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Analysis on temperature effect on the mechanical and tribological properties of titanium nitride thin films

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Abstract. The main goal of this paper is to study the influence of the temperature on the mechanical and tribological characteristics of titanium nitride thin films. The titanium nitride thin films were deposited by reactive magnetron sputtering on silicon substrates using a titanium high purity target. The films were deposited in different conditions. Several films were deposited on silicon substrate at room temperature while the others were obtained after the substrate was preheated. The majority of the films were deposited on non-biased substrates while the rest were deposited on substrates to which a negative bias was applied. Once the films were deposited, the characterization was realized by atomic force microscopy investigations determining the topographical parameters as well as the mechanical properties such as the modulus of elasticity and the hardness. The mechanical properties mentioned before were determined at 20 °C, 40 °C, 60 °C, 80 °C and 100 °C in order to establish the effect of testing temperature on the mechanical characteristics. The results highlighted a significant influence of temperature on the mechanical and tribological properties of the investigated titanium nitride thin films.

1. Introduction

In the last decades, the thin films industry has recorded a strong development due to the fact that it allows the obtaining of materials characterized by superior properties for medical, spatial, aeronautical, microelectronics industries etc. Different type of nitrides coatings are often employed for manufacturing products for the industries mentioned before [1-12]. The mechanical, physical, chemical and electrical characteristics of titanium nitride set it forth a wide range of applications such as hard coatings for mechanical tools, protective coating for medical devices, and diffusion barrier in microelectronics and so on [13-16].

Over the years, the elaboration of titanium nitride thin films has been realized by different techniques such as reactive magnetron sputtering, RF (radio frequency) magnetron sputtering, laser ablation, ion-beam deposition and so on [4-6, 13-19]. The deposition parameters play an important role in obtaining thin films characterized by superior mechanical, tribological, electrical or optical behaviour. For that purpose the nature, the temperature or the biasing of the substrate, the nitrogen flow, the pressure, the distance between the target and the substrate, the deposition time require a special attention Silicon [14, 16, 17], steel [5, 18], quartz [13], titanium [19] and static bell-metal (alloy of copper and tin) [4] are reported in the scientific literature as materials used for substrates when depositing titanium nitride. The experimental investigations reported that the deposition of

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titanium nitride thin films was carried out at different temperatures between the room temperature and 600 ºC [4, 5, 13, 14, 16, 17].

The main aim of this paper is to elaborate titanium nitride thin films by reactive magnetron sputtering using different deposition parameters and to characterize them by atomic force microscopy investigations in order to emphasize the influence of testing temperature on the mechanical properties of the elaborated thin films.

2. Materials and experimental procedure

2.1. Materials

Silicon Si (100) substrates were employed for the deposition of titanium nitride thin films. A high purity (99.995 %) titanium nitride target was used for elaborating them. The atmosphere from the chamber in which the deposition was realized was formed by a mixture of argon and nitrogen.

2.2. Experimental procedure

The deposition of titanium nitride thin films was realized by direct current reactive magnetron sputtering. For a starter the silicon substrates were cleaned in an ultrasonic bath with isopropyl alcohol in order to remove any possible impurities. After that they were blown with nitrogen.

The elaboration of the thin films was realized in the chamber of a reactive sputtering facility with a Varian TV551 turbo-molecular pump under a high vacuum of 10^{-7} torr. The pressure inside the chamber was of 1 mtorr. The nitrogen flow rate was 1.2 cm^3/min while the discharge current was of 350 mA. Some substrates were negative biased voltage at -40 V or -90 V. The deposition time was 20 minutes. Three different temperatures were employed for the substrates when depositing the titanium nitride thin films in order to highlight the influence of the substrate temperature on the mechanical and tribological properties of the deposited films. Some films were deposited on substrate at room temperature, others were deposited after the substrates were previously heated at 300 ºC while the rest were elaborated on substrates preheated at 500 °C. During the deposition process, when substrates were preheated at 300 ºC and 500 ºC, the temperature of the substrates was kept constant. An increase of the temperature up to approximately 100 ºC was determined even when the films were deposited at room temperature due to the contact with the plasma. Some of the titanium nitride films were directly obtained on silicon substrates while the rest were elaborated after a titanium buffer layer was previously deposited on the silicon substrate. The thickness of the deposited films was 0.55 μm. The notation and the deposition conditions for the seven kinds of titanium nitride films are given in table 1. Three titanium nitride thin films were deposited for each deposition conditions.

Table 1. The notation and the deposition parameters of the investigated titanium nitride thin films.

Sample notation	Substrate temperature (^{0}C)	Presence/absence of a titanium buffer layer	Substrate bias voltage (V)
TiN-Tirbl_rt	20	Without Tibl*	---
TiN+Tibl_rt	20	With Tibl	---
TiN-Tibl_300	300	Without Tibl	---
TiN+Tibl_300	300	With Tibl	---
TiN-Tibl_500	500	Without Tibl	---
TiN-Tibl_rt-90	20	Without Tibl	-90
TiN-Tibl_rt-40	20	Without Tibl	-40

* Tibl stands for titanium buffer layer while the “rt” represents the room temperature

After the films were deposited, they were characterized from the mechanical and tribological point of view by atomic force microscopy analyses. The nanocharacterization of the deposited films was performed using a XE 70 atomic force microscope. The tests were carried out for a relative humidity of 31 % at a temperature of 23 ^{0}C. The topography and the tribological properties were determined using a NSC35C cantilever. The characteristics of this cantilever given by the manufacturer are: length of 130 µm, width of 35 µm, thickness of 2 µm, force constant of 5.4 N/m and resonance frequency of 150 kHz. A TD23838 nanoindentor was used for determining the mechanical properties. Its characteristics according to the manufacturer are: cantilever stiffness of 272 N/m, tip radius smaller than 25 nm, tip height of 90 µm, tip thickness of 41 µm and cantilever length of 1050 µm respectively. The XEI Image Processing Tool for SPM (Scanning Probe Microscopy) data used both the Oliver and Pharr and the Hertzian models for the interpretation of the obtained data in order to determine the hardness and the modulus of elasticity respectively. In order to study the variation of the mechanical characteristics in regards to the testing temperature, a LDT 5525B temperature controller was used.

3. Results and discussion

After the titanium nitride thin films were deposited as mentioned before, they were characterized by the tribological and mechanical point of view using an atomic force microscope. The mechanical characterization was performed when the investigated thin films were at five different temperatures namely 20, 40, 60, 80 and 100 ^{0}C respectively in order to emphasize the influence of testing temperature on the mechanical characteristics.

3.1. Topographical characterization

3D images of the films were achieved with the XE 70 atomic force microscope. After interpreting the achieved images with the XEI Image Processing Tool for SPM Data, we determined the values of the roughness parameters. Figure 1 presents an image of the software for determining the roughness characteristics of the titanium nitride thin film deposited at room temperature in the presence of titanium buffer layer (TiN+Tibl_rt).

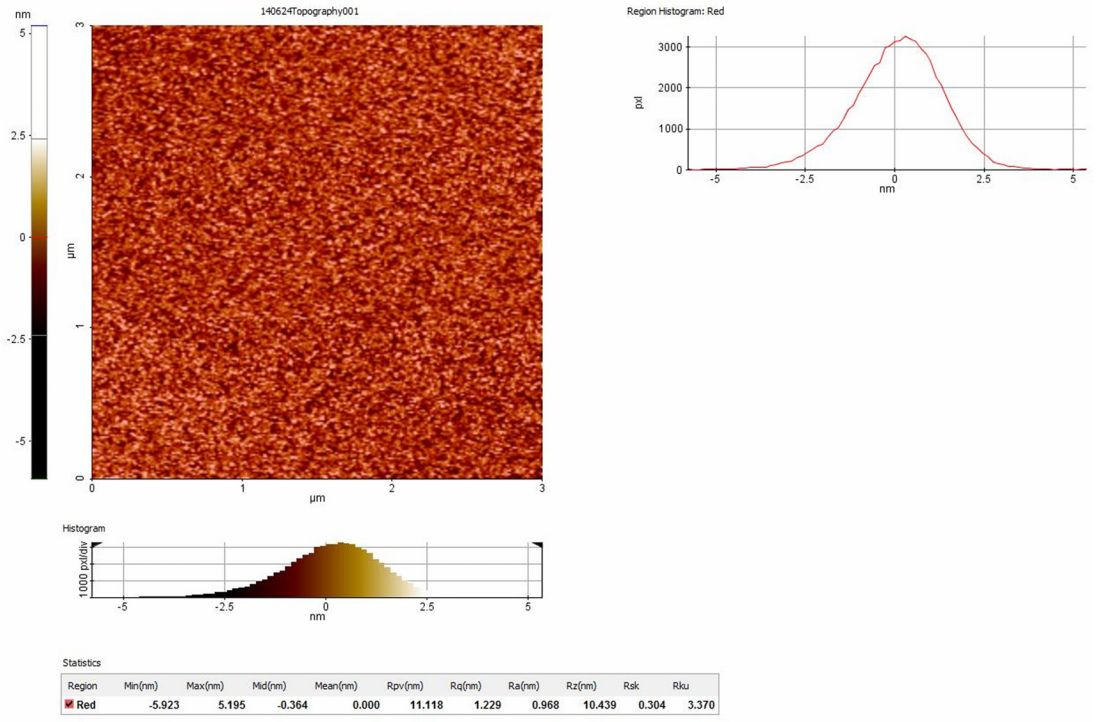


Figure 1. Image of the XEI Image Processing Tools for SPM Data for determining the roughness characteristics of the TiN+Tibl_rt thin film.

Each elaborated thin film was investigated in three different areas, the scanned surfaces being of 5 μm x5 μm. The values of the roughness parameters of interest for the seven kinds of investigated ceramic materials are given in table 2. The R_a represents the average roughness, the R_q is the room mean square, the R_{sk} is the skewness roughness (an asymmetry indicator) while R_{ku} stands for kurtosis roughness (an indicator of the shape of the distribution's tails). We can affirm that the modification of the deposition parameters causes the obtaining of more or less rough surfaces. The increase of substrate temperature leads to the decrease of the average roughness. The negative biasing of the substrate also determines the decrease of the topographical parameter, its effect being stronger than that of the substrate temperature on the same roughness parameter. The titanium nitride thin film deposited at room temperature when a negative bias of -90 V (TiN-Tbl_rt-90) is applied to the substrate is characterized by the smallest value of the average roughness (0.413 nm) while the titanium nitride thin films deposited at room temperature (TiN-Tibl_rt) shows the highest average roughness (1.206 nm).

Table 2. The roughness characterization of the deposited titanium nitride thin films.

Sample	R_a (nm)	R_q (nm)	R_{sk} (-)	R_{ku} (-)
TiN-Tibl_rt	1.206	1.401	0.052	1.843
TiN+Tibl_rt	0.968	1.229	0.304	3.370
TiN-Tibl_300	0.701	0.814	-0.003	1.931
TiN+Tibl_300	0.964	1.246	0.206	3.580
TiN-Tibl_500	0.558	0.860	-2.738	54.501
TiN-Tibl_rt-90V	0.413	0.531	-0.226	3.960
TiN-Tibl_rt-40V	1.092	1.419	-0.005	5.428

3.2. Mechanical characterization

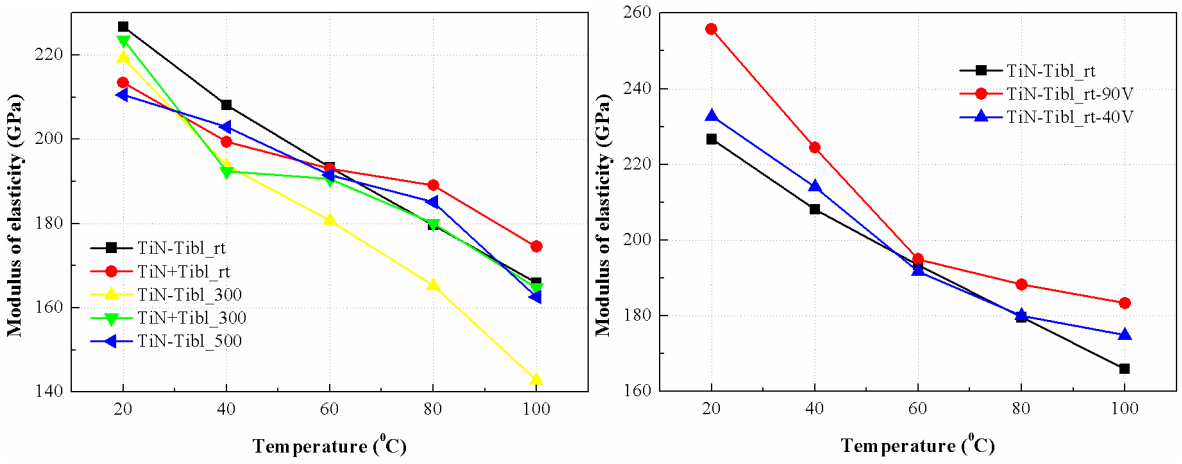
The modulus of elasticity and the hardness are the mechanical properties that were determined by atomic force microscopy investigations. Force vs. Z scan curves were obtained for each sample. The indentations were performed using a force limit of 25 μN. Four indentation tests were performed for each of the five testing temperature. The curves were interpreted with both the Oliver and Pharr method and the Hertzian method to get the values for the hardness and the modulus of elasticity respectively. The Hertzian model was employed for determining the modulus of elasticity due to the fact that this method assumes that plastic deformation doesn't occur between the tip of the indentor and the tested thin film. Figure 2 shows an image of the XEI Image Processing Tool for SPM Data for determining the modulus of elasticity of the TiN-Tibl_rt-90V thin film tested when it was heated at 100 °C. The value of this mechanical property is influenced by the tip shape and the Poisson's ratio of the thin film.

The fluctuation of modulus of elasticity dependent on the substrate temperature when testing from 20 to 100 °C is graphically given in figure 3a. The values of the mechanical parameter decreased indifferent to the deposition parameters when the testing temperature was increased from 20 up to 100 °C. The titanium nitride thin films deposited at room temperature in the presence of a titanium buffer layer (TiN+Tibl_rt) are characterized by the smallest variation of modulus of elasticity in terms of testing temperature (about 18 %) while the biggest variation is specific to the titanium nitride thin films deposited directly on the silicon substrate at 300 °C (TiN-Tibl_300). The thin films deposited on silicon substrate at room temperature show the highest modulus of elasticity (226 GPa). Instead the titanium nitride films deposited at room temperature after a titanium buffer layer was first deposited present the highest modulus of elasticity when testing at 100 °C (175 GPa). When a negative bias is applied to the substrate, an increase of the modulus elasticity is generally determined (figure 3b). A

similar trend as presented before is detachable namely this mechanical characteristic decreases when the testing temperature is increased. The highest values of the modulus elasticity when testing at 20 ^{0}C, 40^{0}C, 60^{0}C, 80^{0}C and 100^{0}C, are characteristic to the titanium nitride thin films deposited at room temperature when a negative bias of -90 V (TiN-Tibl_rt-90) is applied to the silicon substrate. However the films deposited in these conditions present a higher variation of the modulus of elasticity when increasing the testing temperature from 20 ^{0}C up to 100 ^{0}C (28 %) than the titanium nitride thin film deposited at room temperature in the presence of a titanium buffer layer (in this case the variation of the modulus of elasticity was 18 %).



Figure 2. Image of the XEI Image Processing Tools for SPM Data for determining the modulus of elasticity of the TiN-Tibl_rt-90V thin film tested at 100^{0}C.



(a) (b)

Figure 3. The fluctuation of modulus of elasticity up to 100^{0}C dependent on (a) substrate temperature and (b) substrate bias voltage.

Figure 4 presents an image of the XEI Image Processing Tool for SPM Data for determining the hardness of the TiN-Tibl_rt-90V thin film tested at a temperature of 100 ^{0}C. It can be noticed that the value of this mechanical characteristic is influenced, among other things, by the shape of the tip and the Poisson's ratio of both the investigated thin film and the tip.

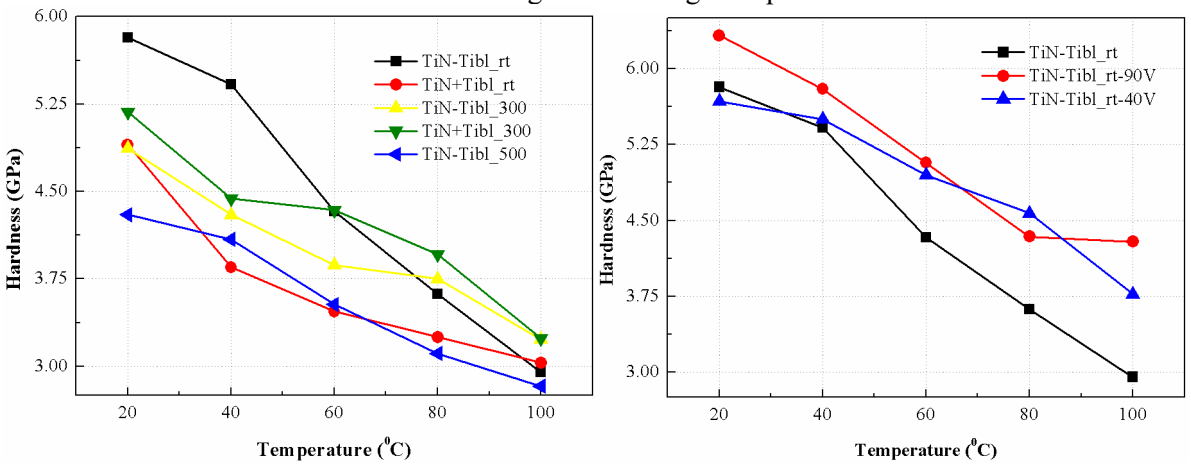


Figure 4. Image of the XEI Image Processing Tools for SPM Data for determining the hardness of the TiN-Tibl_rt-90V thin film tested at 100^{0}C.

The variation of the hardness dependent on both the substrate temperature and substrate bias voltage when testing at temperatures between 20 ^{0}C and 100 ^{0}C are given in figure 5. As expected, the increase of testing temperature up to 100 ^{0}C determines the decrease of the hardness regardless of the substrate temperature or its bias voltage. However, in some cases this decrease is much stronger. The titanium nitride thin films deposited at room temperature directly on the silicon substrate (TiN-Tibl_rt) is characterized by a decrease with almost 50 % of the hardness when the testing temperature is increased from 20 ^{0}C up to 100 ^{0}C. As regards the fluctuation of this characteristic for the samples deposited at different substrate temperatures (figure 5a), when the tests were performed at 20 ^{0}C, the first type of titanium nitride films (TiN-Tibl_rt) presented the highest value of the hardness (about 5.8 GPa) while the films deposited on substrates preheated at 500 ºC (TiN-Tibl_500) are characterized by the smallest hardness (4.3 GPa). When the tests were carried out at 100 ºC, the TiN-Tibl_500 films also showed the smallest hardness but the highest value of this mechanical property was determined for the titanium nitride thin films deposited on substrates preheated at 300 ºC with (TiN+Tibl_300) or without (TiN-Tibl_300) the presence of a titanium buffer layer. The smallest fluctuation of the hardness was pointed out on the films deposited on silicon substrates preheated at 300 ºC (TiN-Tibl_300), in this case the variation being of 33.7 %.

Regarding the variation of the hardness for the samples deposited on negative bias voltage substrates (figure 5b), the results pointed out that in general biasing the substrate causes the increase of

the hardness. The titanium nitride thin films that were deposited at room temperature when a negative bias voltage of -90 V (TiN-Tibl_rt-90V) was applied is characterized predominantly by the highest values of the hardness. This kind of films also presented the smallest fluctuation (32 %) of the mechanical characteristic when increasing the testing temperature from 20 ºC to 100 ºC.

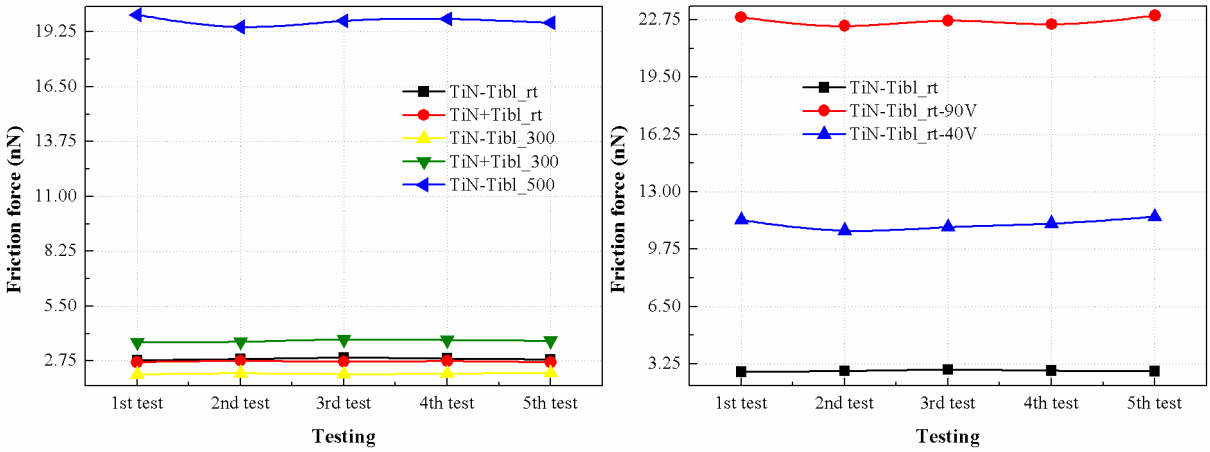


(a) (b)

Figure 5. The fluctuation of hardness up to 100 °C dependent on (a) substrate temperature and (b) substrate bias voltage.

3.3. Tribological characterization

The research also aimed at determining the friction force between the tip of the atomic force microscope and the surface of the investigated films. The fluctuation of this friction parameter as regards the substrate temperature and substrate bias voltage is graphically given in figure 6. In the case of the films deposited on substrates at different temperature without biasing (figure 6a), a significant increase of the friction force was marked out when the titanium nitride films were deposited on substrates preheated at 500 ºC (TiN-Tibl_500). In this case the values of the friction parameter increased more than seven times as compare to that obtained for the thin films deposited at room temperature or at 300 ºC.



(a) (b)

Figure 6. The fluctuation of friction force at room temperature dependent on (a) substrate temperature and (b) substrate bias voltage.

As regards the films deposited on negative biased substrates (figure 6b), it is obviously that applying a bias voltage to the substrate determines a strong increase of the friction force. This increase

is more evident when the applied bias voltage was of -90 V. The thin films deposited in these conditions (TiN-Tibl_rt-90V) is characterized by a friction force of about 23 nN which is eight times higher than the friction force of the samples deposited in the same conditions but without biasing the substrate.

4. Conclusions

Titanium nitride thin films were deposited by reactive magnetron sputtering on silicon substrate at different substrate temperatures, with or without biasing the substrate and in the presence/absence of a titanium buffer layer. The atomic force microscopy investigations marked out that the films deposited at room temperature when biasing the substrate at -90 V are characterized by the smallest average roughness. Regarding the mechanical characteristics, the applying of a negative bias voltage to the substrate causes an increase of both modulus of elasticity and hardness. The two mechanical properties vary when the testing temperature is increased in the sense that their values decrease when increasing the testing temperature. As regards the tribological characteristics, the films obtained on negative bias voltage substrates also present the highest friction force. Future research will aim at characterizing and improving the mechanical, optical and/or tribological properties of titanium nitride films in order to use them when manufacturing components for MEMS applications.

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