Epitaxial growth of $BaTiO_3$ thin films at 600 °C by metalorganic chemical vapor deposition

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$BaTiO_3$ thin films were grown epitaxially on (100) MgO substrates by metalorganic chemical vapor deposition (MOCVD) at a temperature of 600 °C. This substrate temperature is the lowest reported temperature for the growth of epitaxial $BaTiO_3$ films by an MOCVD process. The films had a cube–cube orientation relationship with the substrate and were oriented with an *a*-axis perpendicular to the substrate plane. Nanoscale energy dispersive x-ray spectrometry measurements showed no evidence of interdiffusion between the film and substrate. © *1995 American Institute of Physics.*

The ferroelectric oxide barium titanate, $BaTiO_3$, is a promising material for electro-optic modulators and switches[1,2] because of its very large linear electro-optic coefficient[3] r_{42}. Other potential applications of tetragonal $BaTiO_3$ in photonics include optical memory and optical processing devices[4] (based on a large photorefractive effect in doped material[5]), and frequency doublers[6] for generation of blue/green laser radiation. All of these devices must be fabricated either from bulk single crystals or from epitaxial thin films in order to attain low-loss propagation of the light.

Over the past several years, investigators have reported on epitaxial $BaTiO_3$ thin films grown by a variety of techniques.[7–16] Of these techniques, metalorganic chemical vapor deposition (MOCVD) is very promising for the eventual commercial production of films for photonic devices. The potential advantages of MOCVD over other thin film growth processes include deposition over large areas, high throughput, and uniform coverage of nonplanar shapes. Epitaxial films of $BaTiO_3$ have been grown by MOCVD on (100) surfaces of single crystal $LaAlO_3$,[11,13] MgO,[10,16] and $NdGaO_3$.[12,13]

In any deposition process, the substrate temperature has a strong influence on the microstructure of the film, which ultimately affects the properties. It is favorable to use a low substrate temperature to reduce interdiffusion between the film and substrate in heteroepitaxial growth processes and to minimize the concentrations of undesirable thermally activated defects such as oxygen vacancies, interstitials, and antisite defects. Furthermore, the integration of $BaTiO_3$ electro-optic devices with silicon integrated circuit technology will require that the $BaTiO_3$ films be deposited at the lowest possible temperature in order to minimize the diffusion of dopants in the silicon-based devices.[17]

Annealing studies on amorphous $BaTiO_3$ films have suggested that the lowest temperature for the crystallization of $BaTiO_3$ in thin films is between 400 and 500 °C;[18] however, very small (5–15 nm) epitaxial islands of crystalline $BaTiO_3$ were observed in predominantly amorphous $BaTiO_3$ films grown at 300 °C by MOCVD.[19] To date, much higher substrate temperatures (800–1000 °C) have been used to deposit fully epitaxial $BaTiO_3$ thin films by thermal MOCVD processes.[10–12,16] Chern *et al.*[13] accomplished epitaxial growth at 680 °C by a plasma-enhanced MOCVD process. It is not known if the added energy from the plasma generates structural defects in films in the same manner as thermal energy.

In this letter, we report on the *in situ* epitaxial growth of $BaTiO_3$ thin films on (100) MgO substrates by thermal MOCVD at a substrate temperature of 600 °C. This temperature is 200 °C or more lower than those temperatures used in comparable thermal MOCVD processes.[10–12,16] MgO was selected as a substrate material for several reasons. First, the lattice parameter of MgO ($a_0=4.213$ Å) is reasonably well matched to the lattice parameters of tetragonal $BaTiO_3$ ($a=3.994$ Å, $c=4.038$ Å) at 25 °C. Second, the refractive index of MgO ($n=1.7$ at 0.6 μm) is much lower than that of $BaTiO_3$ ($n=2.4$ at 0.6 μm), facilitating waveguiding in thin $BaTiO_3$ films. Third, MgO does not exhibit a linear electro-optic effect, so interpretation of electro-optic measurements on the films is straightforward.

The films were deposited in an MOCVD system described in more detail elsewhere.[20] The precursors, titanium isopropoxide (TIP) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato) barium hydrate $[Ba(thd)_2\cdot(H_2O)_n]$, were held in stainless steel bubblers. The carrier gas was dried argon (99.997% pure) and the oxidizing gas was dried oxygen (99.5% pure). A set of conditions for epitaxial growth is given in Table I. All gas lines downstream of the $Ba(thd)_2\cdot(H_2O)_n$ bubbler were maintained at a temperature of 240 °C (10 °C above the bubbler temperature) to prevent condensation of $Ba(thd)_2\cdot(H_2O)_n$. A metering valve located immediately downstream of the TIP bubbler was used to control the bubbler pressure. The MgO substrate (dimensions 13 mm×13 mm×0.5 mm) was supported on a SiC-coated graphite susceptor heated by a radio frequency induction generator. The temperature in the center of the susceptor was measured with an ungrounded, sheathed thermocouple; this temperature was calibrated against the substrate surface

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TABLE I. $BaTiO_3$ growth conditions.

Substrate temperature (°C)	600 ± 3[a]
Reactor pressure (kPa[b])	6.67 ± 0.01
Temperature of $Ba(thd)_2\cdot(H_2O)_n$ (°C)	230 ± 1
Temperature of TIP (°C)	25 ± 1
Flow rate of Ar through $Ba(thd)_2\cdot(H_2O)_n$ (sccm)	75.0 ± 0.1
Flow rate of Ar through TIP (sccm)	70.0 ± 0.1
Oxygen gas flow rate (sccm)	300.0 ± 0.1
Pressure over TIP (kPa[b])	37.30 ± 0.01
Deposition time (h)	3.0

[a] The uncertainty given for a variable indicates the observed fluctuation in the value during a deposition experiment.

[b] 1 kPa=7.5 Torr.

temperature as measured with a dual wavelength pyrometer. The error in the substrate surface temperature was estimated to be ±7 °C.

Two $BaTiO_3$ thin films were examined in detail in the present study. The films were transparent and displayed color fringes resulting from variations in film thickness. Observations of the films with a Fizeau interferometer showed a central fringe with an area of at least 50 mm^2, indicating a thickness uniformity of ±40 nm over this region. Transmittance spectroscopy[21] measurements gave thicknesses of 570 and 500 nm at the centers of the two films; the corresponding growth rates were 190 and 170 nm/h, respectively.

The $Ba(thd)_2\cdot(H_2O)_n$ precursor was known to contain Sr,[22] and the concentration of Sr in the films was analyzed in an electron microprobe by wavelength dispersive x-ray spectrometry with a SrF_2 standard. The two films had Sr concentrations of 0.3 and 1.0 at.%. These measurements had a precision of 1% (relative) and an accuracy of 2% (relative). At these low concentrations, the changes in the a and c lattice parameters of tetragonal $BaTiO_3$ due to Sr were calculated to be less than 0.002 Å (0.05%).[23]

Secondary ion mass spectrometry depth profiling measurements on the film containing 1.0 at.% Sr revealed that the composition was uniform to within 1.6% (relative) over the entire depth of the film. There were abrupt changes in the concentrations of Ba, Ti, and Mg at the film/substrate interface, demonstrating that interdiffusion between the film and substrate was minimal. Carbon was not detected in the bulk of the film by Auger spectroscopy (detectability limit=3 at.%).

X-ray diffraction, high resolution transmission electron microscopy and selected area electron diffraction techniques were employed to investigate the epitaxial nature of the thin films. For consistency, all of the results reported below were obtained on the 500 nm thick film that contained 0.3 at.% Sr. The results are typical of those obtained on the other thin film examined in this study.

The conventional x-ray diffraction pattern shown in Fig. 1 contained only peaks corresponding to the 100, 200, and 300 reflections of $BaTiO_3$ and the 200 reflection of MgO, demonstrating that the film was highly oriented. The average parameter calculated from the two-theta values for the three $BaTiO_3$ peaks was 4.000 ± 0.005 Å, which is in close agreement with the published value of $a=3.994$ Å for tetragonal $BaTiO_3$. This indicates that the film was oriented with an a axis normal to the substrate plane.

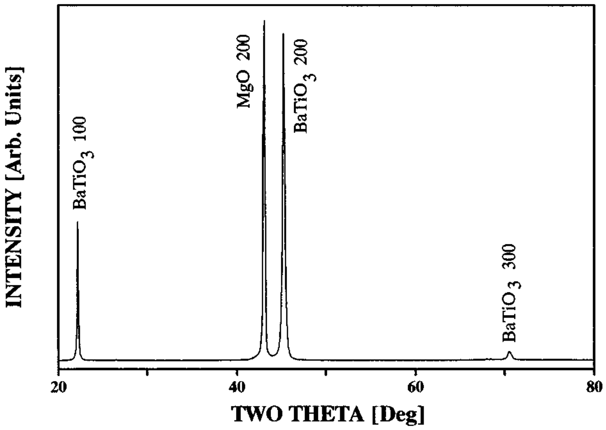

FIG. 1. Conventional x-ray diffraction pattern of a $BaTiO_3$ thin film deposited on a (100) MgO substrate. Theta was intentionally offset by 0.6° in order to reduce the intensity of the strong MgO 200 reflection and thereby improve resolution of the low angle side of the $BaTiO_3$ 200 reflection.

High resolution electron microscopy was used to examine the interface between the film and the substrate. The cross-sectional image shown in Fig. 2 clearly demonstrates continuity of {200} lattice planes across the interface and a sharp film/substrate interface. Composition maps for Ba, Ti, and Mg near the interface were obtained from energy dispersive x-ray spectrometry measurements taken in the scanning transmission mode using a probe diameter of 2–3 nm. The concentrations of Ba and Ti in the MgO substrate and the concentration of Mg in the $BaTiO_3$ film were below the detectability limit of 2 wt.%, indicating that interdiffusion between the film and substrate was low.

Misfit dislocations in the $BaTiO_3$ film were observed along the interface (e.g., see arrow in Fig. 2). These misfit dislocations had a Burgers vector of $\frac{1}{2}\langle 100\rangle_{MgO}$ lying in the plane of the interface. Formation of the dislocations probably occurred during deposition in order to accommodate the

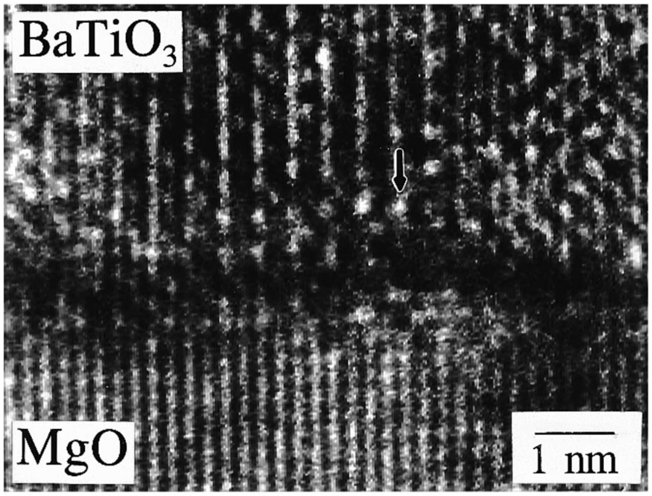

FIG. 2. High resolution electron micrograph of the $BaTiO_3$/(100) MgO interface. The epitaxial nature of the film is clearly evident by sighting down the {200} planes at an oblique angle. A misfit dislocation in the film is indicated by the arrow.

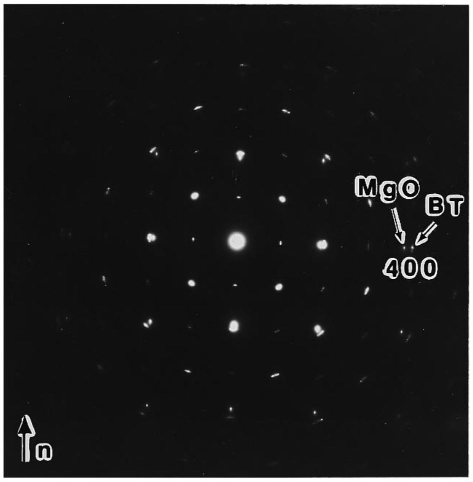

FIG. 3. Selected area electron diffraction pattern showing the cube–cube orientation relationship between the $BaTiO_3$ film and the MgO substrate. The arrow marked *n* indicates the direction normal to the substrate plane.

5.4% lattice mismatch between the substrate and the growing film. A Burgers circuit analysis[24] of the lattice image of an interfacial area gave a dislocation frequency of about one per fifteen unit cells. Since about one dislocation per nine unit cells would be required to fully relieve the lattice mismatch strain, the film may be under residual tensile stress in the plane parallel to the substrate plane. An *a*-axis oriented film (i.e., the larger *c*-axis in the plane of the film), as observed, would partially relieve this stress.

A selected area electron diffraction pattern of a cross-sectional specimen taken with a 0.6 μm diameter aperture centered at the interface is shown in Fig. 3. The patterns show a cube–cube orientation relationship between the $BaTiO_3$ and MgO (i.e., alignment of both the normal and in-plane lattice vectors of the film with those of the substrate), thus confirming that the film is epitaxial. Each higher order $BaTiO_3$ reflection consisted of a set of closely spaced diffraction spots lying on an arc, indicating that different regions of the film were slightly misoriented relative to the $\langle 100 \rangle$ directions in the MgO substrate. The misorientation angle estimated from the extent of the arcing was $\pm 1°$. In the plane of the film parallel to the substrate plane, two sets of $BaTiO_3$ spots (400 and 004) were observed (see arrow labeled BT in Fig. 3), demonstrating that two different orthogonal in-plane orientations of the *c* axis were present. The lattice parameters calculated from these two sets of spots using the MgO diffraction spots as an internal standard were $a=4.008\pm0.006$ Å and $c=4.030\pm0.006$ Å. Only one set of $BaTiO_3$ spots was observed in the plane normal to the substrate plane; the parameter calculated from this set of spots was $a=3.992\pm0.006$ Å. These results confirm that the film was oriented with an *a* axis normal to the substrate plane. The slightly contracted *c* axis and slightly expanded in-plane *a* axis could be due to constraints imposed by the cubic symmetry of the substrate.

The presence of residual strain, as suggested by the interfacial dislocation frequency calculations and the observed differences in the in-plane lattice parameters from the values for bulk $BaTiO_3$, would affect the optical and nonlinear optical properties. The strain-induced change in the indices of refraction would be on the order of 10^{-3}. The piezoelectric induced change in the polarization, and hence the change in the second-order susceptibilities,[25] would be on the order of 10%.

In summary, epitaxial $BaTiO_3$ thin films with an *a*-axis orientation were grown *in situ* on (100) MgO substrates by MOCVD at a temperature of 600 °C. This result demonstrates that epitaxial $BaTiO_3$ films can be deposited at moderate temperatures, thereby increasing the feasibility of integrating $BaTiO_3$ electro-optic devices with silicon integrated circuit technology.

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[1] A. M. Glass, Science **235**, 1003 (1987).
[2] A. M. Glass, Mater. Res. Bull. **XIII**(8), 16 (1988).
[3] P. Gunter, Ferroelectrics **75**, 5 (1987).
[4] See, e.g., Chaps. 10 and 11 in P. Yeh, *Introduction to Photorefractive Nonlinear Optics* (Wiley, New York, 1993).
[5] M. B. Klein, in *Photorefractive Materials and their Applications,* edited by P. Gunter and H.-P. Huginard (Springer, Berlin, 1988), pp. 195–236.
[6] J. A. Armstrong, B. Bloemberger, J. Ducuing, and P. S. Persham, Phys. Rev. **127**, 1918 (1962).
[7] G. M. Davis and M. C. Gower, Appl. Phys. Lett. **55**, 112 (1989).
[8] K. Iijima, T. Terashima, K. Yamamoto, K. Hirata, and Y. Bando, Appl. Phys. Lett. **56**, 527 (1990).
[9] M. G. Norton, C. Scarfone, J. Li, C. B. Carter, and J. W. Mayer, J. Mater. Res. **6**, 2022 (1991).
[10] H. Nakazawa, H. Yamane, and T. Hirai, Jpn. J. Appl. Phys. **30**, 2200 (1991).
[11] L. A. Wills, B. W. Wessels, D. S. Richeson, and T. J. Marks, Appl. Phys. Lett. **60**, 41 (1992).
[12] P. C. Van Buskirk, R. Gardiner, P. S. Kirlin, and S. Nutt, J. Mater. Res. **7**, 542 (1992).
[13] C. S. Chern, J. Zhao, L. Luo, P. Lu, Y. Q. Li, P. Norris, B. Kear, F. Cosandey, C. J. Maggiore, B. Gallois, and B. J. Wilkens, Appl. Phys. Lett. **60**, 1144 (1992).
[14] K. Nashimoto, D. K. Fork, and T. Geballe, Appl. Phys. Lett. **60**, 1199 (1992).
[15] R. A. McKee, F. J. Walker, E. D. Specht, G. E. Jellison, Jr., L. A. Boatner, and J. H. Harding, Phys. Rev. Lett. **72**, 2741 (1994).
[16] P. C. Van Buskirk, G. T. Stauf, R. Gardiner, P. S. Kirlin, B. Bihari, and J. Kumar, in *Ferroelectric Thin Films III,* Mater. Res. Soc. Symp. Proc., edited by B. A. Tuttle, E. R. Myers, S. B. Desu, and P. K. Larsen (MRS, Pittsburgh, PA, 1993), Vol. 310, pp. 119–124.
[17] S. Wolf and R. N. Tauber, *Silicon Processing for the VLSI Era* (Lattice, Sunset Beach, CA, 1986), Vol. 1, p. 57.
[18] P. Li and T.-M. Lu, Appl. Phys. Lett. **59**, 1064 (1991).
[19] T. W. Kim and S. S. Yom, Appl. Phys. Lett. **65**, 1955 (1994).
[20] D. L. Kaiser, M. D. Vaudin, G. Gillen, C.-S. Hwang, L. H. Robins, and L. D. Rotter, J. Cryst. Growth **137**, 136 (1994).
[21] R. Swanepoel, J. Phys. E **16**, 1214 (1983).
[22] F. Wagner, Strem Chemicals, Inc., 7 Mullliken Way, Newburyport, MA 01950 (private communication).
[23] D. F. Rushman and M. A. Strivens, Faraday Soc. Trans. **42A**, 231 (1946).
[24] R. E. Reed-Hill, *Physical Metallurgy Principles,* 2nd ed. (Van Nostrand, New York, 1973), pp. 157–158.
[25] M. DiDomenico, Jr. and S. H. Wemple, J. Appl. Phys. **40**, 720 (1969); **40**, 735 (1969).