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The formation of epitaxial BaTiO$_3$/SrTiO$_3$ multilayers is studied in terms of the growth mechanism by investigating surface morphologies, crystalline orientations, microstructures, and structures of the interfaces, as well as by determining the dielectric properties. Under specific conditions, the epitaxial BaTiO$_3$ films follow a layer-then-island (Stranski-Krastanov) mechanism on (001)-oriented substrates. In view of actual efforts made to grow epitaxial superlattices involving very thin individual layers of BaTiO$_3$ and/or SrTiO$_3$, we have determined that the BaTiO$_3$ films of up to 6 nm thickness do not show any defects and have a sharp BaTiO$_3$–on–SrTiO$_3$ interface. On the contrary, SrTiO$_3$–on–BaTiO$_3$ interfaces within multilayers are rough, probably due to the different growth mechanisms of the two different materials, or due to a difference in the morphological stability of the growth surfaces caused by different surface energies of BaTiO$_3$ and SrTiO$_3$ and by different mobilities of the Ba and Sr atoms reaching the SrTiO$_3$ and BaTiO$_3$ layers, respectively. [DOI: 10.1143/JJAP.41.6633]

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1. Introduction

Actual efforts are being concentrated on reducing the size of electronic devices. A related challenge is that of finding new materials or improving the dielectric properties of existing materials used in the fabrication of ceramic capacitors and dynamic random access memories (DRAMs) which require a high dielectric constant in the case of small dimensions. Due to a large dielectric permittivity at $T > T_c$, a moderate coercive field and a large electro-optic coefficient, BaTiO$_3$ and Ba-rich solid solutions (Ba,Sr)TiO$_3$ are attractive in applications as memory cells, IR detectors, and metal organic chemical vapor deposition, 4) sol-gel 5) and laser ablation methods, 6)

Several methods have been considered in order to enhance the value of the capacitance, especially for a film thickness below 100 nm. 7) Theoretical studies on the relation between the internal stress and the dielectric properties were carried out based on thermodynamics using Devonshire’s or Slater’s model. 8) The preparation of (Ba,Sr)TiO$_3$ thin films was performed by reactive evaporation, 2) r-f-sputtering, 3) metal organic chemical vapor deposition, 4) sol-gel 5) and laser ablation methods, 6)

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growth mechanisms and the influence of the growth parameters can be found in ref. 11. The microstructures of the BaTiO$_3$ thin films and the BaTiO$_3$/SrTiO$_3$ interfaces were investigated by cross-sectional high-resolution transmission electron microscopy (HRTEM) in a JEOL 4010 electron microscope at a primary beam energy of 400 keV. In order to study the crystallographic orientation, XRD $\theta$–$2\theta$ scans, and $\phi$ scans were performed using a Philips X’Pert MRD four-circle diffractometer with Cu K$_\alpha$ radiation and a parallel-plate collimator in front of the detector with a $2\theta$ resolution of 0.1°. Pt electrodes with 100 nm thickness and 0.15 mm diameter were deposited by rf-sputtering through a metallic mask at room temperature. Electrical characterization was performed using a TF Analyzer 2000 ferroelectric tester (AixACCT) and a Hewlett Packard HP 4195A impedance analyzer. C–V measurements were carried out applying an ac signal with an amplitude of 10 mV at 1 MHz, while a dc bias was swept at a rate of 0.2 V/s from 0 to $V_{\text{max}}$ and vice-versa with a delay time of 0.5 s.

3. Results and Discussions

The classical theory of film nucleation and growth states that the film growth mode depends on thermodynamics, i.e. on the surface energies of both the film and substrate, and on the film-substrate interface energy.12–14 Overall, the details of the epitaxial film growth are clearly influenced by a number of parameters including growth method, substrate temperature, oxygen pressure, film thickness, and lattice mismatch. Moreover, the surface state of the substrate has an important influence on the early stages of film growth. In order to properly study the growth mechanism, a well-defined reference surface morphology is required. Therefore, SrTiO$_3$:Nb substrates were subjected to a specific chemical and thermal treatment in order to obtain vicinal surfaces with atomically flat single terminated terraces. The details of substrate preparation and the effects of etching and annealing treatment, respectively, on the final substrate surfaces have been discussed elsewhere.11 The surface morphology of the vicinal SrTiO$_3$:Nb (001)-oriented substrates with a miscut angle of 0.1° after chemical and thermal treatments following the optimal procedure, consists of well-defined terraces of 150 nm to 250 nm width with straight and sharp terrace edges [Fig. 1(a)]. The height of the steps is 0.4 nm which corresponds to one unit cell of SrTiO$_3$, indicating a unique surface termination.

Epitaxial BaTiO$_3$/SrTiO$_3$ multilayers deposited by PLD are discussed in terms of surface morphology, structure of the interfaces between BaTiO$_3$ layers and SrTiO$_3$ layers, and dielectric properties. Multilayers with overall thicknesses of 5, 25, 50, 75, and 125 nm were grown using different deposition times of 1, 5, 10, 15, and 25 min, respectively. The nominal thickness of a BaTiO$_3$ layer is defined as the typical thickness the layer would have if it were to grow in the layer-by-layer mode, and is thus a measure of the amount of deposited material. The overall thickness of BaTiO$_3$/SrTiO$_3$ multilayers is defined as the sum of the nominal individual thicknesses of all the layers involved. The surface morphologies of some of these BaTiO$_3$ layers on top of epitaxial BaTiO$_3$/SrTiO$_3$ multilayers having different thicknesses are shown in Figs. 1(b)–1(f). The same deposition time has been used to grow each layer of BaTiO$_3$ or SrTiO$_3$. The details of surface morphology show that the Stranski-Krastanov mode governs the growth of a BaTiO$_3$ layer on a previous SrTiO$_3$ layer in a BaTiO$_3$/SrTiO$_3$ multilayer, as well as on the SrTiO$_3$ substrate. The film atoms initially form one or several complete monolayers on the substrate surface [Fig. 1(b)], and subsequently 3D clusters nucleate on these layers due to the stress induced by the lattice mismatch [Fig. 1(c)], cf. ref. 11. On further deposition, grains become larger due to the coalescence of several small grains which grow together [Fig. 1(d)]. This feature is well seen in Figs. 1(e) and 1(f) for BaTiO$_3$/SrTiO$_3$ with an overall thickness of 75 nm and 125 nm, respectively. Grains are “connected” and grow together forming a columnar structure, which was indeed observed to develop for thicker films. Considering thin BaTiO$_3$ layers, stresses are expected to arise both along the interface and perpendicular to it. The strain introduced in the BaTiO$_3$ layer by the in-plane mismatch between BaTiO$_3$ and SrTiO$_3$ is relaxed with increasing thickness of the BaTiO$_3$ layer.15 A related dependence of the lattice parameter on film thickness in an epitaxial system with a small lattice mismatch such as for BaTiO$_3$ (tetragonal lattice parameters at room temperature $a = 0.3994$ nm; $c = 0.4038$ nm) on SrTiO$_3$ (cubic lattice parameter $a_c = 0.3905$ nm) has been reported.16–18 The lattice mismatch is defined as $(\alpha_{\text{film}} - \alpha_{\text{substrate}})/\alpha_{\text{substrate}}$. The lattice mismatch between BaTiO$_3$ and SrTiO$_3$ is 2.28% along the $a$ direction, while along the $c$ direction it is 3.4%.

That the Stranski-Krastanov growth mechanism is followed.
by the BaTiO$_3$ layers under our deposition conditions is confirmed by HRTEM analysis (Fig. 2). The interface between the first BaTiO$_3$ layer and the SrTiO$_3$ substrate is well-defined and sharp. As has been shown earlier in detail, a thin (between 2 and 5 nm thick) uniform “wetting” layer covers the SrTiO$_3$ substrate, before BaTiO$_3$ islands begin to appear. The islands are shown in Fig. 2(a) for a 15-nm-thick BaTiO$_3$ film. Figure 2(b) shows the beginning of BaTiO$_3$ island formation (arrows) on a uniform, continuous BaTiO$_3$ layer of about 3 to 4 nm thickness on top of a 5-nm-thick SrTiO$_3$ layer. The roughness of the top BaTiO$_3$ layer decreases with increasing the number of multilayers for the same overall thickness of 15 nm of a BaTiO$_3$/SrTiO$_3$/BaTiO$_3$/SrTiO$_3$/BaTiO$_3$ multilayer [Fig. 2(c)]. Also grain boundaries and occasional breaks inbetween BaTiO$_3$ islands are no longer present in the multilayers, a feature which is preferable for the electrical measurements. In the diffraction pattern taken from a sample region around the film/substrate interface [Fig. 2(d)], the reflections of BaTiO$_3$ and SrTiO$_3$ are well separated, indicating a well relaxed state of the BaTiO$_3$ lattice. The following orientation relationship was revealed by the diffraction pattern:

\[
\begin{align*}
(001)/(100) & \quad \text{BaTiO}_3 \parallel (001) \quad \text{SrTiO}_3; \\
[100]/[001] & \quad \text{BaTiO}_3 \parallel [100] \quad \text{SrTiO}_3.
\end{align*}
\]

The limited resolution of the diffraction patterns makes it difficult to resolve the tetragonality of the BaTiO$_3$ lattice, i.e. to differentiate between $m00$ and $00m$ BaTiO$_3$ reflections.

In order to investigate the orientation of BaTiO$_3$ thin films more precisely, X-ray diffraction $\theta$–2$\theta$ and $\phi$ scans were performed (Fig. 3). $00m$ peaks from the SrTiO$_3$ substrate and $m00/00m$ peaks of the BaTiO$_3$ film reveal the epitaxial film growth in the (pseudo-) cube-on-cube orientation [Fig. 3(a)]. It is impossible to discriminate between $(m00)$ and $(00m)$, i.e. between the $a$ and the $c$ orientation of BaTiO$_3$ ($c/a = 1.01$) because of the 0.1° resolution limit of our diffractometer in $2\theta$. Figure 3(b) shows $\phi$ scans using the 211 ($2\theta = 56.2°$ and $\psi = 34.9°$) and 110 ($2\theta = 31.6°$ and $\psi = 45.0°$) reflections of BaTiO$_3$ including also the contribution from the 112 ($2\theta = 55.9°$) and 101 ($2\theta = 31.5°$) reflections, respectively, since these are close to each other.

An important feature of the BaTiO$_3$/SrTiO$_3$ multilayers is that up to a 6 nm thickness, the BaTiO$_3$ films show no defects and have sharp BaTiO$_3$/SrTiO$_3$ interfaces (Fig. 4). This feature is significant in view of actual efforts to grow epitaxial superlattices involving very thin individual layers of BaTiO$_3$ and/or SrTiO$_3$. Moreover, it has been observed that the epitaxial SrTiO$_3$ film inserted inbetween two BaTiO$_3$ layers promotes good crystallinity of the second BaTiO$_3$ layer. Figure 4 shows a cross-sectional TEM image and a more detailed HRTEM image of a BaTiO$_3$/SrTiO$_3$ multilayer with increasing thickness of the BaTiO$_3$ layers inbetween SrTiO$_3$ layers of constant thickness. Multilayers of this type should reveal effects related to the relaxation of strain with increasing BaTiO$_3$ layer thickness.

Tetragonal BaTiO$_3$ exhibits ferroelectric distortions due to displacements of the Ba$^{2+}$ and Ti$^{4+}$ cations relative to the O$^{2-}$ anions, leading to a net dipole per unit area$^{19}$ and resulting in the $c/a$ lattice distortion of 1.01. A lattice mismatch of 2.28% along the $a$ direction, and that of 3.4% along the $c$ direction are present in BaTiO$_3$/SrTiO$_3$ multilayers. In these multilay-
The relaxing of mismatch strain in the BaTiO$_3$ layers with an overall effect on the dielectric and ferroelectric properties. The lattice mismatches can be expected to occur, resulting in an interaction between the “ferroelectric” distortion and the lattice. An XRD $\theta$–$2\theta$ scan of a 320-nm-thick BaTiO$_3$ film is shown in Fig. 3(a). The peaks labelled as $m00/m0m$ are the BaTiO$_3$ film peaks. Those indicated by filled squares are the SrTiO$_3$ substrate peaks, while those indicated by filled circles and triangles are the substrate peaks originating from the remaining Cu–K$_{\alpha}$ radiation and from the W–L$_\alpha$ radiation, respectively. The latter stems from the tungsten contamination of the X-ray target. (b) X-ray diffraction $\phi$ scans recorded from the same sample using the 222 reflection of the SrTiO$_3$ substrate, and the 112/211 and 101/110 reflections of the BaTiO$_3$ film.

Fig. 3. (a) XRD $\theta$–$2\theta$ scan of a 320-nm-thick BaTiO$_3$ film. The peaks labelled as $m00/m0m$ are the BaTiO$_3$ film peaks. Those indicated by filled squares are the SrTiO$_3$ substrate peaks, while those indicated by filled circles and triangles are the substrate peaks originating from the remaining Cu–K$_{\alpha}$ radiation and from the W–L$_\alpha$ radiation, respectively. The latter stems from the tungsten contamination of the X-ray target. (b) X-ray diffraction $\phi$ scans recorded from the same sample using the 222 reflection of the SrTiO$_3$ substrate, and the 112/211 and 101/110 reflections of the BaTiO$_3$ film.

ers, an interaction between the “ferroelectric” distortion and the lattice mismatches can be expected to occur, resulting in an overall effect on the dielectric and ferroelectric properties. The relaxing of mismatch strain in the BaTiO$_3$ layers with increasing layer thickness, and a reduction of this interaction with increasing thickness of the individual BaTiO$_3$ layers can be expected, cf. ref. 16. Dielectric investigations of our samples of the type shown in Fig. 4 are underway.

In addition to the expected reduction of strain with increasing thickness of the individual BaTiO$_3$ layers, the development of a columnar structure in thick layers has to be taken into account (Fig. 5). Figure 5(a) shows this columnar structure in a single, about 200-nm-thick BaTiO$_3$ film, while Fig. 5(b) reveals the presence of a columnar structure in the individual, about 200-nm-thick, BaTiO$_3$ and SrTiO$_3$ layers of a thick multilayer. Most interesting, the morphology of the BaTiO$_3$–on–SrTiO$_3$ interfaces is different from that of the SrTiO$_3$–on–BaTiO$_3$ interfaces (Fig. 5): While the former interfaces are planar and sharp, the latter are rather rough, playing a certain periodicity of the morphology (“waviness”). This feature can most probably be explained as being due to the different growth mechanisms of the two materials, or due to a difference in the morphological stability of the growth surfaces caused by different surface energies of BaTiO$_3$ and SrTiO$_3$ and by different mobilities of the Ba and Sr atoms reaching the SrTiO$_3$ and BaTiO$_3$ layer, respectively. A similar asymmetry has recently been described by Dubourdieu et al.$^{20}$ showing that Ba penetrates far into the neighboring SrTiO$_3$ layer, while Sr does not enter the neighboring BaTiO$_3$ layer.

Measurements of the dielectric properties have been performed comparing BaTiO$_3$ films and BaTiO$_3$/SrTiO$_3$ multilayers of a different number of individual layers, but equal overall thickness. Figures 6(a) and 6(b) show a similar dependence of the effective dielectric constant and the dielectric loss on the overall film thickness. Below an overall thickness of 75 nm, the dielectric constant linearly decreases with decreasing overall thickness, and it is independent of the number of multilayers, which points to the presence of some interface effect. For thick films, the value of the dielectric constant is close to the bulk value, which confirms the good crystallinity of the films. The dielectric loss saturates for a thickness above 300 nm, and linearly decreases below a thickness of 75 nm [Fig. 2(d)].

The values of the dielectric constant of our BaTiO$_3$ films and BaTiO$_3$/SrTiO$_3$ multilayers are in good correspondence with those published by other groups. The dielectric constant ranges from 240$^{21)}$ to 900$^{22)}$ for BaTiO$_3$/SrTiO$_3$ multilayers of 30 nm and 100 nm overall thickness. A maximum value of 1000 for the dielectric constant was measured for a 580-nm-thick BaTiO$_3$ film by Hayashi and Tanaka$^{23)$ which is in good correspondence to our result for thick films. A more detailed study of the dielectric properties of our multilayers is in progress.

4. Conclusion

With the background aim of improving the dielectric properties, epitaxial BaTiO$_3$/SrTiO$_3$ multilayers grown by PLD on SrTiO$_3$ (001) substrates have been studied in terms of surface morphology, crystalline orientation, microstructure, film/substrate interface morphology, and dielectric properties. The Stranski-Krstanov growth mode has been found to govern the growth of a BaTiO$_3$ layer on the preceding SrTiO$_3$ layer, as has been observed previously for BaTiO$_3$ films on a SrTiO$_3$ substrate. Up to a 6 nm thickness, the BaTiO$_3$ films show no defects and have sharp BaTiO$_3$/SrTiO$_3$ interfaces. In multilayers consisting of thick individual layers, an asymmetry of the morphology has been observed between SrTiO$_3$–on–BaTiO$_3$ and BaTiO$_3$–on–SrTiO$_3$ interfaces. This feature is most probably due to the different growth mechanisms of the two different materials, or due to a difference in the morphological stability of the growth surfaces caused by different surface energies and different mobilities of the Ba and Sr atoms reaching the SrTiO$_3$ and the BaTiO$_3$ layer, respectively. Below an overall thickness of 75 nm, the dielectric constant shows a linear decrease with decreasing overall thickness and does not depend on the number of multilayers.
Fig. 4. TEM cross-sectional view (left) and HRTEM view (right) of epitaxial BaTiO$_3$/SrTiO$_3$ multilayers with different thicknesses of the individual BaTiO$_3$ layers of 2 ML, 4 ML, 8 ML, 12 ML, 20 ML, and 40 ML (ML–monolayer).

Fig. 5. (a) TEM cross-sectional view of an epitaxial BaTiO$_3$ film (150 nm thick) grown on a SrTiO$_3$ substrate. (b) TEM cross-sectional image of an epitaxial BaTiO$_3$/SrTiO$_3$ multilayer grown on a SrTiO$_3$ (001) substrate. The thickness of the individual BaTiO$_3$ layers is about 260 nm, and that of the individual SrTiO$_3$ layers is about 210 nm.

Fig. 6. (a) Dependence of the effective dielectric constant and (b) dielectric loss on the overall thickness of BaTiO$_3$/SrTiO$_3$ multilayers of different numbers of individual layers.

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