Effect of epitaxy on interband transitions in ferroelectric KNbO₃

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Abstract

Very large lattice strain and strain-induced polarization are achieved in KNbO₃ using epitaxial growth of a thin KNbO₃ film onto a (001)-oriented SrTiO₃ single-crystal substrate. We demonstrate experimentally that epitaxy produces dramatic changes of interband transitions in the film compared to those of a reference KNbO₃ crystal: the energies of transitions change, some transitions are substantially suppressed and new ones appear in the film. A comparison of the experimental observations with theoretical calculations points to yet unexplored phenomena. Our results indicate that optical refraction and electro-optical coefficients of ferroelectric films can be controlled by epitaxial growth, which is of importance for emerging photonic and optoelectronic applications.

1. Introduction

Potassium niobate KNbO₃ (KNO) belongs to a family of perovskite-structure oxide ferroelectrics. High optical transparency and large index of refraction in the visible range, excellent nonlinear optical properties, and high dielectric susceptibility of ferroelectric crystals, especially KNO, have long been used in optical devices [1–3]. However, large single crystals are difficult to grow and they are not suitable for integrated photonic and optoelectronic applications. These issues can be mitigated by the use of single-crystal-type epitaxial ferroelectric thin films [4]. Additionally, thin films can be deposited on low-refractive index substrates, leading to strong optical confinement, high optical power density, and other improvements in performance. Efficient photovoltaic, optoelectronic, and plasmonic devices using optically active epitaxial ferroelectric films have already been demonstrated [5–8]. To bring the potential of perovskite-structure ferroelectric films to fruition, it is important to understand how epitaxy-related effects alter the optical properties of ferroelectric oxides.

The lattice structure of heteroepitaxial films can differ significantly from that of single-crystal prototypes. Epitaxial growth of thin films on dissimilar substrates may result in the formation of new structural phases and the emergence of electronic and optical properties that do not exist in bulk crystals. Moreover, a mismatch between the lattice parameters of the substrate and film material and/or a difference in thermal expansion coefficient can produce significant strains, which in turn affect the physical properties of the film. In particular, biaxial in-plane strain has been shown to enhance (or induce) ferroelectric polarization in perovskite oxides [9–11], to reduce bandgaps in epitaxial films of semiconductors, nonpolar metal oxides, and perovskite-type paraelectrics [12–14], and to result in complicated bandgap behavior in ferroelectrics [14, 15]. Studies on how crystal symmetry, lattice strain, and ferroelectric polarization influence the optical properties of heteroepitaxial ferroelectric thin films are only at the very beginning.

The main tool for theoretical studies of perovskite oxide ferroelectrics is first-principles analysis. First-principles calculations of the electronic band structure, density of states (DOS), and ferroelectric polarization have been performed for a number of perovskite oxides. Most often, theoretical results are expressed in terms of the electronic band structure, describing the allowed energy states (valence and conduction bands) in momentum space. From semiconductor physics it is known that interband electronic transitions, which are responsible for the optical properties, can be related to Van Hove singularities in the DOS. In turn, the singularities in the DOS are related to critical points (CPs) in the band structure. A theoretical model of CPs in a
parabolic band approximation (CPPB) was developed for semiconductors decades ago [16, 17]. The CPPB model has been and continues to be used extensively for the analysis of interband transitions in semiconductor materials. One key attribute of this approach is the accurate extraction of CP energies. Consequently, by comparing the experimentally determined energies with first-principles calculations it is possible to assign CPs to specific points in the Brillouin zone (BZ) and thus to verify theory. Recently, the CPPB approach has been extended to perovskite oxide paraelectrics [18–20]. The assignment of CPs, however, has been difficult. More extensive experimental studies of interband transitions are therefore vital not only for a better knowledge and understanding of optical properties, but also for the development of more extensive first-principles theory of ferroelectrics. It should be stressed that interband transitions determine optical refraction and electro-optic coefficients in ferroelectrics [21]. This suggests that tuning of these transitions by epitaxial growth can lead to new optical properties and device applications. Studies of interband transitions in epitaxial films are thus of practical importance for emerging thin-film photonics and optoelectronics using ferroelectrics.

Here we experimentally demonstrate dramatic changes of interband transitions produced by epitaxy in KNO. We apply CP analysis in order to quantify the changes in an epitaxial KNO film compared to a KNO crystal.

2. Experiment

An epitaxial KNO film with a thickness of 4 nm was selected for this study. The film was grown by pulsed laser deposition on a (001)-oriented SrTiO3 (STO) single-crystal substrate at a temperature of 973 K. As a target we used dense ceramic KNO pellet synthesized at the Institute of Solid State Physics, Riga, Latvia [22]. To ensure proper oxygen stoichiometry in KNO, high purity oxygen with a pressure of 20 Pa was used during deposition and the pressure was raised to 800 Pa during post-deposition cooling [23]. The crystal structure and the lattice strains in KNO were analyzed by high-resolution transmission electron microscopy (HRTEM) imaging on a JEOL 2200FS TEM with double Cs correctors, operated at 200 kV.

The optical properties of the KNO film were explored by variable-angle spectroscopic ellipsometry (VASE) using an J. A. Woollam ellipsometer. The ellipsometric data were collected over a spectral range from 0.74 to 9.0 eV and at different angles of incidence between 65° and 75°. The ellipsometric angles (Δ, ψ) were extracted with an accuracy of 0.2° for Δ and 0.04° for ψ. The data analysis was performed using the WVASE32 software package and the procedure developed by Woollam [24, 25]. The experimental ellipsometric spectra of the film were fitted using a model considering a stack of semi-infinite substrate, film, surface-roughness layer, and ambient air. The optical properties of the surface-roughness layer were represented by a Bruggeman effective medium approximation [26]. We used a two-step analysis. A multi-oscillator model was employed to determine the initial dielectric function and layer thicknesses. Then the thickness was fixed and a point-by-point fit was used to accurately extract the dielectric function. The achieved mean square error was in the range of 0.1–0.25, demonstrating high reliability of experimental results. The dielectric functions of the STO substrate and the reference KNO crystal were determined using separate independent measurements. Prior to the measurements on a platelet KNO crystal with a size of approximately (5 mm × 5 mm × 1 mm), the surface of the crystal was epitaxially polished and the crystal was heated to 840 K (above the temperature of the para-to-ferroelectric phase transition) and cooled to room temperature without electric-field poling. This resulted in a polydomain ferroelectric state in the crystal.

The real and imaginary parts of the complex dielectric function, ε₁ and ε₂, were analyzed using derivative spectra. The dielectric function (ε = ε₁ + iε₂) can be presented in the following form in the vicinity of a parabolic CP [27, 28]:

\[ \varepsilon(E) = C - A \exp(i\phi)(E - E_0 + i\Gamma)^\gamma, \]  

(1)

where the parameters are the amplitude A, phase projection factor φ describing the type of CP and excitonic effects, threshold energy E₀, broadening parameter Γ, and exponent γ related to the dimensionality of the CP. Here, E is the photon energy and C is the non-resonant part of the dielectric function due to other CPs. The second derivative of the dielectric function for a two-dimensional CP is given by:

\[ \frac{d^2\varepsilon}{dE^2} = \frac{A \exp(i\phi)}{(E - E_0 + i\Gamma)^{2+\gamma}}. \]  

(2)

The derivative spectra were obtained by numerical differentiation of the smoothed dielectric functions and were subsequently fitted to expression (2). The smoothing was performed using Savitzky–Golay filtering [29] implemented in Origin software [30]. The selection of filtering parameters is found to affect the widths and the amplitudes of the fits. The energies, which are most important for our study, are less affected. For simplicity and
ease of comparison between the film and the crystal, we focus on the energies and the types of transitions. Correspondingly, the phase angles were assumed to be $\phi = 0, 0.5, 1, \text{or} 1.5\pi$ in the fits based on expression (2).

3. Results and discussion

3.1. Epitaxy

The room-temperature bulk crystal structure of KNO is orthorhombic with lattice parameters $a = 5.697$ Å, $b = 5.723$ Å, and $c = 3.971$ Å. The lattice parameter of the corresponding pseudo-cubic perovskite subcell is $a_{\text{bulk}} = 4.016$ Å. At the deposition temperature of 973 K, KNO exhibits a cubic crystal structure with a lattice parameter that is about 3% larger than that of STO [31]. As a result, cube-on-cube pseudomorphic epitaxy of KNO on STO (001) is expected. The mismatch between KNO and STO compresses the in-plane lattice parameter of the perovskite KNO unit cell and it enhances the out-of-plane lattice constant. Because of this, a new ferroelectric tetragonal $c$-phase with out-of-plane polarization along the [001] direction can be stabilized in KNO films on STO [10]. KNO films can only grow with a tetragonal structure up to a critical thickness, beyond which the strain starts to relax [32–34]. The small thickness of the KNO film in this study (4 nm) was specifically selected because it ensures nearly uniform strain and lattice tetragonality throughout the film, as shown below.

HRTEM imaging and selected area electron diffraction (SAED) analysis (figure 1) evidence the single-crystal structure of the KNO film. The epitaxial relationship between the film and the substrate is cube-on-cube type KNO(001)[100]//STO(001)[100]. Streaking of the diffraction spots appears in SAED along the out-of-plane axis only, indicating full coherency between the in-plane lattices of KNO and STO despite their relatively large mismatch. Strain relaxation through the formation of a regular dislocation network does not occur. With the exception of small areas around a few isolated misfit dislocations (see mark in figure 1(a)), the KNO film is strained uniformly.

As expected, the out-of-plane lattice parameters of KNO and STO differ. The crystal structure of KNO can be interpreted as tetragonal. Fast Fourier transformation of the HRTEM image indicates a tetragonality of approximately $c_{\text{film}}/a_{\text{film}} = 1.029$, where $a_{\text{film}}$ and $c_{\text{film}}$ are the in-plane and the out-of-plane lattice parameters of the KNO film. The room-temperature in-plane lattice strain in KNO can be characterized as $s_a = (a_{\text{film}}/a_{\text{bulk}} - 1)$, and the out-of-plane strain as $s_c = (c_{\text{film}}/a_{\text{bulk}} - 1)$. Compared to the bulk perovskite subcell, the KNO film experiences an anisotropic lattice strain of $s_a = -2.8\%$ and $s_c = 0.15\%$. A ferroelectric polarization of up to 60 $\mu$C cm$^{-2}$ can be achieved in such tetragonal KNO films [35].

Ferroelectric ordering in the KNO film is confirmed by HRTEM analysis of a nanodomain with an accurate crystallographic alignment along [010] (white dotted box in figure 2(a)). Although unambiguous identification of Nb, K and O ions is not possible in this phase-contrast image, off-centering of Nb and/or O can be estimated by the relative out-of-plane displacement of the Nb–O plane from the center of the KNO unit cell. The result of this analysis is shown in figure 2(b). The off-centering amounts approximately 0.1 Å, which suggests the formation of a non-centrosymmetric tetragonal ferroelectric $c$-phase in the KNO film.
3.2. Dielectric function

Room-temperature spectra of the dielectric function were extracted from the VASE data for the KNO film and the reference KNO crystal (figure 3). The spectra of $\varepsilon_1$ exhibit maxima at photon energies of approximately 4 eV and 8 eV (figures 3(a) and (c)) and corresponding maxima are seen in the spectra of $\varepsilon_2$ (figures 3(b) and (d)). The obtained dielectric functions with two maxima agree qualitatively with those revealed using reflectance spectroscopy on an orthorhombic KNO crystal [36]. However, a closer inspection evidences that the shape of $\varepsilon_1(E)$ in the tetragonal film differs from that in the orthorhombic crystal (compare figures 3(a) and (c)). The difference between the film and the crystal is even more obvious in the spectra of $\varepsilon_2(E)$ as seen from figures 3(b) and (d).
It should be mentioned that band-structure calculations have been carried out for the paraelectric cubic phase [37–42] and also for the tetragonal and the rhombohedral phases of KNO [41, 42]. The calculations indicate practically similar band structures for all these phases [41, 42]. The present picture of the KNO band structure includes a high-energy valence-band complex which is formed by oxygen O 2p states that are strongly hybridized with Nb 4d states. The nine valence bands at the \( \Gamma \)-point are comprised of three levels with triple degeneracy. The splittings are produced by the crystal field and the electrostatic interaction between mainly O 2p and Nb 4d orbitals. The topmost valence bands consist of oxygen 2px, 2py states. There are six bands in the conduction-band edge at the \( \Gamma \)-point. They arise from the Nb 4d \( t_{2g} \) and Nb 4d \( e_g \) orbitals, separated by energy of approximately 4 eV, and the K 4s orbital. The lowest conduction band arises predominantly from Nb 4d \( t_{2g} \) states with a small O 2p mixing, and it is nearly flat from the \( \Gamma \) point through the \( \Delta \) and X points. The indirect bandgap is located between the topmost valence band at the R point and the bottom of conduction band at the \( \Gamma \) point (R \( \rightarrow \) \( \Gamma \) transition).

The calculated band structure is practically insensitive to the calculation method and crystal phase [37–42]. The main interband transitions determining the dielectric function of KNO in the spectral range of 3–10 eV have been ascribed to those at the X point with energies of approximately 5 eV and above 7 eV, at the \( \Gamma \) point at around 6 eV, and at the M point at approximately 9 eV [40, 42]. The broad dielectric peaks at 4–5 eV in the KNO crystal and the film may therefore be related to optical transitions at the X point of the BZ.

In order to better characterize the difference between optical properties of the film and the crystal, the second derivative of the experimental dielectric function was inspected. The derivative spectra and fits based on expression (2) are shown in figure 4 for the epitaxial KNO film and the reference KNO crystal. The derivatives lack line-like features in the spectral range of 5–6.5 eV in the film and 6.4–7.7 eV in the crystal. The strongest line at approximately 4 eV is clearly seen in all spectra. Also, another line at approximately 8 eV is present in all spectra. Except these two lines, the spectra of the epitaxial film differ from those of the crystal.

The changes of interband transitions in the epitaxial film compared to the crystal are further analyzed by comparing the energies and types of the clearest CPs in the derivative spectra. Table 1 summarizes the fitting parameters obtained for CPs in the film and the crystal. Despite small uncertainties in energies, the differences between the energies of interband transition in the film and crystal are obvious.

Compared to the crystal, the changes in the film include a lowering of the energy (red-shift) by approximately 0.2 eV for the main CP around 4 eV: the energy is \( E_0 = 4.23 \) eV in the film compared to that of 4.41 eV in the crystal. Simultaneously, an opposite shift (blue-shift), or an increase of energy by approximately 0.2 eV is observed for the high-energy CP around 8 eV: the energy is \( E_0 = 8.42 \) eV in the film compared to that of
8.20 eV in the crystal. Besides these energy shifts in opposite directions, the lines with the energies of 4.00, 4.72, 5.60, and 5.90 eV, which are present in the spectra of the crystal, are suppressed in the spectra of the epitaxial film. Instead, new lines with the energies of 3.56, 4.80, 6.92, and 7.24 eV are found in the spectra of the epitaxial film compared to those of the crystal. Since the types and the energies of the suppressed and new lines do not match, it is impossible to ascribe the new lines to shifts in band energies.

The observed changes of interband transitions produced by epitaxy can be compared with theoretical predictions [14, 15]. Based on first-principles calculations and assuming no changes in the valence-band energies, one may expect a decrease of the conduction-band energy in the film due to higher lattice symmetry and anisotropic lattice strain therein [14, 15]. A uniform red shift of the conduction-band DOS in the tetragonal phase compared to that in lower symmetry phases has been suggested [15]. Such a shift would correspond to a simultaneous red shift of all CPs in the strained tetragonal film compared to the orthorhombic stress-free crystal.

The red shift in the film is found for one CP only (4.23 eV). The equally large shift in the opposite direction is found in the film for another CP (8.42 eV). This blue shift is in striking contrast to the theoretically predicted behavior of a strained tetragonal KNO film [15]. Additionally, the detected new transitions in the film compared to those in the crystal suggest that also the shape of DOS can be affected by epitaxy. Thus, the theoretically predicted tendencies are insufficient for explaining the observed changes in the film compared to the crystal.

We note that an alternative interpretation of band-structure effects in KNO films may include band splitting. For instance, the CP with energy of 4.41 eV in the crystal may be split into two CPs with energies of 4.23 and 4.80 eV in the film as illustrated in figure 5(a). Qualitatively, the splitting can be ascribed to the influence of long-range ferroelectric polarization. The polarization can be thought of as contributing to the crystal field, and as such it affects the energies, splitting, and degeneracy of band levels [43]. Compared to the crystal, the ferroelectric polarization is significantly enhanced in the epitaxial film due to the presence of anisotropic lattice strain therein [10]. The strain-induced increase of polarization can widen energy separation between the bands [14]. The observed blue shift of the high-energy CP (8.42 eV in the film) is in line with this possibility. Simultaneously, the strain-induced polarization may lead to band splitting and thus be responsible for the apparent red shift of the lower-energy CP (4.23 eV in the film). Also the low-energy CP in the film (3.56 eV) might be caused by splitting due to ferroelectric polarization because strain-induced red shift of DOS can hardly explain its appearance (Figure 6b). The nature of the low-energy transitions is of especial practical interest as these transitions can significantly influence the bandgap behavior and the optical properties in the visible spectral range. We stress, however, that band splitting is unlikely causing all the CP changes in the KNO film.

### Table 1. Fitting parameters for the main critical points in the epitaxial KNO film and the reference KNO crystal.

| Energy (eV) | π, A, Γ | Energy (eV) | π, A, Γ |
|------------|--------|------------|--------|
| 3.56 ± 0.02 | 1.5 | 0.40 ± 0.05 | 0.20 ± 0.02 | 4.00 ± 0.02 | 1 | 1.5 ± 0.10 | 0.28 ± 0.02 |
| 4.23 ± 0.01 | 0 | 1.60 ± 0.03 | 0.23 ± 0.01 | 4.41 ± 0.01 | 0 | 6.0 ± 0.20 | 0.21 ± 0.01 |
| 4.80 ± 0.02 | 0.5 | 1.05 ± 0.05 | 0.27 ± 0.03 | 4.72 ± 0.02 | 1 | 1.5 ± 0.10 | 0.20 ± 0.02 |
| 6.92 ± 0.02 | 1.5 | 0.80 ± 0.05 | 0.40 ± 0.03 | 5.60 ± 0.03 | 0.5 | 0.6 ± 0.10 | 0.24 ± 0.02 |
| 7.24 ± 0.03 | 1 | 0.40 ± 0.05 | 0.40 ± 0.03 | 5.90 ± 0.03 | 1 | 1.8 ± 0.10 | 0.20 ± 0.03 |
| 8.42 ± 0.02 | 0 | 0.80 ± 0.02 | 0.40 ± 0.02 | 8.20 ± 0.01 | 0 | 1.5 ± 0.10 | 0.22 ± 0.02 |

**Figure 5.** The derivative $d^2 \varepsilon_2/dE^2$ as a function of photon energy $E$ in the epitaxial KNO film and the KNO crystal. For convenience of comparison, the derivative in the film is multiplied by 4.
Thus, significant changes of interband transitions are found in the epitaxial KNO film compared to the KNO crystal. This implies that effects of epitaxy may be more complex than a simple increase or decrease of band energies. In particular, ferroelectric polarization may play a more critical role than previously assumed. The long-range ferroelectric polarization may affect the energies, splitting, and degeneracy of band levels. Correspondingly, the optical properties of epitaxial films may be strongly influenced by variations of the polarization, which in turn are correlated to changes in lattice symmetry and/or strain. The crystal structure, strain, and ferroelectric polarization in epitaxial films can be tuned by selecting an appropriate combination of film and substrate materials. This may be used to tailor optical properties of the films.

4. Conclusions

Large lattice strain is achieved in epitaxial cube-on-cube-type perovskite tetragonal KNO film on a (001) SrTiO$_3$ single-crystal substrate as evidenced by HRTEM analysis. The optical dielectric function in the spectral range of 0.74–8.6 eV is experimentally determined by spectroscopic ellipsometry in the epitaxial KNO film and a reference KNO crystal. The dielectric function of the epitaxial film is found to differ significantly from that of the crystal. Analysis of interband transitions using derivatives of the dielectric function reveals dramatic changes of the energies and types of transitions in the film compared to those in the crystal. These changes are discussed in relation to epitaxially induced changes of crystal symmetry, presence of anisotropic lattice strain, and strain-enhanced ferroelectric polarization in the film. It is suggested that the energies, splitting, and degeneracy of band levels are strongly influenced by the ferroelectric polarization of the KNO film. Such variations of ferroelectric polarization, either caused by changes in lattice symmetry and/or strain, may be used to tailor the optical properties of epitaxial films in photonic and optoelectronic devices.

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