel is larger than the heat conductivity of glass. As is known, structure of Ta films is strongly depended on the substrate temperature. We believe that in the same situation the steel substrate is colder than glass because of higher heat conductivity, leads to weaker crystallinity of the films deposited on steel substrate.

Using known Scherrer's formula the grain size of samples for all deposited films is less than 10 nm, but these results are not confirmed by AFM micrographs. Difference between grain size of thin film extracted from Scherrer's formula and AFM micrographs

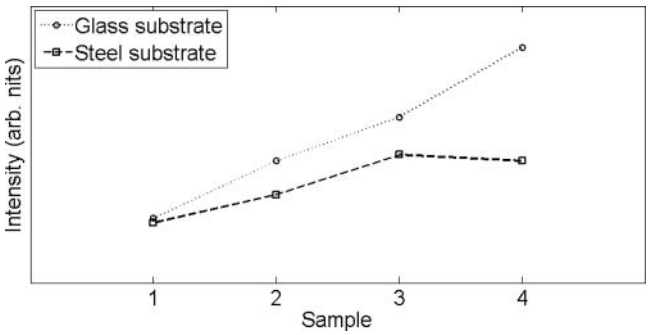

Figure 2. Rate of phase transition of (330) preferred orientation of the films.

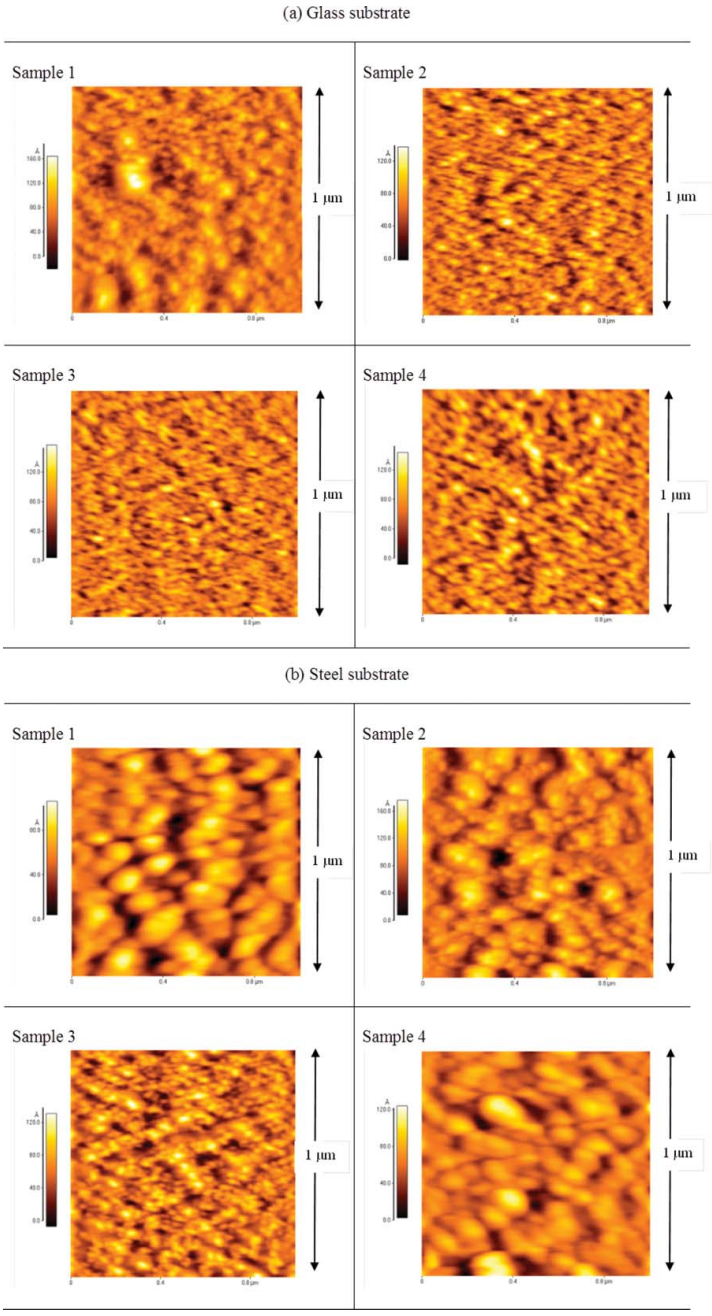

Figure 3. The 2D AFM micrographs of deposited films on (a) glass and (b) steel substrates.

has been reported before [12,16,17]. Two-dimensional (2D) AFM micrographs of samples are presented in Fig 3(a) and (b) for both substrates. For the samples deposited on glass substrate, the average grain size of the film is about 30 nm for sample 1, which is decreased to about 20 nm for samples 2 and 3 and again is increased to about 30 nm for sample 4.

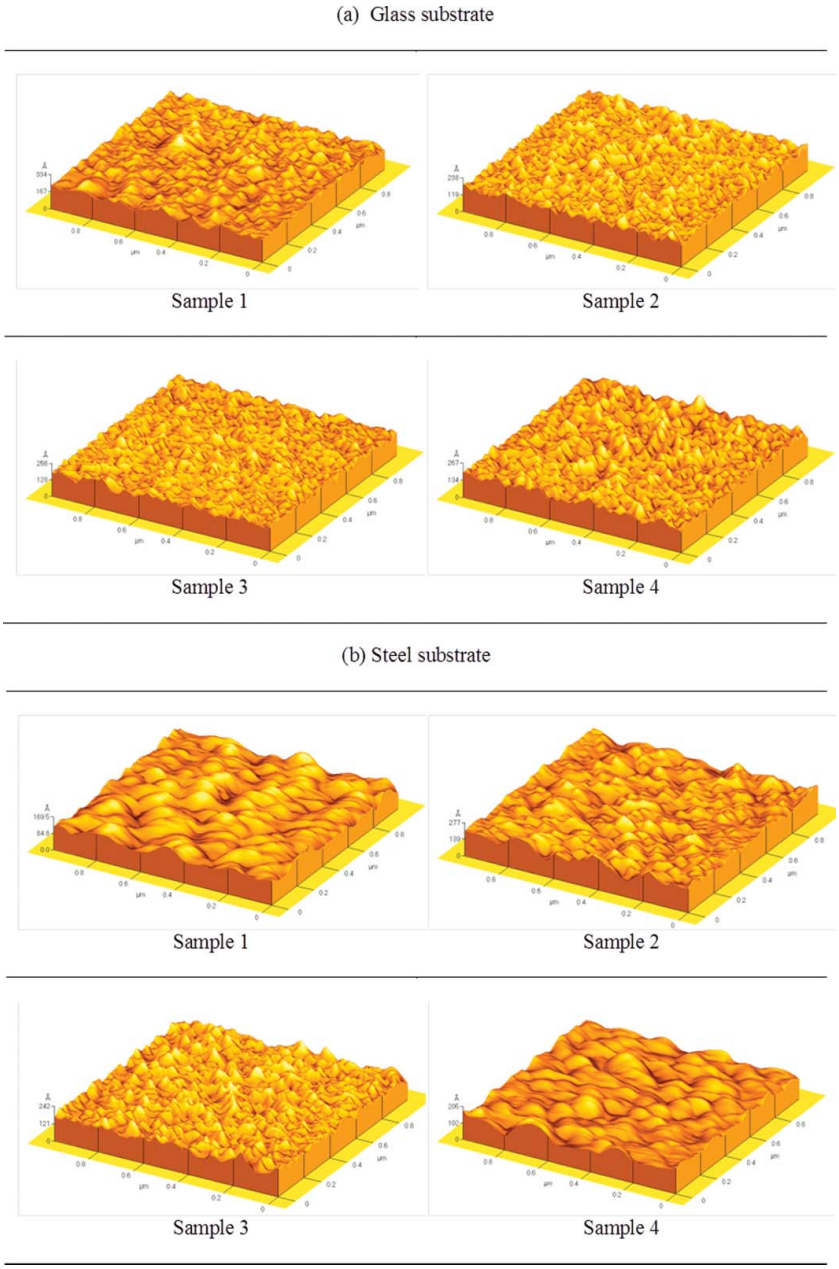

Figure 4. The 3D AFM micrographs of deposited films on (a) glass and (b) steel substrates.

In the case of films deposited on steel substrate, this magnitude is larger. The grain size of sample 1 on steel substrate is about 130 nm that is decreased to about 120 and 100 nm for samples 2 and 3, respectively, but is increased to about 140 nm for sample 4. It can be concluded that for Ta thin films deposited on glass substrate the grain size is differed between 20 and 30 nm while this important magnitude is between 100 and 140 nm for the films on steel substrate. Regarding the higher temperature of the glass substrate, this result

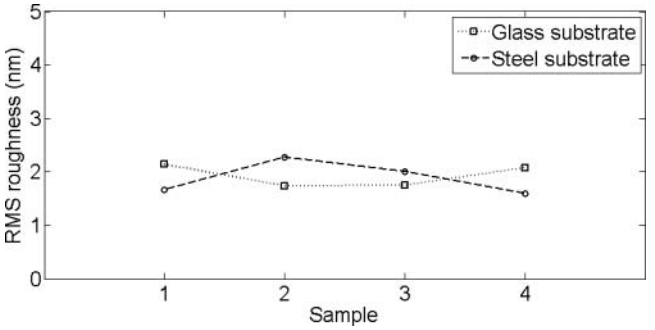

Figure 5. RMS roughness of the deposited films on glass and steel substrates.

is in contrast with the presented result in Ref. [18]. Furthermore the steel surface shows a high surface roughness in comparison with glass and hence, shadowing effect may also decreases the mean grain size.

3.2. Morphology of the Ta Films

Three-dimensional (3D) atomic force micrographs of samples deposited on BK7 glass and 304 steel substrates are shown in Fig 4(a) and (b), respectively, and RMS roughness of films is presented in Fig. 5. The scanning area is $1 \times 1\ \mu m^2$. The deposited films on glass substrate have small conical structure. Size of cones is decreased with increasing the time of deposition for samples 1–3 but is increased for the case of sample 4. Ta films on 304 steel substrates at first have a nodule-like structure. Size of nodules is decreased with deposition time. Sample3 has conical structure while sample 4 again has nodule-like structure. Effect of film structure is clear in the crystallinity of deposited samples. Increasing the conical structure of films is because of increasing their crystallinity that can be observed in the intensity of XRD pattern. RMS roughnesses of different samples are similar in the same order.

3.3. Thickness and Electrical Resistivity

Thickness of deposited films was measured by profilemeter that is presented in Fig. 6. Measurement shows that the rate of deposition of Ta on the glass substrate in the condition of this experiment is approximately constant. This rate is about 15 nm per minute.

The sheet resistance of deposited films on BK7 glass substrates measured with four point probe device is presented in Fig. 7.The sheet resistance is decreased with increasing

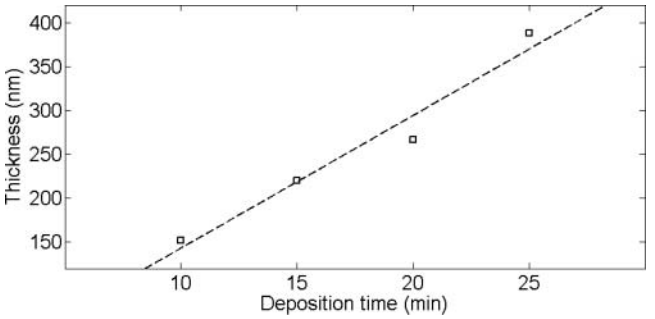

Figure 6. Thickness of deposited films on glass substrate as a function of deposition time.

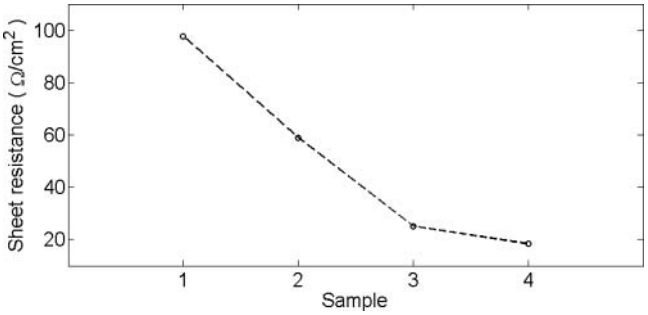

Figure 7. Sheet resistance of samples deposited on BK7 glass substrate.

the thickness of deposited films which is a natural result for conductor films. Furthermore, the crystallinity of samples is very effective in decreasing of tantalum films resistivity. But the noticeable point is the high resistivity of our samples in comparison with similar works. The reported resistivity for tetragonal phase of tantalum thin films is between 170 and 210 $\mu\Omega$-cm [4].

In our case by multiplying the sheet resistance to film thickness, this magnitude is calculated to be between 600 and 1500 $\mu\Omega$-cm. It can be explained by considering the grain size of deposited films. Nanosize grains of tantalum do not forma complete conductor film, because of few numbers of atoms in each grain. From one point of view, diffraction of charge carrier at the voided grain boundaries leads to larger sheet resistance and from other point of view, small size grains is a kind of porous bulk structure leads to larger resistivity. Furthermore, the level of impurities that was mentioned before can be another reason for higher resistivity of samples.

3.4. Reflectance and Transmittance of Ta Films

The UV-Vis-NIR reflectance and transmittance spectrum of deposited samples on glass substrate are presented in Figs 8 and 9, respectively. Reflectance of samples is increased with increasing sample thickness as well as wavelength of the probe beam. Transmittance of samples is decreased with increasing the thickness of sample that is a natural behavior of thin films. But the magnitude of transmittance of samples in the 200 and 2000 nm wavelengths is large in comparison with one expected from tantalum. Using $\rho = 131$ nΩ-m for tantalum, the skin depth of tantalum for this range of electromagnetic wave is between

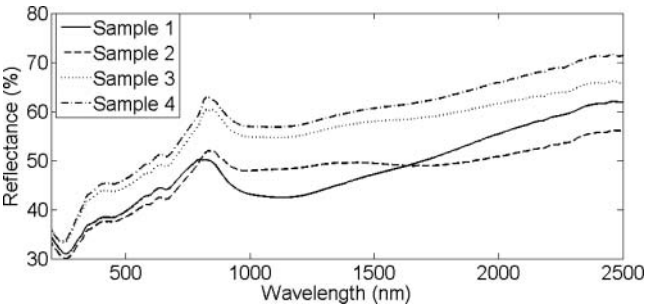

Figure 8. Reflectance of samples deposited on glass substrate.

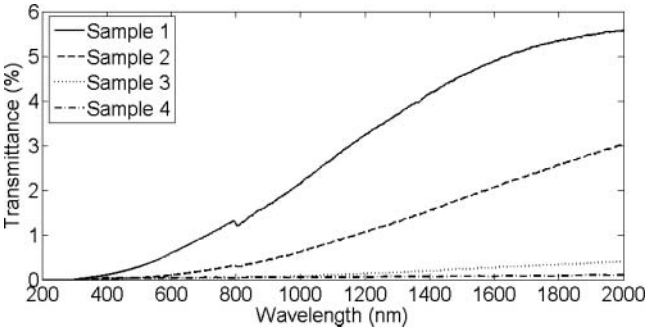

Figure 9. Transmittance of samples deposited on glass substrate.

6.65×10^{-3} μm and 1.4×10^{-2} μm, much more smaller than the thickness of the deposited films. Actually, tantalum films deposited on glass substrate have more than 30% energy absorption in the range of 500 to 2000 nm wavelength, which is not the behavior of an ideal conductor. It can be explained by the fact that in nanosize range the conduction band is not formed completely due to the small number of atoms in the grains, leads to non-zero magnitude of transmission and small amount of absorption.

4. Conclusions

The Ta films were deposited on BK7 glass and 304 steel substrates by direct current magnetron sputtering of a pure tantalum target at room temperature. In this work, the effects of deposition time on the properties of tantalum films with tetragonal crystalline structure have been investigated. It is observed that in this experimental condition tantalum thin film with nanosize grains are formed on both glass and steel substrates. Size of grains for deposited films on glass substrate is 20–30 nm while on steel substrate grain size of deposited films is 100–140 nm. Properties of films are influenced by the substrate temperature even if the difference is so small due to heat conductivity of two materials such as glass and steel. Electrical and optical behavior of such a nanosize grains film are far from typical conductors since the conduction band is not formed in such a small grain size materials. Diffraction of charge carrier at the voided boundaries between grains and the size of grains are two important parameters effective on sheet resistance of such films. So the resistivity of films is larger than presented magnitudes in similar reports. Transmittance of deposited films on glass substratein 200–2000 nm wavelengths is also larger than the expected transmittance magnitudes of typical tantalum films.

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