DEFECT STRUCTURE OF SEMICONDUCTING AND
INSULATING EPITAXIAL OXIDES

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Defect Structure of Semiconducting and Insulating Oxides

The investigation of the defect structure of semiconducting and insulating and epitaxial oxide has focussed on several aspects including (1) the epitaxial growth of $(\text{BaSr})\text{TiO}_3$ over the entire solid solution range (2) the study of point defects in epitaxial BaTiO_3 using temperature dependent conductivity measurements and deep level optical spectroscopy (DLOS) and (3) preliminary studies of their non-linear optical properties.

MOCVD deposition of perovskites: Based on our earlier work for the MOCVD of polycrystalline and epitaxial deposition of SrTiO_3 thin films, we developed the methodology for preparing epitaxial BaSrTiO_3 . A strategy we used to improve the MOCVD process was to prepare precursors with sufficient and stable volatility in collaboration with Prof. T. Marks of Northwestern Univ. This was accomplished by fluorination and encapsulation of the metal ion in a sterically saturating ligand. The introduction of neutral donor ligands such as polyethers to the metal complex reduces oligomerization. To implement this design criteria, we used $\text{Ba}(\text{hfa})_2(\text{tetraglyme})$ (hfa = hexafluoroacetylacetonate, $(\text{C}_5\text{HF}_6\text{O}_2)$) which exhibits significantly improved volatility and vapor pressure stability in comparison to $\text{Ba}(\text{fod})_2$ (fod = hepta-fluorodimethyl octanedionate) and $\text{Ba}(\text{dpm})_2$.

For the growth of epitaxial BaSrTiO_3 , a low pressure, two-zone horizontal quartz reactor was used. Titanium tetraisopropoxide [TPT , $\text{Ti}(\text{OC}_3\text{H}_7)_4$], $\text{Sr}(\text{hfa})_2(\text{tetraglyme})$ and $\text{Ba}(\text{hfa})_2(\text{tetraglyme})$ were employed as the metalorganic precursors. The sources were transported to the reaction zone by an argon carrier gas. Oxygen bubbled through water served as the reactant gas. To obtain an epitaxial layer, LaAlO_3 was used as the substrate. The crystallographic similarity between LaAlO_3 and $(\text{BaSr})\text{TiO}_3$ promotes epitaxy. The $\text{BaSrTiO}_3/\text{LaAlO}_3$

system has a lattice mismatch of 3.0 -5.1%, which is comparable to that of the BaTiO₃/MgO system (4.2%) used in previous studies.

The BaSrTiO₃ thin films were deposited over a temperature range of 750-840°C. For a substrate temperature of 800°C, the deposition rates ranged from 0.2 to 1.5 microns/hr. Typical film thicknesses were 0.2 - 2.0 microns.

For optimal source temperatures, single phase BaTiO₃ films were deposited. The films displayed only the (hoo) reflection planes, which indicated an a-axis preferred orientation. The full width half maximum of the (200) peak was 0.4 - 0.8°. The x-ray phi-angle scan of the (220) diffraction planes for BaSrTiO₃ showed the requisite, fourfold symmetry which confirmed in-plane epitaxy.

Point defect characterization: To determine the point defect structure of the ferroelectric thin films, transient photocapacitance spectroscopy was used. The technique involves measuring the time resolved photocapacitance. For these studies, a Schottky diode or metal-insulator-semiconductor (MIS) structure is used. In the latter case, the ferroelectric oxide serves as the insulator. We have developed and applied this technique to the study of defects in both SrTiO₃ and BaTiO₃. For these measurements, the sample was illuminated with chopped monochromatic light from a 250W quartz lamp equipped with a Zeiss double-prism monochromator. The observed transient photocapacitance was measured with a Boonton capacitance meter interfaced to a personal computer. The time derivative of the photocapacitance was recorded as a function of the photon energy while continuously varying the energy over the spectral region of 1.0 to 3.5 eV. Photocapacitance transients were measured over the time period of 0.4 -50 msec. The system can detect electronically active defect concentrations at levels of the order of 10^{12}cm^{-3} in layers less than a micron thick. Both shallow and deep

level defects can be determined.

Using transient photocapacitance spectroscopy, the defect structure of BaTiO₃ thin films grown on (100) Si was examined. The concentration, optical cross section and associated energy levels of both native and impurity defects in as-grown and BaTiO₃ thin films were evaluated. A series of deep level defects with peak energies of $E_v + 1.8$, $E_v + 2.4$, $E_v + 2.7$, $E_v + 3.0-3.1$ and $E_v + 3.2-3.3$ eV were observed in the as-grown films. Upon vacuum annealing, the concentration of the traps at $E_v + 3.0$ and $E_v + 3.2$ eV increased while the concentration of the traps with levels at $E_v + 1.8$ and $E_v + 2.4$ eV decreased. Based upon defect chemical arguments, the levels at $E_v + 3.0-3.1$ and $E_v + 3.2-3.3$ eV are attributed to oxygen vacancies which are present in concentration of the order of 10^{14} cm⁻³ in as-grown films and 10^{15} cm⁻³ in annealed films. The mid-gap levels are ascribed to impurities specifically Fe and Fe-related defects which are present in concentrations of the order of 10^{14} cm⁻³. It is important to note that no acceptor levels attributable to titanium or barium vacancies were observed. The films were always n-type even for oxygen partial pressures of 0.01 atm. From the aforementioned photocapacitance data and electrical resistivity measurements, a defect model was developed whereby singly ionized oxygen was the dominant defect in the thin films. The relevant defect equilibrium constants are currently being calculated and compared to theory.

Nonlinear optical properties: For large scale fabrication of nonlinear optical (NLO) devices, it is crucial to have reliable, high quality thin films. Among potential NLO materials, BaTiO₃ is a particularly promising candidate because of its high second-order nonlinear optical susceptibility and electro-optic coefficients. We have investigated the suitability of BaTiO₃ thin films prepared by MOCVD for second harmonic generation (SHG).

The BaTiO₃ films investigated were deposited on LaAlO₃ and were highly textured, with the a-axis perpendicular to the film plane. SHG properties were measured using a Q-switched Nd:YAG laser at a wavelength of 1.064 micrometers. Simultaneous corona poling of the films was carried out during SHG measurements. Upon corona poling of the films at temperatures near the Curie temperature, the second-order non-linear optical susceptibility, d_{33} , of the poled films reaches 7.5 pm/V. This value is comparable to that of bulk BaTiO₃ along the c-axis suggesting that the majority of the film grains were aligned with the c-axis parallel to the film normal after poling. The enhanced second-harmonic generation shows a very slow decay at room temperature.

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Structure of Organometallic Chemical Vapor Deposited BaTiO_3 Thin Films on LaAlO_3

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BaTiO_3 thin films grown on LaAlO_3 by organometallic chemical vapor deposition were characterized with cross-sectional high resolution transmission electron microscopy. Epitaxy was confirmed for the films grown on (100) oriented substrates. The films displayed an a axis orientation. The interface between the film and substrate was nearly atomically abrupt. Partial relaxation of the films was observed as a result of misfit dislocation formation.

Key words: $\text{BaTiO}_3/\text{LaAlO}_3$, HRTEM, OMCVD

Recently, increased effort has concentrated on the low temperature deposition and characterization of thin film BaTiO_3 because of its potential applications in microelectronics, nonlinear and electro-optics, as well as optical information storage.^{1,2} Many of these applications require films with low defect density. Epitaxial films have been successfully deposited by rf-magnetron sputtering,³ reactive evaporation,⁴ laser ablation,⁵ and recently, by organometallic chemical vapor deposition (OMCVD).^{6,7} Using high resolution transmission electron microscopy (HRTEM) in conjunction with x-ray diffraction, we have examined the detailed microstructure of thin film BaTiO_3 prepared by OMCVD for the first time. High resolution transmission electron microscopy indicates that the films are indeed epitaxial. The defect structure of the films is evaluated.

The BaTiO_3 films were deposited by OMCVD in a low pressure, two-zone horizontal quartz reactor. The titanium and barium precursors were $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{Ba}(\text{C}_5\text{HF}_6\text{O}_2)_2$ (tetraglyme). The details of the growth process are described elsewhere.⁶ The BaTiO_3 films were deposited on (100) LaAlO_3 at 800°C. The structural similarities between BaTiO_3 ($a = b = 3.994\text{\AA}$, $c =$

$4.038\text{\AA}$) and LaAlO_3 ($a = 3.79\text{\AA}$) promote epitaxy. LaAlO_3 has a distorted perovskite structure at room temperature, which undergoes a structural phase transition from the rhombohedral to the cubic phase at 435°C. The $\text{BaTiO}_3/\text{LaAlO}_3$ system offers a lattice mismatch of 5.4%. The thickness of the deposited film was 0.5 microns.

Cross sectional TEM samples were prepared by mechanically thinning the samples to less than ten microns and then ion milled. An accelerating voltage of 6–7 keV at an incident angle of 20° was used during the milling process. Ion-polishing was accomplished at 3 keV and at an angle of 20°. High resolution transmission electron microscopy was performed with either a Hitachi-9000 or Hitachi 2000 electron microscope and the electron beam was focussed along the [100] direction of LaAlO_3 .

X-ray diffraction measurements were performed with a Rigaku diffractometer using CuK_α radiation. X-ray diffraction confirmed that the films deposited at 800°C were primarily BaTiO_3 with Ba_2TiO_4 as a minor secondary phase. The BaTiO_3 has a preferred orientation with the a axis perpendicular to the substrate surface. Phi scans of the (220) diffraction planes showed fourfold symmetry indicating in-plane epitaxy.

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Fig. 1. High resolution electron micrograph showing epitaxial growth of a BaTiO₃ thin film on LaAlO₃. The misfit dislocations are indicated.

Fig. 2. High resolution electron micrograph showing an additional Ti-O atomic layer near the interface labeled AA' which displays lattice bending.

The lattice images in the high resolution cross-sectional TEM micrograph shown in Fig. 1 confirm that BaTiO₃ has a preferred orientation. The one-to-one correspondence of the lattice images of the film and the substrate shown in Fig. 1 clearly indicates that the film is epitaxial with the substrate. However, as illustrated in Fig. 1, the observed BaTiO₃ lattice image near the substrate/film interface shows that the unit cell is compressed along the direction parallel to the interface but elongated in the direction perpendicular to it. The ratio of the lattice constants (in plane/out of plane) was determined directly from the HRTEM micrograph to be 0.98 for the material near the interface. Away from the interface, the ratio approaches the theoretical value of 1.01 for bulk BaTiO₃. The strained region extends more than 40 nm into the film.

The quality of the film/substrate interface was evaluated using HRTEM. An abrupt BaTiO₃-LaAlO₃ interface structure is observed in Fig. 2. No evidence of secondary phase formation is noted. The BaTiO₃

Fig. 3. High resolution electron micrograph showing the existence of a secondary phase grain near the BaTiO₃-LaAlO₃ interface.

lattice image is seen from the bottom of the jog in the interface indicating nearly atomically abrupt interfaces can be obtained. It is also seen that BaTiO₃ lattice bends along the interface just above the jog. The bending is attributed to lattice expansion of the film along the growth direction within the jog area.

Although sharp BaTiO₃-LaAlO₃ interfaces are observed, numerous structural defects are found within the first ten atomic layers of the film. It is expected that a high concentration of point defects may exist in this region as a result of ion beam damage or growth, since the interface is a region of high excess free energy. However, point defects cannot be identified directly by TEM under normal imaging conditions. Nevertheless, if the density of point defects is quite large, the defects can aggregate to form an additive atomic layer. An additional layer is indeed observed in the region labeled AA' in Fig. 2. In addition, the periphery of this additive layer constitutes an edge dislocation with a Burgers vector equal to 1/2 [001].

While the sharp interface is observed in most regions, in some regions, a reaction layer approximately two unit cells thick is observed at the BaTiO₃-LaAlO₃ interface. As shown in Fig. 1, the lattice image of the interface is not as clear as in the film or the substrate indicating the existence of a disordered layer. This disordered layer may result from local chemical inhomogeneities at the substrate surface formed during the initiation of growth. Away from this disordered region, there is a region with a width of 200–300 Å corresponding to the first two to three minutes of growth, which is easily thinned by ion milling. This implies that the region is atomically disordered or consists of a secondary phase. The existence of these atomically disordered regions indicates that the initial stage of growth is not sufficiently stable. These instabilities during the first few minutes of film growth presumably result from the introduction of the oxidation gas during the growth process, which may result in composition fluctuations. Initial electron energy

loss spectroscopy measurements indicate that this region is barium rich (10). In addition to the disordered region at the interface, a minor secondary phase, also observed in x-ray diffraction, was verified in Fig. 3, and is approximately 200Å in diameter.

High resolution transmission electron microscopy indicates that the interface between the film and the substrate is semi-coherent. The mismatch between the BaTiO₃ and the LaAlO₃ is partially accommodated by the formation of an array of misfit dislocations at the interface. The measured distance between dislocations is about 16 unit cells, which corresponds to a misfit strain of approximately 6.25%. This is to be compared to the calculated misfit strain for a coherent interface of 6.5% at room temperature for *a* axis oriented films. The misfit dislocation extends approximately ten unit cells as shown in Fig. 1. The lattice image indicates that the misfit dislocation consists of two partials which are separated by about six unit cells. Some stacking disorder is evident between the two partials. Further analysis is required to confirm the detailed defect structure. As to why partial dislocations are formed in this system, the energetics must be considered. Since the ionic radius of barium (0.198 nm) and titanium (0.132 nm) are larger than lanthanum (0.169 nm), and aluminum (0.118 nm) respectively, the elastic energy of a perfect dislocation would be expected to be higher than that of the defect structure observed.

In summary, cross-sectional high resolution transmission electron microscopy reveals that epitaxial BaTiO₃ films can be deposited on LaAlO₃ by OMCVD. Nearly atomically abrupt interfaces are achieved, although in some regions evidence of interfacial disorder was noted. The layers are nearly completely

relaxed by the formation of an array of misfit dislocations. Evidence of the formation of impurity phases is noted.

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Second harmonic generation and crystalline structure of corona poled BaTiO₃ thin films

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Second harmonic generation from a 1.064 μm fundamental was measured on BaTiO₃ thin films derived from metalorganic chemical vapor deposition. Significant enhancement of the second harmonic generation was observed upon poling of the film using corona discharge. The second harmonic intensity of the poled film was studied as a function of the incident fundamental polarization, showing that there was no in-plane symmetry in the poled films. The measured macroscopic second-order nonlinear optical coefficient of the poled film, d_{33}^{film} , is ~ 7.5 pm/V. This value is comparable to that of the bulk BaTiO₃ along c -axis, $d_{33}^{\text{BaTiO}_3}$, suggesting that the majority of the crystalline c -axis of the poled film was aligned to the film normal.

1. Introduction

Nonlinear optical (NLO) thin films have been under intense research in recent years for their vast potential in photonic applications [1]. BaTiO₃ is a particular promising candidate for such applications because of its high second-order nonlinear optical susceptibility, electrooptic coefficients, and desirable ferroelectric properties [2,3]. Recent studies have shown that the second harmonic generation (SHG) from BaTiO₃ thin films can be significantly enhanced by the corona poling of the film [4]. The dielectric and ferroelectric properties measured from the contact poled films also showed significant improvement resulting from the direct electric field poling [5]. It is important, both for scientific and practical purposes, to understand the structural change of the film resulting from the electric field poling and the consequent influences of this change on the optical and electrical properties. In this paper, we report the studies on the SHG properties of BaTiO₃ thin films influenced by the corona poling. The second harmonic (SH) intensities were studied as a function of the incident fundamental polariza-

tion to determine the crystalline orientation of the poled film.

2. Experimental procedure

BaTiO₃ thin films were deposited on (100) LaAlO₃ substrates using metalorganic chemical vapor deposition (MOCVD) [6]. The films studied were highly textured with the crystalline a -axis perpendicular to the film plane. The average grain size of the film is ~ 0.2 μm , and the film thickness ranged from 0.2–0.5 μm . The SH intensities from the BaTiO₃ films were measured using a Q -switched Nd:YAG laser at a wavelength of 1.064 μm . The SH intensities from the sample (I_s) and from a Y-cut α -quartz reference (I_0) were measured simultaneously, and the intensity ratio I_s/I_0 was taken as the measured result to eliminate the influence of the laser output fluctuation. The corona poling of the film was achieved by applying a high voltage of up to +10 kV between a tungsten needle placed ~ 3 mm above the film and a grounded plane at the back side of the substrate. The measured intensity ratio from the film

was calibrated by the SH intensity ratio (I_Q/I_0) of a Y-cut α -quartz sample at the same position (corresponding to the second-order nonlinear optical coefficient, $d_{11}=0.34$ pm/V) [2]. The sample arrangement for SHG measurement and corona poling is illustrated in fig. 1. For the in-situ SHG measurement during poling, both incident fundamental and transmitted SH light beams were p-polarized. The details of the SHG measurements and the poling procedure are described elsewhere [4].

For film thickness much smaller than the coherence length, the effective second-order nonlinear optical susceptibility of the BaTiO_3 film, with both the fundamental and the SH signals in p -polarization, is determined by [4]

$$d_{\text{eff}} \sim \frac{l_{c,Q}}{l_s} \left(\frac{n^2(2\omega)n(\omega)}{n_Q^2(2\omega)n_Q(\omega)} \frac{I_s/I_0}{(I_Q/I_0)T} \right)^{1/2} d_{11,Q}, \quad (1)$$

where $l_{c,Q}$ is the quartz coherence length, l_s is the film thickness, $n(\omega)$ and $n(2\omega)$ are the film index of refraction at the fundamental and SH frequencies, $n_Q(\omega)$ and $n_Q(2\omega)$ are that of the quartz, $d_{11,Q}=0.34$ pm/V is the second-order nonlinear optical coefficient of α -quartz, and T is the transmission of the film/substrate to the SH light (the transmission loss was mainly due to the light scattering in the twinned LaAlO_3 substrate). Bulk BaTiO_3 n values [2] were used for the calculation of d_{eff} .

3. Results and discussions

Figure 2 is an X-ray diffraction $\theta/2\theta$ scan of an as-deposited BaTiO_3 film used in the SHG measurement. The strong film peaks observed are attributed to the (100) and (200) BaTiO_3 reflections, and no visible (110) or {101} peaks were present, indicating a strong preferred orientation of the film with a -axis perpendicular to the film plane. The SHG measurements on the as-deposited films yielded d_{eff} values in the range of 10^{-1} – 10^0 times $d_{11,Q}$. These values are much smaller than what one would expect based on the bulk values (the non-zero second-order nonlinear optical coefficients of the bulk BaTiO_3 are $d_{33} \sim 6.8$, $d_{31} \sim 15.7$, and $d_{15} \sim 17.0$ pm/V) [2]. Our initiative for corona poling of the BaTiO_3 films was partly motivated by this low d_{eff} value measured from the as-deposited films. In addition, for BaTiO_3 films deposited on Pt coated MgO, a substantial increase of the film dielectric constant was observed when the bias voltage applied across the film exceeded a threshold voltage of ~ 50 – 100 kV/cm [5]. This is an indication that the lattice dipoles within the film reoriented under the external electric field. Furthermore, it has been reported that both the electrical and optical properties of bulk BaTiO_3 were significantly improved by the electric field poling [7]. Upon poling the BaTiO_3 film using corona discharge at $\sim 115^\circ\text{C}$ (near the bulk BaTiO_3 Curie temperature $T_c \sim 120^\circ\text{C}$), significant enhancement of SHG was measured

Fig. 1. The sample arrangement for SHG measurement and corona poling of BaTiO_3 thin films.

Fig. 2. X-ray diffraction $\theta/2\theta$ scan of a BaTiO_3 thin film measured. Strong peaks from (100) and (200) BaTiO_3 reflections are indicated.

Fig. 3. SH intensity from a BaTiO_3 thin film measured in-situ during a poling procedure. During A→B, the film was heated to $\sim 115^\circ\text{C}$ at zero poling voltage, then the voltage was gradually increased to a threshold voltage of ~ 6 kV. During B→C, the poling voltage gradually increased to 8 kV. During C→D, the film temperature was gradually lowered while maintaining a 8 kV poling voltage. At D, the poling voltage was turned off as room temperature was reached (from ref. [4]).

from the film (as shown in fig. 3). The in-situ SHG measurements yielded values of $d_{\text{eff}} \sim 3.5$ pm/V during poling at 115°C , and $d_{\text{eff}} \sim 2.7$ pm/V immediately after poling (at room temperature). A relatively fast decay of the SH intensity from the film was observed during the first two days after poling, it was followed by a much slower decay over the next several months. Measurement on the stabilized poled film two days after poling yielded a $d_{\text{eff}} \sim 2$ pm/V.

The measured d_{eff} resulted from the SH intensity

generated from the BaTiO_3 film projected to the p-polarization (see fig. 1). Due to the polycrystalline nature of the films investigated, the SH intensity from which d_{eff} was calculated was contributed from many grains within the film at different crystalline orientations. To compare the measured d_{eff} with what would be expected from a BaTiO_3 thin film, the distribution of the grain orientation and the symmetry of BaTiO_3 film need to be considered. Tetragonal BaTiO_3 has a lattice dipole along the c -axis, coinciding with the optical axis. This lattice dipole is the origin of the ferroelectric properties associated with BaTiO_3 . In the as-deposited film, the a -axis is aligned to the film normal, with the c -axis randomly ordered in the film plane. During the poling process, presumably, the lattice dipole was aligned by the external electric field created from the corona discharge, resulting the c -axis reoriented to the film normal. Consequently, the SH intensities generated from different grains of the film became constructive to each other. The above interpretation provides an explanation for the measured SH intensity increase arising from the poling of the film, and is consistent with the X-ray diffraction data obtained from the film before and after the poling [4].

In analyzing the crystalline structure of the film before and after the poling, it is reasonable to assume that for the as-deposited film, there was no preferred orientation in the film plane. The electric field along the film normal during poling should not introduce order into the film plane. Thus, the symmetry of the poled film, as a whole, can be described by the space group $C_{\infty v}$. For this symmetry, the second order nonlinear optical coefficient of the film is given by [8]

$$\begin{pmatrix} d_{31} & d_{32} & d_{33} \\ & d_{24} & d_{15} \end{pmatrix}. \quad (2)$$

This is the macroscopic second-order nonlinear optical susceptibility of the poled film averaged over many crystal grains within the film. The elements $d_{31} = d_{32} = d_{15} = d_{24}$.

Using the electric field projection, one can derive from eq. (2) that, the p-polarized SH intensities from the p- and s-polarized incident fundamentals are

$$I_{p \rightarrow p} = (3d_{31}^{\text{film}} \sin \theta \cos^2 \theta + d_{33}^{\text{film}} \sin^3 \theta)^2 I^2(\omega), \quad (3)$$

$$I_{s-p} = (d_{31}^{\text{film}} \sin \theta)^2 I^2(\omega), \quad (4)$$

where θ is the incident angle within the film, $I(\omega)$ is the intensity of the incident fundamental, and

$$d_{\text{eff}} = 3d_{31}^{\text{film}} \sin \theta \cos^2 \theta + d_{33}^{\text{film}} \sin^3 \theta, \quad (5)$$

is the effective second-order nonlinear optical susceptibility of the film measured from the in-situ SHG measurement during poling, for which both the incident fundamental and the transmitted SH lights are p-polarized.

From eqs. (3) and (4), and also considering the SH Fresnel factor at the incidence, we have [9]

$$d_{33}^{\text{film}}/d_{31}^{\text{film}} = [f(\theta) (I_{p-p}/I_{s-p})^{1/2} - 3 \cos^2 \theta] / \sin^2 \theta, \quad (6)$$

where $f(\theta)$ is the SH Fresnel factor, which was calculated to be ~ 0.79 using the refractive index of bulk BaTiO₃.

After measuring the p-polarized SH intensities at p- and s-polarized incident fundamentals, the ratio $d_{33}^{\text{film}}/d_{31}^{\text{film}}$ for the entire poled film can be calculated using eq. (6). Then, with eq. (5), the values of d_{33}^{film} and d_{31}^{film} can be calculated from the measured d_{eff} . For this purpose, a half wave plate was placed between the front polarizer and the sample. By rotating the axis of the half wave plate, the incident polarization was rotated in the plane perpendicular to the incidence plane (as shown in fig. 1).

Figure 4 is the p-polarized SH intensity measured from a film right after the corona poling. The SH intensity was plotted as a function of the angle (ϕ) between the incidence plane and the incident polarization (with $\phi=0^\circ$ corresponds to p→p, and $\phi=90^\circ$ corresponds to s→p). The almost perfect fitting of the SH intensity to $I = (A \cos^2 \phi + B \sin^2 \phi + C \cos \phi \sin \phi)^2 I^2(\omega)$, with $C=0$, shows that there was indeed no in-plane symmetry for the poled film [10]. A ratio of $(I_{p-p}/I_{s-p}) \sim 14-17$ was consistently measured for several poled films. Using $(I_{p-p}/I_{s-p}) \sim 15$, a ratio of $(d_{33}^{\text{film}}/d_{31}^{\text{film}}) \sim 3.6$ was calculated from eq. (6).

For $d_{\text{eff}} \sim 2.7$ pm/V, measured immediately after the corona poling of the film, a d_{33}^{film} of ~ 10 pm/V and $d_{31}^{\text{film}} \sim 2.9$ pm/V was calculated using eq. (5).

Fig. 4. P-polarized SH intensity measured from a poled BaTiO₃ film plotted as a function of the incident fundamental polarization (ϕ) (with $\phi=0^\circ$ corresponds to p→p, and $\phi=90^\circ$ corresponds to s→p). Also plotted is the fitted result for the data to $I = (A \cos^2 \phi + B \sin^2 \phi)^2 I(\omega)^2$ and $I_{p-p}/I_{s-p} = 15$.

The more stabilized d_{eff} value of ~ 2.0 pm/V measured two days after poling resulted in a d_{33}^{film} of ~ 7.5 pm/V and $d_{31}^{\text{film}} \sim 2.1$ pm/V. Comparing these values to the bulk BaTiO₃ values, one can see that in the stabilized poled film $d_{33}^{\text{film}} \sim d_{33}^{\text{BaTiO}_3}$, while $d_{31}^{\text{film}} \ll d_{31}^{\text{BaTiO}_3}$. This strongly indicates that, for the crystal grains in the poled film, the majority of the c-axes were aligned parallel to the film normal while the a- and b-axes were predominantly randomly ordered in the film plane. The measured result of $d_{33}^{\text{film}} > d_{33}^{\text{BaTiO}_3}$ immediately after poling is also interesting. It may indicate an additional contribution to the SHG of the film from the DC field induced electronic second-order nonlinearity by the surface charge. Induced surface charge may arise from the migration of the ionic charge carriers, such as oxygen vacancies, under the poling electric field. Once the electric field was removed, the induced surface charge was gradually depleted, as indicated by the relatively fast decay of the SH intensity from the poled film during the first two days after poling [4].

The SH intensity of the film at different incident polarization was also measured at various times after poling. Although the SH intensity of the poled film gradually decreased due to the structural relaxation, the ratio (I_{p-p}/I_{s-p}) stayed relatively constant over the same period of time. This may indicate that the c-axis oriented crystal grains in the poled film gradually relaxed back to the a-axis textured orientation.

Kwak et al. suggested that for the perovskite ferroelectric thin films, with the films thickness below a critical thickness (i.e., for PbTiO_3 , $\sim 0.25 \mu\text{m}$), the predominantly a -axis textured film possessed a minimum of free energy considering the contributions from elastic energy, domain-wall creation, polarization, and spontaneous strains of the film [11]. The Coulomb energy arising from the depolarization field of the neighboring grains does not favor the c -axes aligned to the same orientation. Thus, for the a -axis textured film, a "randomly" ordered c -axes orientation in the film plane is energetically favored. Once a poled crystalline grain relaxed back to the a -axis textured state, the c -axis remained randomly ordered in the film plane. Averaging over many grains, the SH intensities generated from these relaxed grains cancelled out each other just as before the poling. Even though the percentage of the c -axis aligned grains decreased due to the relaxation of the poled structure, the ratio ($d_{33}^{\text{film}}/d_{31}^{\text{film}}$) remained the same because this value was mainly contributed by those poled grains not yet relaxed.

4. Summary

In conclusion, a significant increase of SH intensity was observed from BaTiO_3 thin films as a result of corona poling of the film. The dependence of the SH intensity from the poled film on the incident polarization indicated that the majority of the crystalline c -axis was aligned to the film normal. This shows that the electric field poling of BaTiO_3 thin films is

an effective way to improve its nonlinear optical properties.

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On the microstructure, chemistry, and dielectric function of BaTiO₃ MOCVD thin films

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Thin films of BaTiO₃ deposited on (100)LaAlO₃ substrate by metal-organic chemical vapor deposition (MOCVD) are investigated using several electron-optical techniques. Combined high resolution transmission electron microscopy (HRTEM), electron energy loss spectrometry (EELS), and convergent beam electron diffraction (CBED) indicate a substantial influence of lattice strain on the structural and optical characteristics of BaTiO₃ films. Spatially resolved EELS and CBED studies indicate that the substrate influence persists up to about 40 nm away from the interface. The changes in the dielectric function of the films, as inferred from spatially resolved EELS, appear to correlate well with internal lattice strain in the films as deduced from convergent beam electron diffraction (CBED).

I. INTRODUCTION

There has been considerable interest in recent years in the development of ferroelectric perovskite thin films. The outstanding optical, dielectric, and ferroelectric properties of perovskites, coupled with the ability to deposit epitaxial single crystal thin films, make these materials extremely desirable for electro-optic and memory storage devices.^{1,2}

The properties of thin films depend critically on the deposition conditions and on the nature and character of substrate-film interface. It is well established that substrate-film interactions can have a profound influence on the character and properties of deposited thin films.^{4,5} It is also known that a lattice misfit at the interface may result in formation of misfit dislocations (after a "critical" thickness of the film⁴), which generally deteriorate the properties. Furthermore, mismatch of the thermal expansion coefficients of the thin film and substrate can induce residual stresses in the films, which in turn may degrade the properties of the thin films. Other strain relaxation mechanisms include domain formation^{5,6} in perovskite thin films. A small amount of internal strain may have a large effect on the electronic and optical structure of thin films. Therefore, the influence of spatially varying strain on the electronic and optical properties of the films is of considerable interest. The effective width of these strained regions plays a significant role in numerous properties related to internal interfaces.⁷

Recently, the deposition of high quality epitaxial films of BaTiO₃ on a (100)LaAlO₃ substrate by metal-organic chemical vapor deposition (MOCVD) has been demonstrated.³ The bulk phase composition and epitaxial quality were controlled by adjusting the reactant

partial pressures and deposition temperatures. In-plane epitaxy was confirmed using x-ray diffraction and high resolution transmission electron microscopy (HRTEM).

In this paper, we provide a detailed analysis of substrate-film interface and the thin films to further our understanding of the microscale character and interfacial disorder of the BaTiO₃ MOCVD thin films. Moreover, we report the use of spatially resolved parallel detection electron energy loss spectrometry (EELS) and convergent beam electron diffraction (CBED) techniques to understand the spatial extent of the substrate-thin film interactions in the BaTiO₃-LaAlO₃ system. We have also explored the possible longer range influence of the substrate-film interface on the microstructure, chemistry, and dielectric functions of the constrained thin films.

II. EXPERIMENTAL

Epitaxial BaTiO₃ was deposited on LaAlO₃ by metal-organic chemical vapor deposition. Barium(hexafluoroacetylacetonate)₂(tetraglyme)-(Ba(hfa)₂.tet) and titanium (IV)tetraisopropoxide (TPT) were chosen as the organometallic precursors with argon as the carrier gas. The films were deposited in a two-zone, low-pressure horizontal quartz reactor. The details of growth parameters are reported elsewhere.³

Thin foils for TEM were prepared by sandwiching two films, face-to-face, with an epoxy, followed by conventional polishing and ion beam thinning to obtain cross-sectional specimens. TEM experiments were carried out using a 200 kV cold field emission gun atomic resolution analytical electron microscope (ARAEM, Hitachi HF-2000), which is equipped with a Gatan 666 parallel EELS detector and a Gatan CCD camera for HREM imaging.⁸ Since Ba L peaks and Ti K peaks

significantly overlap in the x-ray emission spectra, we resorted to EELS for the confirmation of local elemental chemistry using the standards approach.⁹

III. RESULTS AND DISCUSSION

Figure 1 is an HRTEM image of a BaTiO₃ thin film including the substrate-film interface indicating excellent epitaxy. The substrate-film interface is extremely sharp and devoid of extensive reconstruction. Chen *et al.*¹⁰ have previously reported that the lattice misfit between the film and the substrate is accommodated by a regular array of misfit dislocations.

Occasionally, small islands of an amorphous phase were observed at the substrate-film interfaces. One such amorphous island is shown in Fig. 2(a). EELS spectra from such islands always indicated excess barium, as can be inferred from the background-subtracted integrated intensities of individual edges in the EELS spectrum of Fig. 2(b). The elemental ratios of such regions are close to 2:1:4, for Ba, Ti, and O respectively, within about 10% error (using an external BaTiO₃ standard), indicating the presence of an amorphous Ba₂TiO₄ phase. Surprisingly, the presence of such islands does not seem to hinder the epitaxial growth of the subsequent film.

We now focus our attention on the outer sections of the thin film which are expected to be relaxed and relatively free of any substrate influence. Figure 3 shows an EELS spectrum of the film taken from about 100 nm away from the substrate-film interface. The integrated (background-subtracted) edge intensity ratios of O K, Ti L₂₃, and Ba M₄₅ edges conform to the expected ratios for stoichiometric BaTiO₃. These results indicate good stoichiometry of BaTiO₃ in the outer sections. Figure 4 is a high resolution and high dispersion view of Ti L₂₃ EELS absorption edge obtained from the same region as

Fig. 3. The spectral shape and L₃/L₂ intensity ratio (i.e., energy loss near edge structure, ELNES⁹) of Ti L₂₃ agree very well with an external BaTiO₃ standard. Figure 5 is the loss function of the same section (i.e., 100 nm away from the interface) of the BaTiO₃ thin film derived from the low loss portion of the EELS spectrum. The loss function is virtually identical to the spectrum obtained from a bulk BaTiO₃ single crystal. Since the loss function in EELS is intimately connected to the dielectric function,^{9,11} the changes in EELS loss function spectral features can be associated with changes in the dielectric properties of the solid. The remarkable similarity in the ELNES of Ti L₂₃ edges and the loss functions of the film and the external BaTiO₃ standard indicates that the near neighbor coordination and the local electronic structure (and the dielectric function) of the outer sections of BaTiO₃ thin films are virtually identical to those of the external BaTiO₃ standard. These results indicate that the outer regions (>100 nm) of BaTiO₃ thin films probably possess bulk properties and character.

While the outer sections of the BaTiO₃ thin films indeed have all the characteristics of bulk BaTiO₃, that is not the case near the substrate interface. Spatially resolved low loss EELS data show interesting variation as summarized in Fig. 6. EELS spectra taken closer to the film-substrate interface (spectrum A) appear substantially different from those away from the interface (spectrum C). The loss function, which is related to the imaginary part of the dielectric function [i.e., proportional to $\text{Im}[-1/\epsilon(q, \omega)]$, where $\epsilon(q, \omega)$ is the momentum and frequency dependent dielectric function],^{9,11} varies systematically from the interface region to the exterior. This is reflected in the gradual change in shape and energy of spectral features (indicated by arrows) with distance from the interface. In fact, even the

FIG. 1. An HRTEM image of BaTiO₃ film on LaAlO₃, indicating a sharp and well-defined transition from the substrate to the thin film.

(a)

(b)

FIG. 2. (a) An HRTEM image of BaTiO_3 film-substrate interface containing a small amorphous island. (b) EELS spectrum obtained from the interfacial phase in (a), indicating excess barium.

bulk plasmon energy loss peaks shift to higher values away from the interface, indicating that more valence electrons contribute to the loss spectra away from the interface. CBED high order Laue zone (HOLZ) defect line analysis also indicates variations in the HOLZ lines sharpness and intensity as a function of distance from the substrate-film interface. The right side inset of Fig. 6 is a series of bright-field (BF) CBED disks (zone axis is slightly off- $[106]$ zone) containing a montage of HOLZ defect lines. The HOLZ defect line network exhibits line splitting and broadening close to the interface, indicating substantial elastic strain.¹² The splitting gets weaker away from the interfaces. Unfortunately, it is very difficult to obtain unambiguous values of lattice

parameters from these patterns because of the multi-parameter influence on the HOLZ defect lines.¹² Nevertheless, the HOLZ defect line network does become sharper away from the interface region as can be seen from Fig. 6(c). The systematic variation in HOLZ defect line sharpness indicates gradual decay of strain field away from the interface. The origin of the strain field is expected to be twofold: from the interface misfit dislocations and also perhaps due to thermal stresses because of the different thermal expansion coefficients of LaAlO_3 and BaTiO_3 .

The gradual decay of the strain field as deduced from CBED analysis correlates well with the changes in the EELS spectra. The good correspondence between spa-

FIG. 3. A representative EELS spectrum from about 100 nm away from the interface. The elemental chemistry conforms to that of stoichiometric BaTiO₃ within ~10%.

tially resolved EELS data and CBED HOLZ defect line behavior strongly suggests that the dielectric function of BaTiO₃ is intimately related to the lattice strain in the films. Since the dielectric function dictates the optical and dielectric properties of the material, the combined CBED and EELS results suggest that the optical and dielectric properties of BaTiO₃ MOCVD thin films also vary with lattice strain. It appears, however, that EELS is a more sensitive measure of changes in the dielectric properties. In any case, the influence of the substrate-film interface appears to be vanishingly small more than 40 nm away from the interface. A quantitative relationship between CBED strain analysis and EELS optical functions is not trivial, and ongoing experiments are directed toward this goal.

FIG. 4. Ti L₂₃ EELS edge from the same region as in Fig. 3. The detail ELNES of this edge is identical to that of bulk BaTiO₃ external standard.

FIG. 5. Comparison of the loss function of BaTiO₃ derived from the thin film (100 nm away) and that of an external BaTiO₃ standard. The region (A) consists of inter-/intra-band transitions, region (B) represents collective low energy excitations, while region (C) indicates volume (bulk) plasmon associated with BaTiO₃. An excellent match suggests that the outer portion of the films attains the bulk form.

IV. CONCLUSIONS

Combined HREM, CBED, and EELS analysis of BaTiO₃ MOCVD thin films on LaAlO₃ confirms the previously reported in-plane epitaxial relationship for this system. Some evidence for the formation of Ba-rich second phases and interfacial glassy layers has been identified. However, interestingly, these perturbations do not seem to hinder the eventual epitaxial growth of BaTiO₃.

Spatially resolved EELS and CBED show variations in the structural and optical characteristics of the BaTiO₃ thin film. The changes in CBED patterns and EELS spectra are related to the difference in lattice strain induced by the misfit dislocations, and probably also by the thermal stresses in the film. The CBED and EELS loss function analysis indicates that the BaTiO₃ MOCVD thin films assume bulk characteristics more than 40 nm away from the substrate-film interface. This study demonstrates that internal strains do affect the optical (dielectric) function of the films. Spatially resolved CBED and EELS profiling across interfaces appear to be useful techniques to probe the character of thin films as a function of distance from the substrate.

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FIG. 6. Spatially resolved EELS low loss spectra (A, B, and C). The spectral features (thick arrows) attain bulk BaTiO₃ form as the beam is moved away from the interface. The bulk plasmon edge also shifts to higher energy as the beam is moved away from the interface. The right inset shows variations in CBED HOLZ defect line network (close to [106] zone), indicating systematic decay of strain field as reflected in the sharpness of defect lines. The left inset is the schematic of the profiling experiment, where points "A, B, and C" represent data points for EELS spectra (A, B, and C) as well as CBED patterns shown in the right inset.

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Second-harmonic generation of poled BaTiO₃ thin films

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Second-harmonic generation of 1.064 μm incident light was measured on BaTiO₃ thin films prepared by metalorganic chemical vapor deposition. Upon corona poling of the film, the second-harmonic signal was significantly enhanced. The second-order nonlinear optical susceptibility, d , of the poled film reaches ~ 7.5 times that of the quartz. The enhanced second-harmonic generation shows a very slow decay at room temperature.

Nonlinear optical (NLO) phenomena have been the subject of intense research in recent years for potential applications in optical switches, filters, waveguides, and electro-optic devices.¹⁻³ For the large scale fabrication of NLO devices, it is crucial to have reliable, high-quality thin films with desirable NLO properties. To date, the majority of the work in this regard has focused on poled organic polymer films.^{3,4} The advantages of inorganic thin films include improved structural stability, superior mechanical properties, and better impurity concentration control—all important factors in device fabrication. Among potential inorganic NLO materials, the perovskite BaTiO₃ is a particularly promising candidate because of its high second-order nonlinear optical susceptibility and electro-optic coefficients.^{5,6} Studies have shown that the NLO properties of the bulk, single crystal BaTiO₃ can be further enhanced by the electric field poling of the material.⁷ In this letter, we report the first investigation of the second-harmonic generation (SHG) of BaTiO₃ thin films, and its enhancement with corona poling.

The BaTiO₃ thin films investigated were prepared by metalorganic chemical vapor deposition (MOCVD). The growth process is described elsewhere.⁸ The films were grown *in situ* on (100) LaAlO₃ substrates at 800 °C using Ba(hexafluoroacetylacetonate)₂(tetraglyme) and titanium tetraisopropoxide as precursors. The BaTiO₃ films studied in this work are highly textured with the a axis perpendicular to the film plane. The average grain size as determined by the scanning electron microscopy is $\sim 0.2 \mu\text{m}$. The film thickness is in the range of 0.2–0.4 μm .

SHG properties were measured using a Q -switched Nd:YAG laser at a wavelength of 1.064 μm . The pulse width is 5 ns with a repetition rate of 10 Hz. Figure 1 shows the experimental setup for the SHG measurements and simultaneous corona poling of the film. The laser beam is split so that the second-harmonic (SH) intensities from the sample (I_s) and from a Y -cut quartz reference (I_0) can be measured simultaneously. To eliminate the influence of the laser output fluctuation, the intensity ratio of sample:reference (I_s/I_0) was taken as the measured result. Both the incident fundamental and the transmitted SH light

beams are p polarized by the polarizers P_1 and P_2 , respectively. Narrow-band filters and monochromators are placed before the detectors to ensure that only the SH ($\lambda = 0.532 \mu\text{m}$) intensities are measured. For electric field poling of the film, the sample is placed on a glass slide coated with a thin layer (thickness $\sim 25 \text{ nm}$) of indium-tin oxide (ITO) on one side. A tungsten needle is placed $\sim 3 \text{ mm}$ above the film. Corona poling of the film is achieved by applying a high voltage of up to +10 kV between the grounded ITO coating and the tungsten needle. The poling scheme shown in Fig. 1 enables satisfactory poling of the film without having electric discharge occur at the edges of the film and substrate. A heater is thermally attached to the film so that poling can be conducted at elevated temperatures. For the *in situ* SHG measurements during the poling process, the film normal is tilted 45° to the incident laser beam. The poling procedure was initiated by first heating the BaTiO₃ film to 115 °C (the BaTiO₃ Curie temperature T_c is $\sim 120 \text{ °C}$) with no poling voltage applied. At

FIG. 1. The experimental setup for the SHG measurement and the corona poling of the BaTiO₃ thin films.

$\sim 115^\circ\text{C}$, an electric field was applied to the film by a corona discharge and the SHG was measured *in situ*. The current flow through the corona needle was limited to < 0.1 mA during poling.

For calibration, the SH intensity ratio, (I_Q/I_0) , of a Y-cut α -quartz sample at the same position of the film was measured. The quartz sample was rotated to the maximum SHG orientation at near normal incidence (corresponding to the second-order nonlinear coefficient, $d_{11}=0.34$ pm/V).⁶ Consequently, the second-order nonlinear optical susceptibility, d , of the BaTiO₃ film is determined by comparing the values of I/I_0 and I_Q/I_0 .

For a thin film sample, the SH intensity generated by a fundamental light with intensity $I(\omega)$ is given by^{9,10}

$$I(2\omega) \propto [l_s^2 I^2(\omega) d_{\text{eff}}^2 / n^2(\omega) n(2\omega)] \times [\sin^2(\pi l_s / 2l_c) / (\pi l_s / 2l_c)^2], \quad (1)$$

where l_s is the film thickness, d_{eff} is the measured effective second-order nonlinear optical susceptibility, $n(\omega)$ and $n(2\omega)$ are the index of refraction at frequency ω and 2ω , respectively, and l_c is the coherence length of the film.

Using the bulk BaTiO₃ n values,⁶ the calculated BaTiO₃ coherence length, $l_c = \lambda / 4[n(\omega) - n(2\omega)]$, is much larger than the film thickness l_s . This yields $[\sin^2(\pi l_s / 2l_c) / (\pi l_s / 2l_c)^2] \sim 1$. For the SH intensity ratio of the BaTiO₃ film to the quartz, I/I_Q , the factor $[n^2(2\omega)n(\omega) / n_Q^2(2\omega)n_Q(\omega)] \sim 3.6$ (where the subscript "Q" denotes values for the quartz). Also taking into account the measured transmission, T , of the film/substrate to the SH signal, Eq. (1) becomes

$$I/I_Q \sim (l_s/l_{c,Q})^2 T d_{\text{eff}} / (3.6 d_{11,Q}^2) \quad (2)$$

where $l_{c,Q} \sim 20$ μm is the coherence length of the quartz and $d_{11,Q}=0.34$ pm/V is the d_{11} of the quartz.⁶ The transmission loss is mainly due to light scattering in the twinned LaAlO₃ substrate. This yields

$$d_{\text{eff}} \sim (l_{c,Q}/l_s) [(3.6/T)(I/I_0)/(I_Q/I_0)]^{1/2} d_{11,Q} \quad (3)$$

The real-time SH intensity generated from the film during a typical poling experiment is shown in Fig. 2. A very low SH intensity was measured during the initial heating of the film, with no poling voltage applied. The poling voltage was then gradually increased after the film temperature stabilized at $\sim 115^\circ\text{C}$. For all the films studied, a threshold poling voltage of ~ 5 – 6 kV was observed below which little change of the SH signal was measured. The SH intensity steadily increased above the threshold poling voltage. After poling the film for 20 min at 8 kV, the SH intensity reached a plateau. At this point, the temperature was gradually lowered while maintaining an applied voltage of 8 kV; a decrease of the SH intensity was observed during the cooling. This decrease is presumably related to the changes of the tetragonal lattice structure and the associated lattice dipole. Finally, the electric field was removed after the film reached room temperature.

Prior to poling, the as-deposited BaTiO₃ film displayed a d_{eff} [calculated from Eq. (3)] of ~ 1.9 times $d_{11,Q}$. During the poling process at 115°C , the maximum SH intensity

FIG. 2. SH intensity from a BaTiO₃ thin film measured *in situ* during the poling procedure. During A–B, the film was heated to $\sim 115^\circ\text{C}$ at zero poling voltage, then the voltage was gradually increased to a threshold voltage of ~ 6 kV. During B–C, the poling voltage gradually increased to 8 kV. During C–D, the film temperature was gradually lowered while maintaining an 8 kV poling voltage. At D, the poling voltage was turned off as room temperature was reached.

was recorded which yielded a d_{eff} of ~ 10.3 times $d_{11,Q}$ (~ 3.5 pm/V). Immediately after poling, a d_{eff} of ~ 7.9 times $d_{11,Q}$ (~ 2.7 pm/V) was measured at room temperature. For comparison, the nonzero second-order optical nonlinear coefficients of bulk BaTiO₃ are reported to be $d_{33} \sim 6.8$, $d_{31} \sim 15.7$, and $d_{15} \sim 17.0$ pm/V.⁶ To determine whether or not the substrate was contributing to the enhanced SH signal, the same poling and *in situ* SHG measurements were conducted on the LaAlO₃ substrates. No observable SHG was measured. To determine stability, the enhanced SHG of the poled films was monitored over a period of ~ 60 days at room temperature. As shown in Fig. 3, except the first two days, a very slow decay was observed for over two months after the poling. During this period, d_{eff} dropped to ~ 5 times $d_{11,Q}$ (~ 1.7 pm/V). The poling and SHG measurements of the film were also conducted at room temperature, where a much smaller enhancement of the SH intensity was observed.

The measured SH intensity for the textured BaTiO₃ film presumably results from contributions of many grains within the film having different crystal orientations. To

FIG. 3. SH intensity generated from the poled film measured during a period of ~ 60 days after poling. Except an initial decay, very slow relaxation was observed from the poled structure.

FIG. 4. X-ray diffraction ($\theta/2\theta$) scans of a BaTiO_3 film taken before and after the corona poling. The (100) peak of the as-deposited film shifted to a lower angle after the poling.

compare the measured d_{eff} with what would be expected for a BaTiO_3 thin film, the distribution of grain orientation and the symmetry of BaTiO_3 needs to be considered. Tetragonal BaTiO_3 has a lattice dipole along the c axis. Its optical axis coincides with the c axis. In the as-deposited a -axis textured film, the c axis lies in the film plane with its orientation randomly ordered. This randomness in c -axis orientation explains the low SHG of the film measured prior to poling. During poling, the surface charge on the film created by the corona discharge gives rise to a substantial electric field normal to the film plane. The interaction between the lattice dipole and the electric field aligns the c axis parallel to the film normal. This alignment results in the SH intensities generated from the d_{33} 's of the poled crystal grains being constructive to each other. Consequently, a significant enhancement of SHG is observed from the poled film. However, the poling is not expected to introduce additional order into the a - and b -axis orientations for the poled film. This may explain why the measured effective d_{eff} value is much lower than the d_{31} of bulk

BaTiO_3 . This interpretation of crystal realignment upon poling via the lattice dipole and electric field interaction is supported by the $\theta/2\theta$ x-ray diffraction data obtained from the film before and after the poling. Figure 4 shows that the (100) peak of the as-deposited film shifted to a lower angle after poling. This shift suggests that the film changed from a -axis oriented to c -axis oriented after poling.

In conclusion, SHG has been observed for the first time from BaTiO_3 thin films. A significant enhancement of the SHG is observed upon the corona poling of the film. These results demonstrate that BaTiO_3 thin films prepared by MOCVD are very promising for nonlinear optical applications.

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Defect structure of strontium titanate thin films

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The electrical and optical properties of deep-level defects in SrTiO₃ thin films grown by organometallic chemical-vapor deposition were investigated. Transient photocapacitance spectroscopy was used to determine the deep-level defect structure. Metal/insulator/semiconductor diodes were used for these measurements. The dominant defects in the SrTiO₃ consisted of a series of deep-level trapping states with energies in the range of $E_v + 2.4$ to $E_v + 3.15$ eV and a series of shallower traps near the conduction-band edge. The defect concentration ranged from 10^{14} to 10^{18} cm⁻³ in the as-grown films.

I. INTRODUCTION

In recent years there has been a renewed interest in the ferroelectric thin films as high-dielectric-constant materials. As a result of advances in thin-film deposition technology, high-quality high-dielectric-constant films of SrTiO₃, (Ba,Sr)TiO₃, and (Pb,Zr)TiO₃ (PZT) have been prepared.¹ The point defect structure of these complex oxide films is important since it controls their electrical properties. Previous reports on the defect structure of these perovskite titanate oxides have been almost exclusively limited to bulk samples, single crystal or ceramic. In this article we report on the electrical and optical properties of deep-level defects in SrTiO₃ thin films as determined by transient photocapacitance spectroscopy.

II. EXPERIMENT

A. Sample preparation

SrTiO₃ films were deposited by low-pressure, organometallic chemical-vapor deposition (OMCVD) onto silicon substrates as described elsewhere.^{2,3} The film thickness was in the range of 300–750 nm. The films deposited on (100), 2 Ω cm *p*-type silicon were polycrystalline and exhibited resistivities greater than 10^9 Ω cm and dielectric constants up to 100.⁴

Postdeposition vacuum reduction of the films was performed in a hot-wall furnace at 0.1 Torr. Samples were inserted in a quartz tube sealed on one end. At the end of the vacuum reduction treatment the sample was rapidly removed from the furnace to quench in the defects created in the films.

For transient photocapacitance measurements metal/insulating/semiconductor (MIS) diodes were used. Semi-transparent electrodes of 100-Å-thick gold or nickel were evaporated onto the SrTiO₃ surface. Aluminum formed an ohmic contact to the backside of the silicon substrate. The capacitor area was 11.8 mm².

B. Electrical measurements

Transient photocapacitance spectra were recorded at 77 K while biasing the MIS diodes in the accumulation region with a field of 10^4 V/cm. For photocapacitance measurements the samples were illuminated with monochromatic light from a 250 W Oriel quartz-halogen lamp dispersed through a Zeiss MM12 double-prism monochromator. Light pulses 100–150 ms in duration were obtained with an electromechanical shutter. Following excitation the samples were allowed to relax in the dark to the quasiequilibrium capacitance value. The time-dependent capacitance signal was measured with a capacitance meter operating at 1 MHz. The time derivative of the photocapacitance for a specified interval was recorded as a function of the photon energy while continuously varying the photon energy.⁵

III. THEORY OF TRANSIENT PHOTOCAPACITANCE MEASUREMENTS

When a MIS diode is illuminated with sub-band-gap light, a photocapacitance signal arises from the population or depopulation of traps originating in (i) the semiconductor, (ii) the semiconductor-insulator interface, and (iii) the insulator. The time derivative of the photocapacitance is a direct measure of the trap concentration.⁶ Provided the charge is trapped at defects uniformly distributed throughout the insulator and retrapping is negligible, the change in the capacitance upon illumination with respect to time is given by

$$\left. \frac{d(C)}{dt} \right|_{t=0} = \left. \frac{d(Q/V)}{dt} \right|_{t=0} = \left(\frac{qAd_i}{V} \right) \left. \frac{dn_i}{dt} \right|_{t=0}, \quad (1)$$

where Q is the total trapped charge, n_i is the concentration per unit volume of electrons trapped at deep level states, A is the diode area, d_i is the insulator thickness, and V is the effective bias voltage. Because the capacitance signal measured in the transient photocapacitance technique is obtained during the short illumination pulses, only a fraction of the traps in the insulating layer is filled by the light. The total concentration of traps N_t is related to the concentration of trapped electrons n_i by the expression⁶

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FIG. 1. Measured photocapacitance response of a Au/SrTiO₃/p-Si MIS diode at 77 K. The light was turned on at $t=0$ and turned off at $t=100$ ms.

$$\left. \frac{dn_t}{dt} \right|_{t=0} = \sigma \Phi N_t, \quad (2)$$

where σ is the trap capture cross section and Φ is the incident light intensity. By combining the above equations the total trap concentration is given by

$$N_t = \left(\frac{1}{\sigma \Phi} \right) \left(\frac{V}{qdA} \right) \left(\frac{dC}{dt} \right) \Big|_{t=0}. \quad (3)$$

To calculate the trap concentration, the capture cross section was assumed to be 10^{-16} cm², the atomic cross section.

IV. RESULTS AND DISCUSSION

A. Transient photocapacitance measurements

1. Spectral response

Figure 1 shows the typical transient photocapacitance response for a MIS structure with a SrTiO₃ dielectric film. The photocapacitance response of the SrTiO₃ MIS structure at 77 K showed a rapid increase for short times, 0.4–3 ms, after opening the shutter ($t=0$) followed by a gradual rise for longer times. After closing the shutter, the signal slowly decays to the dark photocapacitance value. In contrast upon illumination, the photocapacitance of a Au/p-Si Schottky diode quickly saturated in less than 4 ms, whereas after cessation of the illumination, the capacitance decayed to the dark capacitance value in less than 5 s. The slow response of the SrTiO₃ MIS structures indicates the presence of deep-level traps.

To determine the origin of the deep traps, the spectral response of the photocapacitance was measured over the spectral range of 1.0–3.5 eV. As shown in Fig. 2, the transient photocapacitance spectra of the as-grown SrTiO₃ MIS structures showed several positive peaks. By changing the interval at which the slope was measured, it was possible to separate the contributions of the trapping states. For the spectrum labeled (a) in Fig. 2 measured over the time intervals from 0.4 to 2 ms, a sharp peak was observed at 1.24 eV, two broad peaks at 1.68 and 2.09 eV, and a weak shoulder at 2.5 eV. For spectra measured for times greater than 2 ms, the same sharp peak at 1.25 eV appeared

FIG. 2. Transient photocapacitance spectra of a Au/SrTiO₃/p-Si diode measured over the interval from (a) 0.4 to 2 ms, (b) 3 to 10 ms, (c) 10 to 30 ms, and (d) 30 to 50 ms.

and several broad photocapacitance peaks were observed for higher photon energies [Figs. 2(b)–2(d)].

As for the traps responsible for the observed photocapacitance peaks, they involve interface states or states in the silicon. Evidence for the identification of the deep-level traps as interface states comes from the comparison of photocapacitance spectra of control samples consisting of either a bare silicon substrate or an oxidized silicon substrate prepared at the same temperature and growth conditions as the SrTiO₃ films. As in the case of the Au/SrTiO₃/Si structure, a sharp peak at 1.26 eV with an onset of 1.1 eV was observed in the Au/oxidized silicon control sample for spectra measured for trapping times from 0.4 to 150 ms as shown in Fig. 3. This was attributed to the photogeneration of carriers in the silicon substrate ($E_g=1.17$ eV at 77 K). Likewise, in the Au/silicon Schottky diode control sample, a similar peak was observed. The oxidized silicon substrate showed an additional peak at 1.72 eV for spectra measured at short time intervals of 0.4–2.0 ms similar to

FIG. 3. Transient photocapacitance spectra of a Au/SiO₂/p-Si diode measured over the interval from (a) 0.4 to 3 ms, (b) 10 to 30 ms, and (c) 30 to 50 ms.

that observed in the as-grown SrTiO₃ films [Fig. 3, spectrum (a)]. This peak is apparently due to trapping states in a silicon dioxide layer formed at the SrTiO₃/silicon interface. Formation of an oxide layer at the SrTiO₃/silicon interface was previously suggested to explain the anomalous thickness dependence of the dielectric constant of the SrTiO₃ films.⁴

The transient photocapacitance spectra of the as-grown SrTiO₃ MIS structures were also found to depend on the metal electrode. Figure 4 shows transient photocapacitance spectra recorded for the same sample with a 100 Å gold and 100 Å nickel contact to the SrTiO₃ film. For measurement times of less than 2 ms the dominant peak is

FIG. 4. Transient photocapacitance spectra of a SrTiO₃/p-Si sample measured over the interval of 0.4–2 ms with (a) a 100 Å gold electrode to the SrTiO₃ films and (b) a 100 Å nickel electrode to the SrTiO₃ film.

FIG. 5. Transient photocapacitance spectra of a Au/SrTiO₃/p-Si diode measured over the interval from (a) 5 to 10 ms and (b) 10 to 30 ms.

observed at 2.08 eV in the spectrum of the Au/SrTiO₃/p-Si diode. In contrast, this peak was not seen in the spectrum of the sample with a nickel electrode. The deep level at 1.9–2.1 eV is apparently due to a trapping state at the Au/SrTiO₃ interface.

Defects associated with the SrTiO₃ film were observed in transient photocapacitance spectra measured from the slope for time intervals longer than 3 ms and photon energies greater than 1.4 eV. Since these transitions were not observed in the spectra of either the etched or oxidized silicon control samples, this indicates these defects are in the SrTiO₃ film. For these measurements, the diodes were biased in the accumulation region and were equilibrated in the dark; therefore, the positive capacitance signal results from the filling of empty trapping levels in the oxide films. Thus, the deep levels are referenced to the valence-band edge. As is evident in Fig. 5, the detailed spectra observed depend on the measured time interval.

Altogether ten trapping states were observed in the as-deposited SrTiO₃ films as listed in Table I. Table I also lists the deep-level trap concentrations calculated for several as-deposited SrTiO₃ films. The trap concentrations ranged from 4×10^{14} to 8×10^{17} cm⁻³. The calculated trap concentrations showed that the dominant defects had energies in the range of 2.4–3.16 eV.

2. Defect Identification

Several of the observed defect states are attributed to extrinsic defects. The photocapacitance peaks B, D, C, and F, at $E_v + 1.86$ – 1.95 eV, $E_v + 2.4$ – 2.48 eV, $E_v + 2.1$ – 2.2 , and $E_v + 2.83$ – 2.88 eV listed in Table I are tentatively ascribed

TABLE I. Trap concentration calculated from the transient photocapacitance spectra of several as-grown samples. The capture cross section was assumed to be 10^{-16} cm².

Photocapacitance peak energy (eV)	Trap concentration (cm ⁻³ × 10 ⁻¹⁶)				
	BF141-8	BF186	BF187	BF189	BF142-3
A $E_v + 1.43$	...	...	...	0.4	...
B $E_v + 1.86-1.95$	1	0.3	0.3	0.3	...
C $E_v + 2.1-2.2$	0.1	...	0.04	...	...
D $E_v + 2.4-2.48$	40	5	10	20	4
E $E_v + 2.56-2.64$	80	10	30	30	20
F $E_v + 2.82-2.85$	50	20	20	...	...
G $E_v + 2.94-3.02$	0.6	7	3	30	10
H $E_v + 3.07-3.16$	50	10	...	20	0.9
I $E_v + 3.19-3.24$	...	...	10	...	0.5
J $E_v + 3.33-3.35$	4	6	...	...	...

to iron impurities. In all the as-grown samples, the B and C transitions at 1.86–1.95 and 2.1–2.2 eV, respectively, appeared as weak peaks in the photocapacitance spectra, while the D and F transitions at 2.4–2.48 and 2.83–2.88 eV were more intense (Fig. 5). Both the B and D photocapacitance peaks at $E_v + 1.86-1.95$ and $E_v + 2.4-2.48$ eV appeared as doublets in the spectra of all the as-grown films, while the C and F photocapacitance peaks at $E_v + 2.1-2.2$ and $E_v + 2.83-2.88$ eV were observed in the spectra of some samples and not observed in other samples.

For comparison, Blazey *et al.* reported similar doublets in the optical-absorption spectra of single-crystal SrTiO₃ doped with iron^{7,8} and aluminum.⁹ At 25 K the absorption spectra of iron-doped single-crystal SrTiO₃ consisted of a weak peak at 2.09 and a strong peak at 2.82 eV. The quenching behavior of the electron-paramagnetic-resonance (EPR) spectra measurements confirmed that the two peaks were due to Fe⁴⁺ defects. Doping the same crystals with aluminum forced the iron impurities into a higher valence state. The optical-absorption spectra in this case consisted of a weak peak at 1.99 eV and stronger absorption at 2.53 eV.^{7,9} The quenching behavior of the EPR and optical-absorption spectra confirmed that the absorption bands were due to Fe⁵⁺. The doublet observed in the optical-absorption spectra was explained as transitions involving a splitting of the valence band.

As to the origin of the transition-metal impurities, they presumably originate from the strontium precursors. Further purification of the precursor should result in lower metallic impurity concentrations in the films.

Several of the defect levels observed by photocapacitance are tentatively attributed to native defects in the SrTiO₃ films. This is supported by vacuum annealing experiments. Figure 6 shows the effect of vacuum reduction at 950 °C on the photocapacitance spectrum of a Au/SrTiO₃/p-Si MIS diode. For the spectrum measured over the interval of 100–150 ms, the as-grown sample showed a weak photocapacitance peak at 3.35 eV [Fig. 6, spectrum (a)]. However, after 8 and 16 h in vacuum at 950 °C, strong peaks were observed at 3.25 and 3.33 eV and a weak shoulder at 3.01 eV [Fig. 6, spectra (b) and (c)]. A similar trend was observed in the transient photocapacitance spectra of other SrTiO₃ films reduced under vacuum.

Taking the band-gap energy of SrTiO₃ at 77 K as the reported value of 3.4 eV,¹⁰ the threshold energy of the photocapacitance peaks indicates that these defects are 0.2–0.4 eV below the conduction-band edge.

As to the origin of the deep-level traps observed after vacuum reduction, several investigators have previously reported trapping states in bulk SrTiO₃ with activation energies $E_c - E_t$ in the range of 0.06–0.37 eV and attributed them to oxygen-vacancy-related defects. Amodei and Roach¹¹ reported a trap at $E_c - E_t = 0.105$ eV from the temperature dependence of the free-carrier absorption of undoped, single-crystal SrTiO₃. Morin and Oliver¹² observed a similar band of electron traps at $E_c - E_t = 0.06-0.12$ eV in the thermally stimulated current spectra of single-crystal SrTiO₃. These dominant electron traps were attributed to oxygen vacancy or iron transition-metal/oxygen vacancy defects. A second band of defects was reported by Maksimov *et al.*¹³ in vacuum-reduced polycrystalline SrTiO₃. The temperature dependence of the conductivity revealed a trapping level at 0.35 eV below the

FIG. 6. Effect of vacuum reduction on the transient capacitance spectra of a Au/SrTiO₃/p-Si sample measured over the interval from 100 to 150 ms: (a) as-grown; (b) vacuum reduced at 950 °C for 8 h; and (c) vacuum reduced at 950 °C for 16 h.

conduction band. These authors attributed these defects to double ionized oxygen vacancies in good agreement with the value predicted by theoretical calculations. Nakano and Ichinose¹⁴ also reported a band of defects at $E_c - E_t = 0.28 - 0.37$ eV in reduced, polycrystalline (Sr,Ca)TiO₃. They associated this defect with ionized oxygen vacancies. Thus, the transient photocapacitance peaks at $E_v + 3.25$ and $E_v + 3.33$ eV observed in the present study are tentatively ascribed to oxygen vacancies. Their concentrations are estimated to be of the order of $10^{16} - 10^{17}$ cm⁻³ as noted in Table I.

V. CONCLUSIONS

Transient photocapacitance was performed on SrTiO₃ films prepared by organometallic chemical-vapor deposition. A total of ten trapping states with peak energies at $E_v + 1.43$, $E_v + 1.86 - 1.95$, $E_v + 2.1 - 2.2$, $E_v + 2.4 - 2.48$, $E_v + 2.56 - 2.64$, $E_v + 2.82 - 2.85$, $E_v + 2.94 - 3.02$, $E_v + 3.07 - 3.16$, $E_v + 3.19 - 3.24$, and $E_v + 3.33 - 3.35$ eV were observed in the as-deposited SrTiO₃ films. The trap concentration ranged from 4×10^{14} to 8×10^{17} cm⁻³. The dominant traps in the as-deposited films were attributed to iron. For vacuum-annealed films, the dominant traps were attributed to oxygen vacancies. Evidence for the formation of interfacial traps at an oxide layer at the SrTiO₃/silicon

interface and for traps at the Au/SrTiO₃ interface was also found by transient photocapacitance measurements.

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THE DEFECT STRUCTURE OF BaTiO₃ THIN FILMSFerroelectrics
III

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ABSTRACT

The defect structure of BaTiO₃ thin films grown on (100) Si was examined using transient photocapacitance spectroscopy. The concentration, optical cross section and associated energy levels of both native and impurity defects in as-grown and annealed BaTiO₃ films were evaluated. Deep level defects with peak energies of $E_v + 1.8$, $E_v + 2.4$, $E_v + 2.7$, $E_v + 3.0-3.1$ and $E_v + 3.2-3.3$ eV were observed in the as-grown films. Upon vacuum annealing, the concentration of the traps at $E_v + 3.0$ and $E_v + 3.2$ eV increased while the concentration of the traps at $E_v + 1.8$ and $E_v + 2.4$ eV decreased. The levels at $E_v + 3.0-3.1$ and $E_v + 3.2-3.3$ eV are attributed to oxygen vacancies. The other levels are tentatively ascribed to Fe and Fe related defects.

INTRODUCTION

Considerable interest in BaTiO₃ ferroelectric thin films has emerged due to its dielectric and non-linear optical properties [1]. These properties are strongly influenced by point and extended defect structures. While the point defect structure of BaTiO₃ ceramics has been extensively studied [2-4], much less is known about the defect structure of thin films. Recently, both textured and epitaxial BaTiO₃ thin films were prepared by metalorganic chemical vapor deposition (MOCVD) at temperatures of 800°C [5,6]. The extended defect structure of the films deposited on LaAlO₃ was evaluated using high resolution transmission electron microscopy [7,8]. However, determining the point defects is much more difficult due to their low concentration in thin films. In this paper, the point defect structure of BaTiO₃ thin films is determined using transient photocapacitance spectroscopy. The associated energy level, concentration, and optical capture cross section of the defects present in the BaTiO₃ thin films are reported. Initial measurements indicate the presence of oxygen vacancies in as-grown and annealed films.

EXPERIMENTAL

Sample Preparation

BaTiO₃ thin films were grown by low pressure metalorganic chemical vapor deposition (MOCVD) at 800°C. Barium hexafluoroacetylacetonate:tetraglyme (Ba(hfa)₂(tetraglyme)) and titanium tetraisopropoxide (99.999%) were chosen as the metalorganic precursors. Two grades of Ba(hfa)₂(tetraglyme) (low purity (99+%) and high purity (99.999%)) were used for growth to examine their effect on the resulting electrical properties of the thin films. The substrates consisted of thermally oxidized p-type Si ($\rho = 1-2 \Omega\text{-cm}$), where the SiO₂ layer was 100-300Å. The growth conditions are described in detail, elsewhere [5,6]. X-ray diffraction showed that the BaTiO₃ thin films grown on SiO₂/Si were polycrystalline with a random orientation.

Metal-insulator-semiconductor (MIS) BaTiO₃/SiO₂/Si diodes were fabricated for transient photocapacitance measurements. Semi-transparent Au electrodes (100Å) with an area of 0.118 cm² were evaporated onto the BaTiO₃ surface. To insure the integrity of the electrical contact, a thicker (350-500Å) Au dot ($1.88 \times 10^{-3} \text{ cm}^2$) was evaporated on top of the transparent electrode. Evaporated aluminum formed an ohmic contact to the backside of the Si substrate. For vacuum annealing, the metal contacts were removed and the samples were heated to 950°C at 10^{-4} Torr for time intervals ranging from 4-20 hours.

The resistivity of the BaTiO₃ films was calculated using the linear region of the current-voltage curves from the MIS diode. The as-deposited films had resistivities ranging from 10⁸-10⁹ Ω-cm. However, the highly textured BaTiO₃ films grown on LaAlO₃ with a low purity and high purity Ba precursor were semi-insulating ($\rho = 200$ -1000 Ω-cm) [8] and insulating ($\rho = 10^6$ -10⁷ Ω-cm), respectively [9].

Transient Capacitance Spectroscopy Measurements

Transient photocapacitance spectroscopy of the MIS structures was measured using a technique initially described by Chantre et al. for the study of semiconductors [10]. Recently, this technique has been extended to evaluate MIS structures [11,12]. For this measurement, chopped light from a 250W Oriel quartz-halogen lamp dispersed through a Zeiss monochromator was focussed onto the diode cooled to 80K. Photocapacitance was measured with a capacitance meter at 1MHz. Spectra were recorded while negatively biasing the MIS diodes in the accumulation region with a field of 10⁴ V/cm. The transient photocapacitance was measured for time intervals of 10-100 msec. Following illumination, the sample was equilibrated in the dark for 5 to 7 sec. The time derivative of the photocapacitance was plotted as a function of photon energy.

Upon illumination of an MIS diode, a photocapacitance signal can arise from emptying or filling of traps in (1) the semiconductor, (2) the semiconductor-insulator interface, (3) the SiO₂/BaTiO₃ interface, (4) the insulator, or (5) the BaTiO₃/metal interface. However, the contributions from different traps can be spectrally and temporally resolved. The time derivative of the photocapacitance is a direct measure of the trap concentration. Provided the charge is only trapped at defects uniformly distributed throughout the insulator and retrapping is negligible, the time derivative of the photocapacitance is given by [11]:

$$dC/dt|_{t=0} = d(Q/V)/dt|_{t=0} = (qAd_i/V) dn_t/dt|_{t=0} \quad (1)$$

where Q is the total trapped charge, q is unit charge per electron, A is the diode area, d_i is the insulator thickness and V is the effective bias. Since short illumination times are used, only a fraction of the traps in the insulator layer are populated. The total concentration of traps, N_t, is related to the concentration of trapped electrons, n_t, by the expression [10,12]:

$$dn_t/dt|_{t=0} = \sigma\Phi N_t \quad (2)$$

where σ is the optical cross section of the trap and Φ is the intensity of the light. Combining Eq. 1 and 2, the total trap concentration is given by

$$N_t = (1/\sigma\Phi) (V/qd_iA) dC/dt|_{t=0} \quad (3)$$

The optical cross section is obtained by measuring the capture rate of an electron, c_a, by the trap, given by

$$c_a = \sigma_a\Phi \quad (4)$$

The capture rate of an electron is determined from the fit of a semi-log plot of the photocapacitance as a function of time [13]. Substituting the intensity of light and measured capture rate, c_a, into Eq. 4, the optical cross section of the trap is obtained.

RESULTS AND DISCUSSION

As-Deposited BaTiO₃ Films

The photocapacitance response of a typical BaTiO₃/SiO₂/Si MIS diode is plotted as a function of the illumination time in Figure 1. For a photon energy of 2.7 eV (Fig. 1 curve a), the photocapacitance increases rapidly up to 10 msec and then begins to saturate. For an excitation energy of 3.17 eV, the photocapacitance increases at a slower rate (Fig. 1 curve b).

The time derivative of the photocapacitance signal is shown as a function of energy for the above sample deposited with a high purity Ba source (Fig. 2a). Transient photocapacitance peaks were present at $E_v + 1.2$, $E_v + 1.4$, and $E_v + 3.1$ eV. A shoulder was also observed in the spectrum at $E_v + 3.2$ eV (Fig. 2a). For comparison, the transient photocapacitance spectrum of a typical BaTiO₃ film grown with a low purity precursor obtained for a 20-40 msec time interval is shown in Fig. 2b. In addition to the peaks at $E_v + 1.2$, $E_v + 1.4$, and $E_v + 3.1$ eV, a broad transition with a peak at $E_v + 1.8$ eV and a shoulder at $E_v + 2.4$ eV is observed in the lower purity film.

To determine the origin of the transitions observed in the BaTiO₃ MIS diodes, the transient photocapacitance of a control sample, SiO₂/Si MIS diode was examined. The transient photocapacitance spectrum of a SiO₂/Si control sample measured using a 20-40 msec time interval has peaks at 1.2-1.3, 1.4 and 2.4 eV (Fig. 3). The 1.25 eV peak with a threshold energy of 1.1 eV arises from the photoexcitation of intrinsic carriers in Si. The possible identity of the levels at 1.4 and 2.4 eV are only suggested here by comparing to other work. The level at 1.4 eV was previously observed as a shoulder in transient photocapacitance spectroscopy of MIS structures with thermally grown SiO₂ on Si and attributed to a defect in the SiO₂ layer [12]. Additionally, the peak at 2.4 eV was previously observed with photo-depopulation/injection measurements on similar structures and was attributed to Na in the SiO₂ [14]. The Na in the SiO₂ layer is presumably a contaminant in the deionized water used during oxidation. The peaks at 1.25 and 1.4 eV have the same energy and shape in both the BaTiO₃/SiO₂/Si (Fig. 2) and SiO₂/Si (Fig. 3) spectra. This indicates that these peaks are of common origin and involve transitions in the SiO₂/Si. However, the broad transition in Fig. 2(b) with a shoulder at 2.4 eV is not attributed to defects in the SiO₂/Si layer.

Fig. 1. The time dependent photocapacitance response of a typical BaTiO₃ MIS diode at two excitation energies.

Fig. 2. Transient photocapacitance obtained at a 20-40 msec time interval for a BaTiO₃ film grown with a) a high and b) a low purity precursor.

From the comparison of the BaTiO₃ and SiO₂/Si MIS diode spectra, the transient photocapacitance peaks at E_v+1.85, E_v+2.4, E_v+3.0-3.1 and E_v+3.2-3.3 eV are attributed to transitions in the BaTiO₃ film. The optical capture cross section of these defects is related to the time dependence of the photocapacitance (Eq. 4). The measured optical cross section, σ , for the defects with energy less than 2.9 eV is 10⁻¹⁴ cm²; whereas, 10⁻¹³ cm² is obtained for traps at higher energies. Upon substitution of the appropriate values for σ into Eq. 3, a trap concentration of 10¹³-10¹⁴ cm⁻³ was estimated for the various defect levels. The measured levels, their concentration and optical capture cross section for several BaTiO₃ films are listed in Table I.

Fig. 3. Transient photocapacitance spectrum at a 20-40 msec time interval for a SiO₂/Si MIS diode.

Table I. The associated energy level, light intensity, optical cross section and concentration of the defects in several as-grown BaTiO₃ films measured with transient photocapacitance. Peak energies are referenced from the valence band. Samples 297, 298, and 302 were prepared using a high purity Ba precursor.

Energy (eV)	Φ (cm ⁻² .sec ⁻¹)	σ (cm ²)	Trap Concentration (cm ⁻³)				
			256	279	297	298	302
1.7-1.9	1.6x10 ¹⁴	10 ⁻¹⁴	10 ¹³	3x10 ¹³	--	--	--
2.4	7x10 ¹⁴	10 ⁻¹⁴	2x10 ¹³	1x10 ¹⁴	--	--	--
2.7-2.8	8x10 ¹²	5x10 ⁻¹⁴	6x10 ¹³	--	--	--	--
3.0-3.1	4x10 ¹²	10 ⁻¹³	7x10 ¹³	8x10 ¹³	10 ¹⁴	10 ¹³	3x10 ¹³
3.2-3.3	2x10 ¹²	10 ⁻¹³	3x10 ¹³	9x10 ¹³	7x10 ¹³	10 ¹³	8x10 ¹³

Since the defect levels at E_v+3.0-3.1 and E_v+3.2-3.3 eV were observed in both low and high purity films, they are likely to be related to native defects (Table I). On the other hand, the defect levels at E_v+1.8 and 2.4 eV are tentatively attributed to the residual impurities since they are only seen in the lower purity films (Table I).

Vacuum Reduction Experiments

To identify the traps with levels at E_v+3.0-3.1 and E_v+3.2-3.3 eV in BaTiO₃, the samples were reduced in a vacuum (PO₂ ~ 10⁻⁵ Torr) at 950°C and the transient photocapacitance was subsequently measured (Fig. 4). The peak intensity of the levels at E_v+3.0-3.1 eV and E_v+3.2-3.3 eV increased following vacuum reduction, which suggests that these defects are related to oxygen vacancies. This observation is

Fig. 4. Transient photocapacitance at a 20-40 msec time interval for an a) as-grown and b) 12 hour vacuum reduced film.

consistent with previous optical absorption measurements of vacuum reduced single crystal BaTiO_3 , where the absorption peak at $E_v + 3.0\text{eV}$ was attributed to oxygen vacancies [15]. Furthermore, theory predicts that the energy levels associated with oxygen vacancies in BaTiO_3 will lie near the conduction band [16,17] of BaTiO_3 , 3.5 eV [18,19].

Further analysis of the vacuum annealed samples derived from the 99+% pure Ba precursor showed that the measured photocapacitance peak intensity of the levels at $E_v + 1.8$ and $E_v + 2.4\text{eV}$ decreased (Fig. 5a), while a new peak at $E_v + 2.65\text{eV}$ (Fig. 5b) developed. In contrast, vacuum reduction of films derived from the high purity precursor did not show these transitions that lie deeper within the bandgap. Therefore, these trapping levels are believed to be impurity related. Since Fe is one of the most abundant impurities in undoped bulk BaTiO_3 [20], these defects most likely involve iron. This is consistent with photoconductivity measurements which identified an Fe related trap at $E_v + 2.6$ eV in $\text{Fe}:\text{BaTiO}_3$ [21]. In addition, electron paramagnetic resonance and optical absorption measurements of single crystal $\text{Fe}:\text{BaTiO}_3$ showed that Fe^{4+} yielded an absorption peak at 2.69 eV, which correlates well with the peak at $E_v + 2.65\text{eV}$ in the BaTiO_3 films [22]. Other optical absorption studies have shown Fe related defects with peaks at $E_v + 2.34$ and $E_v + 2.48$ eV [23]. We propose that the changes in the peak intensities for the mid-gap levels, after vacuum reduction may result from the reduction of Fe^{5+} to Fe^{4+} . Therefore, the levels in the as-deposited films at $E_v + 1.85$ eV and $E_v + 2.4\text{eV}$ may be Fe related.

CONCLUSIONS

In summary, transient photocapacitance spectroscopy has been used to determine the energy levels, optical cross section, and concentration of deep level defects in BaTiO_3 thin films. The defect levels at $E_v + 3.0\text{--}3.1\text{eV}$ and $E_v + 3.2\text{--}3.3\text{eV}$ in the BaTiO_3 films are attributed to native oxygen vacancies with a concentration of ($\sim 10^{14}\text{ cm}^{-3}$) and $\sigma = 10^{-13}\text{ cm}^2$. In addition, the transient photocapacitance of BaTiO_3 films indicated the presence of residual impurity related defects, tentatively ascribed to Fe impurities. These traps had energies of $E_v + 1.8\text{eV}$, $E_v + 2.4\text{eV}$ and $E_v + 2.7\text{--}2.8\text{eV}$ with $\sigma = 10^{-14}\text{ cm}^2$. A detailed model for the defect structure of BaTiO_3 thin films based on resistivity and transient capacitance will follow in future papers.

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Fig. 5. Transient photocapacitance spectra at a 20-40 msec time interval for an a) as-grown and 12 hour reduced and b) 20 hour reduced BaTiO_3 film.

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**FERROELECTRIC PROPERTIES OF a -AXIS
TEXTURED BaTiO_3 THIN FILMS**

Ferroelectrics III

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ABSTRACT

Ferroelectric and dielectric properties were measured for BaTiO_3 thin films prepared by metalorganic chemical vapor deposition which were highly a -axis textured. No ferroelectric hysteresis was observed from the as-deposited BaTiO_3 films on Pt coated MgO. Upon applying an electric field exceeding a threshold electric field, $E_t \sim 50 - 100$ kV/cm, a ferroelectric hysteresis was observed. A spontaneous polarization $P_s \geq 15$ $\mu\text{C}/\text{cm}^2$ was measured for the textured films.

INTRODUCTION

The realization of ferroelectric thin films for electronic applications such as nonvolatile memories and dielectric thin films relies on the growth of high quality films on conducting substrates. While epitaxial growth of BaTiO_3 thin films on insulating substrates such as LaAlO_3 and SrTiO_3 has been reported[1,2], the film deposition on metallic substrates has been generally less successful. To date, only deposition of randomly oriented BaTiO_3 films on metallic substrates were reported using metalorganic chemical vapor deposition (MOCVD). In this paper, we report the successful growth of highly a -axis textured BaTiO_3 thin films on Pt coated MgO, and their measured ferroelectric and dielectric properties.

EXPERIMENTAL PROCEDURE

The BaTiO_3 thin film deposition process was similar to that reported earlier[1]. A Pt layer of ~ 1 μm thick was sputtered on (100) MgO substrates. A BaTiO_3 thin film was subsequently deposited on Pt via MOCVD. Both a -axis textured and randomly oriented BaTiO_3 films were obtained. The textured films were obtained only on the highly (100) textured Pt layer. The film thickness is in the range of 0.3 - 1.0 μm . For electrical characterization, Al dots of 350 μm diameter were evaporated on to the film which served as the top electrical contacts. Part of the film was etched away to expose the Pt bottom electrode. Fig. 1 shows the sample configuration for the electrical properties measurement. The ferroelectric hysteresis of the film was measured using a modified Sawyer-Tower circuit[3] with a 600 Hz sinusoidal applied field. The dielectric properties were measured using a computer interfaced Hewlett-Packard impedance analyzer. A DC bias voltage was applied across the film through a voltage source also controlled by the computer. The amplitude of the AC signal used for the impedance measurement was 20 mV.

Fig. 1. Sample configuration for electrical measurements on BaTiO₃ thin films.

RESULTS AND DISCUSSIONS

Fig. 2 is a x-ray diffraction $\theta / 2\theta$ scan of a highly *a*-axis textured BaTiO₃ film. The strongest diffraction peaks were from (100) and (200) BaTiO₃ reflections. The (110) or {101} reflections were very weak, indicating a highly preferred orientation of the film with the *a*-axis aligned parallel to the film normal. The average grain size of the film is $\sim 0.2 \mu\text{m}$ as determined from the surface morphology using scanning electron microscopy and atomic force microscopy. Fig. 3 shows the measured frequency dependence of the film's dielectric constant and dissipation factor in the frequency range of 200 Hz to 1 MHz. The dielectric constant, $\epsilon \sim 10$, measured for the as-deposited films was low compared to the values for bulk BaTiO₃ single crystals ($\epsilon_c \sim 200$ and $\epsilon_a \sim 4000$) [4] and that reported for BaTiO₃ thin films ($\epsilon \sim 100 - 550$) [5,6,7]. The measured dissipation factor, $D \sim 0.03$, showed little dispersion over the measured frequency range. The as-deposited film generally exhibited no observable ferroelectric hysteresis.

Fig. 2. X-ray diffraction $\theta / 2\theta$ scan of a BaTiO₃ thin film deposited on Pt coated MgO substrate.

Fig. 3. Dielectric constants measured from the as-deposited film, and after $E > E_t$ was applied across the film.

After a DC electric field exceeding a threshold electric field, E_t , was applied across the film, the dielectric constant increased substantially, usually by one order of magnitude to $\epsilon \sim 100$ (Fig.3). Concurrently the dissipation factor increased to $D \sim 0.1$. Nevertheless the film remained highly resistive. The increased dissipation factor corresponded to a resistivity of $300 \text{ M}\Omega\text{-cm}$ across the film. This was in agreement with the directly measured film resistance. The dielectric constant remained at this value after withdrawing of the applied DC field. E_t measured for different films and contacts ranged from $\sim 50 - 100 \text{ kV/cm}$. Also plotted in Fig. 3 is the film's dielectric constant and dissipation factor measured at zero bias voltage after $E > E_t$ was applied.

A ferroelectric hysteresis was observed after the threshold field was exceeded. Fig. 4 shows the measured uncompensated hysteresis loop for an *a*-axis textured film after an electric field, $E > E_t$, was applied. The hysteresis was obtained at the maximum amplitude of the sinusoidal voltage source. Due to the extremely high coercive electric field of the film, saturation of the hysteresis was not observed as indicated by the slightly rounded shape of the hysteresis loop. The rounding of the hysteresis before saturation was also observed in the randomly oriented film where the coercive field was much lower and saturation can be reached. From the hysteresis after $E > E_t$ was applied, the values of spontaneous polarization $P_s \geq 15 \mu\text{C}/\text{cm}^2$, remanent polarization $P_r \sim 13 \mu\text{C}/\text{cm}^2$, and coercive electric field $E_c \sim 220 \text{ kV}/\text{cm}$ were determined. (For comparison, the reported values for bulk single crystal BaTiO_3 are $P_s \sim 26 \mu\text{C}/\text{cm}^2$ and $E_c \sim 5 \text{ kV}/\text{cm}$)[4].

Fig. 4. Ferroelectric hysteresis measured after an electric field $E > E_t$ was applied across an *a*-axis textured BaTiO_3 thin film.

The measured electrical properties can be related to the crystalline structure of the BaTiO_3 thin film. For the *a*-axis textured film, the *c*-axis lies in the film plane. The depolarization energy arising from the lattice dipole interaction favors the *c*-axis of the different grains being "randomly" oriented in the film plane. This *c*-axis orientation configuration, combined with the strain and the fine grained structure of the film, may contribute to the low dielectric constant and the lack of ferroelectric hysteresis observed from the as-deposited BaTiO_3 thin films[8].

Upon poling with an external electric field, the lattice dipoles in the ferroelectric crystals are aligned to the field direction. For bulk BaTiO_3 , poling was achieved with moderate electric fields ($0.5 - 2 \text{ kV}/\text{cm}$) near the Curie temperature[9]. The change of the dielectric constants of BaTiO_3 films as illustrated in Fig. 3 can be attributed to the poling of the film. Due to the small film thickness, very high electric field (orders of magnitude higher than the poling field of the bulk BaTiO_3) could be applied across the film, thus enabling the film to be poled at room temperature. At the threshold field, the lattice dipoles were aligned by the electric field, resulting in the *c*-axes being oriented to the film normal. As a result of this lattice dipole alignment, relatively high dielectric constants and ferroelectric hysteresis loops were observed after the threshold field was exceeded.

The ferroelectric and dielectric properties measured from the BaTiO_3 thin films depended on the film's crystalline structure. Table 1. lists the properties measured for the *a*-axis textured and the predominantly randomly oriented BaTiO_3 thin films derived from MOCVD. Also listed are the electrical properties of the BaTiO_3 thin films reported by other research groups. In

comparison, the charge storage parameters (P_s , P_r) presented in this work were the highest among the reported values for BaTiO₃ thin films so far.

Table 1. The electrical properties of the MOCVD derived BaTiO₃ thin films and those reported by other research groups.

Method	substrate	Crystal Quality	Properties	Reference
MOCVD	Pt	a-axis textured	$P_s \geq 15 \mu\text{C}/\text{cm}^2$ $P_r \sim 13 \mu\text{C}/\text{cm}^2$ $E_c \sim 200 \text{ kV}/\text{cm}$ $\epsilon \sim 100$, $D \sim 0.03 - 0.1$	This work
MOCVD	Pt	random	$P_s \sim 16 \mu\text{C}/\text{cm}^2$ $P_r \sim 10 \mu\text{C}/\text{cm}^2$ $E_c \sim 70 \text{ kV}/\text{cm}$ $\epsilon \sim 100$, $D \sim 0.03 - 0.1$	This work
Reactive evaporation	(100)Pt	(100) epitaxy	$P_s \sim 11 \mu\text{C}/\text{cm}^2$ $P_r \sim 4.7 \mu\text{C}/\text{cm}^2$ $\epsilon \sim 550$ (1 kHz), $D \sim 0.01-0.05$	Iijima et. al, 1990[5]
r.f. magnetron sputtering	Pd	random	$\epsilon \sim 100 - 330$	Shi et. al, 1991[6]
MOCVD	NiCr/BaTiO ₃	random	$\epsilon \sim 250$	Kwak et. al, 1991[7]

For bulk single crystal BaTiO₃ : $P_s \sim 26 \mu\text{C}/\text{cm}^2$, $E_c \sim 1.5 \text{ kV}/\text{cm}$, $\epsilon_c \sim 200$, $\epsilon_a \sim 4000$. from Merz et. al, 1953[4].

SUMMARY

Highly a-axis textured BaTiO₃ thin films were deposited on the Pt coated MgO substrates using MOCVD. Dielectric and ferroelectric properties were measured for the films. Upon poling of the film, spontaneous polarization of $\geq 15 \mu\text{C}/\text{cm}^2$ was achieved. The poled films exhibited polarization parameters comparable to that of the bulk single crystal BaTiO₃.

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