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MULTILAYER HETEROPHASE ELECTRONIC MATERIALS

Charge Carrier Transport Mechanism in High-κ Dielectrics and Their Based Resistive Memory Cells

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Abstract—Current-voltage characteristics of thin dielectric films of HfO_x in p-Si/HfO_x/Ni structures are analyzed. Experimental results are compared with various theoretical models: the Poole–Frenkel trap ionization model, the multiphonon trap ionization model, and the Schottky effect at the Ni/HfO_x interface. It is shown that in spite of the good qualitative description of the experimental results by all models, only the multiphonon trap ionization model provides a quantitative description of the data..

Keywords: amorphous films, high-κ dielectrics, hafnium oxide.

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INTRODUCTION

As the linear dimensions of memory cells are reduced, silicon oxide, which has been used as a gate dielectric in silicon field-effect transistors for half a century, can no longer meet the technological requirements. Therefore, silicon oxide in memory cells is replaced by high-κ dielectrics [1]. The use of such dielectrics involves problems of charge accumulation in traps and large leakage current compared to the amount of electrons under the gate. It is assumed that oxygen vacancies act as traps responsible for charge accumulation in hafnium oxide [2]. Due to the high rate of reprogramming of the cell (~10 ns) and the large number of reprogramming cycles (10^6–10^{12}), resistive random access memory (ReRAM) [3–5] has been actively developed as an alternative to the flash memory based on floating gate and silicon nitride. The operating principle of resistive memory is a reversible change in the resistance upon application of a voltage pulse. It is generally agreed that resistive memory switching is due to the formation and annihilation of oxygen vacancies [2, 6]. Oxygen vacancies also act as the charge carrier traps and play a key role in charge transport in dielectrics. To design optimal ReRAM devices and gain a full understanding of the reprogramming mechanism of ReRAM cells, it is necessary to comprehensively study the transport properties of the active dielectric storage medium.

Currently, there are several models of charge transport in dielectrics based on the ionization of traps. Figure 1 schematically shows the following scenario of charge transport in dielectrics: (a) Frenkel ionization of an isolated Coulomb trap, which involves reducing the energy barrier by applying an electric field [7]; (b) hopping between overlapping Coulomb centers with decreasing energy barrier in the electric field, the so-called Poole effect [8, 9]; (c) multiphonon ionization of an isolated neutral trap (i.e. at low trap density N) [10]; (d) phonon-assisted tunneling of charge carriers between overlapping traps at high N [11]. In addition, electric current can be limited by electron emission from metal to dielectric. Figure 1e depicts the

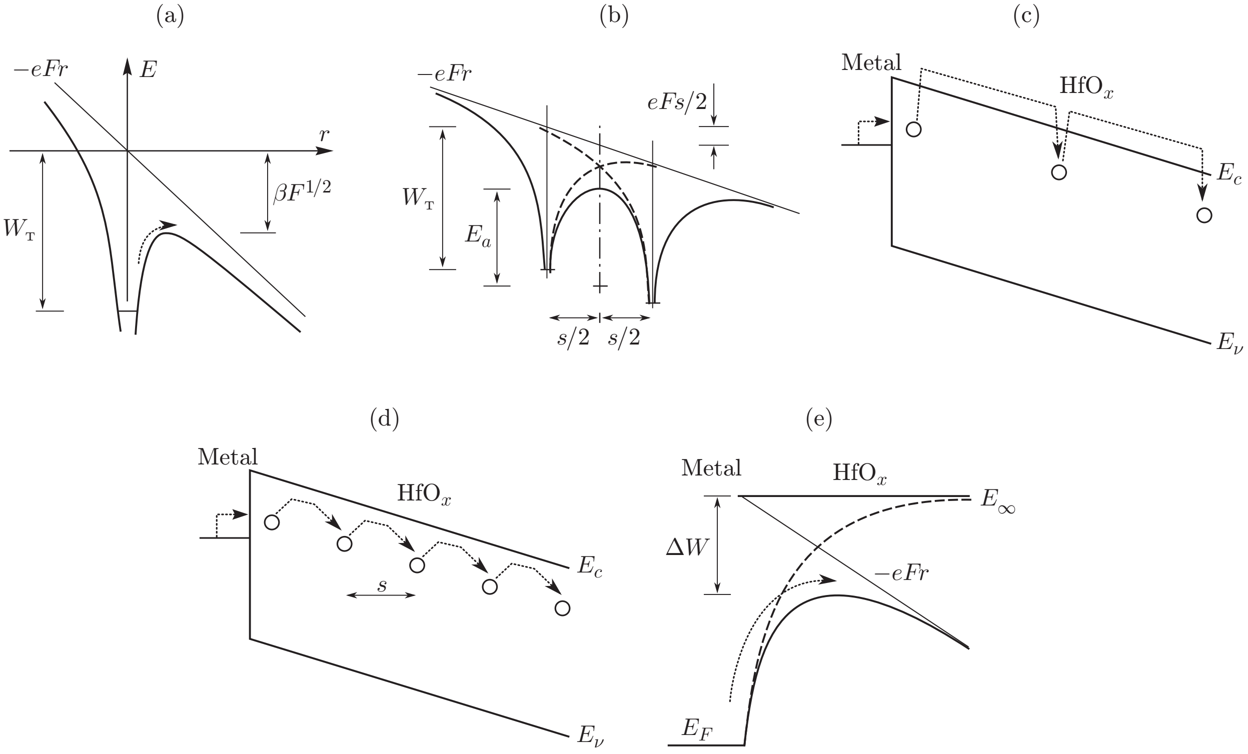

Fig. 1. Charge transport models in dielectrics (for explanation, see the text).

Schottky effect, i.e., a decrease in the energy barrier for electrons upon application of an electric field [12]. An attempt to account for the effect of electron localization in a dielectric film was made in [13], but the experimentally observed exponential dependence of the ionization probability on the electric field was neglected. Exponential dependence of the trap ionization probability is predicted by the both the Frenkel effect and the multiphonon ionization of traps.

In the literature, there are a number of papers on the charge transport mechanism in high-κ dielectrics where the authors qualitatively compare the experimental results with the Poole–Frenkel model without numerical comparison of the properties of the samples and films such as the concentration of traps N, the frequency factor ν, and the relative dielectric constant ε_∞. However, upon completion of all calculations, one obtains nonphysical values of these parameters — either too high or too low.

At present, HfO$_x$ has been extensively studied as a promising storage medium for ReRAM. The objectives of this study is to investigate the transport mechanisms in HfO$_x$ and to compare the experimental and calculated results in terms of models that predict the trap location and the exponential dependence of trap ionization on the electric field, i.e. the Poole–Frenkel and multiphonon trap ionization models.

EXPERIMENTAL

The HfO$_x$ films studied in this paper were grown by physical vapor deposition on Si p- and n-type substrates. The thickness of the HfO$_x$ films was 8–20 nm. Structural analysis revealed an amorphous structure of the HfO$_x$ films. A thin layer of Ni was deposited on the top as an electric contact of circular shape with a radius of 70 μm for transport measurements. The ReRAM effect was studied in Si/TaN/HfO$_x$(8 nm)/Ni structures. The current-voltage (I-U) characteristics were measured at temperatures of $-40\ldots+200$ °C.

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS

Current-voltage characteristics of thin HfO$_x$ films at various temperatures are presented in Fig. 2. Analysis shows that the experimental results can be qualitatively interpreted in terms of the Poole–Frenkel models. However, the calculated value of the frequency factor $\nu \sim 10^{21}$ s^{-1} for $T = -40$ °C is much higher than the characteristic value $W_{\text{t}}/h \sim 1$ eV$/h \sim 10^{14}$ s^{-1} [7] and the calculated relative dielectric constant $\varepsilon_\infty = 10$ is

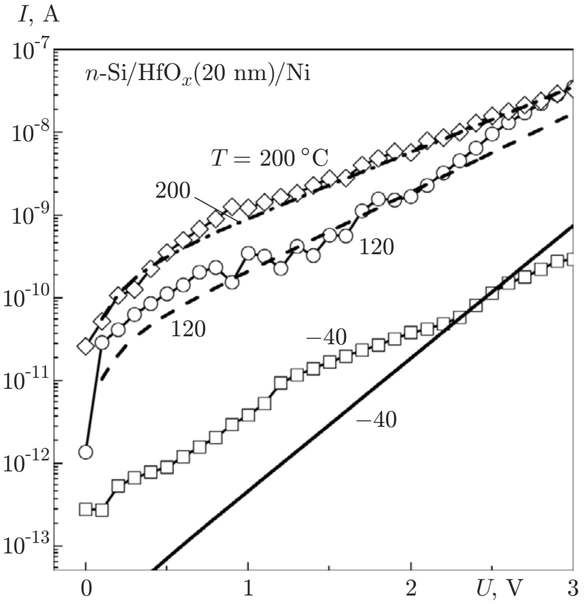

Fig. 2. Experimental (points) and calculated (curves) current-voltage characteristics of the p-Si/HfO$_x$(20 nm)/Ni structure at temperatures of −40, 120, and 200 °C. The calculation was performed for the model of phonon-assisted tunneling of charge carriers between traps.

much higher than the relative dielectric constant of hafnium oxide $\varepsilon_\infty(\mathrm{HfO_2}) = 4$. Hereinafter, W_t is the thermal ionization energy of the trap and h is the Planck constant.

The multiphonon trap ionization model does not describe the experimental data because of different slopes in the coordinates $\log(I)$-U at different temperatures.

Compared with the Frenkel effect, the relative dielectric constant obtained in terms of the Schottky effect $\varepsilon_\infty = 2.5$ is less different from $\varepsilon_\infty(\mathrm{HfO_2})$. The calculated current is several orders of magnitude higher than the experimentally measured values, i. e. the Schottky effect model does not describe the experimental data quantitatively despite the qualitative agreement.

Phonon-assisted tunneling between traps [5]

$$J = eN^{2/3}\nu,$$

$$\nu = 2\frac{\sqrt{\pi}\hbar W_\mathrm{t}}{m^* s^2\sqrt{2(W_\mathrm{opt} - W_\mathrm{t})}}\exp\Big(-\frac{W_\mathrm{opt} - W_\mathrm{t}}{2kT}\Big)\cdot\exp\Big(-\frac{2s\sqrt{2m^* W_\mathrm{t}}}{\hbar}\Big)\cdot\sinh\Big(\frac{eFs}{2kT}\Big), \tag{1}$$

fairly adequately represents the experimental I-U characteristics, both qualitatively and numerically. Here e is the electron charge; $\hbar = h/2\pi$; $s = N^{-1/3}$ is the characteristic distance between traps; k is the Boltzmann constant; F is the electric field in the dielectric. Multiparameter fitting of (1) gives values of the thermal energy of trap ionization in HfO$_x$, $W_\mathrm{t} = 1.25$ eV, the optical energy of the trap $W_\mathrm{opt} = 2.5$ eV, the effective mass $m^* = 0.1m_e$, $N = 4\cdot 10^{19}$ cm^{-3}, and the frequency factor $\nu \sim 10^{14}$ s^{-1}. The calculated dependences are shown in Fig. 2 by curves of different types.

Current-voltage characteristics of the Ni/HfO$_x$/TaN structure at different temperatures are shown in Fig. 3. These curves have a characteristic hysteresis, which indicates switching from a high-resistive state (HRS) to a low resistive state (LRS) upon application of a voltage pulse. Applying a voltage of opposite polarity switches the system from the LRS to the HRS, i.e. the Ni/HfO$_x$/TaN structure can be used in ReRAM cells. The HRS is well described by the model of phonon-assisted tunneling of charge carriers between traps. As before, the experimental data can be interpreted in terms of other models, but there is no quantitative agreement. The results of simulation of the I-U curves of the HRS state at different temperatures are also shown in Fig. 3 by curves of different types.

Problems related to the mechanisms of formation of the LRS state are beyond the scope of this paper. The question of describing the LRS state also remains open. To date, it is generally agreed that this state

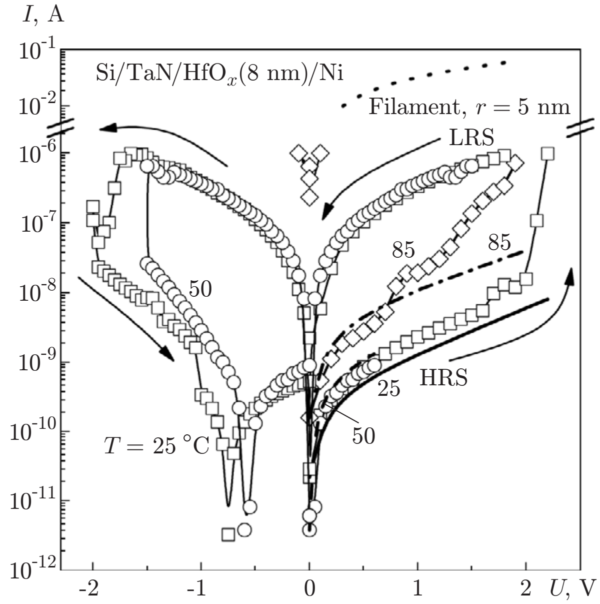

Fig. 3. Experimental current-voltage characteristics of the hysteresis (points) in the Ni/HfO$_x$(8 nm)/TaN structures and simulation of the high-resistance state using the model of phonon-assisted tunneling of charge carriers between traps (curves) at temperatures of 25, 50, and 85 °C.

is due to the formation of conducting filaments or nanowires [14, 15] ~10 nm in diameter. Nevertheless, the calculated current through such a filament is much higher than the experimental values (dotted curve on the upper right of Fig. 3). We believe that this state is formed through the formation of oxygen vacancies, but the chemical composition of the filaments is HfO$_x$ with $x \ll 1$, and not Hf as suggested in [14, 15]. A more detailed description of this state requires further investigation.

The role of holes also remains a debatable question. The simulation results presented here took into account only the contribution of electrons. However, it has previously been shown that the transport in thin films HfO$_x$ is bipolar, i.e. it is carried out by both electrons and holes [16].

CONCLUSIONS

This paper presents the results of an experimental study of the transport mechanism in thin HfO$_x$ films. The experimental data were compared with five different models of trap ionization. It is shown that all the models qualitatively describe the experimental data, but quantitative agreement is obtained only for the model of phonon-assisted tunneling of charge carriers between traps.

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