Charge transport mechanism in amorphous alumina

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The charge transport mechanism in amorphous Al_2O_3 was examined both experimentally and theoretically. We have found that electrons are dominant charge carriers in Al_2O_3. A satisfactory agreement between the experimental and calculated data was obtained assuming the multiphonon ionization mechanism for deep traps in Al_2O_3. For the thermal and optical trap ionization energies in Al_2O_3, the values $W_T=1.5$ eV and $W_{opt}=3.0$ eV were obtained. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3151861]

High-*k* dielectric aluminum oxide Al_2O_3 with a high value of dielectric permittivity ($\varepsilon=10$) is a good candidate to replace gate SiO_2 layers ($\varepsilon=3.9$) in metal-oxide-semiconductor field-effect transistors.[1,2] Amorphous alumina has a band-gap energy of $E_g \approx 6.2$ eV and a barrier height for electrons at the Si/Al_2O_3 interface of $\phi^e=2.0$ eV.[3] In comparison with HfO_2, Al_2O_3 films exhibit low leakage currents.[4,5] Amorphous aluminum oxide (alumina) is used as a blocking layer in flash memory cells based on quantum dots and silicon nitride.[6–12] Some authors interpreted the conduction in Al_2O_3 within the framework of the Pool–Frenkel model.[13,14] The purpose of the present work is an experimental and theoretical study of the conduction mechanism in amorphous Al_2O_3 films. The multiphonon ionization mechanism is applied to explain the Al_2O_3 conduction.[15,16] Previously, the multiphonon ionization mechanism for deep traps was employed to describe various phenomena in semiconductors and dielectrics.[6,15–17]

The atomic layer deposition method was used to grow 14- and 20-nm-thick Al_2O_3 films on (100)-oriented *p*-type Si substrates from trimethylaluminum $Al(CH_3)_3$ and H_2O. The grown Al_2O_3 films were then given a 5 s anneal in dry nitrogen ambient. As the contact, an Al electrode with area of 5×10^{-3} cm^2 was used. The conductivity measurements of the p-$Si/Al_2O_3/Al$ structures were made in a cryostat at temperatures ranging from 77 to 400 K. The refraction index *n* of the Al_2O_3 films measured by ellipsometry at wavelength 6328 Å was found to be 1.73, yielding a value of 3.0 for the high-frequency dielectric constant $\varepsilon_\infty=n^2$. The band-gap energy in the investigated Al_2O_3 films determined by electron energy loss spectroscopy was found to be 6.2 eV.

The current-voltage characteristics were measured at fixed temperature with the voltage rate of 0.2 V/s. In all experiments, a weak, long-term relaxation of the current was observed at a constant Al potential and fixed temperature. Note that a similar relaxation was previously observed in Si_3N_4.[18] The curves of current versus temperature were measured at a fixed gate potential with the rate of heating of 1 K/s. The energy diagrams of p-$Si/Al_2O_3/Al$ structure at zero, positive, and negative potentials applied to the Al electrode are shown in Fig. 1.

The measurements of shifts of capacitance-voltage (*CV*) curves in the p-$Si/Al_2O_3/Al$ structures at both polarities of biases demonstrated that only a negative charge accumulates in Al_2O_3. This experiment proved the density of occupied electron traps in Al_2O_3 to be high, amounting to $\approx10^{19}$ cm^{-3}. Therefore the conduction in thick Al_2O_3 films is limited by a bulk stored charge and by the rate of ionization of deep traps.

To find the dominant contribution from electrons or holes to the Al_2O_3 conduction, the current-voltage characteristics of the p-$Si/Al_2O_3/Al$ structures in the dark and under illumination were measured.[19,20] At negative bias [see Fig. 1(b)] and in the dark the measured current is large and caused by electrons injected from the Al electrode (Fig. 2). At a positive bias [see Fig. 1(c)] the current in the dark is not large and rapidly saturates with bias magnitude (solid curve in Fig. 2) because of minority carriers (electrons) injected from the *p*-type semiconductor substrate. However, under illumination the current increases (dashed curve in Fig. 2)

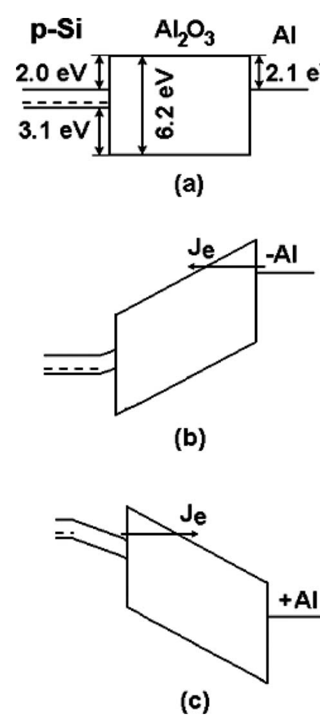

FIG. 1. The energy diagram of the p-$Si/Al_2O_3/Al$ structure at zero (a), negative (b), and positive (c) potentials applied to the Al electrode.

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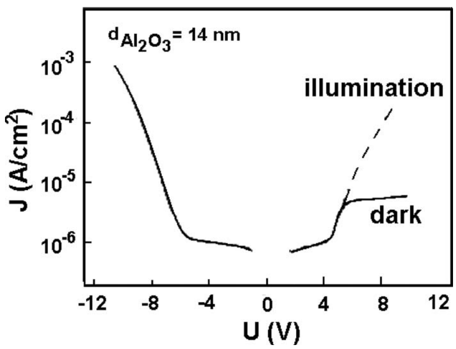

FIG. 2. Current-voltage characteristics of a p-Si/Al_2O_3/Al structure measured at both voltage polarities at the Al electrode. The dotted curves are the current-voltage characteristics of illuminated p-Si/Al_2O_3/Al structure.

due to electrons additionally photogenerated in p-type substrate. Thus, experiment indicates a monopolar (electron) mechanism of Al_2O_3 conduction.

The charge transport in Al_2O_3 is described within the framework of one-dimensional monopolar model involving Shokley–Read–Hall equations and the Poisson equation. This is done much in the same manner as for Si_3N_4.[21] To describe the ionization in Al_2O_3, a model assuming multiphonon ionization of traps was used.[15] We assume that, initially, the electron traps are neutral with a short-range capturing potential for electrons. Each trap can be represented as an "oscillator" or a "core" embedded in the Al_2O_3 lattice, for which the energy of trapped electrons linearly depends on the oscillator coordinate.[15] The trap characteristics are the phonon energy $W_{ph}=\hbar\omega$, the thermal ionization energy W_T, and the optical ionization energy W_{opt}. The external electric fields provides for enhanced ionization. For the rate of trap ionization, the quantum-mechanical approach[15] yields the following expression:

$$P = \sum_{n=-\infty}^{+\infty} \exp\left[\frac{nW_{ph}}{2kT} - S\coth\frac{W_{ph}}{2kT}\right] I_n\left[\frac{S}{\sinh(W_{ph}/2kT)}\right] \times P_i(W_T + nW_{ph}),$$

$$P_i(W) = \frac{eF}{2\sqrt{2m^*W}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF}W^{3/2}\right),$$

$$S = \frac{W_{opt} - W_T}{W_{ph}}. \quad (1)$$

Here, I_n is the modified Bessel function and $P_i(W)$ is the charge-carrier tunneling probability for a triangular barrier of height W.

The experimental curves of electric current versus temperature (dots) and the calculated dependences (solid line) are shown in Fig. 3. The experimental curves were measured at a negative bias, i.e., in the accumulation mode. The best fit of experimental curves with theoretical ones yields an electron capture cross section of 5×10^{-15} cm^2 and a trap density of 2×10^{20} cm^{-3}. From the data obtained at low temperatures and high electric fields, the effective electron mass and the energy W_{opt} were estimated. At a temperature close to the liquid-nitrogen temperature, when tunnel escape from traps dominates, the best agreement between the experiment and the calculations was obtained assuming an effective electron mass $m^*=0.4m_o$ and $W_{opt}=3.0$ eV. In low electric fields

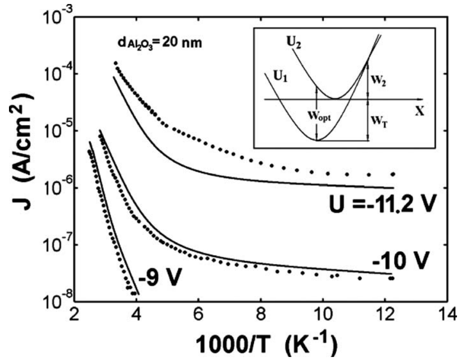

FIG. 3. Curves of current vs temperature for a p-Si/Al_2O_3/Al structure (dots) measured at various negative potentials at Al and the same curves calculated by the theory of multiphonon trap ionization (solid curves). Trap parameters used in the calculations are as follows: W_T=1.5 eV, W_{opt}=3.0 eV, W_{ph}=0.05 eV, $m^*=0.4m_e$, $N_t=2\times10^{20}$ cm^{-3}, and $\sigma=5\times10^{-15}$ cm^2. The inset shows the configuration diagram. U_1 is the potential energy of empty trap and U_2 is the energy of trap filled with an electron.

at high temperatures, the rate of trap ionization is defined by the barrier height for thermal ionization, W_T+W_2, where $W_2=(W_{opt}-2W_T)^2/4(W_{opt}-W_T)$ (see the inset in Fig. 3). The best agreement between the experimental and calculated data was obtained assuming W_T=1.5 eV and W_{ph}=0.05 eV. Hence, for the ratio between the optical and thermal trap ionization energies, we obtain $W_{opt}/W_T=2$, which value translates into $W_2\approx0$ eV. Previously, the same proportion between the energies W_{opt} and W_T was observed in Si_3N_4.[21]

Figure 4 compares the experimental current-voltage characteristics measured at various temperatures (dots) with the curves calculated by the model of multiphonon ionization (solid curve). The experimental curves of current versus voltage were measured at a negative potential at the Al electrode. A satisfactory agreement between the experimental and calculated data was obtained assuming the same parameter values as in modeling the current-versus-temperature curves.

To summarize, the conduction in Al_2O_3 was examined, both experimentally and theoretically, in a broad range of electric fields and temperatures. We have found that electrons are dominant charge carriers in Al_2O_3 independent of bias polarity. The theory of multiphonon trap ionization was shown capable of providing an adequate description to experimental data with realistic values of physical parameters of deep traps in the dielectric.

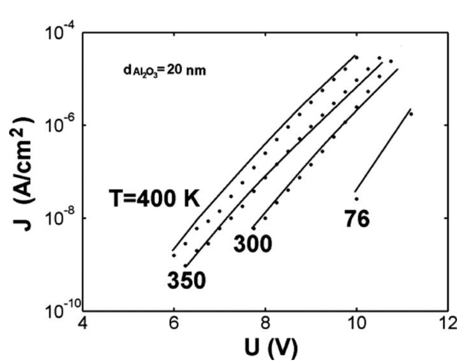

FIG. 4. Current-voltage curves of a p-Si/Al_2O_3/Al structure measured at various temperatures (dots) and at a negative potential at Al and calculated by the theory of multiphonon trap ionization (solid curve). Trap parameters used in the calculations are as follows: W_T=1.5 eV, W_{opt}=3.0 eV, W_{ph}=0.05 eV, $m^*=0.4m_e$, $N_t=2\times10^{20}$ cm^{-3}, and $\sigma=5\times10^{-15}$ cm^2.

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