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Investigation of microstructural and optical properties of $(K,Ba)(Ni,Nb)O_{3-\delta}$ thin films fabricated by pulsed laser deposition

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ABSTRACT

Perovskite-type ferroelectrics are increasingly being studied for applications in solar-energy conversion because of their efficient ferroelectric polarization-driven carrier separation and above-bandgap generated photovoltages. $(K,Ba)(Ni,Nb)O_{3-\delta}$ ferroelectric films, a highly promising and low-cost absorber layer material for solar cells, have been fabricated on $Pt(111)/Ti/SiO_2/Si(100)$ substrates for the first time, using a modified pulsed laser deposition method. Well-crystallized near-stoichiometric $(K,Ba)(Ni,Nb)O_{3-\delta}$ film was obtained by adjusting the target–substrate distance to 50 mm and setting the substrate at an oblique angle of $\sim 11^\circ$ from the plume axis. Microstructural characterizations show the as-grown film exhibits a single-phase perovskite structure with a dense and uniform surface. The optical absorption spectrum of $(K,Ba)(Ni,Nb)O_{3-\delta}$ has two main peaks, i.e., a significant peak at the intermediate energy adjacent to a much larger peak at higher photon energy, which indicates intraband multiple electronic transition. The present results could be crucial for potential solar-energy device applications.

1. Introduction

Ferroelectric thin films have great applications in electro-optic devices, nonvolatile memory, and dynamic access memory [1,2]. Various methods, both vacuum-based and non-vacuum based techniques, such as pulse laser deposition (PLD), metalorganic chemical-vapor deposition, sol-gel processing, and streaming process for electrodeless electrochemical deposition (SPEED), have been employed in fabricating epitaxial and polycrystalline films [3–6]. Among them, one advantage of the vacuum-based techniques is the versatility afforded by the possible use of multiple evaporation/sputtering sources, thereby providing considerable control over the film composition and phase profile. As a precise thin film fabrication technique in vacuum, PLD is widely considered to be a very applicable approach to deposit high-quality films with complex compositions because it has the superiority of offering stoichiometric preservation during materials transfer from target to substrate and good crystallinity due to the highly energetic species [7]. Recently, ferroelectric films continue to attract much attention due to their light-absorbing properties [7,8]. Although photovoltaic (PV) effect observed in ferroelectrics is very promising, most well-studied perovskite oxides have a wide bandgap (E_g) of above 3.0 eV in the ultraviolet region [9], which is undesirable for solar cells, where the optimum gap is around 1.4 eV.

In order to improve the PV efficiency, a lot of efforts have emphasized electronic structure modification of ferroelectric oxides to engineer bandgaps that span the solar spectrum. Grinberg et al. described a family of single-phase solid oxide solutions made from low-cost and non-toxic elements using a solid-state method: $(K,Ba)(Ni,Nb)O_{3-\delta}$ [10]. These oxides exhibit both ferroelectricity and a wide variation of bandgaps in the range of 1.1–3.8 eV, which will be the most promising candidate as visible-light-absorber for solar cells. Similar results have also been reported in our previous works [11], and the synthesized ferroelectric ceramics have a narrow E_g of below 1.5 eV matching the solar spectrum, which creates opportunities for innovation in PV cells and state of the art optoelectronic devices. As we all know, compared with bulk materials, thin films occupy more important position in the field of actual device preparations. Therefore, the research on ferroelectric PV $(K,Ba)(Ni,Nb)O_{3-\delta}$ films was imperative.

In this letter, we have successfully prepared the $[KNbO_3]_{0.9}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_{0.1}$ (KBNNO) film by PLD method for the first time and investigated the film's structure, surface morphology, and optical properties. This work can establish a good basis for the further research of ferroelectric KBNNO films in solar devices and advance the ferroelectric PV field. In addition, our modified PLD method can also be used to prepare other

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multicomponent films especially those containing volatile elements.

2. Experimental details

The KBNNO thin film was grown on Pt(111)/Ti/SiO_2/Si(100) substrate by PLD method using an excimer KrF laser (248 nm, 8 Hz, 3 J/cm^2). The target was a 20 mm diameter disk of high-density KBNNO ceramics and the substrate was placed parallel to the target. Taking the dispersion of K species in plume into account, the substrate was set oblique from the plume axial direction. The schematic diagram of the configuration is shown in Fig. 1 (a). Based on the spatial segregation effects reported by Urbassek and Sibold [12], the lighter species in the plume statistically get the higher velocity in the adiabatic expansion regime and the energy is transferred from the light particles to the heavy ones during the collisions between particles in the plume. As a result, the lighter species decelerate and will hence be more likely to be scattered out of the plume axial direction and spread at a large oblique angle from the plume axis. Furthermore, the larger the oblique angle it spreads, the more likely will it be scattered back to the target surface. On the contrary, the heavier species accelerate and move more centrally in the direction of the plume axis after collision with lighter species and will be less likely to be scattered back to the target surface than the light species. Because the atomic mass of K is the lightest among cations of KBNNO, K species is more likely to spread at a large oblique angle from the axial direction of the plume, which induces K deficiency of films deposited on the substrate. So, in our experiment, to avoid efficiently the K deficiency, the substrate was set at an oblique angle of $\sim 11^\circ$ from the plume axis. In addition, the parameters among the deposition were also optimized. The key parameters used to grow the KBNNO film are summarized in Fig. 1(b).

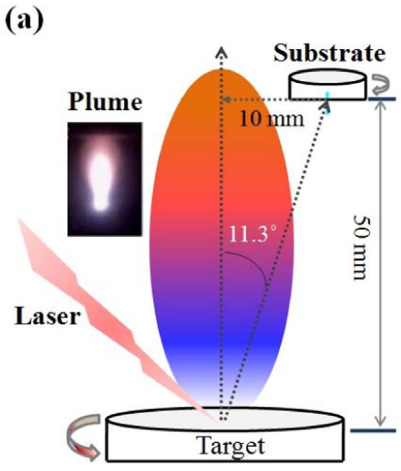
X-ray diffraction (XRD, Bruker D8 Advance, with Cu Kα radiation) was used to identify the crystal-structure of the KBNNO film. The surface micrograph and chemical composition were measured by scanning electron microscopy (SEM, Philips XL30FEG) with an energy dispersive X-ray (EDX) spectroscopy analyzer. The optical absorption of the film sample was determined by ultraviolet–visible–near-infrared (UV–vis–NIR) spectrophotometer (cary500, USA Varian) equipped with integration sphere.

3. Results and discussion

Fig. 2 shows the XRD pattern of the KBNNO film to be consistent with a single-phase perovskite structure, at least within the detection limits of the instrument, and no impurity phases are observed, as compared with the standard peaks taken from JCPDS (71-0945). In our previous experimental results [11], $KNbO_3$ ceramics has been shown to be an orthorhombic (*Amm*2) perovskite, and the different peak shapes were involved as the composition changes, where Bragg reflections for KBNNO ceramics are fully indexed as cubic perovskites. This indicated a structural transition from orthorhombic to cubic. However, from the XRD peaks of KBNNO film, the splitting of the doublet characteristics of the orthorhombic/tetragonal structure is not observed clearly, except the peaks at around 45°, which reveals a pseudo-cubic structure [13], as shown in the inset of Fig. 2.

Grain structure and porosity of KBNNO film have been investigated by using SEM. Fig. 3(a) shows the SEM morphology image of the sample. Well-crystallized and crack-free film was obtained since favorable grains were identified and interlinked densely. The KBNNO film possesses a microstructure of quadrate and quite uniformly distributed grains, whose average grain size is 400 nm. In addition, the elemental composition of the KBNNO film is presented in Fig. 3(b). The EDX analysis result can confirm the molar ratio of elements is near stoichiometric as expected.

The UV–vis–NIR absorption spectra of the KBNNO film on Pt (111)/Ti/SiO_2/Si(100) substrate was shown in Fig. 4(a). The optical bandgap can be estimated from the tangent lines in the plot of the Kubelka-Munk function $(\alpha h\nu)^2$ versus $h\nu$ for the direct bandgap material, where α is absorbance and $h\nu$ is photon energy [14,15], as shown in the inset of Fig. 4(a). It can be seen that the absorption spectrum has a small but significant peak at the intermediate energy adjacent to a much larger peak. The plot for bandgap determination has two slopes, where at low photon energy the slope leads to finding the low gap of 1.85 eV, whereas at higher photon energy there is another slope that gives a gap 2.51 eV. We can speculate the reason for this phenomenon based on many previous studies [9,16–18] and the schematic diagram of the intraband transition were shown in Fig. 4(b). The 2.51 eV gap can be due to the band-to-band transition from hybridized Ni 3*d* and O 2*p* to Nb 4*d* states. The 1.85 eV gap may originate from the intraband transition of Ni 3*d* orbitals, namely, the electron leaps from d_z^2 to $d_{x^2-y^2}$ orbital. With such a low E_g, the KBNNO film could potentially provide great applications in solar-energy devices.



(b)

Parameters	Values
Laser source	KrF
Wavelength	248 nm
Energy density	3 J/cm^2
Repetition rate	8 Hz
Target	KBNNO
Substrate	Pt(111)/Ti/SiO_2/Si(100)
Distance	50 mm
Substrate temperature	750 °C
Base pressure	5.4×10^{-4} Pa
Oxygen pressure	10 Pa
Film growth time	30 min

Fig. 1. (a) Schematic diagram of deposition configuration with the substrate oblique from the plume axial direction. (b) Optimized parameters for the KBNNO film prepared by PLD.