Comparative study of electron-beam crystallization of amorphous hafnium oxides HfO_2 and HfO_x ($x = 1.82$)

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Abstract

The phase transformations of stoichiometric HfO_2 and non-stoichiometric HfO_x oxides grown by ion-beam sputtering-deposition during their electron beam crystallization were investigated. It was found that the sequences of crystalline phase formations in stoichiometric and non-stoichiometric oxides are significantly different. An amorphous HfO_2 film crystallizes first to form monoclinic α - HfO_2 phase nanocrystals and then tetragonal β - HfO_2 phase nanocrystals. In non-stoichiometric HfO_x oxides ($x = 1.82$), in contrast to HfO_2 oxides, hexagonal α -Hf phase metal clusters were initially present. During the crystallization process, the metallic α -Hf phase growth was observed first with the simultaneous appearance of the monoclinic α - HfO_2 phase. Then the orthorhombic- γ - HfO_2 phase appeared, while the α -Hf phase growth ceased. The composition of the investigated non-stoichiometric HfO_x oxides was chosen to be the same as in the dielectric layer of resistive memory cells (ReRAM). The crystallization of oxides was carried out in a local region, the sizes of which are comparable with the size of the ReRAM filament. This made it possible to partially project the crystallization results onto the forming and switching processes in ReRAM cells.

Keywords Amorphous dielectrics · Electron-beam crystallization · HfO_2 · Non-stoichiometric oxides · ReRAM

1 Introduction

An electron microscope beam can be used to crystallize amorphous oxide dielectrics. This is convenient because the crystallization and investigation of its results are carried out in a vacuum column of an electron microscope without extracting the sample into the air. For example, using electron beam crystallization, structural transformations were studied in a variety of amorphous stoichiometric oxides: ZrO_2 [1], Cr_2O_3 [2], ReO_3 [2], Al_2O_3 [3], Fe_2O_3 [4], Ni_2O_3 [5], HfO_2 [2, 6]. However, there are no reports on electron-stimulated crystallization of amorphous non-stoichiometric oxides. Non-stoichiometric oxides have been attracting increasing attention of researchers due to the fact that non-stoichiometric transition metal oxides are used in

intensively developing resistive memory devices (ReRAM) [7–11]. The ReRAM memory cell is a metal-dielectric-metal (MDM) structure. A peculiarity of the ReRAM memory cell is the possibility of reversible resistance switching from the low-resistance to high-resistance state by applying voltage pulses of a certain magnitude and polarity. It is known that the switching mechanism of such devices is based on structural transformations during the local fast annealing of the MDM structure by electric current, resulting in the formation/rupture of a conducting filament in the dielectric layer. At first sight, heating the dielectric medium by electric current and by a high-energy electron flow are essentially different processes, but this is not quite true. According to the Bethe-Bloch formula, electrons with an energy value of ~ 200 keV lose their energy in a medium mainly due to

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atomic ionization [12]. This ionization occurs both by the Auger mechanism and by direct ejection of electrons from internal atomic levels. As a result, hot electrons are formed, and they then excite the electrons from the valence band generating electron–hole pairs. Ultimately, electrons lose their energy due to the electron–phonon interaction and the recombination of electron–hole pairs occurs, which leads to the medium heating. In the case of dielectric breakdown, electrons in a strong electric field are accelerated to energies sufficient for impact ionization with the formation of electron–hole pairs. As a result, an avalanche-like increase in the number of hot secondary electrons and electron–hole pairs occurs. The recombination of electron–hole pairs and the electron–phonon interaction lead to the heating of dielectric medium. Thus, from the energy point of view, the heat sources, during the braking of high-energy electrons and during the impact ionization in a strong electric field, are the same. The difference between these methods of heating a dielectric lies in the energy spectrum of hot electrons. However, the relaxation time of the crystal electronic subsystem is $\sim 10^{-14}$ s [13], which is less than the time period of lattice atomic vibrations [13, 14].

Therefore, when the restructuring of the atomic structure occurs, there are no hot electrons and the process proceeds as if the medium was heated by electric current. Of course, the energy spectrum of an electron gas formed by high-energy electron irradiation can differ significantly from the one formed during the dielectric breakdown, but this is a second-order effect. The characteristic hot electron thermal relaxation length in a solid is about 3 nm [15]. This means that the heat generation region is actually determined by an electron beam diameter. Therefore, electron beam crystallization allows the crystallization process in the local area with dimensions determined by the electron-beam diameter.

The aim of this work is a comparative study of the structural transformations in stoichiometric and non-stoichiometric hafnium oxides using electron beam crystallization. The electron beam diameter used in this work was several tens of nanometers, which is comparable with the filament size in ReRAM. The HfO_x film composition “ x ” corresponded to the composition of the films used in ReRAM devices. Therefore, the study of crystallization due to the local heating in a spot with a diameter of several tens of nanometers is of interest for modeling the structural transformations in the ReRAM device filament.

2 Methods

The stoichiometric oxide (HfO_2) and non-stoichiometric oxide (HfO_x) films with a thickness of about 30 nm were deposited by the ion-beam sputtering deposition (IBSD)

method [16]. The residual pressure in the vacuum chamber before the deposition was 10^{-4} Pa. High purity hafnium metal targets ($\text{Hf} > 99.9\%$) were used for sputtering. The targets were sputtered by 1.2 keV Ar^+ ions. The ion current density on the target amounted to 1.5 mA/cm^2 and was constant. A high purity oxygen flow ($\text{O}_2 > 99.999\%$) was fed into the vacuum chamber to obtain metal oxides. The oxygen pressure in the growth area can be varied, which makes it possible to obtain HfO_x films of various compositions “ x ”. Amorphous carbon-coated copper grids with the 3 mm diameter were used as substrates (S147-3 Holey Carbon Film 300 Mesh Cu (50)). The films were grown at room temperature. Their thickness and growth rate were determined using a quartz sensor (Maxtec Inc.). Two samples were grown for the studies at partial oxygen pressures (P_{O_2}) of 3.6×10^{-3} Pa and 1.8×10^{-3} Pa. The X-ray photoelectron spectroscopy (XPS) studies of the hafnium oxide films grown at the similar P_{O_2} values showed that pressure 3.6×10^{-3} Pa yields films with $x = 2$ (stoichiometric), whereas pressure 1.8×10^{-3} Pa yields films with $x = 1.82$ (non-stoichiometric) [17]. Unlike stoichiometric HfO_2 films, HfO_x ($1.77 < x < 1.82$) films showed their visible switching of conductivity in ReRAM cells and were suitable for creating memory elements [18].

The structural transformations in local surface areas of the prepared films were initiated by the electron beam in a transmission electron microscope (TEM) “JEOL JEM-2200rs” column. These transformations were initiated locally in a spot ranging in size from 20 to 200 nm and, correspondingly, at the electron beam densities ranging from 10^8 to 10^6 A/cm^2 . The film crystal structure was studied at the electron beam density of $1.3 \times 10^4 \text{ A/cm}^2$. The accelerating voltage of the electron microscope was 200 keV. The microscope resolution was about 4 Å.

The scale of the TEM images in our work did not allow us to distinguish the exact boundaries of individual crystalline phases. The analysis of diffraction patterns was carried out in the regions sized $50 \times 50 \text{ nm}^2$ or more. The concentration of crystalline phases formed in an amorphous medium cannot be determined solely by the diffraction reflection analysis. Instead, we qualitatively determined the increase of the particular phase concentration by the appearance of new reflections of the same phase from the other crystalline planes in the diffraction patterns. These new reflexes indicate that a new nanocrystal of the particular phase appeared, but with a different orientation relative to the electron beam. At the same time, the nucleation of nanocrystals with the same orientation relative to each other is quite unlikely.

In order to interpret the obtained diffraction patterns, the following cards from international databases were used: HfO_2 — monoclinic, $P12_1/c1$ 14, card 1528988; tetragonal, $P4_2/mnm$ 136, card mp-776532; orthorhombic,

Pbca 61, card 1544410; Hf – hexagonal, *P6₃/mmc* 194, card 9008501.

3 Results

The TEM images of a $50 \times 50 \text{ nm}^2$ HfO_2 film before and after the exposure to an electron beam with different exposure times are shown in Fig. 1. The initial film surface morphology was uniform, and the microdiffraction pattern showed that the film structure was amorphous (Fig. 1a). The film was annealed in the local area by a 30 s exposure to an electron beam with the 150 nm diameter, and its crystallization was observed. First, the crystal seed of the monoclinic $\alpha\text{-HfO}_2$ phase appeared (Fig. 1b, dark spot).

Then the monoclinic phase and the appearance of the tetragonal $\beta\text{-HfO}_2$ phase traces (not shown in the microdiffraction pattern) were observed (Fig. 1c, microdiffraction pattern). The irradiation for 90 s led to the tetragonal $\beta\text{-HfO}_2$ phase growth, whereas the number and size of the $\alpha\text{-HfO}_2$ microcrystals in the monoclinic modification did not change (Fig. 1d, microdiffraction pattern). The dynamics of the HfO_2 film phase composition change under the influence of the electron beam is presented in Table 1. It should be noted that no metal phase formation in the amorphous HfO_2 film was observed at the used electron beam intensities.

For the non-stoichiometric hafnium oxide film, the crystallization rate under the electron beam influence turned out to be much lower than that of stoichiometric HfO_2 , although the same electron beam diameter was used initially. To increase the exposure intensity, the transverse

Table 1 Dynamics of changes in the HfO_2 film phase composition under the influence of an electron beam

t (s)	HfO_2	
	Monoclinic $\alpha\text{-HfO}_2$	Tetragonal $\beta\text{-HfO}_2$
0	–	–
30	+	–
60	++	+
90	++++	++

t, the exposure time; +, the presence of reflexes of a certain plane in the electron diffraction pattern. An increase in the number of + reflects a phase concentration increase in the film

electron beam size was reduced to 50 nm. This also led to the change of the electron beam cross-section shape from round to triangular.

Crystalline inclusions were present in the diffraction pattern of the initial non-stoichiometric HfO_x film. This is evidenced by the individual reflexes corresponding to the planes of metallic $\alpha\text{-Hf}$ in the hexagonal phase (Fig. 2a). After the irradiation for 60 s, the diffraction pattern changed: the planes corresponding to the crystalline $\alpha\text{-HfO}_2$ phase in the monoclinic modification appeared (Table 2). At the same time, the number of nanocrystals corresponding to the $\alpha\text{-Hf}$ phase increased.

In contrast to the stoichiometric amorphous HfO_2 film, for which the 30 s electron beam exposure led to the appearance of monoclinic $\alpha\text{-HfO}_2$ and tetragonal $\beta\text{-HfO}_2$ phases, the 60 s exposure time and increased exposure

Fig. 1 Bright-field electron microscopy: **a** the initial HfO_2 film, **b** after irradiation with electrons for 30 s, **c** 60 s, **d** 90 s and the corresponding microdiffraction patterns. The electron beam diameter during irradiation was 150 nm

Fig. 2 Bright-field electron microscopy: **a** the initial HfO_x film and after the electron irradiation for 60 s (**b**), 180 s (**c**), 240 s (**d**) and the corresponding microdiffraction patterns. The electron beam size is ~ 50 nm. The beam shape is triangular

Table 2 Dynamics of changes in the HfO_x film phase composition under the influence of an electron beam

t, s	HfO_2			Hf
	Tetragonal $\beta\text{-HfO}_2$	Monoclinic $\alpha\text{-HfO}_2$	Orthorhombic-I $\gamma\text{-HfO}_2$	Hexagonal $\alpha\text{-Hf}$
0	–	–	–	+
60	–	+	–	++
120	–	++	–	++
180	–	+++	+	++
240	–	++	++	++

t, the exposure time; +, the presence of reflexes of a certain plane in the electron diffraction pattern. An increase in the number of + reflects a phase concentration increase in the film

intensity were not sufficient for the tetragonal phase formation in the non-stoichiometric amorphous HfO_x film. A further irradiation for 120 s led to an increase in the crystalline $\alpha\text{-HfO}_2$ concentration in the monoclinic modification. In addition, the amount of the metallic $\alpha\text{-Hf}$ phase was not changed, and the tetragonal $\beta\text{-HfO}_2$ phase did not appear in the film. The exposure for 180 s led to the appearance of the orthorhombic-I $\gamma\text{-HfO}_2$ phase instead of the tetragonal $\beta\text{-HfO}_2$, which appeared upon the similar exposure in the stoichiometric HfO_2 film. The amount of the metallic $\alpha\text{-Hf}$ phase in the film remained at the same level. A further increase in the exposure time to 240 s led to an increase in the number of diffraction reflections corresponding to orthorhombic $\gamma\text{-HfO}_2$, while the amount of the monoclinic $\alpha\text{-HfO}_2$ phase decreased. No metallic $\alpha\text{-Hf}$ phase growth was observed at this point.

As noted above, electron beam crystallization can be used to simulate the structural transformations in the filament of a ReRAM cell. We tried to simulate the forming and switching processes in a ReRAM cell. For this, the amorphous HfO_x film was exposed to a focused electron beam with the smallest possible diameter (about 20 nm). The exposure duration was chosen such that the appearance of the metallic $\alpha\text{-Hf}$ phase nanocrystals was observed (they have a darker colour in the bright-field TEM image) (Fig. 3a). The appearance of the metal phase occurred simultaneously with the monoclinic $\alpha\text{-HfO}_2$ phase formation in the same region. The irradiated 20 nm region periphery remained amorphous at the same time.

It was assumed that interstitial oxygen was formed during the metal phase formation and that it was displaced to the periphery of the irradiated region due to diffusion. In this case, it is reasonable to assume that the interstitial oxygen atoms should return to the 20 nm region upon a repeated heating. Taking this into account, the electron beam was defocused to the 200 nm diameter for the repeated but weaker heating of the film region that overlaps the initial one. Thus, the conditions were created for annealing the crystallization region and its periphery at lower temperatures. Interstitial oxygen was expected to oxidize the metal clusters and reduce the number of reflections from the metal phase. The phase composition of the 20 nm region and periphery was again studied after the second electron beam irradiation (Fig. 3b). It was found that the crystalline phase composition in the 20 nm region did not change significantly. The disappearance of metallic $\alpha\text{-Hf}$ phase reflections was not observed. However, an increase in the number of reflections corresponding to the

Fig. 3 Bright-field electron microscopy of the HfO_x film after the electron irradiation and the corresponding microdiffraction patterns. **a** Irradiation by the electron beam with a characteristic cross-section size of ~ 20 nm. **b** Second irradiation of the same film region by the electron beam with the 200 nm diameter. X denotes the crystallization region, Y and Z denote the peripheral regions

monoclinic α - HfO_2 phase was observed in the peripheral region.

4 Discussion

Previously, the electron beam crystallization of an amorphous stoichiometric HfO_2 film and study of its structure were carried out by Bagmut [19]. In this work, it was found that the monoclinic α - HfO_2 phase microcrystals were formed and grown under the action of an electron beam in the amorphous HfO_2 film. Then the appearance of the crystalline tetragonal β - HfO_2 phase was also observed. Our results coincide with the results of this work, although the film synthesis method is different. Influenced by an electron beam, the monoclinic α - HfO_2 and then the tetragonal β - HfO_2 phases also appear in the amorphous hafnium oxide film grown by IBSD (Fig. 4).

Fig. 4 Schematic representation of the amorphous HfO_2 and HfO_x film structural transformations at the electron beam crystallization

According to the Rep. [20–23], the formation temperature of the α - HfO_2 phase is close to 1670 °C. The formation temperature of the tetragonal β - HfO_2 phase is around 2200 °C. It seems that the electron beam irradiation of the investigated HfO_2 film region was sufficient enough to heat it up to such high temperatures. Usually, the phase diagrams of crystalline modifications existence are given for bulk materials in which the contribution of the surface to the crystal formation enthalpy is insignificant. For thin films, the surface contribution increases with decreasing film thickness and becomes predominant at film thicknesses of about several lattice constants of the crystal. In our case, the oxide film thickness is 30 nm, which significantly exceeds the unit cell size (≈ 0.5 nm). Of course, if we talk about phase transformations, the important question is the nucleation and growth kinetics of a new crystalline phase. In this case, the thin film surface can be the nucleation site of a new phase, which ultimately leads to a decrease in the phase transition temperature. However, the effect of the thickness and hetero-boundaries of oxide layers on the electron beam-stimulated local crystallization is beyond the scope of this work and may be the subject of further research.

It can be seen from our experimental results that the non-stoichiometric HfO_x film ($x < 2$) grown by the IBSD method initially contains the α -Hf metal clusters of hexagonal modification. This corresponds to the previous data on the HfO_x ($x < 2$) films composition of obtained by the XPS method [17]. The formation of α - HfO_2 nanocrystals of

the monoclinic phase occurred upon the electron beam heating of the dielectric film for 60 s. The appearance of the orthorhombic- γ -HfO₂ phase was observed after 180 s of exposure. It is an interesting result, since this phase did not appear in the investigated stoichiometric HfO₂ film. The orthorhombic- γ -HfO₂ phase is typically formed under high mechanical pressure in the film, and its formation temperature range is 1250–1400 °C [23]. For its formation, doping HfO₂ with atoms of a large ionic radius can be used [24, 25]. The other common way for its formation is the synthesis of ZrHfO₂ solid solution [26, 27] followed by high-temperature annealing, which results in the film mechanical stresses. Apparently, due to the formation of α -Hf metal clusters during the electron beam crystallization of non-stoichiometric oxides, mechanical stresses appear in the film sufficient to convert α -HfO₂ to the orthorhombic γ -HfO₂ phase (Fig. 4).

A further increase in the heating time (240 s) does not lead to a significant change in the phase composition. Thus, the metal α -Hf phase concentration increased only in the first 60 s of electron beam irradiation and did not change significantly after that. Since the metal α -Hf clusters were initially present in the HfO_x film, the most probable mechanism of their growth is the process of oxygen vacancies precipitation on their surfaces. In this case, ceasing the metallic cluster growth is possible if the area surrounding them is depleted with oxygen vacancies. Therefore, the metallic clusters should be surrounded by a stoichiometric hafnium oxide shell without oxygen vacancies.

It is known that, after the forming of a ReRAM cell, a filament is formed in the dielectric layer and it determines the cell conductivity [28–30]. During the cell switching operations, the filament changes its structure resulting in its conductivity change, i.e. the ReRAM cell state. The changes in the filament structure should be reversible, since the ReRAM cell endurance reaches 10¹⁰ cycles [31]. According to modern models [32, 33], the filament structure changes as a result of reversible redox chemical reactions. For the reduction reaction, the presence of oxygen vacancies in the filament is necessary, and for oxidation reaction, interstitial oxygen is needed. The unresolved issue in these models is the question of how interstitial oxygen and oxygen vacancies can simultaneously accumulate in the area surrounding the filament without entering into the recombination reaction. Our experiments on the local electron-beam crystallization show that oxygen vacancies in the filament come together to form metal clusters. In addition to the formation of metal clusters, the formation of stoichiometric oxide depleted in oxygen vacancies occurs simultaneously (Fig. 3). As a result, metal clusters are surrounded by a HfO₂ oxide layer. The stoichiometric oxide shell is, firstly, a reservoir for the interstitial

oxygen accumulation necessary for the filament oxidation, and, secondly, it protects it from the recombination with oxygen vacancies present in large quantities in the original non-stoichiometric oxide outside the filament. It can be assumed that, when switching from a low-resistance to a high-resistance state in a ReRAM cell, metal clusters in the filament are oxidized by interstitial oxygen. When switching from a high-resistance to a low-resistance state, the reverse process occurs: metal clusters restore with the release of interstitial oxygen into the shell from stoichiometric oxide, and in such amount that will then be needed for oxidation.

5 Conclusion

The phase transitions induced by the electron-beam crystallization of stoichiometric HfO₂ and non-stoichiometric HfO_x films deposited by the IBSD method were studied. It was established that an amorphous HfO₂ film crystallizes with the formation of nanocrystals: first the monoclinic α -HfO₂ and then tetragonal modification of β -HfO₂. The formation of metal clusters did not occur. In contrast to HfO₂, metal clusters were immediately present in the hexagonal α -Hf phase in the HfO_x ($x = 1.82$) film after its synthesis. First, the monoclinic α -HfO₂ phase appeared and the metal phase growth was observed. The γ -HfO₂ phase in the orthorhombic- γ modification then appeared, which was not observed for the HfO₂ films. At the same time, the metallic α -Hf phase growth ceased, and it indicated the end of the process of oxygen vacancies precipitation on the surface of metal clusters. The formation of the orthorhombic phase γ -HfO₂, which can exist at room temperatures only at high pressures (~4 GPa), allows us to make an assumption that mechanical stresses arise in the films in the crystallization process due to the presence of α -Hf metal clusters.

The composition of the HfO_x ($x = 1.82$) films selected for the study, as well as the small size of the crystallization region (50 nm), allowed us to partially project the results obtained on the processes occurring during the forming and switching in ReRAM cells. These results suggest that the ReRAM filament structure consists of metal clusters surrounded by a stoichiometric oxide shell. The existence of this shell is fundamentally important for substantiating the mechanism of the ReRAM cell switching in models based on redox chemical reactions in the filament.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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