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The effects of substrates on the thin-film structures of $BaTiO_3$

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Barium titanate ($BaTiO_3$) thin films prepared on magnesia, silicon and strontium titanate substrates by r.f. sputtering has been investigated. As a function of substrate and annealing temperatures, the crystal structure and shape were examined by X-ray diffraction and scanning electron microscopy. Thin films were grown on both MgO and silicon substrates; they were amorphous when deposited on MgO if the substrate temperature was less than 450 °C, while for those grown on silicon the temperature had to be less than 500 °C. Above these elevated temperatures, the films were crystalline, with cubic symmetry. After annealing the thin films on magnesia, the crystal structure changed from cubic to tetragonal phase above 1100 °C; the annealing thus caused the grain growth of the $BaTiO_3$. The thin films on $SrTiO_3$ were found to be *c*-axis oriented tetragonal films for a substrate temperature above 500 °C.

1. Introduction

Barium titanate ($BaTiO_3$) is a material which in bulk crystalline form exhibits a high dielectric constant and below the Curie temperature of 120 °C is ferroelectric. Obtaining thin films of $BaTiO_3$ with properties approaching those of bulk $BaTiO_3$ would both contribute general insight into thin-film physics and also have application in the microelectric industries. Extensive work has been done using the r.f. sputtering and other thin-film fabrication techniques [1–4]. Nagatomo *et al.* [2] reported the relationship between the substrate temperature and total gas pressure for the fabrication of $BaTiO_3$ films on platinum and fused quartz substrate by r.f. planar-magnetron sputtering. They obtained various structural films with no phase transition occurring. Another paper on the preparation of $BaTiO_3$ films by sputtering [5], described the dependence of amorphous, cubic and tetragonal phase transitions on the substrate and annealing temperatures. Recently, the *c*-axis oriented $BaTiO_3$ epitaxial films with a smooth surface have been fabricated on $SrTiO_3$(1 0 0) using the pulsed-laser deposition technique [6].

In this paper, the preparation and characterization of thin films of $BaTiO_3$ are reported. The effects of temperature and substrate material in this experiment are discussed, using the X-ray diffraction and scanning electron microscopy results.

2. Experimental procedure

A Joel Model-430RS r.f. sputtering system was used to make the $BaTiO_3$ thin films on MgO, silicon and $SrTiO_3$ substrates. A chromel–alumel thermocouple was attached to control the temperature of the substrate. The target was formed into a disc at a static pressure of 1.38×10^7 Pa and fired at 1250 °C for 1 h in order to make it easier to handle with mechanical force by the conventional ceramic process. The distance between the target and substrate holder was 30 mm. The sputtering chamber was initially evacuated to a base pressure of 3×10^{-3} Pa, then argon gas, controlled with separate flowmeter, was introduced into the sputtering chamber through a manually controlled needle valve. The substrate was clamped on a stainless-steel substrate holder maintained in the temperature range 25–700 °C. The sputtering conditions are summarized in Table I. The thickness of the sputtered films was fixed at 1 μm by the thickness monitor (model TM-200R) which was calibrated using a Dektak 3030(Auto II Programmable Stage Profiler) by measuring the height of a step produced by masking a region of the substrate during deposition. The microstructure and crystallographic properties of the thin films grown on MgO(1 0 0), Si(1 1 1) and $SrTiO_3$(1 0 0) crystals were analysed under the same

TABLE I. Summary of sputtering conditions

Target-to-substrate distance	30 mm
Sputtering gas	100 vol % Ar
Gas pressure	1 Pa
R.f. input power	150 W
Deposition rate	40–50 nm s^{-1}
Substrate temperature	25–700 °C

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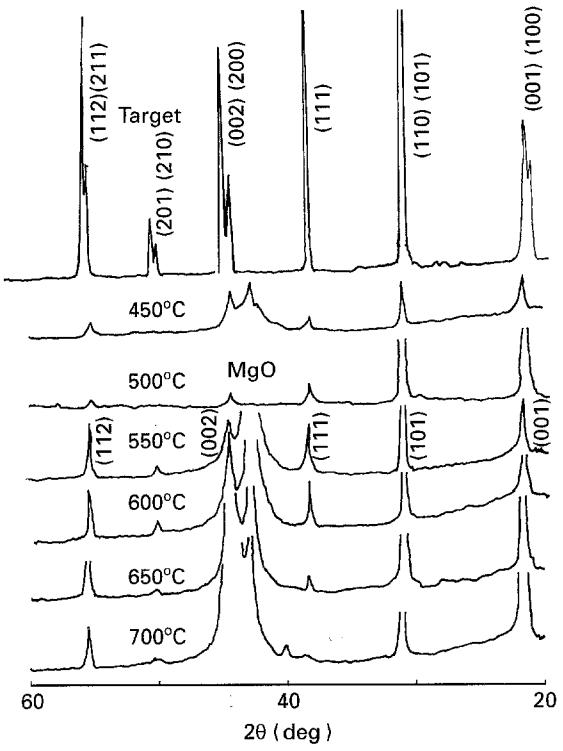

Figure 1 XRD patterns of $BaTiO_3$ films on MgO.

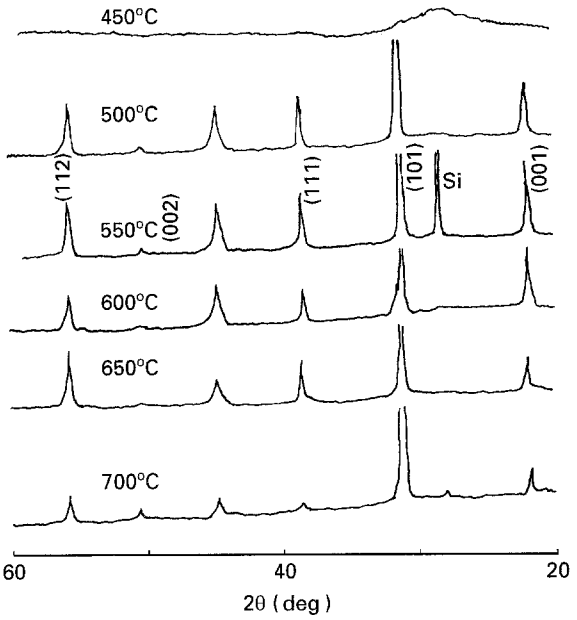

Figure 2 XRD patterns of $BaTiO_3$ films on silicon.

sputtering conditions as in Table I. $BaTiO_3$ has two crystal structures (cubic and tetragonal) which were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The anneals in air were also performed using different temperatures to study the structure change of the $BaTiO_3$. This phase transition was caused by the thermal annealing of the thin films. Grain sizes were determined in different ways; for sizes less than 100 nm we measured the half-width of the X-ray diffraction peak and Scherer's formula [7]; for larger grains, direct measurements were made on scanning electron micrographs.

TABLE II Crystal systems and lattice constants

	Crystal system	Lattice constant (nm)
$BaTiO_3$	Tetragonal	$a = 0.3994$, $c = 0.4038$
	Cubic	$a = 0.4031$
MgO	Cubic	0.4213
Si	Cubic	0.5431
$SrTiO_3$	Cubic	0.3905

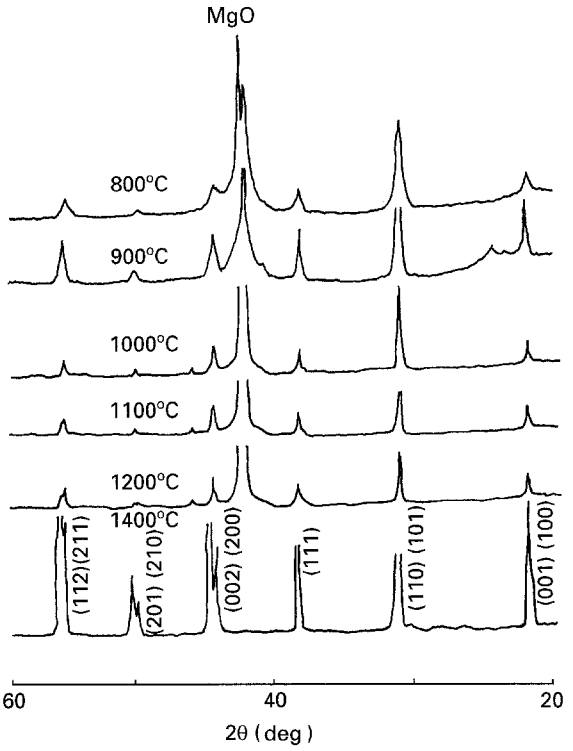

Figure 3 XRD patterns of annealed films on MgO.

3. Results and discussion

Films were prepared using substrates of different materials, namely MgO, silicon and $SrTiO_3$. The crystalline structure of the thin films was investigated by varying the substrate and annealing temperatures with different substrates.

3.1. MgO, silicon substrates

Figs 1 and 2 show the XRD patterns of the thin films of $BaTiO_3$ sputtered in pure argon on MgO and silicon substrates, respectively. The film sputtered at room temperature showed an amorphous phase but when the substrate temperatures were kept above 450 °C on MgO and 500 °C on silicon, $BaTiO_3$ films with the cubic polycrystalline structure were obtained. However, when the substrate temperatures were increased, the sputtered atoms had a surface mobility large enough for the crystalline structure to form. As in Thornton's structural zone model [8], the structure of sputtered films was dependent on the substrate temperature and gas pressures. Also, the substrate temperature influenced the crystallity of the film, as evinced by the sharp peaks in the diffraction pattern. In all films deposited on the substrates above 450 °C on MgO and 500 °C on silicon, the $BaTiO_3$ films

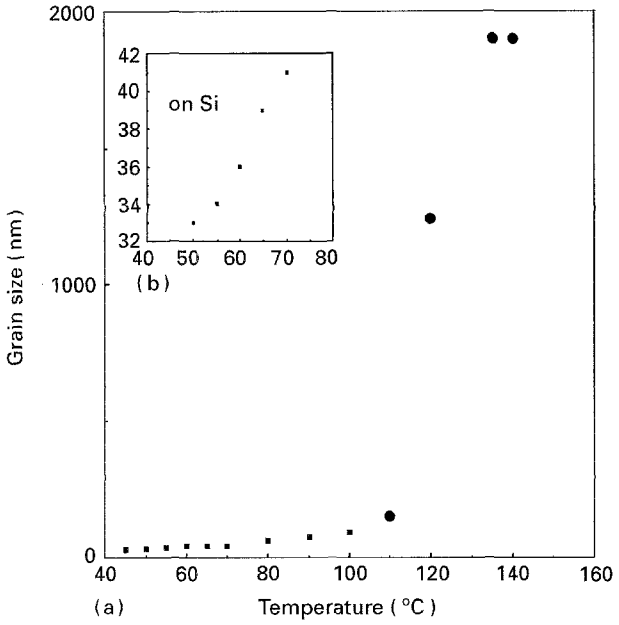

Figure 4 Grain size versus temperature on (a) MgO and (b) silicon substrates. (●) Tetragonal, (■) cubic.

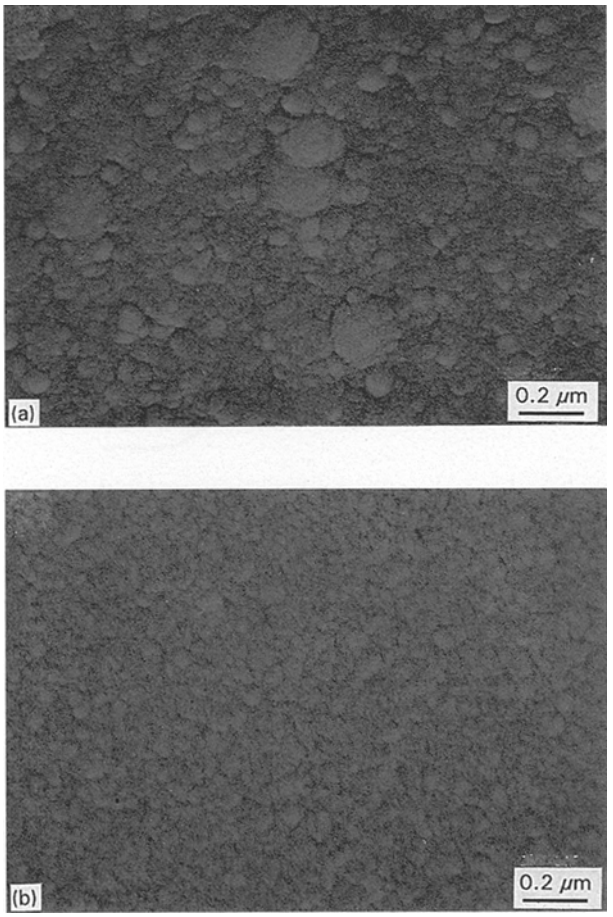

Figure 5 Scanning electron micrographs of $BaTiO_3$ films formed on the substrate at (a) 500 °C and (b) 700 °C.

appear to be cubic. Table 2 shows the crystal system and lattice constants of $BaTiO_3$, MgO, silicon and $SrTiO_3$. The grain sizes of the thin films ranged from 330–470 nm on MgO from 450–700 °C substrate temperatures in this study, which agree with Iijima's report [9]. The decrease in the full-width at half

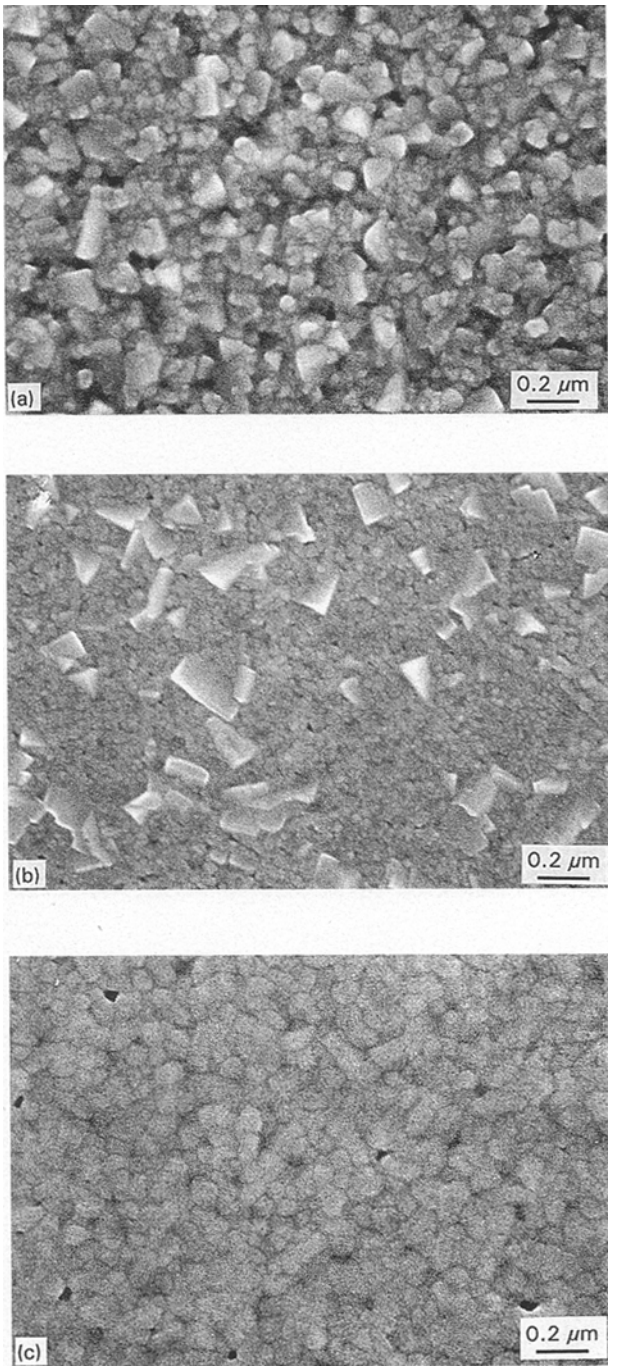

Figure 6 Scanning electron micrographs of $BaTiO_3$ films annealed for 1 h at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, (e) 1200 °C, and (f) 1400 °C.

maximum (FWHM) is caused by the increase of the grain size calculated from FWHM which agrees with the grain size determined by SEM. The thin films on the MgO were annealed at various temperatures to increase the grain size, and those were compared with the dependence on the grains of thin films. Fig. 3 also shows the XRD patterns of the $BaTiO_3$ thin films on MgO annealed from 800–1400 °C. Fig. 4 shows the grain size calculated from the (1 1 0) diffraction peak by FWHM and measured from scanning electron micrographs versus substrate and annealing temperatures. The surface morphology of as-grown and annealed films were observed by SEM. The grain sizes were determined by the average intercept lengths of the linear intercept method [10]. The scanning

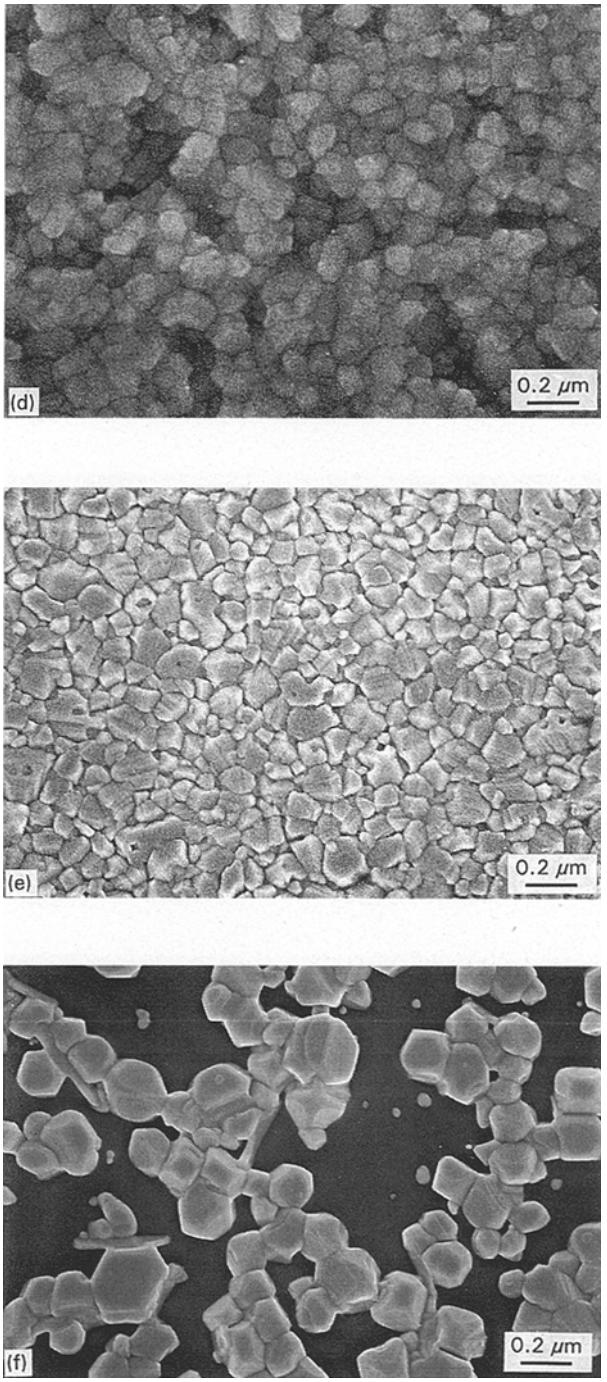

Figure 6 continued

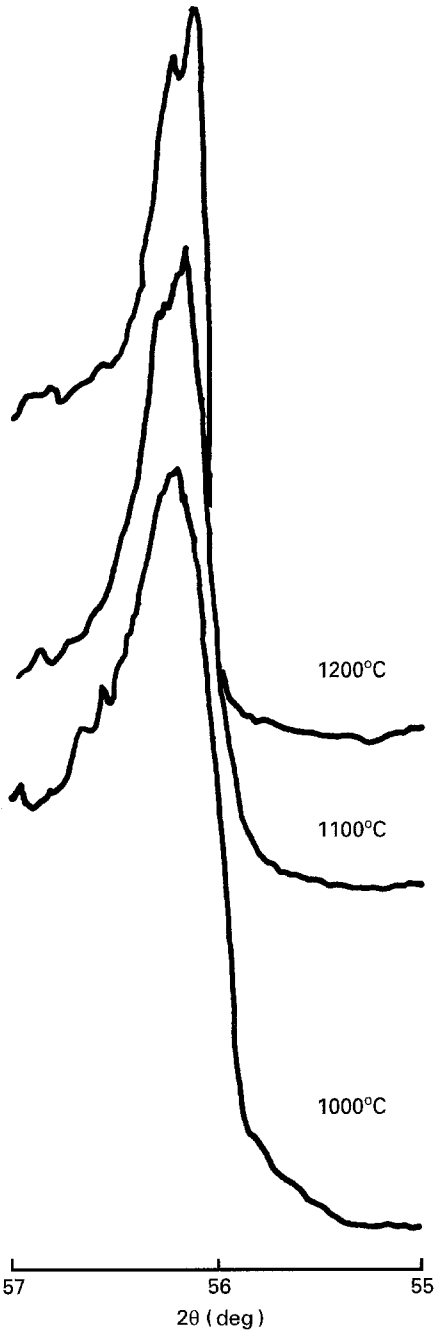

Figure 7 XRD peaks (1 1 2).

electron micrographs in Fig. 5 show the morphologies of the $BaTiO_3$ thin films on MgO; at 500 °C the grains grown were inhomogeneous and at 700 °C they were homogeneous as in Thornton's structural zone model [8].

The scanning electron micrographs in Fig. 6 show the sequence of grain growth at the various annealing temperatures. The peak broadening of the XRD pattern in Fig. 3 for annealing temperatures of 800 and 900 °C were wider than those at higher temperatures, and the morphologies of the grains from scanning electron micrographs in Fig. 6 were duplex which ranged from 62–100 nm and 77.6–150 nm at 800 and 900 °C, respectively. From these phenomena it seemed that the grain growth rate was partly faster. When the annealing temperature was increased, the grain size increased homogeneously as follows; 95.1 nm at 1000 °C, 160 nm at 1100 °C, 1.21 μm at 1200 °C, 1.9 μm at 1350 and 1400 °C. These trends are in good agreement with previous results for the particle-size dependence. For particle sizes less than 120 nm, the symmetry at room temperature is cubic, while for larger particle sizes, the tetragonal, ferroelectric phase is found [5, 11]. The larger surface energies of the smaller grain sizes are considered to cause the appearance of the higher energy phase (cubic), of $BaTiO_3$ [5, 11].

In Fig. 7, the XRD peaks of the (1 1 2) index showed the appearance of the split which indicates the cubic to tetragonal phase change. At higher temperatures, 1350 and 1400 °C, a large grain growth sets in, as a result of which continuous gaps appear in the films shown in Fig. 6. The grains are quite well developed up to

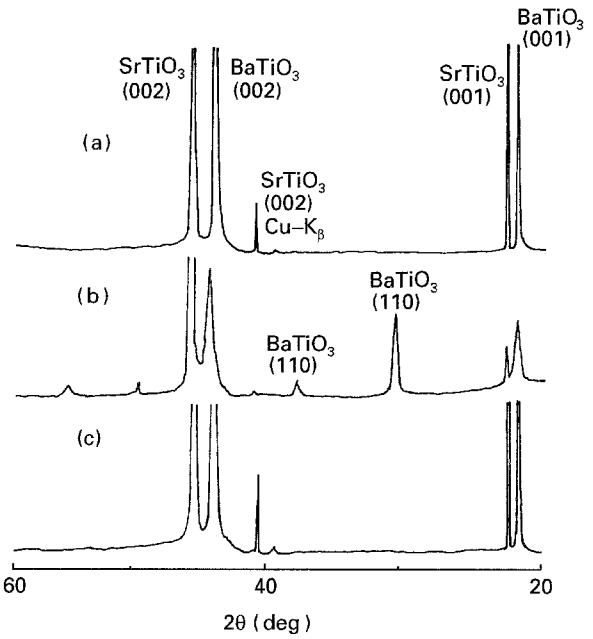

Figure 8 XRD patterns of $BaTiO_3$ films on $SrTiO_3$ at various temperatures: (a) 500 °C, (b) 700 °C (annealed and the film deposited at room temperature), (c) 700 °C (annealed and the film deposited at 500 °C).

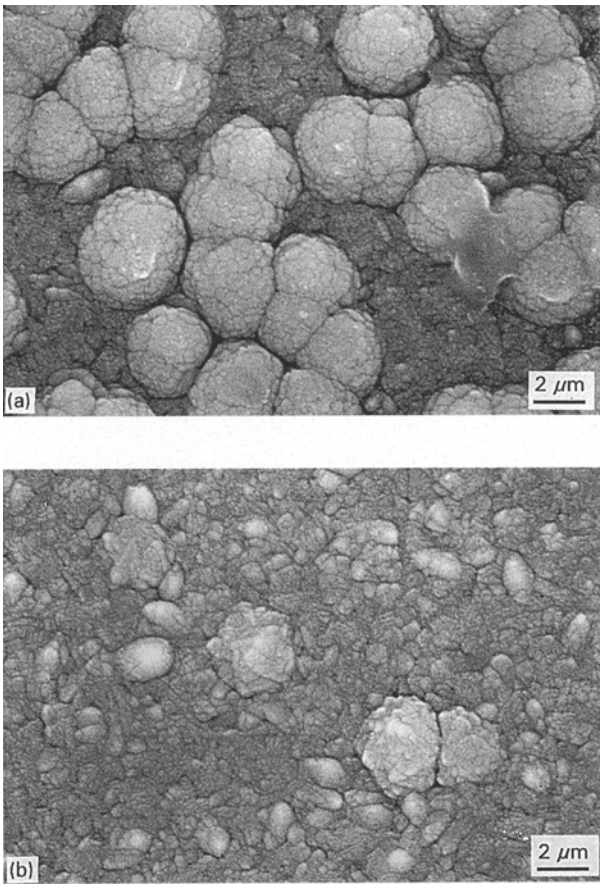

Figure 9 Scanning electron micrographs of $BaTiO_3$ films on $SrTiO_3$ at various temperatures: (a) 500 °C, (b) 600 °C, (c) 1000 °C (annealed and the film deposited at room temperature), (d) 1000 °C (annealed and the film deposited at 500 °C).

1.9 μm or larger, as perovskite structures. The grain sizes from the photographs show the compatibility with the results from the FWHM of the XRD patterns.

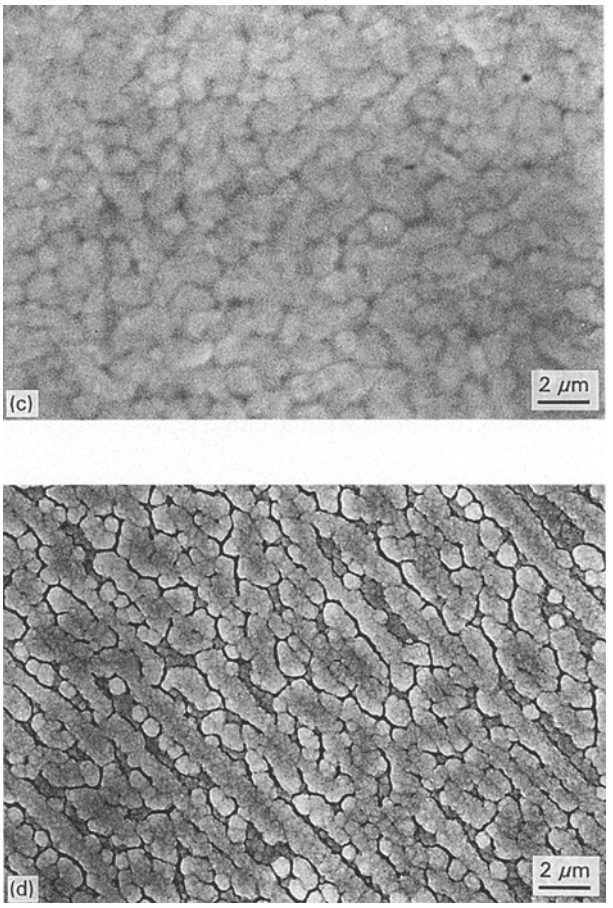

Figure 9 continued

3.2. $SrTiO_3$ substrate

Many of the peaks of the $BaTiO_3$ thin films on the MgO and silicon substrates corresponded to the cubic phase (Figs 1 and 2), but the $BaTiO_3$ thin films on $SrTiO_3$(1 0 0) showed only (0 0 1) and (0 0 2) peaks of tetragonal $BaTiO_3$. The result of the XRD patterns for as-prepared films at 500 °C substrate temperature and that for annealed films are shown in Fig. 8. The *c*-axis oriented films of 500 °C substrate temperature, and films annealed at 700 °C oriented and deposited at 500 °C, are shown in Fig. 8a and c. However, the films annealed at 700 °C from amorphous films deposited at room temperature showed the polycrystalline cubic phase (Fig. 8b). The SEM results in Fig. 9a and b show the 0.4 μm agglomerates on the small-grained $BaTiO_3$ matrix which were confirmed by secondary-ion spectroscopy (SIMS) for the films deposited at 500 and 600 °C. The preference of the tetragonal phase on $SrTiO_3$ might be due to the resemblance of the atomic stacking between $BaTiO_3$ and $SrTiO_3$: atomic mixing of barium and strontium in the deposition process of sputtered atoms reduces the surface energy of the nuclei, so that the lower energy tetragonal phase could be grown much more easily. Fig. 9c and d show that the grains have connected; the directions are also shown.

4. Conclusion

Thin films of $BaTiO_3$ were prepared by using the r.f. sputtering system. The structural characteristics of the

thin films depend on the substrate and annealing temperatures. The films were cyrstalline on MgO if the substrate temperature was greater than 450 °C and crystalline on silicon if the temperature was above 500 °C. The structure of the thin films annealed above 1100 °C was tetragonal. However, the films on $SrTiO_3$ showed different morphology and crystal structure: they were found to show *c*-axis oriented tetragonal phase above 500 °C, according to the grain agglomerated size of 0.4 μm. The $BaTiO_3$ films deposited at 500 °C retained the orientation at the annealing temperatures. However, the amorphous $BaTiO_3$ thin films deposited at room temperature changed from amorphous to polycrystalline cubic phase.

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