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Memory effect of Al-rich AlN films synthesized with rf magnetron sputtering

Y. Liu, T. P. Chen,[a] and P. Zhao
School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

S. Zhang
School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore

S. Fung
Department of Physics, The University of Hong Kong, Hong Kong

Y. Q. Fu
Department of Engineering, University of Cambridge, Cambridge, United Kingdom

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Al-rich AlN thin film, which is deposited onto *n*-type Si substrate by radio frequency sputtering of Al target in an argon and N_2 gas mixture, can exhibit a large memory effect as a result of charge trapping in the Al nanoparticles/nanoclusters embedded in the AlN matrix. For the metal-insulator-semiconductor structure with a 60 nm Al-rich AlN thin film, a voltage of −15 V applied to the metal electrode for 10^{-6} s causes a flatband voltage shift of ~1.5 V. Both electron trapping and hole trapping are possible, depending on the polarity of the applied voltage. In addition, whether the electron trapping or the hole trapping is the dominant process also depends on the charging time and the magnitude of the voltage. The Al-rich AlN thin films provide the possibility of memory applications with low cost. © *2005 American Institute of Physics*.
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Aluminum nitride (AlN) film has attracted significant interest due to its various applications such as surface acoustic wave (SAW) devices and light-emitting applications.[1–5] AlN thin film can be deposited with a number of techniques such as reactive evaporation, magnetron sputtering, pulsed laser deposition, and hybrid techniques such as plasma- or ion-assisted depositions.[6–8] With its high thermal conductivity,[9] reasonable thermal match to semiconductors (such as Si, GaAs, and GaN) and small lattice mismatch[9,10] and wide band gap (6.2 eV),[4] AlN thin film could be used as a gate dielectric for field-effect transistors. In this work, it is shown that besides the application as a gate dielectric, an AlN thin film containing excess Al nanoparticles exhibits a memory effect which can be used for nonvolatile memory devices. The Al-rich AlN thin film is deposited on Si substrate by radio frequency (rf) sputtering to form a metal-insulator-semiconductor (MIS) structure. Charge trapping/distrapping in the Al nanoparticles leads to a shift in the flatband voltage (V_{FB}) of the MIS structure. The situation here is similar to the memory effect observed for SiO_2 thin films containing Si nanocrystals (nc-Si), which has attracted great interest.[11,12] The charge storage ability of the Al-rich AlN thin films provides the possibility of memory applications with low cost.

A series of 60 nm thick Al-rich AlN films were deposited on *n*-type, (100)-oriented Si wafers. The deposition was carried out by rf (13.56 MHz, 300 W) magnetron sputtering of a pure Al target in a gas mixture of argon and nitrogen. A constant flow rate (either 0.5 or 4 sccm) of Ar was maintained, while the flow rate of N_2 was varied from 4 to 20 sccm. A 20 nm aluminum layer was then deposited to form the gate electrode. The wafer backside was coated with a layer of aluminum with a thickness of about 1 μm after removing the initial oxide. Finally, an alloying process was conducted at 425 °C in N_2 ambient to form Ohmic contacts. X-ray photoemission spectroscopy (XPS) analysis was performed using a Kratos AXIS spectrometer with monochromatic Al $K\alpha$ (1486.71 eV) x-ray radiation. The energy scale of the XPS spectrum is calibrated with the binding energy of the C 1*s* peak which is due to the surface contamination. Figure 1(a) shows the XPS peak of Al 2*p* core level of an Al-rich AlN thin film. Based on a previous study,[15] the Al 2*p* peak of the AlN film should be decomposed into three components, i.e., Al, AlN, and Al_2O_3 which is due to the existence of residual oxygen during the sample preparation. Indeed, as shown in Fig. 1(a), such a peak decomposition is necessary and reasonable, and the Al component indicates that the film is Al-rich. Depth profiling of XPS analysis has been conducted on the samples, and it is found that there are some O and C impurities existing in the films from the surface to a depth of ~5 nm. The transmission electron microscopy (TEM) image shown in Fig. 1(b) suggests the existence of Al nanoparticles/nanoclusters embedded in the AlN matrix. The experiment of charging/discharging the Al nanoparticles embedded in AlN thin film 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.

Figure 2(a) shows the *C-V* characteristics obtained by sweeping the voltage from 5 V to −5 V first and then from −5 V back to 5 V. A flatband voltage shift of ~1 V is observed from Fig. 2(a). The large flat-band voltage shift indicates significant charge trapping in the Al-rich AlN film. The charge trapping is concerned with the Al nanoparticles/nanoclusters embedded in the AlN thin films and/or the deep level of antisite defect due to excess Al. For the former case, the situation is very similar to that of Si-rich SiO_2 (i.e., SiO*x*,

[a]Electronic mail: echentp@ntu.edu.sg

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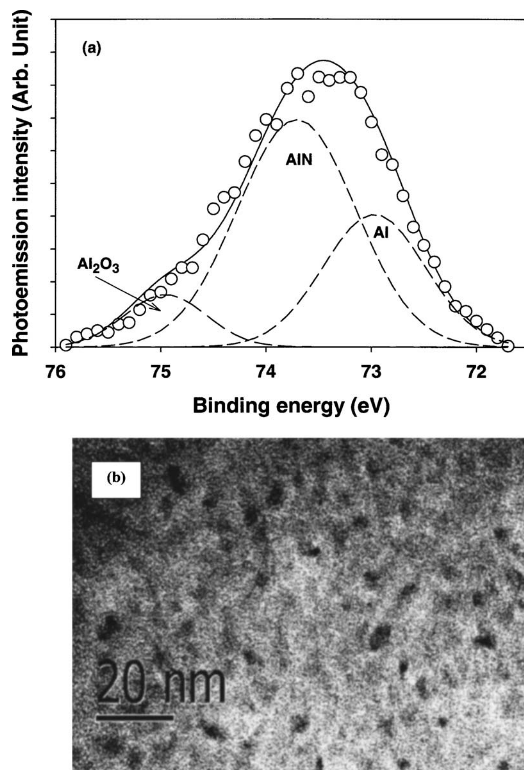

FIG. 1. Peak decomposition of Al 2*p* core level of an Al-rich AlN thin film (a) and the TEM image of an Al-rich AlN film (b).

$x<2$) thin films where charge trapping in the Si nanoparticles leads to a flat-band voltage shift.[13,14] In the latter case, the deep level of antisite defect[16] can trap electrons injected from the gate or the substrate, leading to a flat-band voltage shift. We have measured the flatband voltage shift as a function of the Al:N ratio. As shown in Fig. 2(b), the flat-band voltage shift increases with the Al:N ratio, and there is almost no flat-band voltage shift when the ratio approaches 1 (i.e., the situation of stoichiometric AlN film). This measurement confirms that the flat-band voltage shift is due to the presence of excess Al.

Both positive and negative charge trapping in the Al nanoparticles are possible, depending on the gate voltage applied. As shown in Fig. 3(a), the application of −6 V to the gate for 5 s shifts the *C-V* characteristic to the negative with a negative flatband voltage shift of ~0.4 V (i.e., $\Delta V_{FB} \approx -0.4$ V) indicating a positive charge trapping in the Al nanoparticles. In contrast, as shown in Fig. 3(b), the application of +7 V for 5 s leads to a positive flatband voltage shift of about 1 V (i.e., $\Delta V_{FB} \approx +1$ V), indicating negative charge trapping in the Al nanoparticles. These results show that the charge trapping depends on the voltage (both the polarity and magnitude of the voltage) applied. It will be shown later that the charge trapping (not only the charge amount but also the charge polarity) is also determined by the time of voltage application. The capability of charge storage in the Al nanoparticles and the large effect on the flatband voltage shift provide the possibility of the application of the Al-rich AlN thin films in memory devices.

The MIS structure used in this study has a metal (Al) gate electrode and a *n*-type Si substrate. Therefore, the negative charge trapping in the Al nanoparticles is due to the electron injection from either the gate electrode or the *n*-type Si substrate depending on the polarity of the applied voltage;

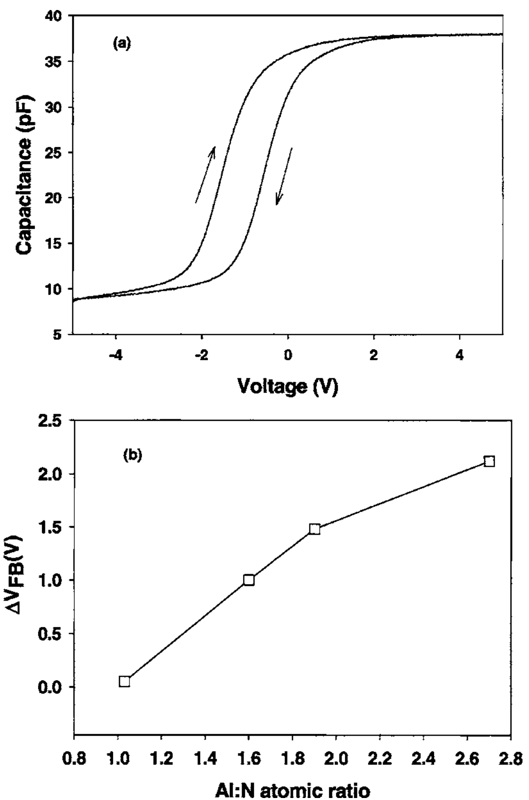

FIG. 2. Double-sweeping *C-V* characteristics of a MIS structure with Al-rich AlN film as the gate dielectric (a) and flatband voltage shift (ΔV_{FB}) caused by the double sweeping (i.e., the sweepings of the voltage from 5 V to −5 V and then from −5 V back to 5 V) as a function of Al:N ratio (b).

and the positive charge trapping is due to the hole injection from the substrate only as the probability of hole injection from the metal gate is extremely low. Under a negative gate voltage with a magnitude sufficiently larger than the value of the flat-band voltage, the surface region of the *n*-type Si substrate will be inverted into *p*-type. In this case, under the influence of the negative gate voltage, electrons can be injected from the gate electrode into the Al-rich thin film, and at the same time holes can be also injected into the thin film from the substrate inversion layer. As holes are minority carriers in the *n*-type substrate, the hole injection is limited by the thermal generation of the holes in the substrate. Therefore, not only the magnitude of the gate voltage but also the time (i.e., the charging time) of the voltage application determines which of the two competing processes (i.e., the electron injection from the gate and hole injection from the substrate under the negative gate voltage) is the dominant one. This argument is directly supported by our experimental results, as discussed later. On the other hand, under a positive gate voltage electrons will be injected into the thin film from the *n*-type substrate where electrons are the majority carriers. Most of the electrons and holes that are injected into the conduction band and the valence band of the AlN thin film, respectively, are collected by the gate or the substrate, leading to a gate current or a substrate current, respectively. At the same time, some of the injected electrons and holes are trapped in the Al nanoparticles, causing a positive and a negative flatband voltage shift, respectively.

The scenario of negative gate voltage discussed above is clearly demonstrated by Fig. 4(a) which shows the flat-band voltage shift as a function of charging time at the gate volt-

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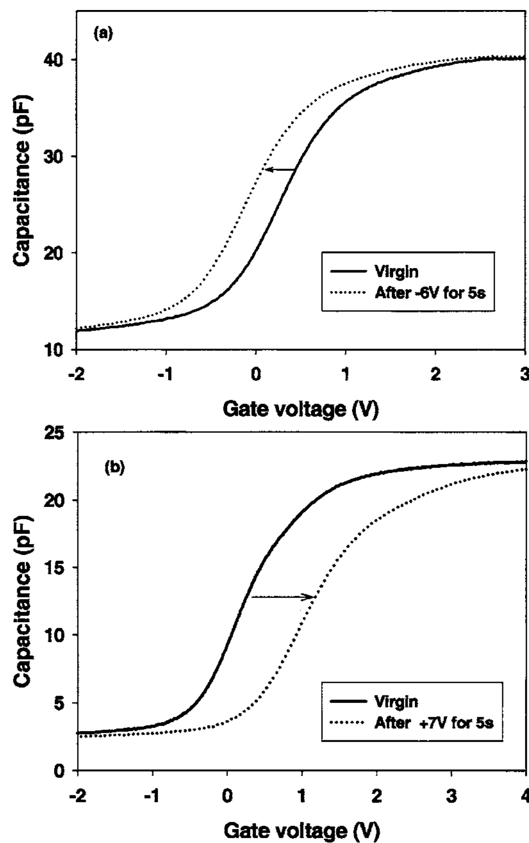

FIG. 3. Shifts in *C-V* characteristics after an application of −6 V for 5 s (a) and after an application of 7 V for 5 s (b).

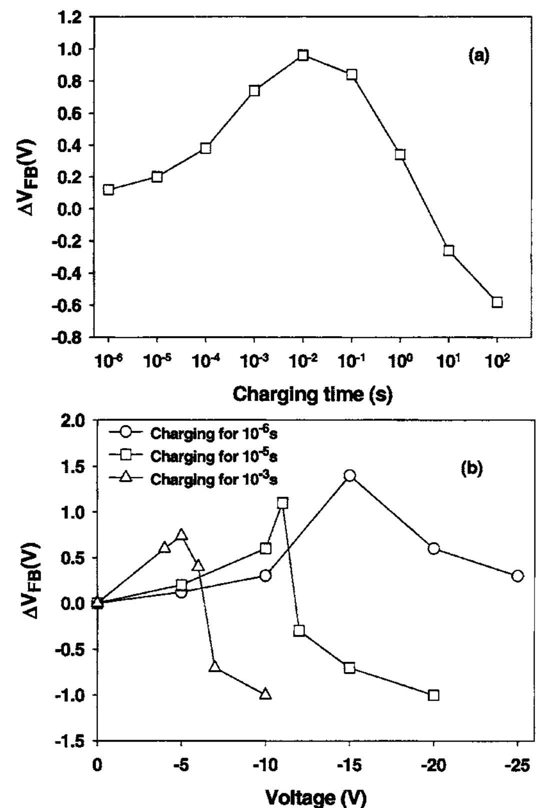

FIG. 4. (a) ΔV_{FB} as a function of charging time at −5 V; and (b) ΔV_{FB} as a function of negative voltage for various charging time.

age of −5 V. As can be seen in the figure, for the charging time shorter than 10^{-2} s, there is a positive flat-band voltage shift (i.e., the $\Delta V_{FB}>0$) and the shift increases with the charging time, indicating that the electron injection from the gate electrode (and thus electron trapping) is the dominant process. However, for charging time longer than 10^{-2} s, the ΔV_{FB} decreases with the charging time and the ΔV_{FB} becomes negative when the charging time is longer than ~3 s. This shows that the hole injection from the *n*-type substrate (and thus the hole trapping) becomes dominant when a sufficiently long time is allowed for the generation of a large amount of holes for the injection. The significance of the competition between the electron injection from the gate and the hole injection from the substrate under a sufficiently negative gate voltage is highlighted by the large difference in the flat-band voltage shift between the charging time of 10^{-2} s ($\Delta V_{FB}\approx +1$ V) and the charging time of 10^{2} s ($\Delta V_{FB}\approx -0.6$ V) as shown in Fig. 4(a).

The competition between the electron injection from the gate and the hole injection from the substrate under negative gate voltage is affected by the magnitude of the gate voltage also, as shown in Fig. 4(b). For the charging time of 10^{-6} s, in the gate voltage range of 0 to −15 V, the ΔV_{FB} is positive and it increases with the magnitude of the gate voltage, indicating that the electron injection from the gate is the dominant process; in the gate voltage range of −15 to −25 V, the ΔV_{FB} decreases with the magnitude of the gate voltage but is still positive, indicating that the hole injection from the substrate is becoming important but is still not the dominant process. When the charging time is increased, the hole injection from the substrate is enhanced. For example, for the charging time of 10^{-3} s, the ΔV_{FB} becomes negative (and thus the hole injection becomes dominant) when the magnitude of the gate voltage is larger than ~6.5 V.

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