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Influence of residual stress on mechanical properties of TiAlN thin films

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ABSTRACT

Mechanical properties of TiAlN thin films with different residual stress, which were fabricated with magnetic filtered vacuum arc evaporation deposition method on silicon substrate, have been investigated. The mechanical properties of TiAlN thin films vary with the residual stress existed in TiAlN thin film. For a lower residual stress, the nanoindentation hardness (H) and modulus (Er) of TiAlN thin film are 18.96 and 210.16 GPa respectively. With the increasing of the residual stress, the H and Er of TiAlN thin film decline from 18.96 and 210.16 GPa to 16.9 and 185.9 GPa respectively. High residual stress induces the decreasing of the H and Er of TiAlN thin film. The empirical expressions of H and Er versus the mean residual compressive stress (σ) have been obtained for the TiAlN thin films.

1. Introduction

Titanium aluminum nitride (TiAlN) exhibits extreme hardness, high melting point, chemical inertness and good thermo-dynamical stability. For these reasons, TiAlN thin films are usually used as thermal barrier, contact materials in microelectronics, catalytic and decoration of surface, wear protections and fuel cell interconnect. Owing to their applications, investigations on TiAlN thin film have been carried out in the fields of fabrication, mechanical, physical and chemical properties of TiAlN thin film [1–7].

The residual stress existed in thin films directly affects the mechanical properties of thin films, such as hardness, elastic modulus and adhesive strength between film and substrate. In the recent years, extensive efforts are carried out to understand the interdependence between the residual stress in the film and substrate or deposition parameters because of the influence of residual stress on their applications [8,9]. Falub C. V. has reported the results of the fiber texture dependence of the anisotropic residual stress state induced by distortion in arc-evaporated TiAlN thin films [10]. Zhao S. S. has analyzed the depth distribution of residual stress in TiAlN thin film [11]. M. Ahlgren et al. show the influence of bias variation on residual stress and texture in TiAlN PVD coatings [12]. Other investigation results on the effect of the residual stress that existed in hard films have been reported [13], and most of the efforts are in order to obtain a TiAlN thin film with lower residual stress. Until now, only few investigations on the influence of the residual stress on mechanical properties of TiAlN thin films have been reported [14,15].

In the present study, mechanical properties of TiAlN thin films with different residual stress have been investigated. The empirical formulas of H and Er versus the mean residual compressive stress (σ) and the influence mechanism have been discussed.

2. Experimental details

TiAlN thin films with a thickness of about 600 nm were synthesized by the magnetic filtered vacuum arc evaporation deposition with a N_2 flux of 8 sccm. The base pressure of chamber was lower than 5×10^{-4} Pa. Substrate was (100) polished silicon wafer with a thickness of 545 μm. Titanium–aluminum alloy (Ti-47.5Al-2.5V-1Cr) was used as cathode material for the fabrication of TiAlN thin film. Before film deposition, Si substrates were cleaned by ion sputtering under negative bias of 3 kV for 5 min. Residual stress of TiAlN thin film was controlled by the thickness of gradual layer introduced into the interface between TiAlN thin film and Si substrate. The thickness of gradual layer varied from 0 nm to 300 nm which were controlled by the deposition time. The flux of N_2 increased step by step gradually from 0 to 8 sccm during the deposition of gradual layer, in which twenty steps were used to prepare the gradual layer and the increment of nitrogen flow rate for each step was about 0.4 sccm. The content of TiAlN phase in gradual layer was varied step by step from 0 to 100% with twenty steps, and gradual layer was composed of TiAl and TiAlN phases. Finally, TiAlN thin film with a thickness about 600 nm was fabricated with a N_2 flux of 8 sccm on the surface of gradual layer.

The microstructure and phase structure of TiAlN thin film were determined by the use of Scanning Electron Microscope (SEM, Hitachi S-4800) and X-ray Diffractometer (Rigaku, D/Max-2400). The H and Er were determined by the use of MML Nano Test equipment with a load resolution of 30 nN, in which the indentor penetration depth was about 100 nm more or less than the thickness of TiAlN thin film (600 nm). At that time, influence of silicon substrate on the H and Er of TiAlN thin film was very small because the indentor penetration

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depth was less than one of the six film thicknesses (including TiAlN thin film and gradual layer). The residual stress of film was measured using the substrate curvature technique in which the curvature was measured by laser beam deflection apparatus. The average stress σ in the TiAlN films was determined by means of Stoney's formula [16]:

$$\sigma = \frac{E_s h_s^2}{6(1-\nu_s)h}\left(\frac{1}{R}-\frac{1}{R_i}\right) \tag{1}$$

where the subscript S refers to the substrate, E (131 GPa for silicon) and ν_s (0.28 for silicon) are Young's modulus and Poisson's ratio of silicon substrate, respectively, h and h_S are thicknesses of coating and substrate, respectively and R and Ri are the substrate curvature radii of the original Si wafer and the coated Si wafer.

3. Results and discussion

Fig. 1(a) shows a microstructure SEM image of the TiAlN thin films fabricated on (100) silicon substrate with magnetic filtered vacuum arc evaporation deposition method. Fig. 1(b) is a XRD spectrum of the TiAlN thin films on Si substrates, inset shows the part of the diffraction spectrum in the range from 59 to 64°. From Fig. 1, it can be seen that the TiAlN thin film is composed of columnar crystal grains in which the mean diameter of the grain is about 100 nm. There are four peaks to be observed in the XRD spectrum (seen Fig. 1(b)), and the intensity of peak located at 61.8° is composed of the diffraction pattern of TiAlN-220 and amorphous structure in gradual layer (seen inset in Fig. 1(b)). Comparing the intensity of peaks, the intensity of diffraction pattern of TiAlN-111 is far higher than that of the diffraction pattern of TiAlN-220. According to columnar crystal grains observed in the TiAlN thin film and XRD spectrum, the main orientation of the columnar crystal grain is [111]. The thickness of the TiAlN thin film is about 600 nm. The thickness of gradual layer is about 100 nm. These results are accordant with the designed data.

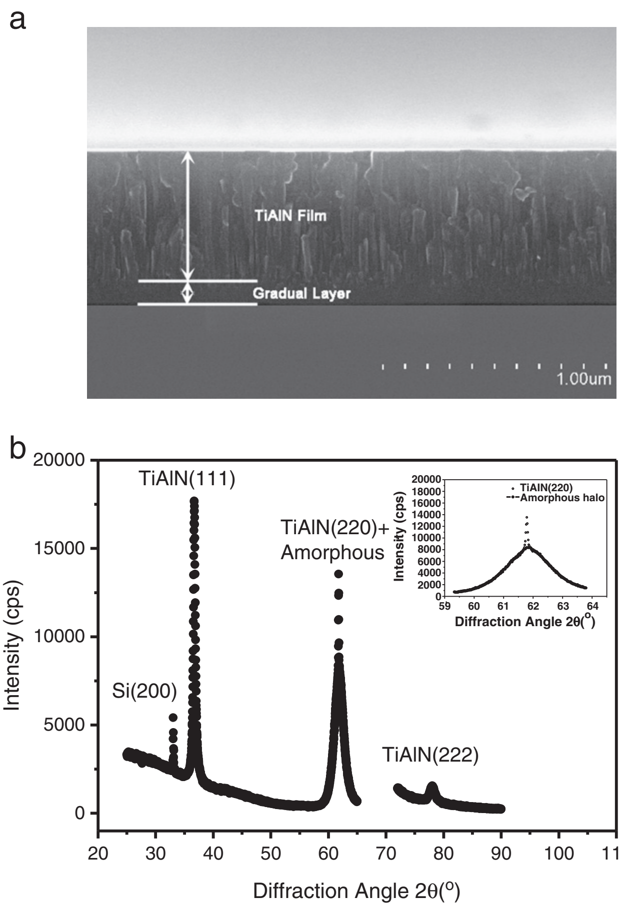

Fig. 1. (a)Cross-section SEM image of the TiAlN thin film with a gradual layer thickness of 100 nm; (b) XRD spectrum of the TiAlN thin film, inset in Figure 1 (b) is part of the diffraction spectrum in the range from 59 to 64°.

Fig. 2 gives results of the H and Er of the TiAlN thin films versus the thickness of the gradual layer. With the increasing of the gradual layer thickness, the H varies from 15.86 GPa to 18.96 GPa, and the Er varies from 185.93 GPa to 210.16 GPa. The maximum H and maximum Er are 18.96 GPa and 210.16 GPa respectively for the gradual layer thickness of 300 nm. It is indicated that the thickness of the gradual layer introduced into the interfaces between the TiAlN thin film and Si substrate affects the hardness H and modulus Er of the films.

For ceramic film/substrate pairs, there is usually a residual stress existed in the ceramic film due to the difference of their structures, thermal expansion coefficients and mechanical properties. The gradual layer introduced into the interface between ceramic film and substrate is an efficient approach for the reducing residual stress of ceramic film. Fig. 3 shows a variation of the residual stress of the TiAlN thin film on the thickness of gradual layer. For the TiAlN thin film/Si substrate pair, the residual stress is high as −1.58 GPa due to un-existence of the gradual layer, and is a compressive stress. With the increasing of the gradual layer thickness, the residual stress

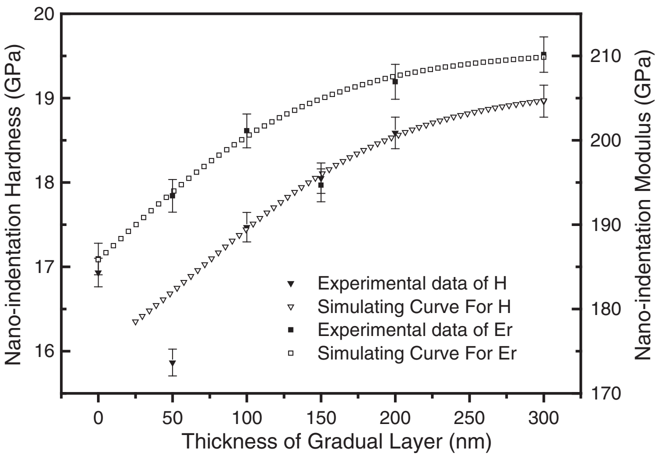

Fig. 2. Variations of the nanoindentation hardness (H) and modulus (Er) versus the residual stress of the TiAlN thin film.

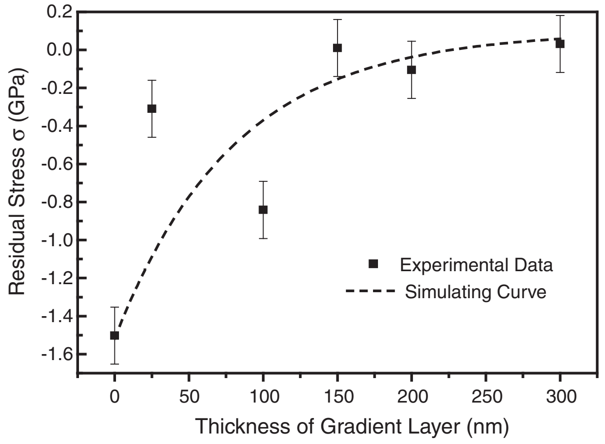

Fig. 3. Residual stress of the TiAlN thin film varied with the thickness of the gradual layer.

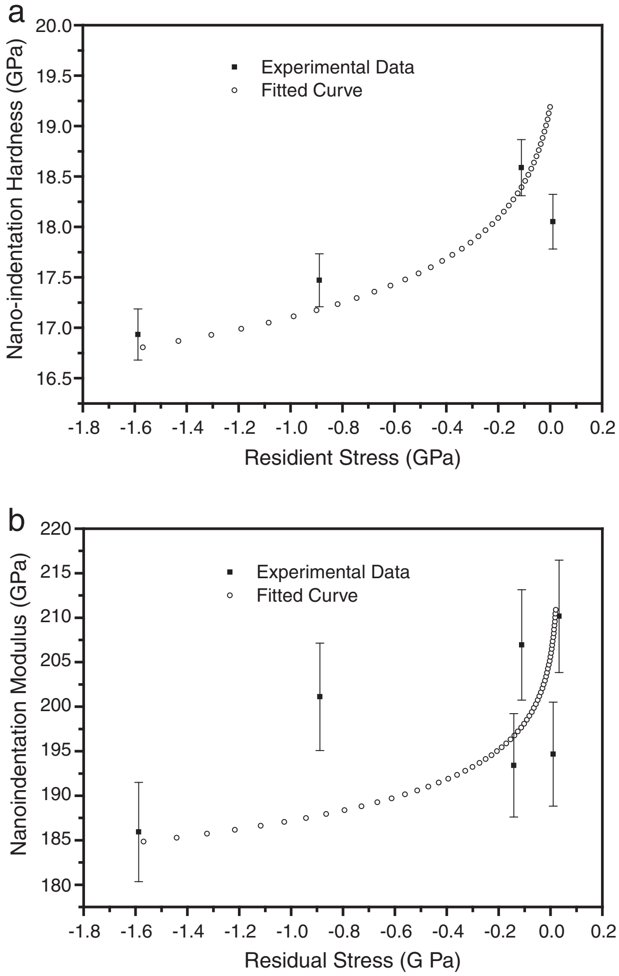

Fig. 4. Data of the residual stress versus the nanoindentation hardness (H) (a) and modulus (Er) (b) of the TiAlN thin film.

decreases gradually. Very low residual stress in the TiAlN thin film, such as 0.01–0.10 GPa, can been obtained when the thickness of the gradual layer is larger than 200 nm. It is indicated that the gradual layer in the TiAlN thin film/Si substrate pairs can be used to control the residual stress.

Comparing the data of Figs. 2 and 3, it can be observed that the variation of the H and Er should be induced by the residual stress of the TiAlN thin film. Fig. 4 shows the variation of the H and Er versus the residual stress of the TiAlN thin film. The H and Er of the TiAlN thin film are 15.86 GPa and 185.93 GPa respectively for a higher residual stress, i.e. −1.58 GPa. With a decreasing of the residual stress of the TiAlN thin film, the H and Er will increase, and reach at the maximum value when the residual stress trend to zero. Those data illuminate that the residual stress existed in the TiAlN thin film affects the mechanical properties of the TiAlN thin film. The data in Fig. 4 are fitted by a Logarithm Function, and we can obtain the empirical expressions of the H and Er versus the compressive stress σ in the TiAlN thin films. The empirical expressions are respectively:

$$\overline{H} = 18.7183 - 0.6865\ln(0.5036 - \overline{\sigma}) \tag{2}$$

$$\overline{Er} = 199.6450 - 5.3399\ln(0.3758 - \overline{\sigma}) \tag{3}$$

where $\overline{H}$ is a mean nanoindentation hardness of film, $\overline{Er}$ is a mean nanoindentation modulus of film and $\overline{\sigma}$ is a residual compressive stress existed in film ($\overline{\sigma}<0$). From the fitted expressions, we can see that the first part at the right of expressions is the intrinsic hardness and modulus of film with a thermal equilibrium structure. The second part shows a deviation of the mechanical properties induced by the residual stress existed in film, and minus "−" illuminates that residual stress makes hardness and modulus of film reducing in the form of a Logarithm decay function with the increasing of the residual stress. According to the fitted expressions, we can calculate the H and Er of the TiAlN films from the residual compressive stress σ, and also obtain the residual compressive stress σ from the H and Er of the TiAlN films.

The residual stress existed in thin films directly affects the mechanical properties of thin films, such as hardness and elastic modulus, and reduces the adhesive strength between film and substrate. In the TiAlN thin film fabricated by the magnetic filtered vacuum arc evaporation deposition method, there is a residual stress existed in the films, and the residual stress induces the decreasing of mechanical properties of the TiAlN thin films. Low residual stress should be needed for the applications of the TiAlN thin films due to the adhesive enhancement between TiAlN thin film and substrate. At the same time, the TiAlN thin films can show an excellent mechanical property. For the TiAlN thin films without residual stress, the characteristic H and Er calculated by the empirical equations are 19.1892 GPa and 204.9139 GPa respectively.

4. Conclusions

The TiAlN ceramic thin films with higher mechanical properties have been fabricated by the magnetic filtered vacuum arc evaporation deposition method. The maximum H and maximum Er are 18.96 GPa and 210.16 GPa respectively for the TiAlN thin film, when the residual stress of the TiAlN ceramic thin films is about 0.01–0.1 GPa. The H and Er of the TiAlN ceramic thin films are affected by the residual stress existed in the film. With the increasing of the residual stress to 1.58 GPa, the H and Er of the TiAlN films gradually decrease to 15.86 GPa and 185.93 GPa respectively. The empirical expressions fitted with Logarithm function between the residual stress and hardness or modulus have been obtained, and can be used to approximately calculate the H and Er of the TiAlN films.

Acknowledgments

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