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Influence of Nitrogen Content on the Structural and Mechanical Properties of TiN Thin Films

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Titanium nitride coatings have been used very successfully in a variety of applications because of their excellent properties, such as hard and decorative coatings and also diffuse barriers in semiconductor technology. These coatings are of interest because they exhibit a number of properties similar to metals (such as goods electrical conductivity) while retaining characteristics (covalent bonds, hardness and melting point) found in insulating materials. In this work, TiN films have been deposited by RF reactive magnetron sputtering (13.56 MHz) from a titanium metallic target at different nitrogen partial pressures (4mTorr to 10mTorr).

We've been studied the effect of the sputtering pressure and nitrogen partial pressure on the properties of titanium nitride films prepared by RF reactive magnetron sputtering. The deposited films were characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) , micro-indentation and Fourier transform infrared spectrum (FTIR).

Keywords: TiN- Coating- Sputtering-Magnetron-

1. Introduction

Titanium nitride is a well-known material, which shows excellent mechanical properties (high hardness and high wear resistance), low electrical resistivity, high chemical and thermal stability, and interesting optical properties (colors varying from gold to dark brown), have been applied in areas such as abrasion resistant coatings on tool steels, decorative coatings in architecture, diffusion barrier layers in semiconductor devices and flat panel displays [1-3].

The structure and properties of TiN have been studied in detail by several researchers [4-6]. These coatings have been prepared by different techniques and sputtering is one of the most successful techniques, but mainly focusing on DC magnetron sputtering [7-9]. The deposition of TiN films by sputtering has important specific advantages such as low levels of impurities and easy control of deposition rate. This method also enables the production of thin films of various morphology and crystallographic structure.

In spite of this successful application of TiN as hard coating, the understanding of how the hardness is influenced by the composition, structure, adhesion and the substrate bias is not very well known.

In our previous work [10,11], a magnetron sputtering has been used to deposit Ti/TiN multilayer at ambient temperature and low pressure. The mechanical properties were found to depend on the roughness of the Ti interlayer. The application of a sufficient negative bias voltage Vb on the substrates during reactive RF magnetron sputtering of titanium greatly improves the hardness of the films and the nature of the coating. We also found that the application of substrate bias removes the oxygen and the carbon impurities and form stoichiometric TiN

The electrical and optical properties of TiN have been studied in another of our previous work[12], we demonstrate the strong influence of the deposition time of TiN on the *I-V* behavior. As the TiN thickness increases, the series resistance increases. We found also the value of the refractive index of the TiN layers varied between 1.04 and 1.09, values close to that of air. The value of the extinction coefficient *K* indicates that the TiN layers are transparent in the near-infrared region.

In this work, the attention was given to the study of the structure, the composition of titanium nitride deposits, which have a considerable influence on their hardness. The deposited coatings were characterized by energy dispersive spectroscopy (EDS) and observed by means of atomic force microscopy (AFM), X-ray diffraction (XRD), micro-indentation and Fourier transform infrared spectrum (FTIR).

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2. Experimental Details

The TiN thin films were deposited by R.F.(13,56MHz) reactive planar magnetron sputtering from a high purity Ti (99,999%) target onto Si (100). The reactive radiofrequency magnetron sputtering system "home made reactor" used in this experiment consists mainly of three sections as shown in Fig.1: deposition chamber, pumping device and RF power supply with a matching network.

The deposition chamber consists of a cylindrical stainless steel reactor of 230mm diameter and 250mm high. In the chamber, all substrates are mounted at the midpoint of a circle planetary substrate holder (diameter 100mm). The distance between the target Ti and the substrate holder is about 30mm. The pressure control device consists of a penning and a baratron gauges. The gases used are high-purity argon (99,99990%) as the working gas and nitrogen (99,99990%) as the reactive gas. Before introducing the gases into the chamber, the reactor is pumped down to 10^{-6} mbar using secondary diffusion pump. After cleaned pumping, the gas mixture is introduced in a constant flow rate.

The deposition time was adjusted based on previous deposition rate data [10, 11]in order to deposit films with maximum thickness of 250-350nm.

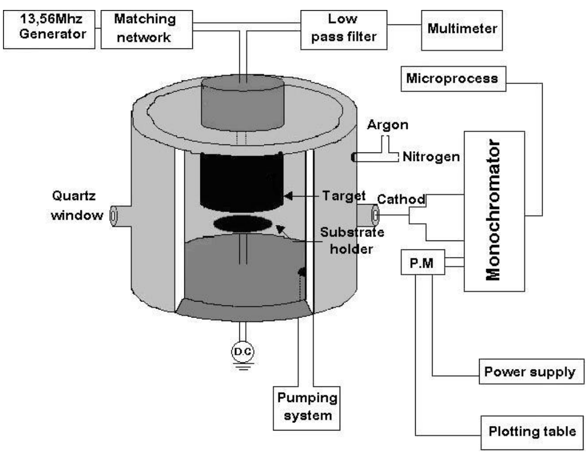

Fig. 1 Experimental set up

3. Results & Discussion

The first step of our study was the optimisation of the deposition conditions in order to obtain good quality layers and good adhesion. TiN monolithic films deposited directly onto the substrate under the same sputtering conditions peeled off partly. Therefore, it was found that the multi-layered thin films were more adhesive to the alloy than the monolithic films [13]. It is believed that Ti interlayer have played important role during the growing of the outer layer grains, in fact the titanium grains serve as nuclei. So the adhesion of the layers depends on the roughness of these interlayers. We have analyzed the influence of the substrate bias voltage on the deposition of Ti films [10]. Indeed, the roughness of Ti films depends on substrate bias voltage. When reaching a high substrate bias voltage, the adhesion of the film seems poor. However, substrate bias voltage corresponding to -25 and -50V give more adherent films. So for our experiment the first layers of titanium films have been grown under fixed parameters (Power: 100W, Deposition time: 20mn, Argon pressure: 1Pa, Substrate bias voltage: -25V).

Secondly for the optimization of the color of the TiN films , we have analyzed the influence of the substrate bias voltage on the color and the composition of our deposits layers. It was clear that the color depends on the substrate bias voltage[11]. In fact, for a substrate bias voltage $|Vb|>50V$, oxygen and carbon impurities were not detectable and the film had an attractive golden yellow colour . But when $|Vb|\leq 50V$ the film contains carbon and oxygen as impurities, which cause the color of the film to be brown. .Other investigations have pointed out the presence of oxygen in TiN films prepared by DC or RF sputtering [14,15]. The oxygen and carbon impurities in the TiN film were effectively removed by applying substrate bias voltage. When applying the substrate bias of -50V, the oxygen and carbon impurities were nearly completely removed from the TiN film and the film revealed golden yellow color, the characteristic TiN color. This result indicates that the oxygen and the carbon impurities are relatively weakly bonded on the growing film surface and they are readily removed by the bombardment of high energy ions and neutrals [16-18]. For deposition of TiN films, the deposition parameters were kept constant except the bias voltage and the N_2 partial pressures. The main deposition parameters were showed on Table 1.

TABLE 1. Deposition parameters

Power	Total Pressure	Deposition time
400 Watt	0,5 Pa	60min

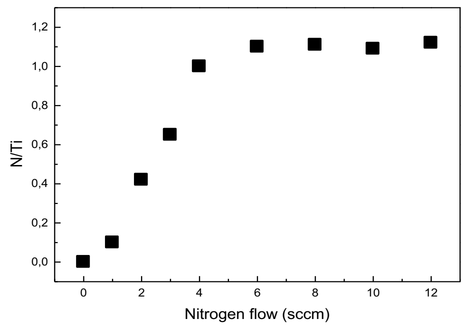

Fig. 2: The variation of N/Ti ratio of TiN films with nitrogen flow

The results show that the deposition rate decreased with increasing N_2 partial pressure. This decrease is due to the difference in the sputtering yield caused by the nitriding of Ti to TiN on the Ti target surface.

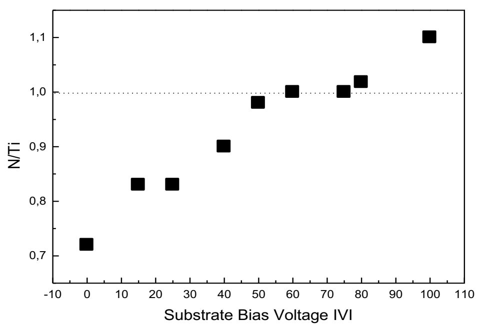

Fig. 3 The variation of N/Ti ratio of TiN:films with substrate bias (N_2/Ar= 4/20, 400W,60min)

Figure 2 represents the dependence of the stoichiometry (N/Ti ratio) of TiN films on nitrogen flow. The N/Ti ratio increase with increasing the nitrogen flow. First slowly from 0 to 0,1, and leads to steeper increase of the nitrogen content up to 1 (50at.%) , for the 4sccm , which corresponds to the stoichiometric composition. For higher flows (> 4sccm), the nitrogen content rises only slightly.

The N/Ti stoichiometry ratio in the TiN film with the substrate bias voltage is represented on Fig 3. It's clearly shown for the substrate bias <-50V, the N/Ti ratio is found to be less than 1, it's due to the presence of oxygen and carbon. The N/Ti ration is approximatively 1 for the high bias substrate voltage till 80V; it's due to the removal impurities.

Figure 4 shows the FTIR spectra of these two samples 1 and 2 (under respectively 4mTorr and 10mTorr). They are similar. The sharp absorption peak near 480cm^{-1} is assigned to vibration level of Ti-N bond [18], while the absorption peak near 1060cm^{-1} is assigned to vibration level of Si-O bond. With increase of nitrogen gas flow rate, the absorption peak near 480cm^{-1}becomes stronger, which denotes more Ti-N bond in the films. The same results was also observed by L.I.Wei [20]

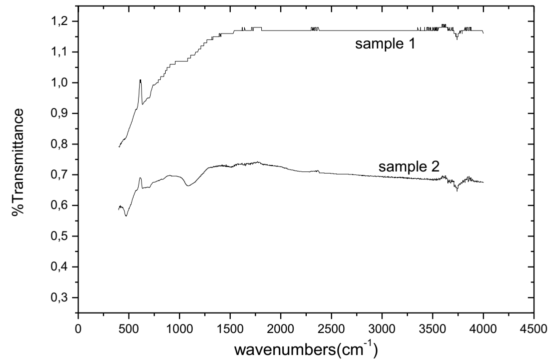

Fig. 4 The FTIR spectra of sample 1 (4mTorr) and 2 (10mTorr) at 400W and 60Min

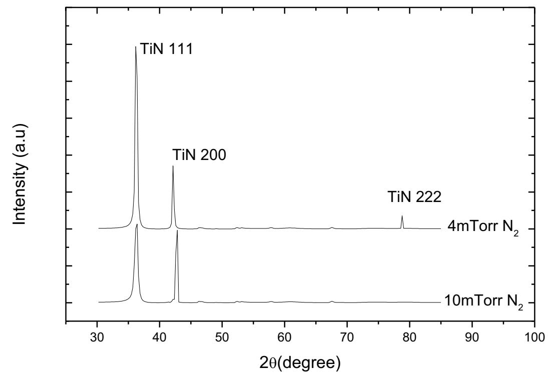

Fig. 5: Effect of N_2 partial pressure on the texture of films deposited by RF magnetron sputtering (400W,60min)

XRD patterns of the coating in thin film mode (off-set angle= 2°) were recorded in D8 Advanced Brucker. The X-ray source was a Cu-Kα radiation.

Figure 5 shows textures investigated with XRD, of two samples of TiN films deposited under various N_2 partial pressures. Both films show the same structure, TiN with a rocksalt faced-centred cubic crystal structure, for an increase in nitrogen partial pressure, the preferred orientation of the film changed from TiN (111) to TiN (200). The same trend was also reported by T.Q.Li & all [21].

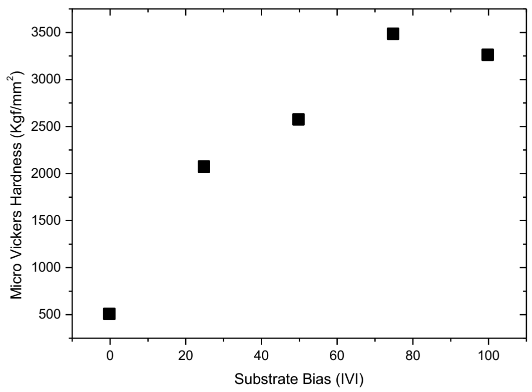

Fig. 6 Variation of the microhardness with the substrate bias (400W, 60min)

Figure 6 shows the variation of the microhardness with the substrate bias. The measured hardness is increased with the increasing of the substrate bias then shows the maximum value from – 75V. The measured hardness at zero bias voltage is thought to be low due to the columnar structure which is not dense, so the inclusion of oxygen and carbon impurities as demonstrates in previous work [10,11].

With increasing nitrogen content the films become harder, where the hardness value varies from approximatively 500 Kgf/mm^2 for pure titanium, up to 3200 Kgf/mm^2 for an optimal nitrogen content of 40at. % (Fig. 7).

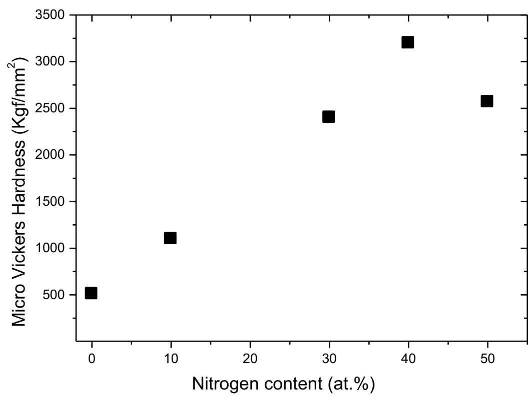

Fig. 7: Variation of microhardness as a function of the nitrogen content (400W, 60min)

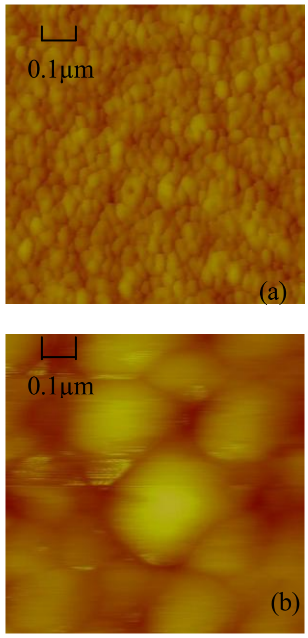

Fig. 8: AFM Topography of TiN thin film of two samples: sample (a) at -60V and sample (b)at -20V.

The surface profile is expected to give an indication on the growth and morphology of the columns and to provide trends on the mechanical strength of coatings. An example of the topography recorded for TiN is illustrated in Fig. 8. In general, the plan view topography consists essentially of hemispherical, rounded hillock units. These units seem to correspond to the columns growing. The average grain size is about 40 nm and 100 nm respectively for the substrate bias Vb=-60 V(a) and Vb= - 20V(b). The hardness of the sample is about 3464kg/mm^2 and 1985kg/mm^2 .

Films deposited at -60V exhibited high hardness probably due to denser structure and grain refinement produced under the enhanced plasma bombardment.

The hardness increase and the surface roughness decreases with an increase in the substrate bias. The increase in the hardness of the coatings is attributed to a decrease in crystallite size [22]

4. Summary

In this work, the TiN films have been deposited onto silicon (100) by reactive RF magnetron sputtering at ambient temperature and low pressure. The effect of the nitrogen content and substrate bias on the composition and the structure of TiN films have been studied.

The application of substrate bias effectively removes the oxygen and the carbon impurities and form stoichiometric TiN. The films show a columnar structure, but in the case of high substrate bias smoother and denser film is produced.

The increase of nitrogen content changes the preferred orientation of the films and their hardness.

5.References

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