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Comparison of TiN films produced by TDEAT ($\text{Ti}[\text{N}(\text{C}_2\text{H}_5)_2]_4$), TDMAT ($\text{Ti}[\text{N}(\text{CH}_3)_2]_4$), and a new precursor TEMAT ($\text{Ti}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$)

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ABSTRACT

TiN films have been deposited by chemical vapor deposition (CVD) from a new TiN precursor, tetrakis(ethylmethylamino)titanium (TEMAT), and compared with those from tetrakis(diethylamino)titanium (TDEAT) and tetrakis(dimethylamino)titanium (TDMAT) in terms of film quality and conformality. The TDEAT process at 350°C provides films with low resistivity of $\sim 2500 \mu\Omega\text{-cm}$ and 30% carbon. In addition, films deposited from TDEAT contain no oxygen and show good stability in resistivity with time. Furthermore, this process provides bottom-coverage ranging from 65% at 275°C to 30% at 350°C. In contrast, excellent bottom-coverage of $\sim 90\%$ over $0.5 \mu\text{m}$ contact holes is obtained by the TDMAT process. However, films deposited from TDMAT are air-reactive upon air-exposure, resulting in a large increase in resistivity when exposed to air. The use of TEMAT, possessing physical properties between those of TDMAT and TDEAT, allows less air-reactive and better crystalline films, compared with TiN films from TDMAT. It is also observed that the carbon level is $\sim 2\text{x}$ lower than that in TiN films from TDEAT. Furthermore, this process provides good step-coverage in $0.35 \mu\text{m}$ contacts with an aspect ratio of 2.9. Consequently, the TEMAT process can be an attractive choice for sub- $0.5 \mu\text{m}$ application.

INTRODUCTION

TiN film has been widely used as a diffusion barrier material for Al metallization and as an adhesion/nucleation layer for chemical vapor deposited blanket tungsten. The TiN CVD was reported from various organic chemistries including $\text{Ti}(\text{NR}_2)_4$, where $\text{R}=\text{Me}$ and Et , complexes. Both TDMAT and TDEAT are the most commonly reported organometallic sources for TiN because of their commercial availability.[1-6] MOCVD of TiN films from TDMAT has been well characterized. The process provides excellent step-coverage. However, it produces unstable films, i.e., they are air-reactive and have a high resistivity and a high level of oxygen contamination.[7,8] On the contrary, TiN films from TDEAT

have lower resistivity, negligible level of oxygen contamination, and show excellent stability in resistivity when exposing the films to air. But the TDEAT process yields a relatively degraded conformality, compared with the TDMAT process.[9,10] Therefore, we examined a new process that could improve step-coverage without suffering a degraded film properties.

In this work, a new titanium compound (TEMAT), possessing physical properties between those of TDMAT and TDEAT, prepared by U.P.Chemical, Korea. has been explored. The results have been compared with those from TDMAT and TDEAT in terms of film quality, impurity contents, step coverage, and reaction mechanism.

EXPERIMENTAL

Thermally oxidized wafers as well as silicon patterned wafers were used as starting material. TiN films were deposited at 250–350°C and 1 Torr in a load-locked single wafer type MOCVD reactor using a titanium-precursor (< 99.999%). The base pressure of the reactor was $\sim 2 \times 10^{-6}$ Torr. Metal organic precursor was introduced to the reactor by the bubbler type liquid delivery system with 400 sccm of He carrier gas(< 99.9999%). Since each precursor has the different vapor pressure, different bubbler temperature was employed to obtain sufficient vapor pressure: 100°C for a TDEAT process; 50°C for TDMAT; 65°C for TEMAT. TDEAT has a vapor pressure of about 0.2 Torr at 100°C while TDMAT and TEMAT have similar vapor pressure of 0.5 Torr at 50°C and 65°C, respectively.

The sheet resistance and thickness were measured by the four-point probe and the surface profilometer, respectively. Cross-sectional scanning electron microscopy(SEM) was used to determine the step coverage over 0.35–0.50 μm contacts with 2.0–3.0 aspect ratios. Auger electron spectroscopy(AES) depth profiling of the samples revealed the contents of elements including titanium, nitrogen, carbon, and oxygen. X-ray photoelectron spectroscopy(XPS) was employed to identify chemical bonding configuration of elements in TiN films.

RESULTS

The results of the deposition rate experiments can be seen in the Arrhenius plots in Fig. 1. As the data shows, in the temperature between 250 and 350°C, the curves show the high positive temperature activation energy: 1.0 eV of activation energy for the TEMAT process; 1.1 eV for TDMAT; 0.6 eV for TDEAT. Therefore, it can be concluded that all the reactions are surface-reaction limited. When deposition is done in the surface reaction limited, the step coverage of the films would be excellent. In fact, similar results are found in these experiments at the low temperature of 250 to 275 °C. But, TiN deposition at 350°C provides different level of conformality with different chemistry of organometallic precursor. Fig. 2 shows the step-coverage in contact holes with aspect ratio of 2.0 – 3.0 obtained at 250 – 350°C and 1 Torr using three different organo-metallic precursors. The bottom

coverage provided by the TDEAT process decreases from 65% at 275°C to 30% at 350°C. In contrast, the use of TDMAT has improved bottom coverage to more than 90% in films deposited at 350°C. In addition, the TiN films from TDMAT has very specular surface, which is probably due to amorphous structure. For a TEMAT process, 50-90% of bottom coverage is obtained over 0.35μm contact holes with an aspect ratio of 2.9. TiN film has a little rough surface inside contact holes and appears to consist of crystalline grains. X-ray diffraction analysis reveals better crystallinity in TEMAT-TiN than TDMAT-TiN films.

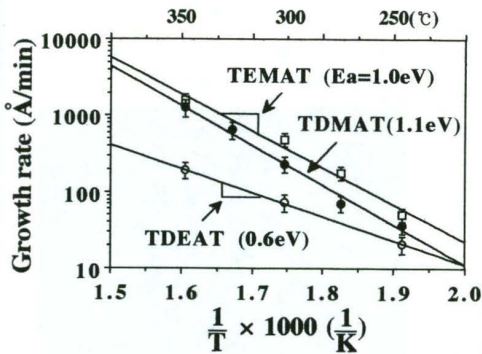


Figure 1. Arrhenius plots for growth rate dependence on temperature.

Fig. 3 shows the dependence of resistivity on substrate temperature. As the temperature increase, a significant dependence is seen. The resistivity rapidly decreases with increasing the temperature up to 350°C , then level off as the temperature continue to increase. The relatively high resistivity of the MOCVD TiN films is mainly due to a porous microstructure and impurities of the films. Therefore, increasing the deposition temperature increases the film density, leading to the reduction in resistivity. The minimum resistivity obtained at 350°C deposition is in the range of 2500-3500 μΩ-cm, depending on the precursor type. Lowest resistivity of ~2500 μΩ-cm is attained using TDEAT precursor while the resistivity of ~3500 μΩ-cm obtained using TEMAT and TDMAT precursors. MOCVD TiN generally undergoes oxygen-stuffing to the level of ~20% oxygen or more when exposed to air, leading to a large increase in resistivity. The experiments were carried out at 350°Cdeposition to identify the effect of the precursor type on the stability of TiN film in resistivity. Fig. 4 shows the different dependence of TiN resistivity variation on different organic-metal precursors. TDMAT produces unstable TiN film. The resistivity of TDMAT-sourced TiN film is on the order of 3500 μΩ-cm as-deposited and increases up to 14,000 μΩ-cm upon air-exposure. Similar, but less increase in resistivity during air-exposure is observed of TiN film deposited from TEMAT. TDEAT precursor produces very stable TiN film with the negligible change in resistivity after air-exposure. These different reactions of TiN films with air might be attributed to their different degree of density. AES depth profiling of the films in Fig. 5, reveals different contents of impurities in TiN films. The films deposited from TEMAT and TDMAT contain roughly 10% oxygen, 18% carbon

while TiN film from TDEAT has low level of oxygen(< Auger detection limit) and ~30% carbon. It is speculated that oxygen contained in TiN films from TDMAT and TEMAT originated from the ambient, which is probably due to their less-dense microstructures. It is also noted that much lower level of carbon was detected in TEMAT- sourced TiN films than TDEAT-sourced TiN films. We speculated that β -hydride elimination may take place during the ethylmethylamido fragmentation in the thermolysis of TEMAT and allow deposition of titanium films with lower carbon impurities, which was discussed more fully in a paper elsewhere.[11]

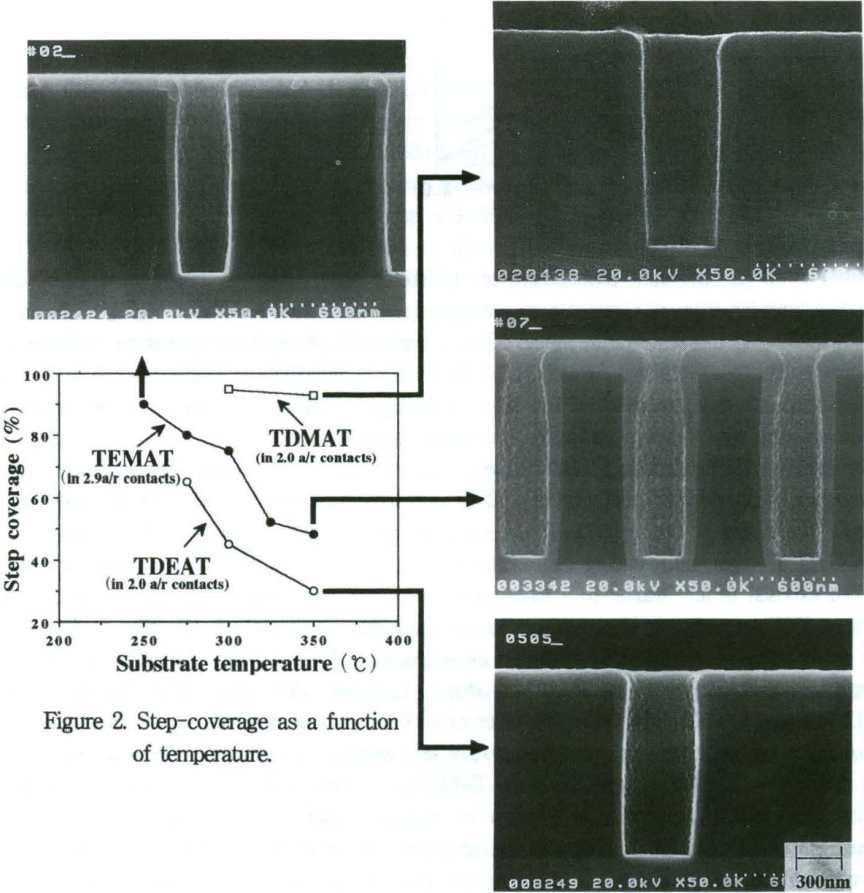


Figure 2. Step-coverage as a function of temperature.

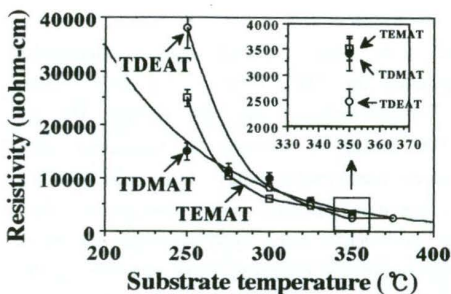


Figure 3. TiN resistivity as a function of substrate temperature.

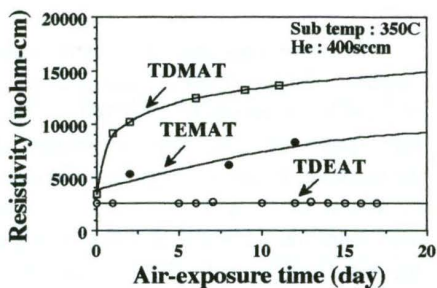


Figure 4. TiN resistivity variation as a function of air-exposure time.

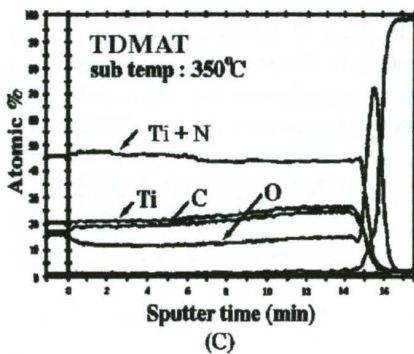
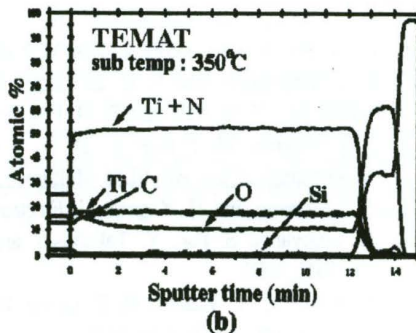
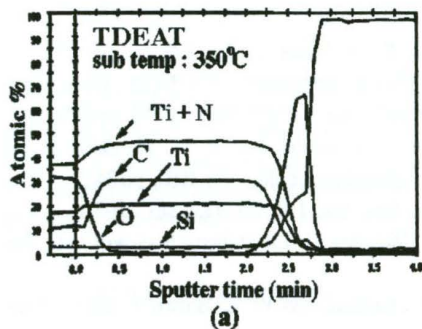


Figure 5. AES depth profiles of TiN films deposited from (a) TDEAT, (b) TEMAT, (c) TDMAT, respectively

CONCLUSIONS

We have compared TiN films deposited from three different organic chemistries including TDEAT, TDMAT, and TEMAT. Operating the TDEAT process at 350°C allows films with low resistivity of $\sim 2500 \mu\Omega\text{-cm}$, no oxygen content, and 30% carbon. Also the high quality of TiN films is reflected by the negligible increase in resistivity upon air-exposure. In addition, step-coverage obtained by this process ranges from 65% at 275°C to 30% at 350°C. A TDMAT process provides the most excellent step-coverage of $\sim 90\%$ over $0.5\mu\text{m}$ contact holes. However, it produces air-reactive films upon air-exposure. Since the active-reaction with air is mainly due to the less dense microstructure, this film quality needs to be improved further for its better application as a diffusion barrier. The use of TEMAT, possessing physical properties in between ^{high} of TDMAT and TDEAT, allows less air-reactive and better crystalline films than TiN films from TDMAT. Furthermore, relatively good step-coverage in $0.35\mu\text{m}$ contacts with an aspect ratio of 2.9 achieved by this process makes a TEMAT process an attractive choice for sub- $0.5\mu\text{m}$ application.

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