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ABSTRACT

Currently, it is generally accepted that the charge transport in dielectrics is limited by the Coulomb trap ionization in a strong electric field (Frenkel effect). In the present work, the charge transport mechanism in La:HfO_2 was experimentally studied, and four theoretical conductivity models—the Frenkel effect of Coulomb trap ionization, Hill-Adachi model of overlapping Coulomb potentials, Makram–Ebeid and Lannoo model of multiphonon isolated trap ionization, and Nasyrov-Gritsenko phonon-assisted tunneling between traps—were quantitatively analyzed. It was shown that the charge transport mechanism in La: HfO_2 is qualitatively described by the Frenkel effect, but the Frenkel effect predicts an abnormally low trap concentration value and a large high-frequency dielectric constant value, which is not consistent with the experiment. The charge transport in La:HfO_2 is quantitatively described by the model of phonon-assisted tunneling between neighboring traps.

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Hafnium oxide (HfO_2) was considered as a paraelectric material. In 2011, it was found that HfO_2 doping, including lanthanum, leads to the appearance of the ferroelectric effect.[1] The presence of the ferroelectric effect in doped HfO_2 opens up the possibility of developing a terabit scale non-volatile Ferroelectric Random Access Memory (FeRAM). Except for thermal silicon oxide (SiO_2), other dielectrics, such as almost stoichiometric Si_3N_4, Al_2O_3, Ta_2O_5, HfO_2, and ZrO_2, and the corresponding nonstoichiometric compounds, such as $SiN_{x<4/3}$, $AlO_{x<3/2}$, $TaO_{x<5/2}$, $HfO_{x<2}$, and $ZrO_{x<2}$, contain high trap concentrations in the range of 10^{18}–10^{22} cm^{-3}. These traps can localize injected electrons and holes, and they are responsible for leakage current. Traps in a dielectric can play both a negative and positive role.

In metal-dielectric-semiconductor devices, the leakage current through traps in the gate dielectric can lead to an undesirable power dissipation and heating of silicon devices.[2] On the other hand, the localization effect of electrons and holes for deep traps in dielectrics is widely used in flash memory devices for recording and storing information.[3,4] The formation and annihilation of traps due to oxygen vacancies underlie the next generation of high-speed resistive flash memories.[4,5]

Currently, it is widely accepted that the charge transport in dielectrics is limited by the Coulomb trap ionization in a strong electric field (Frenkel effect) (inset in Fig. 1).[6] The charge transport in Si_3N_4,[7,8] Al_2O_3,[9,10] Ta_2O_5,[11,12] HfO_2,[13,14] and ZrO_2[15,16] is qualitatively interpreted in terms of the Frenkel effect model. However, it has recently been established that the charge transport in Si_3N_4,[16,17] Al_2O_3,[18] HfO_2,[19,20] ZrO_2,[21] and $Hf_{0.5}Zr_{0.5}O_2$[22] is not quantitatively described by the Frenkel effect. The charge transport in Si_3N_4[16,17] and Al_2O_3[18] is limited by the multiphonon isolated trap ionization, and the charge transport in HfO_2,[19,20] ZrO_2,[21] and $Hf_{0.5}Zr_{0.5}O_2$[22] is limited by the phonon-assisted tunneling between traps. Thin (~10 nm) doped films are intensively studied as an active storage medium in the next generation of nonvolatile FeRAM.[1] Leakage currents in the active medium of doped HfO_2 can lead to an undesirable excessive power dissipation and heating of memory devices. Therefore, it is important to know the charge transport mechanism of doped HfO_2 in order to predict the power dissipation in memory devices. The aim of this work is an experimental study of the charge transport mechanism in La:HfO_2 and its quantitative comparison with theoretical models.

We studied TiN/La:HfO_2(10 nm)/TiN samples. We used the p-type silicon substrate (100) with the resistivity of 12 Ohm cm. A 10 nm thick TiN layer was grown on a silicon substrate using the atomic layer deposition technology at 320 °C. $TiCl_4$ was used as a precursor at room temperature. The synthesis was carried out in NH_3 + Ar plasma. 10 nm thick La: HfO_2 films were deposited using atomic layer deposition. The chamber temperature was 235 °C. The precursors

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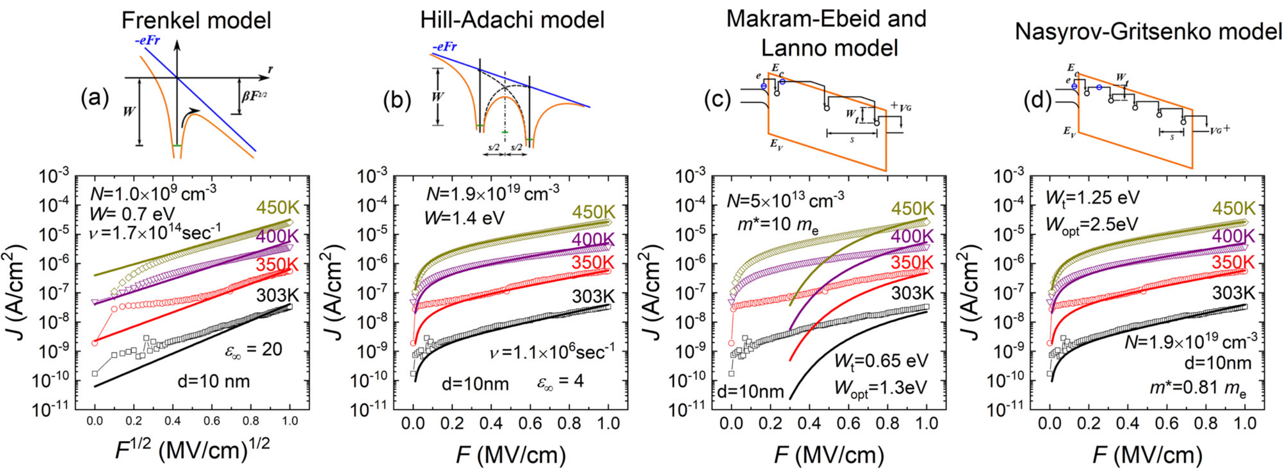

FIG. 1. Experimental current density–electric field characteristics of La:HfO$_2$ and the simulation data (a) obtained by the Frenkel effect model in coordinates lg(J) $\sim \sqrt{F}$; (b) by the Hill-Adachi model in coordinates log (J) $\sim F$; (c) by the Makram-Ebeid and Lannoo model in coordinates log (J) $\sim F$; and (d) by the Nasyrov–Gritsenko model in coordinates log (J) $\sim F$. Above is a schematic representation of the charge transport models.

were Hf(NCH$_3$C$_2$H$_5$)$_4$ (TEMAH) at a heating temperature 100 °C and La (iPrCp)$_3$ at a heating temperature 170 °C. The reactant was O$_2$ + Ar plasma. Fast thermal annealing was used at the temperature of 500 °C for 30 s in the N$_2$ atmosphere. The upper TiN electrode had an area equal to 7.1×10^{-4} cm^2. The fabricated La:HfO$_2$ film structure was crystalline. The study of photoelectron spectra showed that the obtained La:HfO$_2$ compound is a mixture of HfO$_2$ (85%) and La$_2$O$_3$ (15%).

To compare the experimental data and theoretical model, the simulation method of least absolute deviations (LADs) was used. It consists of the theoretical model parameter selection process until the maximum deviation value (20%) of the theory from the experiment is reached. Due to the current expressions Log $I \sim U$ or $I \sim e^U$, the maximum deviation has the form

$$\Delta_{\max} = \left| \mathrm{Log}\left(\frac{I_{teor}}{I_{\exp}}\right) \right| \times 100\%. \tag{1}$$

At the beginning, the theoretical model parameters of one temperature are selected. In our case, it is 450 K. The trap ionization energy is determined independent of the current temperature dependence; the greater the number of experimental temperatures is, the more accurately the ionization energy is found. With four temperature dependences, we guarantee the accuracy for the second decimal place of the trap ionization parameter. Also, a weak electric field is not always taken into account in the simulation process since, at weak electric fields, there is a dynamic process of charging/discharging traps. In our case, it is less than 0.2 MV/cm. In addition, in a weak field, it is also possible to limit the current by the injection process at the metal-dielectric contact. Using this simulation method at $\Delta_{\max} < 20\%$, we have this accuracy of parameters: $\varepsilon_\infty = \varepsilon_\infty \pm 0.2$, $W = W \pm 0.01$, $W_t = W_t \pm 0.01$, $W_{opt} = W_{opt} \pm 0.02$, $\nu = \nu \pm 0.1$, $N = N \pm 0.1$, and $m^* = m^* \pm 0.02$.

To account for the shift of voltage-polarization loops, our measurements were carried out in this mode: each new measurement was made on a new contact pad. Since the film is quite homogeneous and the contacts were obtained with a close areal accuracy, the model parameter deviations should not exceed 5%, and this fits the parameter error.

The experimental current density–electric field (J–F) characteristics of La:HfO$_2$ are shown in Fig. 1(a) at the coordinates corresponding to the Frenkel effect[6,23] (1),

$$J = eN^{2/3}P,\ P = \nu \exp\left(-\frac{W - \beta_F\sqrt{F}}{kT}\right), \quad \beta_F = \left(\frac{e^3}{\pi\varepsilon_\infty\varepsilon_0}\right)^{1/2}. \tag{2}$$

Here, J is the current density, F is the electric field, $N = s^{-3}$ is the trap concentration, s is the distance between traps, P is the trap ionization probability, $\nu = W/h$ is the attempt to escape factor, $\varepsilon_\infty = n^2$ is the high frequency permittivity, and n is the refractive index.

The refractive index of La:HfO$_2$, measured at the wavelength of a helium-neon laser using ellipsometry, is $n = 2.0$. Therefore, the La:HfO$_2$ high-frequency permittivity is $\varepsilon_\infty = n^2 = 4$. The slope of the experimental J–F characteristics of La:HfO$_2$ in the coordinates lg(J) $\sim \sqrt{F}$ gives parameter $\varepsilon_\infty = 20$ in the Frenkel model. The trap energy in La: HfO$_2$ lies in the range of 0.7–0.8 eV. The J–F characteristics of La:HfO$_2$ are satisfactorily described by the Frenkel effect with the trap energy of $W = 0.7$ eV. According to the original Frenkel work,[23] the attempt to escape factor for the trap energy $W = 0.7$ eV corresponds to $\nu = W/h \approx 1.7 \times 10^{14}$ s^{-1}. With such an attempt to escape factor, the trap concentration in the Frenkel model should be equal to $N = 1.0 \times 10^9$ cm^{-3}. The simulated data at 450 K and 400 K meet the LAD requirement. For 350 K and 303 K, the LAD works only in a strong field (more than 0.5 MV/cm) for simulated curves. If such an error is ignored, the deviation of the trap concentration and attempt to escape factor parameters does not exceed half of the order of magnitude. This means that an error in the simulating parameters is not able to explain the discrepancy between the obtained simulating results and expected theoretical results. Therefore, the experimentally obtained anomalously low trap concentration and an anomalously large high frequency permittivity value indicate that the Frenkel effect does not quantitatively describe the charge transport in La:HfO$_2$.

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The exponential increase in the leakage current with the increasing trap concentration is predicted by the overlapping Coulomb potential Hill–Adachi model,[24,25]

$$P = 2\nu \exp\left(-\frac{W - \frac{q^2}{\pi\varepsilon_\infty\varepsilon_0 s}}{kT}\right)\sinh\left(\frac{eFs}{2kT}\right). \quad (3)$$

The J–F characteristics in the Pool coordinates $\lg(J) \sim F$ are presented in Fig. 1(b).

The leakage current increases, and the slope of the curve $\log(J) \sim F$ decreases with the increasing temperature in La:HfO$_2$. In the Hill model, this is explained by an increase in the trap concentration [Fig. 1(b)]. The high-frequency permittivity value $\varepsilon_\infty = 4$, determined for La:HfO$_2$, is in good agreement with the experiment. For energy $W = 1.4$ eV, the attempt to escape factor in the Hill model should be equal to $\nu = 3.3 \times 10^{14}\,\text{s}^{-1}$. Therefore, the Hill model of overlapping Coulomb potentials explains the slope of the J–F characteristic, but does not explain the anomalously low attempt to escape factor value $\nu = 1.1 \times 10^6\,\text{s}^{-1}$.

According to the Makram-Ebeid and Lannoo (ME–L) model, the charge transport in a dielectric is caused by the multiphonon isolated trap ionization.[26] The trap ionization probability in the ME–L model is described by the following expressions:

$$P = \sum \exp\left(\frac{nW_{ph}}{2kT} - \frac{W_{opt} - W_t}{W_{ph}}\coth\frac{W_{ph}}{2kT}\right) \times I_n\left(\frac{W_{opt} - W_t}{W_{ph}\sinh(W_{ph}/2kT)}\right)P_i(W_t + nW_{ph}), \quad (4)$$

$$P_i = \frac{eF}{2\sqrt{2m^* W}}\exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF}W^{3/2}\right). \quad (5)$$

Here, W_t is the thermal energy trap, W_{opt} is the optical energy trap, W_{ph} is the phonon energy, and m^* is the effective electron mass.

In the ME–L multiphonon model, an electron tunnels, through a phonon absorption, into the dielectric conduction band [inset in Fig. 1(c)]. For the simulation, the trap parameters $W_t = 0.65$ eV, $W_{opt} = 1.3$ eV, and $W_{ph} = 60$ meV were chosen for the quantitative coincidence of the model curves with the experimental data in a strong electric field. These trap parameters correspond to the abnormally high effective electron mass value $m^* = 10\,m_e$ and the abnormally small trap concentration value $N = 5 \times 10^{13}\,\text{cm}^{-3}$ [Fig. 1(c)]. These simulating results meet the 20% LAD requirement only in strong fields (more than 0.9 MV/cm). Thus, the ME–L model does not quantitatively describe the charge transport in La:HfO$_2$.

The Nasyrov–Gritsenko (NG) model was proposed in Refs. 27 and 28. In this model, an electron is excited from the ground state, due to the phonon absorption, and then it tunnels to a neighboring trap (see the inset in Fig. 4). In the NG model, the electron tunnels to a neighboring trap due to the large overlap integral. The ionization trap probability in the NG model is given by the following expression:[27,28]

$$P = \frac{2\sqrt{\pi}\hbar W_t}{m^* s^2\sqrt{2kT(W_{opt} - W_t)}}\exp\left(-\frac{W_{opt} - W_t}{W_{ph}}\right) \times \exp\left(-\frac{2s\sqrt{2m^* W_t}}{\hbar}\right)\sinh\left(\frac{eFs}{2kT}\right). \quad (6)$$

The NG model quantitatively describes the J–F characteristics of La:HfO$_2$ at reasonable trap parameters, which are shown in the inset in Fig. 1(d). The obtained values of $W_t = 1.25$ eV and $W_{opt} = 2.5$ eV for La:HfO$_2$ correspond to the thermal and optical trap energies in HfO$_2$.

In this paper, four trap ionization models were used to explain the charge transport in La:HfO$_2$ in a strong electric field. The Frenkel model gives an unphysically low trap concentration and a fourfold higher high-frequency permittivity value. The Hill–Adachi model of overlapping Coulomb centers quantitatively explains the slope of experimental J–F characteristics, but predicts an unphysically low attempt to the escape parameter value. The multiphonon ME–L model does not describe the charge transport in La:HfO$_2$. The NG model quantitatively describes the increase in the La:HfO$_2$ conductivity with the increasing temperature.

The trap concentration in the NG model is the same as in the Hill–Adachi model of overlapping Coulomb traps. The difference between the models is that the Hill–Adachi model assumes the presence of positively charged traps and the NG model assumes the presence of neutral traps.

The thermal trap energy value $W_t = 1.25$ eV and optical trap energy value $W_{opt} = 2.5$ eV obtained in the NG model in hafnium oxide doped with lanthanum (La:HfO$_2$) coincide with the thermal and optical trap energies in undoped hafnium oxide.[19,20,29,30] In Ref. 20, it was found that the traps in undoped HfO$_2$ are caused by oxygen vacancies. The coincidence of the thermal and optical trap energies in HfO$_2$ and in La:HfO$_2$ indicates that the traps in La:HfO$_2$ are due to oxygen vacancies, similar to HfO$_2$. Thus, we can conclude that the charge transport in La:HfO$_2$ is also rather due to the presence of oxygen vacancies in HfO$_2$ than to the doping with the La impurity. Based on this conclusion, a practical recommendation can be made to reduce undesirable leakage currents in the active La:HfO$_2$ medium in FeRAM. The NG theory predicts an exponentially strong decrease in the leakage current with a decrease in the trap concentration. Annealing HfO$_2$ in the N$_2$ atmosphere decreases the trap concentration,[31] but the annealing in the N$_2$ atmosphere may deteriorate ferroelectric properties, as it was reported for Hf$_{0.5}$Zr$_{0.5}$O$_2$ in Ref. 32. On the other hand, annealing Hf$_{0.5}$Zr$_{0.5}$O$_2$ in the O$_2$ atmosphere does not change ferroelectric properties. We assume that this will be the same in the case of La:HfO$_2$. Since the traps in La:HfO$_2$ are caused by oxygen vacancies, the trap concentration responsible for leakage currents can be reduced by annealing La:HfO$_2$ in oxygen or in oxygen plasma.

In conclusion, the charge transport mechanism in La:HfO$_2$ was experimentally studied at different temperatures. The experimental data were analyzed based on four trap ionization mechanisms: the Frenkel model of isolated Coulomb trap ionization, the Hill–Adachi model of overlapping Coulomb traps, the Makram-Ebeid and Lannoo model of multiphonon isolated neutral trap ionization, and the Nasyrov–Gritsenko model of phonon-assisted tunneling between traps. It was shown that the widespread Frenkel model does not quantitatively describe the charge transport in La:HfO$_2$. The Hill–Adachi and Makram-Ebeid and Lannoo models do not describe the charge transport in La:HfO$_2$. The Nasyrov–Gritsenko model of phonon-assisted tunneling between traps at a high trap concentration quantitatively explains the slope of J–F characteristics and gives the thermal trap energy value of $W_t = 1.25$ eV and optical trap energy value of $W_{opt} = 2.5$ eV. The coincidence of the thermal and optical trap

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energies in HfO_2 and in La:HfO_2 indicates that the traps in La:HfO_2 are due to oxygen vacancies.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim, J. Müller, A. Kersch, U. Schroeder, T. Mikolajick, and C. S. Hwang, Adv. Mater. **27**(11), 1811–1831 (2015).
[2] 1J. Robertson and R. M. Wallace, Mater. Sci. Eng., R **88**, 1–41 (2015).
[3] V. A. Gritsenko, in *Thin Films on Si: Electronic and Photonic Applications*, edited by V. Narayanan, M. Frank, and A. A. Demkov (World Scientific Press, 2016), pp. 273–322.
[4] V. A. Gritsenko and D. R. Islamov, *Physics of Dielectric Films: Charge Transport Mechanisms and Physical Basics of Memory Devices* (Parallel, 2017).
[5] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y. B. Kim, C. J. Kim, D. H. Seo, S. Seo, U. I. Chung, I. K. Yoo, and K. Kim, Nat. Mater. **10**, 625–630 (2011).
[6] J. Frenkel, Phys. Rev. **54**, 647 (1938).
[7] S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
[8] H. Bachhofer, H. Reisinger, E. Bertagnolli, and H. von Philipsborn, J. Appl. Phys. **89**, 2791 (2001).
[9] M. Specht, M. Stadele, S. Jakschik, and U. Schroder, Appl. Phys. Lett. **84**, 3076 (2004).
[10] C.-C. Yeh, T. P. Ma, N. Ramaswamy, N. Rocklein, D. Gealy, T. Graettinger, and K. Min, Appl. Phys. Lett. **91**, 113521 (2007).
[11] E. Atanassova, A. Paskaleva, N. Novkovski, and M. Georgieva, J. Appl. Phys. **97**, 094104 (2005).
[12] K. V. Egorov, D. S. Kuzmichev, P. S. Chizhov, Y. Y. Lebedinskii, C. S. Hwang, and A. M. Markeev, ACS Appl. Mater. Interfaces **9**, 13286–13292 (2017).
[13] Z. Xu, M. Houssa, S. D. Gendt, and M. Heyns, Appl. Phys. Lett. **80**, 1975 (2002).
[14] D. S. Jeong, H. B. Park, and C. S. Hwang, Appl. Phys. Lett. **86**, 072903 (2005).
[15] G. Jegert, A. Kersch, W. Weinreich, U. Schröder, and P. Lugli, Appl. Phys. Lett. **96**, 062113 (2010).
[16] J.-H. Hur, S. Park, and U.-I. Chung, J. Appl. Phys. **112**, 113719 (2012).
[17] K. A. Nasyrov, V. A. Gritsenko, Y. N. Novikov, E.-H. Lee, S. Y. Yoon, and C. W. Kim, J. Appl. Phys. **96**(8), 4293–4296 (2004).
[18] N. Novikov, V. A. Gritsenko, and K. A. Nasyrov, Appl. Phys. Lett. **94**, 222904 (2009).
[19] D. R. Islamov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Appl. Phys. Lett. **105**, 222901 (2014).
[20] V. A. Gritsenko, T. V. Perevalov, and D. R. Islamov, Phys. Rep. **613**, 1–20 (2016).
[21] D. R. Islamov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Optoelectron., Instrum. Data Process. **50**(3), 310–314 (2014).
[22] D. R. Islamov, T. V. Perevalov, V. A. Gritsenko, C. H. Cheng, and A. Chin, Appl. Phys. Lett. **106**, 102906 (2015).
[23] J. Frenkel, Tech. Phys. USSR **5**(8), 685–695 (1938).
[24] R. M. Hill, Philosoph. Mag. **23**(181), 59–86 (1971).
[25] H. Adachi, Y. Shibata, and S. Ono, J. Phys. D: Appl. Phys. **4**(7), 988–994 (1971).
[26] S. S. Makram-Ebeid and M. Lannoo, Phys. Rev. B **25**, 6406 (1982).
[27] K. A. Nasyrov and V. A. Gritsenko, J. Appl. Phys. **109**, 093705 (2011).
[28] K. A. Nasyrov and V. A. Gritsenko, J. Exp. Theor. Phys. **112**, 1026–1034 (2011).
[29] T. V. Perevalov, V. S. Aliev, V. A. Gritsenko, A. A. Saraev, V. V. Kaichev, E. V. Ivanova, and M. V. Zamoryanskaya, Appl. Phys. Lett. **104**, 071904 (2014).
[30] K. A. Nasyrov and V. A. Gritsenko, Phys. Usp. **56**, 999–1012 (2013).
[31] D. R. Islamov, V. A. Gritsenko, and M. S. Lebedev, Microelectron. Eng. **178**, 104–107 (2017).
[32] T. Shimizu, T. Yokouchi, T. Oikawa, T. Shiraishi, T. Kiguchi, A. Akama, T. J. Konno, A. Gruverman, and H. Funakubo, Appl. Phys. Lett. **106**, 112904 (2015).

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