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The Deposition of Electro-Optic Films on Semiconductors

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Highly epitaxial, dense potassium niobate thin films can be reproducibly grown on various substrates including magnesium oxide, magnesium spinel, and potassium tantalate by ion-beam sputter deposition. A strong correlation between lattice mismatch and epitaxial film quality can be made as films on potassium tantalate, which possess the lowest lattice mismatch, displayed the smallest amount of grain tilt. Lower optical losses were measured for thinner potassium niobate films as streak lengths of greater than 8 mm were observed. The dominant loss mechanism in these films can be attributed to volume scattering, possibly originating from twin domains or low angle grain boundaries. Second harmonic generation of green light has been demonstrated for these potassium niobate thin film planar waveguides both in the bulk and waveguide configurations.

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1. Introduction

This is the annual report of the project period (1 Jan 1991 - 30 April 1994) covering research undertaken under sponsorship of the Office of Naval Research. The report covers the period from 1 May, 1993 until 30 April, 1994.

The total project objectives include the deposition of $KNbO_3$ thin films on silicon, sapphire and gallium arsenide substrates; the design of simple electro-optic devices; and the addressing of issues of scaleup.

The focus of our research in this final year are categorized into the following:

1) We have already developed a systematic processing procedure that produces highly epitaxial dense $KNbO_3$ thin films. The current obstacle in thin film waveguides concerns the lack of understanding in the waveguide loss mechanisms. Therefore, a significant effort has been made in correlating film microstructure and materials properties with optical losses.

2) We have pursued the nonlinear applications of $KNbO_3$ thin films as $KNbO_3$ is an excellent material for second harmonic generation. A blue laser light source would allow a higher density packing to be achieved on optical recording disks. Frequency doubling can occur in a $KNbO_3$ planar waveguide such that an infrared laser beam converts to its second harmonic in the blue spectrum. We have collaborated with Battelle Memorial Institute for these SHG measurements and have had encouraging success in producing green light from $KNbO_3$ thin film planar waveguides.

3) A collaboration with DuPont has resulted in the development of an ion-assisted deposition system and a novel MOCVD deposition system. These systems allowed us to exploit various processing advantages offered by each technique and extend our understanding of $KNbO_3$ film growth and microstructure.

The accomplishments of the period are summarized below. Further details can be found in the publications which are included as Appendices.

2. Accomplishments - NCSU

2.1 Background

The development of compact, blue or green lasers to increase optical recording density on disks has been a primary motivation for the research in nonlinear materials. An infrared laser beam can be converted efficiently to the green or blue by second harmonic generation by using high quality nonlinear materials under the appropriate conditions. Although many materials such as KTP, KDP, $LiNbO_3$, $BaTiO_3$ have demonstrated SHG, low conversion efficiencies, impractical for a viable device, have resulted. One reason for such poor efficiency is that much of this research has centered around bulk crystals where there is little beam confinement and consequently low power densities as compared with thin film waveguides. Second, although researchers have generated blue light from $LiNbO_3$ thin films, the nonlinear properties and damage threshold of $LiNbO_3$ are not favorable.

$KNbO_3$ possesses one of the highest figures of merit for second harmonic generation, and in waveguide form, it is superior to most other materials presently being used. However, high optical losses are currently a continuing problem that limits the device efficiency. Several factors are generally known to contribute to dielectric optical losses, predominantly microstructural defects and interface roughnesses. Therefore, the focus of the research has included both an investigation of the materials properties that affect optical losses as well as an exploration of the potential of using $KNbO_3$ thin films for second harmonic generation.

2.2 Processing of $KNbO_3$ Thin Films

$KNbO_3$ thin films have been grown on various single crystal substrates including MgO, $MgAl_2O_4$ (spinel), and $KTaO_3$ to provide a variety of film properties and optical losses. An ion-beam sputter deposition technique has been developed and optimized to produce highly epitaxial and dense $KNbO_3$ thin films. Nb and KO_2 targets are sequentially sputtered by an xenon ion source via computer control, thus allowing a layer by layer growth to be implemented. The optimal processing parameters include: growth temperature ranging from 650 to 700°C, beam voltage of 800 volts, oxygen pressure of 1 X 10^{-4} Torr, and interdiffusion layers of about 10 Å.

Another critical factor for epitaxial film growth is substrate surface quality. All substrates are at least cleaned in acetone, methanol, and deionized water prior to mounting with silver paste on the deposition holder. In addition, MgO substrates are annealed at 1150°C for 14 hours to eliminate any hydroxides that may have formed. Next, substrates are cured at 120°C to bake off solvents from the silver paste and ensure good thermal contact. With this careful substrate preparation, very low substrate surface roughness, rms (root mean square) values of 8 to 15 Å, can be achieved.

2.3 Characterization of $KNbO_3$ Thin Films

X-ray diffraction is systematically used to confirm a single orthorhombic film orientation for the $KNbO_3$ thin films. X-ray rocking curves and Rutherford backscattering spectroscopy channeling provide information about the grain tilt and misorientation, in turn revealing the epitaxial integrity of the films. Both measurements revealed the $KNbO_3$ films to possess highly epitaxial orientation. X-ray rocking curve FWHM values of 0.25°, 0.30°, and 0.84° were detected for films on $KTaO_3$, spinel, and MgO, respectively, while channeling displayed minimum yields of 7%, 9%, and 18%, respectively, for the niobium peak. A strong correlation between the lattice mismatch and the grain tilt can be made, as the lowest amount of grain tilt was detected for films on $KTaO_3$ where the lowest lattice mismatch occurs. Atomic force microscopy measures the surface roughness of the films. Low film surface roughnesses with rms values of only 13 to 37 Å were found. These results are discussed in detail in Appendix 3.

The film refractive indices were found to be close to the bulk $KNbO_3$ refractive index values. The TE (light polarized in the film plane) film refractive indices range from 2.27 to 2.29 while for the TM (light polarized perpendicular to the film plane) mode, 2.20 to 2.23 were measured. The TE and TM bulk refractive indices for our film orientation are 2.274 and 2.222, respectively. The closeness of these film values to the bulk suggests that these films are very dense.

The optical losses were analyzed by a optical fiber method. An optical fiber scans the scattering light as seen from the film waveguide surface and the intensity is digitized to a nanovoltmeter. For dielectric optical waveguides, the dominant loss mechanism is scattering losses. Thus, the optical fiber method for loss measurement is appropriate under the assumption that the total optical losses of the films are comprised basically of the scattering losses measured. Guided light streaks of > 8mm were found for KNbO3 films of ~950 to 1200 Å, while thicker films exhibited shorter streaks of only 2 to 3 mm. The optical losses were calculated to be around 30 dB/cm for the thinner films while > 50 dB/cm losses were measured for the thicker films. Since, the microstructure and surface roughness of the films did not change with thickness, one possible explanation for the disparity in losses is discussed in the following section.

Two types of scattering losses exist: surface and volume scattering. Surface scattering is attributed to the inhomogeneous boundaries at the substrate/film and film/air interfaces. Any roughness of these interfaces allows the field to scattering incoherently. However, surface scattering should decrease as the film thickness increases due to a reduced number of reflections. This effect is the opposite of the trend that we observe. On the other hand, the volume scattering phenomenon would yield the behavior we observe. Volume scattering is comprised of microstructural defects including grain boundaries and impurities. If indeed the film-material properties are not changing with thickness, then the actual film losses should not be changing either. However, as the thickness of the films decreases, more of the field is propagating in the low loss single crystal substrate. Therefore, the *total losses measured* for the waveguide decrease as the film thickness decreases. There are two possible factors for the high volume losses. First, 90° twin domains form upon transforming from the tetragonal to the orthorhombic orientation. Light attenuation occurs as these domain boundaries are traversed. Second, although the amount of grain misorientation has been found to be small, nevertheless these low angle grain boundaries can contribute to the scattering losses in a similar fashion as the twin domains. Appendix 4 contains additional information regarding $KNbO_3$ optical loss theory.

3.0 Second Harmonic Generation - Battelle/NCSU Collaboration

A Nd:YLF laser source with wavelength of 1.053 um was used as the fundamental beam for SHG measurements in the $KNbO_3$ thin film planar waveguides. Under mode-locked operation, 80 psec, 100 MHz pulses were first directed through the sample transversely. Thereafter, a harmonic beam splitter transmits the fundamental beam to a beam block while the second harmonic is reflected through a tilted 532 nm bandpass filter onto a ground-glass screen. Strong green light was observed for $KNbO_3$ films with thicknesses varying from 4600 to 6500 Å. Next, a $KNbO_3$ film on an MgO substrate with a varying thickness from 2200 to 2800 Å was coupled to with a 90° rutile prism in a waveguiding mode. A 3 to 4 mm green light streak can be seen when coupling in the TM_0 mode. We believe that the TM_0 mode (at 1.053 um) is phase-matching with the TE_1 mode (at 5265 Å) by modal dispersion at a film thickness of about 2300 Å. This is the first demonstration of SHG by a $KNbO_3$ thin film in a waveguide configuration. Furthermore, we expect these films will similarly demonstrate SHG of blue light with the appropriate laser source. We are currently establishing a collaboration with researchers equipped with a 860 nm wavelength laser. More details of the SHG experiments can be fcund in Appendix 5.

4.0 Accomplishments - DuPont/NCSU Collaboration

4.1 Ion-assisted Rf Sputter Deposition

An ion-assisted deposition process consisting of a filamentless rf ion source was used as another $KNbO_3$ film deposition technique in order to capitalize on its unique advantages and to better understand the relationship between processing parameters and film properties. The benefits of using ion-assisted growth include the increased mobility at the growth surface which in turn, allows for a lower growth temperature. Not only can film homogeneity be improved upon due to the enhanced diffusion, but the lower processing temperature is desirable for semiconductor integration.

4.2 MOCVD

MOCVD is used for the first time to grow $KNbO_3$ thin films. A high deposition rate, large area deposition, and conformal converage are among the technique's attractions. Solid metalorganic source materials are passed through a very sharp temperature gradient allowing them to immediately sublimate, upon which a He carrier gas transports the materials through heated tubes to the reaction chamber. Molecular oxygen is then introduced to the gases prior to entering the chamber to ensure a sufficient amount of oxygen for oxide film growth. The film stoichiometry and growth rate can be controlled by adjusting the flow rate of the sources through the temperature gradient. Appendix 1 and 2 are referred for further information on the work done at DuPont.

Publications

Appendix 1. "Processing Thin Films of $KNbO_3$ For Optical Waveguides," T. M. Graettinger, D. J. Lichtenwalner, A. F. Chow, O. Auciello, and A. I. Kingon, ISIF 1994 Proceedings, submitted to Integrated Ferroelectrics.

Appendix 2. "Growth of Epitaxial $KNbO_3$ Thin Films," Thomas M. Graettinger, P. A. Morris, A. Roshko, A. I. Kingon, O. Auciello, D. J. Lichtenwalner, and A. F. Chow, submitted to MRS Symposium Proceedings 1994, Epitaxial Oxide Thin Films and Heterostructures.

Appendix 3. "Epitaxial $KNbO_3$ Thin Films on $KTaO_3$, $MgAl_2O_4$, and MgO Substrates," A. F. Chow, D. J. Lichtenwalner, R. R. Woolcott, Jr., T. M. Graettinger, O. Auciello, and A. I. Kingon, Appl. Phys. Lett. **65**(9), 1073, 1994.

Appendix 4. "Microstructural and Optical Properties of Potassium Niobate Thin Films," Alice F. Chow, Daniel J. Lichtenwalner, Thomas M. Graettinger, James R. Busch, Orlando Auciello, and Angus I. Kingon, submitted to ISAF 1994.

Appendix 5. "Second Harmonic Generation in Potassium Niobate Thin Films," A. F. Chow, D. J. Lichtenwalner, O. Auciello, and A. I. Kingon, to be submitted to Appl. Phys. Lett.

Appendix 1

151F94: Submitted to Integrated Ferroelectrics

PROCESSING THIN FILMS OF $KNbO_3$ FOR OPTICAL WAVEGUIDES

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Abstract Thin film waveguides of ferroelectric materials hold great promise for use in active integrated optics devices because of the high optical confinement possible in a thin film structure. $KNbO_3$ is an attractive material for active devices because it possesses large nonlinear optical susceptibilities and large electro-optic coefficients. $KNbO_3$ films with low optical losses are required to produce efficient devices. Epitaxial films of $KNbO_3$ (110) have previously been deposited on single crystal MgO (100) using ion beam sputtering techniques. However, these films contained microstructural defects due to the large lattice mismatch (>4.0%) between $KNbO_3$ and MgO which resulted in high optical losses. Recent work has focused on determining the relationships between microstructure and optical loss through the use of lattice matched substrates. Film composition, epitaxial quality and optical properties of $KNbO_3$ films deposited on MgO and $MgAl_2O_4$ have been investigated and are compared.

INTRODUCTION

Crystalline optical waveguides hold great promise for use in integrated optics because high power densities can be maintained over long interaction lengths. Waveguides of ferroelectric materials are of special interest because of their generally strong nonlinear optical, electro-optic, and photorefractive effects. Currently one application of technological importance which uses the nonlinear optical properties of these materials is second harmonic generation (SHG). SHG has been proposed as a viable route to producing a compact, blue laser. Blue light is considered necessary for the next generation of optical storage devices, and has many uses in the laser writing and medical fields because the smaller wavelength means increased resolution. Efficient SHG of GaAs lasers is possible in ferroelectric materials and has been demonstrated in thin films of $LiNbO_3$[1,2] and $BaTiO_3$,[3] among others. Many technological challenges to producing a commercial device based on thin film materials still remain. The greatest of these challenges is fabricating a thin film waveguide with low enough optical loss to permit blue light generation of sufficient power for applications. This paper presents an investigation of the processing of $KNbO_3$ thin films and relates the optical properties to growth characteristics.

PROCESSING OF $KNbO_3$ FILMS

Bulk crystal growth of $KNbO_3$ has been studied for nearly 45 years. The phase diagram of the Nb_2O_5-K_2O system, first reported by Reisman and Holtzberg,[4] reveals that $KNbO_3$ melts incongruently. Thus solution growth techniques have been limited to growth from K_2O-rich melt compositions. Little is therefore known about the effects of composition on the structure and properties of $KNbO_3$. Thin film processing techniques, many of which are non-equilibrium processes, promise the ability to surpass the limits of solution crystal growth. The region of the phase diagram around stoichiometric $KNbO_3$ can then be studied.

Determining the limits of the solid solubility region for $KNbO_3$ are an important first step toward understanding the effects of composition on the perovskite structure of $KNbO_3$. Thin films of $KNbO_3$ with K/Nb cation ratios ranging from 1.35 to 0.66 were grown on single crystal MgO (100) substrates using an ion beam co-sputter deposition system which has been described in detail previously.[5] During film growth a niobium target and a potassium superoxide, KO_2, target were sputtered simultaneously in the presence of molecular oxygen. Changes in the cation ratio were achieved by independently controlling the ion beam energy and current on each target. Typical growth conditions for near stoichiometric $KNbO_3$ films are given in Table I.

X-ray diffraction was used to determine the limits of the single phase region of $KNbO_3$. A selected group of theta-two theta diffraction patterns from this study are shown in Figure 1. Figures 1(a) and 1(b) show the diffraction patterns of potassium-rich films with cation ratios (K/Nb), determined from Rutherford backscattering spectroscopy (RBS),

Table I Processing conditions for $KNbO_3$ thin films.

Parameter	Value
KO_2: Ion Beam Energy	500 eV
KO_2: Ion Beam Current	11 mA
Nb: Ion Beam Energy	750 eV
Nb: Ion Beam Current	16 mA
Xe Pressure (Sputtering Gas)	2.0×10^{-4} torr
O_2 Pressure	1.0×10^{-4} torr
Growth Temperature	600-700°C

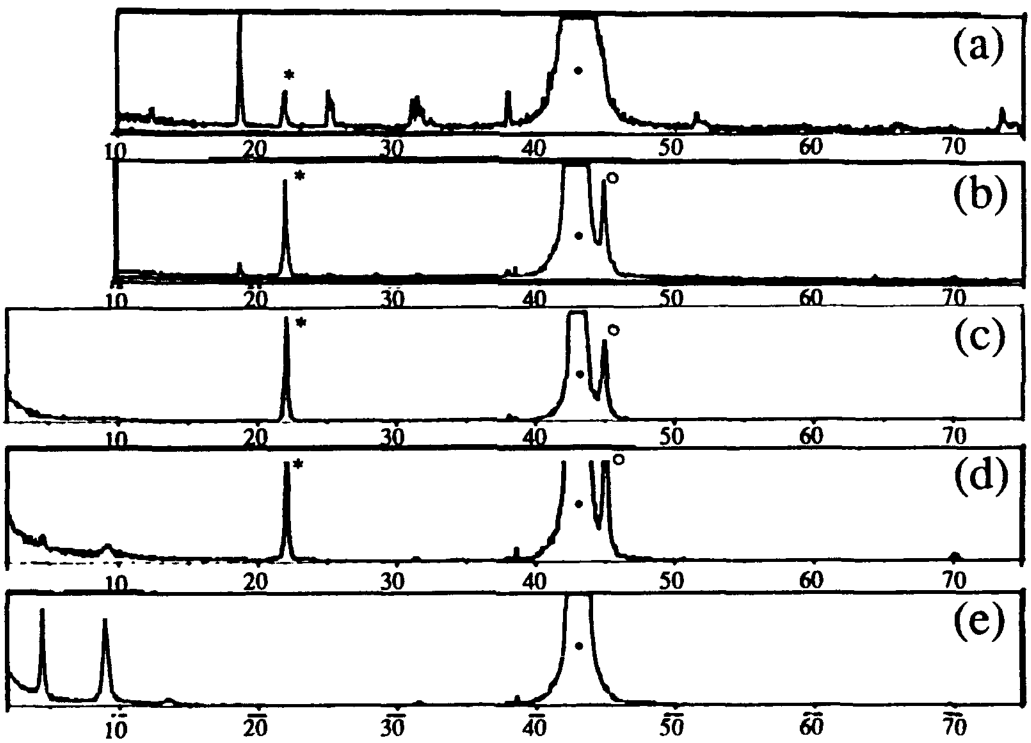

Figure 1 X-ray diffraction patterns of potassium niobium oxide thin films showing the phase evolution as the cation ratio (K/Nb) changes from (a) 1.35, (b) 1.18, (c) 1.00, (d) 0.77, to (e) 0.66. [* $KNbO_3$ (110), • MgO (200), ∘ $KNbO_3$ (220)]

of 1.35 and 1.18, respectively. Figure 1(b) reveals the presence of second phases in the thin film. As the composition becomes further potassium rich, as shown in Figure 1(a), more second phase(s) form as evidenced by more, and more intense, diffraction peaks not due to the $KNbO_3$ phase. The limit of the single phase region of $KNbO_3$ on the potassium-rich side can be conservatively estimated to be reached at a cation ratio of 1.10±5%. The second phase(s) which form above this limit can not be matched to those expected from Reisman and Holtzberg's phase diagram.[4] Instead, metastable phases have apparently formed during the non-equilibrium growth process.

Figures 1(d) and 1(e) represent x-ray diffraction patterns of niobium-rich, potassium niobium oxide thin films. As seen in Figure 1(e), the $KNbO_3$ phase disappears entirely from the diffraction pattern as the cation ratio reaches 0.66. The limit of the single phase region of $KNbO_3$ was reached at 0.80±5%. Thus the $KNbO_3$ perovskite structure will tolerate a larger potassium deficiency than niobium deficiency before second phases begin forming. It should be noted that the limits of the single phase $KNbO_3$ region determined in this study may differ when using other processing parameters, or for other growth techniques.

The $KNbO_3$ phase which appears in Figures 1(a) through 1(d) is highly oriented (110) normal to the substrate. The following sections present results of our investigation of the epitaxial quality of these (110) oriented $KNbO_3$ films.

<u>Epitaxy of Ion Beam Sputter Deposited $KNbO_3$</u>

Thin films of $KNbO_3$ were grown on single crystal MgO (100) and single crystal $MgAl_2O_4$ (100) substrates using the ion beam sputter deposition process described above. MgO and $MgAl_2O_4$ were chosen for this study for their reasonably small lattice mismatch and chemical inertness to the perovskite $KNbO_3$. Table II summarizes the lattice parameters of these two substrates and their lattice mismatch with (110) oriented $KNbO_3$. Since $KNbO_3$ is orthorhombic at room temperature, the lattice mismatch between the cubic substrates and both in-plane lattice parameters of $KNbO_3$ (3.973Å and 4.035Å) are given in the table. It is clear from the table that $MgAl_2O_4$ is much better lattice matched to $KNbO_3$ than MgO. Thus it was expected that films deposited on $MgAl_2O_4$ would show a higher degree of epitaxy.

All $KNbO_3$ films grown on MgO (100) and $MgAl_2O_4$ (100) were highly oriented (110) normal to the substrate. Typical x-ray diffraction patterns of these films are shown in Figure 2(a) and Figure 3(a). It was discovered previously through pole figure measurements that $KNbO_3$ films on MgO display a lattice tilt of 1-1.5° about the substrate normal.[5]

Table II Physical properties of substrates used for $KNbO_3$ film growth.

	MgO (100)	$MgAl_2O_4$ (100)
Lattice Parameter, Å	4.213	8.083
Lattice mismatch, %	6.0, 4.4	1.7, 0.1
Bulk refractive index	1.736	1.723

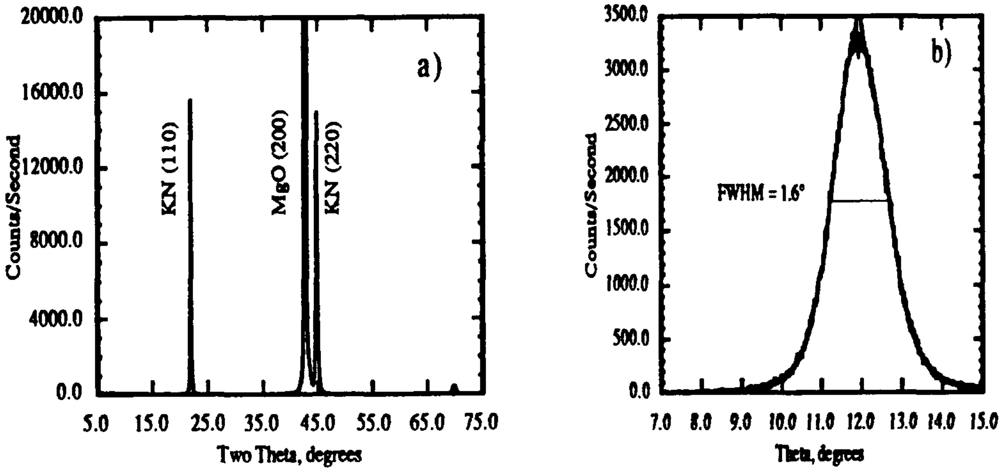

Figure 2 (a) A typical x-ray diffraction pattern of a $KNbO_3$ thin film on MgO, and (b) a rocking curve measurement of the $KNbO_3$ (110) diffraction peak for the film in (a).

In addition, the tilt occurs along all four in-plane substrate [100] directions, evidencing the presence of 90°, 180°, and 270° rotated grains. The x-ray rocking curve measurement of the (110) diffraction peak of a typical $KNbO_3$ film on MgO is shown in Figure 2(b). The width of the rocking curve, FWHM=1.5°, also confirms the misorientation of $KNbO_3$ films on MgO. The lattice tilt and grain rotations accommodate the strain induced in the films on MgO due to the >4% lattice mismatch. Much less lattice tilting is expected for films on $MgAl_2O_4$ whose lattice mismatch is less than 2%. Figure 3(b) shows the rocking curve measurement of the (110) $KNbO_3$ diffraction peak of a film on $MgAl_2O_4$. The FWHM=0.6 is indeed much smaller than the films on MgO, indicating a higher degree of epitaxy for these films. The optical properties of $KNbO_3$ / $MgAl_2O_4$ films which will be discussed below indicate that the grain rotations seen in films deposited on MgO exist in these films as well.

Epitaxy of Ion-assisted Ion Beam Sputter Deposited $KNbO_3$

The ion beam co-sputter-deposition process described above was modified by the addition of a filamentless rf ion source. The rf ion source was used to bombard the growth surface at normal incidence with low energy oxygen ions. Ion-assisted film growth can provide many beneficial effects for film growth including increasing the activity of depositing species which promotes compositional homogeneity and film adherence. In addition, lower processing temperatures may be possible

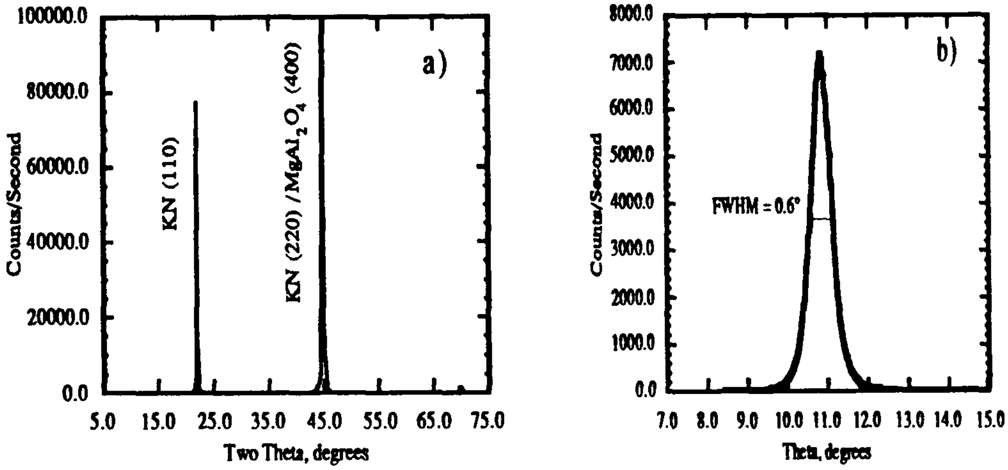

Figure 3 (a) X-ray diffraction pattern of a (110) $KNbO_3$ thin film on $MgAl_2O_4$, and (b) a rocking curve measurement of the $KNbO_3$ (110) diffraction peak for the film in (a).

with ion-assisted growth which may be necessary for integration with semiconductor processing. Nucleation and growth mechanisms can also change, modifying film morphology and microstructure. However, the current study focused on investigating the effects of ion-assisted growth on film orientation and epitaxial quality.

For this study $KNbO_3$ films were again grown on MgO and $MgAl_2O_4$ substrates. Typical processing conditions are shown in Table III. X-ray diffraction patterns reveal that the film (110) axis is normal to the substrate as it was for films deposited without ion-assist. However, the lattice spacing is slightly enlarged compared to the (110) spacing of unassisted films. This comparison is shown in the x-ray diffraction patterns in Figure 4(a) where the (110) peak for the ion-assisted film has shifted to a slightly lower angle. It can also been seen in Figure 4(a) that the (110) diffraction peak of the ion-assisted film is much broader and less symmetrical than the peak of the unassisted film. This is a qualitative indication that the oxygen ion-assist beam has worsened the quality of the $KNbO_3$ films. The rocking curve measurement, shown in Figure 4(b), quantitatively reveals in dramatic fashion that the epitaxial quality of the ion-assisted $KNbO_3$ films is inferior to that of films deposited without ion-assistance. The FWHM of the rocking curve of a $KNbO_3$/ $MgAl_2O_4$ film has increased to over 2° compared to a value of 0.6° for an unassisted film [Figure 3(b)].

The increase in lattice parameter for ion assisted films has been attributed to impurity incorporation. The RBS spectrum shown in Figure

Table III Process parameters for ion-assisted growth of KNbO3 thin films.

Process Parameter	Value
KO2: Ion Beam Energy	850 eV
KO2: Ion Beam Current	13 mA
Nb: Ion Beam Energy	1000 eV
Nb: Ion Beam Current	10 mA
Xe Pressure (Sputtering Gas)	2.0×10^{-4} torr
O_2^+ Energy	50 eV
O_2^+ Current	10 mA
O_2 Pressure	1.0×10^{-4} torr
Growth Temperature	600-700°C

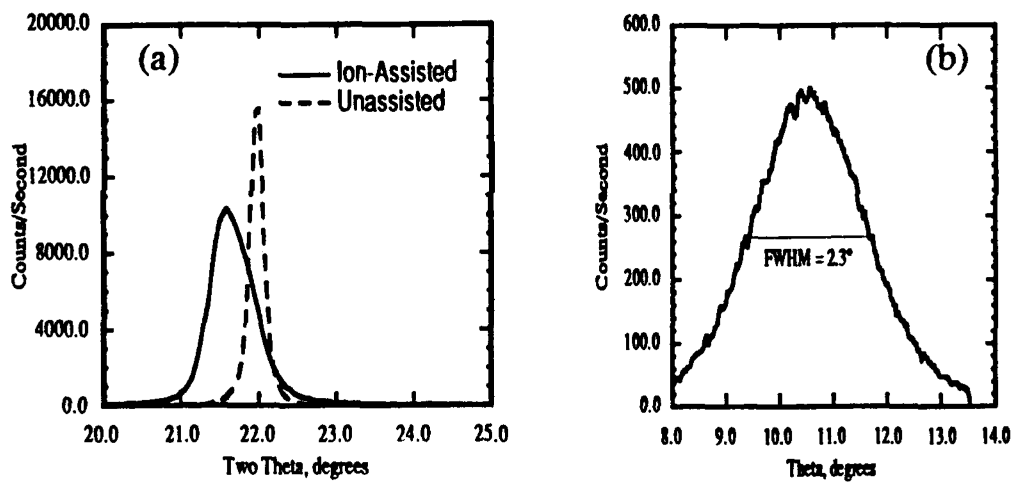

Figure 4 (a)KNbO3 (110) diffraction peaks for ion-assisted and unassisted films. (b) A rocking curve measurement of the KNbO3 (110) diffraction peak for an ion-assisted film.

5 reveals that the ion-assisted films contain Fe and Xe impurities. The Fe impurity has been traced to the stainless steel ring electrode inside the discharge chamber of the rf ion source. For future work it may be possible to replace this electrode with a niobium electrode which would eliminate the source of contamination. The Xe detected is trapped primary sputtering gas that has been trapped in the film during growth. Changing the incidence angle of the oxygen ion-assist beam may reduce this gas incorporation. However, the position of the rf ion source is fixed in the current deposition system. Morphology and microstructure of ion-assisted films has yet to be studied. If the impurities can be eliminated the ion-assisted KNbO3 films may yet show improved characteristics.

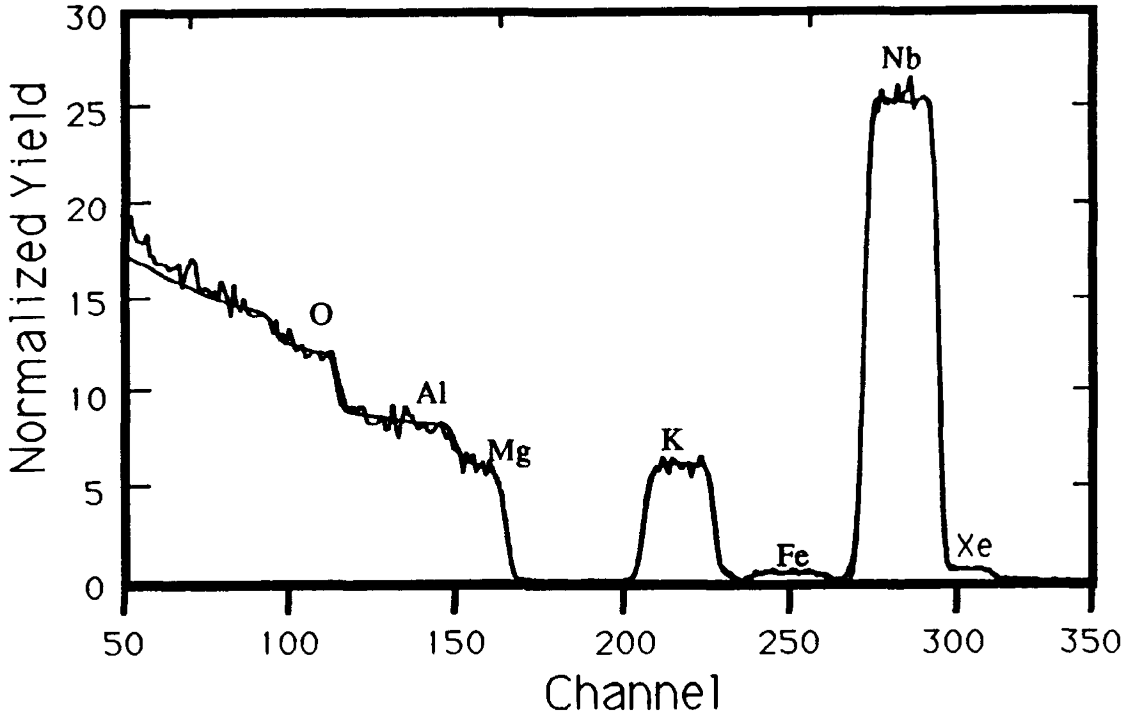

Figure 5 A Rutherford backscattering spectrum of an ion-assisted $KNbO_3$ film showing the presence of Fe and Xe impurities.

OPTICAL CHARACTERIZATION

Optical properties of both ion-assisted and unassisted ion beam sputter deposited $KNbO_3$ thin films were measured using a rutile prism coupler. The refractive indices of the films were determined using the numerical technique developed by Ulrich and Torge.[6] Unassisted $KNbO_3$ films on both MgO and $MgAl_2O_4$ substrates had refractive indices of 2.28 for TE modes and 2.22 for TM modes. The value for the TM modes is very near the bulk value of 2.2221 expected for a (110) oriented crystal. A single crystal $KNbO_3$ film would be expected to have birefringence between orthogonal TE modes. However, no birefringence was observed for orthogonal TE modes in these films. The grain rotations that were observed in the x-ray analyses above lead to a single, averaged refractive index for TE modes in the films.

The refractive indices measured for ion-assisted deposited films were slightly lower than the indices measured for unassisted films. The refractive index for TE modes was 2.26 while the index for TM modes was 2.18. Again no birefringence was observed for TE modes. The decrease in the refractive indices results from the presence of Fe and Xe impurities in the films as discussed above. These impurities increased the lattice parameter of the films thereby lowering the density of the films which is known to reduce the refractive indices.

Optical losses were measured by optically coupling to the $KNbO_3$ thin films with a rutile prism and observing the light streak traveling through the films. These observations lead to several qualitative conclusions about the $KNbO_3$ thin films. First it was found that TM modes have lower losses than TE modes. Second, thin films (1000-1300Å) have significantly lower losses than thicker films (>1500Å). Third, films on MgO have lower optical loss than films on $MgAl_2O_4$; and finally, that losses were so high in ion-assisted thin films that no light streaks could be observed. An analysis of each of these conclusions will follow below.

The high optical loss of guided TE modes relative to TM modes can be understood from an analysis of reflection and refraction at grain boundaries. In the x-ray analysis above, it was found that grain rotations of 90°, 180°, and 270° exist in $KNbO_3$ films. While there is no change in refractive index as a TM mode crosses a grain boundary, there is a refractive index change of 0.11 that occurs as a TE mode crosses a boundary. This index change causes reflection and refraction to occur at these boundaries depending on the angle of incidence of the guided light. The grain size of the $KNbO_3$ films is on the order of 1000Å, so thousands of these boundaries must be crossed in order for a TE mode to propagate an appreciable distance in the film. Therefore propagation is prohibited by light scattering due to reflection and refraction, leading to high optical loss.

The second conclusion above stated that thin films had lower optical loss than thick films. This statement is more evident for TM modes since losses for TE modes in all films are high and are dominated by reflection and refraction at grain boundaries as discussed above. To determine the nature of this observation, the electric field distributions for a thin film (1180Å) and for a thick film (1965Å) were plotted. The field distributions normalized to the Poynting vector are shown in Figure 6. It is clear from the field distributions that much of the optical energy of the guided mode is traveling through the substrate in the thin film. Since the substrate is a single crystal of high optical quality, naturally the thinner film has lower total optical loss for the guided light. Work is currently in progress to determine whether the source of optical loss in the films is due to interface or bulk effects.

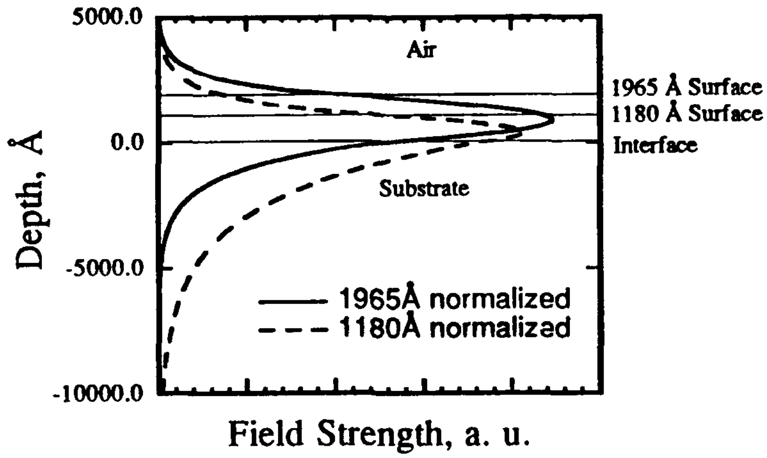

Figure 6 Optical field distributions in $KNbO_3$ thin films.

It is currently unclear why films on MgO have lower optical loss than films on $MgAl_2O_4$. Initially films on $MgAl_2O_4$ were expected to have lower optical loss because of the higher degree of epitaxy discussed earlier in this work. It is suspected that interface effects which do not impair the epitaxial relationship, possibly diffusion between film and substrate, are the source of the higher optical loss. Finally, the high optical losses in ion-assisted $KNbO_3$ thin films are attributed to defects in the film resulting from impurity incorporation and to possible interface damage resulting from bombardment by oxygen ions. Work is continuing to separate and quantify these effects.

SUMMARY

In summary, the single phase region of $KNbO_3$ was investigated to understand the effect of composition on phase formation. The single phase region was determined by x-ray diffraction measurements and RBS spectra to lie between the K/Nb cation ratios of 1.10±5% and 0.80±5%. The epitaxial quality of stoichiometric $KNbO_3$ films deposited on single crystal MgO (100) and single crystal $MgAl_2O_4$ (100) substrates was analyzed through x-ray rocking curve measurements. Films on $MgAl_2O_4$ were found to possess much less misorientation as evidenced by a rocking curve FWHM of 0.6 compared to a FWHM of 1.6 for films on MgO. The addition of a low-energy oxygen ion-assist source to the deposition process was found to degrade the quality of epitaxy on both substrates due to impurity incorporation.

The waveguiding properties of the KNbO3 films were also studied. The refractive indices were measured using a rutile prism coupler and were found to be near bulk values, TE=2.28 and TM=2.20. No in-plane birefringence was observed due to grain rotations which result from lattice mismatch between film and substrate. The refractive indices of ion-assisted films were reduced to TE=2.26 and TM=2.18 by the incorporation of Fe and Xe impurities during processing. Optical losses were also observed in these films. Thin KNbO3 films (1000-1250Å) on MgO substrates demonstrated the lowest optical losses of the films studied.

ACKNOWLEDGMENTS

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Appendix 2

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GROWTH OF EPITAXIAL $KNbO_3$ THIN FILMS

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ABSTRACT

$KNbO_3$ possesses high nonlinear optical coefficients making it a promising material for frequency conversion of infrared light into the visible wavelength range using integrated optical devices. While epitaxial thin films of $KNbO_3$ have previously been grown using ion beam sputtering,[1] defects (i.e. grain boundaries, domains, surface roughness) in these films resulted in high optical losses and no measurable in-plane birefringence. Previous films were grown on MgO substrates, which have a >4% lattice mismatch with $KNbO_3$. In the work reported here, we have grown films on MgO, $MgAl_2O_4$, $NdGaO_3$, and $KTaO_3$ to investigate the role of lattice mismatch on the resulting film quality. Films have also been grown with and without oxygen ion assistance. The orientations, morphologies, and defects in the films were examined using x-ray diffraction and AFM to determine their relationships to the growth conditions and substrate lattice mismatch.

INTRODUCTION

Applications for ferroelectric oxide thin films have increased rapidly in the last ten years. One application that is currently receiving much attention is second harmonic generation, SHG, which allows infrared laser diode wavelengths to be frequency doubled to the blue region of the visible spectrum. Coherent blue light is desired for many next-generation applications, such as optical recording and laser printing, where the smaller wavelength leads to increased resolution. Ferroelectric oxides are an important class of materials for SHG because of their generally large nonlinear optical coefficients. High quality thin films of these oxides are desirable for integrating active waveguides with current laser diode technology. However, many technological challenges remain to be solved to produce device quality ferroelectric thin films. These challenges include producing a low optical loss thin film and, additionally, meeting the requirements for SHG. SHG has been demonstrated in thin films of $LiNbO_3$[2,3] and $BaTiO_3$,[4] among others, but few have met the additional requirements of a low loss waveguide which is necessary for efficient SHG. It is becoming clear to researchers in this field that controlling the microstructure of these films will be necessary to achieving the goal of efficient SHG. The deposition process and the epitaxial quality and surface morphology of $KNbO_3$ thin films are investigated in this work as a step toward understanding the influences of microstructure on optical properties.

ION BEAM SPUTTER DEPOSITION

An ion beam co-sputter deposition system, which has been described previously,[1] was developed for the growth of complex oxide thin films. Ion beam sputtering is well known to produce dense, smooth films, which are very important criteria for optical quality films. A co-deposition route was chosen for the ability to independently control the cation stoichiometry. A niobium and a potassium superoxide, KO_2, target were sputtered simultaneously by Xe ion beams from 3 cm Kaufmann-type ion sources. By independently controlling the ion energy and ion current on each target, the desired film composition could be achieved. Figure 1 clearly illustrates this ability of the deposition system. In Figure 1(a) the ion energy of the beam sputtering the KO_2 target was varied from 500 to 750 eV while all other deposition parameters remained constant. These changes in ion energy resulted in changes in the K/Nb cation ratio from 0.9 to 1.85, determined from Rutherford backscattering spectra (RBS), as shown. Similarly, Figure 1(b) shows the control of cation stoichiometry by changing the ion current on the Nb target. It was experimentally determined that single phase $KNbO_3$ thin films resulted for cation ratios between 0.80 and 1.10 (±0.05). This single phase region is considerably wider than expected from the phase diagram determined by Reisman and Holtzberg[5] for the Nb_2O_5-K_2O system. Table I lists the typical processing parameters for the growth of stoichiometric $KNbO_3$.

EPITAXIAL GROWTH OF $KNbO_3$

$KNbO_3$ thin films were grown on single crystal MgO (100) and single crystal $MgAl_2O_4$ (100) substrates because of the reasonably good lattice match that exists between $KNbO_3$ and

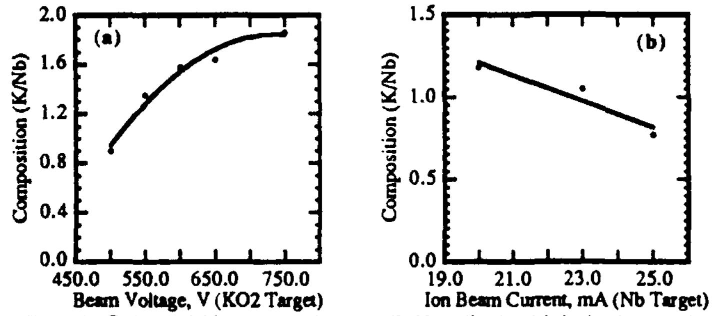

Figure 1 Cation stoichiometry can be controlled by adjusting (a) the ion beam voltage, or (b) the ion beam curent.

Table I Typical processing parameters for ion beam sputter deposition of $KNbO_3$ thin films.

Parameter	Unassisted Deposition	Ion-assisted Deposition
KO_2: Ion Beam Energy	500 eV	850 eV
KO_2: Ion Beam Current	11 mA	13 mA
Nb: Ion Beam Energy	750 eV	1000 eV
Nb: Ion Beam Current	16 mA	10 mA
Xe Pressure (Sputtering Gas)	2.0×10^{-4} torr	2.0×10^{-4} torr
O_2 Pressure	1.0×10^{-4} torr	1.0×10^{-4} torr
O_2^+ Energy	N. A.	50 eV
O_2^+ Current	N. A.	10 mA
Substrate Temperature	600-700 °C	600-700 °C
Growth Rate	0.30 nm/min.	0.25 nm/min.

Table II Summary of lattice parameters of $KNbO_3$ and substrate materials, including lattice mismatch.

	Lattice Parameter, nm	Lattice Mismatch, %†
$KNbO_3$ ($\bar{1}10$)	0.4036	N.A.
$KNbO_3$ (001)	0.3973	N.A.
MgO (100)	0.4213	4.4, 6.0
$MgAl_2O_4$ (100)	0.8083	0.1, 1.7
$KTaO_3$ (100)	0.3989	0.4, -1.2
$NdGaO_3$ (001)	0.3863	-2.8, -4.3

†First number listed is the lattice mismatch with $KNbO_3$ ($\bar{1}10$). Second number listed is lattice mismatch with $KNbO_3$ (001).

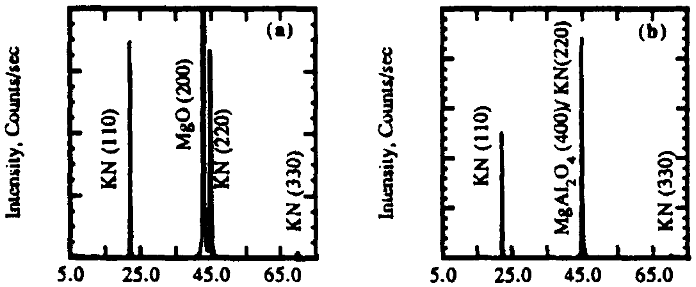

Figure 2 Theta-two theta x-ray diffraction patterns of $KNbO_3$ thin films on (a) MgO (100), and (b) $MgAl_2O_4$ (100).

these materials. Table II summarizes the lattice mismatch between the in-plane lattice parameters of (110) oriented $KNbO_3$ and those of the MgO and $MgAl_2O_4$ substrates. Theta-two theta x-ray diffraction patterns of all films show that the $KNbO_3$ grows highly (110) oriented on these substrates. Figure 2 shows typical diffraction patterns of $KNbO_3$ films on both these substrates. It is important to note that all films were (110) oriented in contrast to the (001) orientation which is the other pseudo-cubic direction of the perovskite unit cell. At the growth temperature, >600 °C, $KNbO_3$ is cubic, so it would be reasonable to expect some (001) orientation to occur. However, no (001) orientation has been observed in x-ray diffraction patterns for any $KNbO_3$ films grown in this study. An analysis of the structural transformations that occur during cooling from the growth temperature reveals why the (110) orientation is preferred.[6] X-ray diffraction rocking curve measurements were used to investigate the epitaxial quality of the $KNbO_3$ thin films. The rocking curve yields a quantitative measure of the misorientation of the thin films due to lattice tilting that results from defects in the microstructure. However, it does not measure in-plane misorientations, or twist, which are also common in heteroepitaxial growth of oxides. Typical rocking curves of $KNbO_3$ thin films on MgO (100) and $MgAl_2O_4$ (100) are shown in Figure 3. It is clear from the FWHM of the rocking curves that the films on $MgAl_2O_4$ possess higher epitaxial quality than those on MgO. This result is expected from the much smaller lattice mismatch between $KNbO_3$ and $MgAl_2O_4$ that was shown in Table II. In addition to the larger lattice mismatch, it is believed that the quality of the MgO surface prior to deposition plays a very important role in determining the

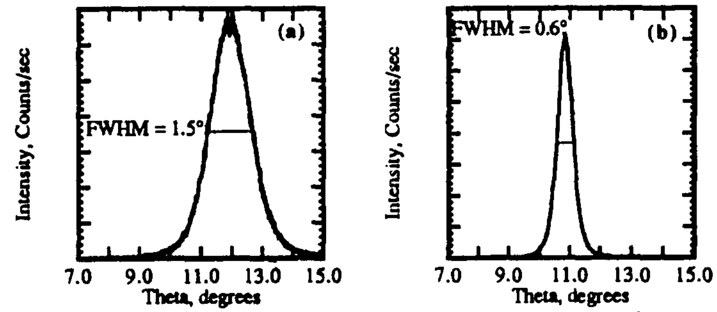

Figure 3 X-ray diffraction rocking curve measurements of the (110) diffraction peak of $KNbO_3$ thin films on (a) MgO (100), and (b) $MgAl_2O_4$ (100).

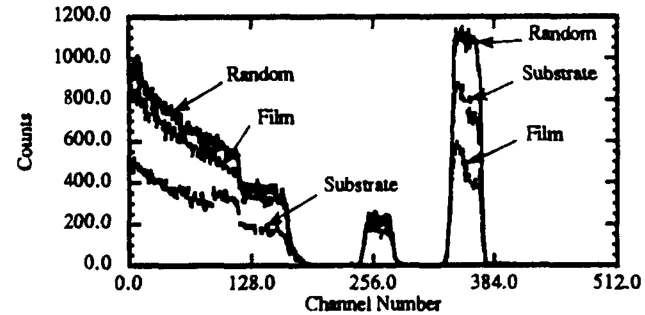

Figure 4 Rutherford backscattering spectra of a $KNbO_3$ thin film on MgO (100), including the spectra showing minimum channeling yields for the film and the substrate.

FWHM of the rocking curve. The rocking curve measurements also reveal that the [110] axis of most $KNbO_3$ films grown on MgO is tilted 1.0-1.5° away from the substrate normal.

RBS channeling was also used to determine the epitaxial quality of $KNbO_3$ films deposited on MgO. Figure 4 shows the random and channeled spectra of one of these films. By determining the minimum scattering yield, χ_{min}, of the film, the misorientation of the film with respect to a single crystal can be quantified. Experimentally it was found that more imperfections exist on the K sublattice than on the Nb sublattice. χ_{min} of the Nb signal was measured to be 37% while χ_{min} of the K signal was calculated to be only 71%. Although the channeling measurement is more sensitive to imperfections on the K sublattice,[7] the cause(s) of the greater imperfection on the K sublattice is unclear at this time. The tilt of the [110] axis is also evident in this measurement. The minimum scattering yields of the substrate and film do not occur at the same beam incidence angle. In fact the minimum yields are found one degree apart, as expected from the rocking curve measurements.

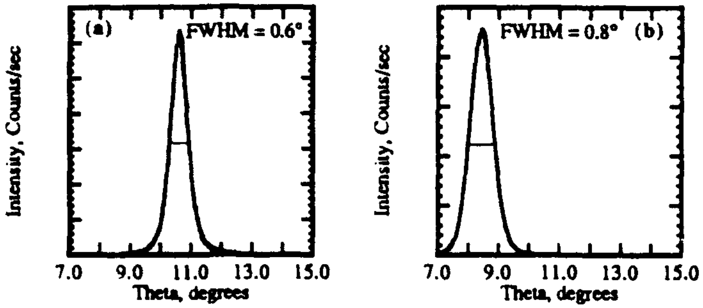

Figure 5 X-ray diffraction rocking curve measurements of the (110) diffraction peaks of (a) a $KNbO_3$ film deposited on Nb_xO_y/MgO, and (b) a $KNbO_3$ thin film deposited on MgO (100)-2°.

MgO is an important substrate for the growth of active optical waveguides because MgO can be grown on GaAs. High quality $KNbO_3$ thin films grown on MgO could then be easily integrated into planar optical device structures which would include both the AlGaAs laser source and the active element. It is thus necessary to improve the epitaxial quality of the $KNbO_3$ films on MgO. Two routes to improving the epitaxial quality of these films have been undertaken and show encouraging results. The first involves the deposition of a niobium oxide transition layer between the MgO substrate and the $KNbO_3$ film. It was shown previously that rotations of the $KNbO_3$ unit cell on top of the MgO surface.[8] In the present study, approximately 5 nm of niobium oxide was first deposited on the MgO (100) surface at the $KNbO_3$ growth temperature. $KNbO_3$ growth was initiated immediately after this layer was complete. The rocking curve of a $KNbO_3$ film grown on top of a niobium oxide transition layer is shown in Figure 5(a). Figure 5(a) reveals a marked improvement in the quality of the $KNbO_3$ film. The FWHM of the rocking curve has been reduced from 1.5° to 0.64°. The structure of the niobium oxide layer has not yet been investigated, but it is believed that this layer eases the lattice mismatch between $KNbO_3$ and MgO resulting in a better oriented film.

The second route to improving the quality of $KNbO_3$ on MgO involves the use of MgO substrates polished slightly off-axis. Polishing the substrate slightly off-axis may induce some anisotropy in the $KNbO_3$ film growth which is not present when films are grown on the on-axis cubic MgO surface. Figure 5(b) shows the rocking curve of a $KNbO_3$ film grown on an MgO substrate whose surface was polished approximately two degrees off the (100) surface. Once again the FWHM of the rocking curve was improved (FWHM = 0.87°), although not to the extent of the improvement seen with the niobium oxide transition layer. It should be emphasized that these are initial results and further improvement in the epitaxial quality of the $KNbO_3$ films on MgO may be realized by optimizing the growth conditions.

Surface quality and optical properties of epitaxial $KNbO_3$ thin films

The quality of the surface of a waveguiding thin film must be very high to prevent optical loss due to modal conversion and surface scattering. An atomic force microscope (AFM) was used to quantify the surface roughness of $KNbO_3$ thin films deposited on MgO. Figure 6 shows the evolution of the surface morphology as film thickness increases. Figure 6(a) is an AFM

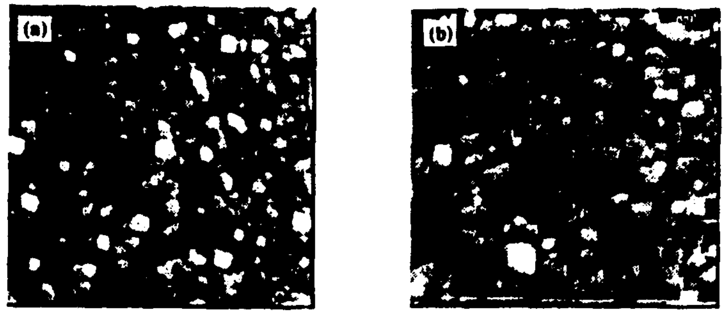

Figure 6 AFM images of the surfaces of $KNbO_3$ thin films (a) 100 nm thick, and (b) 200 nm thick. The images are 2 μm square and the gray scale is 30 nm.

image of the surface of a $KNbO_3$ film which is slightly less than 100 nm thick. This image shows that the peak-to-valley surface roughness is approximately 30 nm. The average grain size of this film, as seen in the image, is approximately 100 nm. Figure 6(b) shows an AFM image of a 200 nm thick film. While the peak-to-valley roughness has remained nearly constant, the grain size of the film has more than doubled. The increased grain size can lead to a degradation of waveguiding properties because *light scattering is known to increase as grain size gets nearer to* the wavelength of the propagating light. Control of grain size may thus be necessary to achieve high quality waveguides for integrated optical applications.

The refractive indices and waveguide losses of sputtered $KNbO_3$ thin films were measured using prism coupling techniques and the details of these measurements have been reported previously.[9] While no in-plane birefringence was observed, the measured refractive indices, TE = 2.28 and TM = 2.20, are very near the expected bulk refractive indices of 2.277 and 2.222, respectively. Optical waveguiding losses were measured to be as low as 10 dB/cm for films 100-120 nm thick. However, no correlation could be determined between the AFM measurements *and the optical loss. It is believed that optical losses due to microstructural defects and surface* imperfections are very large, and the low-loss waveguiding is simply the result of a weakly confined mode propagating through the thin film/substrate waveguide structure.

ION-ASSISTED EPITAXIAL GROWTH OF $KNbO_3$

Thin films of $KNbO_3$ were also grown using an ion-assisted deposition process. A filamentless rf ion source was used to bombard the growth surface with 50 eVoxygen ions. Ion-assisted deposition is known to provide many beneficial effects to film quality. Among the potential advantages of incorporating ion-assisted growth with the ion beam sputter deposition process described above are modifications to the nucleation and growth mechanisms, lower growth temperature, and increased activity at the growth surface. Through ion-assisted growth it may be possible to control the film microstructure including the grain size. A lower growth temperature could be advantageous for integrating these films with current semiconductor processing, and increased activity of the depositing species may improve compositional homogeneity which is important for low-loss optical waveguiding.

The first studies of ion-assisted $KNbO_3$ film growth focused on determining the epitaxial quality achievable using the technique. Typical processing parameters are shown in Table I. $KNbO_3$ films were grown on MgO (100), $MgAl_2O_4$ (100), $KTaO_3$ (100), and $NdGaO_3$ (001) substrates. Lattice constants of these substrates and their lattice mismatch with $KNbO_3$ are shown in Table II. $KTaO_3$, and $NdGaO_3$ were chosen in addition to the MgO and $MgAl_2O_4$ substrates for their unique lattice matching to $KNbO_3$. $KTaO_3$ possesses the smallest lattice

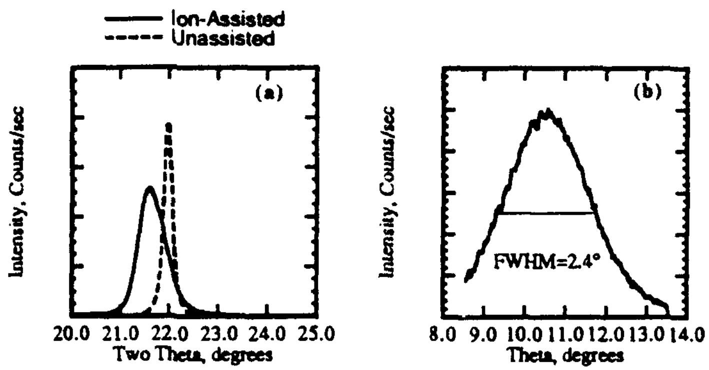

Figure 7 (a) A comparison of the $KNbO_3$ (110) diffraction peaks for films grown with and without ion assistance. (b) The x-ray diffraction rocking curve measurement of the $KNbO_3$ (110) diffraction peak for a film deposited with ion assistance.

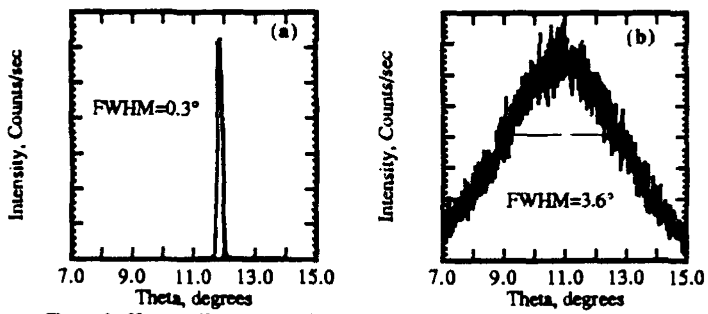

Figure 8 X-ray diffraction rocking curve measurements of the $KNbO_3$ (110) diffraction peak for films deposited on (a) $KTaO_3$ (100), and (b) $NdGaO_3$ (001).

mismatch of any of the substrates used in this study providing the potential for very high quality $KNbO_3$ film growth. The lattice parameters of $NdGaO_3$, on the other hand, are strictly smaller than those of $KNbO_3$ which is unique to the group of substrates used in this study. The deposition temperature during film growth was kept in the 600-700°C range, so that results could be easily compared to films grown without ion assistance.

All $KNbO_3$ films grown with ion assistance were highly (110) oriented. However, the lattice parameter of $KNbO_3$ films on MgO, $MgAl_2O_4$, and $NdGaO_3$ was found to be slightly enlarged. Figure 7(a) shows a comparison of the (110) diffraction peaks of an ion-assisted film and an unassisted film. The lattice parameter of the ion-assisted film has increased by 1.4%, as seen by the shift to a lower two-theta angle. The broadening of the (110) peak of the ion-assisted films is also indicative of a smaller grain size or film strain. The rocking curve of this film, shown in Figure 7(b), reveals that the epitaxial quality has diminished. The FWHM of the rocking curve has increased to more than two degrees compared to 0.6 degrees for the film shown in Figure 3(b). RBS analysis of ion-assisted $KNbO_3$ films revealed the presence of Xe and Fe impurities. These impurities are believed to be responsible for the lower film quality. The Xe in the films is trapped primary sputtering gas, while the Fe is believed to come from sputtering of the stainless steel ring electrode inside the discharge chamber of the rf ion source. The impurity incorporation may be substantially reduced by changing the incidence angle of the oxygen ion bombardment and replacing the stainless steel electrode with another metal such as niobium which would minimize film contamination.

The $KNbO_3$ films on single crystal $KTaO_3$ (100) exhibited the highest epitaxial quality of all of the films deposited with ion assistance. The x-ray rocking curve measurement of one of these films is shown in Figure 8(a). The FWHM of the rocking curve is 0.3° which is at the limit of resolution of the diffractometer used for the measurement. Xe and Fe impurities were also observed in the films on $KTaO_3$. However, due to the very low lattice mismatch between film and substrate these impurities did not diminish the crystal quality as determined by x-ray measurements. In contrast, $KNbO_3$ films deposited on $NdGaO_3$ (001) were of poor epitaxial quality. Figure 8(b) shows the x-ray rocking curve of a film on $NdGaO_3$. The FWHM of the rocking curve is well over three degrees, the largest of all film/substrate combinations. In addition, the films grown on $NdGaO_3$ adhered poorly and exhibited a tendency to peel off the substrate.

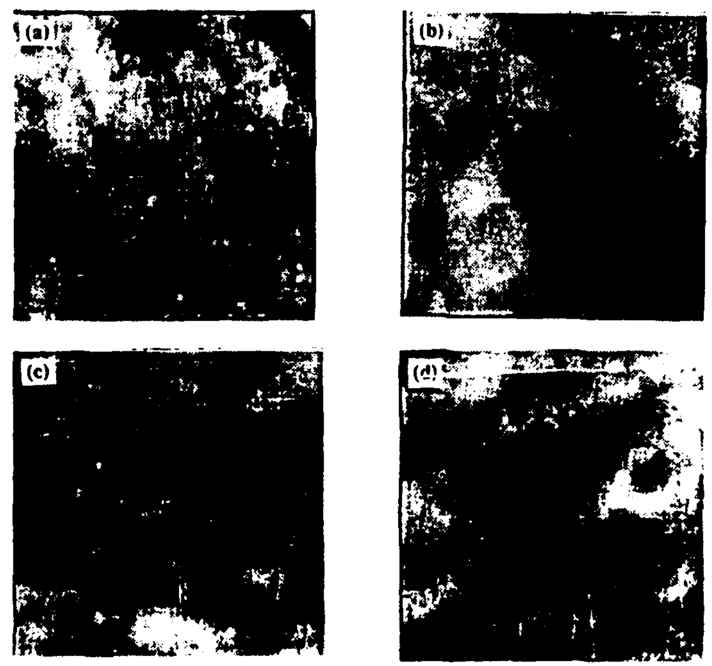

Figure 9 AFM images of $KNbO_3$ thin films deposited with ion assistance on (a) MgO (100), (b) $MgAl_2O_4$ (100), (c) $KTaO_3$ (100), and (d) $NdGaO_3$ (001). The images are 1.25 x1.25 μm square and the gray scales are 5, 100, 30, and 10 nm,respectively.

Surface quality and optical properties of epitaxial ion-assisted $KNbO_3$ thin films

The surface quality of $KNbO_3$ films grown with ion assistance was also investigated using the atomic force microscope. AFM images of films grown on MgO (100), $MgAl_2O_4$ (100), $KTaO_3$ (100), and $NdGaO_3$ (001) substrates are shown in Figure 9. $KNbO_3$ films grown on MgO are shown to have the smoothest surface with a peak-to-valley roughness of 5 nm. This result is an improvement over unassisted films, but it must be further improved for optical waveguiding applications which require very smooth interfaces to prevent scattering and modal conversion. Films on the other substrates were rougher, with a 400 nm thick film on $MgAl_2O_4$ the roughest, 100 nm peak-to-valley. The surfaces of films deposited on $KTaO_3$ and $NdGaO_3$ had intermediate values of roughness, 30 and 20 nm, respectively. The grain size of the films grown with ion assistance is difficult to determine from the AFM images, but it is believed to be smaller than that of the films grown without ion assistance. This smaller grain size may reduce optical scattering in waveguides, as discussed above. If the smaller grain size can be combined with a smoother surface, the films on MgO deposited with ion assistance may be favorable for waveguiding applications if impurity incorporation can also be minimized.

The optical properties of ion-assisted $KNbO_3$ films were also measured with prism coupling techniques and were also reported previously.[9] The measured refractive indices were 2.26 for TE modes and 2.18 for TM modes which are slighlty lower than the indices measured for unassisted films. The lower indices are attributed to a small decrease in density caused by the presence of Fe and Xe impurities which increased the lattice parameter of the assisted films. Optical losses were greater than 50 dB/cm and could not be measured using the fiber probe technique, and thus no correlation with the AFM measurements could be made.

MOCVD GROWTH OF ORIENTED $KNbO_3$ FILMS

$KNbO_3$ thin films were grown for the first time using an MOCVD process.[10] The deposition system, shown schematically in Figure 10, uses solid metalorganic sources. These sources are passed through a very sharp temperature gradient where they sublimate immediately and are transported with He carrier gas to the reaction chamber through heated tubes. The use of the sharp temperature gradient ensures that the source is not exposed to high temperatures over long periods of time, avoiding the difficulty of maintaining a stable vapor pressure over the source during the entire growth process. The cation stoichiometry is controlled by adjusting the feed rate of the metalorganic sources through the temperature gradient. Similarly, the deposition rate can be controlled by scaling the feed rate of both sources. Molecular oxygen, O_2, is added to the gas mixture before entering the reaction chamber so that sufficient oxygen is available for oxide film growth. Typical processing parameters for MOCVD film growth are given in Table III.

Table III Process parameters for MOCVD growth of $KNbO_3$ thin films.

Process Parameter	Value
Source 1	$K(C_{11}H_{19}O_2)$
Source 1: T_{sub}	450 °C
Source 1: Feed Rate	$7.3\text{-}9.7\times10^{-5}$ mol/min.
Source 2	$Nb(C_{11}H_{19}O_2)_4$
Source 2: T_{sub}	325 °C
Source 2: Feed Rate	1.2×10^{-5} mol/min.
Base Pressure	100 mtorr
Operating Pressure	10 torr
He (1) Flow	300 sccm
He (2) Flow	15 sccm
O_2 Flow	300 sccm
Substrate Temperature	650-700 °C
Growth Rate	3.0 nm/min.

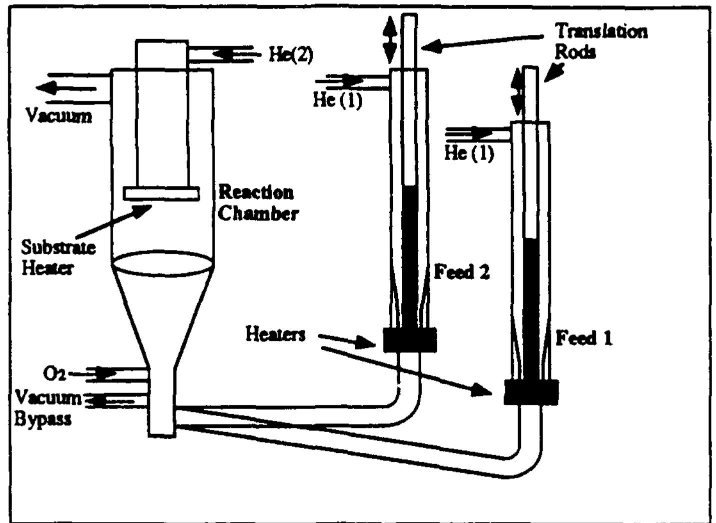

Figure 10 Schematic drawing of the MOCVD system used for the growth of $KNbO_3$ thin films.

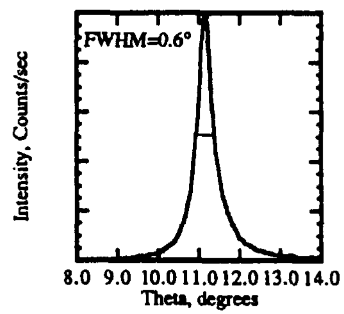

Figure 11 X-ray diffraction rockin curve measurement of the $KNbO_3$ (110) diffraction peak of an MOCVD $KNbO_3$ thin film.

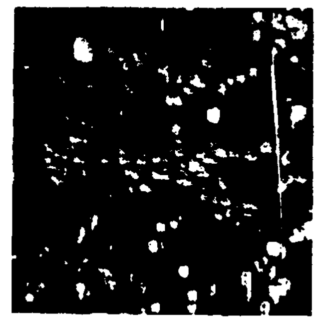

Figure 12 An AFM image of the surface of an MOCVD K NbO3 thin film. The image is 3μm square and the gray scale is 100 nm.

MOCVD $KNbO_3$ films were grown only on $MgAl_2O_4$ (100) substrates, and were found to be highly (110) oriented. Figure 11 shows the rocking curve of a MOCVD $KNbO_3$ film. The FWHM of the rocking curve is 0.6° in keeping with the ion beam deposited films on $MgAl_2O_4$ without ion assistance. However, the surface quality of these initial MOCVD films was found to be considerably below the quality of all the ion beam sputtered films. Figure 12 shows the AFM image of an MOCVD film surface. The peak to valley roughness is 100 nm, nearly equal to the thickness of the film. It is believed that the surface quality of the MOCVD films may be improved by optimizing the processing parameters, particularly the substrate temperature and the deposition rate which was 10 times greater than the deposition rate of the sputtered films.

SUMMARY

The epitaxial quality of $KNbO_3$ thin films grown using ion-assisted and unassisted ion beam sputter deposition was investigated. Key influences of processing conditions on the epitaxial quality were identified. Of these influences, the lattice mismatch between film and substrate was found to have the most prominent effect on epitaxial quality. $KNbO_3$ thin films on $KTaO_3$ (mismatch $\leq 1.2\%$) deposited with ion assistance were found to have the narrowest x-ray rocking curve, 0.3°. However, Fe and Xe impurities were incorporated into the films during the deposition process as a result of the oxygen ion bombardment. Films deposited with ion assistance on MgO, $MgAl_2O_4$, and $NdGaO_3$ substrates had wider rocking curves than films deposited without ion assistance. Two routes were found to further improve the epitaxy of $KNbO_3$ films deposited on MgO without ion assistance. A niobium oxide interlayer and the use of off-axis MgO substrates were found to reduce the width of the rocking curves of $KNbO_3$ films by 60% and 47%, respectively. The surface quality of the films deposited by ion beam sputtering was investigated using atomic force microscopy. Peak-to-valley roughness as low as 5 nm was measured for $KNbO_3$ films deposited on MgO with ion assistance.

$KNbO_3$ thin films were grown for the first time using a solid source MOCVD growth process. Cation stoichiometry and growth rate were controlled by individually adjusting the feed rates of the potassium and niobium metalorganic sources. A rocking curve FWHM of 0.6° was measured for films deposited on $MgAl_2O_4$ which is comparable to the results achieved using sputter deposition. The AFM image of an MOCVD film surface revealed the film was very rough. By optimization of the process parameters it is hoped that surface roughness can be improved in the future.

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Appendix 3

Epitaxial $KNbO_3$ thin films on $KTaO_3$, $MgAl_2O_4$, and MgO substrates

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Epitaxial potassium niobate ($KNbO_3$) thin films have been deposited on $KTaO_3$ (100), $MgAl_2O_4$ (100), and MgO (100) substrates using ion-beam sputter deposition. X-ray-diffraction results show that $KNbO_3$ films have orthorhombic (110) orientation on all three substrates. Rutherford backscattering channeling analysis of $KNbO_3$ films on $KTaO_3$, $MgAl_2O_4$, and MgO exhibits minimum scattering yields (χ_{min}) of 7%, 9%, and 18% for the Nb peak, respectively. This illustrates how the quality of epitaxy improves as the lattice mismatch decreases. Prism-coupling measurements reveal near-bulk refractive indices of about 2.27 for TE modes and 2.22 for TM modes for films on each substrate.

$KNbO_3$ is a promising material for nonlinear-optical (NLO) and electro-optical (EO) applications. It possesses large nonlinear-optical coefficients, and its high electro-optic figure of merit makes it superior to the widely used material, lithium niobate, for integrated-optical phase and amplitude modulators.[1,2]

Several groups have demonstrated the growth of $KNbO_3$ thin films;[3–6] however, films of good optical quality, critical for competitive optical-waveguide devices, are difficult to produce. Thin films used for optical applications should generally be single phase, dense, smooth, stoichiometric, and epitaxial, with as few structural defects as possible. All these properties are important for minimizing light-propagation losses and maximizing NLO and EO effects. An understanding of $KNbO_3$ epitaxial film growth mechanisms is important for optimizing film properties.

In this work, the properties of epitaxial $KNbO_3$ thin films on $KTaO_3$ (perovskite), $MgAl_2O_4$ (spinel), and MgO (rocksalt) substrates are investigated in order to clarify the substrate effects on the epitaxial growth of $KNbO_3$. All three substrates have cubic symmetry. The orthorhombic $KNbO_3$ phase has lattice parameters of $a = 5.721$ Å, $b = 5.695$ Å, $c = 3.973$ Å, and corresponding refractive indices of $n_a = 2.168$, $n_b = 2.279$, and $n_c = 2.329$.[1,7] The three substrates used here provide different lattice and refractive-index mismatches with potassium niobate, as listed in Table I. The properties of $KNbO_3$ films grown on each substrate are presented, and key factors that control film growth, microstructure, and optical properties are discussed.

Ion-beam sputter deposition of $KNbO_3$ thin films has been accomplished using a computer-controlled, sequential layer-by-layer growth technique.[8] A single ion source is used to sequentially sputter targets of niobium and potassium superoxide (KO_2). Substrate temperatures range from 650 to 700 °C, and the oxygen pressure is held at 1×10^{-4} Torr. The MgO and spinel substrates were purchased from Advanced Composite Materials and Commercial Crystal Systems, respectively, while the $KTaO_3$ substrates were provided by Oak Ridge National Laboratory.

The deposited films and substrate materials were analyzed using a variety of techniques. Substrate roughness was measured using atomic force microscopy (AFM). X-ray diffraction (XRD) was used to determine the lattice parameter, phase, and orientation of the $KNbO_3$ films. X-ray-diffraction rocking curve measurements were used to measure grain tilt of the films. Rutherford backscattering spectrometry (RBS) provided film composition and thickness, while ion channeling revealed the epitaxial quality of the $KNbO_3$ films. A prism-coupling technique was used to obtain refractive indices.[10]

Substrate surface roughness can not only directly influence the film surface but impede the epitaxial growth process, since surface steps can induce the growth of (041) tetrahedral twin domains.[11] Atomic force microscopy of the

TABLE I. Bulk properties of $KTaO_3$, $MgAl_2O_4$, and MgO, with comparison to those of $KNbO_3$ (110). Measured properties of $KNbO_3$ (110) films on each substrate are also included.

Substrate	$KTaO_3$ (100)	$MgAl_2O_4$ (100)	MgO (100)
Bulk lattice parameter[a] (Å)	3.989	8.083	4.213
Bulk refractive index[b]	2.225	1.723	1.736
Bulk lattice mismatch, $KNbO_3$ $[\bar{1}10]$, [001]	−1.2%, 0.4%	0.1%, 1.7%	4.4%, 6.0%
Measured FWHM XRD rocking curve	0.25°	0.30°	0.84°
Measured film RBS/channeling, χ_{Nb}	7%	9%	18%
Measured film refractive index, TE, TM	2.27, [illegible]	2.27, 2.23	2.28, 2.21

[a]Reference 8.
[b]Reference 9.

[a]Also at MCNC, Electronics Technology Division, Research Triangle Park, NC 27709-2889.

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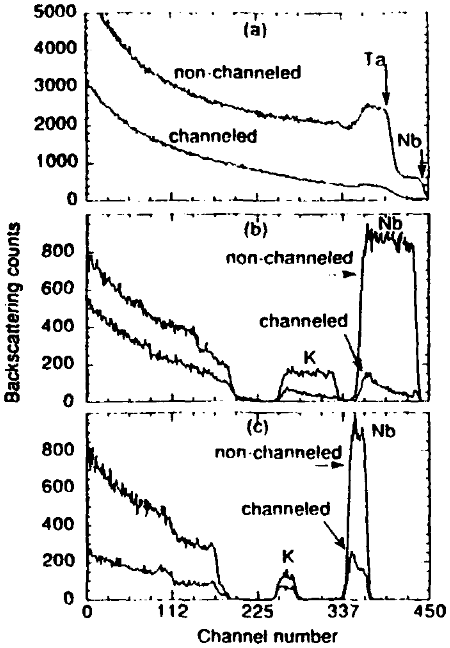

FIG. 1. RBS spectra obtained using unchanneled and channeled configurations are plotted for $KNbO_3$ (110) films on (a) $KTaO_3$ (100), (b) $MgAl_2O_4$ (100), and (c) MgO (100).

substrate surfaces shows that $KTaO_3$ had the lowest surface roughness, with rms roughness of 8 Å, while the rms roughness of the spinel and MgO surfaces was 10 and 26 Å, respectively. The as-received MgO surface contains arrays of "columns" which can be 100 Å or more in height. These are believed to be due to magnesium hydroxide growth. Annealing the MgO substrate at a temperature of ~1200 °C improves the roughness to a rms value of 9 Å. Therefore, a similar roughness can be achieved on each substrate. AFM also detected typical grain sizes of 1000–3000 Å for the $KNbO_3$ films.

X-ray diffraction showed that the $KNbO_3$ films on all substrates are single phase and the orthorhombic [110] is normal to the substrate surface. For the $KNbO_3$ (110) orientation a lattice parameter of 4.036 Å is expected perpendicular to the surface plane. The (110)-plane spacing measured for all films ranged from 4.02 to 4.05 Å. Rocking curve measurements of the $KNbO_3$ (110) peak revealed a full width at half maximum (FWHM) value of 0.84° for $KNbO_3$ on MgO substrates, 0.25° for films on $KTaO_3$, and 0.30° for films on $MgAl_2O_4$, as listed in Table I.

RBS/channeling spectra are shown in Fig. 1 for $KNbO_3$ films on $KTaO_3$ [Fig. 1(a)], $MgAl_2O_4$ [Fig. 1(b)], and MgO [Fig. 1(c)]. Values of minimum channeling, χ_{min}, were obtained in a 10-channel energy window by comparing the lowest point in the channeled spectra, just below the surface peak, with an unchanneled spectrum. $KNbO_3$ on $KTaO_3$ had a χ_{min} of 7% for the Nb peak. Films on spinel show slightly higher χ_{min} values, 9% for Nb, while results for $KNbO_3$ on MgO showed the highest χ_{min}, 18% for Nb. The higher χ_{min} values for $KNbO_3$ on MgO suggest a larger amount of either grain tilt, grain misorientation, or other defects.

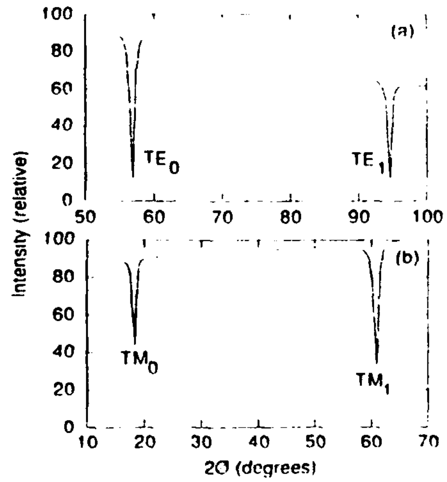

FIG. 2. Coupling curves of uncoupled, reflected intensity vs coupling angle for $KNbO_3$ (110) films on $MgAl_2O_4$ (100), are shown for (a) TE modes and (b) TM modes.

RBS also showed that all of the films are deficient in potassium, with a K to Nb cation ratio in the range of 0.7–0.95. Increasing the amount of KO_2 sputtered does not cause a composition change when deposited at 650–700 °C, although at lower temperatures, 550–600 °C, the films can become potassium rich and not optically translucent. Energy-dispersive x-ray analysis reveals the presence of sodium in some films, which may partially compensate for the potassium deficiency and allow the films to possess a single orientation and near-bulk refractive indices as shown later. A possible source for the sodium is the superoxide pressed KO_2 targets. Potassium vacancies might also be filled by hydrogen atoms.

The refractive indices were measured by coupling a He-Ne (6328 Å) laser beam into the films using the prism-coupling method.[10] Coupling curves for a $KNbO_3$ film with a thickness of 5000 Å on a spinel substrate are shown in Fig. 2. The narrow coupling width is indicative of a smooth film with uniform thickness. Typical refractive indices measured for all films are 2.22 and 2.27 in the TM (light polarized along $KNbO_3$ [110]) and TE modes (light polarized in the film plane), respectively, as shown in Table I. The index of $KNbO_3$ (110) films is smaller than $KTaO_3$ in the TM mode, so TM-mode film coupling is not possible for this case. The measured refractive index for TM modes compares very favorably with the bulk refractive index of $KNbO_3$ [110], 2.222. The refractive indices of the TE modes of our films were measured in two orthogonal propagation directions and were found to be similar in each direction, which indicates that 90° domain orientations exist on all substrates. Therefore, the refractive index for the TE modes should reflect an average value (2.274) between the indices of $KNbO_3$ [$\bar{1}$10] and [001], 2.222 and 2.329, respectively. The fact that our indices so closely approach the bulk values indicates that the films are very dense over a range of film compositions. No dependence of refractive index on composition was detected.

In-plane lattice spacings for single-crystal $KNbO_3$ with (110) orientation would be 3.973 Å [001] and 4.036 Å [$\bar{1}$10].

Table I lists the calculated lattice mismatches for each film/substrate system. The x-ray-diffraction rocking curve and RBS/channeling data show that a smaller amount of grain tilt (higher degree of epitaxy) was observed for the $KNbO_3$ films on $KTaO_3$ and spinel substrates, where a smaller lattice mismatch occurs, compared to films on MgO substrates. This is a clear indication that lattice mismatch is a key factor in achieving good epitaxial quality. Better epitaxial quality suggests fewer structural defects, which should improve the optical quality of the films.

The reason why the $KNbO_3$ (110)-film orientation occurs can be explained based on the following discussion. The lattice parameter of ~4.02–4.05 Å observed for all $KNbO_3$ films by x-ray diffraction indicates that the shortest ⟨100⟩ axis ([001], c=3.973 Å) is parallel to the substrate surface plane (in-plane). At the growth temperature, the fact that both our film and substrate are cubic suggests that the film is (001) oriented with the in-plane ⟨100⟩ axes aligned parallel to those of the substrate. The cubic-to-tetragonal transformation results in two "short" axes and one "long" axis of $KNbO_3$.[1] At least one of the short axes must lie along the substrate surface.

As the film transforms to the orthorhombic phase, there is a slight lattice distortion that leads to the lengthening of one of the original short axes, which becomes the [110] orthorhombic direction. The other short axis remains essentially unchanged, becoming the [001] direction. Since there are no stresses perpendicular to the growth direction, the short axis normal to the substrate plane would be less energetically inhibited to lengthen, thus leaving the remaining short axis to be in the film plane. Similarly, in the other case where if both the short axes were in the film plane, one axis will lengthen and leave the other short axis still in the plane. Thus a short axis would always lie in the plane of the substrate, resulting in the (110)-oriented orthorhombic $KNbO_3$ we observe.

The occurrence of grain tilts and 90° domain orientations can be further understood by considering the $KNbO_3$ phase transformations from cubic (at growth temperature) to tetragonal (~435 °C), and then to orthorhombic (~225 °C) during cooling. During deposition, misfit dislocations are expected to form to accommodate the lattice mismatch between the film and substrate. This may result in "tilts" and "twists" of the film grains with respect to the substrate. Upon cooling, more tilting may occur depending on the thermal-expansion-coefficient mismatch. The phase transformation can induce twin formation and also can affect the magnitude of the grain tilt. Due to the $KNbO_3$ (110) orientation and its orthorhombic structure, in which there is a slight asymmetry of the two ⟨100⟩ long axes, an additional tilt of 0.13° from the normal towards one of the two in-plane $KNbO_3$ ⟨110⟩ directions occurs. The cubic nature of the substrates allows for the tilts and twins to occur in any of the equivalent 90° directions. This limits the x-ray-diffraction rocking curve to a minimum FWHM value of ~0.26° for the fine-grained, unpoled thin films.

Both the XRD rocking curves and RBS/channeling data show a higher quality of epitaxy for $KNbO_3$ on $KTaO_3$ and $MgAl_2O_4$ compared with films on MgO, indicating that a smaller lattice mismatch is the key to improving epitaxy and minimizing low-angle boundaries. Tilts and twins may be a significant factor limiting propagation losses. The lower substrate roughnesses of $KTaO_3$ and $MgAl_2O_4$ substrates and the corresponding lower film roughnesses should result in lower surface scattering losses due to a smoother interface and film surface.

We have deposited high-quality, dense, epitaxial $KNbO_3$ films on $KTaO_3$, $MgAl_2O_4$, and MgO substrates. Despite the observed potassium deficiency, the $KNbO_3$ films are dense as suggested by the bulk refractive indices observed. $KNbO_3$ films on $KTaO_3$ and $MgAl_2O_4$ have better epitaxial orientation than those on MgO, confirming that lattice mismatch is a key issue in producing high-quality epitaxial films. The varying quality of epitaxy of the films and the refractive-index differences between substrates should provide information regarding the dominant loss mechanisms for $KNbO_3$ thin-film waveguides on different substrates. The optical losses are presently being investigated and the results will be reported in a forthcoming publication.

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Appendix 4

MICROSTRUCTURAL AND OPTICAL PROPERTIES OF POTASSIUM NIOBATE THIN FILMS

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ABSTRACT

A potassium niobate thin film waveguide is an ideal candidate for producing a compact blue laser source by second harmonic generation. However, good epitaxial quality films are difficult to produce and high optical losses are a continuing problem. This paper investigates the microstructural and optical properties of $KNbO_3$ thin films to better understand the origin of optical waveguide losses. Epitaxial, dense $KNbO_3$ thin films have been grown on MgO, $MgAl_2O_4$, and $KTaO_3$ substrates by ion-beam sputter deposition. X-ray diffraction, rocking curves, Rutherford backscattering spectroscopy, ion-channelling, field emission scanning electron microscopy, and atomic force microscopy were used to analyze the orientation, epitaxial quality, grain size, and surface roughness of the films. Optical properties including refractive index and optical scattering losses have been characterized by prism-coupling and an optical fiber loss measurement method. The dominant loss mechanism in these film waveguides is discussed. Green light by second harmonic generation has been produced in the transverse and waveguide modes in $KNbO_3$ films.

INTRODUCTION

A short wavelength laser source is necessary to increase the density of present optical recording systems. Green or blue light can be generated from an IR laser by second harmonic generation (SHG) using a nonlinear optical material. Several problems continue to hinder efficient frequency doubling. First, few materials possess high nonlinearity and can be easily phase-matched for the appropriate wavelengths. In addition, bulk crystals that have demonstrated SHG in the blue or green spectral region produce too little power. (At least 5 mW of power is necessary for many practical applications.) [1] Potassium niobate possesses very high nonlinear constants and one of the highest figures of merit for producing SHG. [2] Also, $KNbO_3$ thin films offer field confinement and thus, high conversion efficiency as well as ease of phase-matching by use of modal dispersion. Lithium niobate thin films have demonstrated SHG blue light. However, its bulk nonlinear optical properties are inferior to those of $KNbO_3$ and the second harmonic power produced was weak. [3] Ultimately, thin film waveguides will be desired for high power conversion. Nevertheless, high quality $KNbO_3$ thin films are difficult to grow due to potassium volatility at the growth temperature. A high degree of epitaxy and defect minimization are necessary for low waveguide losses. Thus, the origin of losses must be pinpointed, and microstructure and film processing must be synergistically controlled.

We report the growth of $KNbO_3$ thin films with a high degree of epitaxy, and correlate film microstructures with optical properties. Films were grown by ion-beam sputter deposition. X-ray diffraction (XRD) and x-ray rocking curves were performed to analyze film orientation and grain tilt, respectively. Rutherford backscattering spectroscopy (RBS) revealed film composition information while RBS/channelling detected the grain tilt and misorientation of the films. Substrate and film surface roughnesses were determined by atomic force microscopy (AFM). Field emission scanning electron microscopy displayed the film surface morphology. Refractive indices were calculated from prism-coupling measurements and an optical fiber attachment allowed optical scattering losses to be measured. Highly epitaxial, dense $KNbO_3$ thin films have produced green light by SHG in the transverse and waveguide modes.

ION-BEAM SPUTTER DEPOSITION

Ion-beam sputter deposition was used to produce $KNbO_3$ thin films on MgO (100), $MgAl_2O_4$ (100), and $KTaO_3$ (100) substrates. A computer-controlled, sequential rotating target assembly consists of potassium superoxide (KO_2) and niobium targets that are alternately sputtered by an xenon ion beam. [4] Thus, composition is controlled by programming the ion beam dwell time on each target. Each layer deposited in one rotation of the targets is only 5-10 Å to allow for interdiffusion to form a homogeneous film. The deposition rate is about 10 Å/min. and film growth occurs at 650-700°C. Table 1 summarizes the important sputter deposition parameters.

Table 1. Ion-beam deposition parameters for $KNbO_3$ thin film growth.

Beam energy	800 eV
Beam current	15 mA
Xe^+ source gas pressure (torr)	1.4×10^{-4}
O_2 gas pressure (torr)	2.5 x 10-4
Deposition temperature	650-700°C
Deposition rate	10 Å/min.

MICROSTRUCTURAL PROPERTIES

Orientation

The d-spacings of the planes parallel to the sample surface can be detected through standard theta-two theta x-ray diffraction. $KNbO_3$ films on all substrates under typical growth conditions show a single $KNbO_3$ (110) orientation with d-spacings in the range of 4.02-4.04Å. This corresponds to one of the longer axes of the orthorhombic $KNbO_3$ cell. Films deposited at temperatures lower than 600°C often contain additional grain orientations such as the $KNbO_3$ (111).

X-ray diffraction rocking curve analysis provides information about the grain tilt of the films. The samples were 'rocked' about the $KNbO_3$ [110]. Any misorientation or tilt of the film grains will broaden the width of the rocking curve. XRD rocking curves of $KNbO_3$ films are shown in Figure 1 and reveal FWHM values of 0.25, 0.30, and 0.84° on $KTaO_3$, $MgAl_2O_4$, and MgO, respectively.

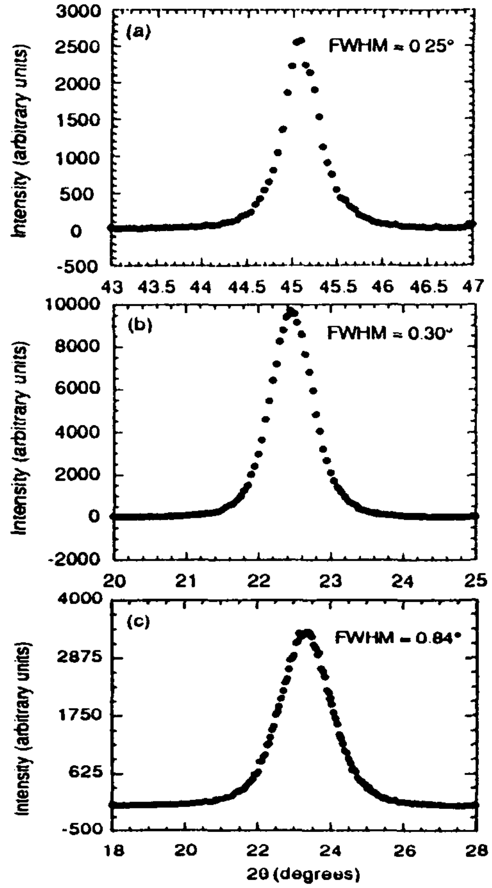

Figure 1. X-ray diffraction rocking curves of $KNbO_3$ [110] on (a) $KTaO_3$, (b) $MgAl_2O_4$, and (c) MgO substrates.

Composition and grain tilt

Rutherford backscattering spectroscopy was used to analyze the composition and thickness of the films. $KNbO_3$ films are found to possess K to Nb ratios in the range of 0.60 to 0.90. The potassium deficiency does not seem to affect the properties of the films. For instance, in XRD, only the $KNbO_3$ (110) orientation exists and near bulk refractive index values are measured (as discussed later) for all films despite the K deficiency. It is believed that Na atoms arising from impurities in the KO_2 targets compensate for the K deficiency. A $KNbO_3$ film was deposited on a beryllium substrate to allow low mass atoms to be detected in the RBS spectrum without being obscured by the substrate peak. Sodium was found to exist throughout the thickness of the film. Thus, it is likely that Na substitution on the K sub-lattice preserves the integrity of the $KNbO_3$ unit cell and further, has little influence on some film properties such as the refractive index.

RBS/channeling measurements were performed by aligning the beam along the [110] film direction. The amount of scattering from the film would reveal the amount of film misorientation, defects, and other scattering centers. Channelling can only occur if films are of good epitaxial quality. In all cases the film was found to be aligned with the substrate in the perpendicular growth direction as the minimum film channeling direction corresponds to that of the substrate. $KNbO_3$ films on $KTaO_3$ and spinel substrates displayed the lowest channeling yields with χ_{min} of only 7% and 9% for the Nb peak, respectively, while $KNbO_3$ films on MgO showed a χ_{min} of 18 %. A single crystal $KTaO_3$ substrate displayed a χ_{min} of 3% which illustrates the high degree of epitaxy of these films. However, films on MgO possess significantly more grain tilt. These results correlate with the XRD rocking curve data shown above.

Surface morphology

Field emission scanning electron microscopy was used to characterize the surface microstructure and grain size of the films. $KNbO_3$ films on MgO and spinel contained grains of 1000 to 1200 Å in size as shown in Figure 2. Larger grain sizes of ~ 3000Å and also 90° oriented domain structures were found for films on $KTaO_3$.

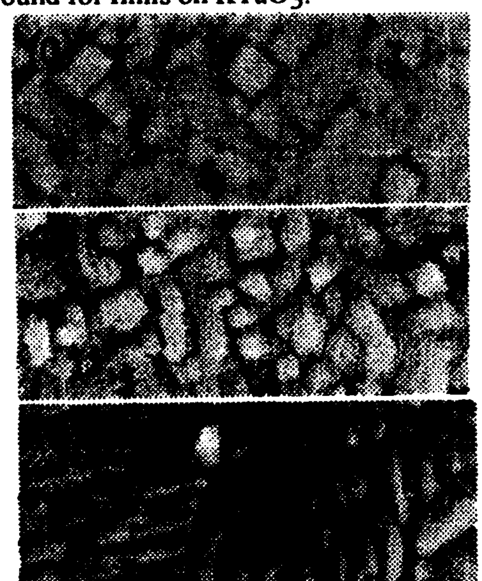

Figure 2. FESEM micrographs of $KNbO_3$ on (a) MgO, (b) $MgAl_2O_4$, and (c) $KTaO_3$ substrates

Surface roughness of both the films and substrates were analyzed by atomic force microscopy. Substrate surface roughness minimization is key for lowering optical scattering at the interfaces and for optimizing epitaxial film growth. Regions of 5 by 5 microns were scanned for all samples. MgO substrates displayed a root mean square (rms) roughness value of 23 Å with maximum features of 196 Å in height. These periodic large structures are believed to be due to hydroxide formation on the MgO surface. Annealing of the MgO substrates for 14 hours at 1150°C resulted in an rms value of only 13 Å with maximum features of 95 Å. Spinel substrates showed rms values of 14 Å and large features of 270 Å. Upon annealing both the rms and the maximum feature height increased appreciably. The rougher spinel surface can be attributed to either the nature of the more complex spinel structure where several different atomic surfaces are possible, or due to vendor preparation. $KTaO_3$ substrates exhibited the lowest surface roughness with an rms of 8 Å and a maximum height of 56 Å. The surface roughness of the $KNbO_3$ films were found to be low, with rms values varying from 13 to 37 Å.

OPTICAL PROPERTIES

Refractive index

The prism coupling technique was used to evaluate the refractive index of the thin films. [5] A He-Ne laser (6328 Å) is focused on a rutile prism clamped to the sample. The beam can be either polarized in the TE (polarized in the plane of the film) or TM (polarized perpendicular to the film) mode. When the propagation constant of the He-Ne beam in the prism matches that of the film, the overlap of the light waves in the airgap between the prism and film allows the light to couple into the film/waveguide. The incident angles which produce coupling conditions are used to calculate the refractive index and thickness of the film. If two coupling angles (two waveguide modes) can be detected, both the thickness and refractive index can be calculated independently. Otherwise, one parameter must be known to calculate the other. Refractive indices measured for all films are 2.21 and 2.28 in the TM and TE modes , respectively. The bulk refractive index of $KNbO_3$ [110] in the TM orientation is 2.222. The refractive indices of the TE modes of our films were measured in two orthogonal propagation directions, but no birefringence was measured, which indicates that 90° domain orientations exist on all substrates. Therefore, the bulk refractive index for the TE modes should reflect an average value between the indices of $KNbO_3$ $[\bar{1}10]$ and [001], 2.222 and 2.329. Figure 3 displays the $KNbO_3$ film refractive indices as a function of composition. Consequently, the fact that the refractive indices fall so close to the bulk values suggest $KNbO_3$ films are dense despite the potassium deficiency.

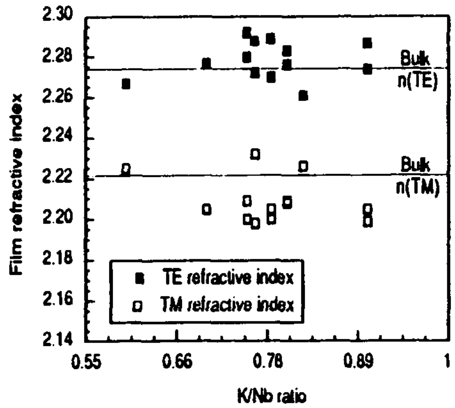

Figure 3. Refractive index of $KNbO_3$ (110) measured in the TE and TM modes versus composition

Scattering losses

Optical waveguide losses can be measured by analyzing the light streak observed in the film when coupling occurs. Longer light streaks suggest lower scattering losses. $KNbO_3$ films on MgO and spinel show higher losses for thick films (>1500 Å) than thinner (~1000 Å) films. Streak lengths of >8 mm can be observed for the latter cases as compared to only 2-3 mm for the thicker films. For our apparatus, losses can only be measured accurately for films with streak lengths of >5 mm. An optical fiber is mounted on a micrometer that allows movement along the length of the streak. The intensity of the light scattered at the surface of the streak is detected and quantified by a photodiode and connected to a nanovoltmeter. The losses can then be calculated by taking the slope of $10\log(I/I_o)$ versus distance along the light streak where I = intensity of the measurement point and I_0 = initial intensity collected by the first point near the prism. Optical waveguide losses of ~34 dB/cm were found for $KNbO_3$ films of ~1100 Å, while even higher losses of >50 dB/cm were detected for thicker (>1500 Å) films .

Second harmonic generation

A Nd:YLF laser source with a wavelength of 1.053 µm with ~80psec, 100 MHz pulses under mode-locked operation was used as the source beam for SHG measurements. A harmonic beam splitter transmits the fundamental wavelength to a razor blade beam block, and reflects the second harmonic through a tilted 532 nm bandpass filter onto a ground-glass screen. First, $KNbO_3$ samples of thickness varying from 4600 to 6500 Å were placed perpendicular to the beam direction. By visual inspection of the screen, strong green light was observed for four samples of $KNbO_3$ thin films on both MgO and $KTaO_3$ substrates. Laser currents of only 28 to 30 A (at 30A, 275 watt/pulse was detected) were necessary to generate strong green light. Saturation of the signal seem to occur at 30 A. A $KNbO_3$ sample of ~2400 Å in thickness was then coupled with a 90° rutile prism. A 3-4 mm green light streak was seen in the TM_0 mode using currents of 31 to 33 A. These SHG results will be discussed in detail in an upcoming paper.

DISCUSSION

Three types of loss mechanisms exist: scattering, absorption, and radiation.[6] However, for dielectric thin films, the predominant contribution to losses are typically scattering losses. Scattering is subdivided into volume and surface scattering. Surface scattering losses are attributed to both light scattered from the film surface and the film/substrate interface. As the thickness of the film increases, the surface scattering losses decrease for a given coupling angle and arbitrary propagation length. As the mode number increases, the surface scattering will likewise increase, for the number of reflections within the waveguide increases duly. Therefore, properties that affect these losses are film and substrate roughness, and the particular mode or coupling angle.

Volume losses originate from scattering due to imperfections such as point defects, dislocations, and grain boundaries, found in the bulk of the waveguide. Figure 4 illustrates the phenomenon of volume scattering. Our data shows that the optical waveguide losses increase as the thickness of the film increases in the case of $KNbO_3$ films on MgO and spinel. This indicates that volume scattering losses are indeed dominating. When the films are just above the thickness criterion for waveguiding of the first mode, the majority of the field is propagating in the low loss single crystal substrate, and thus, low scattering losses are observed. As the film thickness increases, the amount of the optical field propagating in the film increases, and thus volume losses become a greater proportion of the total losses.

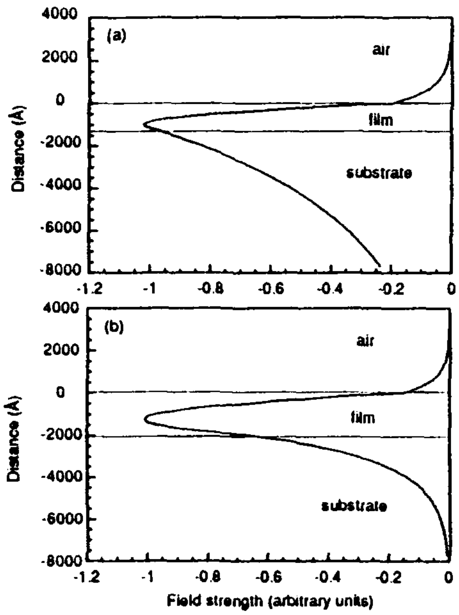

Figure 4. Modal distribution versus distance for the TM=0 mode and wavelength 6328 Å for a $KNbO_3$ waveguide on MgO substrate for film thickness (a) 1200 Å and (b) 2000 Å

The x-ray diffraction rocking curve and RBS/channeling data show a correlation between lattice mismatch and grain tilt. $KNbO_3$ films on spinel and $KTaO_3$, where a smaller lattice mismatch exists, exhibited less grain tilt as compared to films on MgO. At the deposition temperature, the $KNbO_3$ film is cubic. Misfit dislocations form to accomodate the lattice mismatch which may result in 'tilts' and 'twists' of the grains. These lattice imperfections can be a significant contributor to bulk scattering. During cooling, the film first transforms to the tetragonal phase at ~435°C. It is during the second transformation to the orthorhombic structure (~225°C) where twin domains may form. The cubic symmetry of the substrates allows the in-plane orientations to be accomodated in any of the four equivalent 90° directions. Light waves travelling in the film will therefore experience refractive index changes as they traverse the twin domains resulting in attenuation. The coarse and fine grain structure as seen in the FESEM micrographs gives additional evidence of the bulk scattering that is occurring in the films.

SUMMARY

Epitaxial dense $KNbO_3$ thin films have been grown on MgO, $MgAl_2O_4$, and $KTaO_3$ substrates by ion-beam sputter deposition. X-ray diffraction shows a single $KNbO_3$ (110) orientation for all films. RBS revealed K to Nb ratios ranging from 0.60 to 0.90. The potassium deficiency of the $KNbO_3$ films can be explained by sodium incorporation from impurities found in the KO_2 sputtering targets. AFM measurements reveal smooth films when grown on high quality substrate surfaces. Prism coupling measurements show films to possess near bulk TE and TM refractive indices of 2.28 and 2.21, respectively. The optical waveguide losses in the films can be attributed primarily to volume scattering, possibly originating from the coarse and fine grain structure and/or twins formed during structural transformations. $KNbO_3$ thin films have demonstrated SHG of green light from a Nd:YLF laser source in the transverse and waveguide modes with film thicknesses of 4600-6500 Å and ~2400 Å, respectively. The strong green light seen at low currents and small film thicknesses indicate the high nonlinearity of the $KNbO_3$ films, the high quality of these $KNbO_3$ thin films, and the potential for producing a blue laser source.

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This research is supported by the Office of Naval Research under Contract No. N0014-91-1307. We thank Dr. N. R. Parikh at University of North Carolina-Chapel Hill for providing the Rutherford backscattering spectroscopy equipment, and Dr. L. A. Boatner at Oak Ridge National Laboratory for supplying the $KTaO_3$ substrates.

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Appendix 5

Second harmonic generation in potassium niobate thin films

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Green light produced by second harmonic generation has been observed in an epitaxial $KNbO_3$ thin film planar waveguide of orthorhombic-phase produced by ion-beam sputtering deposition on a (100)-oriented MgO single crystal substrate. A Nd:YLF laser beam, with a wavelength of 1.053 μm and ~80 ps, 100 MHz pulses under mode-locked operation, was coupled into the waveguide using a rutile prism, and a green light streak 3 to 4 mm long was seen in the guide. The TM_0 mode of the input beam was phase-matched to the TE_1 mode of the second harmonic at a film thickness of 2300 Å. Second harmonic generation was also observed in a bulk configuration on thicker (4600-6500 Å) films on both MgO and $KTaO_3$ substrates.

PACS number:

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Currently, red laser beams of wavelengths of ~780 nm are used to read optical discs. A source of shorter wavelength, having a smaller beam size, would allow for denser packing of data on the disc. The drive for increasing optical recording density has stimulated the development of nonlinear materials for frequency doubling. Using such materials, an infrared source laser can be used to produce blue or green light via second harmonic generation (SHG). Up to four times the present disc storage capacity has been demonstrated using SHG from a $KNbO_3$ single crystal.[1]

For reasons of compactness, ruggedness, and high conversion efficiency, it is desirable in optical disc applications for the SHG to take place in an optical waveguide.[2] The confinement offered by the waveguide structure allows high optical power densities to be maintained over long interaction lengths; both these factors increase the SHG conversion efficiency. In addition, if the effective waveguide thickness can be appropriately adjusted, the modal dispersion of the guide can be utilized to achieve phase matching under a wider variety of conditions than possible in the bulk material.[3,4] The deposition of waveguide films suitable for SHG on crystalline substrates of lower refractive index is of particular interest for hybrid integration of the guide with diode lasers and other optical components.[5] Among SHG materials, crystalline $KNbO_3$ is notable for its large figure of merit for SHG, broad transparency range, high resistance to optical damage, and suitability for noncritical phase matching of laser diodes.[6] Some properties of $KNbO_3$ are summarized in Table I. $KNbO_3$ crystals are not inexpensive to grow and prepare, and it is difficult to form waveguides in crystals of this material by simple diffusive or ion-exchange processes.[7] Moreover, it is not possible, using bulk crystals, to obtain noncritical phase matching at room temperature for wavelengths below 857nm.[8] Thus it is not surprising that there has been considerable interest in obtaining thin crystalline films of $KNbO_3$ by various deposition methods. Relatively thick, multimode films have been prepared by liquid phase epitaxy.[9] Epitaxial films have been made by the sol-gel method on (211) $SrTiO_3$[10] and on Pt-coated (100) MgO[11], but no optical properties have been

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reported. Recently the pulsed-laser deposition technique has been used to grow epitaxially oriented, stoichiometric $KNbO_3$ films on (100) MgO substrates using K-rich targets[12], again no optical properties have been reported. Schwyn and Thony and co-workers prepared waveguiding $KNbO_3$ layers by rf sputtering on MgO and magnesia-alumina spinel substrates.[13] Their films retained the tetragonal high-temperature $KNbO_3$ phase. They also observed SHG in these films in the bulk configuration. We have recently prepared epitaxial $KNbO_3$ films in the orthorhombic phase on several different substrates using ion-beam sputtering[14], and have observed waveguiding in these films.[15] In this paper, we report on SHG in these samples.

$KNbO_3$ thin films were deposited on MgO and $KTaO_3$ single crystal substrates. Film orientation, epitaxial quality, and substrate and film roughness were characterized by x-ray diffraction and rocking curves, Rutherford backscattering spectroscopy (RBS) and ion-channeling, and atomic force microscopy. Refractive indices were determined by a prism-coupling technique.[16] Second harmonic generation experiments were conducted in the transverse configuration by placing the sample perpendicular to the direction of a Nd:YLF source beam, and also in a waveguided mode using prism-coupling. Calculations for waveguiding conditions and modal dispersion phase-matching are presented.

An ion-beam sputter deposition technique featuring a computer-controlled rotating target assembly was used to deposit $KNbO_3$ thin films.[17] Two KO_2 targets and one Nb metal target are sequentially sputtered using a xenon ion source. Deposition temperatures of 650-700°C and oxygen pressures of about 1×10^{-4} Torr were used. All substrates were cleaned in ultrasonic/acetone, methanol, followed by de-ionized water. MgO substrates were annealed (@ 1150°C for 14 hours) after the cleaning to remove any hydroxide that may have formed on the surface.[14] The deposited films were visually transparent.

X-ray diffraction revealed a $KNbO_3$ (110) orthorhombic orientation for films on all substrates. No other orientations or phases were detected. Both x-ray rocking curves and RBS/channeling determined the films to possess good epitaxial orientation. Films on MgO and $KTaO_3$ showed

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rocking curve FWHM values as low as 0.84° and 0.35°, respectively, and minimum channeling yields of 18% and 7% for the the Nb peak. The single orientation of $KNbO_3$ is critical, for any second phases or other orientations are potential sources for light scattering. The small amount of grain tilt as inferred from the rocking curves and ion-channeling results also suggests that some grain-boundary scattering may occur. More details concerning the $KNbO_3$ film epitaxy and microstructure can be found in a previous paper.[17]

Substrate and film surface roughnesses were measured by atomic force microscopy. The interface and film surface can be significant contributors to scattering losses as nonuniformity of these boundaries causes light to scatter incoherently. Low substrate roughnesses with root mean square (rms) values of 8-10 Å can be achieved for both as-received $KTaO_3$ substrates and annealed MgO substrates. The $KNbO_3$ film surface roughnesses are also low, varying in rms values from 18-37 Å.

Refractive indices were determined using a prism-coupling apparatus in which a He-Ne (632.8 nm) laser is focused onto a rutile prism clamped to the thin film sample. The measured refractive indices are about 2.21 and 2.28 for the TM (light polarized along the $KNbO_3$ (110)) and the TE modes (light polarized in the film plane), respectively. The bulk refractive index values for this film orientation are 2.222 for the TM mode and 2.274 for the TE mode. (The TE value is calculated from an average of the $KNbO_3$ [$\bar{1}$10] and [001] values due to 90° domain orientations.[14]) The fact that the film indices are so close to the bulk values suggests that the films are very dense.

Phase-matching of the fundamental beam with the second harmonic can be achieved by using modal dispersion in thin films.[3] First, the refractive index of $KNbO_3$ as a function of wavelength must be known.[8] The effective index of the film for different modes varies with respect to the film thickness. Thus, by plotting the modal dispersion curves for both the fundamental and second harmonic wavelengths, the thicknesses where phase-matching occurs for particular modes can be pinpointed. Figure 1 displays the modal dispersion curves for a $KNbO_3$ thin film on an MgO substrate at the Nd:YLF laser wavelength of 1.053 μm and the frequency doubled wavelength of 5265 Å. For example, at a film thickness of 2300 Å, the effective index of the TM_0 at 1.053 μm matches that of the TE_1 at 5265 Å as seen in the figure. Therefore, thin film waveguides permit a simpler phase-matching scheme whereby growing films to specific thicknesses allows phase-matching of particular modes to be accomplished.

Figure 2 shows a schematic of the SHG experimental setup. A Nd:YLF laser with a wavelength of 1.053 μm with ~80 psec, 100 MHz pulses under mode-locked operation was used as the source beam. A harmonic beam splitter transmits the fundamental wavelength to a beam block, and reflects the second harmonic through a tilted 532 nm bandpass filter onto a ground-glass screen. First, $KNbO_3$ samples of thickness varying from 4600 to 6500 Å were placed perpendicular to the beam direction in a non-waveguiding mode. Three samples of $KNbO_3$ thin films on MgO substrates and one on a $KTaO_3$ substrate displayed green light as visually detected on the screen. Laser drive currents of only 28 to 30 A (power at 30 A was calibrated at 275 watt/pulse) were necessary to generate strong green light. The signal appeared to saturate at 30 A. Next, we measured SHG in the waveguided configuration. A $KNbO_3$ sample on an MgO substrate with thickness varying from 2200-2800 Å was prepared and then coupled into with a 90° rutile prism. The $KNbO_3$ film was purposely grown with a thickness gradient so that the critical phase-matching thickness could be assured at some area of the sample.[18] At the coupling angle for the TM_0 mode at the fundamental wavelength of 1.053 µm, a 3-4 mm green light streak was observed. Currents of 31-33 A were used. We believe that phase-matching is occurring at a film thickness close to 2300 Å for the TM_0 (@ 1.053 µm) and the TE_1 (@ 5265 Å). The ease of phase-matching in producing strongly visible green light suggests that these $KNbO_3$ thin films have high nonlinearity, and also establishes the potential of $KNbO_3$ thin film waveguides for producing a compact blue or green laser source.

Since modal dispersion allows phase-matching to occur without using crystal birefringence, different orders of modes must be used. The effective refractive index decreases with increasing mode number and wavelength. Therefore, a lower order mode of the fundamental wavelength matches at a higher order mode of the second harmonic. One measure of the conversion efficiency for this case is the mode overlap integral.[19] The shape of the mode depends on the mode order, and the overlap integral for the TM_0 and the TE_1 is not very large, as shown in Figure 3. Other mode selections such as the TM_0 -> TE_2 (which would be phase-matched at 6700 Å) would produce a greater overlap of the fields and second harmonic power. Work on the SHG efficiency of different mode configurations is presently in progress.

In conclusion, high quality epitaxial $KNbO_3$ thin film planar waveguides have been grown by ion-beam sputter deposition. An infrared laser has been used to produce green light by SHG from $KNbO_3$ thin films on both MgO and $KTaO_3$ substrates. Film thicknesses of only 4600 to 6500 Å exhibited strong green light when placed perpendicular to the beam. A green light streak 3-4 mm in length was also observed when a $KNbO_3$ thin film on MgO was coupled at the TM_0 mode. The film thickness was close

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to 2300 Å where modal dispersion phase-matching occurs for the TM_0 at 1.053 μm and the TE_1 at 5265 Å.

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Table 1. Properties of $KNbO_3$

Nonlinear coefficient[a]	1.24×10^{-11} m/V
Refractive index[b]	n_a=2.168, n_b=2.279, n_c=2.329
Lattice parameters[c]	a=5.721 Å, b=5.695 Å, c=3.973 Å
Crystallographic structure	mm2 orthorhombic
Transparency range[a]	0.4-4.5 μm
Damage threshold[a]	150-180 W/cm^2 at 1.064 μm

[a]Reference[20].
[b]Reference[8].
[c]Reference[21].

FIG 1. Modal dispersion curves of the fundamental (1.053 μm) and second harmonic (5265 Å) waveguide modes for $KNbO_3$ thin film on an MgO substrate.

FIG 2. SHG experimental setup for $KNbO_3$ (a) mounted perpendicular to the laser beam and (b) in coupling mode.

FIG 3. Field distribution of the TM_0 at 1.053 μm and the TE_1 at 5265 Å.

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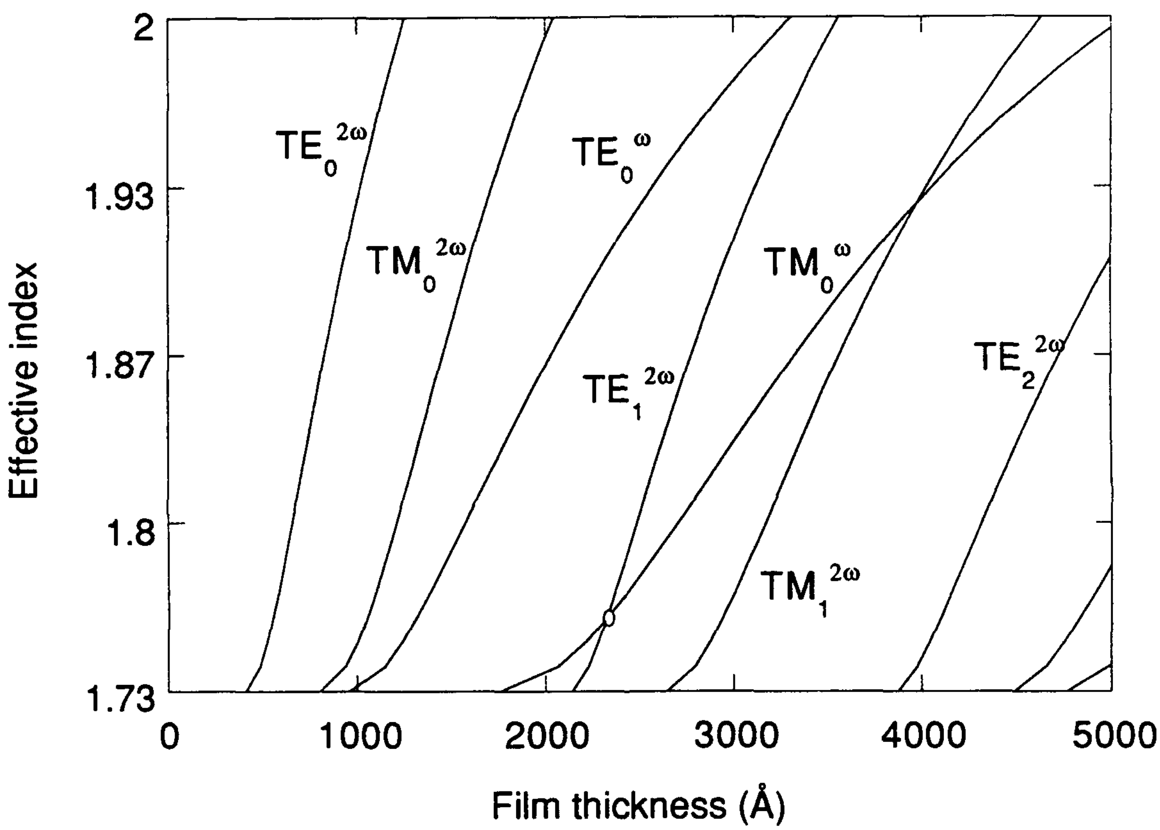
Fig 1. Modal dispersion curves of the fundamental (1.053 um) and second harmonic (5265 Å) waveguide modes for $KNbO_3$ thin film on an MgO substrate.



(a)

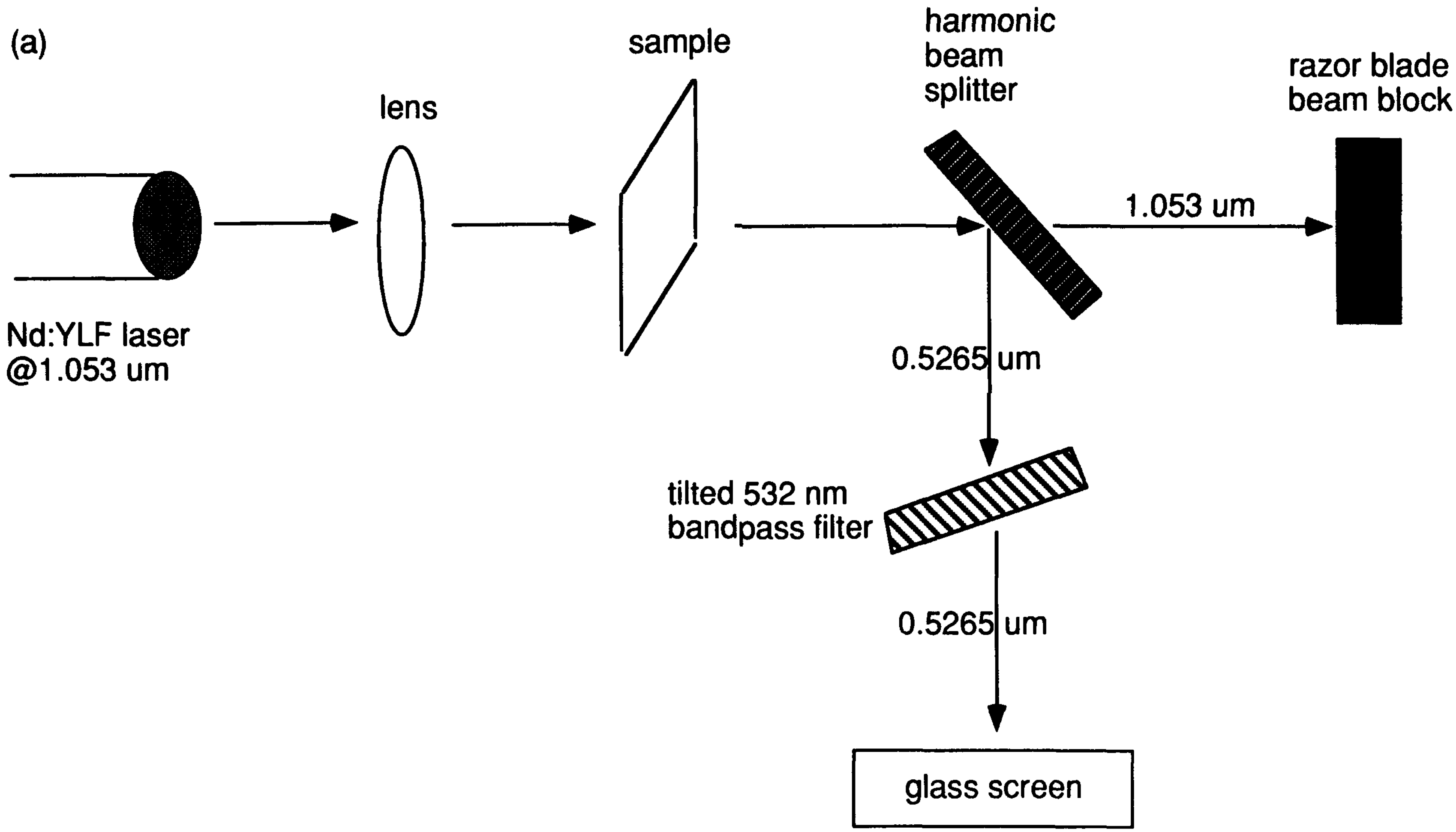


Fig 2. SHG experimental setup for KNbO3 (a) mounted perpendicular to the laser beam

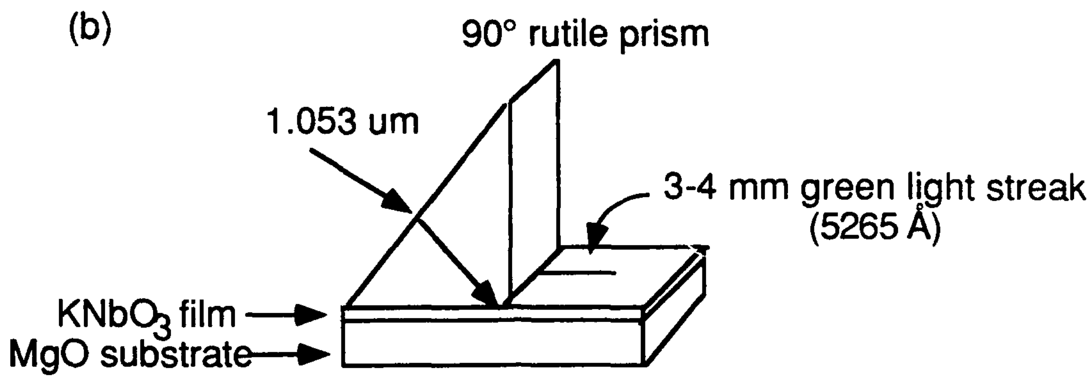


Fig 2. SHG experimental setup for KNbO3 (b) in coupling mode

Fig 3. Field distribution of the TM_0 at 1.053 um and the TE_1 at 5265 Å