Oxidation behavior of titanium nitride films

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The oxidation behavior of titanium nitride (TiN) films has been investigated by using x-ray diffraction, Raman scattering spectroscopy, and field emission scanning electron microscopy. TiN films were deposited onto Si substrates by using cathodic arc plasma deposition technique. After that, the films were annealed in the air at 500–800 °C for 2 h. The x-ray diffraction spectra showed that rutile–TiO₂ appeared above 600 °C. The relative intensity of TiO₂ rapidly increased with temperatures. Only rutile–TiO₂ was detected above 700 °C. Raman scattering spectra indicated the presence of rutile–TiO₂ signals above 500 °C. Meanwhile an additional Si peak appeared at 700 °C in Raman spectra, above which only Si peak appeared. Many nano pores were found on the surface of films annealed at temperatures between 600 and 700 °C in field emission scanning electron microscopy, while the granular structure existed at 800 °C. The as-deposited TiN films had an apparent columnar structure. The thin and dense oxide overlayer appeared at 500 °C, and thicker oxide layer existed above 600 °C. The elongated grain structure with many voids existed in the film at 800 °C. These pores–voids might result from the nitrogen release during the oxidation of the nitride. The oxide layer obviously grows inward indicating the oxidation of TiN films belongs to an inward oxidation. The pre-exponential factor and the activation energy of the oxidation were evaluated by Arrhenius-type relation. These values were $2.2 \times 10^{-6}$ cm²/s and $110 \pm 10$ kJ/mol, which are consistent with those reports in the literature. © 2005 American Vacuum Society.

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I. INTRODUCTION

Titanium nitride (TiN) films, one of the most popular transition–metal nitrides, have become universally accepted coatings due to their high melting points (2950 °C),¹ extreme hardness (2000 kgf mm⁻²),¹ high chemical stability, low electrical resistivity (10–10⁴ μΩ cm),¹ and golden color. The most applications of the films are protective coatings on steels, diffusion barriers in integrated circuit industry, and decorative coatings. The films are frequently subjected to extreme tribological conditions such as highly-applied pressure, high temperatures, and corrosive environments. Therefore, it is important to study the oxidation behavior of the films.

The oxidation of TiN films has been studied by using the thermogravimetric method,² Auger depth profiling,³ and ellipsometry techniques.⁴ The disadvantages of these techniques are that the equipment is quite expensive and lacks of direct proof of the oxide morphology. In their investigations, the oxidation kinetics of TiN films follows parabolic growth dependence.²–⁵ The activation energies deduced from the Arrhenius-type equation are 115.¹ 122.² 136.³ kJ/mol in air, and 155.¹ 203.⁶ and 198.⁷ kJ/mol in oxygen.

So far the morphology of the oxidation of TiN films has not been reported. Therefore, this paper focuses on the investigation of oxidation of TiN films by looking into morphological changes using the field-emission scanning electron microscopy (FESEM). The crystal structure is examined by x-ray diffraction and Raman scattering technique. The oxide growth mode is discussed by analyzing the above obtained results.

II. EXPERIMENTAL DETAILS

A. Deposition of TiN films

The substrates used for this study were p-type (100) Si wafers with a thickness of 725 μm. The TiN films were directly deposited onto the substrates by cathodic arc plasma deposition with an industrial Multi-Arc (now, IonBond) physical vapor deposition system. Prior to deposition, the chamber was pumped down to a base pressure of $6.7 \times 10^{-3}$ Pa. The bias and the current of the substrate were held at −150 V and 2.0 A with a target current of 60 A under $p_{N_2}$ of 3 Pa during deposition. The deposition time was 30 min with the corresponding thickness of the films ~1 μm.

After deposition, the specimens were annealed in flowing air in a gas-tight tube furnace equipped with an oxygen sensor (15% CaO-doped ZrO₂) that was used to monitor partial oxygen pressure, and the flow rate was controlled at 200 sccm using a Unit 8100 mass flow controller. The tempera-
tures were monitored by S-type thermocouples and the temperatures were varied from 500 to 800 °C while the soaking time was held at 2 h throughout this work.

B. Characterization

Changes in the crystal structure of the TiN films after annealing were investigated by x-ray diffraction (Mac-Science MXP3, \( \lambda_{Cu} = 0.154 \) nm) operating at 40 kV and 30 mA. The collection interval and scanning rate were 0.02° (\( \theta/2\theta \) mode) and 5°/min, respectively. The relative integrated intensity of oxide was defined as \( I_{TiO_2}/(I_{TiN} + I_{TiO_2}) \), where the I represents the integrated intensity of the diffraction peak, which was evaluated from the XRD spectra by using their strongest peak. Micro-Raman scattering experiments were performed using a DILOR XY800 spectrometer with a spectral resolution of 0.6 cm\(^{-1} \) at room temperature in air. An argon-ion laser with the wavelength of 514.5 nm and the diameter of 1 \( \mu m \) was used for excitation and the incident laser power was 8 mW. The spectra were recorded over the wavenumber range from 78 to 718 cm\(^{-1} \) with the integrated time of 600 s, and the spectra then determined their peak position. The calibration of the whole spectra was done by using a He–Ne laser excitation line. A JEOL JSM-6700F FESEM operated at 1.5 kV and 10 \( \mu A \) was used to investigate the morphology changes.

III. RESULTS AND DISCUSSION

A. X-ray diffraction analysis

Figure 1 shows XRD spectra of TiN films on (100) Si substrates as a function of annealing temperatures. As shown in the figure, as-deposited TiN films exhibited a mixed structure with a (111) preferred orientation (JCPDS 38-1420), which is consistent with our previous report on copper substrates. The TiN peak sustained at 500 °C, but the TiN (111) peak splitted into two peaks at 600 °C. An additional rutile–TiO\(_2\) peak (JCPDS 21-1276) appeared at a lower diffraction angle. There are some other small rutile–TiO\(_2\) diffraction peaks at 600 °C. Only the rutile–TiO\(_2\) phase was detected above 700 °C. It is worth noting that the additional small peak appearing at \( \sim 33° \) was attributed to silicon. The relative integrated intensity of rutile–TiO\(_2\), estimated by counting the strongest diffraction peak of TiN-(111) and of TiO\(_2\)-(101) is displayed in Fig. 1(b). The rutile–TiO\(_2\) was formed at 600 °C, and the relative integrated intensity increased dramatically and reached 100% above 700 °C. This result indicates that oxidation occurs at 600 °C with formation of a nonprotective oxide layer.

B. Raman scattering spectroscopy analysis

The surface chemical state was further acquired by the micro-Raman scattering method. Figure 2 represents the Raman shift (cm\(^{-1} \)) as a function of annealing temperatures. The (100) silicon peak showing up at 520 cm\(^{-1} \) is consistent
with the literature data. No signal could be detected for as-deposited TiN films. Nevertheless, three broad peaks were found at 200, 450, and 600 cm\(^{-1}\) over 500–700 °C, which are attributed to the rutile–TiO\(_2\) phase. An additional narrow peak at 520 cm\(^{-1}\) above 700 °C was due to the Si substrate. At 800 °C, all rutile–TiO\(_2\) signals vanished, and (100) silicon signal showed up instead. The micro-Raman scattering spectra indicate that the rutile–TiO\(_2\) layer is formed above 500 °C, and becomes thicker at higher temperature. The silicon peak showing up above 700 °C remains to be explored. The Raman spectra suggested that the silicon gradually diffused out and reached the surface of the films above 700 °C.

C. Field emission scanning electron microscopy analysis

Figure 3 represents the plan-view micrographs of TiN films annealed over 500–800 °C for 2 h in air. A very smooth surface was found over as-deposited TiN films. The value of root-mean-square roughness was 1.0 nm examined by atomic force microscopy (SEIKO SPA 400, tapping mode). There was no significant change at 500 °C. Nevertheless, the nanopores were observed on the film surface at 600 and 700 °C. When the annealing temperature reached 800 °C, a granular structure was found. To further explore the detail information of the oxide, a cross-sectional view of the films was also provided.

Figure 4 displays the cross-sectional micrographs of TiN films as a function of annealing temperatures. The as-deposited TiN possessed an obvious columnar structure with a thickness of 1 μm. A very thin and dense oxide layer formed at 500 °C with a thickness of 80 nm on the top of nitride. Furthermore, the thicker and porous oxide layer with a thickness of 500 nm existed at 600 and 700 °C, meanwhile the thickness of the nitride film was gradually reduced. The nitride film was almost consumed at 800 °C. From the above results, it is clearly seen that the oxide growth was inward; i.e., inward oxidation. Moreover, the voids over the films may result from the nitrogen release during the oxidation. The grain boundaries provide the shortcut diffusion path for oxidation. The oxygen penetrates in the films and further reacts with the nitride to form the oxide.

D. Activation energy of oxidation of TiN films

As mentioned earlier, a grain boundary diffusion process controls the oxidation of TiN films at high oxygen atmosphere, and high temperature. The parabolic rate constant \(k_p(T)\) at the given temperature and oxidation time was roughly deduced from the oxide thickness using the relation:\(^2\)
Hence the $k_p(T)$-value was evaluated from the $d_{OX}$ at a specific temperature for 2 h. Furthermore, the activation energy was evaluated from the Arrhenius-type equation,

$$k_p(T) = k_{p0} \exp \left( \frac{-Q}{RT} \right),$$

where $k_{p0}$ is the pre-exponential factor, $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. Figure 5 represents the logarithm value of $k_p(T)$ as a function of the reciprocal absolute temperature for TiN films in present study together with the literature data in air for the different temperature range. From the linear-regression, the pre-exponential factor ($k_{p0}$) and the activation energy ($Q$) could be estimated as $2.2 \times 10^{-6} \text{ cm}^2/\text{s}$ and $110 \pm 10 \text{ kJ/mol}$ in this work. The value is comparable to the literature evaluating from the figure. Nevertheless, the pre-exponential factor is slightly smaller than that of Ichimura and Kawana, but is consistent with that of Tompkins$^4$ and Hones et al.$^5$ Additionally, the activation energy of the Ti and O diffusion in TiO$_2$ has the similar value, i.e., $257 \text{ kJ/mol}$ for titanium and $251 \text{ kJ/mol}$ for oxygen, respectively, but the value obtained in this work is about half of this value, which may relate to the present films microstructures. It is well documented that the microstructure of the films can influence the rate constant and the activation energy,$^{2,3,5}$ e.g., the columnar structure has the higher rate constant than that of granular structure. From the FESEM observations, the low rate constant and activation energy compared to the bulk diffusion data is attributed to the grain boundaries, since the oxygen diffuses along the grain boundary (shortcut path), which is easier than that dense structure, and further reacts with the nitride to form an oxide.

**IV. CONCLUSIONS**

The oxidation behavior of titanium nitride (TiN) films is investigated by using x-ray diffraction, Raman scattering spectroscopy, and field emission scanning electron microscopy. The rutile–TiO$_2$ appeared above 600 °C in the XRD spectra, in which the relative intensity of TiO$_2$ rapidly increased with temperatures and the surface completely converted to TiO$_2$ above 700 °C. The Raman spectra indicated that the rutile–TiO$_2$ showed up above 500 °C. Nevertheless, the additional Si signals appeared above 700 °C, and at 800 °C only the Si signals existed. A pronounced columnar structure existed in the as-deposited TiN film. A very thin and dense TiO$_2$ formed on the nitride at 500 °C, becoming porous with many voids and an elongated grain structure with increasing temperatures. It is suggested that the TiO$_2$ formation might have resulted nitrogen to release during annealing. The Si has been shown along the grain boundaries of the TiN and TiO$_2$ layer, and reaches the surface for annealing temperatures above 700 °C. From these results, the oxide layer can grow inwardly with increasing temperatures. The pre-exponential factor and activation energy were determined by using the Arrhenius-type relation assuming that oxidation of TiN is a diffusion-controlled process, and the values are $2.2 \times 10^{-6} \text{ cm}^2/\text{s}$ and $110 \pm 10 \text{ kJ/mol}$, respectively, which is consistent with values reported in the literature.

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