Formation and Characterization of Epitaxial Rutile Thin Films on Si Substrate

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1. Introduction

Rutile (TiO₂) has high dielectric constant (ε, 170, ε, 89) together with high refractive index, high chemical stability and high laser damage threshold. This material can be a candidate for dielectric capacitor in future highly integrated dynamic random access memory (DRAM). Epitaxial rutile phase TiO₂ films were successfully deposited on such substrates as MgO² and Sapphire. However, TiO₂ films on Si substrate reported so far could not be grown in highly crystallized form⁶. We describe a new and simple method to form TiO₂ epitaxial films on Si substrate. Rutile phase TiO₂ epitaxial films were obtained by the oxidation of epitaxial TiN films. Crystallinity and dielectric properties of thus prepared TiO₂ films and their successful application to a buffer layer for the growth of BaTiO₃ films are presented.

2. Experimental Procedure

Pulsed KrF eximer laser deposition (248nm, 20ns, 5Hz) was employed to deposit TiN films on Si. Epitaxial TiN films were grown on p-type Si (100) substrates (p = 0.01~0.02 Ωcm) by ablating a hot pressed stoichiometric TiN target at 650°C in vacuum (~10⁻⁶ Torr). The TiN films were subsequently oxidized in 50 mTorr oxygen atmosphere. BaTiO₃ films were grown on thus prepared TiO₂ films by pulsed laser deposition at temperatures higher than 600°C and at oxygen pressures less than 1 mTorr. The crystallinity and in-plane orientation of these films were evaluated by X-ray diffractionmetry and X-ray pole figure, respectively. Al electrodes (~0.8 mm²) were deposited on these films through a shadow mask and Au was deposited on the backside of Si substrate by vacuum evaporation. The I-V and C-V characteristics were measured for the MIS diode structure.

3. Results and Discussion

Figures 1(a) and (b) show the X-ray diffraction patterns of a TiN film grown epitaxially on Si (100) substrate and a TiO₂ film formed by oxidation of the TiN film for 30 min at 780°C in 50 mTorr O₂ atmosphere, respectively. The rutile phase TiO₂ film was grown with (110) orientation. The FWHM values of θ-rocking curve for TiO₂ (110) and (220) peaks of this film were 2.48° and 2.28°, respectively, whereas FWHM for (200) peak of the original epitaxial TiN film was 1.74°. Figure 2 shows the X-ray pole figure of this TiO₂ film. The in-plane orientation of the TiO₂ film was revealed to be TiO₂ [001] // Si [011] and TiO₂ [001] // Si [011]. The (110) planes of TiO₂ rutile phase (a=4.593, c=2.959) oriented in two directions perpendicular to each other. As a comparison, we tried to grow TiO₂ film on Si substrates by directly ablating TiO₂ target. However, we could not grow an epitaxial film, and resulted in the similar results to the previous report⁶.

Figure 1(c) shows the X-ray diffraction pattern of BaTiO₃ film grown on thus prepared TiO₂ / Si at a temperature of 650°C in vacuum. The pattern represents the growth of an epitaxial double-layer (BaTiO₃ / TiO₂) film on Si. The values of FWHM for BaTiO₃(100) and (200) peaks were about 5.5° and 5.7°, respectively. The in-plane orientation was revealed to be BaTiO₃ [010] // Si [010] by X-ray pole figure analysis. In this paper, we treat the crystal structure of BaTiO₃ film as a cubic perovskite, since the rather poor crystallinity prevents us from judging whether it is a-axis or e-axis oriented⁶. Such epitaxial BaTiO₃ / TiO₂ double-layer could also be grown by one step process, i.e., by depositing BaTiO₃.
film at 780°C in 50 mTorr oxygen pressure onto a TiN epitaxial film. In this case, it is presumed that oxygen diffuses into TiN layer through the BaTiO3 film and the transformation of TiN into TiO2 as well as the epitaxial BaTiO3 film growth occur simultaneously. When we deposited BaTiO3 film on TiN / Si at the same temperature (780°C) in vacuum, we obtained epitaxial trilayer structure of BaTiO3 / TiO2 / TiN / Si.

Figure 3 shows schematically the epitaxial relationship of BaTiO3 / TiO2 / Si layers. Here we note that the perovskite lattice of BaTiO3 was aligned on Si in a cube-on-cube manner. Usually, the in-plane orientation of perovskite type dielectric oxide film deposited on Si substrate has a rotation of unit cell by 45°. This is because the lattice constant of perovskite is about a = 3.8 ~ 4.0Å and its diagonal length (√2a) agrees well with the lattice constant of Si (5.43Å). In figure 3, the lattice mismatches between BaTiO3 and TiO2 are 14% and -4.7%, and the values between TiO2 and Si are -25.9% and -16.7%, for the two [110] directions perpendicular to each other. Epitaxial growth can occur in such systems with large lattice mismatch as ours as well as in low-lattice-mismatch ones. In former case, the domain epitaxial growth is presumed to occur to minimize the strain energy. In our systems, 6 unit cells of BaTiO3, match with 7 unit cells of TiO2, in one direction (residual mismatch δ = 0.3%), and 21 unit cells of BaTiO3, match with 20 unit cells of TiO2, in the other direction (δ = 0.065%). On the other hand, 4 unit cells of TiO2 match with 3 unit cells of Si (δ = 1.2%), and 6 unit cells of TiO2 match with 5 unit cells of Si (δ = 0.04%).

Figure 4 shows the I-V(J-V) curve of a MIS (Al / TiO2 / p-Si) diode. The leakage current through TiO2 film was rather high value of about 10⁻⁹ A/cm² at 2.5V. The electrical resistivity at 2.5V corresponded to 1.5x10¹⁰ Q cm. A typical C-V characteristics is shown in Fig. 5. It shows hysteresis, suggesting the existence of interface or oxide trap sites. The dielectric constant at 1 MHz evaluated from the maximum capacitance value at the accumulation region was 25. The I-V(J-V) characteristics of BaTiO3 (400nm) / TiO2 (90nm) / Si layer deposited by one step process represented excellent insulating properties up to 40V (0.8MV/cm). The leakage current was less than 5x10⁻⁶ A/cm² and electrical resistivity was about 10¹⁵ Q cm at 10V. A symmetrical I-V curve was obtained regardless of the polarity of the gate voltage. The dielectric constant of this double-layer dielectric film was evaluated to be about 100 at 1 MHz from C-V measurement. The dielectric constant of BaTiO3 film was calculated to be 370 by taking the two series capacitor layers into account. The capacitance of this double-layer should be further increased by reducing the TiO2 film thickness.

In conclusion, the epitaxial TiO2 film could be obtained on Si substrate by oxidation of epitaxial TiN film. This layer was shown to be useful not only as a capacitor but also as a buffer layer for the deposition of other dielectric or ferroelectric oxide films.

REFERENCES

Fig. 1 X-ray diffraction patterns of (a) TiN film deposited on Si at 650°C, and (b) TiO2 film formed by annealing above TiN / Si for 30 min at 780°C in 50 mTorr O2 atmosphere, and (c) BaTiO3 film deposited on TiO2 / Si layer at 650°C in vacuum.
Fig. 2 X-ray pole figure of the TiO₂ film on Si (100) substrate. The poles are taken for TiO₂ {101} planes.

Fig. 3 The schematic diagram representing the in-plane orientation relationship between BaTiO₃ (BTO), TiO₂ (TO) and Si substrate.

Fig. 4 I-V (J-V) curve for a MIS (Al / TiO₂ (120nm) / Si) diode.

Fig. 5 Typical C-V curve for TiO₂ film with thickness of 120nm.