Preparation of Compositionally Graded TiN–AlN and TiN–SiNx Films from Alkoxide Solutions by Liquid Injection Plasma CVD Method

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Four kinds of compositionally graded (CGed) AlN–TiN and SiNx–TiN films were prepared on a Si wafer substrate at about 700 °C by a plasma chemical vapor deposition (CVD) technique designed to inject alkoxide solutions (titanium tetra-ethoxide, aluminum tri-buthoxide, and hexa-methyl-disiloxane) stabilized with tri-ethanol-amine into a thermal Ar/N₂/H₂ plasma. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrical resistivity. The relative atomic concentrations of N, Ti, Al, Si, O, and C were determined by X-ray photoelectron spectroscopy (XPS). It was shown by XRD and XPS that CGed AlN-TiN films formed with monolithic AlN and TiN composition on surface and substrate, respectively, with corresponding changes of Al and Ti as a function of distance from the interface. Similarly, CGed SiNx–TiN films were prepared, with complementary changes of their Si and Ti contents. The existence of SiNx was assumed from the presence of Si-N bonding in N1s and Si2p XPS spectra, despite the lack of XRD diffraction peaks related to silicon nitrides. CGed AlN-TiN films were 1–3 μm thick and showed the formation of flower-like agglomerated particles consisting of regular 0.2–0.3 μm fine particles on the surface, whereas spherical particles of 3 μm size are formed on surface of CGed SiNx–TiN films. The electrical resistivity of the films changed from 300 to 7 × 10⁴ Ω cm, depending on the type of CGed film.

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1. Introduction

Titanium nitride (TiN) is technologically important because of its low resistivity (several tens μΩ cm), good hardness and chemical stability, and high melting point (>3000 °C). TiN films are also used as coatings on cutting tools, because they are harder than alumina and thermally stable to 3000 °C. Aluminum nitride (AlN) and silicon nitride (Si₃N₄) exhibit useful properties such as high thermal conductivity and high electrical resistivity, and are thus widely used as electronic substrates where high thermal conductivity is required and as protective coatings.

The preparation of TiN and AlN films by plasma-enhanced CVD (PECVD) combined with a thermal or r.f. plasma has been reported by several authors. In the preparation of these films, metal halogenides such as TiCl₄, AlCl₃, and SiCl₄ have been used as a starting source, but these tend to leave a small amount of ammonium chloride or chlorine in the films, which degrades the properties of the films. To overcome these problems, a metal-organic (MO) CVD process using tetrakis-(dimethyl amino) titanium (TDMAT), tri-methyl aluminum (TMA), and hexa-methyl-disilazane has been developed for the low temperature preparation of TiN, AlN, and SiNₓ films, respectively. While these organometallic compounds are useful sources for making these nitride films, they have to be handled very carefully because of their strong tendency to absorb moisture, their high toxicity and their explosiveness in air.

Ti, Al or Si-containing alkoxide are interesting alternative sources for the preparation of the nitride films, because they are easily handled in ambient atmosphere, inexpensive and have emit of no toxic exhaust fumes. One of the authors (S. S.) has reported, for the first time, the preparation of TiN and AlN films from titanium tetra-ethoxide and aluminum tri-buthoxide solutions by thermal PECVD. The preparation method of these nitride films was developed by examining factors influencing the optimum conditions for the preparation of the films. He extended the work to the preparation of composite nitride films, (Ti₁ₓAlₓ)N, and studied the effects of the Al content on the mechanical and electrical properties.

As described above, TiN film coating is useful for cutting tools, but is readily oxidized in use, resulting in the degradation of the mechanical properties. Composite TiN/AlN films have the advantage that the alumina formed on oxidation protects the film from the further oxidation. However, the oxidation of exposed surface TiN is not avoided. It is of interest to produce compositionally graded (CGed) films of AlN–TiN with AlN and TiN on the respective surface and substrate, accompanied by complementary changes of Al and Ti contents in the film. These are expected to show high resistance to oxidation, because if the AlN exposed on the surface is oxidized, the resulting oxidation-resistant alumina covers the film and prevent oxidation of the TiN. This idea can also be applied to the preparation of CGed films of Si₃Nₓ–TiN, with the improved hardness and high oxidation resistance of Si₃Nₓ. However, it seems difficult to make the compositions of Ti and Al/Si complementarily change in a film of a few microns in thickness. The present report describes the first preparation of compositionally graded
films of TiN–AlN and TiN–Si₃N₄ of a few microns in thickness from mixed alkoxide solutions by liquid injection PECVD. The electrical resistivity of the CGed films was measured and compared with that of pure TiN.

2. Experimental procedure

2.1 Preparation of CGed films

A schematic diagram of the r.f. thermal plasma apparatus (JHS–15M, JEOL) is shown in Fig. 1. The plasma was composed of a mixture of Ar/N₂/H₂ as the outer tangential gas and Ar as the inner tangential gas; these gases were also used to spray the mixed alkoxide solutions into the plasma flame. A water-cooled holder supporting the substrate for film deposition was located at the center of the chamber. The temperature, which was measured at a tip of the holder with a thermocouple, was about 700°C, depending on the shape of plasma, which was affected by the N₂ flow rate. The further details are reported elsewhere.¹⁵

Titanium-tetra-ethoxide (Ti(OCH₃)₄, TTEO), aluminum-tri-buthoxide (Al(OC₄H₉)₃, ATBO), and hexa-methyl disiloxane ((CH₃)₃SiOSi(CH₃)₃), HMDS) were used as starting materials for the preparation of the CGed TiN–AlN and TiN–Si₃N₄ films. A stabilizing agent of tri-ethanol-amine (N(CH₂CH₂OH)₃, TEA)) was added to mixed solutions of TTEO and ATBO or TTEO and HMDS to prevent precipitation of the hydroxide. Each alkoxide was dissolved in dried ethanol or toluene at a molar ratio of 1:1 to 1:3. Two kinds of CGed AlN–TiN films were prepared; AlN and TiN deposited on the surface and substrate, respectively, with complementary change of Al and Ti in the film (designated AlN/TiN), and vice versa (TiN/AlN). Two kinds of CGed TiN–Si₃N₄ films were also prepared (Si₃N₄/TiN and TiN/Si₃N₄). For the CGed films to be prepared, the feeding rate of the two alkoxide solutions was complementarily changed with time, maintaining the total feeding rate at 0.1 ml min⁻¹ using two HPLC pumps (GULLIVER PU–980, JASCO corporation), as shown in Fig. 2. For the CGed AlN/TiN films, for example, the TTEO solution was fed into the plasma for the first 25 min at a rate of 0.1 ml min⁻¹, after which the feeding rate of the TTEO was decreased with time for 20 min while increasing the feeding rate of the ATBO solution, and the ATBO solution alone was fed for the last 25 min. The substrate used in this experiment was the (100) face of Si wafer (10 mm diameter × 0.5 mm thick), which had been treated with 46% HF solution for 10 min, followed by ultrasonic cleaning in acetone, ethanol, and deionized water and successive drying at 50°C.

2.2 Characterization

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 N, Ti, Al, Si, O, and C were determined by X-ray photoelectron spectroscopy (XPS) (Shimadzu 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 ratios. The surface and cross-section of the film were observed by scanning electron microscopy (SEM) (JEOL, JSM–6300F). The thickness of the film was determined from the cross-sectional SEM observation. The electrical resistivity of the compositionally graded films was measured parallel to the substrate using a four-probe method at room temperature.

3. Results and discussion

3.1 Compositionally graded TiN–AlN films

As described above, two kinds of CGed AlN–TiN films were prepared, with AlN and TiN on the respective surface and substrate, and vice versa. Figure 3 shows the XRD patterns of CGed AlN/TiN and TiN/AlN films. Sharp peaks of AlN and TiN are observed in the two films, probably because they are thin (about 1 μm). The composition of N, Al, and Ti, and the impurities O and C in the AlN/TiN film was analyzed as a function of depth by etching (Fig. 4). The surface AlN layer removed at the etching times less than 20 min is contaminated with much oxygen and carbon. In samples etched for more than 20 min, the N content is increased, maintaining the atomic percentage at 23–34 at.%. It is deserved that the Al content continuously decreases from 38 to 10 at.%, in contrast to the Ti content which complementarily increases from 5 to 28 at.%. The impurity O content is high in the film, but decreases to 14 at.%) near the substrate. Carbon is also present at a level of 8 at.% in the...
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Fig. 3. XRD patterns of compositionally graded AlN//TiN and TiN//AlN films. x, unidentified peak.

Fig. 4. Changes in the depth direction of atomic percentages of N, Ti, Al, O, and C in AlN//TiN films. ▲ N, ▼ Al, ■ Ti, ◊ O, ○ C.

Figure 5 shows the composition change of the CGed TiN//AlN film. Much oxygen is also present (42 to 13 at.%) in the film etched for 20 min, resulting in an insufficient region of Ti and N. After 20 min etching, the N content is maintained at a level of 34–39 at.%, with the O suddenly decreasing to 13 at.% and leveling off. The Ti content is maintained at 30–34 at.% and decreases gradually after 20–100 min etching, in contrast to the Al content which complementarily increases from 4 at.% on the surface to 40 at.% near the substrate. The carbon is maintained at 6–13 at.%, gradually decreasing toward the substrate. It is concluded that the CGed AlN//TiN and TiN//AlN films are formed, with complementarily changing contents of Ti and Al, and vice versa, even though a certain amount of the O and C impurities are present. The bonding states of O were determined from the O1s XPS spectra, showing the presence of TiO2 and Al2O3 at 530.5 and 532.0 eV, respectively, in both films, which also changed complementarily with depth. The existence of TiO2 and Al2O3 was also confirmed by the results in the Ti2p XPS spectrum at about 2.5 eV higher than the Ti2p peak assigned as TiN (called a satellite peak) and at 532.0 eV in the Al2p XPS spectrum of the whole film. The C1s spectra showed the existence of TiC and free carbon peaks at 282.0 and 284.6 eV, respectively, in the film rich in TiN. Al4C3 and free carbon peaks were detected at 282.5 and 284.5 eV, respectively, in the Al2p and C1s XPS spectra of the film rich in AlN.

The surface and cross section of both AlN//TiN and TiN//AlN films were observed by SEM (Fig. 6). The film is about 1 µm thick. In the AlN//TiN film (Figs. 6(A) and (A')), agglomerated cauliflower-like particles 0.5–1 µm in size, consisting of primary 0.1 µm sized particles, are formed on the surface. These cauliflower-like particles are also loosely packed together at the top surface. However, dense columnar particles are seen inside the films. In the TiN//AlN film, larger cauliflower-like particles 1–3 µm in size, consisting of regularly 0.2 µm-sized particles, are also seen on the surface. The cross-sectional observation shows the film to be 2 µm thick, containing large cauliflower-shaped particles lying on a lower layer consisting of relatively dense columnar particles. Interrupted growth observation of both films failed to show such cauliflower-shaped particles, but regular submicron-sized particles were observed. Therefore, it seems that the cauliflower-shaped particles are formed as a result of sudden growth from these small particles acting as nuclei at extended growth times.

3.2 Compositionally graded TiN–SiNx films

Figure 7 shows the XRD patterns of CGed SiNx//TiN and
TiN//SiNₓ films prepared from mixed solutions of HMDS and TTEO containing stabilizing TEA. It is seen that the diffraction peaks of TiN appear in both films, but no peak related to silicon nitrides is found. As shown by Nₓ XPS of the etched SiNₓ//TiN film (Fig. 8), the Si–N bonding can be recognized at 397.5 eV in sample etched for 25 min, after which the peak decreases or overlaps with that of Ti–N; a similar trend was seen in Si₂p XPS, showing that the Si–N peak appeared at 102.0 eV, which became smaller with depth and diminished near the substrate. Therefore, it is concluded that amorphous silicon nitride is formed in the whole film, designated as SiNₓ.

Changes of the concentrations of N, Si, Ti, O, and C with depth in the SiNₓ//TiN film are shown in Fig. 9. The first 10 min of etching removed the concentrated impurities O and C from the SiNₓ surface. After removal of the impurities, the N content increases to 46 at.%, becoming constant with depth. Concomitantly, the Si content rises to 38 at.%, then gradually decreases from 30 at.% over two-thirds of the film depth towards the substrate. The Ti content then drops steeply to 3 at.%, in contrast to the Ti which concomitantly increases to 35 at.% near the substrate. The O and C impurities occur at less than 6 at.% over most of the film depth, but increase slightly near the substrate. Similar trends in the change of the composition were observed in the TiN//SiNₓ films (Fig. 10). After removing the contaminating O and C at the TiN surface, the N content becomes almost constant at 44–48 at.% over the whole film. The Ti rises to the relatively lower level of 26 at.%, decreasing with depth, while the Si exists at 10 at.%, increasing with the decrease of Ti. In both films, the Ti content in the whole film was less than expected, suggesting that this component is more difficult
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than Si to incorporate into the film. It was found that the compositionally graded SiN\textsubscript{x}/TiN films, and vice versa, can be formed by liquid injection plasma CVD method using the alkoxide solutions. The O and C impurities result from TiO\textsubscript{2}/SiO\textsubscript{2} and TiC/SiC/free carbon, as indicated by Ti\textsubscript{2p}, Si\textsubscript{1s}, and C\textsubscript{1s} XPS spectra.

Cross-sectional observations of SiN\textsubscript{x}/TiN and TiN/SiN\textsubscript{x} films are shown in Fig. 11. Spherical particle 3 µm in size are formed on the outermost surface of the SiN\textsubscript{x}/TiN film, beneath which ≈1 µm particles are seen. As observed from Fig. 9, these particles can be regarded as amorphous SiN\textsubscript{x}. The cross-section shows the film to be 3 µm thick and dense, containing particles piled up from the substrate and growing larger toward the surface. Agglomerated particles 1-3 µm size composed of 0.3 µm grains are formed at the surface of TiN/SiN\textsubscript{x} film, similarly to TiN/AIN film. The film is 3 µm thick and shows to be dense near the substrate.

3.3 Electrical resistivity of the CGed films

Table 1 shows the electrical resistivity of the four CGed films. As reported in our previous paper, the pure TiN film prepared from TTEO without TEA stabilizer showed an electrical resistivity around 300 µ\textOmega cm. The addition of TEA greatly reduced the value to 60-80 µ\textOmega cm, as listed in Table 1. The resistivity of the AIN/TiN and TiN/AIN films is one and two order of magnitude larger, respectively, than the pure TiN film. The resistivity value of the CGed AIN/TiN or SiN\textsubscript{x}/TiN film is smaller than that of TiN//

AlN or TiN//SiN\textsubscript{x}, suggesting that the surface effect of the TiN phase with a high electrical conductivity is not reflected in the CGed film, probably because the higher concentrations of O and C impurities are concentrated near the surface.

4. Summary

Compositionally graded AlN/TiN and SiN/TiN films were prepared on Si substrates at about 700°C by plasma CVD capable of injecting mixed solutions of Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, Al(OC\textsubscript{4}O\textsubscript{7})\textsubscript{3}, and/or (CH\textsubscript{3})\textsubscript{3}SiOSi(CH\textsubscript{3})\textsubscript{3} containing stabilizing solution of N(CH\textsubscript{2}CH\textsubscript{2}OH)\textsubscript{3} into thermal Ar/N\textsubscript{2}/H\textsubscript{2} plasma. A complementary change of Ti and Al, and Si and Ti contents with depth was achieved by changing the feeding rate of each alkoxide solution with time. By this means, it was possible to prepare the CGed AIN//TiN films with the AlN and TiN compositions on the respective surface and substrate, accompanied by complementary changes of Al and Ti with depth, and vice versa. Similarly, the CGed SiN\textsubscript{x}/TiN and TiN/SiN\textsubscript{x} films were prepared by this liquid injection CVD method. The films achieved a thickness of 1-3 µm and show the formation of cauliflower-like agglomerated particles consisting of fine 0.2-0.3 µm-sized particles on the surface. Columnar and dense microstructure was observed in the deeper region of the CGed AIN//TiN and SiN\textsubscript{x}/TiN films, respectively. The electrical resistivity of the films changed from 300 to 7 x 10\textsuperscript{4} µ\textOmega cm, depending on the type of the CGed films.

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Table 1. Electrical Resistivity of Compositionally Graded Films (µ\textOmega cm)

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<th></th>
<th>pure TiN\textsuperscript{1}</th>
<th>pure TiN\textsuperscript{2}</th>
<th>TiN/AlN</th>
<th>AIN/TiN</th>
<th>SiN\textsubscript{x}/TiN</th>
<th>TiN/SiN\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure TiN\textsuperscript{1}</td>
<td>300</td>
<td>60 - 80</td>
<td>1 x 10\textsuperscript{4}</td>
<td>1 x 10\textsuperscript{3}</td>
<td>300</td>
<td>7 x 10\textsuperscript{4}</td>
</tr>
<tr>
<td>pure TiN\textsuperscript{2}</td>
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\textsuperscript{1}prepared without TEA, \textsuperscript{2}prepared with TEA
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