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THIN-FILM PEROVSKITES - FERROELECTRIC MATERIALS FOR INTEGRATED OPTICS

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ABSTRACT

Optical guided wave (OGW) devices, based on $LiNbO_3$ or GaAs, are commercially available products with established markets and applications. While $LiNbO_3$ presently dominates the commercial applications, there are several drivers for the development of improved electro-optic (EO) materials. If the appropriate crystal quality could be obtained for thin-film $BaTiO_3$ supported on MgO for example, or for an integrated $BaTiO_3$/MgO structure on silicon or GaAs, then the optimum OGW device structure might be realized. We will report on our results for the growth of optical quality, epitaxial $BaTiO_3$ and $SrTiO_3$ on single-crystal MgO substrates using source shuttering molecular beam epitaxy (MBE) techniques. We will also discuss how these materials can be integrated onto silicon. Our MBE studies show that, for this important class of perovskite oxides, heteroepitaxy between the perovskites and alkaline earth oxides is dominated by interfacial electrostatics at the first atomic layers. We have been able to demonstrate that a layer-by-layer energy minimization associated with interfacial electrostatics leads to the growth of high quality thin films of these materials. We have fabricated waveguides from these materials, and the optical clarity and loss coefficients have been characterized and found to be comparable to in-diffused waveguide structures typically represented by Ti drifted $LiNbO_3$.

INTRODUCTION

The field of integrated optics is remarkable in that it started from ideas that did not have existing implementations in real material systems(1). The basic building blocks envisioned by its inventors simply did not exist. The field grew out of a desire to take optical communication systems that did exist as prototype communication optical components and to miniaturize them onto a single substrate. Specifically, the optical components suggested by the original proposal were thin films of electro-optic (EO) and lasing materials deposited onto suitable substrates. Initial attempts to develop such materials failed because the polycrystalline films that resulted from deposition technologies available at the time were not as optically clear as the bulk, single crystal materials the films were modeled after(2). As a result of these attempts, it was recognized early on that what was needed were single crystal, epitaxial thin film/substrate material systems that could be developed into optical guided wave (OGW) devices.

Largely because of the lack of optimum, thin film EO materials for switching applications, Ti drifted $LiNbO_3$ has emerged as the only practical candidate for device development and commercialization(3). While this system enjoys considerable success in OGW device applications, inherent limitations associated with embedding waveguides in a bulk ferroelectric continue to point to the need for thin film materials. For device speed and efficiency, the ideal waveguide structure consists of a thin film material with a large electro-optic coefficient deposited onto a material possessing a small microwave dielectric coefficient. A ferroelectric member of the perovskite oxides, i.e. $BaTiO_3$, as a thin film structure of $BaTiO_3$ on MgO has recently been shown to be a candidate alternative to Ti drifted $LiNbO_3$ technology. The large EO coefficient of $BaTiO_3$ coupled with the small microwave dielectric constant of the alkaline-earth-oxide substrate could substantially improve device speed and efficiency(4). If the

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appropriate crystal quality could be obtained for thin-film $BaTiO_3$ supported on MgO for example, or for an integrated $BaTiO_3$/MgO structure on silicon or GaAs, then the optimum OGW device structure might be realized.

In recent work we have been able to obtain optical quality, epitaxial $BaTiO_3$ and $SrTiO_3$ as thin films on single-crystal MgO. We have fabricated waveguides from these materials. and the optical clarity and loss coefficients have been characterized and found to be comparable to in-diffused waveguide structures typically represented by Ti drifted $LiNbO_3$(5). This is the first demonstration of such optical clarity of $BaTiO_3$ and $SrTiO_3$ grown in thin-film form; these results have been obtained by directly addressing the fundamental requirements of interfacial energy minimization between perovskite and alkaline earth oxides.

Figure 1 is an SEM micrograph that shows a fracture cross-section of a representative $BaTiO_3$ film on (001)MgO; this material was grown by using source-shuttering molecular beam epitaxy (MBE) techniques in ultra-high vacuum. The film is adherent, single phase, and optically clear. The epitaxy is cube-on-cube and uniquely results from a layering sequence that begins at the TiO_2-plane of the perovskite structure. This layering sequence is a requirement for single-orientation, epitaxial growth of a perovskite on MgO. We have successfully grown these high performance ferroelectrics on MgO and are working towards their growth and optical quality development on silicon.

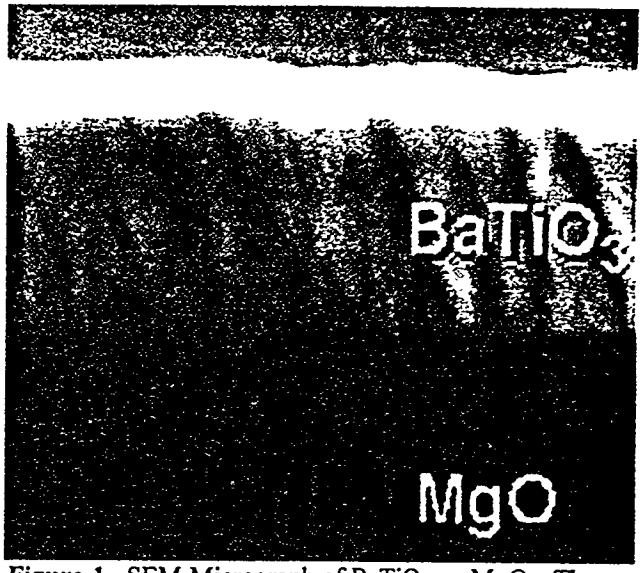

Figure 1. SEM Micrograph of $BaTiO_3$ on MgO. The film is 0.6 microns thick with a single oriention epitaxy on the (001) surface of MgO.

We have found that a layer-by-layer energy minimization associated with interfacial electrostatics leads to the growth of high-quality thin-films of these materials(6). For both $BaTiO_3$ and $SrTiO_3$ a commensurate, stable interface structure exists with MgO that makes it possible to study 2-dimensional phenomena for these perovskites that are only a single unit-cell high or to grow thick adherent films with good optical quality for device applications. To obtain optical quality for these high performance ferroelectrics on silicon it is necessary to solve the problems of heteroepitaxy for not only the perovskite/alkaline earth oxide interface but the alkaline earth oxide/silicon interface as well. Chemical reactivity, thermal elastic strain, lattice mismatch, and electrostatics all play significant roles in developing these structures.

In this paper we summarize the results of our thin-film studies of heteroepitaxy and optical properties for $BaTiO_3$ and $SrTiO_3$ grown on MgO, and we discuss how these materials can be integrated on silicon.

EXPERIMENTAL

The thin films in this study were grown in an ultra high-vacuum MBE system with source shuttering for barium and titanium metal evaporation from effusion cells. The oxygen source was controlled through a channel-plate source to maintain the O_2 pressure at the sample surface

at 1-5 x 10^{-7} torr. MgO substrates were polished using Syton™ polish, washed in methyl alcohol and placed in the MBE chamber. The (001)MgO was annealed on the sample manipulator at 1000°C, cooled to 500°C, and 50 nm of MgO was grown homoepitaxially using an e-beam evaporator. The perovskite growth was then initiated with either a barium or titanium deposition cycle, source-shuttered to a total of 2 nm, and grown at 700°C to final thicknesses required for waveguide mode propagation. We used a co-deposition process where barium, titanium and oxygen arrival was balanced to achieve stoichiometric $BaTiO_3$ (or $SrTiO_3$). For the work on silicon, standard techniques of oxide stripping/formation/thermal reduction are used to obtain reconstructed 2X1 silicon (001) surfaces(7).

Optical loss data were accumulated using a prism coupling technique with video camera light-collection for streak intensity or by directly measuring the transmitted intensity exiting the cleaved end of a planar guide. The details are recently reported by Walker et al(5). This method is an adaptation of the technique originally used by Tien(2). The measured effective indices, n_{eff}, for the modes were calculated based on the coupling angles observed using a 45° rutile prism. The calculated values are derived using the characteristic equations for TE and TM modes for a planar waveguide including the possibility of birefrigence of the film material(8). The effective index of refraction for a particular mode, n_{eff}, is simply related to the coupling angle for the prism, Θ, by

$$n_{eff} = n_{rutile} \sin\left(45° + \sin^{-1}\frac{\sin(\Theta - 45°)}{n_{rutile}}\right) . \qquad (1)$$

The coupling angle Θ, is the angle between the prism face normal for a 45° prism and the guide surface normal.

RESULTS AND DISCUSSION

While our goal is the development of high performance ferroelectrics like $BaTiO_3$ on silicon for electro-optic and ferroelectric device applications, there are several steps that must be accomplished to reach that goal. An oxide-based optical waveguide on silicon requires a low-index optical isolation layer against silicon and a ferroelectric epitaxial guiding layer on the top surface. Significant heteroepitaxy and thermal strain issues arise in developing such a structure. In what follows we discuss these issues as component parts.

$BaTiO_3$ on MgO:

While it is not possible in the present context to describe in detail the characterization of the interface structure, the basic features are summarized as follows(6): For a heteroepitaxial transition between insulating oxides, the interface electrostatics (ion-ion near-neighbor interactions) of the first layers critically determine whether a commensurate structure can develop. For example, in going from MgO to $BaTiO_3$ on the (001) face of MgO, if the transition is initiated at a barium oxide plane, the structure at the interface cannot develop commensurately with the MgO surface. The basic incompatibility results from the large ion-size difference between barium and magnesium. The Mg^{2+} ion is only 0.130 nm in diameter and is accommodated easily in the interstices of oxygen octahedra in the NaCl-type MgO structure(9). The O-O distances along the vertices of the oxygen octahedra containing the Mg^{2+} are 0.297 nm; this distance is very nearly a closest packing separation distance for the O^{2-} ion with its 0.140 nm radius. In the BaO plane of the perovskite, $BaTiO_3$, the equivalent O-O distance is expanded approximately 35% to 0.398 nm as a direct consequence of the 0.274 nm diameter Ba^{2+} ion. The large lattice energy increase that would result from a barium-ion substitution for magnesium in the normal stacking sequence of (001) MgO simply cannot be accommodated and is, of course, not observed as a solid solution or as a commensurate heteroepitaxial system(10,11). One might argue however, that the near equivalence of the 0.595 face diagonal distance on (001) MgO and the 0.554 nm cube edge of BaO would facilitate heteroepitaxial growth. It would not be unreasonable for the resulting 6% lattice mismatch to be accommodated by strain or to be relieved by periodic edge dislocations.

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However, this simple lattice-matching model contains a critical flaw; a 45° -rotated stacking sequence initiated at a BaO plane leaves either all the barium ions on top of magnesium sites or all the oxygen ions on top of oxygen sites. Clearly such near-neighbor ion configurations where either cation-cation or anion-anion repulsive interactions occur in such large numbers leads to a high interfacial energy and an inherent instability.

Figure 2 provides an illustration of the dramatically different result that can be obtained by moving up one plane in the $BaTiO_3$ unit cell to the TiO_2-plane and initiating the growth sequence at that point. A commensurate, atomically flat layer of TiO_2 can form in which every other cation row is vacant over the underlying Mg^{2+} sites. This TiO_2 truncation of (001) MgO satisfies the electrostatic requirements for anion-cation near-neighbor pairs at the interface and is a low-energy, stable truncation of the MgO surface. The missing row of cations in this layer provides the energetically favorable sites for subsequent barium-ion attachment to the crystal surface. As the perovskite growth is continued with alternating barium-and titanium-deposition cycles, $BaTiO_3$ grows layer-by-layer, and strain relief can occur by nucleation of simple edge dislocations maintaining the single orientation cube-on-cube epitaxy(6). The transition from heteroepitaxy to homoepitaxy of the perovskite is completed with the desired single-orientation material and its advantageous long-range structural coherence.

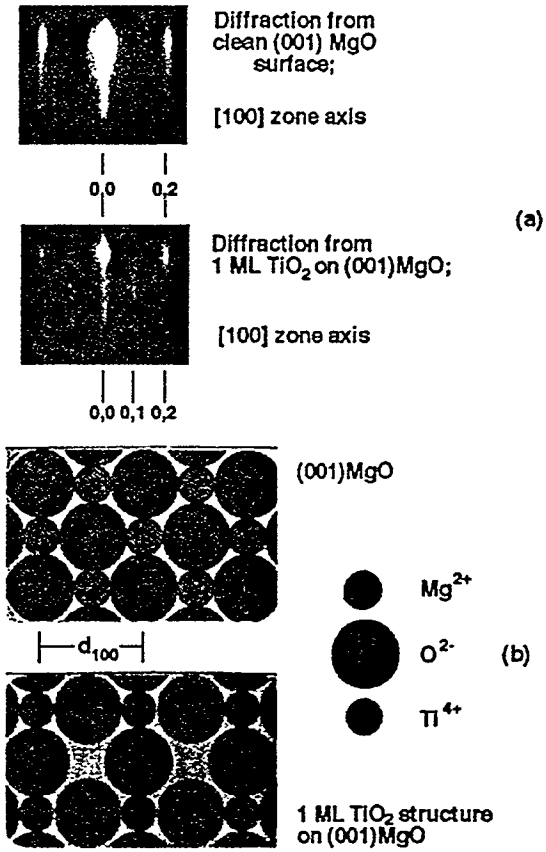

Figure 2 - TiO_2 truncation of (001) MgO.
a) RHEED at the [100] zone axis for clean and TiO_2 -truncated MgO; b) ball models of (001) surfaces.

As outlined above, the optical loss coefficient data for these materials has been obtained using an adaptation of the prism coupling technique originally developed by Tien(2). Walker et al.(5) have recently reported on a detailed study of $SrTiO_3$ thin films on MgO. The measured and calculated values determined from Eq. 1 agree based on bulk values of n_e and n_o for bulk $BaTiO_3$. The optical loss performance meets and exceeds that of state-of-the-art Ti-drifted $LiNbO_3$ waveguides.

<u>MgO on Silicon:</u>
As discussed at the outset the overriding goal of this work is the integration of epitaxial, high crystalline quality ferroelectrics on silicon. We are developing a low-temperature (less than 500°C) growth process that relies on low-index-of-refraction, alkaline earth oxides as optical isolators and high-performance ferroelectrics like $BaTiO_3$ as the optically active waveguide components.

The alkaline earth oxides, BaO, SrO, CaO and MgO are NaCl-type cubic oxides that grow at anomalously low temperatures relative to their absolute melting points (12,13), and in a series

of papers (14-16) we have shown that these oxides grow heteroepitaxially on silicon starting with an exactly lattice-matched $Ba_{0.725}Sr_{0.275}O$. This oxide forms readily on any of the three low index planes of silicon, but a pure {111} plane epitaxy is not obtainable with these oxides since NaCl-type structures have unstable (111) surfaces due to surface dipoles. Epitaxy on (001) and (110) silicon is cube-on-cube, but (111) silicon produces a [111] growth direction normal with (001) facets as a growth habit. These epitaxies are discussed in ref(13), but are all uniquely driven by the same phenomenon on all three faces: large alkaline earth ions,Ba or Sr, order as silicide precursers along the [110] silicon directions common to all three of the low index surfaces of silicon(15).

Two advantages accrue from alkaline earth oxides as the optical isolation layer on silicon: first, a cubic, high-symetry oxide surface can be obtained in heteroepitaxy that is exactly lattice matched to silicon, and second, and perhaps more importantly, this has so far been shown to be the only oxide system for which epitaxial growth occurs at sufficiently low temperatures to be compatible with silicon processing technology. A major disadvantage does present itself however, since all of these oxides are susceptible to hydroxide formation. In the case of BaO, it is instantaneous and uncontrollable if the layer is of any significant thickness. This latter disadvantage is overcome however by minimizing Ba containing layers in a transition that grades the strain to MgO. This transition is discussed in ref(13). We have successfully used alkaline earth oxide strain relaxation to MgO so that a thick (400 nm) optical isolation layer can be obtained. We then use the titanium truncation of MgO discussed above to accomplish the required heteroepitaxial transition to $BaTiO_3$.

We are presently working on domain stabilization and polarization phenomena in composite waveguide structures. We will report our results in subsequent publications.

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