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Preparation of potassium tantalate niobate thin films by chemical solution deposition and their characterization

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Abstract

Potassium tantalate niobate ($KTa_xNb_{1-x}O_3$, (KTN), where $x = 0$, 0.21, 0.36, 0.53, 0.74, 0.82, 0.86, and 1) thin films of perovskite structure were prepared by chemical solution deposition (CSD) on Si and SiO_2 glass substrates. A homogeneous and stable precursor solution was obtained by dissolving potassium, niobium and tantalum isobutoxides in absolute isobutanol and an addition of diethanolamine as a modifier. The film quality was determined by annealing temperature and heating regime, Al_2O_3 "chemical" buffer layer and $KNbO_3$ seeding layer. Optimum conditions for film preparation were found. It was approved by X-ray diffraction (XRD) that the films have the wanted pseudocubic perovskite structure. Infrared transmittance was measured for broad range of Ta/Nb ratios. The spectra show continuous transformation from $KTaO_3$ to $KNbO_3$ and indicate that the optical axis lies in the plane of the film.

Keywords: Films; Tantalates; Chemical solution deposition; Spectroscopy

1. Introduction

Potassium tantalate niobate, $KTa_{1-x}Nb_xO_3$ (KTN), thin films have received a great deal of attention owing to their piezoelectric, pyroelectric, and electrooptic properties. As only KTN films with perovskite structure have these desirable properties, the formation of pyrochlore phase should be avoided at their preparation. The paraelectric cubic perovskite phase of KTN (Ta/Nb = 65/35) is the most frequently studied because it is a promising candidate material for IR detectors and electro-optic devices owing to its very large quadratic electrooptic coefficient and photorefractive effect.[1] Using different procedures including chemical solution deposition (CSD) method, KTN perovskite thin films have been successfully prepared.[1–4] Highly $(1\,0\,0)\langle u\ v\ w\rangle$ oriented KTN(65/35) perovskite films[1] 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[2] 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[2] deposited on (1 0 0)Si, $(1\,-1\,0\,2)Al_2O_3$ and $(0\,1\,-1\,0)SiO_2$. Besides, various substrate types[3] 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[3] that the phase composition of the KTN thin films had a strong dependence 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. 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 of compositions (65/35, 50/50, and 35/65), and deposited on bare and

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Pt-coated (1 0 0)MgO were studied.[4] Pure perovskite phase was grown on both types of substrates at 700 °C with a high degree of preferred (1 0 0) orientation. In summary, 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 (i.e., $SrTiO_3$ or MgO) was used.

This paper describes the preparation of a series of KTN perovskite thin films, covering the entire interval of Ta:Nb ratios, deposited on (1 0 0)Si, and SiO_2 glass substrates, and their characterization by X-ray diffraction (XRD) and infrared spectroscopy.

2. Experimental

$Ta(OCH_2CH(CH_3)_2)_5$, $Nb(OCH_2CH(CH_3)_2)_5$, and $K(OCH_2CH(CH_3)_2)$ were chosen as starting compounds for the synthesis of $KTaO_3$ (KT) and $KNbO_3$ (KN) sols, together with absolute $HOCH_2CH(CH_3)_2$ as a solvent, and 2,2-diethanolamine as a modifier. Detailed procedures for syntheses and handling of precursors and cleaning of the substrates are given elsewhere.[5] In order to minimize the loss of potassium due to the evaporation and reaction with the underlying layers, 5–7% excess of potassium in KTN sols with respect to stoichiometric concentration was used. $Al(OCH_2CH(CH_3)_2)_3$, 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[5]). Unhydrolysed solutions were deposited by spin-coating (Karl Suss Gyrset coater) at 2000 rpm, the samples were then dried (at 110 °C for 5 min) in a drying chamber, and pyrolysed in a preheated furnace. If necessary, the deposition–drying–pyrolysis cycle was repeated until the desired thickness was reached. Finally, the samples were crystallized by annealing. The conditions for the pyrolysis and annealing steps differed according to the deposited layer: the Al_2O_3 buffer layer was pyrolysed at 450 °C for 5 min, and annealed at 800 °C for 60 min; the KTN layers were pyrolysed at 550 °C for 5–10 min. The annealing was carried out under the conditions simulating the rapid thermal annealing technique: the annealed sample was immersed quickly into the muffle furnace preheated at 750 °C and annealed for 5 min (Fig. 1). The composition of KTN 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 and atomic force microscopy (AFM). Further characterization of the perovskite films was done using far infrared spectra. The infrared transmittance on KTN thin films was measured in the spectral range from 30 to 700 cm^{-1} at room temperature using a Bruker IFS 113v Fourier transform spectrometer. The raw experimental spectra show 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.

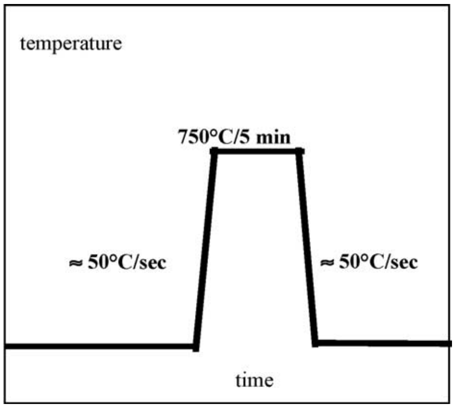

Fig. 1. Scheme of annealing procedure simulating rapid thermal annealing technique.

3. Results and discussion

3.1. Film preparation

This work is a continuation of our previous study[5] dealing with the preparation of $KTaO_3$ (KT) perovskite thin films. It was confirmed that the parameters optimal for the preparation of pure KT layers[5] were suitable also for the preparation of KTN layers with various Ta/Nb ratio.

Concerning the formation of perovskite phase in thin films, two main issues seem to be decisive. The first one is the stability of perovskite phase at higher temperatures and that of pyrochlore phase at lower temperatures. The second one is the high volatility and reactivity of basic potassium towards the acid substrates. In the temperature range from 750 to 850 °C, in a few (2–12) minutes, the perovskite phase is formed in KTN films preferentially, as it can be seen from X-ray patterns of KTN films annealed at various temperatures presented in Fig. 2. Below the lower temperature limit, a pyrochlore phase crystallizes preferentially; above the upper limit the formation of potassium deficit phases as $K_6Ta_{10.9}O_{30}$ is inevitable.

The Al_2O_3 film of thickness above 200 nm is used for chemical separation of the substrate from the deposited film ("chemical" buffer layer). This substantially reduces the loss of potassium due to its reaction with acid substrates such as Si and SiO_2 glass. The influence of the Al_2O_3 film thickness on the preferential crystallization of the KTN perovskite phase is shown in Fig. 3. A pseudocubic KN layer (thickness 60 nm, lattice misfit <2% in comparison with pure KT) was used as a seeding layer promoting the growth of perovskite KTN films via the grain growth from seed islands.

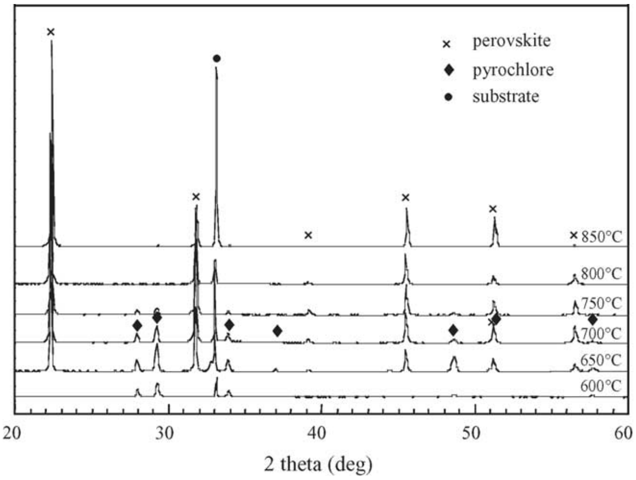

Fig. 2. XRD patterns of KTN films on SiO_2 glass substrate, with Al_2O_3 and KN buffer layers, heat-treated at different temperatures under heating regime simulating rapid thermal annealing technique.

3.2. Film characterization

The series of powder X-ray patterns for KTN films with various Ta/Nb ratio is shown in Fig. 4. The plotted X-ray data are similar and confirm the perovskite-like structure of the KTN films for all Ta/Nb ratios. The diffraction peaks are not split even in the Nb-rich samples (note that bulk $KTaO_3$ is cubic but $KNbO_3$ is orthorhombic at room temperature). This indicates a pseudocubic symmetry of our films, which could be explained by their nanocrystalline character. It is well known that the deviation from the cubic phase is quite reduced for such small crystallites.[6]

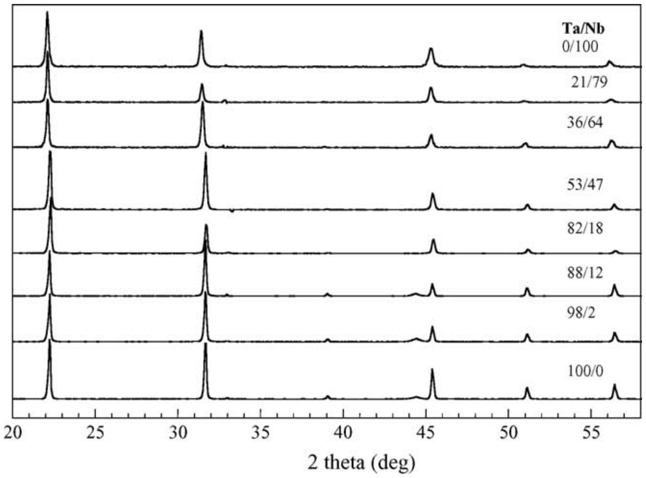

Fig. 4. X-ray diffractograms of KTN films with varying Ta/Nb ratio. Films were deposited on Si and SiO_2 substrates at optimized conditions.

The transmittance spectra for varying Ta/Nb ratio are displayed in Fig. 5. KT keeps the cubic crystal structure over the entire temperature range and its spectrum shows the characteristic patterns for perovskites. It consists of three minima corresponding to the frequencies of the optically active transverse phonons, which can be assigned to F_{1u} irreducible representations of the group theory. They are located[7] at the frequencies 90, 200 and 550 cm^{-1}. The crystal structure of KN at room temperature is orthorhombic with the crystal axes $a \approx c$. Its polarized infrared spectra are generally different along the particular crystal axes. They can be classified[8] by A_1, B_1 and B_2 representations in orthorhombic and A_1 and E in pseudocubic structure. In the latter case, the phonon frequencies are at 60, 198 and 516 cm^{-1} for the E symmetry and at 190, 295 and 600 cm^{-1} for the A_1 symmetry.

The positions of the phonons in Fig. 5 are in reasonable agreement with the data on bulk materials. On contrary to X-ray diffraction, which shows pseudocubic character, infrared spectra of KN display features of strong uniaxial material. As our films are polycrystalline we measured unpolarized spectra and, therefore, our infrared spectra are superpositions of the spectra parallel and perpendicular to optical axis. The

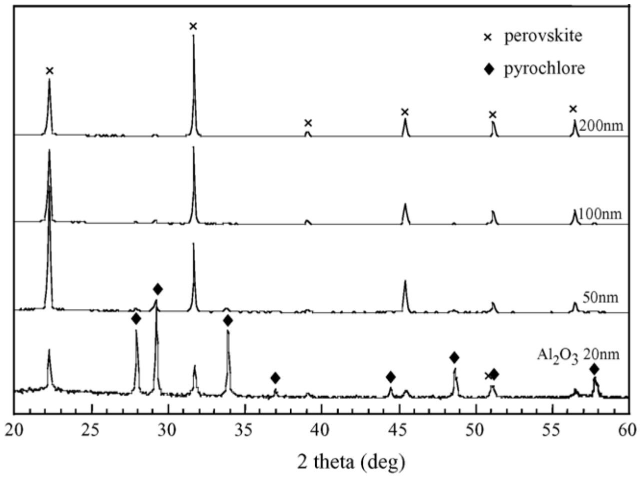

Fig. 3. XRD patterns of KTN films on (1 0 0) substrate with Al_2O_3 buffer layer of different thickness. KN seeding layer (60 nm) and heat treatment simulating rapid thermal annealing were used.

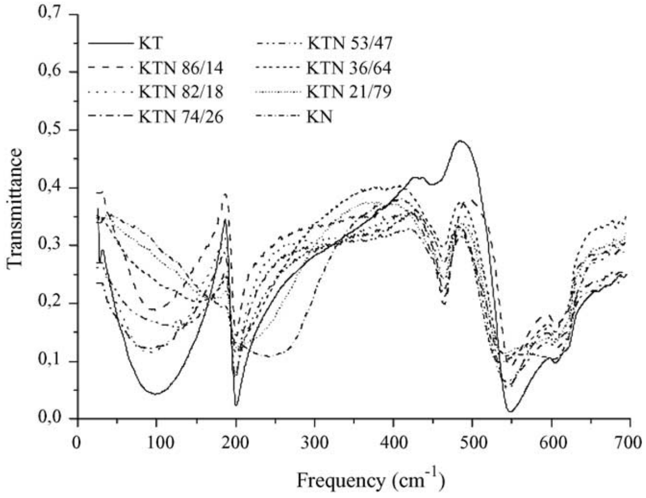

Fig. 5. Concentration dependence of far infrared transmittance spectra on KTN thin films deposited on (1 0 0)Si substrate with Al_2O_3 buffer layer and $KNbO_3$ seeding layer.

continuous transformation from the KT to KN spectrum can be clearly observed with varying Ta/Nb ratio. In the KN spectrum, the A_1 component is quite enhanced. It indicates that the crystallites could prefer the orientation with the optical axis in the film plane. The absolute values of the transmittance depend on the film thickness and its homogeneity. As these parameters vary in our films, we cannot compare them. The position of the minimum is, however, independent of them.

4. Conclusions

A CSD method was used for preparation of polycrystalline $KTa_{1-x}Nb_xO_3$ films on different substrates in the entire range of Ta/Nb ratio. The conditions of their preparation were optimized. It was demonstrated by X-ray diffraction that the films have pseudocubic perovskite structure. Infrared transmittance was measured for eight different Ta/Nb ratios. The spectra show continuous transformation from KT to KN and indicate that the optical axis lies in the plane of the film.

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