

Double perovskite $\text{Bi}_2\text{FeMo}_x\text{Ni}_{1-x}\text{O}_6$ thin films: Novel ferroelectric photovoltaic materials with narrow bandgap and enhanced photovoltaic performance

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ABSTRACT

Double perovskite ferroelectric $\text{Bi}_2\text{FeMo}_x\text{Ni}_{1-x}\text{O}_6$ (BFMNO) thin films were fabricated using the sol-gel method. The thin films have a broad-band absorption in visible light range of 400–650 nm. With the increase of Mo content, the optical bandgap decreases from 2.19 eV to 2.07 eV. More importantly, the as-prepared BFMNO thin films have self-polarization behavior that causes the forming of the depolarization field and build-in field in the thin films. The narrow band gap and strong ferroelectric self-polarization play a crucial part in improving the photovoltaic effect. The thin film of $x = 0.7$ has the optimum open circuit voltage and short circuit current which are 5.41 V and $71.07 \mu\text{A}/\text{cm}^2$ under light illumination of $110 \text{ mW}/\text{cm}^2$. In addition, the photovoltaic effect of the thin film also exhibits a good adaptability in high temperature environment. This work highlights the applications of the BFMNO thin films as a novel high-performance ferroelectric photovoltaic material.

1. Introduction

New energy materials have been considered as the reliable and clean energy materials to replace fossil fuels [1–12]. In recent years, ferroelectric photovoltaic (FE-PV) materials, a peculiar class of solar energy materials, have attracted considerable attention due to low cost, better carrier transfer and high stability of chemical and thermal [13–17]. The FE-PV effect, i.e. the charge separation of photoexcited carriers is driven by ferroelectric polarization, is different from the typical PV effect in semiconductor heterojunction [18–21]. Moreover, the output photovoltage is much larger than the bandgap of the ferroelectric materials [22]. However, the main drawback for most of FE-PV materials is tiny photocurrent [3,23]. Therefore, searching for feasible and high-efficiency method to improve PV effect of FE-PV materials is still a great challenge.

Among the ferroelectrics, BiFeO_3 (BFO) has a large remnant polarization of $90 \mu\text{C}/\text{cm}^2$ and a relatively small band gap of 2.7 eV, exhibiting the potential application in FE-PV field [24]. Indeed, the remarkable visible light PV effect have been observed in BFO crystal, ceramics and films [17,25–27]. However, the PV properties of the pure BFO have not been excellent enough to satisfy researcher. Therefore, some strategies are employed to enhance the PV properties of the BFO

materials. Tuning the bandgap and ferroelectric polarization is the primary method, which can improve the PV performance starting from the intrinsic physical properties of the BFO materials. For instance, ions doping is an effective method to change the electronic structure and crystal structure, resulting in a tuning on bandgap and polarization. Li et al. reported that La doping decreased the bandgap of BFO films to 2.63 eV [28]. Peng et al. found that Nd doping reduced bandgap and enhanced power conversion BFO ceramics [29]. Nechache et al. investigated Cr doped BFO double-perovskite structure $\text{Bi}_2\text{FeCrO}_6$, achieving a high power conversion efficiency of 8.1% by bandgap engineering [15]. In addition, the PV properties the BFO materials are also improved by a constructive PV effect. Fan et al. found that constructive PV effects at both the bulk and the $\text{BiFe}_{0.6}\text{Sc}_{0.4}\text{O}_3/\text{LaNiO}_3$ interface lead to a large PV properties, i.e. engineering the Schottky barrier heights to add a interfacial effect [30]. Huang et al. fabricated p-i-n heterojunction PV devices, where the two junctions favor carrier separation at the p-i and i-n interfaces [31].

In this work, we utilized the two strategies to develop a new BFO based FE-PV thin film and enhance the PV properties. Mo, Ni as the doped elements substituted Fe sites in $\text{Bi}_2\text{FeMo}_x\text{Ni}_{1-x}\text{O}_6$ (BFMNO). Mo, Ni co-doping played an important role in tuning bandgap and ferroelectric polarization of BFO. Moreover, the self-polarization of the thin

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film caused the sloping of the energy band, leading to the forming of the built-in field at the electrode-ferroelectric interface. As a result, the BFMNO thin films exhibited the large photovoltage and photocurrent as well as the excellent adaptability for high temperature. This work provide the strategies to enhance the PV properties of FE-PV materials, and opens up a promising feasible route to development of BFO materials in photoelectricity applications.

2. Material and methods

The $\text{Bi}_2\text{FeMo}_x\text{Ni}_{1-x}\text{O}_6$ (BFMNO) thin films ($x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$ and 0.75) have been fabricated on Si substrate via a sol-gel process. Stoichiometric amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 2-methoxy ethanol to prepare the precursor solution with a concentration of 0.1 mol/L . In order to uniformly disperse the metal ions in the sol-system, simultaneous, improving the stability and decomposition temperature of the citrate, thereby increasing the stability of the colloid, citric acid as the function of complexing agent was added into the solution. In order to compensate for the loss of volatile Bi during high temperature annealing, an excess of 2% bismuth nitrate was added to solution.

The precursor solution was spin-coated onto the Si substrate at 3000 rpm for 20 s and then dried at $150 \text{ }^\circ\text{C}$ for 5 min , subsequently pyrolyzed at $400 \text{ }^\circ\text{C}$ for 10 min , and finally annealed at $600 \text{ }^\circ\text{C}$ for 3 min . The last layer was annealed at $700 \text{ }^\circ\text{C}$ for 10 min to increase densification and crystallization of the BFMNO thin films. Au was used to fabricate the top electrodes. For the PV properties measurements, the lateral structure was adopted. On the top of the films, the symmetric Au top electrodes were fabricated by sputtering method using a vacuum ion sputtering equipment (VIS, GS1600) with current of 4 mA for 15 min , where a rectangular metal mask ($1 \text{ mm} \times 11 \text{ mm}$) was used to control the electrode area.

The optical transmission was measured using a UV-Visible spectrometer (Hitachi U-3900). The phase structure and the cross-sectional microstructure was examined using x-ray diffractometer (XRD, Bruker, D8 Advance diffractometer) and scanning electron microscopy (FESEM, FEI Quanta 200, FEG). The surface topography was measured by an atomic force microscope (AFM, Bruker, Icon). The thin films were not polarized before measuring the electrical and PV properties of them. The current-voltage (J - V) characteristics of the BFMNO films were tested by Keithley electrometer (6517B) and hernia light source (Solar500). The field-induced hysteresis loops (P - E) of the films were measured by a Ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM) at 5 kHz .

3. Results and discussion

Fig. 1 shows the XRD patterns of the BFMNO thin film with $x = 0.7$

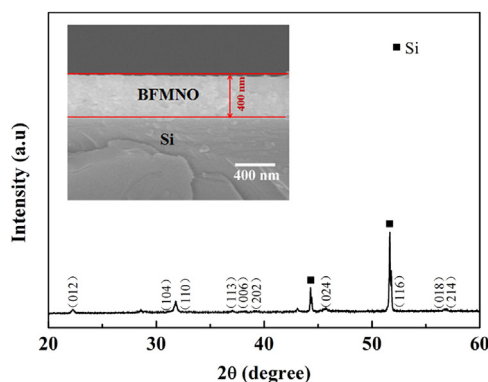


Fig. 1. XRD pattern and cross-sectional SEM image of $x = 0.7$.

deposited on Si substrate. The BFMNO film is crystallized in a rhombohedral perovskite structure with $R3c$ space group [32,33], revealing the polycrystalline nature of the films. No impurity phases are observed except for Si from the substrate. When x exceeds 0.7 , the structure of the film have a change, which does not maintain rhombohedral perovskite structure (Fig. S1). The cross-sectional FESEM image of the BFMNO thin film with $x = 0.7$ is shown in the inset of Fig. 1. The film exhibits a dense and uniform microstructure without any cracks. The thickness of the film is about 400 nm . The other thin films with different components exhibit the same phase structure and cross-sectional microstructure.

The AFM images of the surfaces of the BFMNO thin films show smooth and crack-free (Fig. S2 and Fig. 2). With the increase of Mo content, the grain size shows a decreasing tendency, indicating that the addition of Mo is in favor of grain refinement. In addition, the line roughness of the blue line shows that the roughness increase with the increase of Mo content. The root-mean-square roughness (R) of the surface ($25 \mu\text{m}^2$) for the thin films is also measured. The R increases from 8.2 nm to 9.5 nm when the Mo content increases from 0.2 to 0.7 . When the Mo content exceeds 0.7 , the R reaches to 17.3 nm for $x = 0.75$.

The schematic of the measurement for PV properties is shown in Fig. 3a. In the work, the symmetric Au top electrodes with an inter-electrode distance of 1 mm are fabricated on the top of thin films. Fig. 3b shows J - V characteristics curves of the as-prepared BFMNO thin films measured under light illumination of 40 mW/cm^2 . It is noted that the BFMNO thin films exhibit obvious rectification behavior. More importantly, Mo content has an significant influence on the PV properties. With the increase of Mo content, the open circuit voltage (V_{oc}) and short circuit current (J_{sc}) increase firstly and then decrease, as shown in the Fig. 3c. When x is 0.7 , the thin film has the optimal V_{oc} and J_{sc} , which are up to 1.59 V and $14.5 \mu\text{A/cm}^2$, respectively. However, the PV effect of the thin film with $x = 0.75$ is weakened, which is attributed to the change of the phase structure. Fig. 3d shows the zero bias photocurrent density of the BFMNO thin films with the light being switched on and off. The illumination of light on the specimens surface is turned on and off at a regular interval of 100 s . The BFMNO thin films exhibit a spontaneous and repeatable response to the light illumination, indicating that the PV effect has high stability. It is observed that the J_{sc} of $x = 0.7$ is larger than that of the others thin films under the illumination of light, which almost stays a constant value of $14.5 \mu\text{A/cm}^2$. These results indicate that moderate Mo content is beneficial for the improvement of PV properties. Interestingly, in this work, the BFMNO thin films show obvious PV effect even though the thin films are not polarized. Therefore, it is suggested that the observed PV effect may originate from the ferroelectric self-polarization of the BFMNO thin films. In addition, the fill factors (FF) of the thin films are calculated, where the FF of $x = 0.7$ is 8.6% . The FF of other thin films is also under 10% . The low FF is caused by the fact that the direction of the photo-generated current is opposite to the direction of the polarization, leading to that the current decreases gradually with the increase of the voltage in the first quadrant.

Generally, the PV effect of FE-PV materials is related closely to light absorption capacity and ferroelectric polarization. To further explore the mechanism of the enhanced PV effect, the UV-visible transmission spectra and the P - E hysteresis loops of the BFMNO thin films are measured. Fig. 4a show the UV-visible transmission spectra and absorption coefficient (α) as a function of wavelength of incident light in the BFMNO thin films. The spectra exhibit a broad absorption band which is in the range of 400 – 650 nm , indicating that the thin films have a capacity to absorb a considerable amount of visible light [29]. The spectra are used to estimate the optical bandgap (E_g) of the BFMNO thin films [22]. The optical band gap can be estimated using the Tauc's Law [34]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

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