Magnetron Sputtered nc-Al/α-Al$_2$O$_3$ Nanocomposite Thin Films for Nonvolatile Memory Application

Yibin Li$^{1,2}$, Sam Zhang$^{1,*}$, Y. Liu$^3$, T. P. Chen$^2$, Thirumany Sritharan$^4$, and Cong Xu$^4$

$^1$School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
$^2$Center for Composite Materials, School of Astronautics, Harbin Institute of Technology, P.O. Box 3010, Harbin 150001, P. R. China
$^3$School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore
$^4$School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

In this paper, we developed nc-Al/α-Al$_2$O$_3$ nanocomposite thin films using magnetron sputtering. The nc-Al/α-Al$_2$O$_3$ films were sputtered on $p$-type Si substrates from pure Al target in gas mixture of Ar and O$_2$. X-ray photoelectron spectroscopy and high resolution transmission electron microscope studies confirm that the nanocrystalline Al are embedded in amorphous Al$_2$O$_3$ matrix thus nc-Al/α-Al$_2$O$_3$ nanocomposite forms. This nanocomposite thin film exhibits memory effect as a result of charge trapping.

Keywords: Magnetron Sputtering, nc-Al/α-Al$_2$O$_3$, Nonvolatile Memory.

1. INTRODUCTION

Al$_2$O$_3$ is widely used in mechanical, optical, and micro-electronic applications because of its excellent chemical resistance, good mechanical strength, high hardness, transparency, high abrasive and corrosion resistance as well as insulating.$^{1,4}$ Al$_2$O$_3$ thin films can be synthesized by sol–gel,$^3$ electron-cyclotron-resonance sputtering,$^6$ self-limiting atomic layer deposition$^7$ and so on. Al$_2$O$_3$ thin film can be used as a gate dielectric for field-effect transistor.$^8$ The conduction barrier height of Al$_2$O$_3$ is 2.8 eV$^9$ which is smaller than that of SiO$_2$. This allows for writing at a lower voltage, and it is very beneficial for nanoscale memory devices. Similar to the memory effect observed in SiO$_2$ thin films containing Si nanocrystals (nc-Si/SiO$_2$) or Al-rich AlN thin films (nc-Al/AlN),$^{11-13}$ in the present study, the Al-rich Al$_2$O$_3$ nanocomposite (nc-Al/Al$_2$O$_3$) thin films are deposited on $p$-type Si substrates by radio frequency (rf) magnetron sputtering to form a metal-insulator-semiconductor (MIS) structure. Charge trapping/detrapping in the Al nanocrystals leads to a shift in the flat-band voltage ($V_{FB}$) of the MIS structure. The capability of the Al-rich Al$_2$O$_3$ film indicates that such films may have a potential application in memory devices.

2. EXPERIMENTAL DETAILS

The starting substrate was $p$-type, (100)-oriented Si wafer, which was cleaned through RCA process (removal of the organic and oxide). A series of 60 nm thick Al-rich Al$_2$O$_3$ films were deposited on the cleaned Si wafers via radio frequency magnetron sputtering. The sputtering deposition parameters are listed in Table I. The deposition rate $R$ at various sputtering power densities is determined by $R = \frac{d}{t}$, where $d$ is the film thickness is measured through the cross-sectional image using field emission scanning electron microscope (FESEM, JEOL JSM-6340F, Japan) and $t$ the time taken for the long time deposition. A 100 nm aluminum layer as the gate electrode was then deposited onto nanocomposite thin films. A layer of aluminum with a thickness of about 200 nm was sputtered on the wafer backside after initial oxide was removed by plasma sputtering. The chemical states of the films were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation (15 kV and 10 mA). The base vacuum of the XPS chamber was 2.66 × 10$^{-7}$ Pa. The energy scale of XPS spectra was calibrated with the core level of the C 1s peak which is due to the surface contamination. The high resolution transmission electron microscopy (HRTEM, JEM-2010) was used to observe the nanocrystalline Al embedded in amorphous Al$_2$O$_3$ matrix. An Ar$^+$ ion gun with acceleration voltage of 4 kV and
filament current of 15 mA was used to etch the samples at a gas pressure of $6.65 \times 10^{-6}$ Pa. Positive ion mass depth profiling was conducted using time of flight secondary ion mass spectrometry (TOF-SIMS IV, manufactured by CAMECA/IONTOF, Germany) for elemental distribution. The bombarding Ar ion was operated at 3 keV; Ga$^+$ impingement beam was powered at 25 keV; Ar sputtering area was set as $300 \times 300 \mu m^2$ while the Ga$^+$ impingement area for analyses was $150 \times 150 \mu m^2$. Charging/discharging test was carried out by applying a voltage to the MIS structures with a Keithley 4200 semiconductor characterization system, and capacitance–voltage (C–V) measurements were carried out with a HP4284A LCR meter at the frequency of 1 MHz.

3. RESULTS AND DISCUSSION

Figure 1 shows the XPS profiles of Al 2p core level of the pure Al$_2$O$_3$ and Al-rich Al$_2$O$_3$ thin films, respectively. At lower power density of 3.56 W/cm$^2$, shown in Figure 1(a), the Al 2p profile has only one peak assigned as Al$_2$O$_3$. At this power density, aluminum sputtered from Al target completely reacts with oxygen thus no extra metallic Al is left in the film. However, as Al sputtering power increases, like 4.33 W/cm$^2$, as shown in Figure 1(b), the spectrum can be decomposed into two peaks: the peak located at lower binding energy of 72.7 eV is assigned to the metallic Al, and the other one located at higher binding energy of 75 eV comes from Al$_2$O$_3$. Figure 2 plots the mole ratio of Al over O as a function of power density. At lower power density, like 3.56 W/cm$^2$, the ratio of Al over O is around 0.65, indicating that the film has stoichiometric composition of Al$_2$O$_3$. At high power densities, like 3.95 and 4.33 W/cm$^2$, the ratio of Al over O is higher than 0.65. Namely, Al is rich in the film where the Al-rich Al$_2$O$_3$ film results. This is reasonable because higher power results in higher sputtering yield and thus more Al atoms are sputtered out to enter the film. The microstructure of nanocomposite thin film was observed using HRTEM as shown in Figure 3. Obviously, at the power density of 3.56 W/cm$^2$, there is no evidence that nanocrystalline Al exists in the amorphous Al$_2$O$_3$ matrix. The selected area electron diffraction patterns (shown in Fig. 3(a) inset) also confirm that the film is amorphous. This is in good agreement with XPS result where the Al 2p profile is only assigned to be Al$_2$O$_3$ (also

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
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<tbody>
<tr>
<td>Base pressure (Pa)</td>
<td>$&lt;3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Process pressure (Pa)</td>
<td>0.93</td>
</tr>
<tr>
<td>Power density (W/cm$^2$)</td>
<td>3.56, 3.95, 4.33</td>
</tr>
<tr>
<td>Gas flow rate (Ar/O$_2$ sccm)</td>
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</tr>
<tr>
<td>Target-to-substrate distance (mm)</td>
<td>40</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>Room temperature</td>
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</table>
the Al/O ratio is nearly approaching stoichiometry of 2/3). However, as the power density reaches 3.95 W/cm², the Al nanocrystal (around 5 nm in diameter) is clearly observed, as seen in Figure 3(b). This confirms that the excessive Al forms nanocrystalline Al embedded in the Al₂O₃ matrix. With the power density increasing, like at the power density of 4.33 W/cm², the content of excessive Al increases too, resulting in a bigger size of the nanocrystalline Al, as seen in Figure 3(c) with the nanocrystal size of around 10 nm in diameter. The elemental distribution along thickness direction tested by SIMS is depicted in Figure 4. The interface between nc-Al/Al₂O₃ thin film and silicon substrate is clearly defined.

Figure 5 shows the C–V curves obtained by sweeping the voltage from −5 V to 2 V back and forth. It is observed that there is no flat-band voltage shift occurring at the sputtering power density of 3.56 W/cm². Correlated with the HRTEM image shown in Figure 3(a), it is believed that pure Al₂O₃ (i.e., containing no Al nanocrystals) does not present flat-band voltage shift. For the sample synthesized at 3.95 W/cm², in which nanocrystalline Al exists, a flat-band voltage shift of around 1 V is obtained (Fig. 5(b)). At 4.33 W/cm², the flat-band voltage shift is enhanced for up to 2 V (c.f., Fig. 5(c)). These results lead to a conclusion that the existence of nanocrystalline Al in amorphous Al₂O₃ matrix results in flat-band voltage shift, and the amount of the shift depends on the nanocrystalline content in the film. A large shift indicates significant charge trapping in the Al-rich Al₂O₃ film. The charge trapping is correlated with the Al nanocrystals embedded in the Al₂O₃ thin films. The situation is very similar to that of Si-rich SiO₂ (i.e., SiOₓ, x < 2) thin films where charge trapping in the Si nanocrystals also leads to a flat-band voltage shift. As measured, there is almost no flat-band voltage shift when the Al/O ratio reduces 1.5, i.e., the stoichiometric Al₂O₃ film. As Al/O ratio becomes greater than 1.5, a flat-band voltage shift is obtained.

Figure 6 shows the flat-band voltage shift as a function of the charging duration at various voltages. A negative voltage to the gate results in a negative flat-band voltage shift.
Magnetron Sputtered nc-Al/α-Al2O3 Nanocomposite Thin Films for Nonvolatile Memory Application

Li et al.

Fig. 5. C–V curves of Al-rich Al2O3 films at different power densities: (a) 3.56 W/cm²; (b) 3.95 W/cm²; (c) 4.33 W/cm².

Fig. 6. Flat-band voltage shift of nanocomposite thin film (deposited at the power density of 4.33 W/cm²) at different applied voltage.

4. CONCLUSION

Excessive Al atoms from reactive sputtering of Al target form nano-size crystals distributed in the amorphous Al2O3 matrix. This nc-Al/α-Al2O3 film exhibits a memory effect. Charging and discharging the Al nanocrystals leads to flat-band voltage shift of the Metal Insulator Semiconductor devices. The situation is similar to that of Si-rich SiO2 film, which has already been used in memory applications. As the synthesis of the Al-rich Al2O3 film is very simple and cheap, the Al-rich Al2O3 film provides a possibility of memory applications with low cost.

References and Notes


shift (i.e., $\Delta V_{FB}$ is negative, or the shift is towards the left of the original $C–V$ curve), which indicates a positive charge trapping in the Al nanocrystals. The MIS structure used in this study has a metal (Al) gate electrode and a $p$-type Si substrate. Therefore, the positive charge trapping in the Al nanocrystals is due to hole injection from the substrate. Under a negative gate voltage with a sufficiently large magnitude, the surface region of the $p$-type Si substrate will be enhanced into $p$ plus type. In this case, under the influence of the negative gate voltage, holes can be injected into the thin film from the substrate accumulation layer. At the same time, electrons are also injected from the metal gate. As the holes are the majority charge carriers in the $p$-type substrate, there are no competing processes (i.e., the electron injection from the gate and hole injection from the substrate under the negative gate voltage) occurring. Under this circumstance, electron trapping won’t be observed. This argument is confirmed by our experimental results. As seen in Figure 6, negative $\Delta V_{FB}$ increases with the applied voltage magnitude and charging duration. No positive flat-band voltage shift occurred. The capability of charge storage in the Al nanoparticles and the large effect on the flat-band voltage shift provide the possibility of the application of the Al-rich Al2O3 thin films in memory devices.
Li et al. Magnetron Sputtered nc-Al/\text{Al}_2\text{O}_3 Nanocomposite Thin Films for Nonvolatile Memory Application


Received: 25 February 2007. Accepted: 20 October 2007.