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REMOTE PLASMA ENHANCED METAL ORGANIC CHEMICAL VAPOR DEPOSITION OF TiN FOR DIFFUSION BARRIER

Ju-Young Yun and Shi-Woo Rhee†

Laboratory for Advanced Materials Processing (LAMP), Department of Chemical Engineering,
Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea
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Abstract – TiN films were deposited with remote plasma metal organic chemical vapor deposition (MOCVD) from tetrakis-diethyl-amido-titanium (TDEAT) at substrate temperature of 250-500°C and plasma power of 20-80 W. The growth rate using N_2 plasma is slower than that with H_2 plasma and showed 9.33 kcal/mol of activation energy. In the range of 350-400°C, higher crystallinity and surface roughness were observed and resistivity was relatively low. As the temperature increased to 500°C, randomely oriented structure and smooth surface with higher resistivity were obtained. At low deposition temperature, carbon was incorporated as TiC phase, as the deposition temperature increases, carbon was found as hydrocarbon. At 40 W of plasma power, higher crystallinity and rough surface with lower resistivity were obtained and increasing the plasma power to 80 W leads to low crystallinity, smooth surface and higher resistivity. It may be due to the incorporation of hydrocarbon decomposed in the gas phase. Surface roughness was found to be related to the crystallinity of the film.

Key words: MOCVD, TiN, TDEAT, Plasma, Diffusion Barrier

INTRODUCTION

Titanium nitride (TiN) is an important material in the advanced metallization for ultra large scale integrated (ULSI) circuits. It is used as a diffusion barrier to protect the shallow silicon junctions in the formation of Al contacts on Si because it is very hard and chemically stable [Price et al., 1993; Travis and Fiordalice, 1993; Harper et al., 1989; Roberts et al., 1995; Charatan et al., 1994].

Sputtered TiN was widely accepted for such purpose. However, with the decrease of feature size in silicon devices, physical vapor deposition like sputtering can not give a conformal coverage of a surface and chemical vapor deposition (CVD) process of TiN was required. The most widely studied precursors for CVD TiN are Titanium tetrachloride ($TiCl_4$), tetrakis-dimethyl-amido-titanium (TDMAT), and tetrakis-diethyl-amido-titanium (TDEAT). In these systems, Ti undergoes a one-electron reduction from Ti(IV) of the precursor to Ti(III) in TiN. Much efforts have been devoted toward CVD TiN using $TiCl_4$ [Ianno et al., 1990] and early processes utilized nitrogen and hydrogen at high deposition temperature of around 900-1200°C. Kurts and Gorden lowered the deposition temperature to around 500°C by using ammonia [Sherman, 1990]. But several problems limited the applications of $TiCl_4$ in device manufacturing. The deposition temperature in $TiCl_4$ chemistry was too high for the ULSI application and Cl incorporation in the film, especially at low deposition temperature (<500°C), was of major concern because of the corrosion problem.

In the process of MOCVD with NH_3, particle formation and poor conformality was a problem as a result of its high deposition rate [Prybyla et al., 1993]. To avoid this problem, thermal decomposition process using metal organic source without ammonia was studied. Chemical reaction of TDMAT can be written as

But in this system, hydrogen in ligands activated the bond between carbon and titanium and stable Ti-N-C three membered rings were formed, which leads to the incorporation of hydrocarbon [Lawrence and Bernard, 1992].

In this research, TiN film for a diffusion barrier with remote plasma enhanced MOCVD was studied. The aim of this study is to investigate the deposition conditions such as temperature and plasma power of the reactant on the deposition kinetics and material properties such as crystallinity, morphology and chemical structure of the film.

N_2 plasma was used as a reactant gas for preventing particle formation and breaking chemical bonds of metalcycles. In the selection of precursor between TDMAT and TDEAT, TDEAT was selected because it produced a high quality TiN film as reported in several publications [Raajimakers, 1994; Sun and Tsai, 1994]. By using plasma, we could generate activated species at low temperature and adjust the reaction pathway to reduce the contamination of the films from reaction byproducts [Kulish et al., 1993].

EXPERIMENTAL

Remote plasma MOCVD of TiN films was carried out in a cold wall, single wafer reactor and schematic diagram of the reaction system is shown in Fig. 1. The substrate used was p type Si(100) wafer. TDEAT, yellow liquid precursor at room

†To whom all correspondences should be addressed.

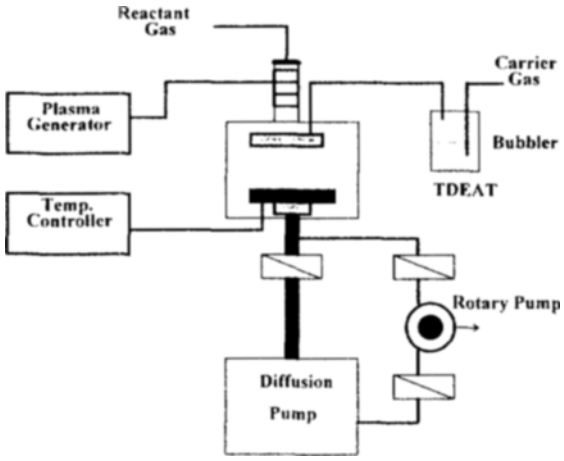


Fig. 1. Schematic diagram of MOCVD apparatus.

temperature, has a vapor pressure of 50 mTorr at 60°C, and was bubbled to be delivered to the reactor through the dispersal ring in the downstream. Nitrogen gas activated by remote plasma system was introduced from the upstream. Deposition was performed over the temperature and the plasma power range of 250-500°C and 20-80 W, respectively. The total pressure was 1 Torr and flow rates of carrier gas with TDEAT and reactant gas were fixed at 10 and 30 sccm, respectively.

Chemical structure was examined by X-ray photo electron spectroscopy (XPS) and the resistivity was measured with four point probe (Veeco Co.). Surface roughness and morphology of TiN films were observed with Autoprobe-CP atomic force microscopy (AFM) at a scan speed of 2 Hz. Structure of deposited films was analyzed with Rigaku D-MAX 1400 X-ray diffractometer (XRD) with Cu-Kα radiation operating at 50 kV and 150 mA.

RESULTS AND DISCUSSION

1. Deposition Rate

Fig. 2 shows temperature dependence of the deposition rate on Si surface, which would explain a growth mechanism by its activation energy for a certain temperature range. With N_2 plasma, 9.33 kcal/mol of activation energy for TiN deposition was obtained in the temperature range of 250-500°C and the deposition rate using H_2 plasma exhibited a similar behavior with Ea=9.70 kcal/mol. The deposition rate using N_2 plasma is lower than that with H_2 plasma. Overall reaction of TiN deposition from TDEAT can be written as

$$(C_2H_5)_2N\diagdown \quad \diagup N(C_2H_5)_2 \\ \quad\quad Ti \xrightarrow{N_2 \text{ or } H_2 \text{ plasma}} TiN(C)+HN(C_2H_5)_2+H_2NC_2H_5 \\ (C_2H_5)_2N\diagup \quad \diagdown N(C_2H_5)_2 \quad\quad +\text{other hydrocarbons}$$

and it is believed that the separation of diethylamino group by the attack of nitrogen radicals is slower than that by the attack of hydrogen radicals. The dependence of TiN deposition rate on the RF power is shown in Fig. 3. The deposition rate reached a maximum value and then decreased with an increase of rf power. At low power, an increase of the power enhanced the deposition rate by the generation of more reactive radicals. However, as the power was further increased, the rate was decreased. It is believed that the precursor was decomposed in the gas phase by the attack of increased nitrogen radicals with increasing RF power and those intermediate species did not participate in the deposition on the surface.

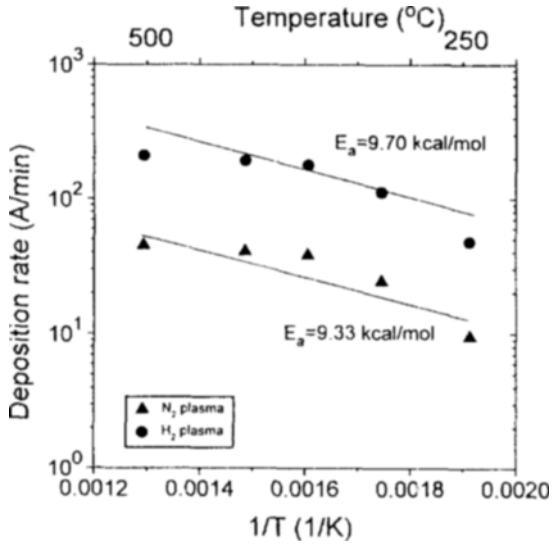


Fig. 2. The effect of substrate temperature on the deposition rate. (40 W, N_2 plasma, deposition time: 20 min)

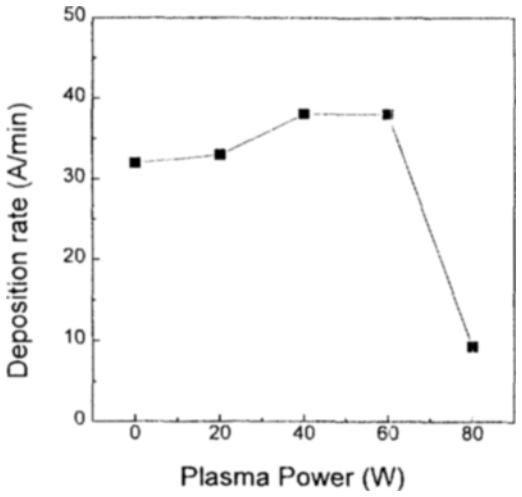


Fig. 3. The effect of plasma power on the deposition rate. (350°C, N_2 plasma, deposition time: 20 min)

2. Resistivity

Resistivity, which depends on deposition temperature, was the lowest within the range of 350-400°C and increased above 400°C (Fig. 4). It is believed that the crystallinity became poor due to the incorporation of thermally decomposed hydrocarbon at the higher temperature. Fig. 5 shows that resistivity was decreased with the plasma power but increasing plasma power to 80 W leads to the increase of the resistivity and this is due to the incorporation of impurities. These results were supported by the following XRD and XPS studies. In this study, we obtained the resistivity of around 1500 μΩcm as the variation of the temperature and plasma power and these results were comparable to other studies using MOCVD [Raajimakers, 1994; Sun and Tsai, 1994]. But the lowering of resistivity is neces-

sary for applications and it is expected that the lower values will be obtained by the variation of other conditions in the further studies.

3. Crystallinity and Morphology

TiN has (111), (200) and (220) peaks at 36.80, 42.61 and 61.97°, respectively according to XRD standard table [Manory, 1994]. Film deposited in the range of 300-400°C exhibited (111), (200) and (220) orientation. It is seen from Fig. 6 that (111) signal was weak at 300°C, but as the temperature increased to 400°C, this signal became stronger. However, the film deposited at 500°C was more randomly oriented. Lowering of crystallinity may be due to the increase of impurities by the decomposition of hydrocarbon at higher temperature. Fig. 7 shows AFM images of surface morphology at different deposition temperatures. At lower temperature, a film was formed with a smooth surface morphology, but, the surface became rough in the range of 350-400°C. However, at higher temperature, smooth surface was observed again (root mean square (rms) roughness=83 Å at 300°C, 870 Å at 400°C and 479 Å at 450°C). It seems that surface roughness is increased with crystallinity. At higher temperature, XRD peak intensity and the rms roughness decreased with higher resistivity. Fig. 8 and 9 show that increasing plasma power to 80 W leads to the decrease of the XRD signals and surface roughness (rms roughness=447 Å at 20 W, 884 Å at 40 W, and 331 Å at 80 W). As the plasma power was increased above some value, the crystallinity and roughness was decreased and resistivity was increased. It may be due to the increase of decomposition of hydrocarbon in the gas phase.

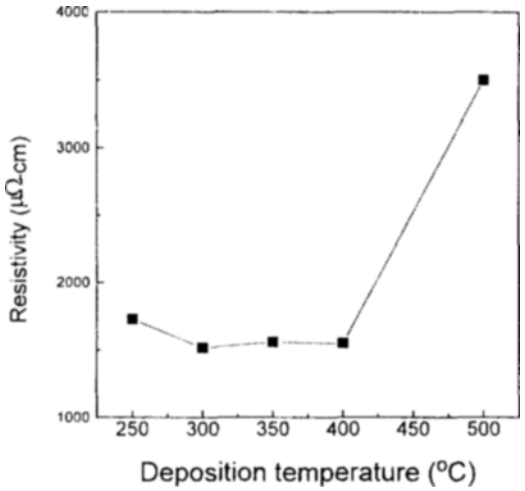


Fig. 4. Resistivity of TiN film at various deposition temperature.
(40 W, N_2 plasma)

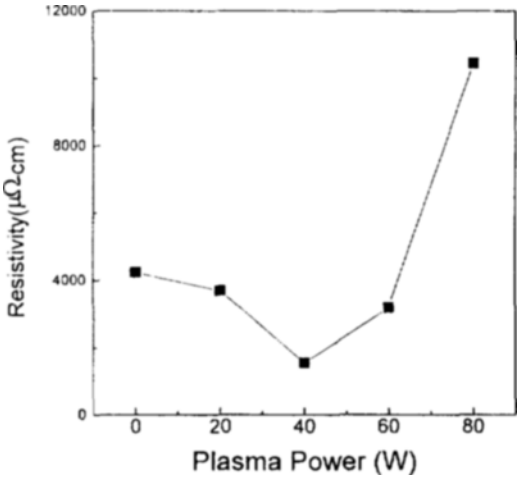


Fig. 5. Resistivity of TiN film at various plasma power.
(350°C, N_2 plasma)

4. Chemical Structure

In MOCVD system, incorporation of impurities in the film

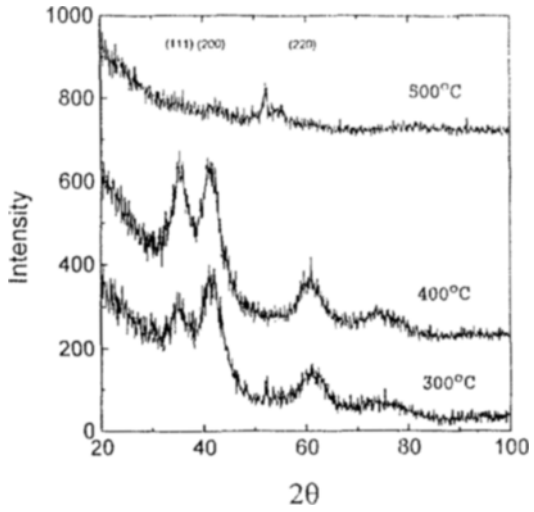
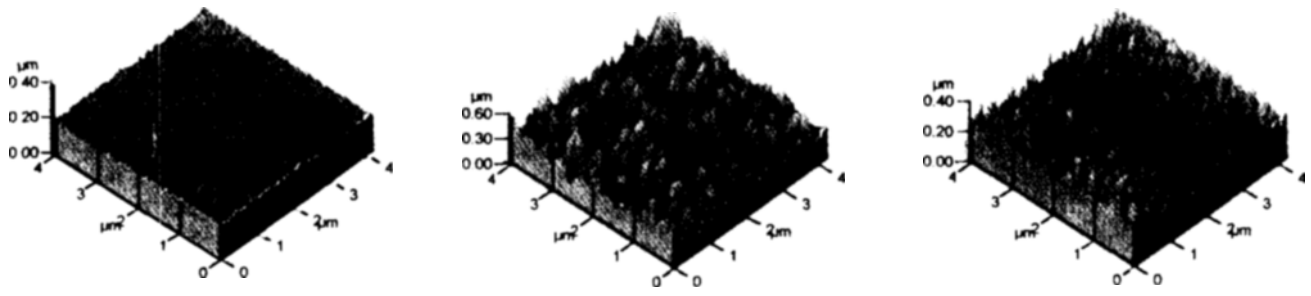


Fig. 6. XRD patterns of TiN at various deposition temperature.
(40 W, N_2 plasma)



(a) (b) (c)

Fig. 7. AFM surface images of TiN film at various deposition temperature.
(a) 300°C, (b) 400°C, (c) 450°C (40 W, N_2 plasma)

because of a incomplete reaction is a problem. In the final state of TiN deposition with MOCVD, only three of four electrons of titanium were bonded to nitrogen and this structure has a high reactivity with impurities. For this reason, TiN reacts readily with hydrocarbons or other radicals. Carbon can be incorporated in the film in different process steps with different bond types such as TiC or hydrocarbon [Coneille et al., 1995] and these contaminants can severely affect the properties of the layer. TiC, formed from direct bonding of carbon to Ti, has some TiN-like properties, however, hydrocarbon incorporated from the decomposition of precursor in the gas phase increases the resistivity.

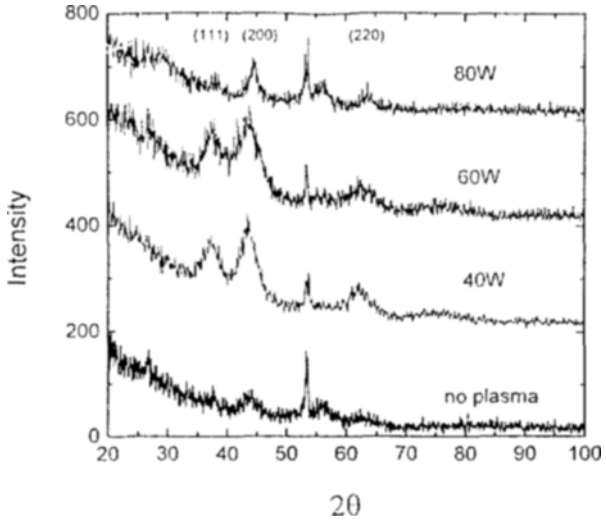


Fig. 8. XRD patterns of TiN at various plasma power.
(350°C, N_2 plasma)

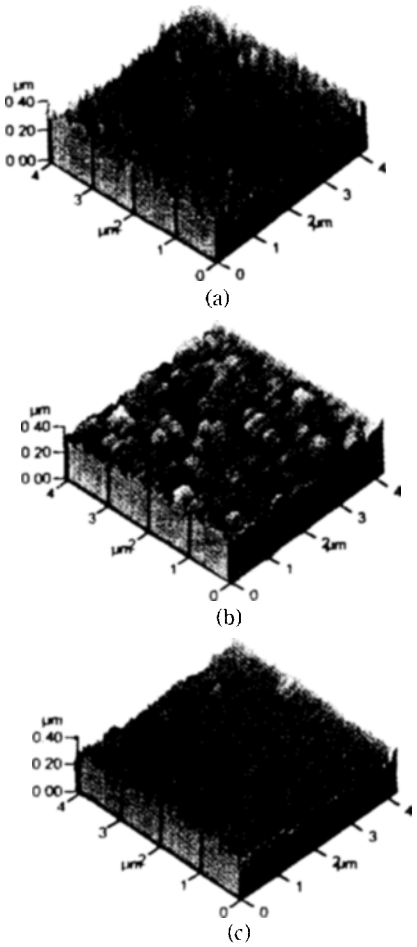


Fig. 9. AFM surface images of TiN film at various plasma power.
(a) 20 W, (b) 40 W, (c) 80 W (350°C, N_2 plasma)

We compared the chemical structure of the film deposited at 400°C with the film deposited at 500°C. The XPS spectra of the C_{1s} region deposited at 400°C and 500°C are shown in Fig. 10. The spectrum at 400°C has two peaks (hydrocarbons at 285 eV, TiC at 282 eV), and the film deposited at 500°C contained organic carbon with little titanium carbon (TiC). At the deposition temperature of 500°C, TiN film had more organic carbon than TiC, and this variation of carbon bonding structure is generally known to be involved in a change of resistivity [Ishihara et al., 1990]. Higher TiC content leads to lower resistivity, and lower resistivity was observed at 400°C as shown in Fig. 4.

CONCLUSION

TiN films were deposited from TDEAT-N_2 plasma, and growth kinetics and film properties were investigated. The de-

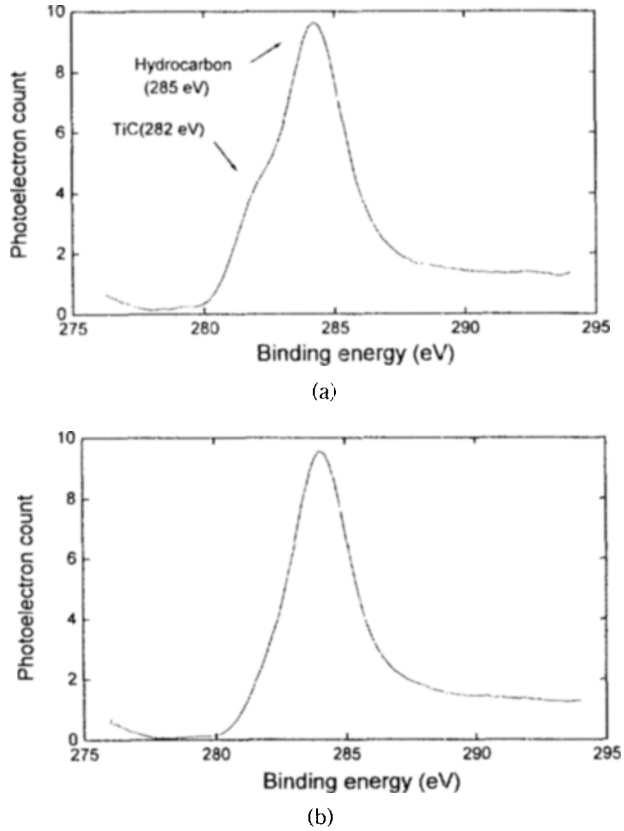


Fig. 10. The XPS spectra of C_{1s} region at various deposition temperature.
(a) 400°C, (b) 500°C (40 W, N_2 plasma)

position rate using N_2 plasma exhibited a similar activation energy with H_2 plasma. The growth rate using N_2 plasma is lower than that with H_2 plasma. Resistivity depends on the deposition temperature and was the lowest in the range of 350-400°C and increased above 500°C. Increasing the plasma power to 80 W leads to the increase of the resistivity. It is believed that these results are due to the incorporation of impurities by decomposition of the hydrocarbon in the higher temperature and plasma power.

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