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Preparation of hafnium oxide thin films by sol–gel method

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Abstract Hafnium oxide (HfO_2) films were grown on SiO_2/Si substrates by a sol–gel method, and their crystalline structure, microstructure and electrical properties were investigated. X-ray diffraction analysis indicated that the monoclinic HfO_2 films could be obtained by annealing at 500 °C. A transmission electron microscopy (TEM) image showed that the films were grown as a spherulite grain structure with a mean grain size of approximately 15 nm. The dielectric constant of the HfO_2 films of 300 nm was approximately 21.6, and the current–voltage measurements showed that the leakage current density of the HfO_2 films was approximately 1.14×10^{-5} A/cm^2 at an applied electric field of 100 kV/cm. The sol–gel method-fabricated HfO_2 films are concluded to be feasible for MEMS applications, such as capacitive-type MEMS switches.

Keywords Hafnium oxide · Thin film · Crystalline structure · Microstructure · Electrical properties

1 Introduction

Hafnium oxide (HfO_2) films have attracted great interest, because of their large number of potential applications in optical coatings and microelectronics [1–5]. The large dielectric constant and good thermal stability when in contact with silicon, makes HfO_2 film a promising candidate to replace the current SiO_2 gate dielectric materials in field-effect devices [4, 5]. It can also be applied a dielectric in microelectro-mechanical systems (MEMS). A novel approach using a PZT/HfO_2 multilayered dielectric for capacitive-type MEMS switches was investigated in our previous work [6]. It is found that compared with Si_3N_4, the use of a PZT/HfO_2 multilayered dielectric enables the realization of a high equivalent dielectric constant of 79–82 and a low leakage current density after a bias stressing time of 4^{10} s, resulting in a an efficient switching isolation and a very low power consumption. Many the techniques have been used to fabricate HfO_2 thin films, such as sputtering [7], the sol–gel method [8], atomic layer deposition [9], and metal–organic chemical vapor deposition (MOCVD) [10]. The sol–gel method generally offers significant advantages in the film fabrication of electronic materials, such as high purity, ease of composition control, relatively low processing temperature and large deposition area [11]. In this study, HfO_2 films were deposited by the sol–gel method on SiO_2/Si substrates and their crystalline phases, microstructures and electrical properties were investigated.

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2 Experimental procedure

SiO_2/Si(100) substrates were prepared by thermally oxidizing (100) silicon wafers. The HfO_2 films were grown by the sol–gel method using a precursor solution prepared by the Kojundo Chemical Laboratory. The films were coated on SiO_2/Si substrates using a spin coater operated at 500 rpm for 10 s and 2,000 rpm for 10 s. The coated films were dried at 120 °C for 5 min and 400 °C for 5 min, and finally crystallized at temperatures ranging from 500 to 750 °C for 30 min. For obtaining more reliable results of XRD analysis, the coating and heat-treatment process was repeated 11 times to obtain thicker HfO_2 films.

The crystal structure of the HfO_2 films was examined by X-ray diffraction (XRD, Rigaku RINT2000, CuKα radiation) analysis. The surface and cross-sectional morphologies of the films were observed by scanning electron microscopy (FE-SEM, JSM-6500F). Cross-sectional TEM specimens were prepared by conventional grinding and polishing. The specimens were ground and polished to a thickness of 20 μm, and were further thinned to perforation by Ar-ion milling using a Gatan precision ion polishing system (PIPS). The microstructures of the films were studied by transmission electron microscopy (HF2000, HITACHI). For measuring the electrical properties of the films, a Pt/Ti film was used as the bottom electrode, and a Pt film (size=ϕ 1.5 mm) was deposited by sputtering to form the top electrode. The dielectric constant and current–voltage (*I*–*V*) characteristics of these HfO_2 films were measured using multifrequency LCR meter (HIOKI 3522-50).

3 Results and discussion

3.1 Crystalline phases of HfO_2 films

First, to obtain a more reliable estimation, the XRD analysis of the thick HfO_2 films with 11 coating cycles annealed at 750 °C was conducted. Figure 1 shows the XRD pattern of the HfO_2 films deposited on SiO_2/Si substrate. As can be seen, distinct diffraction peaks can be observed, and these diffraction peaks are ascribed to the monoclinic phase of HfO_2 [12]. A peak ascribed to either tetragonal or orthorhombic HfO_2, often appearing at 2θ=30.3° in HfO_2 films deposited by atomic layer deposition and sputtering [13–16], was not detected in this study. The HfO_2 films, therefore, mainly crystallized in the monoclinic phase without the tetragonal or orthorhombic phase. There is no preferred orientation in these HfO_2 films, because the relative intensity ratios between all the diffraction peaks are close to those in the HfO_2 powder diffraction patterns [12]. Crystallite size (*t*) can be calculated using the Scherrer formula, t=0.9 $\lambda/(B \cos\theta)$, where λ is the X-ray wavelength, B is the peak width, and θ is the Bragg diffraction angle. The average crystallite size in the HfO_2 films calculated from the (111) and (11-1) diffraction peaks was approximately 15 nm.

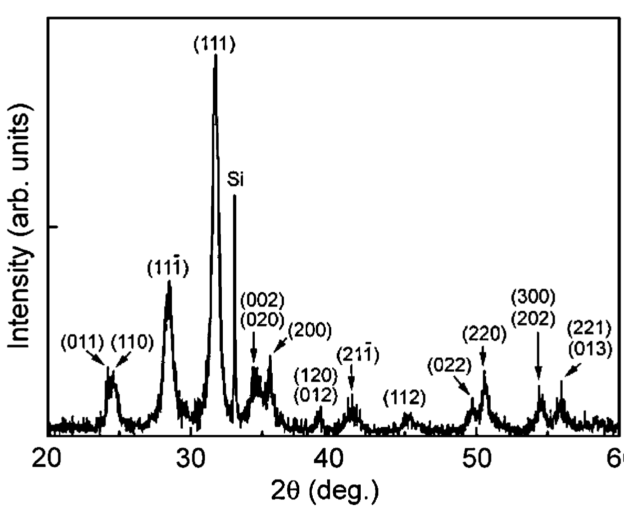

Fig. 1 XRD pattern of HfO_2 films with 11 coating cycles on SiO_2/Si(100) substrates annealed at 750 °C

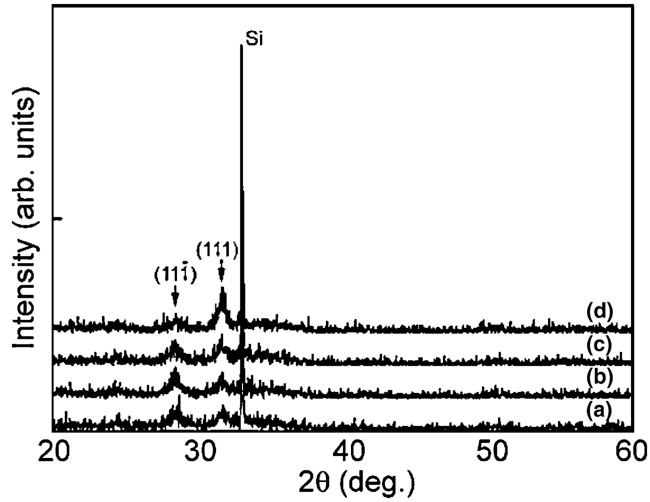

Fig. 2 XRD patterns of single-layer HfO_2 films on SiO_2/Si(100) substrates annealed at (**a**) 500 °C, (**b**) 550 °C, (**c**) 650 °C and (**d**) 750 °C

Figure 2 contains representative results of the XRD analysis of single-layer HfO_2 films annealed at various temperatures on SiO_2/Si substrates. At an annealing temperature of 500 °C, the (111) and (11-1) peaks of monoclinic HfO_2 appear. The peak density of these peaks increases slightly with annealing temperature. These results reveal that monoclinic HfO_2 films can be obtain at the annealing temperature of 500 °C by the sol–gel method, which is significantly lower than that of the HfO_2 films deposited by sputtering [6]. In our previous study, the HfO_2 films were deposited at room temperature by sputtering and then crystallized by postdepositional annealing at a temperature of 600 °C. It is imperative to decrease processing temperature for HfO_2 films for microelectronics and MEMS applications.

3.2 Microstructure of HfO_2 films

Figure 3 shows a cross-sectional TEM image of the HfO_2 film with five coating cycles grown on SiO_2/Si substrate. The thickness of the films is approximately 275 nm. From the result, the thickness of one layer of the HfO_2 film is concluded to be approximately 55 nm. The films consist of densely packed grains with a mean grain size of approximately 15 nm. The grain size obtained by TEM is in very good agreement with that calculated by XRD analysis using the Scherrer formula, as described above. Figure 4 shows a high-resolution electron microscopy (HTEM) image of the HfO_2 films. The measured d spacing of the crystallite shown in Fig. 4 is 0.3162 nm, and is coincident with the (11-1) planes (0.315 nm) of the monoclinic phase of HfO_2. The measured d spacing of monoclinic-phase HfO_2 is also consistent with those calculated by XRD analysis.

3.3 Electrical properties of HfO_2 films

The dielectric constant measurement of the films was carried out at a frequency of 1 kHz using an impedance analyzer. Figure 5 shows the schematic of dielectric constants of HfO_2 films vs sweep frequency. The room temperature dielectric constant of HfO_2 films was 21.6, which is in good agreement with the data in the literature (22) [17] but slightly higher than that of sputter-deposited HfO_2 films (18–20) [5]. The high dielectric constant in this work could be attributed to the high quality of the HfO_2 films, which crystallized well in the monoclinic phase with densely packed grains. The *I*–*V* measurements showed that the leakage current density of the HfO_2 films was 1.14×10^{-5} A/cm^2 at an applied electric field of 100 kV/cm. From their electrical properties, the sol–gel method-fabricated HfO_2 films are concluded to be feasible for MEMS applications, such as capacitive-type MEMS switches.

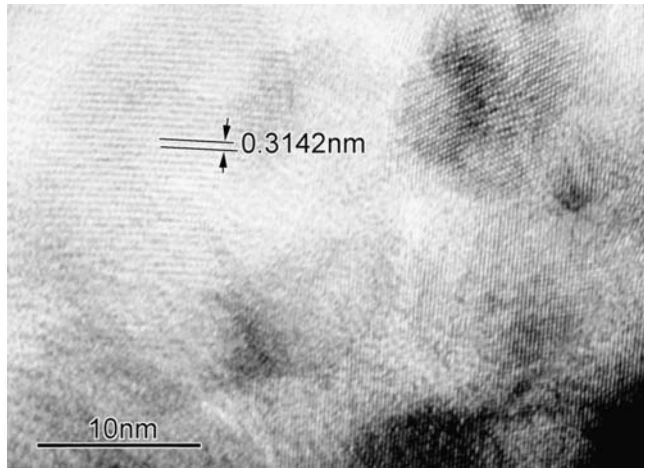

Fig. 4 Cross-sectional HTEM image of HfO_2 films with five coating cycles deposited on SiO_2/Si(100) substrates

4 Conclusions

Hafnium oxide (HfO_2) films were fabricated on SiO_2/Si (100) substrates by a sol–gel method. Their crystalline structure and microstructures were studied by XRD analysis and transmission electron microscopy, respectively. XRD analysis indicated that the monoclinic HfO_2 films could be obtained by annealing at 500 °C on SiO_2/Si substrates. TEM images revealed that HfO_2 films consist of densely packed grains with a mean grain size of approximately 15 nm. The electrical properties of the HfO_2 films were investigated by dielectric constant and current–voltage measurements. From their electrical properties, the sol–gel

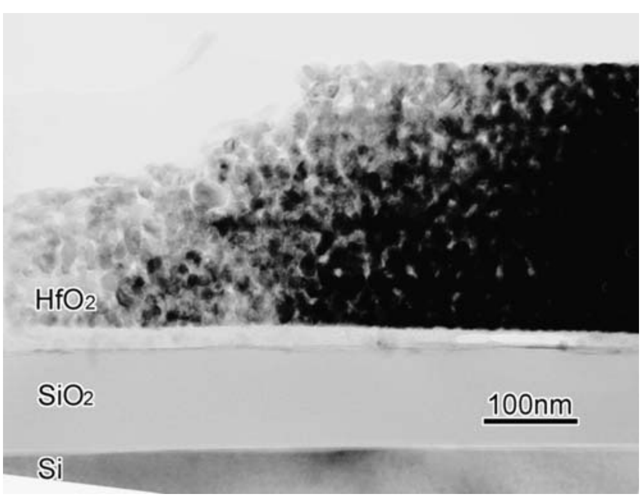

Fig. 3 Cross-sectional TEM image of HfO_2 films with five coating cycles deposited on SiO_2/Si(100) substrates

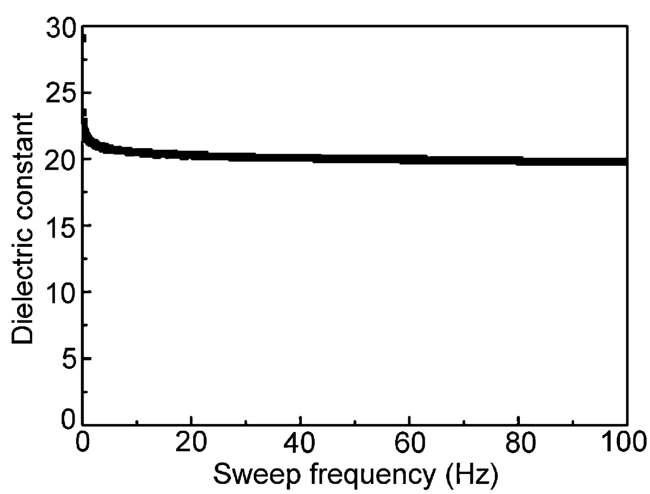

Fig. 5 Schematic of dielectric constants of HfO_2 films vs sweep frequency

method-fabricated HfO_2 films are concluded to be feasible for MEMS applications, such as capacitive-type MEMS switches.

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