Thermo-optical studies of NaNbO₃ thin films

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Abstract. Thermo-optical studies of sodium niobate NaNbO₃ (NN) thin films, deposited by the pulsed laser ablation technique on Si/SrRuO₃ substrates, were performed by spectroscopic ellipsometry in the temperature range 300 - 550°C. Optical constants at the room temperature were measured in the spectral range 250 - 1000 nm. Substantial changes in the refractive index temperature behaviour (taken at λ = 300 nm) were found at temperatures 370, 445, 503, 520, and 532°C, where the first and the last temperatures are the phase transitions \( P \rightarrow R \) and \( S \rightarrow T_1 \), respectively. Other temperatures (445, 503, and 520°C) are suggested as the points of some local structural changes in the NN film.

1. Introduction

An antiferroelectric sodium niobate NaNbO₃ (NN), which is promising lead-free piezoelectric material [1 - 3], undergoes probably the most complex phase transitions with vary in temperature of all perovskites [4, 5], changing its phase from a high-temperature paraelectric (PE) to antiferrodistortive and then reaching antiferroelectric (AFE) phase at 370°C (the symmetries and space groups of the phases formed are indicated in parenthesis). The unit cells of phases \( R \) and \( S \) are the largest reported for a low-symmetry phase of any perovskite. There are several reports [6 - 8], where additional phase transitions between \( R \) and \( T_1 \) were found on NN single crystals: Lefkiwitz (X-Ray, 1966) established unusual phase transitions at 430 - 440°C (detected also by optical observation), 518°C and 526°C; Denoyer (differential thermal analysis (DTA) and x-ray, 1971) – at 523°C; and Glazer (DTA, 1973) – at 530°C while heating and at 512°C while cooling. No other revision of these additional phases of the NN single crystals were attempted for many years, not to mention on results of NN thin films. An instrumental, technical and analytical improvement of the experiments and results makes such a re-examination just in time. We report here the new ellipsometric results, where temperature dependence of refractive index was measured at high temperatures (300 - 550°C) to study the phase transitions of NN thin films. Certainly it would be advisable to determine also the changes of
atomic parameters or specific heat capacity by the temperature of NN thin films, but this has to be left to future study. On the other hand, our thermo-optical results, gives some additional information about optical properties and phase transitions of NN thin films.

2. Experimental

NN thin films were deposited on Si/SrRuO$_3$ (Si/SRO) substrates by PLD using KrF-excimer laser (LPX 300, Lambda Physics) with the wavelength of 248 nm, and the repetition rate of 10 s$^{-1}$ with energy density of 2 - 3 J/cm$^2$. PLD process was accomplished in the vacuum chamber with O$_2$ and Ar atmosphere at a pressure of $\sim 0.03$ mbar. The laser beam was focused on the target material, which was wobbling and rotating in order to minimize the droplet formation. The deposition temperature for NN and SRO was 580°C. The targets of the NN and SRO were made by chemical synthesis technique [9].

The highly conductive oxide SrRuO$_3$ have been used as the bottom electrode due to its stability, not only in oxidizing, but also in inert gas atmospheres up to quite high temperatures [10–12], unlike the high-$T_c$ superconducting thin films, which typically have relatively poor crystalline quality and rough surfaces, and are not fully chemically and thermally stable. High stability of the bottom electrode and processing compatibility with ultra-large-scale integrated circuit fabrication during electrode deposition are very important to realize the integration between the high-permittivity dielectric materials and active devices located on the substrates.

The crystalline structure of the deposited films was analyzed at the room temperature (RT) using Siemens D5000 x-ray diffraction (XRD) equipment with Co anode. The XRD showed that our NN films has an orthorhombic crystal structure (reported in our earlier work [13]), which corresponds to that reported for the single crystals [8, 14 - 16].

RT and temperature dependent optical measurements were performed by means of a J. A. Woollam spectroscopic ellipsometer operating in rotating analyzer mode. The main ellipsometric angles $\psi$ and $\Delta$ were measured in a spectral range from 250 to 1000 nm (1.23 eV till 4.85 eV) at incidence angles of 65, 70 and 75 degrees at the RT. Fitting RT $\psi$ and $\Delta$ we took into account all heterostructures with a top layer of superficial roughness, which was described in terms of the effective medium approximation (EMA) [13, 17]. The Lorentz oscillator for the dielectric function was used to describe the optical properties of NN [17].

There were several models to fit RT results:
1. Substrate/SRO/homogenous film.
2. Substrate/SRO/interface/homogenous film.
3. Substrate/SRO/interface/homogenous film/roughness.
4. Substrate/SRO/interface/inhomogeneous film (mixture of the host material and grain boundaries)/roughness (Figure 1).

The optimal values for the $n$, extinction coefficient $k$, and thickness $d$ for each sample layer were found by Monte-Carlo optimisation of the multilayer model, using licensed software package FilmWizard.

Specially constructed sample holder with PC-controlled heating element allowed the real-time measurements of $\psi$ and $\Delta$ during heating. These measurements were performed in the temperature range 300 - 550°C at 300 nm wavelengths (photon energy $\sim 4.12$ eV) and at the incidence angle of 75 degrees. The given wavelength was chosen because of its near band gap position with purpose to increase the sensitivity of ellipsometric measurements to any phase transitions and structural changes in our films. Near the absorption edge, any structural changes give a considerable contribution to the interband transitions witch can be seen in the refraction and absorption indices changing [18]. So called “effective” values of refractive index $n_{eff}$ as the function of temperature $T$ was calculated using the RT results of NN host material. These $n_{eff}(T)$ values were calculated using easy isotropic model (substrate/SRO/homogenous film/roughness) and therefore can not be used as an absolute
value of refractive index \( n \) changing by \( T \) but it is sufficient for the phase transition detection. Uniformity of the thickness was also considered during calculations, and the roughness was assuming to be constant and equal to the value calculated from RT results. Data are analyzed with the software package WVASE32.

### 3. Results and discussion

Figure 2a illustrates an experimental data and the fourth model numerical fit of the main ellipsometric angles \( \psi \) and \( \Delta \) as a function of the wavelength at the incidence angles 65° and 70° for Si/SRO/NN sample. The RMSE value for the first model was 9, but for the last one 4. The simple models (see “2. Experimental”, models from 1 - 3), could not give such good agreement between measured spectra and calculated one as it was established assuming that the film is a mixture of the host material and the voids. The interface layer between bottom electrode and films was found to be \( \sim 2 – 3 \) nm, but consider of this layer did not gave any improvement of the fitting. Significant difference in the amplitude of the calculated \( \Delta \) in comparison with the measured one is due to the thickness nonuniformity of the films. The thickness distribution of the thin films rise depolarization of the light, which can be seen as the rounded shape of minima and maxima in \( \Delta \) (since \( \Delta \) is very sensitive to the thickness). The high-frequency lattice dielectric constant and the volume fraction of the second (porous) phase of NN material were established to be 1.10 and 35%, respectively. The \( \varepsilon_m \) and band gap energy for the 2nd phase is much lower then that for the host material of NN film.

Optical properties for NN are shown in Figure 2b. The refractive index \( n \) and the absorption index \( k \) increase as the energy increases from 1.17 to 4.24 eV (normal dispersion) and decrease at energy from 4.24 to 4.49 eV (anomalous dispersion), which is usual for dielectric materials in that energy range. The Lorenz oscillator could not characterize optical properties and give acceptable fit to the experimental data at the shorter wavelengths (\( \lambda \approx 350 \) nm). As the result the anomalous dispersion was estimated approximately and calculation of optical properties at this region still have too be improved.

The fundamental absorption edge for each film was determined from the spectral dependence of the imaginary part of dielectric constant \( \varepsilon_2 = 2nk \) by applying the Tauc relation

\[
\hbar \omega \varepsilon_2 = \text{const} \cdot (\hbar \omega - E_g)^l,
\]

where \( \hbar \) is the reduced Planck constant, \( \omega \) is the angular frequency, \( E_g \) – band gap energy, and \( l = 1/2 \) for the allowed direct transitions and 2 for

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![Figure 2a](image1.png)

**Figure 2.** Experimental ellipsometric angles \( \psi \) and \( \Delta \) (open symbols) and their numerical fit (solid line) as a function of wavelength at two angles of incidence for the Si/SRO/NN sample (a); refractive coefficient \( n \) (continuous line) and extinction coefficient \( k \) (discontinuous line) of NN film deposited on Si/SRO substrates (b).
indirect transitions. By extrapolating the linear part, the optical energy gap was deduced at \( (\hbar \omega E_g)^2 = 0 \), giving the fundamental absorption age \( E_g \) for the direct transition (see Tab. 1).

The thickness \( d_{SRO} \) of the SRO, \( d_{NN} \) of NN thin films, and surface layer \( d_{s} \), refractive index \( n_{633} \) at 633 nm, and fitting parameters of the single Lorentz oscillator: optical band gap energy \( E_g \), high-frequency lattice dielectric constant \( \varepsilon_{\infty} \), centre energy of the oscillator \( E_c \), vibrational broadening of the oscillator \( \nu \) and amplitude (strength) of the oscillator \( A \), are summarized in Table 1. Detected \( n \) for Si/SRO/NN sample is lower than that detected for singles crystals, but \( E_g \) is in good agreement with values evaluated for single crystals [21].

An effective refractive index \( n_{eff} \) of NN thin films at 300 nm as the function of the temperature is presented in the Figure 3. Refractive index sharply decreases from 320°C till 370°C with the rate of \( 4 \cdot 10^{-4} \) K\(^{-1}\), then increases with the rate of \( 1 \cdot 10^{-4} \) K\(^{-1}\) till 445°C and \( 0.7 \cdot 10^{-4} \) K\(^{-1}\) till 503°C. The decrees and increase of \( n_{eff} \) at \( T > 503°C \) are with very similar rate of about \((0.5 - 0.7) \cdot 10^{-4} \) K\(^{-1}\).

For perovskite crystals the \( n \) usually increase as the temperature rises [18, 19, 21]. Nevertheless, the polycrystalline film structure, defects and stresses in the film (for example, was found that grain boundaries give significant impact; see the RT ellipsometry results) can change this behaviour dramatically that we can be seen in our case. Moreover, our measurements were performed at shorter wavelengths close to the band gap energy to increase the sensitivity.

The minimum of \( n_{eff} \) at 370°C corresponds to the \( P \rightarrow R \) phase transition. Detected phase transition temperature \( T_c \) of 370°C is in good agreement with our earlier dialectical measurements on similar films [13]. The 370°C transition was established by different techniques by other authors: dialectical measurements on the single crystals [22] and thin films [23], and also on the single crystals by X-ray [4, 7, 8, 15, 24], optics [15, 22] and DTA [7, 24]. In several works the transitions was observed at 360°C [6, 16, 25, 26], and in some works even at \( T > 370°C \) [27, 28].

Evidence of different \( T_c \) of the \( P \rightarrow R \) phase transition (and also others) is very feasible due to the oxygen vacancies

\[ \text{O}_\alpha \leftrightarrow V_\alpha'' + 2e' + \frac{1}{2}\text{O}_2^\uparrow \]

in accordance with the defect chemistry theory [31]: in the sample are formed primarily doubly ionised oxygen vacancies \( V_\alpha'' \) and two electrons which can participate in conductivity. In the case of NN crystal it can be written in a form of

\[ \text{NaNbO}_3 \leftrightarrow \text{NaNbO}_{3-x} + 2xe' + \frac{1}{2}\text{O}_2^\uparrow \]

It was found by Molak [32] that \( T_c \) varies with the concentration of \( V_\alpha'' \). Measurements were performed on NN crystals heated at reduced air pressure thereby causing the generation of \( V_\alpha'' \). The influence of the \( V_\alpha'' \) on the transition \( P \rightarrow R \) was studied, and was established that \( T_c \) is higher for the crystals with greater oxygen nonstoichiometry, ie., for the samples heated at

| Substrate | \( d_{SRO} \) (nm) | \( d_{NN} \) (nm) | \( d_{s} \) (nm) | \( n_{633} \) | \( E_g \) (eV) | \( \varepsilon_{\infty} \) | \( E_c \) (eV) | \( \nu \) (eV) | \( A \) (eV) |
|-----------|------------------|------------------|-----------------|-----------|-------------|-------------|-------------|-------------|-------------|
| Si/SRO    | 16               | 240              | 4               | 2.08      | 3.48        | 3.79        | 4.31        | 0.16        | 1.44        |
lower partial pressure of oxygen: at $2 \cdot 10^{-2}$, $2 \cdot 10^{6}$ and $2 \cdot 10^{8}$ Pa the $T_c$ during heating is 374, 367 and 362°C, respectively. It should be noticed that Molak established the same effect also on Mn$^{2+}$ doped NN crystals. Theoreticians Sobyanin [33] and Levanyuk [34] showed that local fluctuations in the order parameter caused by point defects lead to shifting of $T_c$. Increasing or decreasing of the $T_c$ is depended on the type of frozen in defects, and by this it is possible to explain the observation of different $T_c$. It is possible, according to Molak, that our NN samples and samples of the groups, who determined $T_c > 360°C$ for $P \rightarrow R$ transition, have oxygen nonstoichiometry.

The slope of $n_{eff}$ at the $380°C < T < 445°C$ slightly differ from that of $445°C < T < 500°C$. This rather suspicious transition at ~ $445°C$ was noted in three x-ray studies [6, 29, 30], but described differently in each. Our optical observation is the second evidence for it; the 1st was done by Lefkiwitz. Accourding to our RT measurements, which showed presence of grain boundary influence, this transition can be due to the grain boundary effect. From X-ray was found that during the $P \rightarrow R$ transition the niobium ions displace inside the oxygen octahedral of NN crystal [35]. This is the transition where the strongest changes of the NN structure occur. Due to the presence of $V_{36}$, reduction in valency of niobium ions appears what leads to change in the local field in the neighbourhood of these defects. And what we see at ~ $445°C$ is some kind of relaxation of defects on grain boundaries.

The next light adjustments of $n$ were found to be at $503°C$, $520°C$ and $532°C$. The minimum of $n_{eff}$ at $520°C$ agree with $T_c$ of $S \rightarrow T_1$ [4, 8, 24]. But there are works where $S \rightarrow T_1$ phase transitions were detected to be at $530°C$ [6, 7] or at $T > 530°C$ [28]. So, it is not clear whether our $S \rightarrow T_1$ transition occurs at $520°C$ or $532°C$. Anyhow, these two transitions, which appear around $520°C$, are uncommon. Lefkiwitz established by X-ray unusual phase transitions at $518°C$ and $526°C$ ($T_{S \rightarrow T_1} = 530°C$), Denoyer by X-ray and DTA – at temperature range of $523 - 528°C$ ($T_{S \rightarrow T_1} = 528°C$), and Glazer also by DTA – at $530°C$ while heating and at $512°C$ while cooling. In our case we did not observed $R \rightarrow S$ transition at $480°C$. It might be shifted to the $503°C$ due to the existence of defects in the sample. Phase transition at $520°C$ could be appearance of regions with $T_1$ structure. Because of difference in lattice parameters, strains occur between $T_1$ and $S$ regions and impede the growth of $T_1$ and stabilize the continued existence of $S$ [8]. While temperature keeps rising, the lattice parameter cause changes in strain, at $532°C$ the distribution and magnitude of the strains become critical, regions with $S$ structure starts to disappear and $T_1$ growth has no loner interception. Lefkovitz found that at temperature region of $518°C$ and $526°C$ a negative thermal expansion exists, and explained it by the circumstances of a temperature gradient or a particular type of mechanical stress [6]. It should be also mentioned that because of the high sensitivity of ellipsometric technique to any global and local structural changes, we cannot separate the phase transition taking place in whole films with surface or interface phase transition. Therefore, the next step of our investigation will be study of the found phase transitions by other methods (like specific heat measurements) and development of more complicated ellipsometric model for taking into account possible anisotropy of our films.

4. Conclusion

New optical properties and thermo-optical results on the NN thin films are presented in this work. Refractive and absorption indexes were calculated from the ellipsometric data in the spectral range $250 – 1000$ nm. The band gap energy of NN films was calculated to be 3.48 eV. Several peculiarities in the refractive index temperature behaviour of NN thin films at the temperatures 370, 445, 503, 520 and 532°C were observed. These peculiarities were attributed to the phase transitions taking place in the NN film. Detected phase transition temperatures agree with the others works done by different techniques mainly on NN single crystals.

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6. References

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