

Structural and optical properties of epitaxial BaTiO₃ thin films grown on GdScO₃(110)

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We have prepared 1- μm -thick epitaxial BaTiO₃ thin films on GdScO₃(110) using pulsed laser deposition. The structural perfection of the films was revealed by a rocking curve width of $\Delta\omega=0.13^\circ$ for the 002 BaTiO₃ reflection and a Rutherford backscattering spectrometry/channeling minimum yield, χ_{min} , of 0.5% measured for the Ba signal behind the surface peak. High-resolution transmission electron microscopy revealed an epitaxial relationship between BaTiO₃ and GdScO₃ and a sharp interface between the substrate and the film. The refractive index of the BaTiO₃ film was $n_o=2.329\pm0.002$ and $n_e=2.307\pm0.002$ at a wavelength of 632.8 nm and $n_o=2.248\pm0.002$ and $n_e=2.228\pm0.002$ at a wavelength of 1523 nm. The optical losses were less than 2 dB/cm at a wavelength of 632.8 nm. © 2003 American Institute of Physics. [DOI: 10.1063/1.1575935]

The electro-optic properties of BaTiO₃ are utilized in a number of thin film devices, including modulators. Thin film BaTiO₃ Mach-Zehnder modulators with 95% modulation efficiency were recently demonstrated using epitaxially grown BaTiO₃ on MgO(100).¹ The use of MgO as a substrate can, however, be problematic: it is well known that Ca impurities within the MgO substrates segregate at the substrate surface at high temperatures.^{2,3} Since high temperatures are frequently inevitable, the yield of optically transparent BaTiO₃ films on MgO is limited to about 10% due to such outdiffusion and surface segregation. We present an improvement of this situation by introducing the rare-earth scandates (ReScO₃) as alternative substrates for the growth of epitaxial BaTiO₃ films.

In order to provide high quality heteroepitaxial growth with low dislocation density, the identification of a suitable substrate material is critical. One decisive parameter is the lattice constant of the substrate, which has to closely match the parameters of the thin film. In Fig. 1 the lattice parameters of several frequently used oxide substrate materials together with those of some thin film materials are shown. The arrow indicates the range of lattice constants for Ba_xSr_{1-x}TiO₃. At $x=1$, Ba_xSr_{1-x}TiO₃ becomes pure BaTiO₃. For BaTiO₃ thin films two substrates appear to be the best choice from Fig. 1: KTaO₃ and MgAl₂O₄. Of course, more than the lattice parameter is important.⁴ For example chemical compatibility, thermal expansion match and the stability of the substrates used for epitaxy at elevated

temperatures are also very important. The high growth temperatures, typically 800–850 °C,¹ and the reactive oxygen atmosphere during growth limit the number of substrate candidates. Although the perovskite KTaO₃ is available commercially and has a lattice constant of 3.99 Å (an excellent lattice match to BaTiO₃), it suffers from significant potassium loss at substrate temperatures (T_{sub}) of greater than about 750 °C,⁵ which is less than the growth temperatures mentioned earlier. If the growth temperature stays below 750 °C this substrate could be considered as a good candidate as well. Another problem stems from the thermal expansion coefficient, which over the 25–700 °C temperature range averages $5.9\times10^{-6}/\text{K}$ for MgAl₂O₄.⁶ This is smaller than the average thermal expansion coefficient of $10.1\times10^{-6}/\text{K}$ for

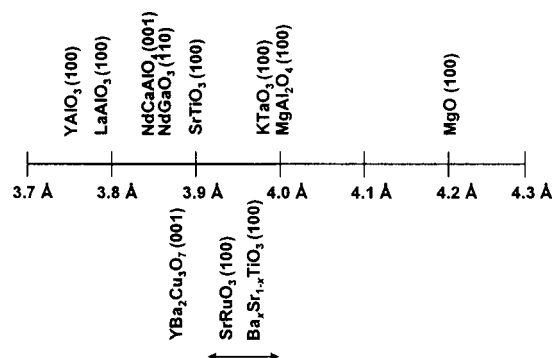


FIG. 1. Approximate lattice constants of the square surface net of several commercially available substrates typically used for the heteroepitaxial growth of oxide thin films. For comparison, the lattice constants of the square surface net of some thin film materials are mentioned below the line. The arrow denotes the lattice parameter range of (Ba,Sr)TiO₃.

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TABLE I. Lattice constants of a class of possible substrate materials: the rare-earth scandates (see Refs. 9 and 10). The lattice parameters a , b , and c of the orthorhombic structure as well as $c/2$ and $\sqrt{a^2+b^2}/2$ are listed for the different materials.

Material	a (Å)	b (Å)	c (Å)	$c/2$ (Å)	$\sqrt{a^2+b^2}/2$ (Å)
LaScO ₃	5.678	5.787	8.098	4.049	4.053
CeScO ₃	5.787	5.626	8.047	4.023	4.036
PrScO ₃	5.770	5.602	8.010	4.005	4.021
NdScO ₃	5.770	5.579	7.999	4.000	4.013
SmScO ₃	5.524	5.750	7.953	3.977	3.987
EuScO ₃	5.502	5.750	7.954	3.977	3.979
GdScO ₃	5.488	5.746	7.934	3.967	3.973
TbScO ₃	5.466	5.727	7.915	3.958	3.958
DyScO ₃	5.440	5.713	7.887	3.943	3.944
HoScO ₃	5.427	5.714	7.895	3.947	3.940

BaTiO₃ over the same temperature range.⁶ This difference can lead to cracks and other defects in BaTiO₃ films grown on MgAl₂O₄. A maximum thickness of 500 nm for crack-free BaTiO₃ on MgAl₂O₄ has been reported.⁷ Thus, no suitable commercially available substrate with good lattice match exists for the growth of BaTiO₃ at elevated substrate temperatures.

We propose the rare-earth scandates for the growth of Ba_xSr_{1-x}TiO₃ and other perovskites with lattice parameters in the 3.94–4.05 Å range as a class of substrates. The rare-earth scandates were previously considered as possible laser crystals.⁸ The lattice parameters of several rare-earth scandates are listed in Table I. The rare-earth scandates are all orthorhombic at room temperature and isostructural with GdFeO₃ (and NdGaO₃, SrRuO₃, etc.). GdScO₃, for example, has lattice constants of $a=5.488$ Å, $b=5.746$ Å, and $c=7.934$ Å and belongs to the space group $Pbnm$. In this structure the (110) plane, spanned by $[1\bar{1}0]$ and $[001]$ directions, provides a nearly square base with $c/2=3.967$ Å and $\sqrt{a^2+b^2}/2=3.973$ Å. As is shown by the last two columns in Table I, the pseudocubic lattice constants of the scandates range from 3.94 to 4.05 Å. Therefore, these materials could be superior to existing substrate options for the epitaxial growth of perovskites with lattice parameters in this range. In this letter we evaluate the rare-earth scandates as useful substrates. One rare earth scandate that is currently commercially available,¹¹ DyScO₃, is lattice matched to SrRuO₃ better than 0.4%. Here we focus on the growth of BaTiO₃ on GdScO₃ to obtain optically transparent films for use as waveguides and electro-optic devices. GdScO₃(110) has the lowest misfit to BaTiO₃ of the rare-earth scandates which are now available commercially.¹¹

BaTiO₃ films were grown by pulsed laser deposition (PLD) using a KrF excimer laser (wavelength 248 nm, pulse length 20 ns, pulse frequency 10 Hz, and a fluence of 2.5 J/cm²).¹² The substrates, single-side polished untwinned GdScO₃(110) single crystals ($5\times10\times0.8$ mm³), were placed 4 cm from the target on a SiC resistive heater. The BaTiO₃ target was a sintered single-phase cylinder. BaTiO₃ films were grown at substrate temperatures ranging from 600 to 800 °C under an oxygen atmosphere of 2×10^{-3} mbar. The crystallinity, epitaxial orientation relationship, and the stoichiometry of the films were investigated by Rutherford backscattering spectrometry and channeling (RBS/C), x-ray

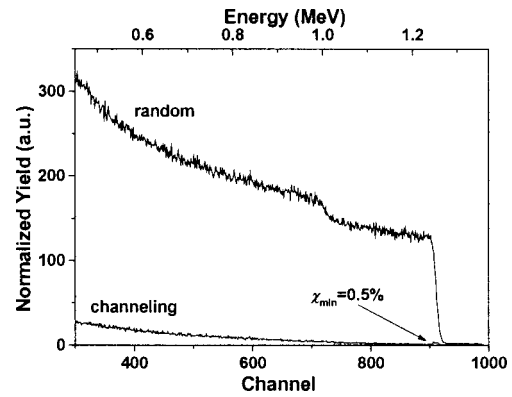


FIG. 2. RBS and channeling measurement of a 1- μ m-thick BaTiO₃ film on GdScO₃ grown at $T_{\text{sub}}=650$ °C.

diffraction (XRD) (θ - 2θ scans, rocking curve measurements, and ϕ scans) with a nonmonochromatic Cu K_{α} source, and high-resolution transmission electron microscopy (HRTEM). The BaTiO₃ film thickness was adjusted to 1 μ m to obtain low loss planar waveguides for optical characterization. The transparency and in-plane and out-of-plane refractive indices of the BaTiO₃ films were measured using a prism coupling setup.¹³

The stoichiometry of the films was established by RBS/C. Comparison of simulated and measured spectra verified a 1:1 Ba:Ti ratio over the entire range of PLD growth conditions investigated. The observed channeling $\chi_{\text{min}}=0.5\%$ (Fig. 2) attests to the high crystalline quality of the BaTiO₃. This value is lower than the lowest values for BaTiO₃ films grown on MgO(100).¹² The lattice parameters determined from XRD analysis were $c=4.08\pm0.01$ Å (out-of-plane) and $a=3.99\pm0.02$ Å (in-plane). These values are comparable to the lattice parameters observed in thick (and thus relaxed) epitaxial BaTiO₃ films grown on SrTiO₃.¹⁴ In addition, the crystalline perfection of the films was corroborated by a full width at half maximum (FWHM) of the 002 reflection of BaTiO₃ grown at 750 °C of $\Delta\omega=0.13^\circ$. All of the BaTiO₃ films had FWHMs below $\Delta\omega=0.4^\circ$, a typical value for BaTiO₃ grown on MgO(100). Even for BaTiO₃ films 1.5- μ m-thick we observed no cracks. This is crucial for optical devices. This indicates that the thermal expansion coefficient of GdScO₃ is reasonably well matched to the thermal expansion coefficient of BaTiO₃.¹⁵

The improved microstructure of the BaTiO₃ films was confirmed by HRTEM. Figure 3(a) shows a low-magnification cross-sectional image revealing the typical mi-

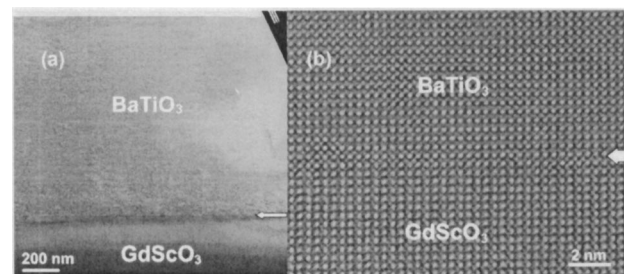


FIG. 3. (a) Cross-sectional TEM of a 1- μ m-thick BaTiO₃ film grown at $T_{\text{sub}}=650$ °C on GdScO₃. (b) Cross-sectional HRTEM of the interface of a BaTiO₃ film grown at $T_{\text{sub}}=650$ °C on GdScO₃. The position of the BaTiO₃/GdScO₃ interface is indicated by the arrows.

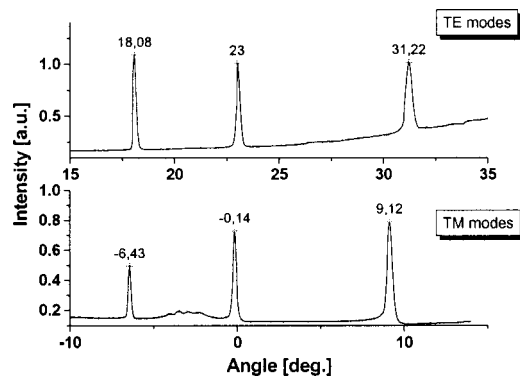


FIG. 4. Bright-line spectra of the TE and TM modes at a wavelength of 632.8 nm in a 1- μm -thick BaTiO₃ film grown at $T_{\text{sub}}=650^\circ\text{C}$ on a GdScO₃ substrate.

crostructure observed. In comparison with BaTiO₃ films grown under similar conditions by PLD on MgO, a lower density of lattice defects was observed. A higher perfection is also obtained at the interface in the BaTiO₃/GdScO₃ system, denoted by an arrow in Fig. 3(b), than in the BaTiO₃/MgO system.¹⁶

Assuming a rectangular homogeneous refractive index profile of the BaTiO₃ film, the TE (in-plane) and TM (out-of-plane) refractive indices were evaluated for a 1- μm -thick film. Figure 4 shows the bright-line angular spectra for TE and TM polarization at a wavelength of 632.8 nm. From these spectra the refractive indices of the film and substrate were calculated. The refractive indices of the BaTiO₃ film are $n_o=2.329\pm0.002$, and $n_e=2.307\pm0.002$ and the refractive index of the GdScO₃(110) substrate is $n=2.08\pm0.01$ at a wavelength of 632.8 nm. Rotation of the sample by 90° yielded the same values of the refractive index, showing that the in-plane index is homogenous. We have also performed these measurements at a wavelength of 1523 nm and the refractive indices are: $n_o=2.248\pm0.002$, and $n_e=2.228\pm0.002$ for the film and $n=2.050\pm0.002$ for the substrate. These values are valid for all of the samples grown in this investigation. The observed values of the refractive index of the substrate are in accordance with prior work.⁸

If we assume that the scattered light intensity is proportional to the total light intensity inside the waveguide, the optical losses in the waveguide can be determined. This assumption is correct for homogenous waveguides, which the planar BaTiO₃ films appear to be from the structural data. For low losses, the accuracy of this method is decreased, but it still gives a good approximation of the film transparency. Figure 5 shows the measured scattering intensity from a planar waveguide grown at 650 °C as a function of propagation length along the waveguide. A damping coefficient of 2.2 dB/cm was calculated from the experimental data. This low coefficient was determined for four different samples. We expect the losses at a wavelength of 1550 nm to be even lower because the losses that come from the surface roughness decrease if the wavelength increases.

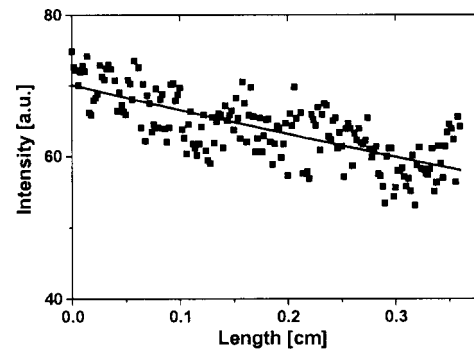


FIG. 5. Scattered intensity from the TE mode for a 1- μm -thick BaTiO₃ film grown at $T_{\text{sub}}=650^\circ\text{C}$ on GdScO₃. The exponential fit gives a loss of 2.2 dB/cm.

Epitaxial BaTiO₃-films grown on GdScO₃(110) exhibit superior structural perfection ($\chi_{\text{min}}=0.5\%$ and $\Delta\omega=0.13^\circ$) compared to BaTiO₃ grown on other substrate materials. The 2.2 dB/cm optical losses measured are comparable to the best values achieved in BaTiO₃ films grown on MgO and are far more reproducible compared to growth on MgO. These results demonstrate the promise of rare-earth scandates as a class of perovskite substrates ideal for perovskites with sub-cell spacing in the 3.94–4.05 Å range.

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