Low-temperature growth of Ti(C,N) thin films on D2 steel and Si(100) substrates by plasma-enhanced metalorganic chemical vapor deposition

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We have deposited Ti(C,N) thin films on Si(100) and D2 steel substrates in the temperature range of 200–300 °C using tetrakis diethylamidotitanium (TDEAT) and titanium isopropoxide (TIP) by pulsed dc plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD). Radical formation and ionization behaviors in plasma are analyzed in situ by optical emission spectroscopy at various pulsed bias voltages and gas conditions. H2 and He+H2 gases are used as carrier gases to compare plasma parameters, and the effect of N2 and NH3 as reactive gas is also evaluated by the reduction of the C content of the films. Polycrystalline Ti(C,N) thin films were successfully grown on either D2 steel or Si(100) surfaces with TDEAT at temperatures as low as 200 °C. For TIP, however, only TiOCN thin films were obtained on Si(100) substrates. The best deposition process is evident for H2 and N2 gas atmospheres and bias voltage of 600 V. The higher film hardness is about 1760 Hk 0.01, but depends on gas species and bias voltage. Compared to TiN films, the Ti(C,N) film grown by PEMOCVD has very good conformability; the step coverage exceeds 85%, with an aspect ratio of more than 3. © 2000 American Vacuum Society. [S0734-2101(00)17504-9]

I. INTRODUCTION

Titanium nitride (TiN) is one of the most studied coating materials among the nitrides because of its excellent wear resistance, chemical stability, and corrosion resistance in strong acids.1 Coated cutting tools and dies (for example, assorted cutting and forming tools coated with TiN, multilayer coatings, and sheet-metal dies coated with TiN and TiC thin films on D2 steel substrates) are representative of the widespread commercial use of this technology in machining and forming operations.2

The growth of TiN thin films by chemical vapor deposition (CVD) is of great interest for achieving conformal deposition. The most widely used precursor for TiN is TiCl4, and this process usually provides good film quality and excellent step coverage.3,4 However, chlorine impurity in the as-grown films and a relatively high deposition temperature (>600 °C) are considered major drawbacks in actual device fabrication. D2 steel which is a Fe alloy with a composition of C (1.5%), Cr (15.0%), Mo (1.0%), and V (1.0%) can easily start surface modification even at 300 °C. To overcome these problems, metalorganic CVD (MOCVD) processes, including plasma-enhanced MOCVD (PEMOCVD) have been suggested.5–7 PEMOCVD offers the possibility of a homogeneous overall coating at relatively low temperatures by activation of the process gas in an electrical discharge. Several recent studies have been done on the relationship between process parameters and layer properties; one process parameter is the use of a proper precursor.8–12

Tetrakis diethylamidotitanium (TDEAT)-based TiN offers a low deposition temperature and is free of chlorine contamination in the film with moderate step-coverage compared to CVD TiCl4-based TiN. Therefore, the improvement film quality using N2/H2 and NH3/H2 plasma or rapid thermal nitration of a TiN film based on a metalorganic precursor is highly desired.

In this study, we tried to grow TiN thin films with high hardness and low carbon content on D2 steel and Si(100) substrates at temperatures as low as 200 °C. A metalorganic compound such as TDEAT was mainly used with pulsed dc PEMOCVD. Titanium isopropoxide (TIP) was also needed to make TiN or Ti(C,N) thin films a substitutional metalorganic compound of TDEAT. To understand the gas-phase reaction chemistry of the MO compounds in the plasma, plasma diagnostics were carried out by optical emission spectroscopy (OES) at various pulsed bias voltages and gas conditions. The advantages of pulsed dc PEMOCVD, which was used in this study, are the growth of the Ti(C,N) thin films with fine surface morphologies and good step coverage at very low deposition temperatures compared with other deposition processes and conditions.

II. EXPERIMENTAL PROCEDURE

Thin films of Ti(C,N) and TiOCN were obtained by the PEMOCVD method, and a pulsed dc with pulse frequency of 10 kHz and duty ratio of 30%–50% was used to make plasma. D2 steel and Si(100) were used as substrates, which were cleaned and etched by the standard procedure. Prior to CVD, the substrate was preheated to 200 °C and sequentially treated with Ar and N2 plasma for 10 min under –600 V bias voltage. Sputtering with Ar plasma was used to make an oxygen-free, reformed surface. N2, which can play a very important role in growing good TiN thin films, was used as a

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seed and reactive gas for the growth of good surface layers to improve the hardness and adhesion between TiN thin films and substrates. The deposition was performed under the discharge voltage of −500 through −700 V, working pressure of about 500 mTorr, substrate temperature of 200−300 °C, bubbler temperature of 50−70 °C, carrier gas of 100−200 sccm, and reactive gas of 10−20 sccm. The deposition lasted 1 h.

Metalorganic compounds of tetrakis diethylamidotitanium (Ti[N(C2H5)2]4) (TDEAT) and titanium isopropoxide (Ti[OCH(CH3)2]4) (TIP) were used as a precursor for the growth of TiN and Ti(C,N) thin films, respectively. To understand the gas-phase reaction chemistry of the MO compounds in the plasma, single Langmuir probe and optical emission spectroscopy were used in situ for plasma diagnostics at various pulsed bias voltage and gas conditions. To characterize the composition ratio, surface morphologies, and hardness of the as-grown films, we used x-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray photo-electron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS), and a micro-Knoop hardness tester.

III. RESULTS AND DISCUSSION

A. Plasma diagnostics

The measurement of plasma density is important for understanding the coating process and the gas-phase reactions. The electron temperature can be obtained from the plasma density and provides a value for the energy of the plasma related to the gas-phase reaction discharge. Therefore, the plasma density and electron temperature are two of the important factors for understanding the thin-film growth and the MO-compound decomposition during the process.

In our PEMOCVD process, the plasma density showed a dependency with pressure and power, but was mainly affected by electron temperature. The electron density \( n_e \) for the general PECVD process is \( \sim 10^{10} \text{cm}^{-3} \). In our process, however, the value of \( n_e \) was in the range of \( 1.2 \times 10^{10} - 6.3 \times 10^{10} \text{cm}^{-3} \), depending on various gas-phase reaction chemistries. In the case of the N2−H2 gas reaction, relatively higher electron temperatures occur because of the difference in 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 lower energy than that of helium (He), because the ionization potential of H2 is relatively low. Thus, the electron and ion density of hydrogen observed was higher than that of He. Nitrogen can also cause electron radiation at low energy and thus have high plasma intensity. In the case of nitrogen, the first ionization potential is 15.5 eV and the energy of the metastable state is 8.5 eV. We also obtained the plasma variable for the same nitrogen magnitude as He/H2 or H2 as a carrier gas with bias voltage in the mixed gas phase. At first, the electron temperature of He/H2−N2 was almost 5 eV and that of H2−N2 was almost 4 eV. We confirmed that the electron temperature increased by changing bias voltages; the difference in electron temperature was about 1 eV with the change of carrier gas. Figures 1(a) and 1(b) show the variation of electron temperature in the plasma as a function of bias voltage [Fig. 1(a)] and of different gas-reaction chemistry [Fig. 1(b)]. However, the electron density of H2−N2 (1.2×10^{10}−1.4×10^{10} \text{cm}^{-3}) was higher than that of He/H2−N2 (8.9×10^{9}−1.2×10^{10} \text{cm}^{-3}). In conclusion, we know that the relation between electron (or ion) density and electron temperature contradicts the trend of different gas-phase reaction chemistries applied in this study.

Optical emission spectroscopy is a powerful tool with which to control the coating process and optimize the layer properties. In this study, 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. In the Ti(C,N) film growth, radicals of CN, CH, NH, and Balmer series\(^{13}\) of N2, N2+, He, H2, and H were observed, as shown in Fig. 1(c). Two important things were found. First, the maximum plasma intensity was obtained when He/H2−N2 mixture gas was used, and He may play an important role in enhancing the plasma intensity. Second, in contrast to the H2−N2 mixture, NH3 decreased the
plasma density of the CN radical and increased CH and NH radicals; therefore it can be expected to decrease the carbon content in the films. It is significant that the OES result is related to the layer properties, such as surface topography and microhardness. In our OES observation, we found that only some species, such as CN, CH, and NH, among all the observed radicals played an important role in determining the layer properties as the main indicator. We believe that CN radicals cause an increase in carbon magnitude and decrease in microhardness, whereas CH radicals cause a decrease in carbon magnitude and an increase in microhardness.

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

Figure 2(a) shows a typical x-ray diffraction pattern of a Ti(C,N) film grown on D2 steel at 200 °C with TDEAT MO compound. It shows a relatively strong TiCN(111) peak at 2θ = 35°, and the other peaks originate from the metal alloy substrate. This means that highly oriented polycrystalline film in the [111] direction was deposited on the D2 steel substrate. In Fig. 2(b), however, only weak diffraction peaks originating from TiN and TiO2 (or TiOCN) were observed from a thin film grown on a Si(100) substrate using TIP and Ar:N2:H2 = 3:1:1 gas conditions. However, stronger peaks appeared when the amount of N2 gas was increased by a factor of 2 [see the upper of Fig. 2(b)].

The surface morphologies of the as-grown Ti(C,N) films with nearly the same film thickness (~1 μm), shown in Figs. 3(a)–3(d), coated under various gas-phase reaction chemistries, were in general quite smooth. However, the domed microstructure was detected in this work when H2–NH3–TDEAT [Fig. 3(b)] and He/H2–N2–TDEAT [Fig. 3(c)] reaction chemistry were especially used, indicating buckling of the coating due to compressive stress. This suggests that H2–NH3 and He/H2–N2 as carrier and reactive gases are not suitable for making very smooth surfaces compared to those of the H2–N2 and He/H2–NH3 reaction 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, even though the carbon content in the film layers is greater than that of H2–NH3–TDEAT. Moreover, the H2–N2 system may play an important role in growing a smoother surface than the He/H2 system.

As for the carrier gas, H2 leads to better surface morphologies than He/H2. Thus, the Ti(C,N) film grown with
H₂–N₂–TDEAT reaction under −600 V of bias voltage shows the best surface condition, and this reaction improves the chemical stability. This indicates that film growth of a superior surface morphology at low temperature can be done using H₂–N₂–TDEAT reaction chemistry. Figures 3(e) and 3(f) are photographs of Ti(C,N) films grown on D2 steel using H₂–N₂–TDEAT and H₂–NH₃–TDEAT reaction chemistry, respectively. As shown in Fig. 3(e), the film is much darker than in Fig. 3(f), which means that the Fig. 3(f) film contains more carbon than the Fig. 3(e) film. This can be explained by the changes in the composition ratio shown in Fig. 4(e).

Figure 4(a) shows the XPS survey spectra obtained from the Ti(C,N) film grown on a Si(100) substrate at 200 °C with H₂–N₂–TIP under −600 V of bias voltage. Typical RBS data, shown in Fig. 4(b), were also obtained for a Ti(C,N) thin film that was grown under the same conditions as in Fig. 4(a) on a Si(100) substrate with H₂–N₂–TDEAT. In contrast to Fig. 4(b), O 1s peaks as well as Ti 2p, C 1s, and N 1s photoelectron peaks are also present in Fig. 4(a), indicating the possibility of TiOCN film formation. In the case of TDEAT, however, it exists only in the surface layers. The evidence is confirmed through the RBS data in Fig. 4(b), which shows no oxygen in the bulk of the film layer. Figure 4(c) shows a variation of the surface concentrations of titanium, nitrogen, and carbon measured by XPS and RBS analysis for the as-grown Ti(C,N) films that were grown with different reactive gases under conditions of −500 V, 50 μs pulse, 100 sccm of carrier gas, and 10 sccm of reactive gas. As shown in Fig. 4(c), when NH₃ is applied as a reactive gas with H₂+TDEAT, the carbon content in the film gave the smallest value (Ti:C:N = 1:2.5:1) among the three gas conditions. This indicates that, as shown in the Fig. 1(c), the CN radical in the plasma can affect the carbon content in the film layers. When TIP was used, however, the composition ratio of Ti to C is almost 4.5 times higher than that of Ti to N, and a considerable amount of oxygen was observed due to incorporation by the precursor itself during CVD.

Figure 5(a) shows the variation of microhardness of Ti(C,N) thin films grown under a bias voltage of −600 V with TDEAT. The hardness of the Ti(C,N) layers, which ranges from 1250 to 1760 Hk 0.01, is influenced by the carbon content in the Ti(C,N) layers. In this study, the greatest hardness, 1760 Hk 0.01, was obtained when H₂ and N₂ gas were used with TDEAT; the lowest hardness, 1250 Hk 0.01, was obtained with He/H₂ as a carrier gas and with NH₃ as a reactive gas. This can be explained by the different gas properties of reaction conditions between H₂–N₂ and He/H₂–NH₃; the H₂–N₂–TDEAT reaction is more chemically stable than the He/H₂–NH₃–TDEAT reaction. Because the H₂ gas is very effective in enhancing the ionization of radicals, only the CH radical among CN, CHₓ, and NH radicals increases the hardness; the H₂–N₂ mixture especially results in a high hardness. Thus, a film with higher hardness can be expected for the H₂ and N₂ gas-phase reaction. This is well predicted by OES analysis, and the bonding state of the carbon can influence the hardness of the layers and a polymeric carbon in the thin films may reduce the hardness. Using TIP, a maximum hardness of 1030 Hk 0.01 was obtained by a TiON thin film grown on a Si(100) substrate under the same conditions as those using TDEAT. Figure 5(b) shows the cross-sectional SEM image of a Ti(C,N) thin film grown on a stepped Si(100) substrate at 200 °C with H₂–N₂–TDEAT. As shown in Fig. 5(b), we obtained a Ti(C,N) film that has a uniform interface with film thickness of 500 nm, indicating quite good adhesion between the Ti(C,N) film layer and the substrate. Figure 5(b) also shows that the film has good step coverage. The reason for the appearance of good adhesion may be attributed to using N₂ gas prior to deposition and/or during deposition because the
III. EXPERIMENTAL

We have deposited Ti(C,N) and TiOCN thin films on D2 steel and Si(100) in the temperature range of 200–300 °C using MO compounds of TDEAT and TIP by PEMOCVD. Highly oriented polycrystalline Ti(C,N) film has been deposited on D2 steel with TDEAT, and poorly crystalline TiOCN films were also grown on Si(100) with TIP at temperatures as low as 200 °C. The as-grown Ti(C,N) films have fine surface morphologies and good step coverage, and the film thickness was 400–600 nm.

We found that H2 gas is very effective in enhancing ionization of radicals, especially the H2–N2 system, resulting in high hardness, whereas NH3 gas greatly reduces the C content of Ti(C,N) thin films. The best hardness, 1760 Hk 0.01, was obtained from a film deposited by H2–N2–TDEAT reaction chemistry. In contrast, the film with the lowest hardness, 1250 Hk 0.01, was grown under He/H2–NH3–TDEAT reaction chemistry. Plasma surface cleaning with N2 gas prior to deposition appears to increase adhesion of as-grown films.

IV. CONCLUSIONS

We have deposited Ti(C,N) and TiOCN thin films on D2 steel and Si(100) in the temperature range of 200–300 °C using MO compounds of TDEAT and TIP by PEMOCVD. Highly oriented polycrystalline Ti(C,N) film has been deposited on D2 steel with TDEAT, and poorly crystalline TiOCN films were also grown on Si(100) with TIP at temperatures as low as 200 °C. The as-grown Ti(C,N) films have fine surface morphologies and good step coverage, and the film thickness was 400–600 nm.

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