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Dielectric and structural characterization of $KNbO_3$ ferroelectric thin films epitaxially grown by pulsed laser deposition on Nb doped $SrTiO_3$

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ABSTRACT

$KNbO_3$ thin films were deposited on $SrTiO_3$ substrates by pulsed laser deposition. The X-ray diffraction patterns highlight an epitaxial growth according to the (011) orientation. This epitaxial growth was then confirmed by Electron Channeling Pattern. In agreement with the structural characteristics the dense microstructure consists in regular and ordered grains. Dielectric measurements were performed in the 20 Hz to 1 MHz frequency range on a $KNbO_3$ thin film grown on 2 at.% Nb doped (100)$SrTiO_3$ substrate in a large range of temperature in order to investigate the paraelectric–ferroelectric transition. Measurements at room temperature revealed a dielectric constant of 450 at 10 kHz and a minimum value of the loss tangent of 0.075 at 100 kHz. Dielectric study in the 20–600 °C temperature range showed a maximum of permittivity at the Curie temperature $T_c = 410$ °C and evidenced a "progressive" first-order phase transition, different from the classical "diffuse" transition.

1. Introduction

Ferroelectric thin films are receiving great attention for many years in order to achieve high performance integrated systems. Indeed the richness of their properties opens the way to a large variety of applications for which miniaturization is required, like Micro Electro Mechanical Systems, nonvolatile Ferroelectric Random Access Memories [1,2], electrooptic waveguides [3], modulators or, more recently, electrically tunable high frequency devices for telecommunication [4]. Among the various ferroelectric compounds investigated, the perovskite-like $KNbO_3$, a lead-free compound, is of first interest in different fields. As an illustration, numerous studies are motivated in the field of optics because of its large electro-optical coefficients [5]. It is also largely studied for its nonlinear optical properties [6] as well as for high refraction indices ($n_a = 2.279$, $n_b = 2.329$ and $n_c = 2.168$ at $\lambda = 632.8$ nm) [5]. In relation with its high piezoelectric coefficients [7] it has consequently been an electromechanical coupling constant of interest for applications like surface acoustic waveguides [8]. Finally a high polarization value of 26 μC/cm^2 was early reported in single crystals [9].

The $KNbO_3$ ferroelectric–paraelectric transition which is of first order for bulk material, is accompanied by a structural change [10]. This compound presents a cubic structure above its Curie temperature which is of 435 °C, is tetragonal below, then orthorhombic at 215 °C (thus at room temperature) and rhombohedral at −72 °C. The lattice constants of the orthorhombic unit cell of $KNbO_3$ at room temperature are $a = 3.9739$ Å, $b = 5.696$ Å, $c = 5.7213$ Å (space group *Amm*2, no. 38) and the polarization vector of the ferroelectric phase directed along the *c* axis.

Many deposition methods are quoted still today in the literature for the growth of $KNbO_3$ thin films such as: ion beam [11], metal-organic chemical vapor deposition [12], spin-coating [13], RF sputtering [14], polymeric precursors [15] and pulsed laser deposition (PLD) [16,17].

We present here the structural and dielectric characteristics of $KNbO_3$ thin films epitaxially grown by PLD on (100)$SrTiO_3$ and Nb doped (100)$SrTiO_3$ single crystals. Dielectric measurements were performed in a wide range of temperature and at different frequencies in order to achieve accurate data on the ferroelectric–paraelectric phase transition (dielectric constant, loss tangent, and Curie temperature).

2. Experimental

2.1. $KNbO_3$ deposition

Potassium niobate thin films were deposited by PLD from home-made sintered targets. $KNbO_3$ powders were prepared by solid state reaction using a conventional ceramic process, from a stoichiometric mixture of K_2CO_3 and Nb_2O_5 powders calcined in air at 1000 °C for 12 h. In order to compensate potassium loss during deposition,

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K-enriched targets were prepared by adding 50 mol % excess of KNO_3 to the $KNbO_3$ powders [18]. Then, cylindrical pellets, 25 mm in diameter and ~5 mm thick, were obtained by liquid phase assisted sintering (12 h at 350 ° C), tacking benefit from the low melting temperature of KNO_3 (342 °C). Deposition conditions were optimized from a systematic study [18] in order to achieve pure $KNbO_3$ thin films with high crystalline quality.

Thin films were deposited at 700 °C under an oxygen pressure of 30 Pa, using a KrF excimer laser (Tuilaser Excistar, pulse duration of 20 ns, $\lambda = 248$ nm), with a focused energy density of ~1.5 J/cm^2, operating at 2 Hz. The laser beam, incident at 45°, was focused on the target which was rotated in a standard vacuum chamber (background pressure of about 5×10^{-4} Pa).

Deposition on textured (111)Pt coated silicon leads to randomly oriented $KNbO_3$ films or at the best textured films. The use of an epitaxial electrode to achieve an epitaxial growth of the films is an alternative. We demonstrated that Pt epitaxial films can be used to epitaxially grow ferroelectric films like $SrBi_2Nb_2O_9$ as well as $KTa_xNb_{1-x}O_3$ [19,20]. However, the coexistence of several competing orientations [20] was frequently encountered in such oxide/metal heterostructures, motivating the choice of a single crystal conducting substrate in view to study the dielectric behavior of high structural quality thin films.

So, during this study, in addition to films deposited on pure (100) $SrTiO_3$ single-crystal substrates, a ~330 nm thick $KNbO_3$ film was grown on a conducting (100)$SrTiO_3$ substrate doped with 2 at.% Nb suitable as a bottom electrode for electrical measurements performed in a standard capacitor configuration. Indeed, high quality epitaxially grown $KNbO_3$ films, similar to films deposited on pure insulating $SrTiO_3$ [18], were expected on this single-crystal substrate.

2.2. Composition, structural and microstructural analyses

The composition of the films was determined by energy dispersive spectrometry using a Link Oxford analyzer implemented on a Jeol 6400 JSM scanning electron microscope which also gives access to Electron Channeling Patterns (ECP). The surface morphology of the films was observed with a field effect emission scanning electron microscope (JEOL F-6301) operated at low voltage (typically 7 to 9 kV) in order to limit charge effects and to achieve a high resolution without the need of metallization of the samples.

The films were characterized by X-ray diffraction (XRD) using a four-circle texture diffractometer (Bruker AXS D8 Discover) operated with Cu $K_{\alpha 1}$ radiation in θ–2θ, ω-scan and φ-scan modes. In-plane ordering was qualitatively checked by ECP which displays a stereographic projection of the films planes along the pole aligned with the microscope axis, due to a systematic drop of backscattered electron yield each time the electron beam reaches a Bragg angle for its wavelength (0.077 Å at 25 keV). ECP is a very sensitive method to probe any in-plane misorientation [21]. Whereas X-ray diffraction probes the film all over its thickness, the probed depth by ECP is typically of a few tens of nanometers in our experimental conditions. Moreover ECP is a powerful method to evidence epitaxial growth (*i.e.* in-plane ordering) when XRD probing in φ-scan or pole figure reaches resolution limit. In fact, 2θ and ψ angles resolution is generally not enough when recording a φ-scan (at ψ around 45° typically) in the case of film and substrate which crystallize in very close crystalline systems with a low mismatch. In the present heterostructure, $SrTiO_3$ has a cubic structure with a lattice constant of 3.905 Å while the orthorhombic structure of $KNbO_3$ can be described in a pseudo-cubic lattice [22] ($a_{pc} \sim 4.0$ Å) leading to a film/substrate lattice mismatch of 2% at room temperature. We verified by a θ–2θ scan recorded at $\psi = 45°$ that the film (001) and substrate (110) diffraction planes were clearly distinguishable to accurately perform φ-scans (Fig. 1). In this case ECP remains a complementary method to probe the epitaxial quality of $KNbO_3$ up to the film surface.

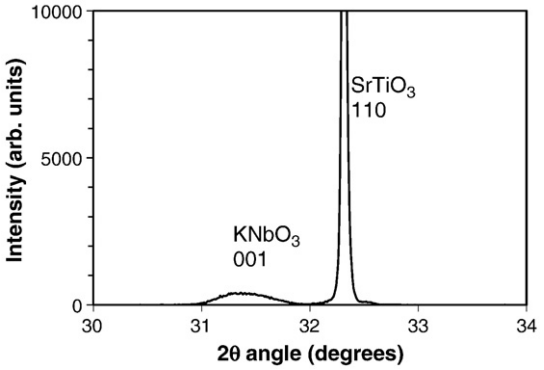

Fig. 1. θ–2θ XRD pattern recorded at $\psi = 45°$ on a $KNbO_3$ film epitaxially grown on Nb doped (100)$SrTiO_3$.

2.3. Dielectric measurements

For electrical characterizations, 150 μm diameter disk shaped Pt top electrodes were prepared by a lift-off process. The dielectric responses were measured in the 20 Hz to 1 MHz frequency range by an automated system using an impedance analyzer HP4192A. The dielectric constant and loss tangent of the film were measured using an alternative voltage of weak amplitude (100 mV).

The Curie temperature was determined from dielectric constant measurements performed in the temperature range 20–600 °C at 1, 10 and 100 kHz. A home-made high-power furnace was used to heat the films in this temperature range. The activation energy values were computed from the response of the a.c. conductivity versus reciprocal temperature with the classical equation $\sigma_{ac} = \sigma_0 \cdot \exp(-Ea/kT)$.

3. Results and discussion

3.1. Structural and microstructural characteristics

In order to optimize the growth conditions of $KNbO_3$ to obtain an epitaxial growth on a single-crystal substrate, we chose to use (100) $SrTiO_3$ substrates. As mentioned above, $SrTiO_3$ crystallizes in a cubic structure ($a = 3.905$ Å at room temperature) and is then an ideal model substrate to study the epitaxial growth of perovskite type materials. The difference in unit-cell constants between the $<100>SrTiO_3$ direction and $<100>_{pc}$ (corresponding to the [110] $KNbO_3$) is equal to 2% at room temperature and 3% at the temperature of growth.

The films thus obtained have a high crystalline quality as attested by the XRD pattern in θ–2θ mode displayed in Fig. 2. It highlights a growth of the film with the (011) orientation (referring to the orthorhombic unit cell). The $\Delta\omega$ value of the width at half maximum of the 011 peak obtained by scanning ω is typically close to 0.2° (Fig. 2). These low values of rocking curves recorded on the 011 peak

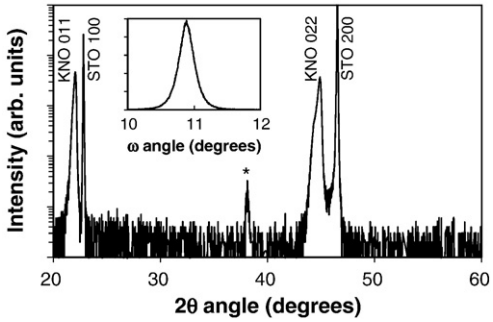

Fig. 2. θ–2θ (a) and ω-scan (b) XRD patterns typical of a $KNbO_3$ film grown on Nb doped (100)$SrTiO_3$; * labeled peak is substrate holder.