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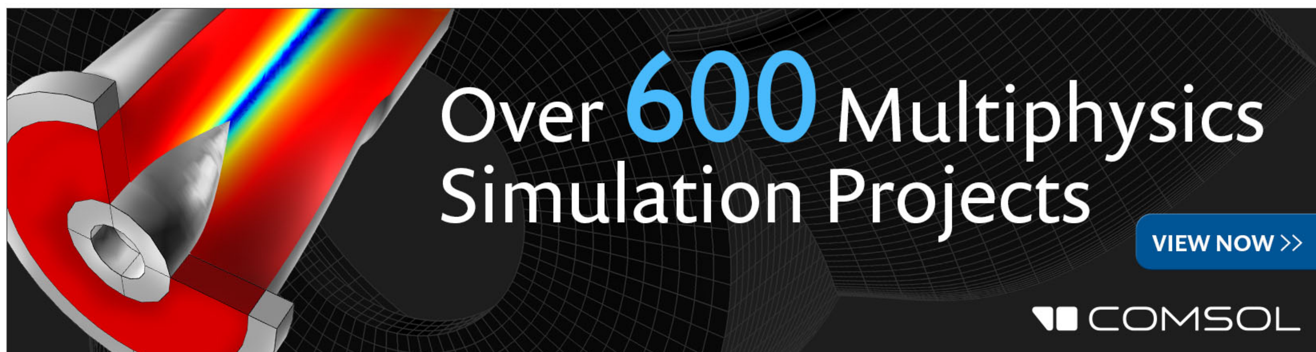

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Structural characterization of aluminum films deposited on sputtered-titanium nitride/silicon substrate by metalorganic chemical vapor deposition from dimethylethylamine alane

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Al films deposited on sputtered-TiN/Si substrate by metalorganic chemical vapor deposition (MOCVD) from dimethylethylamine alane (DMEAA) were characterized using x-ray diffraction (XRD), Auger electron spectroscopy (AES), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The TiN film sputtered on the Si has a preferred orientation along the growth direction with the ⟨111⟩ of the film parallel to the Si⟨111⟩. Sputtering of the TiN film on the Si induced strains at the interface. The TiN/Si interface is flat while the Al/TiN interface is rough. There exist many dislocations at the Al/TiN interface. The Al_2O_3 phase was formed at the Al/TiN interface during the early stages of Al deposition. In the Al grains, there exist many tangled dislocations and a few Al_2O_3 particles. With increasing deposition time, the Al film surface roughness increases. © *1995 American Institute of Physics.*

Multilevel metallization is an indispensable technique in increasing the device packing density in very large-scale integrated circuits (VLSIs). Al and Al alloy films are widely used for such metallization. Generally, Al is deposited by physical vapor deposition (PVD), however, as aspect ratio increases, it is difficult for PVD to fill via holes of deep-submicron size. Chemical vapor deposition (CVD) of Al has the advantages of excellent step coverage and selective growth, which are convenient for such micrometallization.[1–4]

DMEAA is one of the promising candidates for Al CVD because of its relatively high vapor pressure at room temperature (1.5 Torr), its long shelf-life, and its being a liquid and thus providing stable vapor pressure. Moreover, direct Al–C bonds are not present in its molecular structure, which helps to prevent carbon contamination.[3] To improve contact properties, a barrier layer is required for Al metallization in VLSIs. TiN is frequently used as a barrier layer because of its thermal and chemical stability. Although Al CVD on metal films using DMEAA has been reported,[5] the structure of the Al films is still far from clear. We deposited TiN film on Si as a diffusion barrier with reactive sputtering, and then deposited Al films on the TiN/Si substrate by CVD with DMEAA.

The Si(100) wafers having 4° off angle to (100) were used in this study. After a standard cleaning process, TiN film of 500 nm thickness was formed on the Si by direct current magnetron reactive sputtering in a gas mixture of Ar and N_2. Sputtering parameters were as follows: base pressure 5×10^{-9} Torr, process pressure 3 mTorr, sputtering power 6 kW, N_2 flow rate 60 sccm, Ar flow rate 20 sccm, substrate heated to 400 °C during sputtering. Al films were prepared at 190 °C by CVD with DMEAA. DMEAA was fed into the reactor with vapor phase mass flow controller without any carrier gas. The base pressure was 1.1×10^{-6} Torr and process pressure was 0.15 Torr.

The structures of the TiN and Al films were analyzed using a Rigaku D-Max 1400 x-ray diffractometer with Cu $K\alpha$ radiation operating at 50 kV, 150 mA. The depth profiles of elements Al, O, N, Si, and Ti were obtained by a Perkin-Elmer PHI 600 scanning Auger multiprobe. The surface morphology of the TiN and Al films was observed using

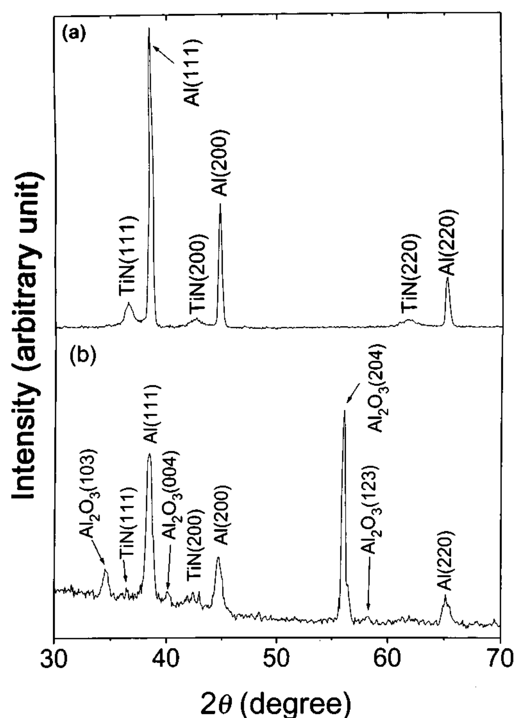

FIG. 1. XRD spectra of the Al films deposited on the TiN/Si substrate for (a) 15 and (b) 1 min, respectively.

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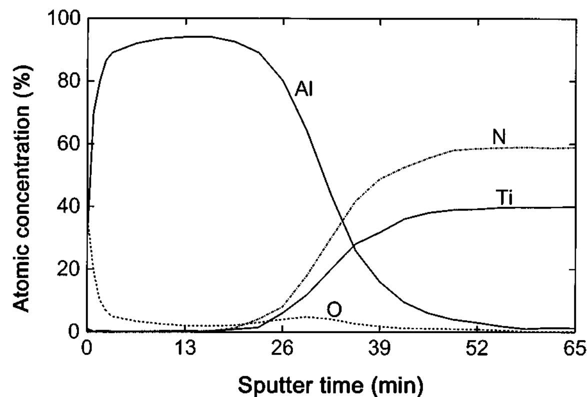


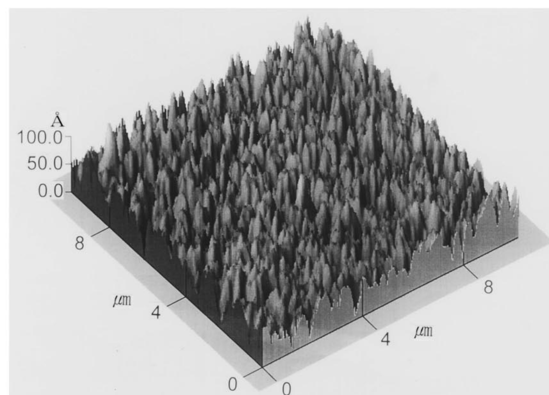
FIG. 2. Typical AES depth profiles from an Al film deposited on the TiN/Si substrate.

an Autoprobe-CP model atomic force microscope. Cross-sectional specimens for TEM were first glued face to face, cut, then ground, dimpled, and thinned by ion milling. TEM observations were conducted using a JEOL JEM-200CX transmission electron microscope operating at 100 kV.

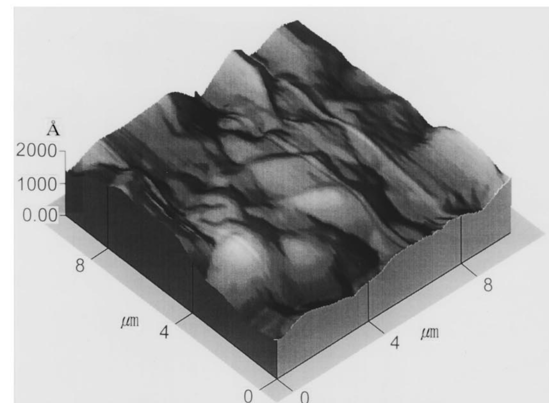
Figure 1 shows the XRD spectra of the Al films deposited on the TiN/Si substrate for 1 and 15 min, respectively. The thickness of the Al films deposited on the TiN/Si substrate for 1 and 15 min was estimated to be about 50 and 1000 nm, respectively, by weight measurement. The TiN film sputtered on Si exhibits strong (111) orientation while the Al films deposited on the TiN/Si substrate show random orientation. This is not in agreement with the results of Al films sputtered on the sputtered-TiN(111) films, where the Al films give (111) orientation.[6] The Al film deposited on the TiN/Si substrate for 1 min shows several peaks from Al_2O_3 in addition to the peaks of both Al and TiN while the Al film deposited on the TiN/Si substrate for 15 min does not. The Al_2O_3 phase is not likely to be from surface native oxide because it was not detected by XRD when the film was thick. This indicates that the Al_2O_3 phase or intermediate layer formed during the early stages of Al deposition.

Figure 2 shows typical AES depth profiles from an Al film deposited on the TiN/Si substrate. A small oxygen peak was observed at the Al/TiN interface near the Al film side. This suggests that Al–O compounds formed at the Al/TiN interface, in good agreement with the XRD results. A Ti–O compound layer was reported to exist on the TiN film surface.[7] The formation of the Al_2O_3 phase at the Al/TiN interface suggests that during Al CVD Ti–O compounds reacted with Al, forming the Al–O compounds. The effect of temperature and other operating variables on the formation of alumina at the interface is not yet known.

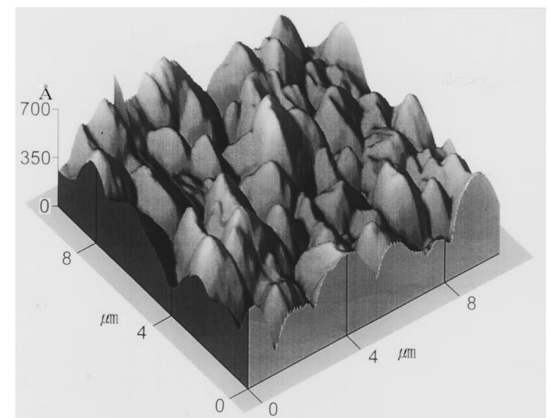
Figure 3 shows the AFM images of the TiN film, and the Al films deposited on the TiN/Si substrate for 1 and 15 min, respectively. The TiN and Al films exhibit rugged surface morphology. The rugged mountains of the TiN film distribute uniformly while those of both Al films do not. With increasing deposition time, the Al film surface roughness increases. The average diameters of the rugged mountains of the TiN film, and the Al films deposited on the TiN/Si substrate for 1



(a)



(b)



(c)

FIG. 3. AFM images of (a) the TiN film, and the Al films deposited on the TiN/Si substrate for (b) 15 and (c) 1 min, respectively..

and 15 min, are 1020, 2160, and 5630 nm, respectively. From the AFM results, however, it is difficult to determine the structure of the TiN and Al films.

Figure 4 shows the bright field cross-sectional TEM images of the Al film deposited on the TiN/Si substrate for 15 min and the Al/TiN interface, respectively. Good sections with homogenous thickness were obtained with the TiN and Al films [Fig. 4(a)]. The thickness of the Al film was found to be about 1000 nm, and that of the TiN film was found to be about 500 nm. The TiN film was found to be made up of very small needlelike grains ~20 nm in width and 200 nm in length, which grow in the direction inclined to the Si at an

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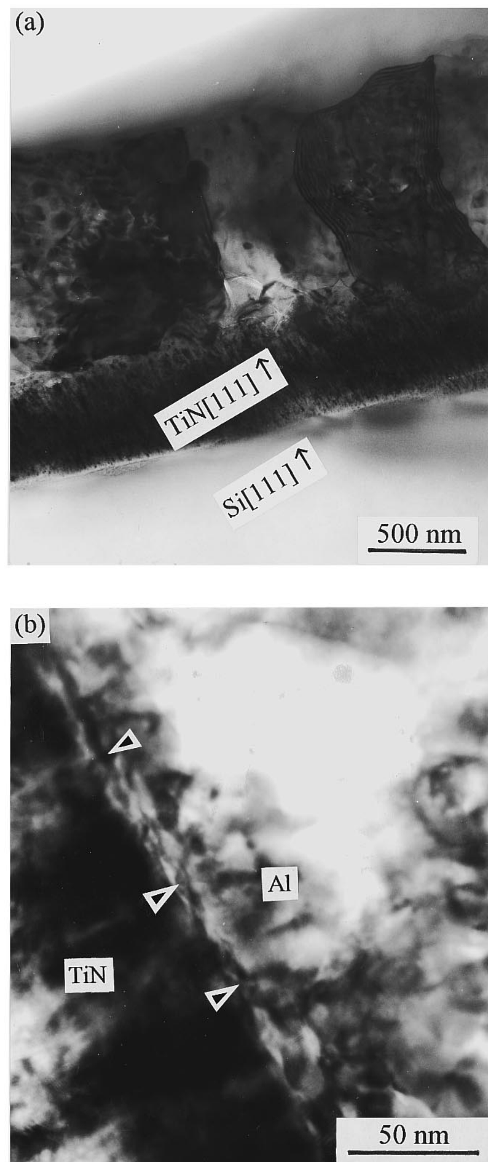

FIG. 4. Bright field cross-sectional TEM images of (a) the Al film deposited on the TiN/Si substrate for 15 min and (b) the Al/TiN interface, respectively.

angle of about 66°. This direction is parallel to the Si⟨111⟩. From the XRD results, it is suggested that the growth direction of the TiN film is ⟨111⟩. Therefore, there is a preferred orientation of the TiN film along the growth direction with the film ⟨111⟩ parallel to the Si⟨111⟩. This is probably because atomic arrangement and interatomic distance of the TiN(111) plane are close to those of the Si(111). Obvious changes in contrast were observed in the Si near the interface [Fig. 4(a)], indicating that the sputtering of TiN film on the Si induced strains at the interface. The Al/TiN interface is relatively rough, and there exist many dislocations [Fig. 4(b)]. An intermediate layer indicated by the arrow in Fig. 4(b) seems to exist at the Al/TiN interface, which might be the Al_2O_3 phase found by XRD and AES. The Al grains were found to have elongated blocklike shape ~600 nm in width and 930 nm in length. Some small Al grains, which were formed at the nucleation stage, were found near the interface. In the Al grains, there exist many tangled dislocations, and a few small particles with a diameter of about 50 nm which were identified as Al_2O_3 phase by selected area diffraction analysis. Al_2O_3 particles cannot nucleate and grow to such size in the Al grains within 30 min at 190 °C. It was also found that there is not any definite orientational relationship between the Al_2O_3 particles and Al matrix. Therefore, a possible reason for the existence of Al_2O_3 particles within the Al grains is that Al_2O_3 particles formed in gas phase because of residual O_2 or H_2O and then deposited together with Al onto specimen surface. DMEAA is unstable in the atmosphere and it readily decomposes into alumina when exposed to air. Because the volume fraction of Al_2O_3 particles is small, it is impossible to detect them by XRD. The existence of Al_2O_3 particles in the Al grains is also one of the reasons why there exist many tangled dislocations in the grains. Compared with the AFM results, it was found that the rugged mountains in the AFM images do not correspond to the grains. It is desirable that grain size should be large and uniformly distributed. Also, the film should be free from impurities. Other researchers showed that impurities like hydrogen,[8] nitrogen,[9] and oxygen[10] have bad effects on the migration resistance of metal lines.

In summary, the TiN film sputtered on the Si has a preferred orientation along the growth direction with the ⟨111⟩ of the film parallel to the Si⟨111⟩. Sputtering of the TiN film on the Si induced strains at the interface. The TiN/Si interface is flat while the Al/TiN interface is rough. There exist many dislocations at the Al/TiN interface. Al_2O_3 phase formed at the Al/TiN interface during the early stages of Al deposition. In the Al grains, there exist many tangled dislocations and a few Al_2O_3 particles. With increasing deposition time, the Al film surface roughness increases.

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