

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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1. Introduction

Potassium tantalate niobate, $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (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 (≈ 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 (100) $\langle uvw \rangle$ oriented KTN(65/35) perovskite films³ were prepared from alkoxide precursors deposited on (100) SrTiO_3 , and (100) MgO and annealed at 700 and 750 °C, respectively. Quite similar films⁴ were also prepared from hydrolysed alkoxide sols deposited on (100) MgO and annealed at 700 °C. Unfortunately, only pyrochlore phase was detected in KTN(65/35) films⁴ deposited on (100)Si, (1–102) Al_2O_3 and (01–10) SiO_2 . Furthermore, various substrate types⁵ were tested for KTN(65/35) film preparation. In addition to the substrates mentioned above, also Pt-coated (111)Si, (100)YSZ, (110) SrTiO_3 , and (012) LaAlO_3 were used. It was concluded⁵ 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 (100) and (110) SrTiO_3 , and (100) 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 ((100)YSZ, (1–102)Al₂O₃, (012)LaAlO₃). Only the pyrochlore phase was observed on the substrates having no structural similarity with the film (amorphous SiO₂ and Pt-coated (111)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 (100)MgO were studied.⁶ Pure perovskite phase was grown on both types of substrates at 700 °C with a high degree of preferred (100) 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 (SrTiO₃, MgO) was used.

The first paper describing the preparation of pure perovskite KT films by chemical solution deposition on various substrates including SiO₂ glass and (100)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(OCH₂CH(CH₃)₂)₅, and K(OCH₂CH(CH₃)₂) were chosen as precursors for the synthesis of KTaO₃ (KT) sol, together with absolute HOCH₂CH(CH₃)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(OCH₂CH(CH₃)₂)₃ with absolute (CH₃)₂CHCH₂OH as the solvent, and 2,2-diethanolamine as a modifier were used for the preparation of the sol for Al₂O₃ buffer layer deposition (see our previous paper⁷). Nb(OCH₂CH(CH₃)₂)₅ and K(OCH₂CH(CH₃)₂) were used for the synthesis of KNbO₃ (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 °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 Al₂O₃ buffer layer was pyrolysed at 450 °C for 5 min, and annealed at 800 °C for 60 min; while the KT layers were pyrolysed at 550 °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 °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 °C. This can be seen from the X-ray patterns of KT films annealed at various temperatures in Fig. 1. Below 750 °C, the pyrochlore phase crystallizes preferentially, above 850 °C the formation of potassium deficit phases as K₆Ta_{10.9}O₃₀ is inevitable.

An Al₂O₃ 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 SiO₂ 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 KTaO₃ films (1200 nm) deposited on SiO₂ glass and (100)Si substrates with Al₂O₃ (200 nm) “chemical” buffer layer and KNbO₃ (60 nm) seeding layer are shown in Fig. 2. It can be seen that the KT films have cubic perovskite structure.

The spectra of KTaO₃ 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.

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