Epitaxial electro-optical $BaTiO_3$ films by single-source metal–organic chemical vapour deposition

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Chemical vapour deposition (CVD) is a promising process for the production of ferroelectric complex oxide films having a large electro-optical coefficient. We report the epitaxial growth of high-quality $BaTiO_3$ films using a single-source CVD process. A variety of epitaxial relationships have been achieved with $BaTiO_3$ films grown cube-on-cube on substrates of large lattice mismatched $LaAlO_3$ and MgO, and ⟨001⟩, ⟨110⟩ and ⟨111⟩ oriented $SrTiO_3$. A large quadratic electro-optic coefficient was measured for CVD-prepared $BaTiO_3$ films. These films also have values of the optic refractive indices and second electro-optic susceptibilities close to those of bulk $BaTiO_3$ crystals, indicating their excellent quality.

$BaTiO_3$ is a material of high interest because of its unusual combination of ferroelectric, electro-optic, piezoelectric and photorefractive properties. $BaTiO_3$ has the largest linear electro-optic coefficient and photorefractive four-wave mixing reflectivity known.[1,2] However, difficulties associated with its bulk crystal growth have limited its practical application. Epitaxial growth of films from the vapour phase is an alternative approach to obtaining large-area, high-purity single crystals because of lower growth temperature, the elimination of crucibles, and the availability of suitable substrates which may suppress the adverse effect of the phase transitions associated with bulk $BaTiO_3$ crystals. Recent advances in complex oxide thin-film processes have opened an unprecedented opportunity for realization of the potential of $BaTiO_3$. The control of the film's orientation is important to utilize its larger tensor component for practical device fabrication, because $BaTiO_3$ has strongly anisotropic properties. Among the linear electro-optic coefficients of $BaTiO_3$ only r_{42} (1640 pm V^{-1}) is significantly larger than those of other commonly used electro-optical materials, such as $LiNbO_3$ (31 pm V^{-1}). There are several reports about the epitaxial growth of $BaTiO_3$ with *a* or *c* axes perpendicular to the substrate surface by various methods such as chemical vapour deposition (CVD),[3] plasma enhanced (PE)-CVD,[4,5] sputtering[6] and laser ablation.[7] CVD is a favourable process for growing epitaxial films. Process scale-up is relatively simple, since, in CVD, the precursor is transported by a carrier gas. This feature makes CVD the method of choice for large-area, low-cost, high-throughput processes for many applications. In this paper, we report the epitaxial growth of $BaTiO_3$ films with ⟨100⟩ or ⟨001⟩, ⟨110⟩ or ⟨101⟩, and ⟨111⟩ directions perpendicular to the surface using a CVD process. These films have optical and electro-optical properties which are very close to those of bulk crystals, demonstrating the high quality of the films.

Experimental

At present, the primary obstacles to the widespread application of CVD in the growth of $BaTiO_3$ thin films are the low vapour pressure and the unstable evaporation behaviour of barium organometallic precursors such as $Ba(thd)_2$ (Hthd = 2,2,6,6-tetramethylheptan-3,5-dione). This results in low throughput and unstable precursor delivery in the conventional MOCVD process. We have developed an innovative liquid source system which provides steady and reproducible vapour phase precursor delivery. The precursors $Ba(thd)_2 \cdot xH_2O$ and $Ti(OPr^i)_2(thd)_2$ were dissolved in a mixture of *n*-butyl acetate and tetraglyme and this solution was used to grow $BaTiO_3$ films; tetraglyme is thought to form an adduct with $Ba(thd)_2$. The formation of the adduct can prevent the barium precursor from oligomerizing and reacting with ambient CO_2, stabilizing the evaporation process of $Ba(thd)_2$.[8] The use of the single liquid source makes the control of the film's stoichiometry significantly easier, because, under given P_{O_2}–T conditions in the reaction chamber, the film composition depends only on the Ba/Ti ratio in the solution and *P*–*T* conditions in the vaporizer. Moreover the precursors are not exposed to high temperature for extended periods, because the solution is delivered to the vaporizer under pulsed conditions. This allows the use of relatively unstable compounds as precursors.

The $BaTiO_3$ thin films were prepared by the CVD process using a single-source delivery system. Growth of the films was performed in the vertical CVD reactor (Fig. 1) with the susceptor rotating at a speed of 100–1000 rpm. The precursor solution was delivered to the vaporizer by a liquid pump and the temperature of the vaporizer was maintained at 235–245 °C. The films were grown at a system pressure of 2 Torr and substrate temperature of 650–700 °C. Argon was used as a carrier gas and a mixture of nitrogen(I) oxide and oxygen was used as the oxidizing agent; the total gas flow was 500 sccm with the partial pressure of oxygen maintained in the range of 0.2–0.5 Torr. The films grew at the rate of 0.5–1 μm h^{-1}. The thickness of the films as measured by a Decktak IIA profilometer was in the range 0.3–5 μm.

Energy dispersive X-ray spectroscopy (EDX System Amray

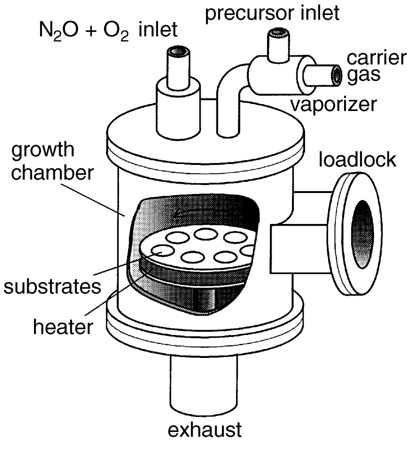

Fig. 1 Vertical CVD reactor used for $BaTiO_3$ film growth

1400) was used to measure the metal composition of the $BaTiO_3$ films. The absolute metal atomic ratios were calibrated using Rutherford back-scattering (RBS) measurements. Only films with a Ba/Ti molar ratio close to unity (±5%) were chosen for further study.

The structural properties of the films were characterized by X-ray diffraction using both θ–2θ and ϕ-scanning techniques (Rigaku four-circle diffractometer).

Results and Discussion

Structural properties of the deposited films

Fig. 2 presents typical θ–2θ X-ray diffraction patterns for $BaTiO_3$ films grown on various substrates. One can see that the films grew epitaxially in the normal directions, since X-ray spectra of $BaTiO_3$ films show only reflections of crystallographic planes with the same indices as those of substrate materials. Using the X-ray data, we found that the lattice constants were 3.995 Å (±0.003 Å) for the films grown on $LaAlO_3(001)$ and 4.006 Å (±0.001 Å) for the films grown on MgO(001). The measured values of the lattice parameter of $BaTiO_3$ films are equally close to both *a* and *c* lattice constants of the $BaTiO_3$ crystals ($a = 3.992$ Å, $c = 4.032$ Å at 20 °C). Therefore, the *a* and *c* orientation can not be distinguished in our films. The question is then whether the shift in lattice parameter values is caused by residual stress or by an incomplete phase transition. However, it has been shown[9] that the films prepared by MOCVD could be reoriented with the *c*-axis parallel to an electric field by the corona poling method.

The films also have excellent in-plane epitaxy as shown by X-ray scanning (Fig. 3). The modulation of the (103) reflection of $BaTiO_3$ grown on $LaAlO_3(001)$ and MgO(001) every 90° indicates that the *a* or *c* axis of $BaTiO_3$ is parallel to the $\langle 001 \rangle$ direction of the substrate material. The alternation of (311) peaks every 72 and 108° for the scan of $BaTiO_3$ films grown on $SrTiO_3(110)$, as shown in Fig. 3, also reveals the high quality of in-plane orientation. The X-ray data show that various epitaxial growth modes can be achieved using the single-source CVD process with single crystalline $BaTiO_3$ films grown on a variety of substrates including large lattice mismatched (5%) $LaAlO_3(001)$ and (6%) MgO(001) and (110),(111) oriented $SrTiO_3$. The epitaxial growth of high-quality $BaTiO_3$ on low refractive index substrates such as MgO ($n = 1.73$) is highly desirable for optical waveguide device applications. The capability of epitaxially grown $BaTiO_3$ with off-crystal axis orientation is also significant for practical optical device design and fabrication in order to use the material's largest electro-optic component.

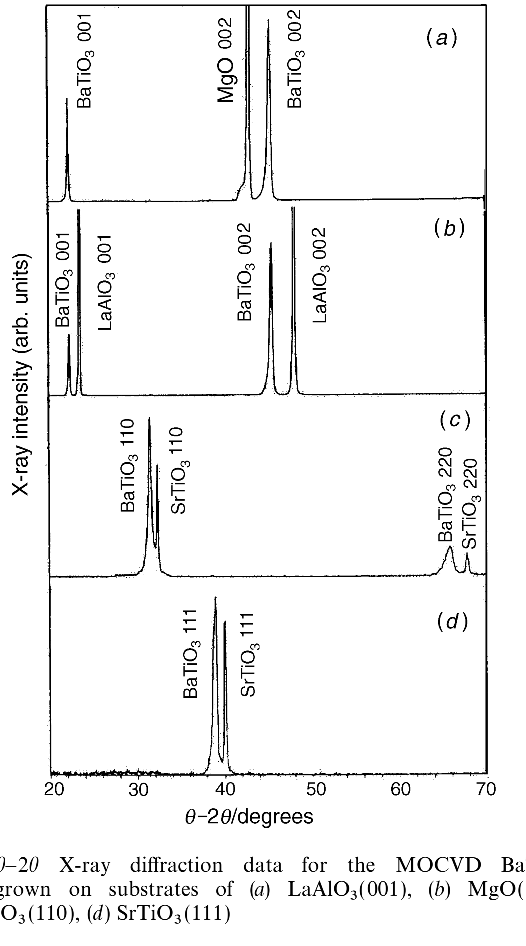

Fig. 2 θ–2θ X-ray diffraction data for the MOCVD $BaTiO_3$ films grown on substrates of (*a*) $LaAlO_3(001)$, (*b*) MgO(001), (*c*) $SrTiO_3(110)$, (*d*) $SrTiO_3(111)$

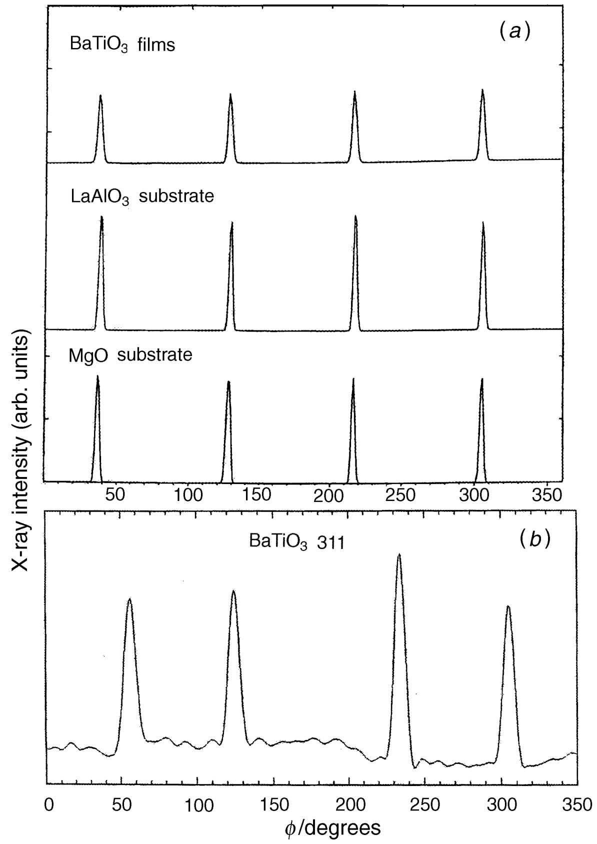

Fig. 3 ϕ-scan of the (103) (*a*) and (311) reflections of a $BaTiO_3$ film grown on $LaAlO_3(001)$, MgO(001) (*a*) and $SrTiO_3(110)$ (*b*)

Characterization of the optical properties

Gas-phase nucleation occurring at high deposition temperature and high partial pressure of oxygen leads to the precipitation and accumulation of fine particles in the growing film which eventually results in high optical losses in the thin film material. We optimized the deposition conditions to diminish gas-phase reactions. A growth temperature as high as 800 °C is needed to form a well crystallized $BaTiO_3$ phase, if only oxygen is used. The utilization of a N_2O–O_2 mixture as oxidizer allowed reduction of the growth temperature to 650–700 °C. This in combination with the low partial pressure of oxygen in the reaction chamber enabled a significant reduction of the gas-phase reaction and growth of transparent $BaTiO_3$ films up to 1.5 µm thick. However, thicker films were translucent.

The optical properties of the films were measured by a Metricon prism-film waveguide coupler. Fig. 4 shows the reflected intensity *vs.* beam angle (θ) for an unpoled $BaTiO_3$ film on a MgO substrate; the minima in the spectra correspond to waveguide modes. Four modes in both TE and TM polarization were observed at a wavelength of 0.6328 µm. The data can be fitted with extraordinary and ordinary refractive indices

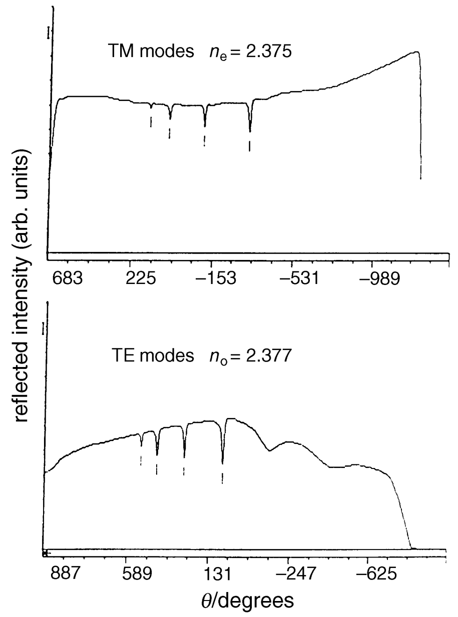

Fig. 4 Results of prism coupling experiments on $BaTiO_3$ films grown on MgO(001)

of $n_e = 2.375$ and $n_o = 2.377$ (±0.005). These values are close to those of bulk $BaTiO_3$ crystals ($n_e = 2.364$ and $n_o = 2.4164$), indicating the high quality of these films. The smaller difference between n_e and n_o in films than that found in bulk crystals may be due to many reasons such as the presence of 90° domains, a reduction in tetragonality as a result of the incomplete phase transition, columnar growth, and unpoled nature of the films. Similar refractive indices (*ca.* 2.3) were also obtained for $BaTiO_3$ films grown on $LaAlO_3$. The refractive index of $LaAlO_3$ is measured to be 2.06 at 0.6328 μm. This value, which is smaller than that of bulk $BaTiO_3$, is sufficient for waveguide fabrication. However, the large light scattering caused by twinning of the substrates makes $LaAlO_3$ less suitable for practical guided optical devices.

A transmission differential ellipsometer was employed to measure the second-order electro-optic properties of the oxide thin film materials. Transmission differential ellipsometry is a phase-sensitive detection method, especially designed for electro-optic measurements of thin-film materials.[9] Coplanar interdigitated electrodes with a gap of 40 μm were fabricated on $BaTiO_3$ films to perform measurements.

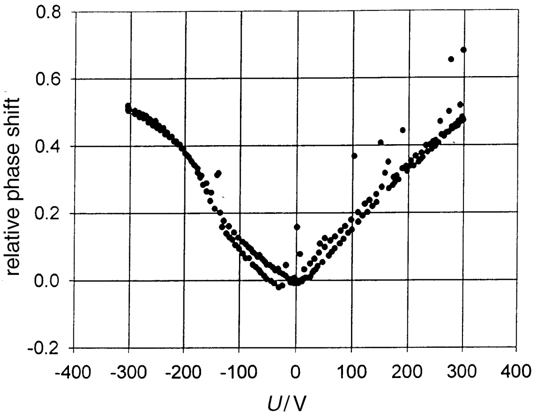

Fig. 5 Dependence of the relative phase shift on applied voltage for a $BaTiO_3$ film on $SrTiO_3$(001)

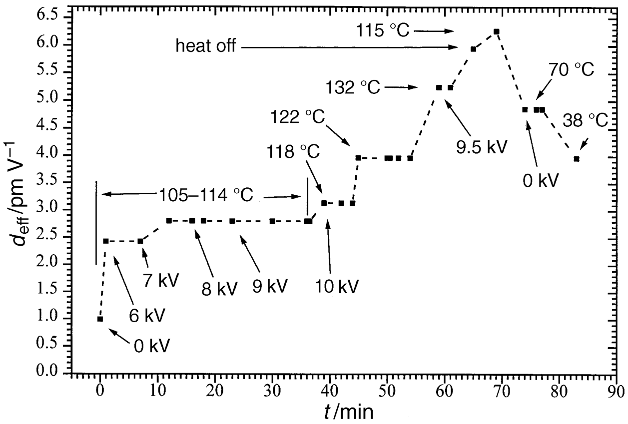

Fig. 6 Effective *d*-coefficient of a $BaTiO_3$ thin film grown on a $LaAlO_3$(001) substrate measured *in situ* (relative to quartz) at the indicated temperatures and with corona poling

Fig. 5 shows the dependence of the phase retardation on the applied voltage. The films demonstrated a quadratic electro-optic behaviour. The value of the second-order electro-optic coefficient (*R*) was calculated using eqn. (1),

$$R = \lambda \Delta \Gamma / (n^3 E^2 L) \qquad (1)$$

where $\Delta\Gamma$ is the relative phase shift, λ is the wavelength in nm, n is the refractive index of the film, E is the density of the electric field in V m^{-1} and L is the film thickness in nm. The R value for a 5 μm thick $BaTiO_3$ film grown on $SrTiO_3$(100) was calculated to be 1×10^{-16} m^2 V^{-2} at 3 V μm^{-1}, being of the same order as that of PLZT (lead zirconate–titanate doped with La), which has the largest quadratic electro-optic effect.

The second-order electro-optic susceptibility (D_{ij}) of the $BaTiO_3$ grown on $LaAlO_3$ and $SrTiO_3$ was measured by a second harmonic generation (SGH) set-up having corona electric field poling. The details of the experiment and calculation are described in ref. 10. The results of SHG measurements of a *c*-axis oriented film on $LaAlO_3$, as shown in Fig. 6, indicate that the film has $d_{33} = 6.2$ pm V^{-1}. This value is comparable to 6.8 pm V^{-1} for bulk $BaTiO_3$ crystals, further indicating the high quality of these films.

Conclusions

We have demonstrated the epitaxial growth of $BaTiO_3$ films on technologically important substrates: low refractive index MgO for potential active optical waveguide device applications, and off-crystal axis oriented (110) and (111)$SrTiO_3$ for efficient electro-optic device development. Excellent epitaxy in these films was confirmed by X-ray diffraction. Guided optical wave propagation in films grown on MgO and $LaAlO_3$ was observed by prism coupling. These films exhibited values of the refractive indices close to those of bulk $BaTiO_3$ crystals. The $BaTiO_3$ films showed first-order quadratic electro-optic behaviour with large electro-optic coefficient *R*. The $BaTiO_3$ films also showed second-order electro-optic susceptibilities similar to those of bulk $BaTiO_3$.

This work was supported by the USAF Rome Laboratory (Contract F19628-93-C-0078) and APRA (Contract DAAAH1-94-C-R144). We thank Xin Di Wu of Los Alamos National Laboratory for the RBS measurement and John Jackson of Metricon for the prism coupling measurements.

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Paper 6/07898B; *Received* 21*st November*, 1996