The Dielectric Constant and Crystalline Size of TiO$_2$ Films Deposited on Silicon by Use of Ionized Oxygen

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Polycrystalline TiO$_x$ films were deposited on silicon at 600 ~ 800 °C by use of 500 eV and 1 keV O ions. The diameters of TiO$_x$ crystallites increased from 4 nm to 18 nm with increasing substrate temperature or decreasing O ion energy. The dielectric constant of ~ 160 ε_0 was fulfilled on the TiO$_x$ film, consisting of crystallite with an average size of 12 nm, deposited at 600 ~ 700 °C.

Key words: titanium-oxide, dielectric constant, crystallite-size, lattice-constant, IBAD

I. INTRODUCTION

Gate-oxide as an important material of metal-oxide-semiconductor field-effect transistors is required to reduce its thickness with downsizing of dynamic random-access memory for future ultra-large scale integration. The conventional oxide and oxide-nitride-oxide triple layers will reach their applied physical limits in terms of reduction of thickness due to a marked increase in the direct tunnel current. Many scientists have participated in the development of high dielectric materials showing sufficiently low leakage current densities. Insulating oxides, such as tantalum oxide (TaO$_x$) [1] and titanium dioxide (TiO$_2$) [2, 3] have dielectric constant much higher than that of silicon oxide, silicon nitride, and oxide-nitride-oxide triplet. Titanium oxide has dielectric constant higher than those of TaO$_x$ [4]. Single-crystalline TiO$_2$ has a dielectric constant of 89 ε_0 for planes normal to the c-axis and 173 ε_0 for planes parallel to the c-axis [2], where ε_0 is the dielectric constant of free-space. The dielectric constant of conventional TiO$_2$ films is small, at most 30 ε_0 [3, 5]. However, the textured O-deficient TiO$_2$ films deposited by an ion-beam assisted deposition (IBAD) [6] had a high dielectric constant of ~ 160 ε_0, approximately as the same as that on bulk TiO$_2$ oriented to the c-axis [7]. As the O-deficient TiO$_2$ films are composed by crystallites with small sizes, we studied the relationship between the dielectric constant and the crystalline size on TiO$_2$ films deposited by IBAD.

2. EXPERIMENTAL DETAILS

P-doped (100) Si wafers of 1 - 2 Ωcm were used in this experiment. After the Si wafers were ultrasonically cleaned subsequently with acetone, solvent natha, methanol, they were immersed in an etchant of HF:H$_2$O: methanol to remove the native oxide layer. Titanium oxide was deposited onto the Si surfaces by an IBAD containing an electron beam evaporation and an ECR ion source [8]. Oxygen ion beams containing O$^+$, O^{2+}, O$_2^+$, etc were applied onto Si surfaces at energies of 0.5 - 1.0

keV, and the intensity was held constant at 0.01 mA/cm^2. Titanium oxide films were deposited in a vacuum of ~ 10^{-2} Pa at substrate temperatures of 500 ~ 800°C in O_2 gas flow of 10 ~ 50 sccm.

The compositions of the TiO_x films deposited on the Si substrates were measured by the Rutherford backscattering spectrometry (RBS) using 2.0 MeV He ions. The detection angle was 165° and the angle of incidence was 60°. The thickness of the TiO_x films was measured using a laser probe roughness tester. The crystalline structures of the TiO_x films were studied using an X-ray diffraction (XRD) meter with a Cu $_{K\alpha}$ source.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction spectra on various TiO_x films deposited by the IBAD. Measured diffraction peaks were indexed by comparing the known rutile TiO_2 [9]. On the TiO_x films, the large diffraction peak was from the (110) plane of rutile TiO_2, and the diffractions from the (101), (200), (211), (220), and (301) planes of rutile TiO_2 were weak. The strongest intensity of the diffraction from the (110) plane was measured on the
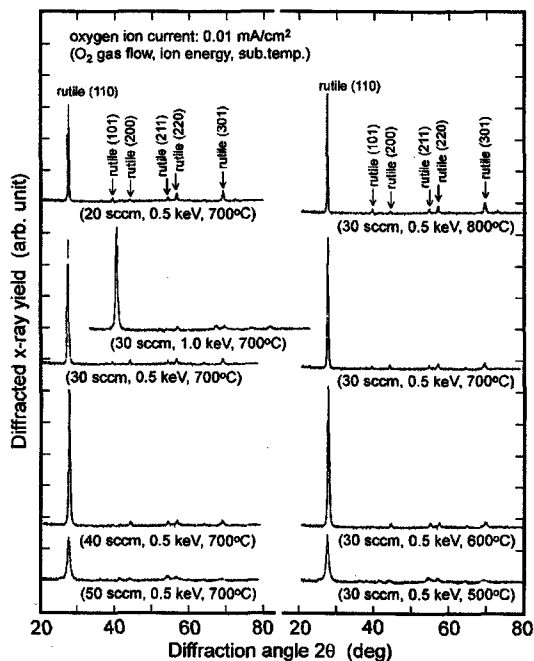

Fig. 1. Typical x-ray diffraction spectra

TiO_x film deposited under the conditions of an O_2 flow rate of 30 sccm and a substrate temperature of 700°C. The intensity of the (110) diffraction depended slightly on O ion energy, for example, as seen for the sample deposited under conditions of O_2 flow rates of 30 sccm and a substrate temperature of 700°C.

The average size of crystallites can be calculated from the full width at half maximum (FWHM) of the XRD peak from the (110) TiO_2 and its peak angle by using Scherrer's relation [10]. As shown in Fig. 2, the TiO_x films were composed with the crystallites with average sizes of 6~17 nm. The average size of the crystallites increased with increasing substrate temperature and O ion current although it decreased with increasing O ion energy. The surfaces of TiO_x films are collided with O ions, and the sputtered thickness is proportional to the energy of O ions [11]. The growth of crystallites is restricted with the sputtering although as the migration of O ions with energies larger than thermal energy on
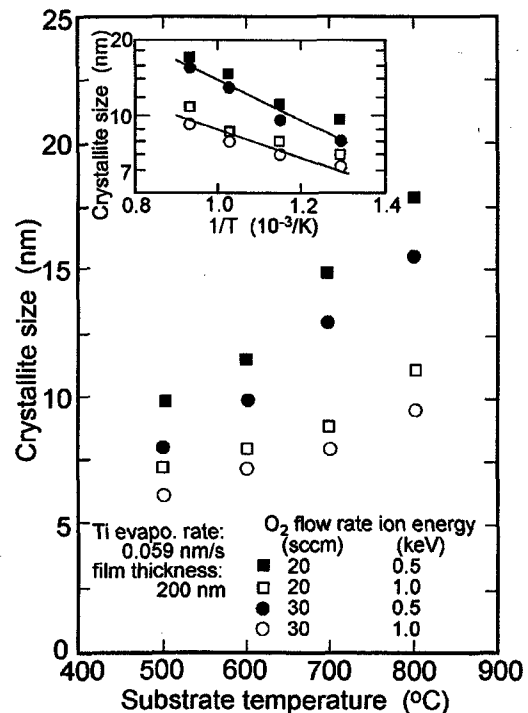

Fig. 2. Calculated average sizes for TiO_2 films. The insert shows the substrate temperature dependence of the crystallite size

substrates is enhanced with the kinetic energy, the crystallite size became larger. The crystallite sizes increased exponentially with increasing substrate temperature as shown in an insert of Fig. 2. This relation can be approximated by ~ exp (- E_a/kT), where E_a is an activation energy. The activation energies of 0.2 and 0.33 eV were obtained on the TiO_x films deposited at the O ion energies of 1.0 and 0.5 keV, respectively. The decrease in the activation energy with an increase in the energy of ions reflects that the growth of crystallites was restricted by collision of energetic ions onto the TiO_x film surfaces.

Figure 3 shows the dielectric constant of the deposited TiO_x films as functions of substrate temperature, O ion energy, and O_2 flow rate. The dielectric constant was obtained from the C - V curve. The dielectric constant increased with increasing substrate temperature, reached a maximum, and then decreased. The dielectric constant varied significantly with the O_2 flow rate on the TiO_x films deposited at the O ion energy of 1 keV. When the TiO_x film was deposited at the O_2 flow rate of 20 sccm, the film surface is collided with the fraction of energetic O ions in the O beam flux greater than when the film
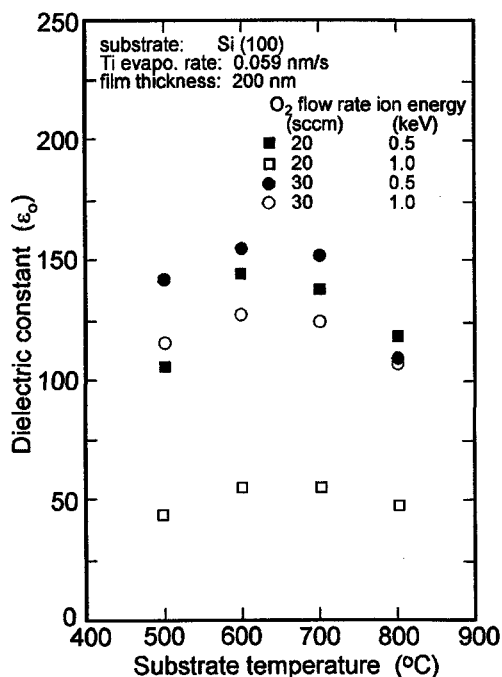
was deposited at the O_2 flow rates larger than 20 sccm. Since the intensity of the O ions was held constant at 0.01 mA/cm^2, the fraction of O ions in the O beam flux increases with decreasing the O_2 flow rate. The number of damaged TiO_x increases with decreasing the O_2 flow rate since the O ion beam current is held constant. Thus, dielectric constants depend remarkably on O_2 flow rates. A similar small dielectric constant is obtained on TiO_2 films deposited by RF sputtering [12].

Figure 4 shows the relationship between the dielectric constant and the crystalline size on TiO_2 films deposited by the IBAD method. The TiO_2 films deposited with the O ion energy of 0.5 keV had a maximum dielectric constant at a crystallite size of about 12 nm, regardless of the O_2 flow rate. On the other hand, the TiO_x films deposited with the O ion energy of 1.0 keV had maximum dielectric constants corresponding to crystallite sizes and the O_2 flow rates: 9 nm for the O_2 flow rate of 20 sccm and 7 nm for the O_2 flow rate of 30 sccm. To deposit TiO_x films with a large dielectric constant by the IBAD method, it is required to optimize the size of the crystallite by adjusting O ion energy and O_2 flow rate. Figure 5 shows the value of a^2c, volume of unit cell, as a function of substrate temperature, which a and c are the lengths of a-

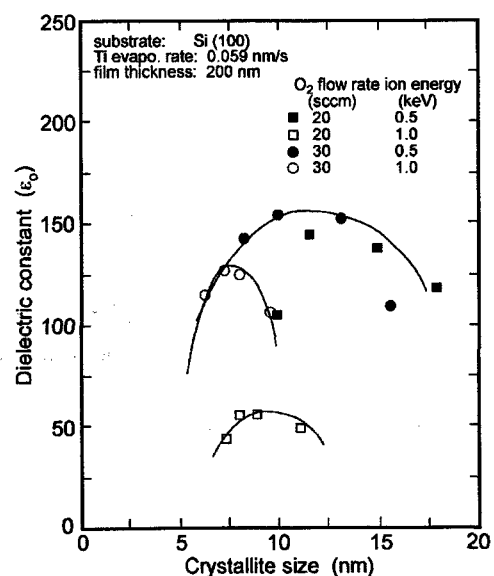Fig. 3. The dielectric constant of TiO_x films

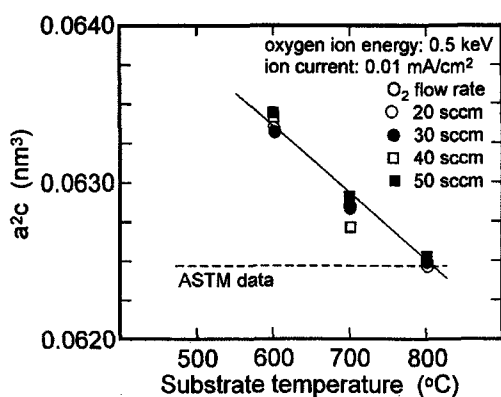
Fig. 4. Crystalline size dependence of dielectric constant

Fig. 5. The value of a²c, volume of unit cell

a- and c-axis on the TiO₂ unit cell, respectively. The value of a^2c on the TiO$_x$ films deposited at substrate temperatures of 600 and 700 °C was larger than that calculated from the ASTM data for rutile TiO₂ [14]. A large value of a^2c suggests to be present a large space around Ti^{+2} ions in the rutile TiO$_x$ unit cell. The Ti^{+2} ions in the rutile TiO$_x$ unit cell enable to displace easily from the O⁻ ions by an applied electric field. Thus, the TiO$_x$ films have a large dielectric constant. The TiO$_x$ films deposited at 800 °C had approximately the same value of a^2c as the ASTM data. Since the value of a^2c decreased with increasing substrate temperature, the dielectric constant on TiO$_x$ films deposited at high substrate temperatures became smaller.

4. CONCLUSION

On polycrystalline TiO₂ films deposited on silicon by use of the IBAD method, the volume of the unit cell increased with decreasing O ion energy and substrate temperature and increasing O₂ gas flow rate, and the space around Ti^{+2} ions in the rutile TiO₂ unit cell became larger. The Ti^{+2} ions in the unit cell on the TiO$_x$ films with large a^2c can be displaced easily for O⁻ ions by an electric field. Thus, the dielectric constant of the TiO$_x$ films increased with increasing the volume of the unit cell, which depended on substrate temperatures, O₂ flow rates,

and O ion energies. Recovery of defects introduced by collision of energetic O ions at high substrate temperatures resulted in small dielectric constant on the TiO$_x$ films. The polycrystalline TiO₂ films consisting of average crystallite size of 12 nm had a dielectric constant of ~ 160 ε₀.

5. ACKNOWLEDGEMENT

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