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Structural and Electrical Characteristics of HfO_2 Films Fabricated by Pulsed Laser Deposition

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1. Introduction

A reduction of device dimensions of metal-oxide-semiconductor field-effect transistors (MOSFETs) requires ultra-thin gate oxide films. However, when the oxide thickness decreases to less than 2 nm, the leakage current density becomes large because of a direct tunneling effect. Therefore we have to replace commonly used SiO_2 films by high-dielectric-constant (high-k) materials because they can avoid the direct tunneling of carriers. From a viewpoint of thermal stability between the high-k materials and Si, gate oxides such as HfO_2, ZrO_2 and La_2O_3 have been attracted much attention [1-3]. HfO_2 has many desirable properties such as a high dielectric constant (~30), high heat of formation (-271 kcal/mol), and relatively large band gap.

In this work, we have grown HfO_2 thin films by a pulsed-laser-deposition (PLD) method and show the relationship between the electrical characteristics and the crystallographic structures of HfO_2.

2. Experimental

HfO_2 films were deposited by PLD with a HfO_2 target on p-Si (100) substrates treated by diluted HF. The HfO_2 film thickness was 15-19 nm. The oxygen gas pressure during the deposition was 10 Pa or 20 Pa and the deposition temperature was 300℃, 400℃ and 530 ℃. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to study the structural properties. For the electrical characteristics, MOS capacitors with an $Al/HfO_2/Si/Al$ structure were fabricated, and capacitance-voltage (C-V) and current-voltage (I-V) characteristics were measured using the MOS capacitors. The frequency in the C-V measurement was 1 MHz.

3. Results and Discussion

Figure 1 shows XRD patterns of HfO_2 films formed on Si (100) substrates at oxygen pressures. The deposition temperature was 300℃, 400℃ and 530℃. The XRD patterns of these samples indicate that HfO_2 films has a polycrystalline monoclinic structure. The HfO_2 film formed at 300℃ is found to have a random-oriented structure from the XRD profile. With increasing the deposition temperature, the intensity of the $(\bar{1}11)$ peak becomes stronger. This fact means that the crystalline HfO_2 is preferentially oriented to $(\bar{1}11)$. The diffraction peak intensity depends also on the oxygen pressure. The peak intensity for 20 Pa is weaker than that for 10 Pa. Therefore, the O atoms in the HfO_2 film have an effect of suppressing the crystallization of the film.

Cross-sectional TEM images of HfO_2 films deposited at oxygen pressures of 10 Pa and 20 Pa are shown in Figs. 2(a) and 2 (b), respectively. The deposition temperature was 400℃. It is found from Fig. 2 that an amorphous layer of about 2 nm thick was formed at the interface between HfO_2 and the Si substrate. However, we confirmed that no interfacial layer was observed when HfO_2 was deposited at an oxygen pressure as low as 1.3×10^{-2} Pa. These results strongly suggest that the interfacial layer consists of SiO_x.

Figure 3 (a) and 3 (b) show C-V characteristics of HfO_2 films at oxygen pressures of 10 Pa and 20 Pa, respectively. At each pressure, deposition temperature was performed at 300 ℃ and 530 ℃. Comparing these C-V characteristics with XRD patterns shown in Figs. 1, the $(\bar{1}11)$ -oriented samples have a large hysteresis in the C-V characteristics. The hysteresis indicates the existence of carrier-injection traps. On the other hand, the HfO_2 films with random-orientation do not show any hysteresis. From these results, the grain boundary structures of polycrystalline HfO_2 is considered to influence the traps of the carrier injection. The typical conduction mechanism of the HfO_2 films was found to be mainly dominated by Poole-Frenkel current (not shown). The Poole-Frenkel current was thought to be also influenced by the grain boundary structures.

4. Conclusions

We have investigated the structural and electrical characteristics of HfO_2 films deposited by a PLD method. It is found that the orientation and morphology of HfO_2 grains are strongly dependent of the deposition temperature. Moreover, the electrical characteristics depend strongly on the grain boundary structures of polycrystalline HfO_2 films.

References

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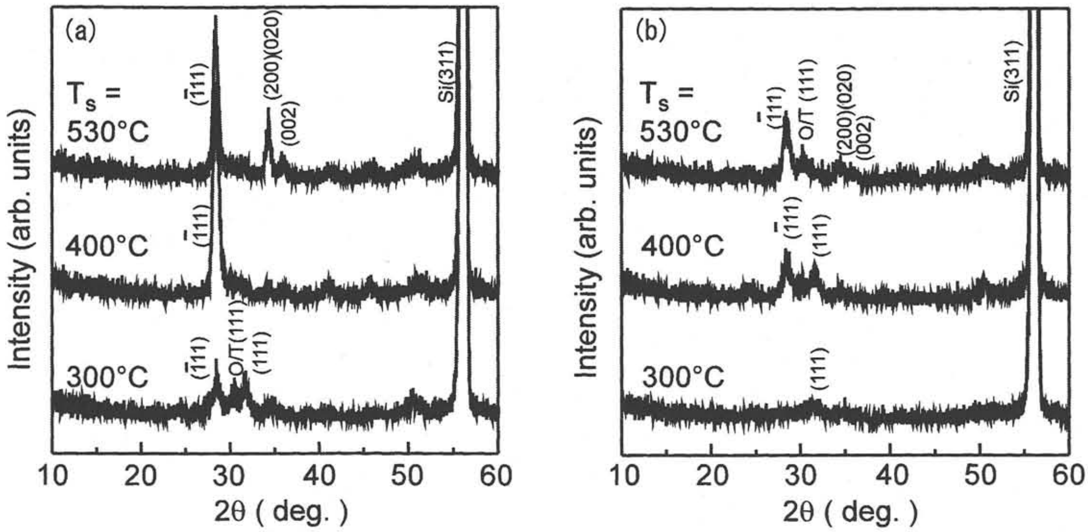

Figure 1 : XRD patterns of HfO_2 films formed on Si (100) substrates at O pressures of (a) 10 Pa and (b) 20 Pa. The deposition temperature was 300℃, 400℃ and 530℃.

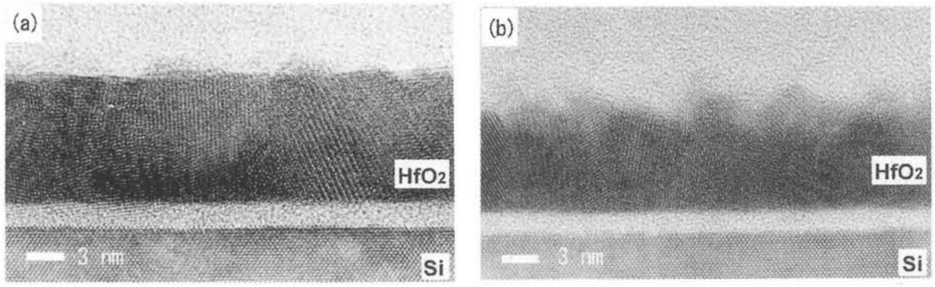

Figure 2 : Cross-sectional TEM images of HfO_2 films formed on Si (100) substrates at O pressures of (a) 10 Pa and (b) 20 Pa. The deposition temperature was 400℃.

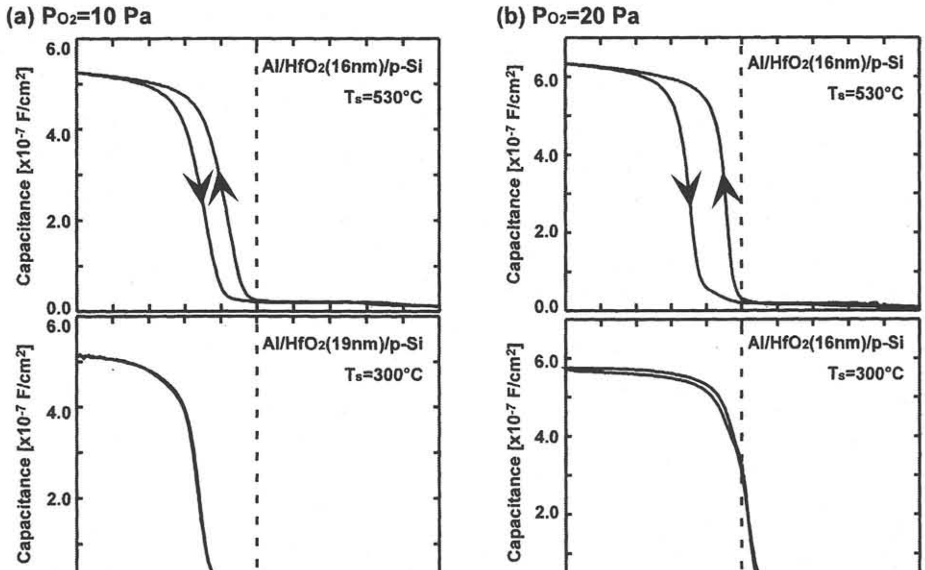

Figure 3 : Capacitance-voltage characteristics of HfO_2/p-Si (100) samples shown in Fig. 1. The mesurement frequency was 1 MHz.