Charging effect of Al_2O_3 thin films containing Al nanocrystals

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In this work, Al_2O_3 thin film containing Al nanocrystals (nc-Al) is deposited on Si substrate by radio frequency sputtering to form a metal-insulator-semiconductor structure. Both electron and hole trapping in nc-Al are observed. The charge storage ability of the nc-Al/Al_2O_3 thin films provides the possibility of memory applications. Charging in the nc-Al also leads to a change in the dc resistance of the thin films, namely, the electron trapping in the nc-Al leads to an increase in the resistance, whereas the resistance is reduced if there is hole trapping in the nc-Al. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2994695]

Recently, Al_2O_3 is considered as a promising candidate for the gate dielectric of field-effect transistors due to its excellent electrical properties such as low leakage current, high dielectric constant (~8), and high breakdown voltage (~9 MV/cm).[1–3] Various techniques such as radio frequency (rf) magnetron sputtering,[4] atomic-layer deposition (ALD),[5] and plasma-enhanced ALD[6] have been used to prepare the Al_2O_3 films. In this work, Al-rich Al_2O_3 film is deposited on Si substrate by rf reactive sputtering to form a metal-insulator-semiconductor (MIS) structure. Transmission electron microscopy (TEM) images show the existence of Al nanocrystals (nc-Al) formed by the excess Al in the Al_2O_3 thin film. Charge trapping/detrapping in the nc-Al leads to a shift in the flat-band voltage (V_{FB}) of the MIS structure, demonstrating the possibility of memory applications of the material system. On the other hand, the charging effect on the current conduction of the thin films is studied also.

The starting substrates were *p*-type, (100)-oriented Si wafers. 60 nm thick Al-rich Al_2O_3 films were deposited on the cleaned Si wafers with rf magnetron sputtering. The rf sputtering of Al target was carried out in O_2 ambient at a power of 310 W. The Ar to O_2 ratio is set to be 60:1. The films were annealed with rapid thermal process at 500 °C for a duration varying from 30 s to 5 min. A 200 nm aluminum layer was then deposited on the top of the thin films to form the gate electrode. The backside electrode was formed with a 200 nm aluminum layer after removing the initial oxide of the Si wafers. 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. Figure 1(a) shows the XPS peak of Al 2*p* core level of an Al-rich Al_2O_3 thin film. The Al 2*p* peak of the film can be decomposed into two components, i.e., elemental Al and Al_2O_3. The Al component indicates that the film is Al-rich. The high resolution TEM image shows that the excess Al form nanocrystals that are embedded in the amorphous Al_2O_3 matrix, as illustrated in Fig. 1(b). Charging/discharging experiments, the current-voltage (*I-V*) measurements and dc resistance measurements were carried out with

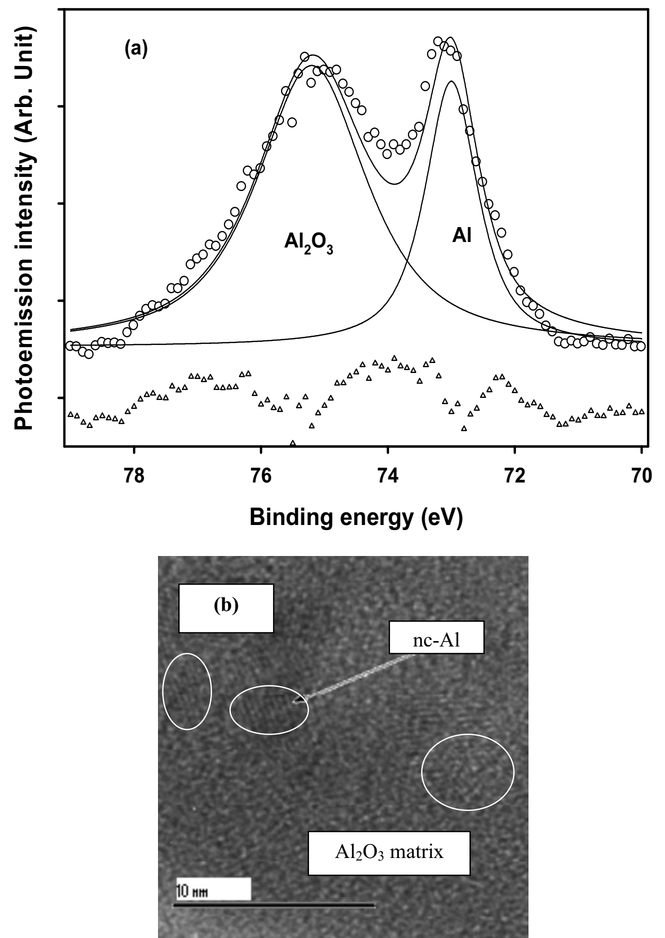

FIG. 1. (a) Peak decomposition of an Al 2*p* core level of an Al-rich Al_2O_3 thin film and (b) TEM image of an Al-rich Al_2O_3 thin film.

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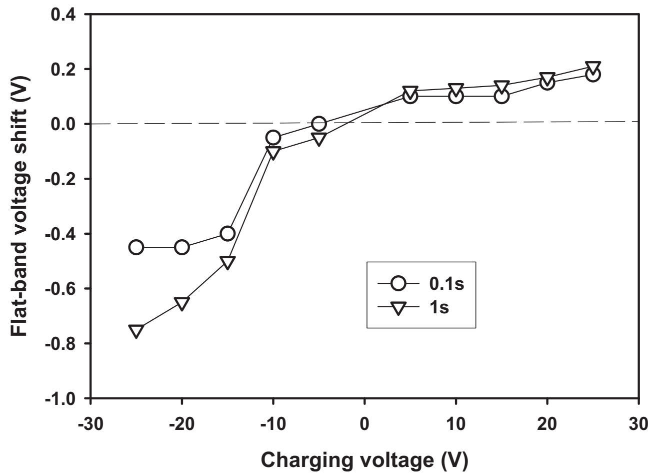

FIG. 2. Flat-band voltage shift as a function of charging voltage for different charging durations.

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.

Both positive and negative charge trapping in nc-Al are possible, depending on the gate voltage applied. For examples, the application of +20 V to the gate for 3 s causes a positive flat-band voltage shift (ΔV_{FB}) of 0.2 V, i.e., $\Delta V_{FB} = +0.2$ V indicating a negative charge trapping in the nc-Al; in contrast, the application of −12 V for 3 s leads to a negative flat-band voltage shift of about 0.5 V, i.e., $\Delta V_{FB} = -0.5$ V, indicating positive charge trapping in the nc-Al. These results show that the charge trapping depends on the voltage polarity. The capability of charge storage in the nc-Al and the effect on the flat-band voltage shift provide the possibility of the application of the nc-Al/Al_2O_3 thin films in memory devices. The charge trapping in nc-Al embedded in Al_2O_3 thin films here is similar to that in Si nanocrystals embedded in SiO_2 thin films[7–10] or in nc-Al embedded in AlN thin film.[11]

Figure 2 shows the flat-band voltage shift as a function of charging voltage for different charging durations. The application of a higher voltage leads to a larger flat-band voltage shift, and the flat-band voltage shift is also increased with the charging time. It is observed that the charge trapping depends on the polarity of the voltage applied. The negative voltage application causes the hole trapping and thus a negative flat-band voltage shift, while the positive voltage leads to the electron trapping and thus a positive flat-band voltage shift. Both holes and electrons are found to be injected from the substrate depending on the polarity of the applied voltage. The capability of charge storage in the nc-Al and the effect on the flat-band voltage shift provide the possibility of the application of the nc-Al embedded Al_2O_3 thin films in memory devices.

The influence of the charge trapping on the current conduction of the nc-Al/Al_2O_3 thin films has been studied. The I-V characteristics shown in Fig. 3(a) were obtained by sweeping the voltage from 0 to +10 V and then from +10 to 0 V. As shown in Fig. 3(a), the second scan exhibits a reduction in the current conduction. Such a current reduction can be explained in terms of the breaking of some tunneling paths formed by the nc-Al due to electron trapping in certain nanocrystals during the I-V measurement. Neutral nanocrystals can form tunneling paths connecting the metal gate to the Si substrate.[12,13] Electrons can be transported along these paths forming the conduction current. The positive I-V measurement can cause electron injection from the substrate and some of them are trapped in nc-Al. Due to the electrostatic interaction with the electrons trapped in the nc-Al, some of the tunneling paths are broken and thus the current is reduced, as shown in Fig. 3(a). The I-V characteristics shown in Fig. 3(b) were obtained by sweeping the voltage from 0 to +6 V before and after applying the negative charging voltage of −10 V to the MIS structure for 0.1 s. As shown in

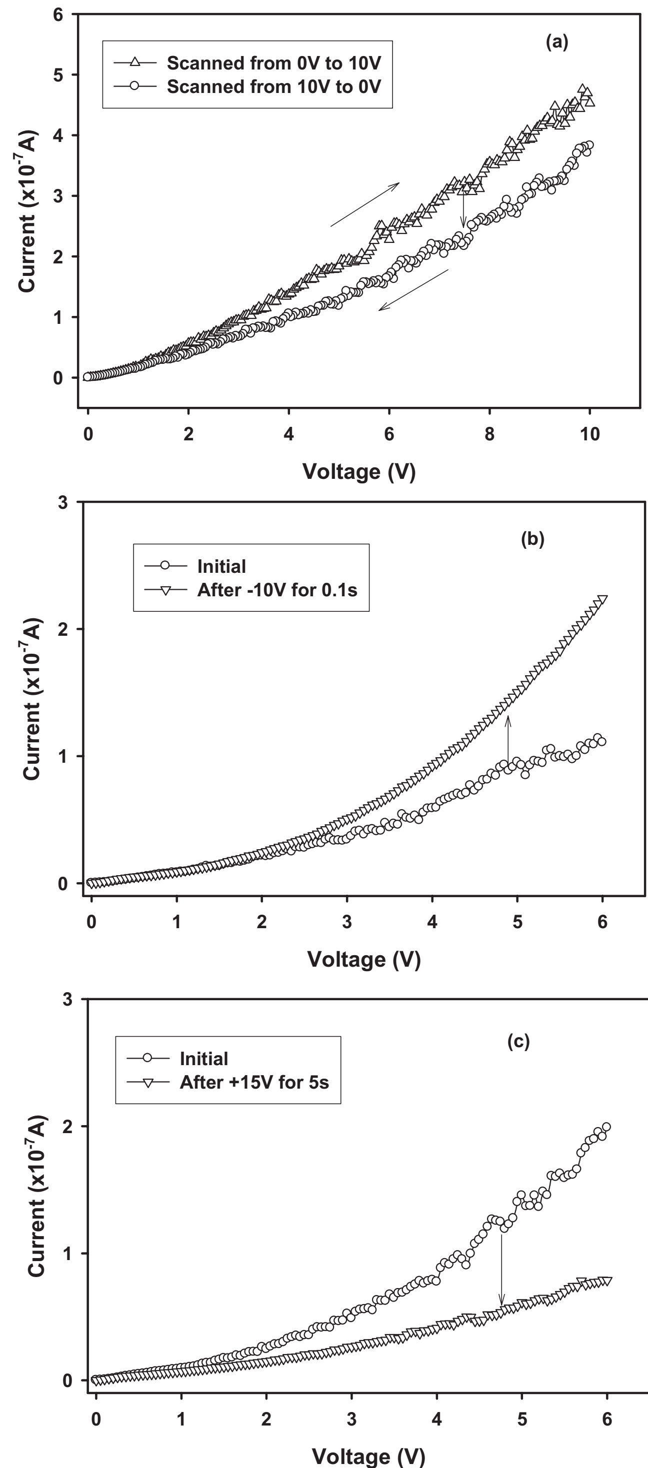

FIG. 3. (a) I-V measurements with voltage sweeping from 0 to +10 V and subsequently from +10 V to 0 V, (b) I-V characteristics before and after the application of −10 V for 0.1 s, and (c) I-V characteristics before and after the application of +15 V for 5 s.

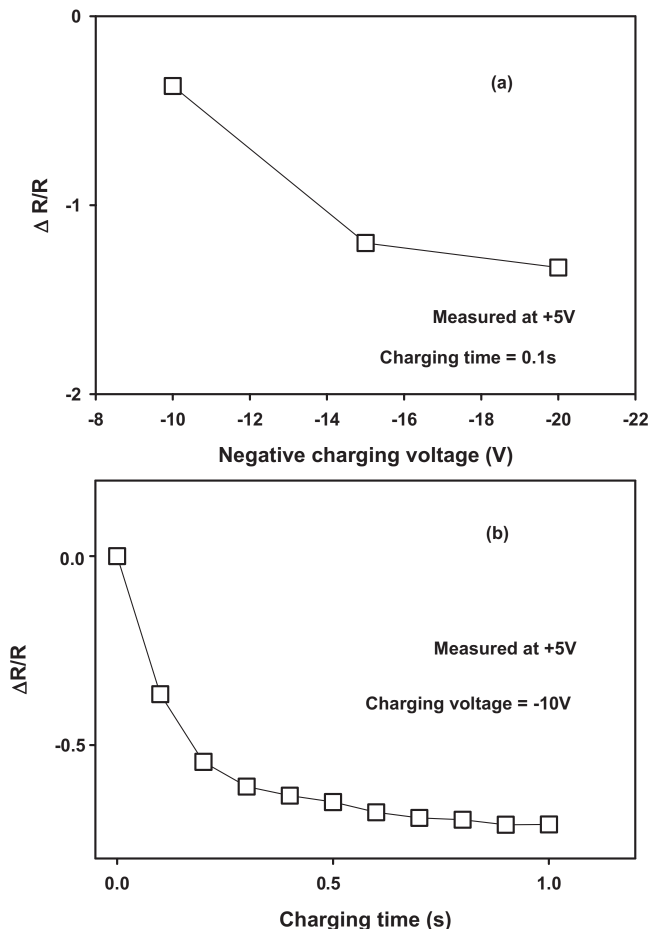

FIG. 4. (a) Change in the dc resistance of the nc-Al/Al_2O_3 thin film as a function of negative charging voltage with a fixed charging time of 0.1 s and (b) change in the dc resistance as a function of charging time with a fixed charging voltage of −10 V. The dc resistance is measured at +5 V.

Fig. 3(b), the application of −10 V for 0.1 s leads to an increase in the current. The increase in the current is due to the hole injection from the substrate under the negative voltage. As more neutral nanocrystals are available as a result of the hole injection, more tunneling paths are formed; in addition, the hole trapping in the nc-Al can also enhance the electron tunneling via the nanocrystals. Therefore, the current conduction increases with the hole injection. The *I-V* characteristics shown in Fig. 3(c) were obtained by sweeping the voltage from 0 to +6 V before and after applying the positive charging voltage of +15 V to the MIS structure for 5 s. The application of +15 V for 5 s leads to a current drop to a lower level. Such a current reduction is due to the breaking of some tunneling paths as a result of more electron trapping in the nc-Al under the application of the positive voltage.

Figure 4(a) shows the dc resistance change ($\Delta R/R$) of the nc-Al/Al_2O_3 thin film as a function of negative charging voltage with a fixed charging time of 0.1 s. The resistance is measured at +5 V. As discussed above, a negative charging voltage can cause hole injection from the substrate and thus an increase in the current conduction. With a larger multitude of the negative charging voltage, more holes are injected into the nc-Al/Al_2O_3 thin film, causing a decrease in the resistance, as shown in Fig. 4(a). A prolonged time of the hole injection further reduces the resistance, as demonstrated by Fig. 4(b).

In contrast to the reduction in the resistance by negative charging voltage, an increase in the resistance is observed for a positive charging voltage. As a positive charging voltage causes electron trapping in the nc-Al due to the electron injection from the substrate, the resistance increases with the decrease in the number of the tunneling paths as a result of the electron trapping. Obviously, the electron trapping and thus the resistance increases with the charging time.

In summary, nc-Al/Al_2O_3 thin films have been prepared with rf magnetron sputtering. The thin films exhibit the capability of both electron and hole trapping in the nc-Al. The charge trapping capability of the thin films provides the possibility of memory applications of the thin films. The influence of charge trapping on current conduction of the thin films has been studied. It is found that the conduction is enhanced with the hole trapping but reduced with the electron trapping.

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