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# Modeling the charge transport mechanism in amorphous $Al_2O_3$ with multiphonon trap ionization effect

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ABSTRACT

The charge transport mechanism in amorphous alumina, $Al_2O_3$, is investigated both theoretically and experimentally. We found that the experimental current–field–temperature dependencies can hardly be understood based on the commonly used Frenkel effect or the thermally-assisted tunneling model. Instead, we suggest that the charge transport in $Al_2O_3$ is related to the ionization of the deep trap by multiphonon tunneling. Excellent agreements between the predicted, the measured data were obtained by using the proposed multiphoton model with the following values of trapping parameters: thermal ionization energy of 1.5 eV, optical ionization energy of 3.0 eV, phonon energy of 0.05 eV, electron effective mass of $0.4m_e$. The density of electron trap and electron capture cross-section of neutral traps are $2 \times 10^{20}$ cm$^{-3}$ and $5 \times 10^{-15}$ cm$^2$, respectively.

## 1. Introduction

Aluminum oxide, $Al_2O_3$, is a material of much interested as an alternative to silicon dioxide, $SiO_2$, for suppressing the gate tunnel current in silicon devices. The aluminum oxide has advantage of high dielectric constant of about 10 [1,2], a large bandgap energy of 6.2 eV and thus a high electron barrier (~2.0 eV) at the Si/$Al_2O_3$ interface [3]. In addition, it was found that $Al_2O_3$ films grown on silicon have lower leakage currents than that of hafnium oxide [4,5] because of the lower trap density in $Al_2O_3$. $Al_2O_3$ films were also proposed to be used as blocking layers in flash memory cells [6–10]. To be used as a blocking layer in flash cells, the leakage current must be extremely low in order to maintain charge storage for a 10 year period at elevated temperatures (85 °C). Thus, a detail investigation on the charge transport mechanism in this material is very important.

Electrical conduction in dielectrics under high electric fields (~5 MV/cm) is often considered to obey the widely-accepted Frenkel trap ionization model [11,12]. However, in high-*k* materials, the leakage current characteristics are often diverged from the Frenkel model [13,14]. It was proposed that the current conduction in $Al_2O_3$ at room temperature is dominated by the Frenkel mechanism [15,16]. A different trap ionization model which assumes that the trap ionization rate in a semiconductor is controlled by a multiphonon mechanism was also proposed in the literature [12,17–19]. As will be demonstrated in this work, the same mechanism is also applicable to the $Al_2O_3$ case. The experimental details will be given in Section 2 and the theoretical background will be given in Section 3.

## 2. Experimental

$Al_2O_3$ films of about 20 nm thick were deposited on (1 0 0) oriented p-type silicon substrates with resistivity of about 5 Ω cm by using atomic layer deposition (ALD) from a trimethylaluminum $Al(CH_3)_3$ and $H_2O$ precursors. Here we used much thick films in order to minimize the effects of interface layer. After deposition, the $Al_2O_3$ films were annealed in a dry nitrogen ambient for 5 s. Electron diffraction pattern indicates that the as-deposited film is amorphous. Aluminum gate contacts with area of $5 \times 10^{-3}$ cm$^2$ were deposited onto the films by thermal evaporation technique. To measure the current conduction of the p-Si/$Al_2O_3$/Al capacitor, the sample was placed in a liquid nitrogen cryostat. All measurements were performed in accumulation mode, *i.e.* with a negative potential applied to the gate metal. Temperature-dependent currents were measured at fixed voltages applied to the gate at a heating rate of 1 K/s. Current–voltage characteristics were measured at fixed temperatures at a voltage ramp of 0.2 V/s. For samples biased at a constant voltage, the measured current displayed a slow relaxation similar to that reported in amorphous silicon nitride $Si_3N_4$ [20]. The nature of the slow current relaxation in both $Si_3N_4$ and $Al_2O_3$ still remains unclear. The high-frequency dielectric constant, $\varepsilon_{opt}$, of amorphous $Al_2O_3$ was calculated with $\varepsilon_{opt} = n^2$, where $n$ is the refractive index which was measured by an ellipsometer

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operated at wavelength of 6328 Å. The high-frequency dielectric constant of $Al_2O_3$ was about 3.0 based on this study.

Since the hole barrier at the $Si/Al_2O_3$ interface, equals to 3.1 eV, is greater than the electron barrier at the $Si/Al_2O_3$ or $Al/Al_2O_3$ interfaces which is about 2.0 eV only [3], electron injection from Al into $Al_2O_3$ dominates the charge transport and the hole injection from Si into $Al_2O_3$ should be negligible at negative bias. That is, the current conduction in $Al_2O_3$ is unipolar and is governed by the electron current only which is similar to the $HfO_2$ case [4].

The electron injection at the $Al/Al_2O_3$ interface was assumed to be controlled by the Fowler–Nordheim (FN) mechanism with thermally-assisted tunneling at the contact [21]. The experimental value of electron effective mass of about $0.45m_e$ was used in the calculations [16]. The charge transport in metal/alumina/silicon structures is normally controlled by the space charges localized at the deep traps of the bulk $Al_2O_3$. The temperature and voltage dependencies of conduction current in $Al_2O_3$ are therefore governed by the corresponding dependencies of trap ionization rate. It was believed that the trap ionization process in dielectrics should involve the Frenkel emission of charge carriers due to the Coulomb barrier lowering under the applied electric fields [9].

## 3. Theory

In the Frenkel model, involving attractive Coulomb potential (see Fig. 1a), the trap ionization probability, $P$, at low electric fields and high temperatures is given by [11]

$$P_{\mathrm{FP}} = \nu \exp\left(-\frac{W_t - \beta\sqrt{F}}{kT}\right) \tag{1}$$

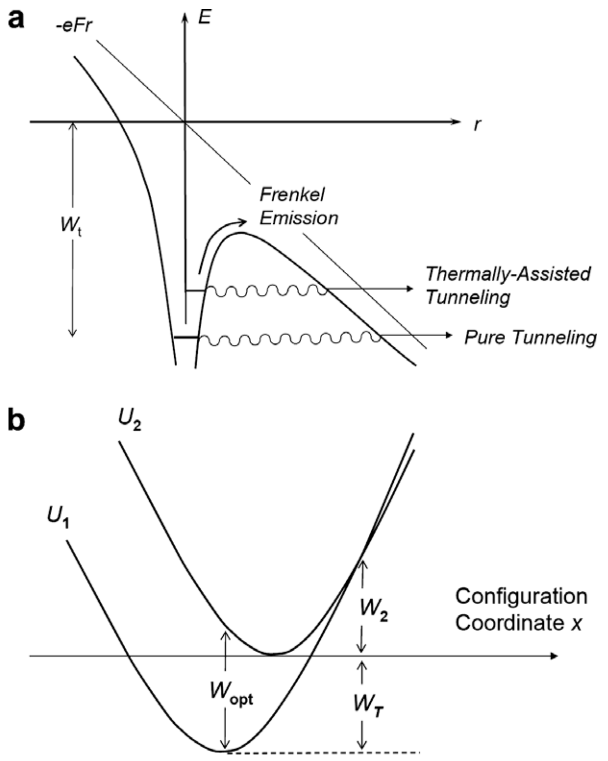

**Fig. 1.** (a) Coulomb trap ionization in a high electric field indicating pure tunneling at high field and at low temperature, thermally-assisted tunneling in the intermediate temperature range, and thermal ionization (Frenkel emission) at weak field and at high temperatures. (b) The configuration diagram for a neutral trap adopted in the phonon-coupled trap model. The potential curves $U_1$ and $U_2$ refer to electron-filled traps and empty traps, respectively.

where $W_t$ is the trap energy, $\beta = \sqrt{e^3/\pi\varepsilon_\infty\varepsilon_0}$ is the Frenkel constant, and $\nu$ is the attempt-to-escape factor; $F$ is the local electric field; $e$ is the electron charge; $\varepsilon_0$ is dielectric constant; and the low-frequency dielectric constant, $\varepsilon_\infty$, is about 10 for $Al_2O_3$.

At high electric fields and at low temperatures the Frenkel model can be further modified by taking into account trap ionization involving thermally-assisted tunneling (TAT) which is given by

$$P_{\mathrm{TAT}} = \frac{\nu}{kT}\int_0^{W_t-\beta\sqrt{F}} dE \times \exp\left(-\frac{E}{kT} - \frac{2}{\hbar}\int_{x_1}^{x_2} dx\sqrt{2m^*(eV(x)-E)}\right) \tag{2}$$

where $V(x) = W_t - \frac{e}{4\pi\varepsilon_\infty\varepsilon_0 x} - Fx$. Here, $E$ is the excited energy level, and $m^*$ is the electron effective mass. The points $x_1$ and $x_2$ are classical turning points and are given by

$$x_{1,2} = \frac{1}{2}\frac{W_t - E}{eF}\left(1 \mp \left(1 - \frac{eF}{\pi\varepsilon_0\varepsilon_\infty(W_t-E)^2}\right)^{1/2}\right) \tag{3}$$

The electron tunneling is treated here within the semi-classical approximation, and the integral over $x$ can be expressed in terms of elliptic integrals. The total trap ionization rate based on this approach is

$$P = P_{\mathrm{FP}} + P_{\mathrm{TAT}} \tag{4}$$

A phonon-coupled trap model was also considered to explain the experimental data. Following the approach of Makram-Ebeid and Lannoo [17], in this model we consider each empty trap as a neutral center presenting an 'oscillator' or 'core', embedded in the $Al_2O_3$ lattice and capable of capturing an electron. The trapping characteristics are governed by the phonon energy ($W_{ph} = \hbar\omega$), thermal energy ($W_T$) and the optical ionization energy ($W_{opt}$) as depicted in Fig. 1b. The rate of trap ionization can be approximated by [17]:

$$\begin{gathered} P = \sum_{n=-\infty}^{+\infty} \exp\left[\frac{nW_{ph}}{2kT} - S\coth\frac{W_{ph}}{2kT}\right] I_n\left(\frac{S}{\sinh(W_{ph}/2kT)}\right) P_i(W_T + nW_{ph}) \\ P_i(W) = \frac{eF}{2\sqrt{2m^*W}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m}}{\hbar eF}W^{3/2}\right), \quad S = \frac{W_{opt}-W_T}{W_{ph}} \end{gathered} \tag{5}$$

where $I_n$ is the modified Bessel function and $P_i(W)$ is the tunnel escape rate through the triangular barrier of height $W$.

## 4. Results and discussion

Fig. 2 shows experimental curves of temperature-dependent currents measured at various bias voltages applied to the samples. Results based on Frenkel effect with trap ionization involving thermally-assisted tunneling are illustrated in solid curves. Here, we assumed that the capture cross-section of the Coulomb potential is $5 \times 10^{-13}$ cm$^2$. At high temperatures and at weak electric fields, the conduction current depends exponentially on temperature. Fitting the experimental curves in the $\ln J$ versus $l/T$ plot yields a trap energy of 1.4 eV and an electron trap density of $5 \times 10^{19}$ cm$^{-3}$. The absolute values of the electric current in the high temperature range and weak fields yield an attempt-to-escape factor of $1 \times 10^9$ s$^{-1}$ which is anomalously low. In the original paper for Frenkel theory [11] the frequency factor $\nu$ is evaluated as $\nu = W_t/h \approx 4 \times 10^{14}$ s$^{-1}$, which is much larger than the present value. Meanwhile, the interpretation of amorphous $Si_3N_4$ conductivity based on the Frenkel effect also results in an anomalously low-frequency factor in the range of $10^6$–$10^9$ s$^{-1}$ [19,22].

At low temperatures, the electric current is almost independent on temperature and can be explained with the trap-assisted tunneling. The effective mass of escaped electron can be evaluated

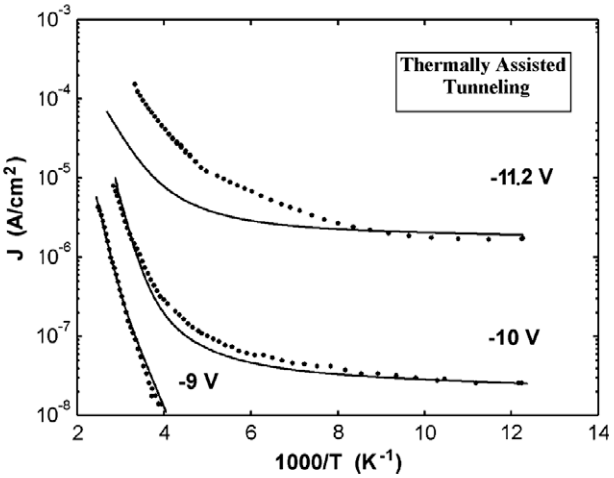

**Fig. 2.** Experimental current–temperature curves measured at different electric fields (dots) with theoretical fitting based on the Frenkel effect with thermally-assisted tunneling trap ionization (curves). The best-fit parameter values are: $W_t = 1.4$ eV; $m^* = 3.5m_e$; $\nu = 1 \times 10^9$ s$^{-1}$; $\sigma = 5 \times 10^{-13}$ cm$^2$ and $N_t = 5 \times 10^{19}$ cm$^{-3}$.

from fitting the experimental dependence with a calculated curve. For $Al_2O_3$, $m^* = 3.5m_e$. An anomalously high effective mass of $m^* = 4.0m_e$ was reported for tunneling ionization of Coulomb traps in amorphous $Si_3N_4$ [19]. Both values suggest that the current conduction in amorphous $Al_2O_3$ can be adequately described neither by the Frenkel effect nor by including trap ionization by thermal-assisted tunneling.

Fig. 3 shows the current–voltage characteristics measured at various temperatures and fitted with the Frenkel model. The values of parameters for traps are identical to those used in the *I–T* calculations. Note that here we used different effective electron masses for $Al_2O_3$ bulk ($m^* = 3.5m_e$) and at the $Si/Al_2O_3$ interface ($m^* = 0.45m_e$). As if the effective electron mass at the interface excess $0.45m_e$, contact-limited conduction would emerge. This effect manifests as a sharp decrease in the electric current as the bias voltage decreases. That is not the case of the present experiments.

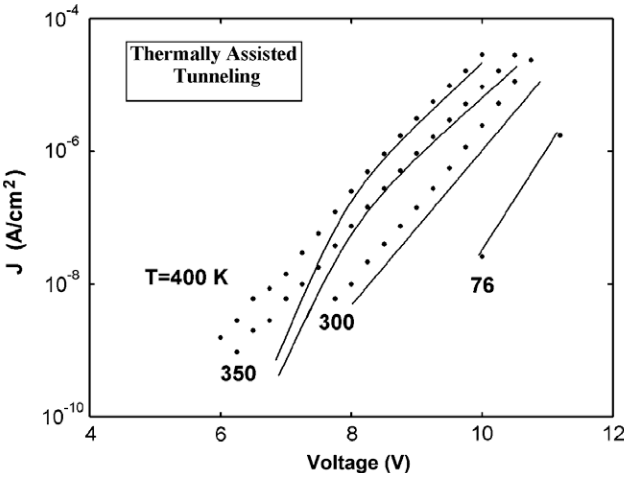

**Fig. 3.** Current–voltage characteristics measured at different temperatures with negative potentials applied to the Al contacts (dots) with theoretical fitting based on the Frenkel effect with thermally-assisted tunneling trap ionization (curves). Best-fit parameters are: $W_t = 1.4$ eV; $m^* = 3.5m_e$; $\nu = 1 \times 10^9$ s$^{-1}$; $\sigma = 5 \times 10^{-13}$ cm$^2$ and $N_t = 5 \times 10^{19}$ cm$^{-3}$.

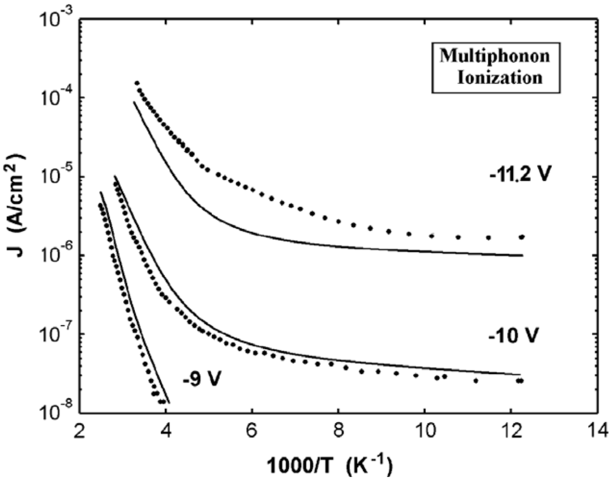

**Fig. 4.** Current–temperature characteristics measured at different negative potentials applied to the Al contact (dots) in comparison with data calculated using quantum multiphonon mechanism (solid line). The parameters used in the simulation are: $W_T = 1.5$ eV, $W_{opt} = 3.0$ eV, $W_{ph} = 0.05$ eV, electron effective mass $m^* = 0.4m_e$, density of electron traps $N_t = 2 \times 10^{20}$ cm$^{-3}$, cross-section of electron capture at the neutral trap $\sigma = 5 \times 10^{-15}$ cm$^2$.

Fig. 4 plots the relationship of electric current versus temperature measured at various potentials. The solid curve was calculated according to the Makram-Ebeid quantum theory of multiphonon trap ionization [17]. From the fitting point of view, Fig. 4 does not yield much better fitting than that in Fig. 2. The rather obvious improvement is that the multiphonon model has a better fit at high temperature and high voltage (see the curve for −11.2 V bias) than the TAT case. However, the accuracy of the fitting is not our primary concern. Our primary concern is that the values of the parameters must be sound physically. The TAT model does not yield reasonable values of the model parameters. Considering the current conduction in $Al_2O_3$ in term of the quantum Makram-Ebeid multiphonon theory [17], the electron cross-section again assumed to be $5 \times 10^{-15}$ cm$^2$ for neutral traps. At low temperatures and at high electric fields, the rate of trap tunnel ionization is defined by the effective mass and the effective barrier height which is close to the optical ionization energy $W_{opt}$ [19]. At temperatures close to the liquid nitrogen temperature, effective mass of $0.4m_e$, optical ionization energy of 3.0 eV and trap concentration of $2 \times 10^{20}$ cm$^{-3}$ were obtained by fitting the experimental data with theoretical curves (see Fig. 4). The effective mass obtained in present study agrees with the experimental and theoretical values reported earlier [16,23,24].

In the case of high temperatures and weak electric fields the trap ionization probability depends on the energies $W_T$ and $W_{opt}$. As shown in Fig. 1b, the combination of these energies defines the trap ionization energy $(W_T + W_2)$. In the quantum multiphonon theory [17], core tunneling under parabolic potentials $U_1$ and $U_2$, respectively, for traps with captured electrons and for empty traps is considered. Hence, the trap ionization energy can be smaller than $W_T + W_2$ in weak electric fields. The best-fit of the experimental data in Fig. 4 yields a $W_T$ value of 1.5 eV. The ratio between the optical and thermal ionization energies of traps in $Al_2O_3$ is $W_{opt}/W_T \approx 2$, resulting in $W_2 \approx 0$ eV. The same result was found earlier for trap energies in $Si_3N_4$ [21]. The best agreement with the experiment was obtained with a phonon energy $W_{ph} = 0.05$ eV.

Fig. 5 shows the current–voltage characteristics measured at various temperatures. Because of the slow current relaxation in $Al_2O_3$ films, the measured current values from a voltage sweep over the range of 6–11.2 V is slightly different to those given by the temperature sweep. As shown in Fig. 5, a satisfactory agreement with the experimental data is achieved. Comparing with Fig. 4, although the fittings were based on different sets of data, the fitting parameters obtained from Fig. 5 are only slightly differ-

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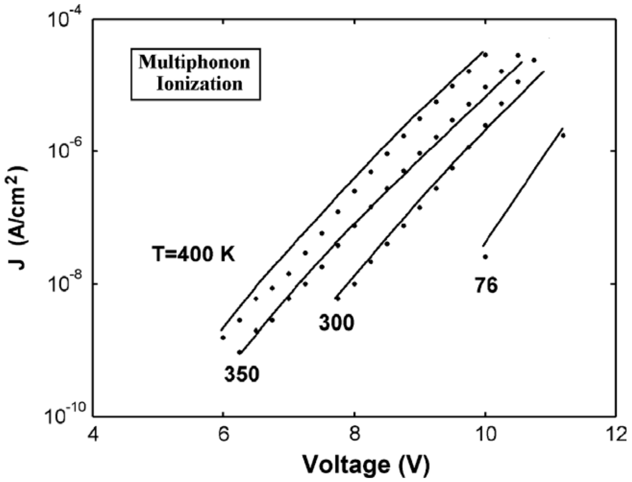

**Fig. 5.** Current–voltage characteristics measured at different temperatures with negative potentials applied to the Al contacts (dots) in comparison with data calculated using quantum multiphonon mechanism (solid line). The parameters used in the simulation are: $W_T = 1.5$ eV, $W_{opt} = 3.0$ eV, $W_{ph} = 0.05$ eV, electron effective mass $m^* = 0.4m_e$, density of electron traps $N_t = 2 \times 10^{20}$ cm$^{-3}$, cross-section of electron capture at the neutral trap $\sigma = 5 \times 10^{-15}$ cm$^2$.

ent to those obtained from the *I–T* fittings in Fig. 4. Similar differences were also found between the *I–T* and *I–V* as given in Figs. 2 and 3, respectively.

In summary, we have demonstrated that the fittings of the experimental *I–T* and *I–V* curves with the Frenkel ionization model (for traps with a Coulomb attractive potential) yields an extremely low attempt-to-escape factor for trapped electrons (which is five orders of magnitude lower than the theoretically-predicted value) and an anomalously high value of the tunneling effective mass (an order of magnitude greater than the experimental value). Hence, the widely-accepted Frenkel model fails to produce a satisfactory description for the current conduction in amorphous $Al_2O_3$. The current conduction in $Al_2O_3$ film should be due to multiphonon ionization of neutral trap.

## 5. Conclusions

We show that the current conduction in amorphous $Al_2O_3$ can be modeled well with the multiphonon ionization of neutral trap in a wide range of temperatures and electric fields. Parameters of electron trap in amorphous $Al_2O_3$ were determined. These results enable accurate prediction of leakage current and charge accumulation at traps in $Al_2O_3$.

It is interesting that the electrical conduction behaviors in amorphous $Al_2O_3$ are similar to that reported in amorphous silicon nitride $Si_3N_4$. In both cases the conduction mechanism is controlled by the multiphonon trap ionization. In addition, the value of the effective electron mass obtained in the present study, $m^* = 0.4m_e$, agrees well with both the experimental value $m^* = 0.45m_e$ and theoretical value obtained previously in band calculations.

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