Preparation and infrared characterization of potassium tantalate thin films

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Abstract

Potassium tantalate $KTaO_3$, (KT) thin films of perovskite structure were prepared by chemical solution deposition (CSD) on Si and SiO_2 glass substrates. Potassium and tantalum isobutoxides were dissolved in absolute isobutanol with an addition of diethanolamine as a modifier to obtain a homogeneous and stable precursor solution. Optimum conditions for film preparation were found. Annealing temperature and heating regime, Al_2O_3 "chemical" buffer layer and $KNbO_3$ seeding layer were the determining factors of the film quality. It was demonstrated by X-ray diffraction (XRD) that the films have the desired cubic perovskite structure. The infrared transmittance spectrum of the films shows three minima corresponding to optical active phonons in the perovskite crystal structure. Their positions are in agreement with the bulk material, except the $14\,cm^{-1}$ shift of the lowest phonon, which has been also observed in other perovskite materials. The temperature dependence of the phonon parameters has been studied too.
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Keywords: Films; Spectroscopy; Tantalates; Chemical solution deposition

1. Introduction

Potassium tantalate niobate, $KTa_{1-x}Nb_xO_3$ (KTN), is an example of ferroelectric/paraelectric solid solutions of particular interest for both applied and basic research. Pure $KTaO_3$ (KT) is an incipient ferroelectric with relatively high permittivity ($\approx$230 at room temperature) remains cubic down to the lowest temperatures. $KNbO_3$ exhibits on cooling a sequence of three ferroelectric phase transitions similar to $BaTiO_3$. KTN thin films have received a great attention owing to their piezoelectric, pyroelectric, and electrooptic properties. It has been used in capacitors for DRAMs, and attracts also attention in the branch of fuel cells research owing to its high-temperature protonic conductivity.[1] KT is expected to be a good material for the application in microwave tunable devices.[2]

Different procedures including chemical solution deposition (CSD) have been used for preparation of KTN thin

films with perovskite structure.[3–6] As only these films have the desirable properties, the formation of pyrochlore phase should be avoided at their preparation. Highly $(1\,0\,0)\langle u\,v\,w\rangle$ oriented KTN(65/35) perovskite films[3] were prepared from alkoxide precursors deposited on $(1\,0\,0)SrTiO_3$, and $(1\,0\,0)MgO$ and annealed at 700 and 750 °C, respectively. Quite similar films[4] were also prepared from hydrolysed alkoxide sols deposited on $(1\,0\,0)MgO$ and annealed at 700 °C. Unfortunately, only pyrochlore phase was detected in KTN(65/35) films[4] deposited on $(1\,0\,0)Si$, $(1-1\,0\,2)Al_2O_3$ and $(0\,1-1\,0)SiO_2$. Furthermore, various substrate types[5] were tested for KTN(65/35) film preparation. In addition to the substrates mentioned above, also Pt-coated $(1\,1\,1)Si$, $(1\,0\,0)YSZ$, $(1\,1\,0)SrTiO_3$, and $(0\,1\,2)LaAlO_3$ were used. It was concluded[5] that the phase composition of the KTN thin films strongly depended on the crystal structure of the substrates, while other processing parameters (chemical additives to sol, annealing regimes) played less important roles. Using substrates $(1\,0\,0)$ and $(1\,1\,0)SrTiO_3$, and $(1\,0\,0)MgO$ with lattice parameters and crystal symmetry close to KTN, the pure perovskite phase was obtained.

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The KTN films contained a varying portion of pyrochlore phase on the substrates which exhibited lower degree of crystallographic matching $((1\,0\,0)YSZ$, $(1-1\,0\,2)Al_2O_3$, $(0\,1\,2)LaAlO_3)$. Only the pyrochlore phase was observed on the substrates having no structural similarity with the film (amorphous SiO_2 and Pt-coated $(1\,1\,1)Si$). The structural, dielectric, and ferroelectric properties of a series of KTN thin films with compositions (65/35, 50/50, and 35/65), and deposited on bare and Pt-coated $(1\,0\,0)MgO$ were studied.[6] Pure perovskite phase was grown on both types of substrates at $700\,^\circ C$ with a high degree of preferred $(1\,0\,0)$ orientation. In all above mentioned papers, the maximum content of Ta in KTN films reached 65%, and preparation of pure perovskite phase was successful only when a crystallographically similar single crystal substrate ($SrTiO_3$, MgO) was used.

The first paper describing the preparation of pure perovskite KT films by chemical solution deposition on various substrates including SiO_2 glass and $(1\,0\,0)Si$ was published by the present authors.[7] The development of this method enabled us to prepare the KT films of a quality suitable for their characterization by far infrared spectroscopy at various temperatures. This is the main topic of the present paper.

2. Experimental

$Ta(OCH_2CH(CH_3)_2)_5$, and $K(OCH_2CH(CH_3)_2)$ were chosen as precursors for the synthesis of $KTaO_3$ (KT) sol, together with absolute $HOCH_2CH(CH_3)_2$ as a solvent, and 2,2-diethanolamine as a modifier. Detailed procedures of precursor syntheses, their handling, and substrate cleaning are given in our previous paper.[7] In order to minimize the loss of potassium due to the evaporation and reaction with the substrate, 5–7% excess of potassium in KT sols with respect to stoichiometric concentration was used. $Al(OCH_2CH(CH_3)_2)_3$ with absolute $(CH_3)_2CHCH_2OH$ as the solvent, and 2,2-diethanolamine as a modifier were used for the preparation of the sol for Al_2O_3 buffer layer deposition (see our previous paper[7]). $Nb(OCH_2CH(CH_3)_2)_5$ and $K(OCH_2CH(CH_3)_2)$ were used for the synthesis of $KNbO_3$ (KN) sol. The KN layer served as seeding layer for KT crystallization. Unhydrolysed sols were deposited on substrates by spin-coating (Karl Suss Gyrset coater) at 2000 rpm. After the deposition, the samples were dried (at $110\,^\circ C$ for 5 min) in a drying chamber, and then pyrolysed in a preheated furnace. If necessary, the deposition–drying–pyrolysis cycle was repeated until the desired thickness was reached. Finally, the samples were annealed to complete the crystallization. The conditions for the pyrolysis and annealing steps depended on the type of the deposited layer: the Al_2O_3 buffer layer was pyrolysed at $450\,^\circ C$ for 5 min, and annealed at $800\,^\circ C$ for 60 min; while the KT layers were pyrolysed at $550\,^\circ C$ for 5–10 min. The annealing was carried out under the conditions simulating the rapid thermal annealing: the annealed sample was immersed quickly into the muffle furnace preheated at $750\,^\circ C$ and annealed for 5 min. The composition of sols and films was determined by means of the volumetric titration and electron microprobe analysis, respectively. The thickness of films was measured by a stylus profilometer, the crystallization behavior was determined mainly by powder X-ray diffraction (XRD) and atomic force microscopy (AFM).

The infrared transmittance on KT thin films was measured in the spectral range from 30 to $700\,cm^{-1}$ and from 10 to 300 K using a Bruker IFS 113v Fourier transform spectrometer. The raw experimental spectra showed interference fringes originating in multiple passage of infrared radiation in the Si substrate. The fringes were eliminated by a Fourier-transform filtering of the transmittance.

3. Results and discussion

3.1. Film preparation

Two main issues seem to be decisive for the formation of perovskite phase in thin films. The first one is the stability of perovskite phase at higher temperatures and of pyrochlore phase at lower temperatures. The second one is the high volatility and reactivity of basic potassium towards the acidic substrates. The perovskite phase in KT films is formed preferentially in temperature range from 750 to $850\,^\circ C$. This can be seen from the X-ray patterns of KT films annealed at various temperatures in Fig. 1. Below $750\,^\circ C$, the pyrochlore phase crystallizes preferentially, above $850\,^\circ C$ the formation of potassium deficit phases as $K_6Ta_{10.9}O_{30}$ is inevitable.

An Al_2O_3 film of thickness above 200 nm is used for chemical separation of the substrate from the deposited ("chemical" buffer layer). This substantially reduces the loss of potassium due to its reaction with acidic substrates as Si and SiO_2 glass. A pseudocubic KN layer (thickness 60 nm, lattice misfit <2% in comparison with pure KT) was used as a seeding layer to promote the growth of perovskite KT films via the grain growth from seed islands. With respect to high annealing temperature it is highly probable that pronounced interdiffusion of Nb and Ta occurred. However, no Nb was detected in KT films by electron probe microanalysis.

3.2. Film characterization

XRD patterns of $KTaO_3$ films (1200 nm) deposited on SiO_2 glass and $(1\,0\,0)Si$ substrates with Al_2O_3 (200 nm) "chemical" buffer layer and $KNbO_3$ (60 nm) seeding layer are shown in Fig. 2. It can be seen that the KT films have cubic perovskite structure.

The spectra of $KTaO_3$ at selected temperatures are displayed in Fig. 3 and show the characteristic patterns for perovskites. They consist of three minima corresponding to the frequencies of the optically active transverse phonons of F_{1u} symmetry. They are located at the frequencies 90, 200 and $550\,cm^{-1}$, which reasonably agree with the data on bulk material. The positions of bulk material frequencies are indicated in Fig. 3 by arrows.
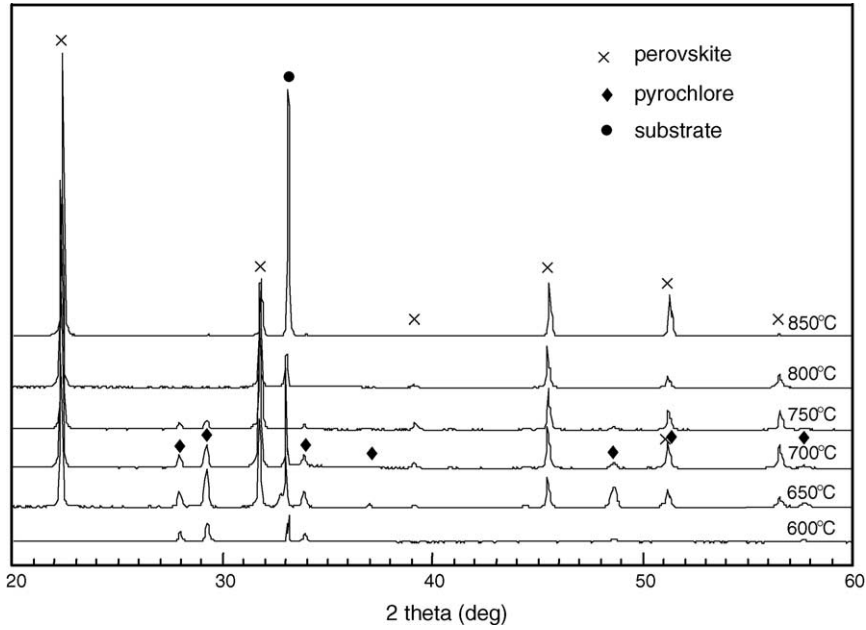
Fig. 1. XRD patterns of KT films on SiO$_2$ glass substrate, with Al$_2$O$_3$ and KN buffer layers, heat-treated at different temperatures under heating regime simulating rapid thermal annealing technique.

To evaluate the parameters of the infrared active modes, we fit the transmittance spectra by a model consisting of a stack of a film and substrate. In our calculation, to include multiple passage of the radiation through the sample, the complex amplitudes of electromagnetic field were summed in the film and the intensity summation was used to evaluate influence of the substrate. The dominant contribution to the complex dielectric function for each layer is given by the phonons, which

can be modeled by the sum of damped harmonic oscillators

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_\infty + \sum_{i=1}^{n} \Delta\varepsilon_i \frac{\omega_{\text{TO}i}^2}{\omega_{\text{TO}i}^2 - \omega^2 + i\omega\gamma_{\text{TO}i}}$$

where $\varepsilon_\infty = n^2$ is the high-frequency dielectric constant, $\Delta\varepsilon_i$, $\omega_{\text{TO}i}$ and $\gamma_{\text{TO}i}$ are dielectric strength, transverse frequency and damping of the ith phonon, respectively. The function
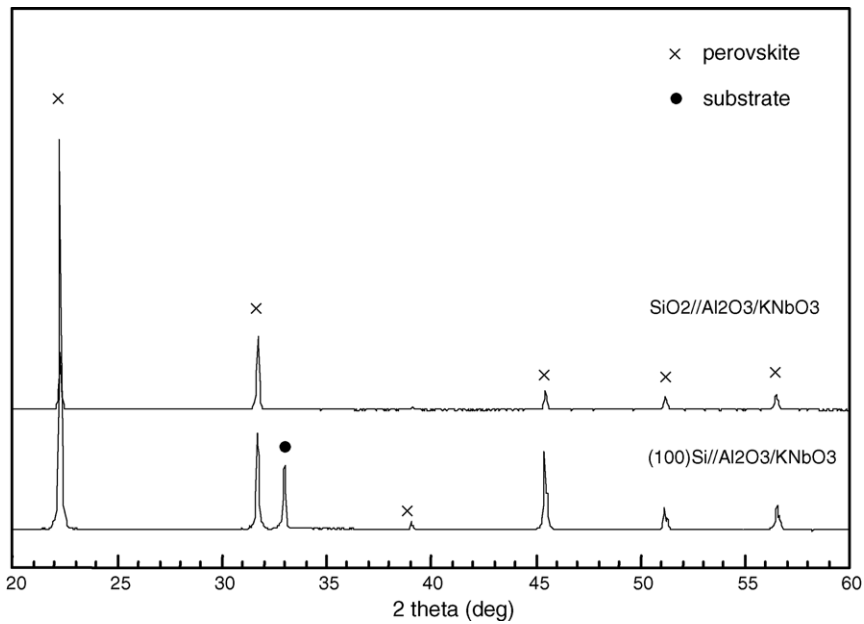

Fig. 2. XRD patterns of KT films on SiO$_2$ glass and (1 0 0)Si substrates, with Al$_2$O$_3$ and KNbO$_3$ buffer layers, annealed at 800 °C for 20 min under heating regime simulating rapid thermal annealing technique.
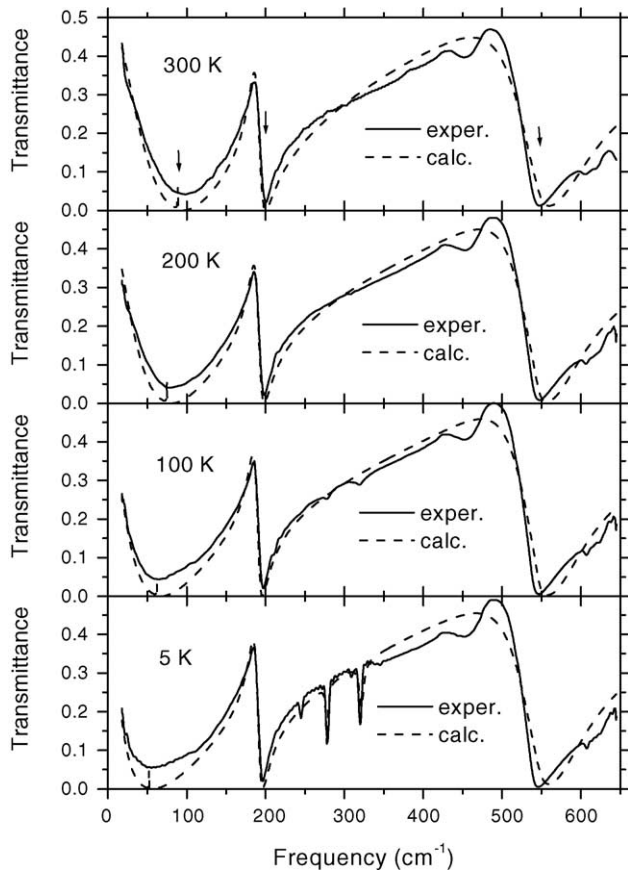
Fig. 3. Temperature dependence of the experimental and fitted transmittance spectra for selected temperatures. The arrows indicate the positions of the frequencies in single crystal bulk.

Fig. 4. Temperature dependence of the frequency of the soft mode for our thin film and single crystal.

$\varepsilon(\omega)$ was used for calculation of the Fresnel formulas for complex transmission and reflection of particular layers. To reduce the ambiguity and errors in the parameter determination, we measure and fit independently also the transmission of the bar substrate and we keep the parameters fixed during the subsequent film fit.

The fitted curves are also shown in Fig. 3 and are compared with the reflectance experiment. Good agreement can be seen between the experimental and fitted curves in all three major absorption features. The minor deviations between the two curves are caused by multiphonon absorption or inhomogeneity of the films. The lowest-frequency mode behaves as a soft mode. KTaO$_3$ is an incipient ferroelectric and the soft mode frequency, therefore, decreases in the entire temperature range on cooling. Its frequency is $90\,\mathrm{cm^{-1}}$ at room temperature and decreases to $54\,\mathrm{cm^{-1}}$ at 6 K. The fitted model frequencies are plotted in Fig. 4. The static permittivity calculated from the model parameters $[\varepsilon(0) = \sum_i \Delta\varepsilon_i + \varepsilon_\infty]$ is 208 at room temperature and increases to 611 at 5 K, ε_∞ is 4.8.

Pure KTaO$_3$ is the model intrinsic quantum paraelectric. This is manifested by the deviation of its dielectric response from Curie–Weiss law at low temperatures. The static permittivity $\varepsilon'(T)$ of a single c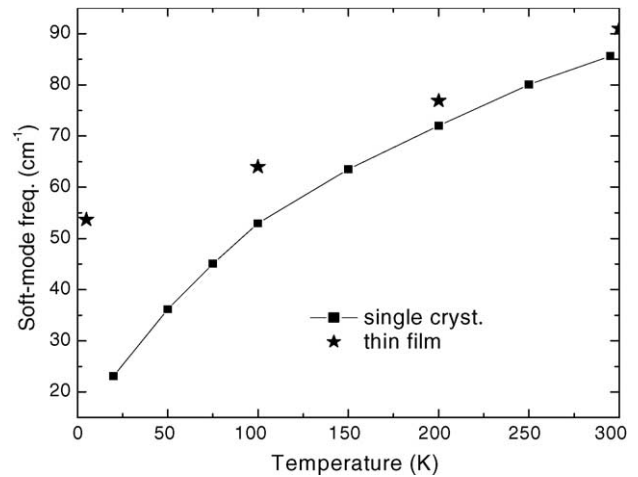rystal at room temperature has a value of 230 and below 20 K approaches a plateau with ε' of 4000. These values are in agreement with hyper-Raman measurements[8] of the soft mode frequency. The comparison of the single crystal results with the parameters of our fit shows that the contribution of all optically active modes observed in infrared to permittivity is lower than the permittivity of the single crystal. The deviation is small for room temperature and becomes markedly enhanced at low temperatures. The decrease in ε' is a consequence of the soft mode stiffening in thin films. This situation is similar to that what was observed in the case of SrTiO$_3$, where it was explained as the result of porosity and center symmetry loss in the thin films.[9]

4. Conclusions

A CSD method was used to prepare polycrystalline KTaO$_3$ films on SiO$_2$ glass and (1 0 0)Si substrates. The conditions of their preparation were optimized. It was demonstrated by X-ray diffraction that the films have cubic perovskite structure. Infrared transmittance at various temperatures was measured and fitted. The lower value for contribution of the infrared active modes to permittivity was explained in analogy with SrTiO$_3$ as consequence the film porosity and loss of symmetry center.

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