CONDENSED MATTER

Forming-Free Memristors Based on Hafnium Oxide Processed in Electron Cyclotron Resonance Hydrogen Plasma

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It is shown that the treatment of stoichiometric HfO_2, which is synthesized by atomic layer deposition, in electron cyclotron resonance hydrogen plasma leads to a significant depletion of the film in oxygen and the formation of nonstoichiometric HfO_x ($x < 2$). The longer the treatment time, the higher the degree of oxygen depletion. The charge transfer in the films under study occurs by phonon-assisted tunneling between oxygen vacancies serving as traps. It has been found that the p^{++}-Si/HfO_x/Ni structures, where the oxide layer is treated in the electron cyclotron resonance hydrogen plasma, have memristor properties: they are reversibly switched between high and low resistance states. The fabricated memristor structures are forming-free.

Hafnium oxide is one of the most promising candidates for an active medium of resistive memory elements (memristors) (resistive random access memory, RRAM) [1]. At present, memristors are already used as working elements of high-speed nonvolatile flash memory matrices [2]. Memristors are also promising for active elements of neuromorphic cognitive systems to simulate the work of a synapse. Hafnium oxide memristors currently exhibit excellent memory performance [3].

Reversible switching of the dielectric layer in memristors (metal–dielectric–metal structures) between high- and low-resistance states is carried out through the electrodiffusion of oxygen vacancies in the oxide layer, leading to the formation or rupture of a conductive filament [4]. Nonstoichiometric oxygen-depleted oxides are often used in memristor structures [5]. The fabrication of memristor structures with an oxygen-depleted oxide layer makes it possible to solve the problem of forming, i.e., the first switching of the structure from the initial state to a low-resistance state that is performed at a voltage significantly exceeding the voltage of subsequent switching and has a stochastic character. Forming is currently one of the key challenges in the development of RRAM matrices. It was shown in [6, 7] that, when using $HfO_{x < 2}$ in memristor structures, no forming procedure is required (so-called forming-free memristors).

One of the methods for fabricating oxygen-depleted oxide films is the treatment of stoichiometric oxide in an electron cyclotron resonance (ECR) hydrogen plasma. This method has proven itself in partial reduction of SiO_2 [8, 9] and V_2O_5 [10]. The advantages of the ECR hydrogen plasma are a high degree of ionization at a low ion temperature and a low combustion pressure (to 10^{-3} Pa), so that the thermal effect on the film surface is negligible during treatment. The method of reducing the oxygen content using the ECR plasma was not used previously for HfO_2; however, it was shown in [11] that the treatment of HfO_2 in radio-frequency argon–hydrogen plasma leads to the improvement in the storage characteristics of memristors based on it.

The purposes of this work are to establish the possibility of fabricating nonstoichiometric oxygen-depleted $HfO_{x < 2}$ films by the ECR hydrogen plasma treatment of stoichiometric HfO_2, which is prepared by atomic layer deposition, and to determine the applicability of the prepared $HfO_{x < 2}$ films as active media of forming-free memristors and to characterize the prepared structures by establishing the mechanism of charge transport.

HfO_2 films 8 nm thick were synthesized by atomic layer deposition (ALD) with a precursor $Hf[N(CH_3)(C_2H_5)]_4$ (TEMAH) and H_2O on a p^{++}-Si (100) substrate doped with boron (0.001–0.005 Ω cm). HfO_2 films were treated in a vacuum setup with a built-in source of the ECR hydrogen plasma with a multipole magnetic system as described in [9]. The

power pumped into the plasma was 76 W (an empirically established optimal value), the bias potential on the substrate was −150 V, and the temperature of the sample holder was 496 K. A series of hafnium oxide films were prepared by treating them in the ECR hydrogen plasma for 0, 6, and 14 min. Using the ellipsometry method, we verified that no etching of the film occurred at the specified treatment parameters.

Memristor metal–dielectric–metal structures were fabricated by depositing 0.3 × 0.3-mm Ni contacts 50 nm thick by electron-beam evaporation. The current–voltage characteristics (CVCs) of p^{++}-Si/HfO_x/Ni resistive switching structures were measured at a Cascade Microtech probe station connected to a B1500A Agilent Technologies semiconductor analyzer. The current–voltage characteristics at temperatures of 300–450 K ($I–V–T$ characteristics) were measured using a Linkam LTS420E heating/cooling stage and a Keithley 6517a electrometer.

X-ray photoelectron spectra (XPSs) were measured on a SPECS spectrometer using the Al $K\alpha$ radiation of a FOCUS-500X-ray monochromator ($h\nu$ = 1486.74 eV) and a PHOIBOS-150-MCD-9 hemispherical analyzer. The O-to-Hf atomic concentration ratio (the parameter x in HfO_x) was determined from the integral intensities of the O $1s$ and Hf $4f$ photoelectron lines after Shirley background subtraction taking into account the corresponding atomic sensitivity factors of the elements [12].

The photoelectron spectrum of the Hf $4f$ level of the initial HfO_2 film is described by a doublet including the Hf $4f_{7/2}$ peak at an energy of 16.9 eV, which corresponds to the Hf^{4+} state in stoichiometric HfO_2 (Fig. 1) [13]. For films treated in ECR hydrogen plasma, the deconvolution of the Hf $4f$ spectra with the same FWHM as that for the initial (raw) film reveals an additional Hf $4f$ doublet with the Hf $4f_{7/2}$ peak at an energy of 16.4 eV. The chemical shift of this peak to the low-energy spectral region indicates the presence of Hf atoms with a lower degree of oxidation in the oxide, which, in turn, shows that the film is oxygen-depleted. The low-energy doublet intensity increases with the exposure time of the sample in the plasma. Therefore, the ECR hydrogen plasma treatment of HfO_2 leads to the formation of oxygen vacancies in the near-surface region of the oxide, and the longer the treatment time, the higher their concentration. According to O $1s$ and Hf $4f$ core levels taking into account the normalization of this ratio to 2 for the initial stoichiometric film, the parameter x = [O]/[Hf] is estimated as 1.97 and 1.95 for films treated in plasma for 6 and 14 min, respectively. Thus, the ECR hydrogen plasma treatment of stoichiometric HfO_2 forms nonstoichiometric oxygen-depleted hafnium oxide $HfO_{x < 2}$, and the longer the treatment time, the lower the x value.
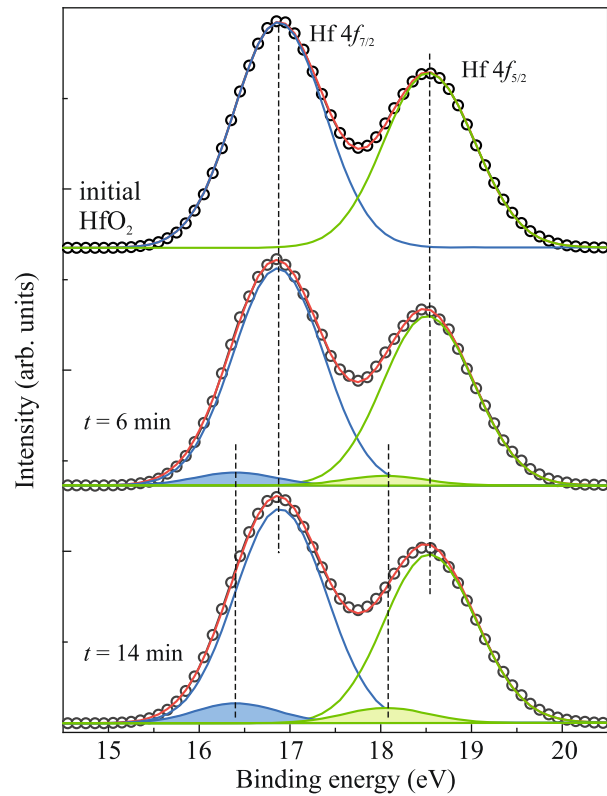

Fig. 1. (Color online) (Circles) Experimental X-ray photoelectron spectra of Hf $4f$ for hafnium oxide films with different treatment times in the ECR plasma in comparison with the (blue and green lines) decomposition components and (red line) their sum.

The accuracy of determining the stoichiometry of oxides using XPSs is not high (~0.01). Since the XPS data indicate the formation of oxygen vacancies in HfO_2 subjected to the plasma treatment and namely oxygen vacancies are responsible for the conductivity of HfO_2 [14, 15], the concentration of vacancies can be determined by analyzing the CVCs of the films under study and the parameter x can be thereby estimated in an alternative way. The conductivity of dielectrics is extremely sensitive to the concentration of defects. However, the accuracy of determining the concentration of oxygen vacancies in the studied films from the CVC analysis depends on a number of assumptions: the choice of the charge transport model and the assumptions that only oxygen vacancies are involved in the conduction and that they are distributed uniformly over the film thickness.

Previously, it was shown that the model describing the $I–V–T$ characteristics of ALD-HfO_2 films at physically correct values of all variable parameters of the model is phonon-assisted tunneling between neutral traps (Nasyrov−Gritsenko model) [14, 15]. Analyzing CVCs, as well as photoluminescence spectroscopy and quantum chemical simulation data, we also

found that the thermal (W_t) and optical (W_{opt}) ionization energies for the oxygen vacancy in HfO$_2$ are 1.25 and 2.5 eV, respectively [14–16]. Thus, for the characterization of ECR plasma-treated HfO$_2$ films in this work, we analyzed the CVCs within the Nasyrov–Gritsenko model with W_t = 1.25 eV and W_{opt} = 2.5 eV. In this model, the analytical expression for the current density j on the field F has the form [17]

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

(1)

Here, e is the elementary charge, m^* is the effective electron mass, k is the Boltzmann constant, N is the trap density, and $s = N^{-1/3}$ is the average distance between traps.

It can be seen that the CVCs for the p^{++}-Si/HfO$_x$/Ni structure, in which the oxide layer was treated for 14 min, at temperatures of 300, 350, 400, and 450 K are described rather well by the Nasyrov–Gritsenko model at the given W_t and W_{opt} values and the variation of only the density N and effective mass m^* (Fig. 2a). The experiment is described by the theory at N = 10.5 × 10^{20} cm^{-3} and m^* = 1.2m_0. As a rule, the transport model used overestimates m^* values since the space charge in the dielectric is ignored in it. The inclusion of the space charge through integration of the Nasyrov–Gritsenko model with the Poisson and Shockley–Reed–Hall equations gives more correct m^* values [18], but this greatly complicates the model. Thus, the analysis of I–V–T characteristics of the p^{++}-Si/HfO$_x$/Ni structure, first, confirms the presence of a high concentration of oxygen vacancies in the oxide layer and, second, indicates that charge transport through hafnium oxide films treated in the ECR hydrogen plasma occurs by the Nasyrov–Gritsenko mechanism.

The CVCs of p^{++}-Si/HfO$_x$/Ni samples with different hydrogen plasma treatment times of hafnium oxide measured at 300 K show that the conductivity of the dielectric increases significantly with the treatment time (Fig. 2b). According to Eq. (1), this is naturally explained by the increase in the concentration of oxygen vacancies. The measured CVCs are described well by the Nasyrov–Gritsenko model using the same parameter values (W_t, W_{opt}, and m^*), only by the variation of the trap density N. The trap densities for structures with the initial hafnium oxide film and films treated in plasma for 6 and 14 min were N = 4.0 × 10^{20}, 5.7 × 10^{20}, and 10.5 × 10^{20} cm^{-3}, respectively. The trap density obtained for the initial film was quite high, but a close value (N = 2.5 × 10^{20} cm^{-3}) was also obtained earlier for the n-Si/HfO$_2$(20 nm)/Ni
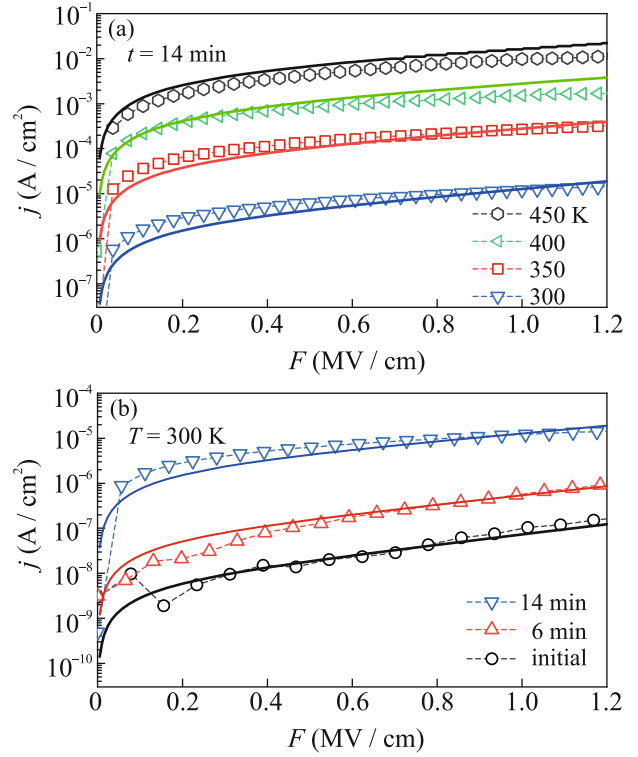

Fig. 2. (Color online) (Symbols) Current–voltage characteristics of the p^{++}-Si/HfO$_x$/Ni(+) structure (a) measured at different temperatures after the 14-min plasma treatment and (b) measured at T = 300 K after the plasma treatment for different times in comparison with the (solid lines) current–voltage characteristics calculated within the Nasyrov–Gritsenko model at W_t = 1.25 eV, W_{opt} = 2.5 eV, and m^* = 1.2 m_0. The trap densities in the initial film and in the films treated for 6 and 14 min are N = 4.0 × 10^{20}, 5.7 × 10^{20}, and 10.5 × 10^{20} cm^{-3}, respectively.

structure with the oxide layer synthesized by the ALD method [15].

Knowing that the mass density of ALD HfO$_2$ is 9.68 g/cm^3 [19], it is easy to calculate the total concentration of elements in strictly stoichiometric oxide: N(O) = 2N(Hf) = 5.54 × 10^{22} cm^{-3}. By subtracting the found concentration of oxygen vacancies from the total oxygen concentration, we can find the atomic ratio x = [O]/[Hf] for the studied films: x = 1.99, 1.98, and 1.96 for the initial film and films treated in the ECR hydrogen plasma for 6 and 14 min, respectively. These values of the parameter x are close to those found from the XPS analysis.

To reveal the applicability of the fabricated HfO$_x$ films as functional layers in memristors, we measured the CVCs of resistive switching of three p^{++}-Si/HfO$_x$/Ni structures where hafnium oxide was treated in plasma for 0, 6, and 14 min (Fig. 3). The limiting current (I_{cc}) for the first switching was chosen such
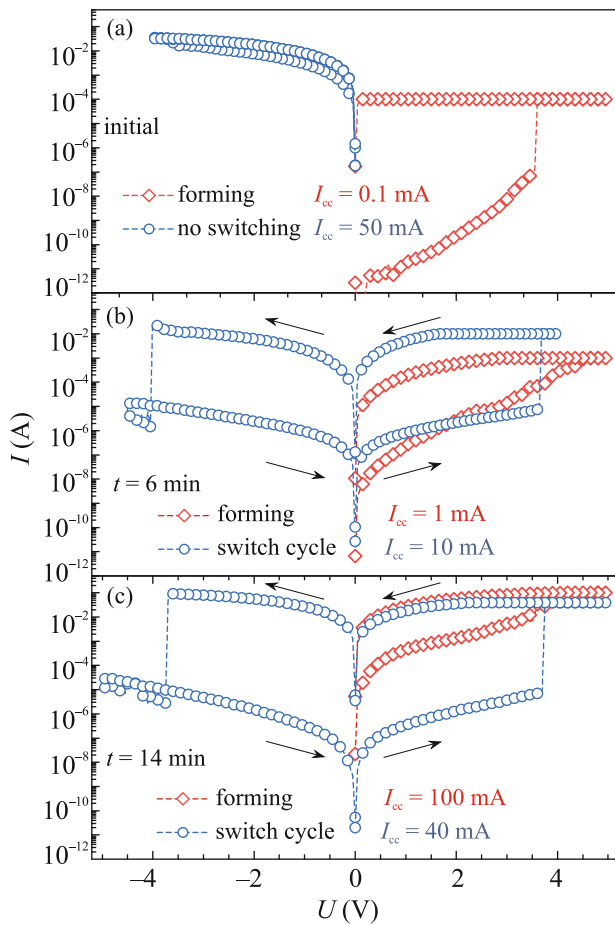
Fig. 3. (Color online) Current–voltage characteristics of resistive switchings of p^{++}-Si/HfO$_x$/Ni memristor structures (a) without and (b, c) with the plasma treatment for (b) 6 and (c) 14 min.

that the memristor was formed without destroying the structure. The structures where the oxide layer was treated in the ECR hydrogen plasma have the typical CVC of a bipolar memristor: they can be reversibly switched between a high resistive state (HRS) and a low resistive state (LRS). Moreover, the longer the treatment time of the hafnium oxide layer in the plasma, the larger the memory window, i.e., the ratio of currents in the LRS and HRS. For structures with oxide layer treated for 6 and 14 min, the ratio of currents in the LRS and HRS at a voltage of 2 V is 5×10^3 and 25×10^3, respectively. For structures with untreated hafnium oxide, no resistive switching is observed. It can be seen on the CVCs of samples treated in the hydrogen plasma for 6 and 14 min that the voltage of the first switching of the studied memristors (forming voltage) does not exceed the voltage of subsequent switchings. In the literature, such memristors are called forming-free ones. The memristor properties of the prepared structures, namely, their

cycling and information storage time, will be studied in detail in subsequent works.

To summarize, using XPS and CVC analysis, we have established that the ECR hydrogen plasma treatment of thin stoichiometric ALD-HfO$_2$ films leads to their depletion in oxygen and the formation of non-stoichiometric HfO$_{x < 2}$. Moreover, the longer the treatment time, the higher the degree of depletion. The parameter x has been estimated by two different methods: by the integrated intensity of the O 1s and Hf 4f XPS levels and by comparing the experimental and calculated CVCs. For the film treated in the plasma for 6 and 14 min, the x values are 1.97 and 1.95, respectively. It has been shown that charge transport in hafnium oxide films treated in hydrogen plasma, as well as in the initial films, occurs through phonon-assisted tunneling between traps, which are oxygen vacancies with thermal and optical ionization energies of 1.25 and 2.5 eV, respectively. It has been established that the p^{++}-Si/HfO$_x$/Ni structures with the oxide layer treated in the ECR hydrogen plasma have the typical CVC of the memristor: they are reversibly switched between high and low resistance states. It has been found that the studied memristors are forming-free since their forming voltage does not exceed the subsequent switching voltage. In this case, the memory window of the resulting memristors increases with the exposure time in the hydrogen plasma. Thus, the ECR hydrogen plasma treatment of stoichiometric HfO$_2$ is an efficient method for fabricating thin nonstoichiometric HfO$_{x < 2}$ films applicable as an active medium of the RRAM resistive memory matrix cell.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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