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Origin of traps and charge transport mechanism in hafnia

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In this study, we demonstrated experimentally and theoretically that oxygen vacancies are responsible for the charge transport in HfO2. Basing on the model of phonon-assisted tunneling between traps, and assuming that the electron traps are oxygen vacancies, good quantitative agreement between the experimental and theoretical data of current-voltage characteristics was achieved. The thermal trap energy of 1.25 eV in HfO2 was determined based on the charge transport experiments. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4903169]

Knowledge about charge transport mechanisms hafnia (hafnium oxide, HfO2) is crucial for modern microelectronics, because high-κ HfO2 is used as a gate dielectric in high-speed MOSFETs and FinFETs and a blocking insulator in Si-oxide-nitride-oxide-silicon-type (SONOS) flash memory cells. Hafnia is a promising candidate to be used as active medium in resistive random access memory (RRAM), which would involve combining the most favorable properties of both high-speed dynamic random access memory and non-volatile flash memory. Hereby, MOSFETs and SONOS need high-κ dielectrics with low leakage currents, while RRAM requires dielectric medium with reversible resistive switching. Managing the process of hafnia films synthesis to control leakage currents can create high-quality devices for various purposes. However, an unresolved physics is the nature of defects and traps that are responsible for the charge transport in HfO2. The atomic structure of defects that affects the localization and charge transport still remains unclear. Currently, the accepted hypothesis is that oxygen vacancies are responsible for charge transport in dielectric. Although many studies have investigated the theory of the atomic and electronic structure of oxygen vacancies in hafnia, direct experimental data regarding the presence of oxygen vacancies in hafnia were reported recently. It was shown that oxygen vacancies in hafnia are responsible for blue luminescence band at 2.7 eV and a luminescence excitation band at 5.2 eV, and a hypothesis that the oxygen vacancies in hafnia act as traps in charge transport through the dielectric was discussed. In this case, thermal energy traps in HfO2 are equal to a half of the Stokes luminescence shift Wl = (5.2 - 2.7)/2 = 1.25 eV.

A lot of studies of the charge transport in dielectrics described experimental results by Poole-Frenkel (PF) mechanism in hafnia-based structures. The most part of HfO2 transport investigations did not get into account neither charge trap density, which depends on thin film fabrication technology, nor phonon influence on electron and hole transport, which might be significant at high temperatures. Only few of investigations explained their results quantitatively as well as qualitatively, getting agreement of the phenomenological parameters such as dynamic permittivity, trap energy, frequency factor, etc. However, these studies involved complex mathematical calculations.

In this letter, phonon-assisted tunneling between traps (PATT) conduction mechanism in HfO2 was developed. Proposed model has simple mathematics and is in good quantitative and qualitative agreement with experimental data. It was clearly shown that oxygen vacancies are responsible for the charge transport in HfO2 and HfO2-based devices.

Transport measurements were performed for metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) structures. For the MIS Si/HfOx/Ni structures, the 20-nm-thick amorphous hafnia was deposited on a n-type Si (1 0 0) wafer by using the atomic layer deposition (ALD) system. Tetrakis dimethyl amino hafnium (TDMAHf) and water vapor were used as precursors. Transport measurements were performed using an Agilent E4980A precision LCR meter.
To describe the experiments quantitatively and qualitatively, we performed simulations based on the PATT model. In this model, the probability of electron tunneling between traps per second is defined as following:

\[
P = \frac{\sqrt{2\pi eFs}}{m^*s^2\sqrt{W_{opt}-W_1}} \exp\left(-\frac{W_{opt}-W_1}{2kT}\right) \times \exp\left(-\frac{2s\sqrt{m^*W_1}}{h}\right) \sinh\left(\frac{eFs}{2kT}\right),
\]

where \( h = \hbar / 2\pi \), \( W_{opt} \) is the energy of optical excitation of the trap, \( m^* \) is the effective mass, and \( s = N^{-1/3} \) is mean distance between traps. The results of this multi-parameter fitting procedure are shown in Fig. 2, graphed in solid lines. This procedure yielded the values of different transport parameters, \( N = 6.8 \times 10^{19} \text{ cm}^{-3} \), \( W_i = 1.25 \text{ eV} \), \( W_{opt} = 2W_i = 2.5 \text{ eV} \), and \( m^* = (0.3-0.4)m_e \) (\( m_e \) is a free electron mass). Quantitatively, there is full agreement between the PATT model and the experimental data. The trap thermal energy value of 1.25 eV that was obtained is close to that of 1.2 eV (Ref. 30) and \( W_i = 1.36 \text{ eV} \) (Ref. 24) observed earlier, and equal to a half of the Stokes luminescence shift.\(^{19}\)

Furthermore, the trap optical energy value of \( W_{opt} = 2.5 \text{ eV} \) is close to the calculated value of 2.35 eV for the negatively charged oxygen vacancy in hafnia reported earlier.\(^{15}\)

Fig. 3 shows the configuration diagram of a negatively charged oxygen vacancy (electron trap) in hafnia. A vertical transition with a value of 2.5 eV corresponds to the optical trap excitation, and transitions of 1.25 eV correspond to thermal trap energy.

The inset in Fig. 2 show experimental capacitance-voltage characteristics of the MIS(PVD) structure at different voltage limits. Positions of the right hysteresis branch of C-V characteristics depend on the voltage limits, while the left
branch is fixed. Sweep voltage directions show that the bulk charge is accumulating on the traps with the voltage growing. These phenomena show that the electron traps are filled only, while the holes traps (if any) are empty. Voltage loop allows us to valuate the density of the filled electron traps \(n_e \approx 3.7 \times 10^{18} \text{cm}^{-3}\), which is less than 20 times than found value of \(N\).

The same procedure was applied to experiment data of the charge transport measurements in MIS(ALD) and MIM structures. Experiment current-voltage characteristics compared with simulations in terms of the PATT model in MIS(ALD) are shown in Fig. 4. Fitting procedure returns the following parameters values: \(N = 2.5 \times 10^{20} \text{cm}^{-3}\), \(W_1 = 1.25 \text{eV}\), \(W_{opt} = 2W_1 = 2.5 \text{eV}\), and \(m^* = 0.8 m_e\). Different values of fitting parameters of MIS(ALD) and MIS(ALD) structures have only the trap density \(N\) and effective mass \(m^*\). The difference of effective mass values is due to bulk space charge (due to captured in traps electrons and holes), which is adequately addressed in Ref. 31. Neither thermal trap energy nor optical trap energy depends on film fabrication technology.

The inset in Fig. 4 shows experimental capacitance-voltage characteristics of the MIS(ALD) structure at different voltage limits. With increasing of the voltage limits, the right hysteresis branch of \(C-V\) characteristics moves right, and the left branch moves left. Using the voltage shifts, one can valuate the density of the filled holes and electron traps: \(5n_h \approx n_e \approx 1.1 \times 10^{19} \text{cm}^{-3}\), respectively. It should be noted that \(n_e \approx N/20\) as well as for MIS(PVD) structures.

The bulk charge due to trapped charge carriers blocks the carriers injections from the semiconductor and metal electrodes at low voltages and leads to deviation of simulated \(I(V, T)\) from experiment data. To simplify Fig. 4, the mismatched data at \(V < 3 \text{V}\) are not shown. To get full agreement of simulations with experimental data, the bulk charge must be taken into account in solving of Poisson’s equation with Shockley-Read-Hall equations for electrons and holes.\(^{31}\)

Fig. 5 shows the experimental data of current-voltage measurements in MIM structures at different temperatures. The solid lines present the results of simulations in terms of PATT model (3). MIM structures have the following parameter values: \(N = 5.5 \times 10^{20} \text{cm}^{-3}\), \(W_1 = 1.25 \text{eV}\), \(W_{opt} = 2W_1 = 2.5 \text{eV}\), and \(m^* = 0.9 m_e\).

An artifact feature of experimental \(I-V-T\) curves shows that the zero current is observed at nonzero but negative voltages as shown in Fig. 5. This phenomenon is due to displacement current

\[
I_D = C \cdot \frac{dV}{dt},
\]

\(C\) is capacity of the sample and \(dV/dt = +0.3 \text{V/s}\) is voltage sweep rate. Taking into account (4) in simulation of \(I-V-T\) characteristics (1) and (3) with found fitting parameters, the artifact feature is described with good agreement as shown by dashed lines in Fig. 5.

The difference between different MIS ad MIM structures in effective mass is due to bulk space charge. However, it is important to notice that the trap’s energy parameters are invariants of grown structures and film fabrication techniques. Consequently, we found that the nature of charge carrier transport in hafnia and hafnia-based structures is
PATT. This charge transport model is more simple than based in quasi-continuous spectra of charge trap energy 1.4–2.4 eV, proposed by Vandelli et al. 

These results combined with spectra measurements and quantum chemical simulations show that, namely, oxygen vacancies are responsible for charge transport in HfOx, and the oxygen vacancies play the role of charge traps.

Previous experiments in charge transfer have demonstrated that hafnia conductivity is bipolar (or two-band): electrons are injected from a negatively shifted contact in the dielectric, and holes are injected from a positively shifted electrode in the dielectric. For the reason of simplicity, the current study took into account electron conductivity only. This assumption is supported by evaluated values of the filled traps densities, when the holes traps are mostly empty. This means that the hole current is much lower than the electron current caused by blocking holes injection from the metal gate due to high barrier for holes on Ni/HfO2 interface.

To summarize, we examined the transport mechanisms of HfO2, demonstrating that transport in hafnium oxide is described by the PATT model. Simulating the current-voltage characteristics of this model and comparing experimental data with calculations revealed the energy parameters of the traps in hafnia: the thermal trap energy of 1.25 eV and the optical trap energy of 2.5 eV. PATT charge transport model describes experiment data results with excellent qualitative and quantitative agreement, while standard PF model has qualitative agreement, while standardPF model has qualitative agreement.