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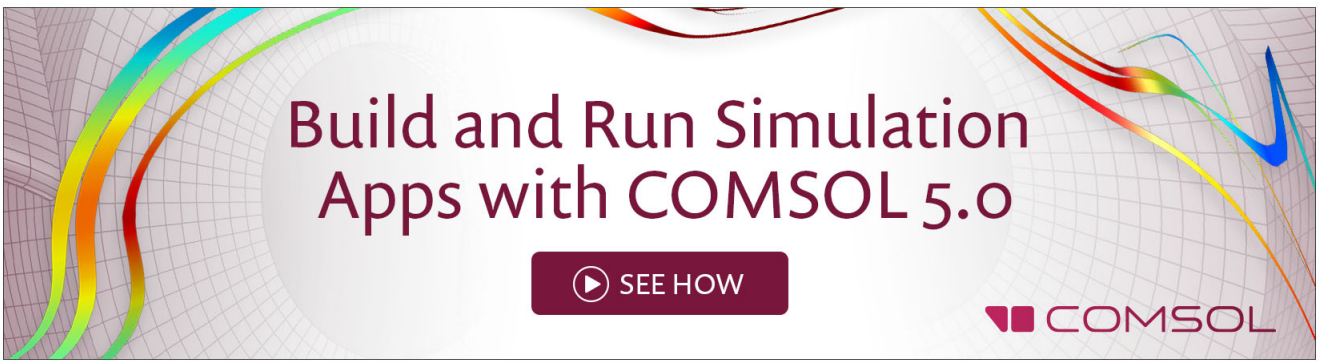

Charge transport in amorphous $Hf_{0.5}Zr_{0.5}O_2$

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In this study, we demonstrated experimentally and theoretically that the charge transport mechanism in amorphous $Hf_{0.5}Zr_{0.5}O_2$ is phonon-assisted tunneling between traps like in HfO_2 and ZrO_2. The thermal trap energy of 1.25 eV and optical trap energy of 2.5 eV in $Hf_{0.5}Zr_{0.5}O_2$ were determined based on comparison of experimental data on transport with different theories of charge transfer in dielectrics. A hypothesis that oxygen vacancies are responsible for the charge transport in $Hf_{0.5}Zr_{0.5}O_2$ was discussed. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4914900]

Knowledge about charge transport of high-κ dielectrics is very important for modern microelectronics. Previous transport studies were based on binary compound like HfO_2 and ZrO_2.[1–3] It was shown that charge transport mechanism in HfO_2 and ZrO_2 is phonon-assisted tunneling between traps.[2,4] The charge transport mechanism of ternary high-κ solid solution $Hf_{0.5}Zr_{0.5}O_2$ still remains unknown.

In this letter, we investigate the charge transport mechanism in $Hf_{0.5}Zr_{0.5}O_2$ by comparison of experimental data with different theories of charge transfer in dielectrics.

Transport measurements were performed for structures $Si/Hf_{0.5}Zr_{0.5}O_2/Ni$. To fabricate these structures, we deposited the 20-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ solid solution films on *n*- and *p*-type Si (1 0 0) wafers by physical vapor deposition (PVD). Pure HfO_2 and ZrO_2 targets were bombarded by electron beams in high vacuum chamber, and Hf_xZr_yO were deposited on the wafer forming $Hf_{0.5}Zr_{0.5}O_2$ films. A Zr/Hf ratio of $\simeq$1 was used. We did not apply any post-deposition annealing to produce the most non-stoichiometric films. The structural properties of grown high-κ $Hf_{0.5}Zr_{0.5}O_2$ dielectric were examined by grazing incidence x-ray diffraction diffractogram (GI-XRD). The structural analysis showed that the resulting $Hf_{0.5}Zr_{0.5}O_2$ films were amorphous. All samples for transport measurements were equipped with round 50-nm-thick Ni gates with a radius of 70 μm. The measurements were performed using a Hewlett Packard 4155B semiconductor parameter analyzer and an Agilent E4980A precision LCR meter.

Optical (dynamic) permittivity ε_∞ of $Hf_{0.5}Zr_{0.5}O_2$ was calculated in the framework of density functional theory using the *ab initio* simulation code QUANTUM ESPRESSO.[5] Electronic structures and dielectric properties of monoclinic $Hf_{0.5}Zr_{0.5}O_2$ using 12-atom cell were simulated. The structure was obtained by replacement of a half hafnium atom to zirconium in monoclinic primitive cell of HfO_2 with following relaxation. The similar approach was described earlier.[6]

Fig. 1(a) shows a set of experimental current-voltage characteristics (*I-V*) of *n*-$Si/Hf_{0.5}Zr_{0.5}O_2/Ni$ structures measured at different temperatures *T* by characters in various shapes and colors. Positive applied voltage corresponds to positive bias on the Ni contact. The leakage current through $Hf_{0.5}Zr_{0.5}O_2$ grows exponentially with the increase in electric field (or applied voltage) and temperature in accumulation mode ($V > 0$).

Experiment results were analyzed by using different models of charge transport in dielectrics

$$I = eSN^{2/3}P, \tag{1}$$

where *I* is the full current through the sample, *e* is the elementary charge, $S = \pi(70\,\mu\text{m})^2$ is the contact square, *N* is the bulk trap density, and *P* is the probability rate of charge

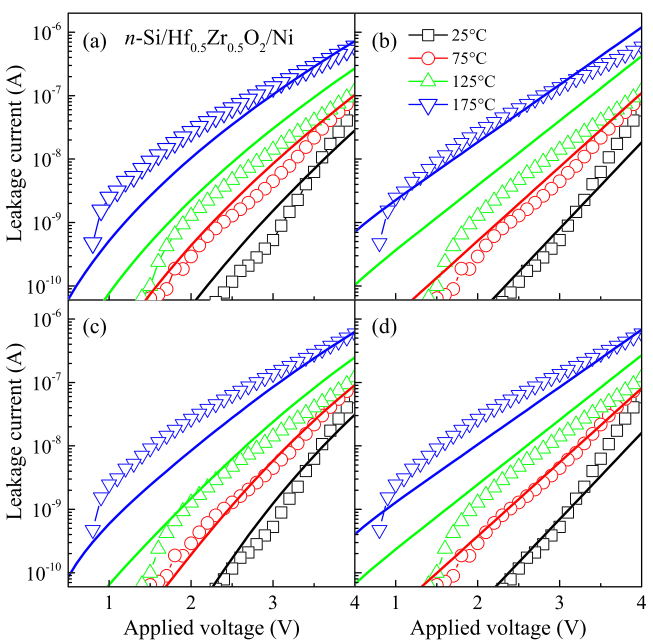

FIG. 1. Experimental (characters) and simulations (solid lines) current-voltage characteristics in *n*-$Si/Hf_{0.5}Zr_{0.5}O_2/Ni$ structures at different temperatures. (a) Frenkel model (2), (b) Hill model of overlapped traps (3), (c) multiphonon trap ionization (4), (d) phonon-assisted tunneling between traps (5).

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TABLE I. Summary table of the values of the fitting parameters obtained from the simulation *I-V* characteristics for *n*- and *p*-Si/ZrO_2/Ni structures in different models: (F) Frenkel model (2), (Hill) Hill model (Poole law) (3), (MPTI) multiphonon trap ionization (4), (PAT) phonon-assisted tunneling between traps (5). The last column represent ranges of expected (reasonable) values (from calculation or literature), if any.

Model	N (cm^{-3})	s	W (eV)	W_t (eV)	W_{opt} (eV)	ν (s^{-1}) (approx.)	ε_∞	m^*/m_e
F	1×10^{7}	50 μm	0.8	…	…	10^{14}	$3.6\div3.7$	…
Hill	3×10^{19}	3.2 nm	$0.9\div1.0$	…	…	$10^{6}\div10^{7}$	5	…
MPTI	2×10^{13}	370 nm	…	0.8	1.6	…	…	0.17
PAT	3×10^{19}	3.2 nm	…	1.25	2.5	…	…	0.23
Exp.	$\sim10^{18}\div10^{21}$	$1\div10$ nm	~1	~1	$\sim1\div3$	$\sim10^{14}\div10^{15}$	$4.8\div5.2$	…

carrier transfer between traps, which depends on the transport model. A mathematical model of well known Frenkel law was introduced in 1938 for isolated trap ionization[7]

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

where ν is the frequency factor which was defined as $\nu\simeq W/h$, W is thermal ionization energy of the trap, $h=2\pi\hbar$ is the Planck constant, β_F is Frenkel coefficient, $F=V/d$ is the electric field, d is the dielectric film thickness, k is the Boltzmann constant, ε_∞ is dynamic permittivity of the dielectric film, and ε_0 is vacuum permittivity (electric constant). Results of simulations (1) + (2) are shown in Fig. 1(a) by solid lines. One can see that Frenkel model describes the experiment data qualitatively very good. However, quantitative fitting procedure returns underestimated fitting parameter values: the slopes of the fitting lines with Frenkel coefficient give the dynamic permittivity $\varepsilon_\infty=3.6\div3.7$, which is lower than $\varepsilon_\infty(HfO_2)=4.4$,[8] $\varepsilon_\infty(ZrO_2)=5.6$,[9] and calculated from the first principals $\varepsilon_\infty(Hf_{0.5}Zr_{0.5}O_2)=4.8\div5.2$. Further fittings return $N=10^7\,cm^{-3}$ and $W=0.8$ eV. Found values of the charge trap density $N=10^7\,cm^{-3}$ at $\nu\sim W/h\simeq2\times10^{14}\,s^{-1}$ correspond to mean distance between traps $s=N^{-1/3}\simeq50\,\mu$m that is comparable to Ni gate size. Taking all these facts into account, one can conclude that there is no quantitative agreement between experiments and Frenkel model, despite that Frenkel model describes the experiment data qualitatively.

Simulating in terms of overlapped traps ionization (Hill model),[10]

$$P=\nu\exp\left(-\frac{W-e^2/\pi\varepsilon_0\varepsilon_\infty s}{kT}\right)2\sinh\left(\frac{esF}{2kT}\right),\tag{3}$$

is in good quantitative agreement with experiments as well as Frenkel model (Fig. 1(b)). However, too low value of frequency factor of $\nu\sim10^7\,s^{-1}$ was obtained. All values of obtained filling parameters are collected in Table I.

Results of simulations by the model of multiphonon trap ionization[11]

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

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

are shown in Fig. 1(c) by solid lines. Here, W_{ph} is phonon energy, W_{opt} is optical energy of the trap, W_t is thermal trap energy, I_n are modified Bessel functions, m^* is the effective mass, and $P_i(W)$ is probability of tunneling trough a triangle barrier of W height. Calculated set of *I-V-T* curves is very close to experimental data; obtained values of fitting parameters include low trap density of $N=2\times10^{13}\,cm^{-3}$, which corresponds to $s=370$ nm. This mean distance between traps is much greater than the film thickness of 20 nm (Table I). Thus, it can be concluded that multiphonon trap ionization does not adequately describe charge transfer in $Hf_{0.5}Zr_{0.5}O_2$.

To get complete vision on the charge transport in $Hf_{0.5}Zr_{0.5}O_2$, experiment data were simulated based on phonon-assisted tunneling between traps[12]

$$P=\frac{\sqrt{2\pi}\hbar W_t}{m^*s^2\sqrt{W_{opt}-W_t}}\exp\left(-\frac{W_{opt}-W_t}{2kT}\right)\times\exp\left(-\frac{2s\sqrt{m^*W_t}}{\hbar}\right)\sinh\left(\frac{eFs}{2kT}\right).\tag{5}$$

Results of this procedure are shown in Fig. 1(d). The experiment data were described quantitatively and qualitatively with the following values of fitting parameters (Table I): $N=3\times10^{19}\,cm^{-3}$, $W_t=1.25$ eV, $W_{opt}=2.5$ eV, and $m^*/m_e=0.23$ (m_e is a free electron mass). Fig. 2 shows the configuration diagram of a negatively charged electron trap. A vertical transition with a value of 2.5 eV corresponds to the optical trap excitation; transitions of 1.25 eV correspond to thermal trap energy.

The same measurements and simulations were performed for *p*-Si/$Hf_{0.5}Zr_{0.5}O_2$/Ni structures. Results are represented in Fig. 3. One can see that all the models describe experimental curves qualitatively. Calculated values of fitting parameters are summarized in Table I. Models of isolated (2) and overlapped (3) charged traps can describe

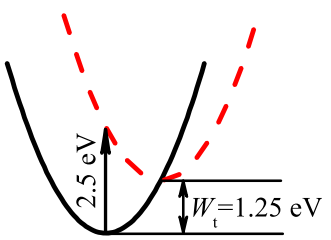

FIG. 2. Configuration coordination energy diagram of trap ionization process on negative charged trap in $Hf_{0.5}Zr_{0.5}O_2$. Lower term is filled ground state, upper term is excited empty state.

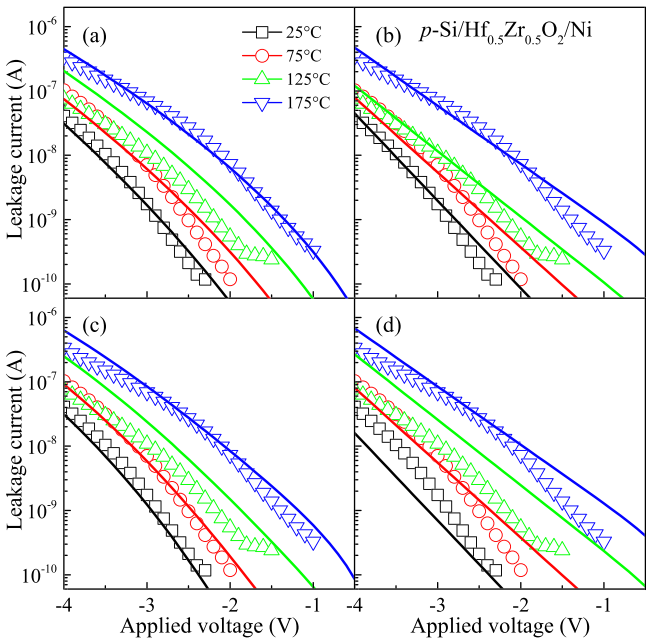

FIG. 3. Experimental (characters) current-voltage characteristics and simulations (lines) in p-Si/$Hf_{0.5}Zr_{0.5}O_2$/Ni structures at different temperatures. (a) Frenkel model (2), (b) Hill model of overlapped traps (3), (c) multiphonon trap ionization (4), (d) phonon-assisted tunneling between traps (5).

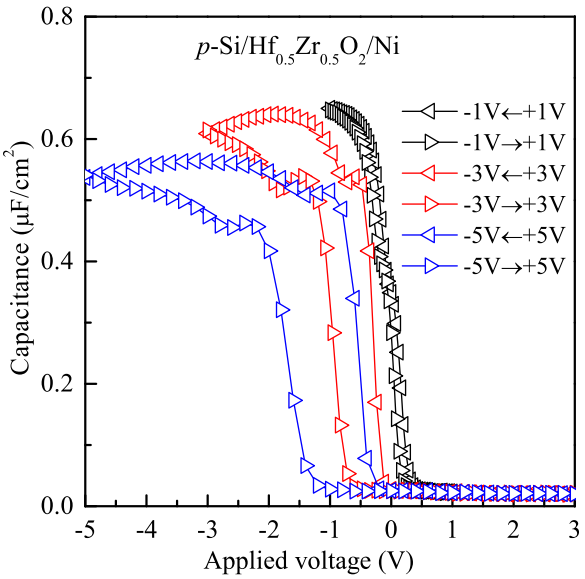

FIG. 4. Experimental capacitance-voltage characteristics in p-Si/$Hf_{0.5}Zr_{0.5}O_2$/Ni structures at different voltage limits.

experiments with inadequate parameters like for n-Si-based samples. Multiphonon ionization of neutral trap (4) has good agreement with experiments at $N = 2 \times 10^{13}\,\mathrm{cm}^{-3}$, which is equal than one got for n-Si/$Hf_{0.5}Zr_{0.5}O_2$/Ni structure by the same transport model. At the same time, calculated curves in terms of phonon-assisted tunneling between traps (5) are close to experimental data with the same parameter values as that obtained for n-Si/$Hf_{0.5}Zr_{0.5}O_2$/Ni samples.

Phonon-assisted tunneling between traps adequately describes charge transport in $Hf_{0.5}Zr_{0.5}O_2$ films on n-Si and p-Si substrates. Taking these into account, we conclude that the model of phonon-assisted tunneling between traps describe charge transport in $Hf_{0.5}Zr_{0.5}O_2$ films. Energy parameters of traps, such as the thermal trap energy of 1.25 eV and the optical trap energy of 2.5 eV, are similar to that in binary oxides HfO_2,[2,13] and ZrO_2.[14]

Capacitance-voltage (C-V) measurements (Fig. 4) show that the increase in voltage amplitude leads to shift of the hysteresis to negative voltages. This phenomenon might be caused by holes trapping on $Hf_{0.5}Zr_{0.5}O_2$ interfaces or in the bulk of the dielectric. C-V shift allows us to valuate the density of the filled hole traps as $n_h^b \lesssim 3 \times 10^{18}\,\mathrm{cm}^{-3}$ in the bulk or $n_h^s \lesssim 6 \times 10^{12}\,\mathrm{cm}^{-2}$ on the surface states. It is not possible to separate percentage of the charge on the surface, and in the bulk, unusual C-V behavior of reducing, the maximum capacity with an increase in the voltage amplitude indicates that the surface charge is significant. However, it should be noted that the number of filled bulk traps $n_h^b \lesssim 3 \times 10^{18}\,\mathrm{cm}^{-3}$ is much lower than total trap density of $N = 3 \times 10^{19}\,\mathrm{cm}^{-3}$. The possible explanation of this difference is the Coulomb repulsion of the charged particles with forming of Wigner-glass-like structures[15] in the bulk of $Hf_{0.5}Zr_{0.5}O_2$.

It was shown that oxygen vacancies are responsible for charge transport via HfO_2 and ZrO_2.[2,13,14] Thus, one can expect that oxygen vacancies are responsible for charge transport in $Hf_{0.5}Zr_{0.5}O_2$ too. To confirm this hypothesis, experiments on photoluminescence and quantum-chemical simulations are required.

Recently, it was reported that orthorhombic crystalline phase of high-κ $Hf_{0.5}Zr_{0.5}O_2$ thin films can be ferroelectrics, being perspective material for application to ferroelectric random access memory (FeRAM).[16–18] Despite that FeRAM has many advantages, retention characteristics of FeRAM devices much to be desired because of the depolarization effect.[19] A possible reason of the depolarization effect is charge leakage via traps of the dielectric. To confirm or refute this hypothesis, transport properties of $Hf_{0.5}Zr_{0.5}O_2$ in amorphous and ferroelectric phases must be compared.

To summarize, we examined the transport mechanisms of amorphous solid solution $Hf_{0.5}Zr_{0.5}O_2$. It was demonstrated that all charge transport models such as Frenkel model, Hill model, multiphonon trap ionization, and phonon-assisted tunneling between traps describe experiment data formally, qualitatively, while only phonon-assisted tunneling between traps describes the charge transport in $Hf_{0.5}Zr_{0.5}O_2$ quantitatively. Comparing experimental current-voltage characteristics with results of simulations revealed energy parameters of the charge traps in $Hf_{0.5}Zr_{0.5}O_2$: the thermal trap energy of 1.25 eV and the optical trap energy of 2.5 eV that are equal to that for HfO_2 and ZrO_2.

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