Preparation and oxidation of composite TiN–AlN films from alkoxide solutions by plasma-enhanced CVD

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Abstract

Composite and compositionally graded (CGed) TiN–AlN films were deposited on Si wafers at 600 °C from Ti- and Al-alkoxide solutions by N_2 plasma-enhanced chemical vapor deposition (CVD). The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Vickers micro-hardness. In the composite TiN–AlN films, the Ti and Al contents varied linearly and complementarily with solution composition, the N content ranging from 35 to 40 at.%. In the CGed films, the Al component decreased complementarily with increasing Ti toward the substrate. Cross-sectional SEM observation showed both films to be about 1 μm thick with a columnar structure. Oxidation of the composite and CGed films was performed at 500, 700, and 900 °C in air for 1 h. The improvement of oxidation resistance in both composite and CGed films is discussed on the basis of the XRD and SEM observations, and the XPS analysis of the oxidized films.
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1. Introduction

Titanium nitride (TiN) has been widely used because of its low electrical resistivity (in order of several tens μΩ cm) and its low friction coefficient. A disadvantage of TiN is its tendency to oxidize rapidly at low temperatures (∼500 °C) to form TiO_2 that readily shears off from the substrate and causes a drastic degradation of its wear resistance. Composite TiN–AlN coatings have attracted much attention because of their improved oxidation resistance at elevated temperatures compared with TiN and because of their improved performance in certain machining operations.[1] Composite TiN–AlN coatings are usually prepared by physical vapor deposition (PVD) technique such as sputtering[2–4] and arc ion plating.[5]

On the other hand, there have been several studies on the preparation of TiN–AlN films by chemical vapor deposition (CVD) at higher temperatures (>1000 °C).[6–8] Compared with the conventional CVD method, plasma-enhanced CVD (PECVD) makes the coating process possible at low temperatures (≲800 °C). Composite TiN–AlN coatings prepared by this method normally involve the use of halogens such as $TiCl_4$ and $AlCl_3$ or $AlBr_3$ as the starting material.[9–11] For example, Kim and Lee prepared TiN–AlN films on high-speed steel or Si wafers by the PECVD technique using a halogen gas mixture.[10,11] Recently, studies have indicated that the oxidation/corrosion of TiN–AlN films is superior to that of TiN alone.[12–14]

Previous work on the use of alkoxide solutions to prepare monolithic nitrde films (TiN, AlN, and SiNx) and their composite films by PECVD used a H_2/N_2 plasma generated at a maximum power of 15 kW.[15–18] It is of interest to investigate whether it is possible to make these nitride films from alkoxide solutions in N_2 plasma without H_2 at higher power (>20 kW). TiN films have previously been reported to form on various substrates from titanium tetra-ethoxide solution ($Ti(OC_2H_5)_4$) in N_2 plasma at a 20 kW power.[19] The present study extends this work on the nitride films in N_2 plasma to the preparation of composite TiN–AlN films and composi-

tionally graded (CGed) AlN–TiN films. The staring materials for the PECVD process in N_2 plasma are alkoxide solutions (titanium tetra-ethoxide $Ti(OC_2H_5)_4$, TTEO and aluminum tri-butoxide $Al(OC_4O_7)_3$, ATBO). The oxidation of TiN films is compared with that of composite TiN–AlN films containing CGed, revealing an improvement in oxidation resistance in the composite films.

2. Experimental procedures

The alkoxides TTEO and ATBO were used as the starting materials. Tri-ethanol amine ($N(C_2H_4OH)_3$) was used to stabilize the TTEO and ATBO and prevent precipitation of the hydroxide. Each alkoxide solution was dissolved in tri-ethanol amine and then dissolved in ethanol. For preparation of composite TiN–AlN films, a mixture of the alkoxide solutions with various mole ratios was fed into a N_2 plasma at a rate of 0.1 ml min^{-1} using a high pressure liquid chromatography (HPLC) pump (GULLIVER PU-980, JASCO corporation). The flow rate of N_2 was fixed at 25 slm. The plasma apparatus and generation conditions are described in detail elsewhere.[15] The substrate used for film preparation was a 100 Si wafer at a temperature of 600 °C.

CGed AlN–TiN films also were prepared, with AlN and TiN compositions on the surface and substrate, respectively, the ratios of Al and Ti in the film being varied complementarily toward the substrate. For this preparation, the feed rate of the two alkoxide solutions was complementarily varied with time, while maintaining the total feed rate at 0.1 ml min^{-1} using two HPLC pumps. The substrate used in this experiment was also a Si wafer.

The phases produced on the film were identified by thin film X-ray-diffractometry (XRD) (RIGAKU, Rint 2000) with Cu Kα radiation. The chemical states of the N, Ti, Al, Si, O, and C were determined by X-ray photoelectron spectroscopy (XPS) (Shimazu Corporation, ESCA-3200) with Mg Kα radiation. The binding energy of the elements was corrected by reference to free carbon (284.6 eV). The relative atomic percentage of the elements in the film was calculated from their XPS peak area ratio. The surfaces and cross-sections of the films were observed by scanning electron microscopy (SEM) (JEOL, JSM-6300F). The thicknesses of the films were determined from the cross-sectional SEM observation. The Vickers micro-hardness of the composite and CGed films was measured at a load of 300 mN.

Oxidation of the composite and CGed TiN–AlN films was carried out in air by heating at a rate of 5 °C min^{-1} to a fixed temperature (500, 700, and 900 °C) and holding at this temperature for 1 h. The phases produced on the film after oxidation were identified by thin film XRD. The surfaces and cross-sections of the oxidized films were observed by SEM. The oxidized CGed films were etched in depth by sputtering with Ar ion and the compositions of Ti, Al, N, O, and C were semi-quantitatively determined by XPS.

3. Results and discussion

3.1. Preparation of composite and compositionally graded AlN–TiN films

Fig. 1 shows the XRD patterns of the composite TiN–AlN films obtained at a range of Al atomic fractions from 0 to 1.0 at intervals of 0.2. The top trace shows the result for a CGed TiN–AlN film. Very sharp peaks corresponding to the rock-salt type TiN structure appear at Al fractions of 0–0.2. As the atomic fraction of Al is increased (Ti:Al = 6:4 and 4:6), these peaks become broaden and shift slightly to higher angles. This slight shift reflects the dissolution of AlN in the TiN structure, as reported previously.[16] A very small, broad peak of AlN appears first at 0.4 Al and becomes sharper with increasing Al content. Only wurtzite-type AlN peaks appear in the 0.8 and 1.0 Al samples. The CGed film shows relatively sharp TiN and AlN peaks; although this film has an AlN surface, as explained later, sharp TiN peaks are also observed, probably because of the thinness of the film. The XRD pattern of the CGed film corresponds to that of the composite films with Ti:Al = 6:4 or 4:6.

The surfaces and cross-sections of the composite and CGed films were observed by SEM (Fig. 2(A)–(E)). Fine 0.1–0.3 μm triangular crystals are compactly formed on the surface at Ti:Al = 8:2, with a columnar film structure about 1 μm thick (Fig. 2(A)); the surfaces and cross-sections of pure TiN films have been found to have a similar microstructure.[19] The columnar crystals become longer with increasing distance from the interface. With increasing Al fraction, the particle sizes increase to 0.3–0.5 μm at Ti:Al = 6:4 and 4:6, with round aggregated particles consisting of 0.1 μm regularly sized grains on the surface (Fig. 2(B) and (C)). The cross-section shows the formation of ~1 μm thick columnar particles. At a Ti:Al ratio of 2:8, the morphology and thickness of the film were similar to those of the 4:6 ratio. In the
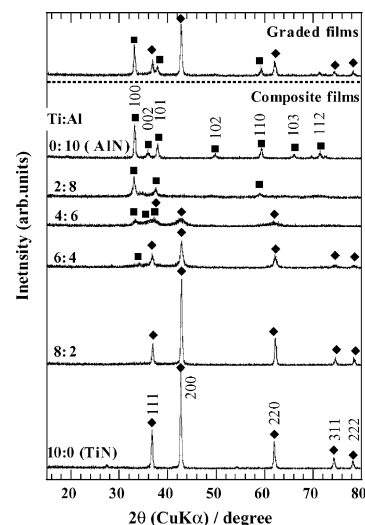

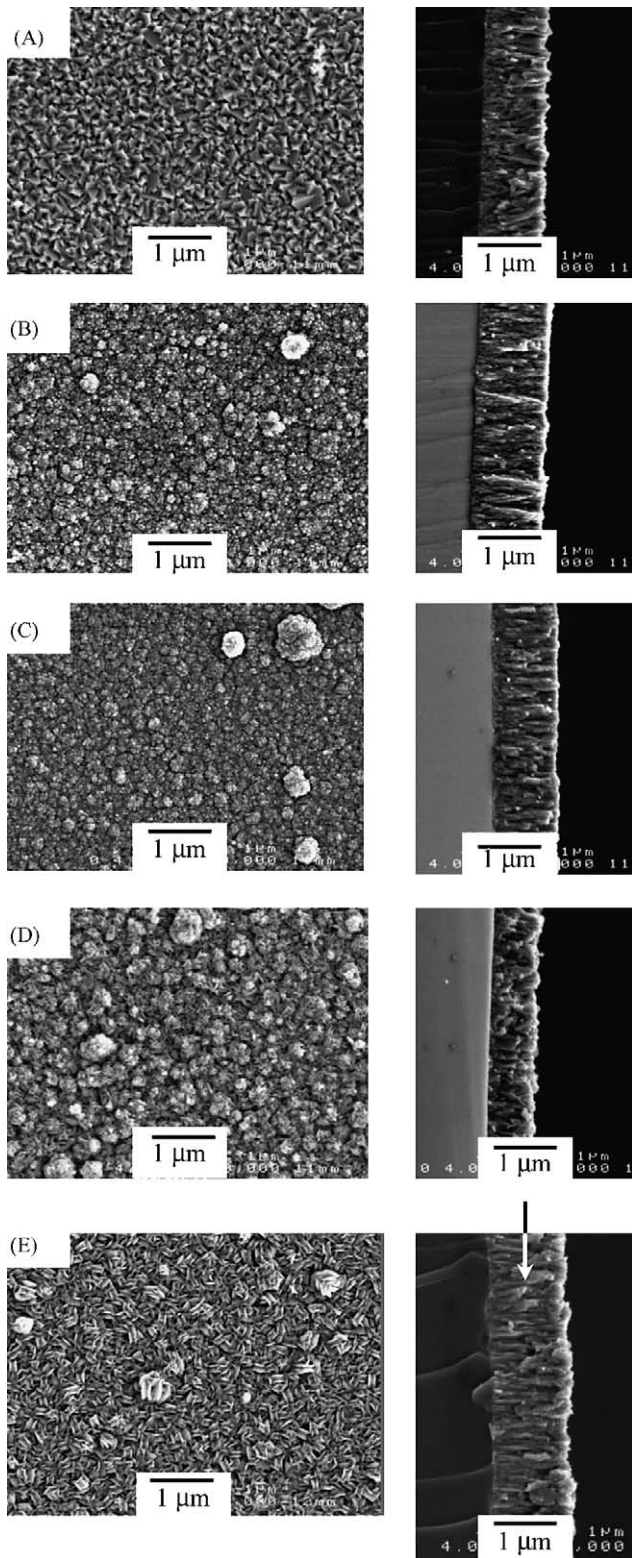Fig. 1. XRD patterns of composite and CGed TiN–AlN films. (♦) TiN and (■) AlN.

Fig. 2. SEM photographs of surface and cross-section of composite and CGed TiN–AlN films. Atomic fraction of Al in composite films; (A) 0.2, (B) 0.4, (C) 0.6, (D) 1.0, and (E) CGed film.
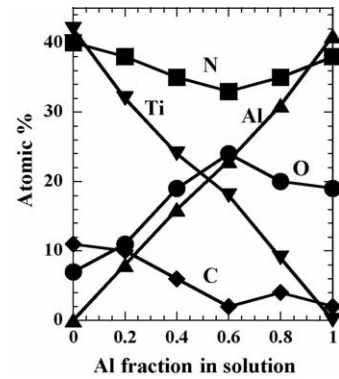

Fig. 3. Changes of atomic percentages of Ti, Al, N, O, and C in composite films with Al atomic fraction.

AlN film (Fig. 2(D)), the surface is covered with 0.2–0.5 μm coagulated particles, consisting of needle-like crystals less than 0.1 μm. The thickness of this coating is about 0.6 μm. The surface of the CGed film (Fig. 2(E)) is coated with aggregated particles consisting of three or four adhering 0.5 μm plate-like crystals oriented normal to the surface. The cross-sectional observation shows the growth of 0.1–0.5 μm long columnar particles in the middle of the two-layer film (arrowed in Fig. 2).

The relative atomic percentages of Ti, Al, N, O, and C elements of the composite films were determined semi-quantitatively from the respective XPS areas, as shown in Fig. 3. The N content remained approximately constant at 35–40 at.% at all Al fractions. The Ti and Al contents varied, in a linear but opposite manner, with Al fraction in solution, indicating the effective deposition of Ti and Al components from the solution without selective etching or removal in N_2 plasma. The oxygen impurity in the film was less than 10 at.% at Al fractions of 0 and 0.2, increasing to about 20 at.% at Al fractions of 0.6–1.0. This oxygen impurity level is higher than approximately 10 at.% found in films previously prepared using $H_2/N_2/Ar$ plasma. In contrast, the carbon impurity was less than 10 at.%, falling to about 5 at.% at Al fractions $\gtrsim 0.6$. This carbon impurity content is lower than the approximate 10 at.% found in previous films.

Fig. 4 shows changes the concentrations of Al, Ti, N, O and C elements of the CGed films with depth from the outer surface to the substrate. After etching for 5 min, the surface was still contaminated with O and C, the compositions at this depth were not taken into account. At the intermediate depth (etching time <20 min), the nitrogen is maintained at 40 at.%, with the oxygen content about 20 at.% and the carbon less than 5 at.%. At greater depths, the oxygen content rapidly decreases toward the interface, with increase in the N content. The Al and Ti contents also change complementarily with depth, the Al composition being 40 at.% at the surface and the Ti 45 at.% at the interface. The Al component appears to draw the oxygen impurity into the films.

The micro-hardness was measured for both the composite and the CGed AlN–TiN films as a function of Al fraction
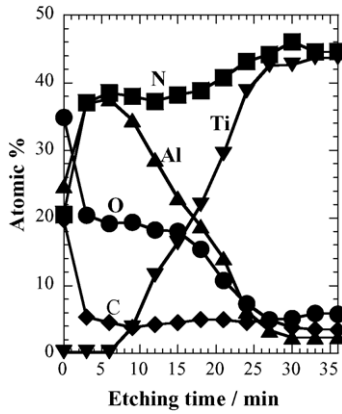
Fig. 4. Depth profile of Ti, Al, N, O, and C in CGed film.

Fig. 6. XRD patterns of composite and CGed films oxidized at 500 °C in air. (♦) TiN, (■) AlN, (●) TiO$_2$(rutile), and (▼) TiO$_2$ (anatase).

(Fig. 5). The values are lower than those reported in several papers (15–20 GPa), probably because the present films possess a columnar microstructure (Fig. 2), which can readily be broken by the Vickers indenter. The relative micro-hardness of the composite film increases with AlN fraction, reaching a maximum at an Al fraction of 0.6, then decreasing as the Al fraction is increased further. The micro-hardness of the composite films was greater than those of the end-member compounds (TiN and AlN). It is interesting to note that the micro-hardness of the CGed films lies between that of composite films with Al fractions of 0.5 and 0.7.

3.2. Oxidation of composite and CGed AlN–TiN films

Fig. 6 shows the XRD patterns of the surface of the composite and CGed films oxidized at 500 °C for 1 h in air. The pure TiN film is oxidized to TiO$_2$ (rutile, ● and anatase, ▼) with a small residual 200 peak of TiN. When a small fraction (0.2) of Al is added to TiN, the oxidation of the composite film does not proceed as rapidly as in the pure TiN film, retaining a strong 200 peak of TiN with the formation of a broad anatase (TiO$_2$) peak. Further additions of Al (Ti:Al = 6:4 or 2:8) do not result in the appearance of any distinct peaks. The occurrence of strong AlN peaks in the oxidized AlN film

indicates relatively little oxidation at 500 °C. At 700 °C, the pure TiN film was completely oxidized to rutile, as seen from the XRD trace (Fig. 7). With the addition of Al fractions of 0.2 and 0.4, the TiN peaks (♦) remain, but peaks of rutile and anatase appear, indicating that the oxidation is suppressed in the composite films. At an Al fraction of 0.6, the oxidized films show only broad TiO$_2$ peaks. At 0.8 Al, the absence of XRD peaks suggests a lack of oxidation at 700 °C, similar to the situation at 500 °C. It is clear from these results that the addition of AlN to the TiN film is effective in improving the oxidation resistance of the TiN. The CGed films displays a remarkable high oxidation resistance compared with that of the composite films, judging by the persistence of strong TiN and AlN peaks and only a small amount of rutile. The surface of both the composite and CGed films oxidized at 700 °C remains almost unchanged, but the micro-hardness is decreased by 10–20% after oxidation.
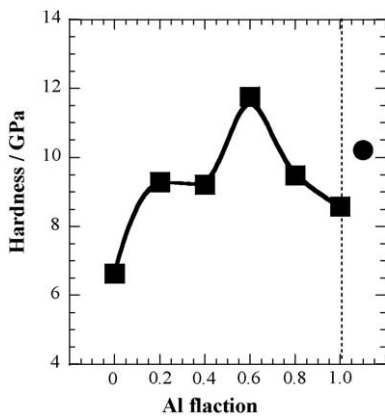

Fig. 5. Relationship between micro-hardness and Al atomic fraction in composite films and CGed film. (■) composite films and (●) CGed films.
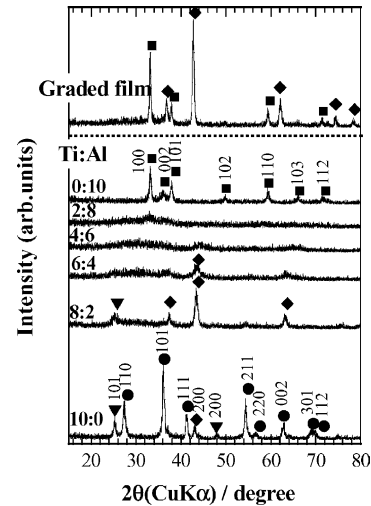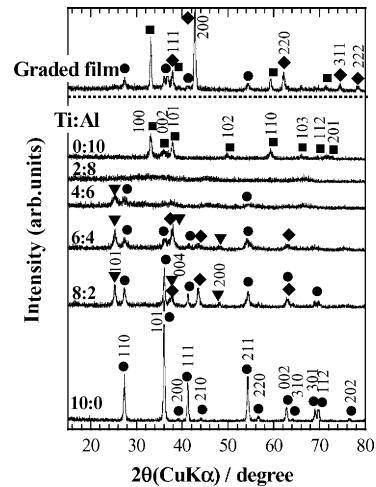

Fig. 7. XRD patterns of composite and CGed films oxidized at 700 °C in air. The symbols are identical to those in Fig. 6.
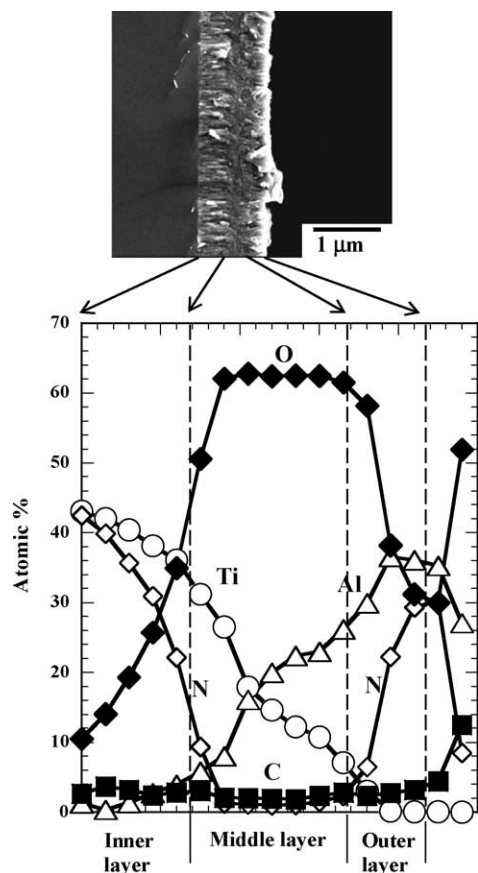
Fig. 8. SEM photograph and the corresponding depth profile of CGed film oxidized at 700 °C in air. The symbols are identical to those in Fig. 6.

Fig. 8 shows a cross-sectional SEM photograph of a CGed film oxidized at 700 °C, with the corresponding compositional depth analysis. CGed films oxidized at 500 °C show a similar microstructure. The oxidized films consist of three layers of similar thickness. The outer layer possesses a collapsed columnar morphology, the middle layer shows a dense structure, while the inner layer retains the columnar particles. The outermost surface was found to be contaminated with O and C, the immediate underlying layer containing Al but not Ti. The N content of this layer decreases and the O content increases toward the middle layer. The XRD trance contains only AlN peaks and no phase related to aluminum oxide, as might be expected in an oxidized film (Fig. 7). Since the unoxidized CGed films contain an O impurity of about 20 at.%, the oxygen content of 30 at.% in the oxidized film suggests the occurrence of partial oxidation. As seen by SEM, oxidation destroys columnar structure of the outer layer. The Al and Ti concentrations in the middle layer change complementarily with depth. This layer contains about 65 at.% O, but no N is detected. Rutile is the only detected crystalline phase by XRD (Fig. 7), but this middle layer may also contain amorphous aluminum oxide or aluminum oxy-nitride. The inner layer contains an increased N/Ti content and an O level, which decreases steeply toward the Al-free substrate. This layer consists of TiN, more probably, TiON. Its carbon con-

tent of about 3 at.% throughout is less than the 5 at.% found in the unoxidized layer, probably because of its removal by oxidation. Since the middle oxide layer is dense, it acts as a barrier to the penetration by oxygen gas, protecting the TiN of the inner layer. It is likely that the vertical fissures in the columnar structure enable the oxygen to readily penetrate deep into the outer and middle layers of the film. Complete oxidation of the CGed film occurs at 900 °C, producing the oxide phase containing no N in the cross-section.

4. Conclusion

Composite and CGed TiN–AlN films about 1 μm thick with a columnar structure were deposited at 600 °C on a Si wafer from Ti- and Al-alkoxide solutions fed into a N_2 plasma at a rate of 0.1 ml min^{-1}. The composite films contain 35–40 at.% N and have Ti and Al contents which change linearly and complementarily with the solution composition. The Al component of the CGed films decreases complementarily with increasing Ti concentration toward the substrate. The Vickers micro-hardness values of the composite films at Al fractions of 0.5 and 0.7 and of the CGed films are double those of the end-member compounds (TiN and AlN). Oxidation studies of the composite and CGed films in air at 500 and 700 °C show an improvement in the oxidation resistance of both the composite and CGed films which can be attributed to the existence of AlN in the former and to a dense oxidized middle layer in the latter.

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