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Growth of highly oriented $ZrTiO_4$ thin films by radio-frequency magnetron sputtering

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$ZrTiO_4$ thin films on Si(100), metals [Al, Ti and Pt coated on Si(100)] and glass were prepared by radio-frequency magnetron sputter deposition. All films on crystalline substrates exhibited a highly preferred orientation in [020], which were evidenced by the full width at half-maximum ($\leqslant 0.046°$) of the associated rocking curves. The structure of the films on glass, depending on the substrate temperature, was either amorphous or random polycrystalline. Good stoichiometric quality and thermal stability have been observed in films on silicon. The X-ray diffraction and transmission electron microscopy selected-area diffraction studies indicated that, after a sequence of annealing up to 650–700 °C, the distributions of Zr and Ti ions in the octahedral cation sites of crystal structure of the films remained disordered.

Zirconium titanate, $ZrTiO_4$, is a material for application in many fields. It is known as a high-temperature (melting point 1820 °C) and high-dielectric material. The reported dielectric constant is 23.8 in the 1kc–10 Mc frequency range.[1] Recently, $ZrTiO_4$-based ceramics also attracted a lot of attention due to its dielectric properties in the microwave frequency regime[2,3] and its chemical bonding characteristics; the latter makes it useful as catalyst[4] and sensor material for humidity measurements.[5] In addition, both of its nominal components, ZrO_2 and TiO_2, in thin film form have been studied intensively in the last decade[6,7] for their high refractive indices and large optical band gaps, useful for making high-precision optical devices. However, $ZrTiO_4$ film itself did not receive detailed attention and its synthesization and properties have not yet been studied. In this letter we report the fabrication of highly oriented $ZrTiO_4$ films using radio-frequency magnetron sputter deposition. We investigated the effect of substrates and thermal anneal on the preferred orientation of the as-grown films. The resulting microstructure and composition of the films are also reported.

The zirconium titanate thin films were sputter deposited by using a 76 mm target made of packed $ZrTiO_4$ powder. The system was arranged in a sputter-up configuration with a horizontal rotatable substrate holder 8 cm away from the target. The base pressure of the sputtering chamber is typically 5×10^{-7} Torr. Prior to film deposition the target was presputtered alone for 15 min. All films were deposited at a fixed rf power level of 250 W and an operating pressure of 10 mTorr which was maintained in the chamber by a mixture of argon and oxygen at a flow-rate ratio of 80/20. The substrate temperature was corrected by precalibration from the value as measured by a thermocouple sitting between the substrate and heating lamps. The substrates used were Corning 7059 glass, p-type Si(100) and metals (Al, Ti, and Pt) coated on Si(100). The crystal structures of the films were analyzed using a Siemens D5000 XRD with Cu Kα radiation and a JOEL 2000FX STEM at 200 KeV.

In the first set (set A) of depositions the substrates were subjected to no intentional heating. The XRD patterns of these as-deposited films on silicon and metals exhibited only a (020) peak [Figs. 1(a)–(d)] at $2\theta = 32.9$ °, referring to axes labeled according to the orthorhombic space group Pbcn. The patterns also show that the underlying coatings of Al and Pt are nonpreferred oriented and that of Ti is (011) oriented. Under the current sputtering conditions, identical growth habit was adopted irrespective of the crystal structures (face-centered cubic, hexagonal, or diamond structure) or the degree of crystal orientation (random, preferred oriented, or single/crystal) of the substrates on which these films were grown. A highly b-axis oriented structure of films on Si(100)

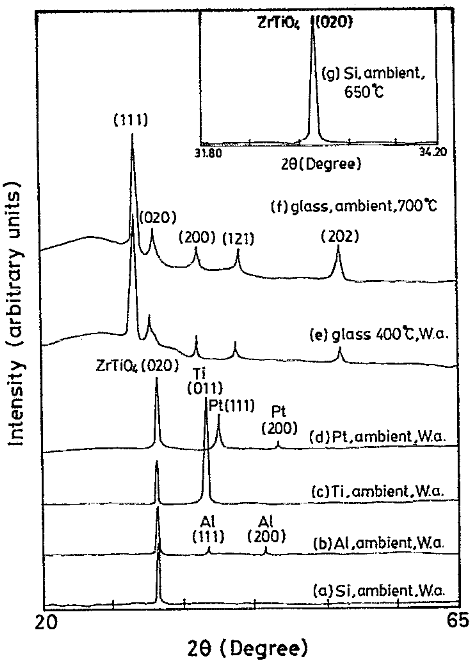

FIG. 1. X-ray diffraction of $ZrTiO_4$ films, three items attached with each curve, (a)–(g), indicate, in sequence,1, the substrates, 2, the substrate temperatures and 3, the annealing temperatures, or without annealing (w.a.).

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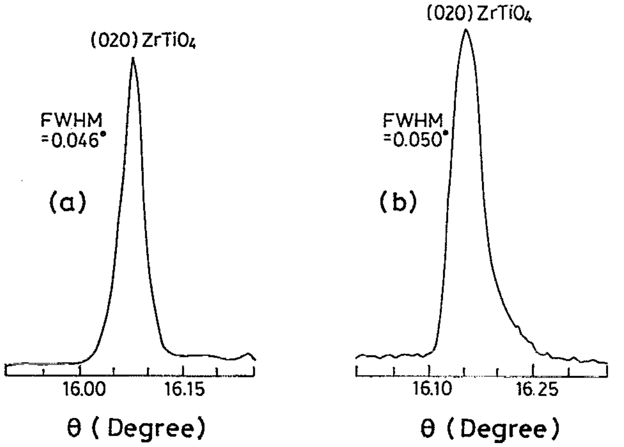

FIG. 2. X-ray rocking curves of the (020) plane for $ZrTiO_4$ films deposited on Si(100), (a) films unannealed, (b) films annealed up to 650 °C for one hour.

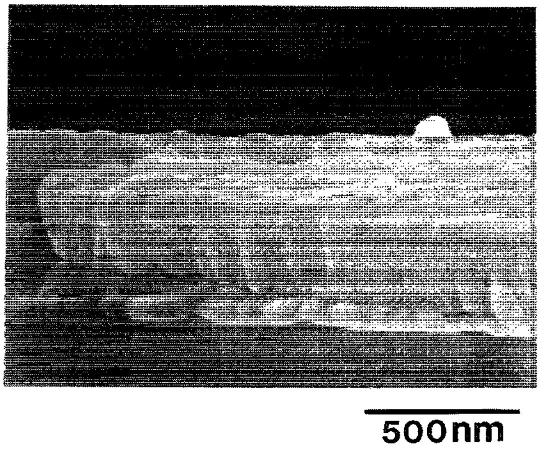

FIG. 3. SEM of $ZrTiO_4$ films as deposited on aluminum.

is evidenced by the (020)-plane rocking curve [Fig. 2(a)] having a full width at half-maximum (FWHM) of only 0.046 ° (±0.005 °). Similar results were obtained for films on Pt(0.046 °), Ti(0.041°) and Al(0.042 °) substrates (curves not shown here). In contrast to the cases for crystalline-type substrate, the structure of films deposited on glass under the set-A conditions proved to be noncrystalline or of very poor structure with not any discernible peak in the XRD spectra except the amorphous broadening.

In set B depositions the crystallinity of films on glass was improved significantly as the substrate temperature was maintained at 400 °C or higher temperatures during deposition and the structure turned out to be randomly oriented [Fig.1(e)]. With the same substrate-heating conditions, the films grown on Si(100) exhibited the (020) growth habit. The XRD results showed that, similar to many other fiber-texture films, the $ZrTiO_4$ films deposited on crystalline substrates also have a close-packed atom plane parallel to the film plane [the unit cell dimensions; a=4.81, b=5.44, c=5.03 Å] Ref. 8, presumably corresponding to a low-energy configuration.[9]

Columnar morphology was observed by, scanning electron microscopy (Fig. 3) on the fractured films as-deposited on aluminum, supporting a growth model in which island nuclei coalesce and grow to form columnar crystallites. The average width of the column is of the order of 100 nm.

Stable $ZrTiO_4$ orthorhombic phase may tolerate a variation of mole ratio of Ti/Zr from 45/55 to 58/42.[10] Stoichiometric analysis of the film composition was performed by EPMA (JOEL JXA-8800M) on a film of thickness 1.2 μm. The measured Ti/Zr ratio is 1.03/1.00. Typical depth profile, analyzed by secondary ion-mass spectroscopy (SIMS) (CAMECA IMS-4f), of the $ZrTiO_4$ films on silicon (Fig.4) shows uniform concentration distributions for both cations.

To evaluate the thermal stability of $ZrTiO_4$ films, the samples on silicon (selected from set A) were carried through a sequence of thermal annealing (in air), 400, 500, and 650 °C each for one hour. The annealed films showed high adhesion and no degradation of appearance. The final FWHM of (020) rocking curve was found to be 0.050 ° [Fig. 2(b)], essentially unchanged from the original one, while the FWHM of (020) 2θ peak reduced from 0.083° to 0.052 ° [Fig.1(g)] due to the relaxation of inhomogeneous strain and/or grain growth of the films. The peak position is at 32.93°, corresponding to b=5.44 Å by Bragg law. A similar annealing process up to 700 °C for one hour led the amorphous films on glass (from set A) to a random crystalline structure [Fig. 1(f)] with the (020) peak at 2θ=32.27°, corresponding to b=5.54 Å.

Detailed studies on the phase transition of $ZrTiO_4$[10–13] that occurs in a temperature range 1100–1200 °C showed that the high-temperature structure having a random distribution of zirconium and titanium ions in available octahedral cation sites could only be completely converted to the low-temperature ordered form (b=5.348 Å) by very slow cooling at 1 °C/h.[11] The ordered phase exhibits nonintegral satellite reflections in electron diffraction patterns associated with the development of a structural modulation along the *a* axis. While the samples prepared by quenching or furnace cooling remain disordered or a structure close to the onset of the tran

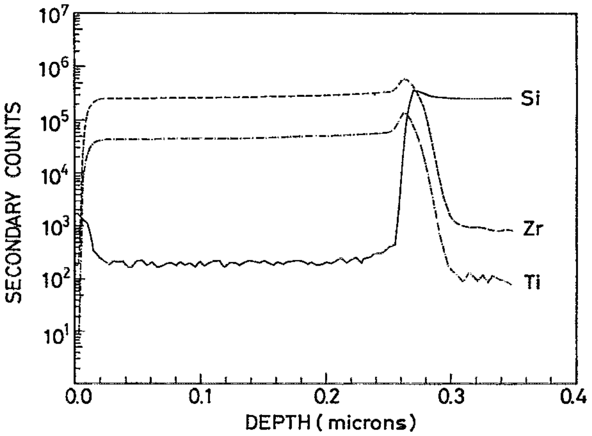

FIG. 4. SIMS depth profile for $ZrTiO_4$ films as deposited on Si(100).

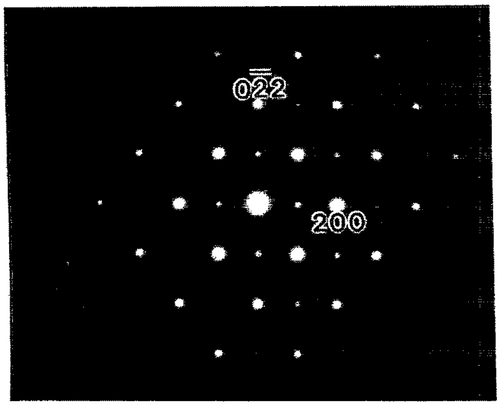

FIG. 5. [011] electron diffraction patterns of annealed $ZrTiO_4$ films on Si(100).

sition, and have the values of b, 5.48–5.50 Å or 5.41–5.45 Å.[8,11] The results obtained from the current XRD studies indicated that, after anneal, the films on glass are still highly disordered, and the films on silicon are on the verge of transition. This point is confirmed by the TEM [011] selected-area diffraction (Fig. 5) of the latter, which displays disordered-type diffraction patterns with no extra reflection in the *a* direction otherwise arising from a superstructure in ordered form.[13]

In summary, thin films of $ZrTiO_4$ have been grown by rf magnetron sputtering method with uniform stoichiometry and Ti/Zr ratios within 3% of that of the target. The films on crystalline substrates exhibited (020) preferred orientation of good crystallographic-alignment quality. The distributions of both cations in octahedral sites of $ZrTiO_4$ structure, after an annealing process which had caused significant strain relaxation and grain growth, remained disordered.

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