Study on plasma assisted metal-organic chemical vapor deposition of Zr(C,N) and Ti(C,N) thin films and in situ plasma diagnostics with optical emission spectroscopy


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Zr(C,N) and Ti(C,N) films were synthesized by pulsed dc plasma assisted metal-organic chemical vapor deposition method using metal-organic compounds of tetrakis diethylamido titanium and tetrakis diethylamido zirconium at 200–300 °C. To change the plasma characteristics, different carrier gases such as H2 and He/H2 were used and, as the reactive gas, N2 and NH3 were added to the gas mixture. The effect of N2 and NH3 gases was also evaluated in the reduction of C content of the films. Radical formation and ionization behaviors in plasma were analyzed by optical emission spectroscopy and mass spectrometry at various pulsed biases and gas conditions. The gas mixture of He and H2 as the carrier gas was very effective in enhancing the dissociation of molecular gases. In the case of N2 addition, N2 as reactive gas resulted in higher hardness. However, NH3 as reactive gas highly reduced the formation of CN radical, thereby greatly decreasing the C content of Zr(C,N) and Ti(C,N) films. The hardness of the film is 1400–1700 HK depending on gas species and bias voltage. Higher hardness can be obtained for a H2 and N2 gas atmosphere and bias voltage of ~600 V. Plasma surface cleaning using N2 gas prior to deposition appeared to increase the adhesion of films on steel. The changes of plasmas including radicals and film properties are illustrated in terms of carrier and reactive gases, as well as pulsed power variation. © 2008 American Vacuum Society. [DOI: 10.1116/1.2944262]

I. INTRODUCTION

Zirconium nitride (ZrN) and titanium nitride (TiN) thin films have useful properties including high hardness, good electrical conductivity, high melting point, and chemical inertness.1 Applications include wear-resistant hard coatings on machine tools and bearings, decorative coating making use of the golden color thermal-control coatings for windows, and erosion-resistant coatings for spacecraft plasma probes.2,3 However, an important new application of ZrN and TiN is as a diffusion barrier layer for metallization in integrated circuits due to its low diffusion rate and good electrical conductivity.4 For all these applications, as feature sizes shrink and aspect ratios grow, the issue of good step coverage becomes increasingly important. It is therefore essential to manufacture conformal coatings of ZrN and TiN.

The growth of ZrN and TiN thin films by chemical vapor deposition (CVD) is of great interest for achieving conformal deposition. The most widely used precursors for ZrN and TiN film growth are ZrCl4 and TiCl4, and these processes usually provide good film quality and excellent step coverage.5,6 However, chlorine impurity in the as-grown films and relatively high deposition temperature (>600 °C) are considered major drawbacks for actual device fabrication. To overcome these problems, metal-organic chemical vapor deposition (MOCVD) processes, including plasma assisted MOCVD, have recently been suggested.7–11 One of the most widely investigated precursors in ZrN and TiN CVD is tetrakis diethylamido zirconium (TDEAZ) and tetrakis diethylamido titanium (TDEAT). TDEAT-based TiN, for example, offers low deposition temperature and is free of chlorine contamination in the film with moderate step coverage compared to TiCl4-based CVD TiN. However, TiN CVD of the TDEAT precursor suffers significant carbon impurity in the films, causing high resistivity. Therefore, improved film quality using N2/H2 and NH3/H2 plasma or rapid thermal nitration of metal-organic-precursor-based ZrN and TiN films is highly desired.

In this study, we tried to grow Zr(C,N) and Ti(C,N) thin films with high hardness and low carbon content on D2 steel and Si(100) substrates at temperature as low as 200 °C by pulsed dc plasma assisted metal-organic chemical vapor deposition (PA-MOCVD) using the metal-organic (MO) compounds of TDEAZ and TDEAT. To understand the gas-phase reaction chemistry of the MO compounds in the plasma, an in situ plasma diagnostic study was carried out by optical emission spectroscopy (OES) and mass spectrometry (MS) at various pulsed bias voltages and gases conditions. The advantage of pulsed dc PA-MOCVD applied in this study is to grow the Zr(C,N) and Ti(C,N) thin films with fine surface morphology and good step coverage at very low deposition temperature compared to other deposition processes.

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TABLE I. The general deposition conditions of Ti(C,N) and Zr(C,N) films used in this work.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ti(C,N)</th>
<th>Zr(C,N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge voltage (V)</td>
<td>−500 to −700</td>
<td>−500 to −800</td>
</tr>
<tr>
<td>Pulse duration (%)</td>
<td>30–50</td>
<td>30–50</td>
</tr>
<tr>
<td>Pulse frequency (kHz)</td>
<td>10</td>
<td>10–40</td>
</tr>
<tr>
<td>Working pressure (Pa)</td>
<td>133</td>
<td>133</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>200–300</td>
<td>200–300</td>
</tr>
<tr>
<td>He/H₂ flow (SCCM)</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>N₂, NH₃ flow (SCCM)</td>
<td>0–10</td>
<td>0–50</td>
</tr>
<tr>
<td>Deposition time (h)</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

II. EXPERIMENT

MOCVD is carried out in a homemade pulse dc PA-MOCVD system to deposit ZrN and TiN thin films. Si(100) and D2 steel were used as the substrates, cleaned and etched using the standard procedure. After cleaning the samples, the substrates were treated with Ar and N₂ plasmas sequentially to make an oxygen-free surface and nucleation sites for ZrN and TiN, respectively. The process of plasma surface cleaning using N₂ gas prior to deposition appears to increase the adhesion of the films on D2 steel. The deposition was carried out for 0.5–1 h at deposition temperatures of 200–300 °C. The temperatures of the substrate were detected by an optical pyrometer. The general process conditions for film deposition are −500 to −800 V discharge voltage, 30%–50% dc pulse duration, 10–40 kHz dc pulse frequency, and 100–200 SCCM carrier gas with 0–50 SCCM N₂ or NH₃ bubbler gas at 133 Pa working pressure. Table I shows the general deposition conditions for the ZrN and TiN films.

Two MO compounds of tetrakis diethylamido titanium (Ti(NEt₂)₄, TDEAT) and tetrakis diethylamido zirconium (Zr(NEt₂)₄, TDEAZ) were used as precursors for growing TiN and ZrN thin films. To understand the gas-phase reaction chemistry of the MO compounds in the plasma, the plasma diagnostics were carried out in situ using OES and MS at various pulsed bias voltages and gas conditions. The films produced by pulsed dc-MOCVD were characterized by x-ray photoelectron spectroscopy (XPS), x-ray diffraction, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The microhardness was also checked with a micro-Knoop hardness tester.

III. RESULTS AND DISCUSSION

A. Study on plasma characteristics and diagnostics

The measurement of plasma density is important in understanding the coating process and gas-phase reaction. The electron temperature can be obtained from the plasma density and has a meaning of an average energy of plasma that occurs from the gas-phase reaction discharges. Therefore, understanding the plasma density and electron temperature is an important factor for thin-film growth and MO precursor decomposition during PA-MOCVD. It is well known that plasma density does not depend on pressure and bias voltage, but it can be influenced by the electron temperature. In our previous results,11 we reported that with increasing bias voltage, plasma density remained constant while electron temperature increased. In the case of N₂–H₂ gas reaction, relatively higher electron temperatures can be made due to the difference of their first ionization potential when He gas is used rather than without that gas. In a plasma state, the ionization of hydrogen gas occurred at a rather lower energy compared to that of helium due to relatively low ionization potential. Thus, the plasma density of hydrogen is higher than that of He at similar process conditions. Nitrogen can also be ionized at a low potential and thus have a high plasma density.

Optical emission spectroscopy is a powerful tool for controlling the coating process and for optimizing both the layer properties and coating process. In this study, therefore, OES was used as a qualitative in situ diagnostic method. By measuring the intensity of the spectral lines it is possible to identify the density of the excited state, by assuming that the
electron density in the plasma remains nearly constant for the experimental conditions. Figure 1 shows the experimental results from the emission spectroscopy during the coating processes for ZrN(a) and TiN(b) thin-film growth, respectively. Figure 1(a) shows the typical OE spectra obtained from ZrN coating processes under bias voltages of −500 and −600 V with different reaction chemistries of Zr–MO systems. The other typical OE spectra obtained from TiN coating processes under bias voltage of −500 V and different gas-phase reaction chemistries of Ti–MO systems are also shown in Fig. 1(b). Figures 2(a) and 2(b) show the variations of relative plasma intensities obtained from Figs. 1(a) and 1(b), respectively, as a function of gas-phase reaction chemistry. In Figs. 2(a) and 2(b), two important observations can be made from our OES study. One is that the maximum plasma intensity was obtained when the He/H2–N2 mixture gas was used and He might play an important role in enhancing the intensity. The other is that in contrast to the H2–N2 mixture, NH3 decreases the plasma density of the CN radical and increases CHx and NH radicals; therefore, it can be expected to decrease carbon content in the films. Because Fig. 1(b) was obtained under a gas-phase reaction condition of 1 Torr and −500 V with different chemistries, the data showed the same behavior as Fig. 1(a), where He will be influenced with increasing electron temperature [see Figs. 2(c) and 2(d)]. This means that the He/H2 mixed gas has a higher electron temperature than H2 gas, and the highest electron temperature can be obtained using NH3, indicating an effective metal-ligand bond cracking.11 In addition, the electron temperature is increased with increasing bias voltage [see Fig. 2(c)]. We thus know conclusively that the relation between electron density (or plasma density) and electron temperature has a contradictory trend with different gas-phase reaction chemistries applied in this study.

Another noticeable thing is that the OES results correlate to layer properties such as surface topography and microhardness. In Figs. 1(a) and 1(b), several excited lines occurred in the discharge at different wavelengths. By comparing the experimentally observed lines by OES with theoretical spectroscopic data, we can identify some important lines. For example, the excited lines at about 337.0, 387.0, and 425.0 nm are attributed to the transitions by NHI, CNI, and CHI, respectively. From our OES experiments, we found that only some species, such as CN, CH, and NH, among all observed lines are the most important as the main indicator determining the layer properties during the coating.
The surface morphologies of the as-grown Ti(C,N) films deposited on D2 steel at 200 °C and −500 V under different plasma chemistry conditions such as (a) He/H2–N2–TDEAT and (b) He/NH3–TDEAT showed a very smooth appearance, as shown in Figs. 4(a) and 4(b). However, the domed microstructure, which is one of the typical surface structures for PA-MOCVD top layers of TiN, as well as TiC, was detected in this work when H2–NH3–TDEAT and He/H2–N2–TDEAT [Fig. 4(a)] reaction chemistry was used. This suggests that H2–NH3 and He/H2–N2 as carrier and reactive gases are not proper for making very smooth surface morphology compared to H2–N2 and He/H2–NH3 systems. This is consistent with the results of OES, XPS, and microhardness measurements, which showed good chemical stability and relatively high hardness for the reaction chemistry of H2–N2–TDEAT, although the carbon content in the film surface is slightly higher compared to that of H2–NH3–TDEAT. The thickness of the as-grown film is about 500 nm according to the cross-sectional SEM measurement. As reported by Eizenberg et al., this good conformability is due to MOCVD Ti(C,N) deposition under conditions in which the surface reaction is controlled in the temperature range 200–300 °C.

The compositions of as-grown films were determined with XPS. Figure 4(c) shows a composition variation of the typical Ti(C,N) film measured by XPS analysis as a function of gas-phase reaction chemistry. The analysis yielded the following stoichiometry: 19.2 at. % Ti, 19.9 at. % N, 58.8 at. % C, and 2.1 at. % O, in the film deposited from H2–N2–TDEAT. A similar composition (not shown here) was obtained: 19.2 at. % Ti, 21.7 at. % N, 57.1 at. % C, and 2.0 at. % O, in the films deposited from H2–NH3–TDEAT. These results are very similar to another report, where the addition of NH3 to the TDEAT led to a decrease in carbon content and an increase in nitrogen content in TiN films. Therefore, it is confirmed that the NH3 reductive reaction in a low-pressure condition causes a decrease in C content in the TiN films. This can be explained with our OES data; that

process. Good layer properties were achieved only for a deposition temperature of 200 °C and the reaction chemistry of He/H2–N2 systems. The highest hardness values obtained for the Ti(C,N) and Zr(C,N) films in He/H2–N2 reaction chemistry were about 1760 and 1680 HK 0.01, respectively [see Figs. 4(d) and 5(d)]. However, by increasing the intensities of CN and CH radicals of dissociated MO compounds in the plasma, the concentrations of CH, C2H, and CNH residual gases are also increased, resulting in the increase in carbon content in the films. With mass spectroscopy, we confirmed gas species in the plasma. Figure 3(a) shows typical mass spectra taken during ZrN film growth under different plasma chemistry conditions. In addition to hydrogen and helium mass peaks, two more peaks at mass numbers of 15 and 28 are observed in the lower picture of Fig. 3(a) due to CH3− radical and N2 molecules, respectively. However, when gas was used as the reactive gas, in the upper picture of Fig. 3(a), three additional mass spectra are clear in the mass range 16–18. We analyzed these spectra as NH2, NH3, and possibly water species, respectively. As shown in Fig. 3(b), we also measured mass spectra during TiN film growth under different plasma chemistry conditions. With increasing negative bias voltage from 500 to 700 V, the mass peak at about m/z = 27, which may be attributed to C2H2−x (x = 0, 1, 2) and/or CNH2−x (x = 0, 1) radical species and directly influenced into carbon and nitrogen contents resulting in different hardness, increases while the other peaks remain constant in intensity. This is in good agreement with our OES results. The CH radical increases the microhardness, but the CN radical decreases the hardness [see Figs. 4(d) and 5(d)]. This is also in good agreement with previous reports that a reduction of the microhardness of films is monitored in situ by the intensity of the plasma-induced optical emission of the CN radical at 387.14 nm. Moreover, the intensity of the CN radical is proportional to the carbon content of the film layer, and the NH3 reactive gas decreases the carbon content but does not effectively increase the hardness. With He and NH3, however, the intensity of CH and NH was increased; otherwise, the CN radical decreases under relatively low bias voltage. Thus, the importance of the CH, CN, and NH species is proved by the correlation with the layer properties in our study. Moreover, plasma surface cleaning using N2 gas prior to deposition appeared to increase the adhesion of as-grown films.

B. Growth of Ti(C,N) and Zr(C,N) thin films

The surface morphologies of the as-grown Ti(C,N) films deposited on D2 steel at 200 °C and −500 V under different plasma chemistry conditions such as (a) He/H2–N2–TDEAT and (b) He/NH3–TDEAT were about 1760 and 1680 HK 0.01, respectively [see Figs. 4(d) and 5(d)]. However, by increasing the intensities of CN and CH radicals of dissociated MO compounds in the plasma, the concentrations of CH, C2H, and CNH residual gases are also increased, resulting in the increase in carbon content in the films. With mass spectroscopy, we confirmed gas species in the plasma. Figure 3(a) shows typical mass spectra taken during ZrN film growth under different plasma chemistry conditions. In addition to hydrogen and helium mass peaks, two more peaks at mass numbers of 15 and 28 are observed in the lower picture of Fig. 3(a) due to CH3− radical and N2 molecules, respectively. However, when gas was used as the reactive gas, in the upper picture of Fig. 3(a), three additional mass spectra are clear in the mass range 16–18. We analyzed these spectra as NH2, NH3, and possibly water species, respectively. As shown in Fig. 3(b), we also measured mass spectra during TiN film growth under different plasma chemistry conditions. With increasing negative bias voltage from 500 to 700 V, the mass peak at about m/z = 27, which may be attributed to C2H2−x (x = 0, 1, 2) and/or CNH2−x (x = 0, 1) radical species and directly influenced into carbon and nitrogen contents resulting in different hardness, increases while the other peaks remain constant in intensity. This is in good agreement with our OES results. The CH radical increases the microhardness, but the CN radical decreases the hardness [see Figs. 4(d) and 5(d)]. This is also in good agreement with previous reports that a reduction of the microhardness of films is monitored in situ by the intensity of the plasma-induced optical emission of the CN radical at 387.14 nm. Moreover, the intensity of the CN radical is proportional to the carbon content of the film layer, and the NH3 reactive gas decreases the carbon content but does not effectively increase the hardness. With He and NH3, however, the intensity of CH and NH was increased; otherwise, the CN radical decreases under relatively low bias voltage. Thus, the importance of the CH, CN, and NH species is proved by the correlation with the layer properties in our study. Moreover, plasma surface cleaning using N2 gas prior to deposition appeared to increase the adhesion of as-grown films.
is, the NH₃ as reactive gas highly reduces the formation of the CN radical and increases CHₓ and NH radicals, thereby greatly decreasing the C content and increasing the N content in the Ti(C,N) films. Very similar behavior has also been observed in Zr(C,N) films. However, because the intensity of the CN radical is proportional to the carbon content in the film layer, the NH₃ did not effectively increase the hardness. Because the He and H₂ mixture gas is very effective in enhancing the ionization of radicals, only the CH radical among CN, CHₓ, and NH radicals increases the microhardness, especially N₂, resulting in high hardness. Thus, a film with higher hardness can be expected for H₂ and N₂ gas-phase reaction chemistry.

The hardness of the Ti(C,N) and Zr(C,N) layers, shown in Figs. 4(d) and 5(d), ranges from 1400 to 1700 HK 0.01 in our work, and is influenced by the carbon content in the layers, as also found by Rie et al.¹⁵ They argued that the bonding state of the carbon influences the hardness of the layers, and polymeric carbon reduces the hardness of the layers compared with carbidic carbon. As the C–C bonds in the layer increase, the hardness decrease and spalling may occur. This is also confirmed with FTIR measurements [see Fig. 5(c)], which show that the more the C=C intensity, the higher the hardness. However, the ratio of C/Ti and O/Ti did not vary as much with deposition temperature compared to that of N/Ti, indicating no noticeable incorporation of carbon and oxygen from either precursors or air with the as-grown films. The hardness values, obtained for the Ti(C,N) and Zr(C,N) films under the same He/H₂–N₂ reaction chemistry, were changed from 1360 to 1680 HK 0.01 with increasing bias voltage from -600 to -800 V; while the hardness value obtained under NH₃–H₂ reaction chemistry without and with He/He/H₂–N₂ remained almost constant in the range 1250–1350 HK 0.01 [see Figs. 4(d) and 5(d)]. Two typical observations are found: One is that He and H₂ mixture, which can enhance the ionization of radicals (especially N₂), could increase the hardness as much as 300 HK 0.01. The other one is that N₂ will be more effective to improve hardness rather than NH₃, and the flow rate of NH₃, which is only effective in reducing carbon contents due to attenuation of CN species formation, does not change the hardness in great deal. The surface morphology of the Zr(C,N) layers deposited under different bias voltages and plasma chemistries such as He/H₂–N₂–TDEAZ at -500 V and He/H₂–NH₃–TDEAZ at -700 V, linked with a domed appearance of the surface topography, changed from a rough
surface to a very smooth surface topography at higher discharge voltages [Figs. 5(a) and 5(b)]. The most ultrafine surface structure was obtained from a Zr\(\text{C,N}\) film deposited with both He/\(\text{H}_2\)–N\(_2\)–TDEAZ [Fig. 5(a)] and He/\(\text{H}_2\)–N\(_2\)–TDEAZ (not shown) at bias voltage of −600 V. Moreover, the \(\text{H}_2\)–N\(_2\) system might play an important role in growing smoother surfaces than those of \(\text{H}_2\)–NH\(_3\) (not shown) or He/\(\text{H}_2\)–NH\(_3\) [Fig. 5(b)] systems. This agrees with previous report\(^{16}\) and indicates that the plasma during deposition, which contains particle energies and densities, can determine the nucleation and growth of the layer.

**IV. CONCLUSIONS**

We deposited Ti\(\text{C,N}\) and Zr\(\text{C,N}\) thin films on Si\(100\) and D2 steel substrates by pulsed dc plasma assisted metal-organic chemical vapor deposition in the temperature range 200–300 °C using tetrakis diethylamido titanium and tetrakis diethylamido zirconium. Very smooth Ti\(\text{C,N}\) and Zr\(\text{C,N}\) films with low carbon and oxygen contents were deposited on the D2 steel surface at temperatures as low as 200 °C. From XPS analysis, a film composition with low oxygen concentration was obtained from the film deposited with \(\text{H}_2\)–NH\(_3\)–TDEAT. Moreover, films grown at higher temperatures by changing gas-phase reaction chemistry also showed nearly the same oxygen concentration, suggesting the stability of the as-grown films.

\(\text{H}_2\) and He+\(\text{H}_2\) gases were used as carrier gases to compare plasma parameters and the effect of \(\text{N}_2\) and \(\text{NH}_3\) gases as reactive gas was also evaluated in the reduction of C content of the films. In this study, we found that He and \(\text{H}_2\) mixture gas is very effective in enhancing the ionization of radicals, especially N\(_2\), resulting in high hardness. However, \(\text{NH}_3\) gas highly reduces the formation of the \(\text{CN}\) radical, thereby greatly decreasing the C content of Ti\(\text{C,N}\) and Zr\(\text{C,N}\) films. The highest film hardness obtained was 1400 HK 0.01 to 1700 HK 0.01, depending on gas species and bias voltage. Plasma surface cleaning using \(\text{N}_2\) gas prior to deposition appears to increase the adhesion of films on cold-forming steel.

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