Influence of Target Material on the Microstructure and Properties of Ti–Si–N Coatings Prepared by r.f.-Reactive Sputtering

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We examined the effects of sputtering conditions and target materials on the microstructure and mechanical properties of Ti–Si–N coatings prepared by r.f.-reactive sputtering. We used composite targets consisting of a Ti (99.99%) plate and Si₃N₄ chips as well as the target consisting of a Ti plate and Si chips. Thin films were synthesized by an r.f. sputtering machine in a facing target-type (FTS) on the substrates of high speed steel. During the deposition, the substrate was heated from room temperature up to ~300°C and a d.c. bias up to ~100 V was applied. Without substrate heating and bias, the hardness of the films increased from 30 GPa for a binary system, reaching a maximum of 37 GPa for a ternary system with a small amount (3–8 at%) of Si. It then decreased to values lower than those of binary systems when Si was more than 10 at%. The hardness of high Si films (containing ~20 at% Si) increased and reached to a maximum value of 40 GPa around at a bias of ~30 V, but the crystallite size of the film increased to ~30 nm. On the other hand, the hardness of the films (containing ~20 at% Si) deposited from the Ti–Si–N target increased with increasing negative bias voltage, being saturated at 38 GPa over ~80 V. Although the crystallite size of the films increased gradually with increasing negative bias, it still remained at about 7 nm at ~80 V. The characteristics of the latter film could be attributed to the formation of a nano-composite structure defined by Veprˇek et al.

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1. Introduction

Transition metal nitride films have been extensively studied and used for hard¹,² or decorative coatings.³,⁴ Recent studies of transition metal nitride films of wear-protective coatings have been aiming to explore multi component systems for improving hardness and/or oxidation resistance. Since Veprˇek et al. presented a theoretical concept for the super-hard “nanocomposite” films and their experimental verification on the Ti–Si–N systems prepared by plasma assisted CVD (PACVD),⁵,⁶ many researchers have extensively studied mechanical properties and/or oxidation resistance of Ti–Si–N coatings⁷–¹⁰ and other systems such as Zr–Si–N,¹¹,¹² Cr–Ni–N,¹³ Ti–Mo–N¹⁴ deposited by PVD.

Among the previous studies on Ti–Si–N coatings, some films fabricated by PVD showed super hardness. However, the results were not always consistent with the theoretical concept of the nanocomposite structure. For example, XRD diffractograms for the superhard Ti–Si–N coatings obtained by some researchers showed not very broad, low-intensity reflections but a strong reflection from large (20–50 nm) grains. This indicates that the relationship between the structure and mechanical property of Ti–Si–N coatings has not yet been satisfactorily elucidated.

To understand the hardening mechanism in terms of structure, a systematical study of mechanical properties and microstructure of coatings with respect to the sputtering parameter is necessary. This study was thus undertaken to investigate the influence of sputtering conditions and target materials on the mechanical properties of r.f.-sputtered Ti–Si–N films.

2. Experiment

Ti–Si–N films were prepared in an r.f. sputtering apparatus which has a pair of targets facing each other (referred to as the Facing Target-type r.f. Sputtering (FTS); Osaka Vacuum Co., Ltd., FTS-2R). Composite target consisting of a rectangular (100 mm × 160 mm × 10 mm thickness) titanium (99.99%) plate and silicon (99.9999%) (10 mm × 10 mm × 0.5 mm thickness) or Si₃N₄ (99.8%) (10 mm × 10 mm × 1.5 mm thickness) chips were sputtered in a mixture of highly purified argon and nitrogen gases (99.9999%). The silicon concentration in the films was controlled by the number of silicon chips stuck on the titanium plates. Mirror-polished silicon wafers and high-speed steel plates (SKH-51) of 25 mm × 25 mm were used as substrates. All the substrates were cleaned ultrasonically with acetone, ethanol and 2-propanol in the sequence before sputtering deposition. The system was first evacuated to a vacuum better than 5 × 10⁻⁵ Pa (≈ 3.8 × 10⁻⁷ Torr) prior to deposition. A deposition of adhesion-layer of Ti–Si on the substrate was followed by the deposition of Ti–Si–N coating.
by reactive sputtering. Based on the result of our previous study of TiN film preparation, the Ar gas flow rate was fixed at 10 sccm, and the flow rate of N₂ gas was brought back gradually from the highest flow rate to 2.5 sccm along the hysteresis loop of reactive sputtering³,⁴,¹² in order to obtain metal-like titanium nitride films. The working pressure was kept at ~0.15 Pa (1.1 mTorr). The r.f. input power (13.56 MHz) for sputter deposition was fixed at 1 kW. In some cases, the substrates were heated up to ~300 °C and/or were applied with a d.c. negative bias voltage up to ~100 V during deposition. Film thickness was monitored between 1.0 and 1.5 μm by controlling the sputtering time.

Indentation hardness and effective Young’s modulus of films were measured for the evaluation of mechanical properties of films. The indentation hardness, \( H_{IT} \), is the resistance to permanent deformation and is defined as follows:¹⁴,¹⁵

\[
H_{IT} = \frac{F_{\text{max}}}{A_p}
\]

where

\( F_{\text{max}} \): is the maximum applied force;
\( A_p \): is the projected (cross-sectional) area of contact between the indenter and the sample determined from the force-displacement curve and a knowledge of the area function of the indenter.

The effective Young’s modulus¹⁶ is determined by the eq. (2):

\[
\frac{E_{IT}}{(1 - \nu_s^2)} = \frac{1}{\frac{1}{E_r} - \frac{1}{E_i}}
\]

where

\( \nu_s \): is the Poisson’s ratio of the sample;
\( \nu_i \): is the Poisson’s ratio of the indenter (for diamond 0.07);
\( E_r \): is the reduced modulus of the indentation contact, which is obtained from the experimentally measured stiffness of the initial unloading data of the indentation;
\( E_i \): is the modulus of the indenter (for diamond 1140 GPa).

As \( \nu_i \) is unknown, the effective Young’s modulus, \( E_{IT}/(1 - \nu_s^2) \) is usually obtained from the indentation measurement.

The indentation was performed by a nano-indentation system (Triboscope, Hysitron Inc.) at room temperature using a triangular Berkovich diamond pyramid. The load was applied on the film plane with a d.c. negative bias voltage up to 100 V using a nano-indentation system (Triboscope, Hysitron Inc.) at room temperature using a triangular Berkovich diamond pyramid. The load was applied on the film plane with a d.c. negative bias voltage up to 100 V.

The crystal structure of films was identified by an X-ray diffractometer (Philips X’pert system) using Cu–Kα radiation with either a thin film mode (incident angle = 1 degree) or 0–20 mode. The crystal size in the direction perpendicular to film plane was estimated by the width of XRD peaks using Scherrer’s equation. The cross section of the coatings was observed by a Field Emission Scanning Electron Microscope (FE-SEM: JSM-7400F, JEOL). The chemical concentration of titanium, nitrogen and silicon of these films were measured by an Electron Probe Microanalyzer (EPMA). X-ray photoelectron spectroscopy (Shimadzu, ESCA-3400) was used to analyze the chemical bonding state of the Ti–Si–N films.

3. Results

Figure 1 depicts the variation of the indentation hardness (\( H_{IT} \)) and the effective Young’s modulus (\( E_{IT}/(1 - \nu_s^2) \)) of Ti–Si–N films that deposited without bias application or substrate heating as a function of Si content. Open or closed marks (circles and squares) in the figure show the values for the coatings deposited using Si chips or Si₃N₄ chips, respectively. A simple analysis of this figure indicates that the indentation hardness (\( H_{IT} \)) or the effective Young’s modulus is mainly a function of Si content, although the target material was expected to be the determinant factor.

The hardness increases with Si concentration, reaching a maximum value of 37 GPa in the range of 5 to 8 at%Si; and then decreases to 22 GPa at 22.5 at%Si. The effective Young’s modulus also reaches to a maximum value of 360 GPa at about 4 at%Si. The variations of these values were different from those of Ti–Si–N films reported in the previous reports.⁹,¹⁰ However, the tendency of the results was relatively similar to that of Ti–Si–N films reported by Diserens et al.,⁷ or Vaz et al.⁸ which were prepared by r.f.-reactive sputtering with applied bias. Figure 2 reveals the dependence of lattice parameter (\( a \)) and crystallite size (\( D \)), which were measured from the XRD peak position and XRD peak width using Scherrer’s equation, on the Si content. The lattice parameter shows the maximum value of 0.432 nm at about 3 at%Si. The crystallite size increases with increasing Si concentration, reaching to 35 nm at about 5 at%Si. With further increment of Si, the grains became smaller. Although both maxima of the lattice parameter (\( a \)) and the crystallite size (\( D \)) are not consistent with each other, they are in the range of the hardness peak position as shown in Fig. 1. The similar relationship was also observed in the previous report of Zr–Si–N films.¹¹,¹² On the other hand, the Ti–Si–N films containing more than 15%Si shows hardness lower than that of TiN films despite the films consisting of nanocrystallites.
less than 10 nm. Ti–Si–N films containing about 20% Si indicated low hardness of ~20 GPa, which is similar to the results reported by other researchers. 5–8)

Sputtering deposition with substrate heating and bias application can cause higher energy of sputtered particles, which frequently results in a phase separation. Two series of Ti–Si–N films (with Ti–Si target: series A, with Ti–Si3N4 target: series B) were deposited at ~300°C under the d.c. biased voltage varying from 0 to ~100 V. Figure 3 shows the XRD patterns of series A-(Ti–Si–N) films with different bias voltages, which were measured by θ–2θ method (a) and by thin film method (grazing angle mode) (b). XRD patterns reveal the presence of only one phase that can be assigned to the cubic B1 NaCl type structure. In Fig. 3(a), the strong (111) peak of the film deposited at ~30 V as compared with the film deposited at 0 V indicates that the application of negative bias voltage increased the grain size and preferred orientation of the films. Although the film at ~30 V shows an extremely strong (111) peak in θ–2θ diffractogram [Fig. 3(a)], it does not exhibit a (111) peak or a (200) peak in the Fig. 3(b). This fact implies that the film has a strong preferred orientation along the direction of film deposition compared to the films deposited over ~30 V. Figure 4 shows the variation in nano-indentation hardness and effective Young’s modulus of series A-(Ti–Si–N) films deposited with Ti–Si target as a function of the applied bias voltage. The indentation hardness of series A films increases drastically with increasing negative bias voltage, reaching to a maximum of 40 GPa at ~30 V. The effective Young’s modulus increases with increasing negative bias voltage, saturating at about 320 GPa. Figure 5 depicts the change of silicon or nitrogen contents and the crystallite size (measured from XRD analysis) in the series A films, as a function of bias voltage. The nitrogen content in the films was kept in the range of 46 to 50 at%. The silicon content decreases with increasing negative bias voltage, and reaches about 0% at ~50 V and below. The crystallite size of the films increases drastically with the increase of negative bias voltage reaching to 30 nm at a bias of ~30 V, at which film showed highest hardness of about 40 GPa.

Figure 6 depicts the variation in nano-indentation hardness and effective Young’s modulus of the series B-(Ti–Si–N) films deposited with Ti–Si3N4 target as a function of the applied bias voltage. The indentation hardness of the B films
increases with increasing negative bias voltage, but saturated at a level of 38 GPa for more than \(-80\) V. The effective Young’s modulus of series B films also increases gradually with increasing negative bias voltage to \(\sim 290\) GPa. Figure 7 illustrates the change of silicon or nitrogen contents in the series B films and the crystallite size, as a function of bias voltage. The nitrogen content decreases from 65 to about 50 at% with increasing negative bias voltage. On the other hand, the silicon content remains constant at about 20% up to \(-80\) V. Although the crystallite size of the films increases gradually with increasing negative bias, it remains at about 8 nm between \(-40\) to \(-100\) V.

Figure 8 shows the cross-sectional view of Ti\(_{42}\)Si\(_9\)N\(_{29}\) (series A) and Ti\(_{29}\)Si\(_{30}\)N\(_4\) (series B) films observed by FE-SEM. Figures 8(a) and 8(a)' reveal that the Ti\(_{42}\)Si\(_9\)N\(_{29}\) film consisted of a fiber structure according to Thornton’s classification\(^{18}\) or a nano-crystalline column.\(^{10}\) From these results, it is obvious that the hardest films fabricated from Ti–Si target consist not of nano-crystalline sphere grains but of nano-columnar grains. As shown in Figs. 8(b) and 8(b)', Ti\(_{29}\)Si\(_{20}\)N\(_{51}\) film exhibits a very fine structure consisting of equiaxed grains as have seen in amorphous or nano-crystal material.

Figure 9 illustrates XPS narrow scan spectra of Si\(_2p\) for Ti\(_{42}\)Si\(_9\)N\(_{29}\) film and Ti\(_{27}\)Si\(_{32}\)N\(_{4}\) film fabricated from Ti–Si composite target (series A) and Ti\(_{29}\)Si\(_{30}\)N\(_{4}\) film fabricated from Ti–Si\(_3\)N\(_4\) composite target (series B). XPS spectra show that the chemical state of silicon in Ti–Si–N films was mainly in the form of Si\(_x\)N\(_9\) regardless of Si content and target material. In the case of the Ti\(_{27}\)Si\(_{32}\)N\(_{4}\) films deposited without substrate bias and heating, however, relatively weak shoulder at \(\sim 99\) eV can be observed, which suggests the existence of some amounts of TiSi\(_y\) or unreacted Si in the film. The spectra for Ti\(_{42}\)Si\(_9\)N\(_{29}\) film and Ti\(_{29}\)Si\(_{30}\)N\(_{4}\) film show no shoulder at \(\sim 99\) eV. Figure 10 shows the development of XPS spectra for Ti–Si–N films fabricated from Ti–Si\(_3\)N\(_4\) composite target with varying substrate bias voltage. Typical peak broadening and relatively weak intensity of the Ti\(_{2p3/2}\) peak was observed, suggesting the improvement of Ti–N bonding.

Figure 11 illustrates the relationship between the nano-indentation hardness and crystallite size of Ti–Si–N films reported by Vepřek et al. The solid line denotes the early data presented by Vepřek and the broken line shows their theoretical calculation. It is important that there is a clear difference between the two kinds of films. The result of Ti\(_{42}\)Si\(_9\)N\(_{29}\) film deposited from Ti–Si target does not fall on the curves. On the contrary, the result of Ti\(_{29}\)Si\(_{20}\)N\(_{51}\) films fabricated from the Ti–Si\(_3\)N\(_4\) composite target is similar to that based on the nano-composite model defined by Vepřek et al.
4. Discussion

As shown in Fig. 4, the indentation hardness of series A films showed the maximum value of 40 GPa at the substrate bias voltage of $-30\,\text{V}$. On the other hand, the Young’s modulus value of the film increased with increasing negative bias voltage, i.e., with increasing bombardment energy. The behavior of the Young’s modulus value could be explained by the increase of film density caused by the peening effect. Besides, densification of films due to the ion bombardment affects most probably the increase of hardness of films. However, negative bias acts as a re-sputtering force to the particles reaching to the substrate at the same time. Despite the similar values of the sputtering yield of Ti and Si atoms, only the Si content in the films decreases with the increase of negative bias voltage as shown in Fig. 5. As is clear from Fig. 1, the addition of Si improves the hardness of TiN, with this hardening effect being more pronounced for Si contents from 5 to $\sim 10\,\text{at}\%$. The decrease of the indentation hardness with further increase of negative bias voltage above $-30\,\text{V}$ could be attributed to the drastic decrement of Si content.

Although the sputtering process is a highly non-equilibrium phenomenon, the reason why Si atoms were re-sputtered more than Ti by applying substrate bias can be understood from the view point of chemical thermodynamics. The tendency of compound formation can be predicted qualitatively using formation free energy (Ellingham diagram). Due to the larger negative free energy of TiN as compared with $\text{Si}_3\text{N}_4$ as shown in Ellingham diagram,
Ti–Si composite target as shown in Fig. 5. Thus, the Si content in the film (Series A films) decreases with increasing negative bias voltage when using bias voltage. Therefore, Si particles on the substrate should be re-sputtered nitriding ratio of Ti atom is higher than that of Si atom. The weak shoulder observed on Si2p narrow scan spectra at 99 eV (Fig. 9) for Ti27Si22N51 film suggests the existence of some amounts of TiSi, or unreacted Si. However, it disappeared by the substrate bias and heating. From the Si2p narrow scan spectra of Ti42Si9N49 film, the peak intensity at 101.5 eV is relatively weak, but the chemical bonding state of Si in the Ti42Si9N49 film is mainly in the form of Si3N4. At the same time, however, we noticed that the hardest film (Ti42Si9N49) consisted of relatively large crystallites (~30 nm in average). The high hardness film (40 GPa) consisting of nano-columnar crystalline TiN grains can not be explained regardless of the existence of Si3N4 phase. 

Based on these considerations, we can conclude that the reactive sputtering using Ti–Si3N4 composite target and substrate heat and bias is an effective technique for preparing Ti/Si3N4 nano-composite coatings by reactive sputtering.

5. Conclusion

Ti–Si–N films have been prepared by r.f. reactive sputtering using Ti–Si or Ti–Si3N4 composite target in the Facing Target-type Sputtering (FTS) system. Microstructure study of these films using XRD, FE-SEM and XPS has drawn the following conclusions:

(1) The indentation hardness and the effective Young’s modulus increase with the addition of a small amount of Si even without heating or applying a bias voltage to the substrate. The hardness and Young’s modulus of Ti–Si–N films reaches a maximum of 37 and 360 GPa in the range from 3 to 8 at%Si.

(2) The indentation hardness of Ti–Si–N films (Ti42Si9N49) deposited from Ti–Si target increased with substrate bias and heating and reaches a maximum value of 40 GPa around at ~30 V. The film consists of nano-columnar TiN grains of ~30 nm in length and a small amount of amorphous Si3N4 phase.

(3) The indentation hardness of Ti–Si–N films (Ti29Si20N51) deposited from Ti–Si target with the substrate bias and heating increased and reached a maximum value of 38 GPa around ~80 V. The film has a nano-composite structure consisting of equiaxed TiN crystal grains of ~8 nm and an amorphous Si3N4 phase.

(4) The increase of hardness with increasing bias voltage of the Ti–Si–N films (Ti29Si20N51) deposited from Ti–Si target could be attributed to the formation of nano-composite structure consisting of TiN nanocrystals embedded in Si3N4 amorphous phase.
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