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Formation and Characterization of Epitaxial Rutile Thin Films on Si Substrate

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Rutile phase TiO_2 films were epitaxially grown on Si(100) substrates by oxidizing epitaxial TiN films deposited by a pulsed laser deposition. The electrical resistivity and dielectric constant of TiO_2 film was $1.5\times10^{10}\Omega$cm and 25, respectively. This film could be used as a buffer layer for the growth of epitaxial $BaTiO_3$ film on Si. The $BaTiO_3$ / TiO_2 double-layered capacitor on Si showed high dielectric constant and very low leakage current of 5×10^{-8}A/cm^2 at 10V.

1. Introduction

Rutile (TiO_2) has high dielectric constant ($\varepsilon_{//}$ 170, $\varepsilon_{\perp}$ 89)[1] 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 TiO_2 films were successfully deposited on such substrates as MgO[2] and Sapphire[3]. However, TiO_2 films on Si substrate reported so far could not be grown in highly crystallized form[4]. We describe a new and simple method to form TiO_2 epitaxial films on Si substrate. Rutile phase TiO_2 epitaxial films were obtained by the oxidation of epitaxial TiN films. Crystallinity and dielectric properties of thus prepared TiO_2 films and their successful application to a buffer layer for the growth of $BaTiO_3$ 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 ($\rho = 0.01\sim 0.02$ Ωcm) by ablating a hot pressed stoichiometric TiN target at 650°C in vacuum($\sim10^{-6}$ Torr). The TiN films were subsequently oxidized in 50 mTorr oxygen atmosphere. $BaTiO_3$ films were grown on thus prepared TiO_2 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 diffractometry and X-ray pole figure, respectively. Al electrodes (~0.8 mmΦ) 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 (t = 90nm) grown epitaxially on Si (100) substrate and a TiO_2 film formed by oxidation of the TiN film for 30 min at 780°C in 50 mTorr O_2 atmosphere, respectively. The rutile phase TiO_2 film was grown with (110) orientation. The FWHM values of ω-rocking curve for TiO_2 (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 TiO_2 film. The in-plane orientation of the TiO_2 film was revealed to be TiO_2 [001] // Si [011] and TiO_2 [001] // Si [0$\bar{1}$1]. The (110) planes of TiO_2 rutile phase (a=4.593, c=2.959) oriented in two directions perpendicular to each other. As a comparison, we tried to grow TiO_2 film on Si substrates by directly ablating TiO_2 target. However, we could not grow an epitaxial film, and resulted in the similar results to the previous report[4].

Figure 1(c) shows the X-ray diffraction pattern of $BaTiO_3$ film grown on thus prepared TiO_2 / Si at a temperature of 650°C in vacuum. The pattern represents the growth of an epitaxial double-layer ($BaTiO_3$ / TiO_2) film on Si. The values of FWHM for $BaTiO_3$(100) and (200) peaks were about 5.5° and 5.7°, respectively. The in-plane orientation was revealed to be $BaTiO_3$ [010] // Si [010] by X-ray pole figure analysis. In this paper, we treat the crystal structure of $BaTiO_3$ film as a cubic perovskite, since the rather poor crystallinity prevents us from judging whether it is a-axis or c-axis oriented[5,6]. Such epitaxial $BaTiO_3$ / TiO_2 double-layer could also be grown by one step process, i.e., by depositing $BaTiO_3$

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 $BaTiO_3$ film and the transformation of TiN into TiO_2 as well as the epitaxial $BaTiO_3$ film growth occur simultaneously. When we deposited $BaTiO_3$ film on TiN / Si at the same temperature (780°C) in vacuum, we obtained epitaxial trilayer structure of $BaTiO_3$ / TiO_2 / TiN / Si.

Figure 3 shows schematically the epitaxial relationship of $BaTiO_3$ / TiO_2 / Si layer. Here we note that the perovskite lattice of $BaTiO_3$ 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°[7]. This is because the lattice constant of perovskite is about $a = 3.8 \sim 4.0$Å and its diagonal length ($\sqrt{2}a$) agrees well with the lattice constant of Si (5.43Å). In figure 3, the lattice mismatches between $BaTiO_3$ and TiO_2 are 14% and -4.7%, and the values between TiO_2 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[8]. In our systems, 6 unit cells of $BaTiO_3$ match with 7 unit cells of TiO_2 in one direction (residual mismatch $\delta = 0.3\%$), and 21 unit cells of $BaTiO_3$ match with 20 unit cells of TiO_2 in the other direction ($\delta = 0.065\%$). On the other hand, 4 unit cells of TiO_2 match with 3 unit cells of Si ($\delta = 1.2\%$), and 6 unit cells of TiO_2 match with 5 unit cells of Si ($\delta = 0.04\%$).

Figure 4 shows the I-V(J-V) curve of a MIS (Al / TiO_2 / p-Si) diode. The leakage current through TiO_2 film was rather high value of about 10^{-5}A/cm^2 at 2.5V. The electrical resistivity at 2.5V corresponded to 1.5×10^{10}Ωcm. 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 $BaTiO_3$ (400nm) / TiO_2 (90nm) / Si layer deposited by one step process represented excellent insulating properties up to 40V (0.8MV/cm). The leakage current was less than 5×10^{-8}A/cm^2 and electrical resistivity was about 10^{13}Ωcm 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 the C-V measurement. The dielectric constant of $BaTiO_3$ 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 TiO_2 film thichness.

In conclusion, the epitaxial TiO_2 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.

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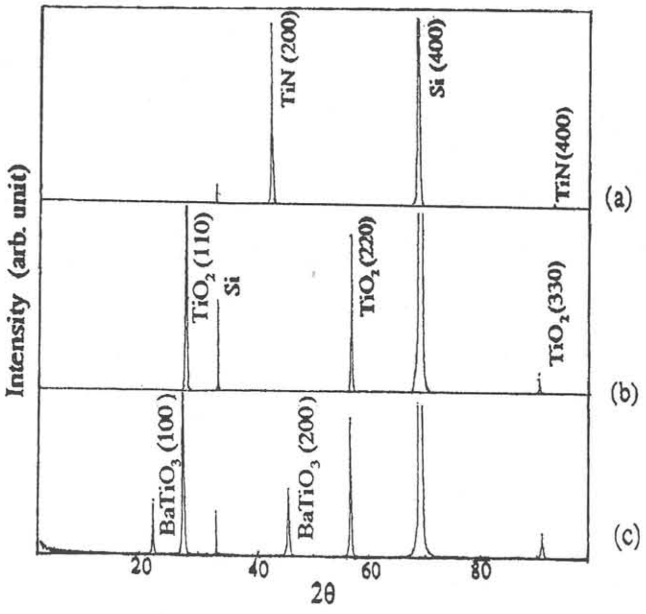

Fig. 1 X-ray diffraction patterns of (a) TiN film deposited on Si at 650°C, and (b) TiO_2 film formed by anneaning above TiN / Si for 30 min at 780°C in 50 mTorr O_2 atmosphere, and (c) $BaTiO_3$ film deposited on TiO_2 / Si layer at 650°C in vacuum.

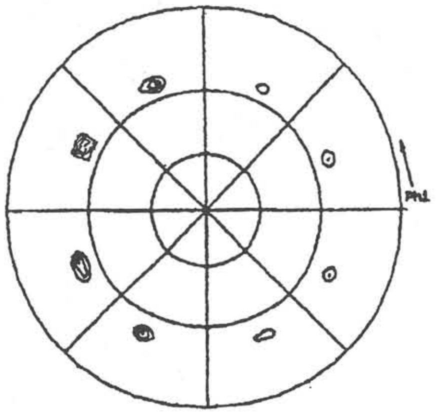

Fig.2 X-ray pole figure of the TiO_2 film on Si (100) substrate. The poles are taken for TiO_2 {101} planes.

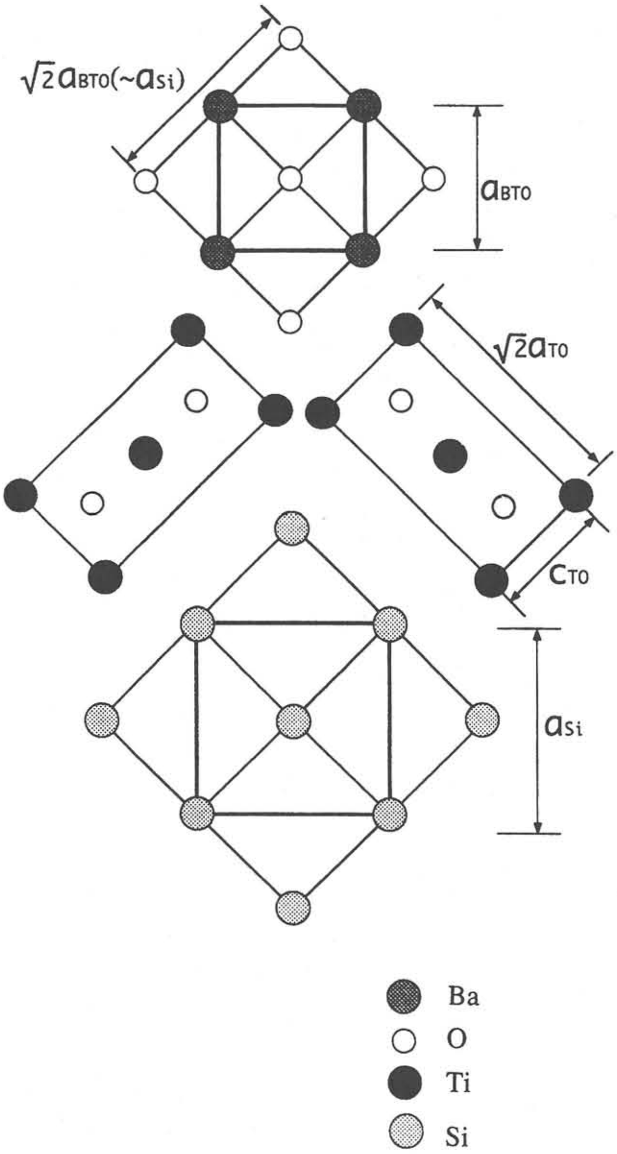

Fig.3 The schematic diagram representing the in-plane orientation relationship between $BaTiO_3$(BTO), TiO_2(TO) and Si substrate.

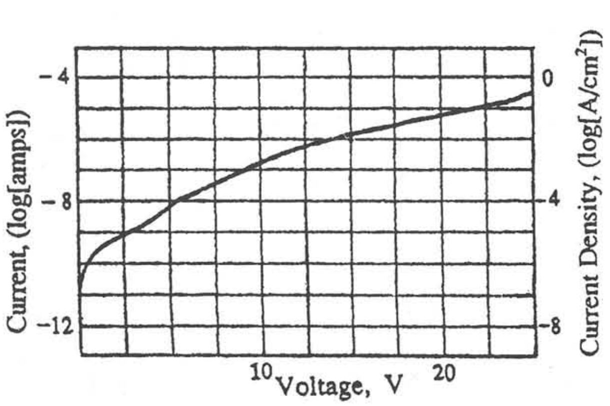

Fig. 4 I-V (J-V) curve for a MIS (Al / TiO_2 (120nm) / Si) diode.

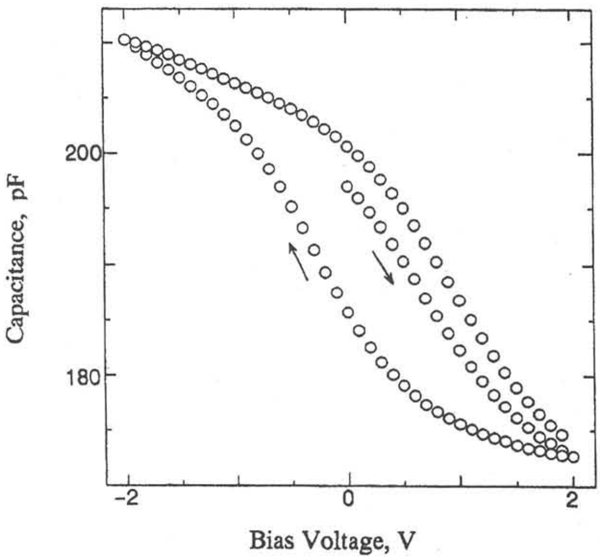

Fig. 5 Typical C-V curve for TiO_2 film with thickness of 120nm.