Nanoscale potential fluctuation in non-stoichiometric HfO$_x$ and low resistive transport in RRAM

V.N. Kruchinin$^a$, V.Sh. Aliev$^a$, T.V. Perevalov$^{a,b}$, D.R. Islamov$^{a,b}$, V.A. Gritsenko$^{a,b,*}$, I.P. Prosvirin$^c$, C.H. Cheng$^d$, A. Chin$^e$

$^a$Rzhanov Institute of Semiconductor Physics SB RAS, 13 Lavrentiev Ave., 630090 Novosibirsk, Russia
$^b$Novosibirsk State University, 2 Pirogov Str., 630090 Novosibirsk, Russia
$^c$Boreskov Institute of Catalysis SB RAS, 5 Lavrentiev Ave., 630090 Novosibirsk, Russia
$^d$Dept. of Mechatronic Engineering, National Taiwan Normal University, 106 Taipei, Taiwan, ROC
$^e$National Chiao Tung University, 300 Hsinchu, Taiwan, ROC

**Abstract**

We study the structure of non-stoichiometric HfO$_x$ films with variable composition using the methods of X-ray photoelectron spectroscopy and spectroscopic ellipsometry. HfO$_x$, to a first approximation, is a mixture of HfO$_2$ and Hf metal with a small amount ($\sim 10–15\%$) of hafnium sub-oxides HfO$_y$ ($y < 2$). Spatial potential fluctuations, due to chemical compound fluctuations, lead to the percolation charge transport in such electronic systems. An application of these phenomena in resistive memory physics is discussed.

**Keywords:** Nanoscale fluctuations, Hafnium sub-oxides, Percolation, Resistive memory

1. Introduction

In modern silicon devices silica SiO$_2$ is superseded by high-$\kappa$ dielectrics, such as HfO$_2$, ZrO$_2$, Ta$_2$O$_5$ etc. Hafnia (HfO$_2$) permittivity depends on the modification varying in the range of 12–40. HfO$_2$ is the promising material for CMOS devices, DRAM capacitors and the memory insulator in Si-Oxide-Nitride-Oxide-Silicon (SONOS)-type flash memory cells [1,2]. Of great interest is the use of non-stoichiometric hafnium oxide HfO$_x$. The variation of chemical composition (stoichiometry) of HfO$_x$ leads to changes in its electronic structure, which opens up the possibility of controlling the physical (optical and electrical) properties. Compared to tetrahedral compounds of silicon, coordination numbers of Hf and O atoms in HfO$_2$ are high. Thus, it is not clear which model describes the structure of non-stoichiometric HfO$_x$. The purpose of the present work is to study the atomic and electronic structure of variable composition HfO$_x$.

2. Synthesis of HfO$_x$ films

HfO$_x$ ($x \leq 2$) films were produced using Hf target ion beam sputtering deposition in oxygen. The composition ($x$-parameter) of HfO$_x$ films was defined by partial oxygen pressure. For our experiments we grew three sets of HfO$_x$ samples at the partial oxygen pressures of $4.4 \times 10^{-4}$ Pa, $1.0 \times 10^{-3}$ Pa, and $3.6 \times 10^{-3}$ Pa. In these conditions we produced two sets of the samples of non-stoichiometric ($x < 2$) films and one set of almost stoichiometric composition ($x \approx 2$), respectively.

Transport measurements were recorded for metal-oxide-metal (MOM) structures of Si/TaN/HfO$_x$/Ni. To fabricate these structures, we deposited 8 nm thick HfO$_x$ films on TaN films (100 nm thick) on Si wafers using physical vapor deposition. A pure HfO$_2$ target was bombarded by an electron beam and HfO$_2$ was deposited on the wafer. No post deposition annealing was applied to produce highly non-stoichiometric HfO$_x$ films. Structural analysis showed that the resulting films were amorphous.

3. Experiment

The core-level Hf$4f_{7/2}$–Hf$4f_{5/2}$ and valence band spectra of HfO$_x$ films were obtained using an XPS machine with monochromatic Al K$_\alpha$ radiation. The dispersive refractive index and absorption coefficient of HfO$_x$ films were determined by means of spectroscopic ellipsometry.

The higher-level electronic-structure calculations were performed using the density functional theory (DFT) with the QUANTUM ESPRESSO software package [3].
The samples for transport measurements were equipped with round 50-nm-thick Ni gates with a radius of 70 μm. The transport measurements were performed using a Hewlett Packard 4155B Semiconductor Parameter Analyzer. The current compliance was set to 1 μA.

4. Results

The XPS spectra of the core-level Hf4f7/2–Hf4f5/2 in HfOx variable composition are shown in Fig. 1. For HfOx, grown at the highest oxygen pressures, a peak is observed at an energy corresponding to the stoichiometric HfO2. Decreasing the oxygen pressure during HfOx synthesis is accompanied by the appearance of XPS peaks corresponding to metal Hf (HfO1.83 and HfO1.55 in Fig. 1). With the decreasing of oxygen pressure, the intensity of the peaks corresponding to metal hafnium increases (HfO1.55). The decomposition of the spectra indicates that in addition to HfO2 and Hf the films have a non-stoichiometric phase of HfOx. Corresponding to this phase, the peaks are located approximately in the middle between the Hf- and HfO2-related peaks as shown in Fig. 1. Thus, according to XPS, HfOx are the mixtures (composites) of stoichiometric HfO2, metal Hf, and the non-stoichiometric phase of HfOx. In the following, we will note HfOx composites which consist of HfOx, Hf and non-stoichiometric HfOx as “non-stoichiometric HfOx,” bearing in mind that HfOx is different from HfOy.

The experimental valence band spectra of HfO2 is in good agreement with the simulated spectra for monoclinic HfO2, as shown in Fig. 2. A proof of the existence of non-stoichiometric hafnia in our films can be obtained from the comparison of the experimental valence-band XPS with the corresponding one calculated from the first principles for m-HfO2 with neutral oxygen vacancy and polyvacancy (Fig. 2). The calculation satisfactorily describes the experiment, even that the XPS spectra are compared for HfO2 in amorphous and monoclinic phases. The presence of the neutral oxygen vacancy in m-HfO2 leads to the defect levels at 3.2 eV.

The spectra of absorption coefficient α for HfOx are shown in Fig. 3. The band gap of amorphous HfO2 is 5.6 eV [4]. The HfOx absorption coefficient increases monotonically with the increasing photon energy E in the range of 1.1–4.5 eV, while, at an energy of E > 4.5 eV, a sharp increase of α takes place. In the range of 1.1–4.5 eV, absorption is low due to the presence of Hf metallic clusters in the films. The significant absorption at E > 4.5 eV is caused by the presence of non-stoichiometric HfOx.

According to XPS and optical absorption experimental data, HfOx consists of metal Hf and a bit of non-stoichiometric HfOx.
Non-stoichiometric HfO$_2$ can be placed between HfO$_2$ and Hf, inside HfO$_2$, and inside Hf. A planar model of HfO$_2$ in terms of the intermediate structure model (IM) is shown in Fig. 4(a) [5]. According to the IM model, HfO$_2$, HfO$_2$, and Hf. It is shown in Fig. 4(b) that the energy diagram of HfO$_2$, taking into account that the Hf work function is 3.9 eV the band gap of HfO$_2$ is $E_g = 5.6$ eV, and electron affinity of HfO$_2$ is $\gamma = 2.1$ eV [6]. According to IM, space fluctuations of chemical composition cause space fluctuations of the band gap in HfO$_2$ (Fig. 4(b)). The band gap HfO$_2$ varies in the range of 0–5.6 eV. The bottom of the conduction band $E_c$ against the energy of an electron in vacuum $E_0$ varies in the range of 2.1–3.9 eV, which leads to $E_c$ fluctuation scope of 1.8 eV. The valence band ceiling $E_v$ against $E_0$ varies in the range of 3.9–7.9 eV. In case of the barrier control by defects in the dielectrics, the $E_c$ fluctuation scope of 1.6 eV is expected [7].

The transport in such system is described by the Éfros-Shklovskii percolation theory [8,9]. This model assumes that excited electrons (or holes) with an energy higher than flow level $E^+(E^0)$ are delocalized, and drive round a random potential transferring the charge. In other words, to be involved in the transport processes, electrons and holes must overcome energy thresholds $W_{\alpha \beta}$. The current–voltage characteristics are exponentials [9]:

$$I \sim \exp \left( \frac{-W_{\alpha \beta}}{kT} \right) \exp \left( \frac{(CeF_{\alpha \beta})^{1/n}}{kT} \right),$$

where $I$ is the current, $e$ is the electron charge, $F$ is the electric field, $\alpha$ is the fluctuations space scale, $V_{\alpha}$ is the energy fluctuation amplitude, $k$ is the Boltzmann constant, $C \approx 0.25$ is a numeric constant, and $v = 0.9$ is a critical index.

To illustrate an application of the proposed model, we analyzed the current–voltage ($I$–$V$) characteristics of HfO$_2$-based element of resistive random access memory (RRAM) in the low resistive state (LRS). The experimental $I$–$V$ characteristics of Si/TaN/HfO$_2$/Ni MOM structures at different temperatures are shown in Fig. 5 by symbols. The calculated $I$–$V$ curves are shown in Fig. 5 by thick lines with different hatching. Fitting the calculated curves (1) to the experimental data allows us to obtain electron percolation level $W_e \approx 1.0$ eV and the space scale of fluctuations $\alpha = 1–2$ nm in HfO$_2$ (Fig. 4).

The charge transport in high resistive state including the artifacts of zero–current potential shifts, were discussed in Ref. [10].

5. Conclusion

According to XPS and optical absorption experiments, HfO$_2$ consists of metal Hf and non-stoichiometric HfO$_2$. The potential fluctuation model was introduced. Based on this model, the charge transfer in the low resistive state of HfO$_2$-based resistive memory was considered. The electron percolation level and the fluctuations space scale were obtained.

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References