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Structural and optical characterization of titanium nitride thin films deposited by magnetron sputtering

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Abstract. Titanium nitride applicability covers different industries such as microelectronics, biomedicine and so on. This paper presents the analysis of the structural and optical properties of titanium nitride thin films for different deposition conditions. The samples were deposited by direct current magnetron sputtering on silicon substrates. The deposition was done at room temperature, on substrates preheated at 300 °C or on substrates that were polarized at -40 V and -90 V respectively. The results indicate a dependency of the structural orientation with respect to the deposition process when this takes place at room temperature. When the deposition was done on a preheated substrate there was no structural orientation. A negative polarization of the substrate leads to the formation of small sized crystallites. Regarding the optical properties, the films showed good semiconductor properties and a low reflectivity.

Introduction

Titanium nitride (TiN) thin films were studied by many researchers due to their excellent properties, especially mechanical and tribological properties, corrosion resistance, wear resistance and thermodynamic stability [1–3]. Due to these properties, titanium nitride thin films can be used in a wide range of applications like: diffusion barriers for micro-electric devices, optical coatings with antireflection and antistatic properties, electrodes, biomedicine and hard coatings for tools and so on [4–9].

The most often used methods to obtain titanium nitride films are: reactive magnetron sputtering, laser ablation, ion beam deposition or plasma assisted chemical vapor deposition and so on [10–14]. The physical-chemical and mechanical/tribological properties of titanium nitride films depend on the deposition parameters. In this regard, different researches present the influence of some deposition parameters such as the deposition rate, deposition time, substrate, the heating or the polarization of the substrate on the topographical, mechanical, tribological, adhesion properties for titanium nitride thin films deposited by DC (direct current) magnetron sputtering. All the results are pointing out a change in these properties with the change in deposition parameters. A possible explanation for this change can be the growth of the deposited films after different preferential orientations.

The present paper is a study concerning the deposition of titanium nitride thin films by DC magnetron sputtering on silicon substrates at different deposition parameters (substrate

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temperature, substrate bias voltage, deposition time) and the structural and optical characterization of the obtained thin films.

Materials and Methods

Deposition of titanium nitride thin films

The deposition of titanium nitride films was done by direct current reactive magnetron sputtering method, using 99.99 % purity titanium target and silicon Si (100) substrate. The experimental procedure details are presented in previously published work of the authors [4]. The parameters for titanium nitride films deposition were: (i) deposition time (10, 20 and 40 minutes) with the substrate (RT) at room temperature, (ii) deposition time (20 minutes) with the substrate at a temperature of 300 °C and (iii) deposition time (20 minutes) and polarization of the substrate at -40 V and -90 V. These studies were conducted in order to determine the influence of the deposition conditions on the structural and optical properties of titanium nitride films destined for MEMS devices applications.

Characterization of titanium nitride thin films

X-ray diffraction analysis was carried out with an Inel Equinox 3000 diffractometer using a cobalt radiation (λ_1=1.7889 Å, λ_2=1.7928 Å). The patterns were evaluated using JPCDS 87-0633. The mean crystallite size and lattice strain were calculated using the Williamson-Hall method. According to this method, the broadening of the diffraction line, β, is given by the sum of the broadening introduced by the crystallite size, β_d, and the broadening introduced by the internal strain, β_ε (equation (1)). These two parameters can be calculated using the equations (2) and (3) as follows [15]:

$$\beta = \beta_d + \beta_\varepsilon \tag{1}$$

$$\beta_d = \frac{K\cdot\lambda}{D\cdot cos\theta} \tag{2}$$

$$\beta_\varepsilon = 4\cdot\varepsilon\cdot tg\theta \tag{3}$$

Where K is Scherrer's constant, λ is the wavelength of the X-ray radiation, D is the mean crystallite size, θ is the Bragg angle while ε represents the internal strain. Starting from the equations mentioned above and the graphical plotting of the dependency $\beta\cdot\cos\theta = f(4\cdot\sin\theta)$, the mean crystallite size and the internal strain can be determined. Thus, the internal strain is given by the line's slope while the mean crystallite size is given by the intersection between the line and the Y axis ($\beta\cdot\cos\theta$).

UV-Vis spectroscopy studies were conducted in order to determine the optical properties of the films. Using an aluminum mirror as reference, the diffuse reflectance spectra were measured at 8° with a Lambda 35 Perkin-Elmer spectrometer equipped with an integrated sphere. The energy band gap of the titanium nitride films was determined based on the Kubelka-Munk function [16].

Results and discussions

XRD patterns of the titanium nitride films deposited at different deposition time are presented in Fig. 1. The crystalline phase of titanium nitride was identified based on JPCDS standard diffraction no. 87-0633. Based on the results obtained using the Williamson-Hall relation, it was observed that the increase in deposition time tends to decrease the structural parameters, i.e. crystallite size, lattice strain and cell volume (Table 1). It was also observed that for a deposition

time of 10 minutes, the titanium nitride film has a textural orientation in the (111) crystalline plane, while when increasing the deposition time to 40 minutes, the preferred orientation of the deposited titanium nitride film changes to the (220) crystalline plane.

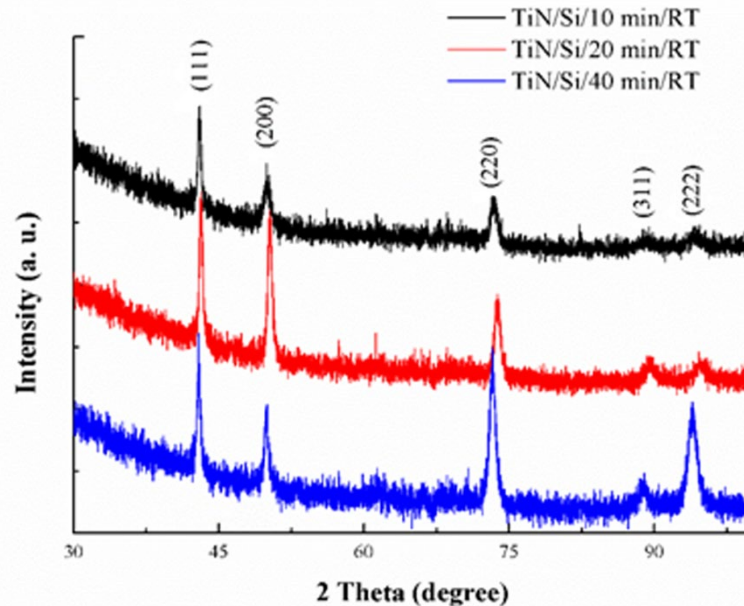

Fig. 1. XRD patterns of titanium nitride thin films deposited at different deposition time on a silicon substrate at room temperature.

The change in the preferred orientation, confirmed by other authors like [10, 14, 17], can be attributed to the increased energy of the bombarding particles from titanium target. Another cause for the change in the structural parameters with the increase in the deposition time can be the change in the preferred orientation, which can deform the cell parameters and to the increased thickness of the film [10]. According to the theoretical calculation, titanium nitride films thickness increased (0.27 µm, 0.55 µm and 1.10 µm) with the deposition time (10, 20 and 40 minutes). However, the change in lattice strain can be explain due to the presence of the $(TiN)_{.76}$ (JCPDS file no. 01-087-0626), $(TiN)_{.88}$ (JCPDS file no. 01-087-0630) and TiN (JCPDS file no. 01-087-0633) compounds in the structure of the deposited films. For instance, the presence of the $TiN_{0.76}$ leads to the change in 2θ angle from 50.68 º (specific to the stoichiometric compound TiN) to 49.97 º in the case of the (200) crystalline plane. The values of the lattice strain given in Table 1 are the average values obtained for each film and they are influenced by the quantity of non-stoichiometric compounds. The presence of non-stoichiometric compounds was also reported by other researchers [18, 19].

Fig. 2 presents the XRD patterns for the titanium nitride film deposited on the silicon substrate preheated at 300 ºC and the titanium nitride film deposited on the silicon substrates negatively biased at -40 V and -90 V respectively, when the deposition time was kept constant at 20 minutes. It is obvious that the deposition parameters have a strong influence on the chemical composition and, implicitly, on the properties of the investigated thin films. As mentioned above, non-stoichiometric compounds exist in the deposited thin films. Their existence determines a shift to the left of the peaks. We assume that the shift is more significant in the case of titanium nitride

thin films that are containing higher quantities of non-stoichiometric compounds. When the silicon substrate was polarized at -40 V and -90 V for a deposition time of 20 minutes, compared to the un-polarized film, it was observed a decrease in crystallite size titanium nitride films (Table 1) from 21 nm for the un-polarized titanium nitride film to 16-17 nm for titanium nitride film for the polarized substrate. According to Benegra et al. [20] a decrease of crystallite size with the increase of negative bias can be explained by the fact that the pulsed power may not only increase the impinging atom energy, but it may also increase the ion current densities.

Table 1. Structural parameters of titanium nitride thin films

Samples	Average crystallite size [nm]	Lattice strain [%]	Cell volume [Å^3]
TiN/Si/10 min	37	0.379	12.73
TiN/Si/20 min	21	0.272	12.70
TiN/Si/40 min	17	0.160	12.69
TiN/Si/20 min/300 ^{0}C	17	0.210	12.70
TiN/Si/20 min/-40 V	17	0.585	12.73
TiN/Si/20 min/-90 V	16	0.930	12.73
TiN/JPCDS 87-0633	-	-	12.73

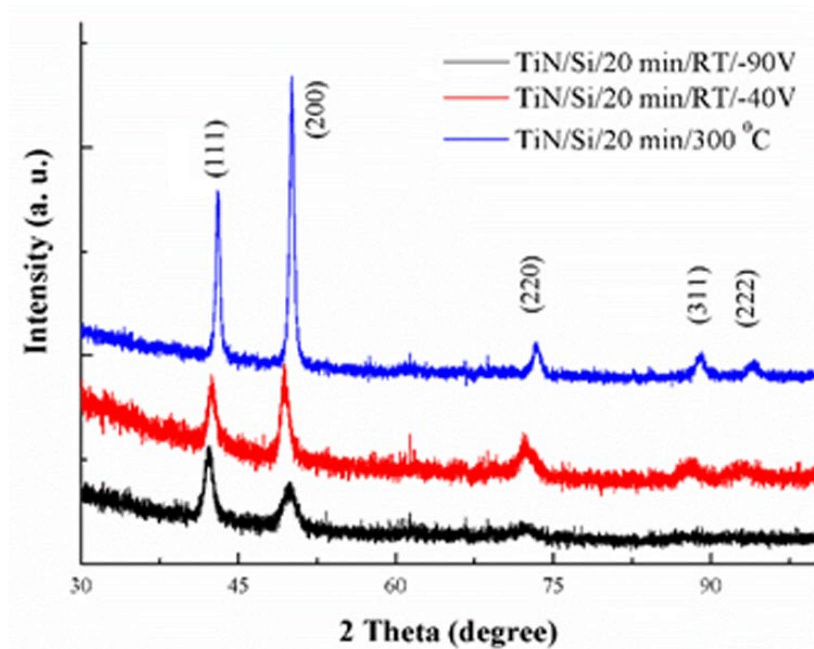

Fig. 2. XRD patterns of titanium nitride films deposited on substrates heated at a temperature 300 °C and polarized at -40 V and -90 V for 20 minutes.

Fig. 3 shows the specular reflectance of titanium nitride films deposited on silicon substrates at room temperature at different deposition times. All the films exhibit a low reflectivity, between 300 nm and 500 nm, but as the wavelength increases to the infrared region, the reflectance also increases, especially for the titanium nitride film deposited for 20 minutes which has a of reflectance nearly 60 %.

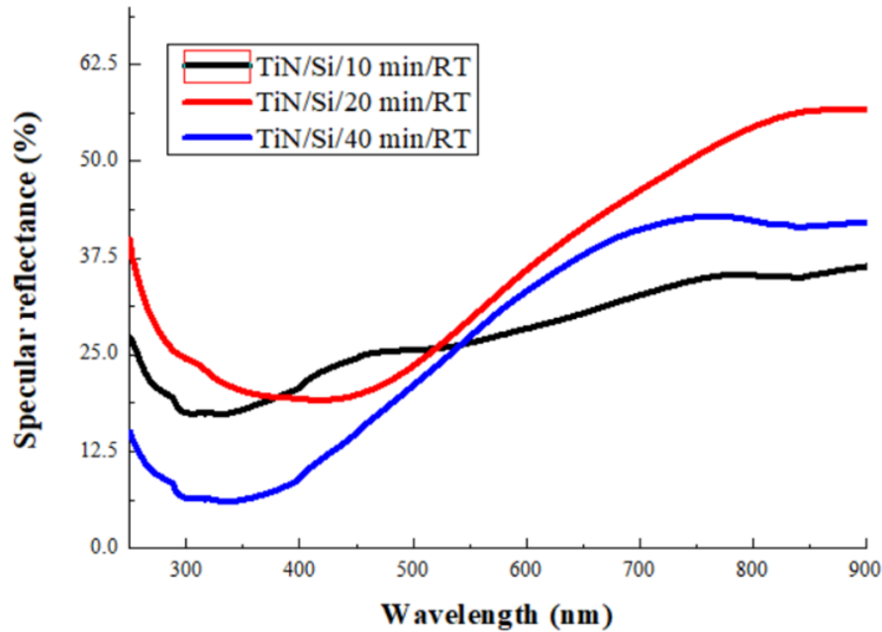

Fig. 3. Reflectance spectra of titanium nitride films deposited at different deposition time on a silicon substrate at room temperature.

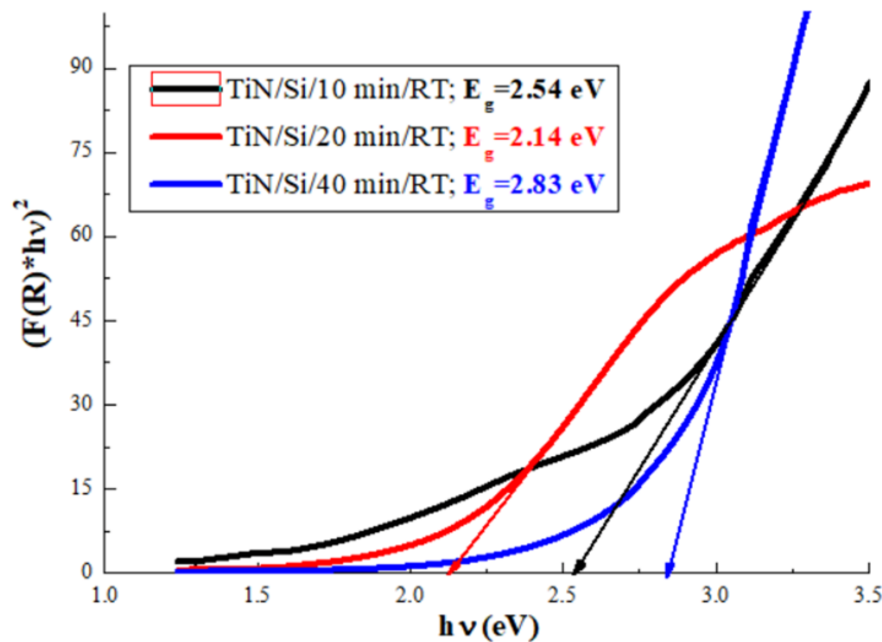

Fig. 4. Energy band gap of titanium nitride films deposited at different deposition time on silicon substrate at room temperature.

The energy band gaps suggest that the titanium nitride films deposited at different deposition times are semiconducting materials (Fig. 4). The titanium nitride film deposited for 20 minutes exhibit a lower energy band gap (2.14 eV) than the films deposited for 10 and 40 minutes, respectively (2.54 eV and 2.83 eV).

A red-shifting in the optical energy of titanium nitride film deposited for 20 minutes, compared to the film deposited for 10 minutes can be attributed to the increase in the film thickness and with the change in the textural orientation from (111) crystalline plane to (220) crystalline plane, which also implied an increase in the roughness of the films [4]. According to Kiran et al. [21] the change in the titanium nitride films thickness causes a shift in the optical edge and therefore a change in the band structure of the films.

Fig. 5 presents the reflectance spectra of the titanium nitride films deposited for 20 minutes on a silicon substrate heated at 300 °C and on substrates, at room temperature, to which a negative bias-voltage of -40 V and -90 V respectively was applied. Compared to the titanium nitride film deposited on the silicon substrate heated at 300 °C, which have a reflectivity between 300 nm and 500 nm, the titanium nitride films deposited on a substrate with different voltage bias, the reflectivity increases to between 500 nm and 900 nm.

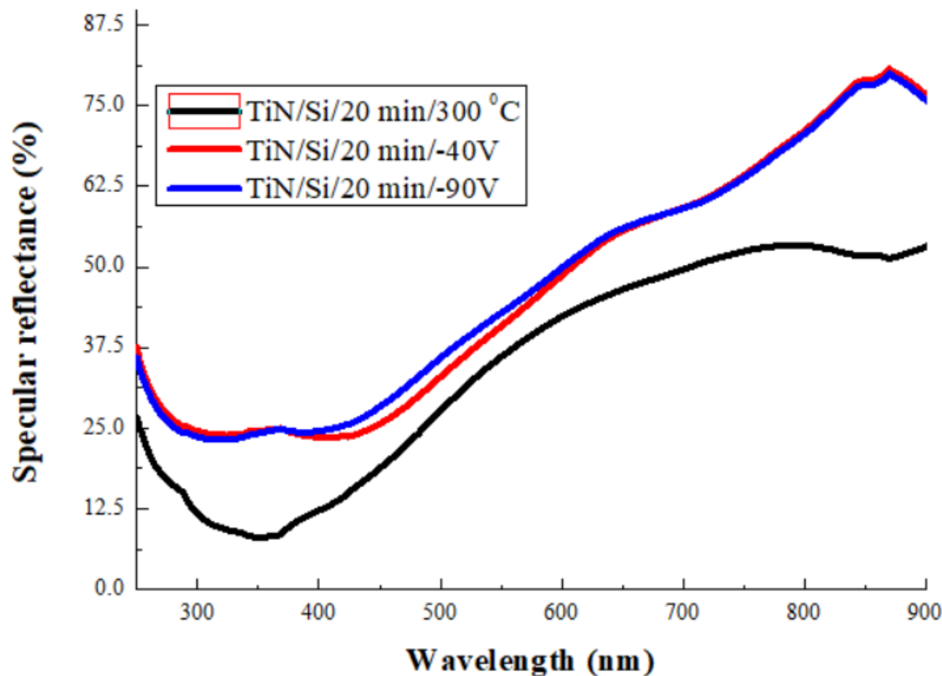

Fig. 5. Reflectance spectra of titanium nitride films deposited for 20 minutes on a silicon substrate preheated at 300 °C and deposited on a substrate at room temperature and polarized at -40 V and -90 V.

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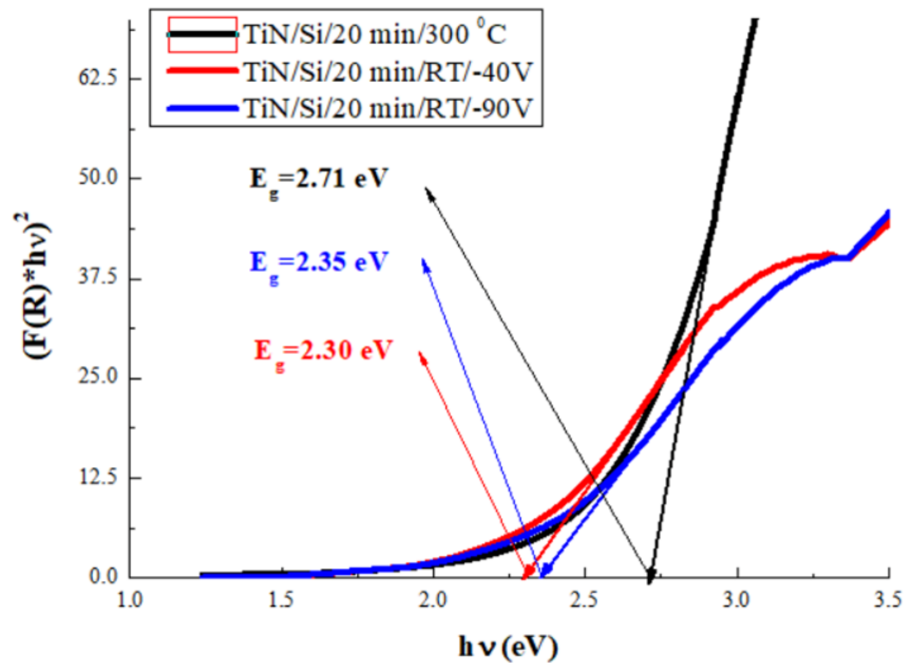

Fig. 6. Energy band gap of titanium nitride films deposited on a silicon substrate preheated at 300 °C and deposited on substrate at room temperature and a voltage bias of -40 V and -90 V.

The crystalline degree of the titanium nitride film deposited on a substrate heated at 300 °C increases compared to the titanium nitride film deposited on un-heated substrate. The energy band gap (Fig. 6) also increases due to the blue-shifting of the optical response. The latter is caused by a decrease in the crystallite size that implies band structure modifications due to cell size and by the fact that titanium nitride film deposited on a heated substrate do not present a textural orientation unlike the titanium nitride film deposited on an un-heated substrate [22]. The blue-shifting of the optical response was also observed for the films deposited at negative bias voltage. This can be also attributed to the decrease in the crystallite size.

It can be concluded that titanium nitride films exhibit semiconducting properties based on the structural and optical characterization of titanium nitride films deposited on silicon substrate at different deposition conditions. As a result, titanium nitride films may have possible applications in solar cells, optoelectronics or microelectronic-mechanical devices.

Summary

The deposition of titanium nitride films on a silicon Si (100) substrate at different deposition parameters influences the structural and optical properties of the material. Thus, when the deposition time increases from 10 to 40 minutes and the deposition is done on silicon substrates at room temperature, the textural orientation changes from (111) orientation to the (220) crystalline plane due to increase in both the energy of the bombarding particles of the titanium target and in the film thickness. Heating of the silicon substrate at 300 °C leads to an increase of crystallinity, but the titanium nitride film does not present a textural orientation. Applying a negative bias voltage to the substrate leads to the formation of titanium nitride films with small crystallite size. By optical means, titanium nitride films exhibit semiconducting properties, with a low reflectivity (between 300 nm and 500 nm), but they increase for a wavelength in the infrared region. The energy band gap of the films is also influenced by structural properties (crystallite size and textural orientation) and film thickness.

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