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Change of electrical properties of $(K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O_3$ thin films induced by gamma-ray irradiation

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ABSTRACT

We investigated the effects of gamma-ray (γ) irradiation on the electrical properties of $(K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O_3$ (KNMN) thin films. The KNMN thin films were prepared on Pt/Ti/SiO_2/Si substrate using a chemical solution deposition method through a spin-coating process and were subject to γ radiation at various total doses from 0 to 3000 kGy. The structural properties as well as the ferroelectric and dielectric properties of the prepared films were examined before and after γ irradiation. We found that their crystalline quality did not vary significantly with an increase in the total dose. It was also observed that the remnant polarization value of the films decreased by ~10%, but the films maintained ferroelectricity even after irradiation up to 3000 kGy. In addition, the dielectric constant of the films decreased with the total dose. The observed variation of the electrical properties on the total dose might be mainly associated with the mobile defects in Mn-doped KNN thin films such oxygen vacancy and the stored energy gained from gamma-rays.

1. Introduction

Ferroelectric substances with the ABO_3 perovskite structure are widely used as materials in electronic devices, including sensors, transducers, and actuators because of their outstanding ferroelectric and piezoelectric properties [1–5]. Among the fields in which electronic devices based on ferroelectric substances are used, devices exposed to high-energy radiation such as in space, nuclear reactors, and military applications are included. Long-term exposure of such electronic devices to radiation is likely to damage the ferroelectric substances owing to the high-energy radiation effects, leading to significant degradation in the sensitivity and lifetime of the devices [2,3]. Therefore, the development of radioactivity-resistant ferroelectric substances are essential for use in high-radiation environments.

Since these radiation-induced degradations are highly relevant to structural defects in ferroelectric substances, many studies have been conducted on the effects of irradiation on the electrical and structural properties of ferroelectric substances to better understand of the degradation mechanism [2–7]. The results of previous studies show that ferroelectric substances with perovskite structures including $Pb(Zr_xTi_{1-x})O_3$ (PZT), which is the most widely used ferroelectric substance in commercialized devices at present, have high radioactivity resistance of 50–100 kGy or greater [2,3,8]. Nevertheless, many studies on the degradation of ferroelectric properties due to irradiation have been also reported. According to the studies, electric properties such as ferroelectricity as well as the dielectric properties of ferroelectric substances decrease as the level of radiation increases [2–7,9] and the degree of decrease in electric properties is largely dependent on the type and quality of the ferroelectric substance [4]. Generally, this radiation-induced degradation in ferroelectric properties is thought to be caused by two main factors: ionizing effect and displacement effect [8,9]. During the irradiation, a large number of electron–hole pairs can also be generated by ionizing effects, which can be trapped in defects. These trapped charges can produce a local field in the

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opposite direction of the external field, resulting in the degradation of polarization switching. High-energy gamma-ray can also displace atoms by transferring energy to lattice atoms through an electron-atom scattering event such as Compton scattering and pair production [10,11], which produces some defects such as interstitials and vacancies. These defects can lead to pinning the domain walls so that they can affect the change of physical properties of materials.

Recently, lead-free materials such as Bi-based compounds [$(Bi_{0.5}K_{0.5})TiO_3$ and $(Bi_{0.5}Na_{0.5})TiO_3$], $BaTiO_3$, and $(K_{0.5}Na_{0.5})NbO_3$ (KNN)-based materials have received considerable attention from an environmental perspective owing to the toxicity of lead [12]. Among several lead-free ferroelectric materials, KNN is a highly promising candidate for replacing lead-based ferroelectric materials because it has a high Curie temperature, relatively high piezoelectric properties, and low coercive fields [13]. However, pure KNN materials possess high leakage current related to defects formed by the evaporation of highly volatile alkaline ions of Na and K. Consequently, various methods including doping and hot-pressing are being investigated to overcome this problem and to improve the piezoelectric properties of KNN. Recently, the effects of Mn doping on KNN materials have been reported by a few research groups [14–16], and the results indicate that small amounts of Mn substitution for Nb could reduce leakage current and enhance ferroelectric/piezoelectric properties [16,17]. It was also shown that the existence of multivalent Mn ions in KNN materials disturbs the formation of oxygen vacancies and decreases domain wall pinning [17]. Despite the fact that Mn-doped KNN exhibits properties comparable to PZT, studies on the effects of irradiation on KNN materials have not yet been reported with the exception of KNO. Therefore, in this work, we prepared $(K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O_3$ (KNMN) thin films and observed the variations in their morphological and electrical properties under γ irradiation.

2. Experimental procedure

KNMN thin films were synthesized on a $Pt/Ti/SiO_2/Si$ (Pt/Si) substrate with 40×40 mm^2 size by chemical solution deposition using the spin-coating method. Sodium acetate, potassium acetate, niobium pentaethoxide, and manganese acetate were used as the starting chemicals to fabricate KNMN precursor solutions. Acetic acid and 2-methoxyethanol were used as solvents and acetylacetone was used as a chelating agent. The detailed preparation procedure of precursor solution is described in Refs [15–18]. To compensate for the volatilization of alkaline metals during the high-temperature annealing process, 10% K and Na excess was added to the precursor solution, and the molarity was adjusted to 0.4 M. KNMN precursor solutions were dropped onto a Pt/Si substrate using a micropipette and spin-coated at 3000 rpm for 30 s. After the spin-coating process, each coating layer was dried at 200 °C for 5 min, then calcinated at 400 °C for 5 min, and finally heat treated at 550 °C for 5 min. The process of deposition, drying, calcination, and heat-treating was repeated 8 times. The final annealing process for the crystallization of films was performed in a preheated tube-type furnace at 750 °C for 30 min. The prepared KNMN films had a thickness of about 500 nm.

Prior to the deposition of Pt top electrodes for electrical measurements, the 40×40 mm^2 KNMN film was diced into dozens of pieces. The detailed process of sample preparation for structural and electrical characterization is given in Fig. 1: (1) A KNMN film with a size of 40×40 mm^2 is synthesized on a Pt/Si substrate. (2) We select a uniform area in the film. (3) We then dice the sample into pieces. The size of each piece is 7×10 mm^2. We can usually get 20 pieces. (4) We deposit Pt top electrodes with 100-μm diameter on all diced films using the photo-lithography and the sputtering method [8]. About 70 electrodes are placed on each film. (5) Electrical properties such as *P-E* loops and dielectric constants are measured for 30 or more electrodes for each film. All the electrodes are individually named. For example, one film is named sample K1 and each electrode in sample 1 is labeled as K1-(1,1), K1-(1,2), K1-(1,3), … .., K1-(2,1), K1-(2,2), K1-(2,3), … .., K1-(3,1), K1-(3,2), K1-(3,3), … .., and so on, as shown in Fig. 1, where K indicates the KNMN film. (6) The diced films were then γ irradiated using a ^{60}Co source at room temperature with a dose rate of 10 kGy/h and different total doses. (7) All the samples are irradiated at the same time, and each sample is irradiated according to the desired irradiation total dose. (8) Changes in the crystal structure and the ferroelectric and dielectric properties of the irradiated films were investigated before and after γ irradiation. The values of remanent polarization (P_r) and dielectric constant (ε) were measured using the same electrode on the same film. (9) For about 30 electrodes, the above steps are repeated. (10) We then calculate the standard deviation from the data obtained from about 30 electrodes of the films. The standard deviation reflects how spread out the numbers is in our samples. And Electrical properties are measured as follows. Here are examples. For the samples irradiated with a total dose of 300 kGy, (1) ΔP_r values were calculated as: $P_{a\ K3\text{-}(1,3)} - P_{b\ K3\text{-}(1,3)}$, where P_a and P_b are the remanent polarization values measured after and before the irradiation. (2) Average ΔP_r values were calculated as: $\{(P_{a\ K3\text{-}(1,1)} - P_{b\ K3\text{-}(1,1)}) + (P_{a\ K3\text{-}(1,2)} - P_{b\ K3\text{-}(1,2)}) + \ldots .. + (P_{a\ K3\text{-}(n,n)} - P_{b\ K3\text{-}(n,n)})\}/n$, where n is the number of electrodes on a sample. (3) Average $\Delta 2P_r$ (%) were calculated as: $\{\Delta 2P_{\ K3\text{-}(1,1)}$ (%) + $\Delta 2P_{\ K3\text{-}(1,2)}$ (%) + … .. + $\Delta 2P_{\ K3\text{-}(n,n)}$ (%)$\}/n$, where n is the number of electrodes, where $\Delta 2P_{\ K3\text{-}(n,n)}$ (%) is $(2P_{a\ K3\text{-}(n,n)} - 2P_{b\ K3\text{-}(n,n)})/2P_{b\ K3\text{-}(n,n)} \times 100$. (4) The standard deviation was calculated with these data. (5) Dielectric constants were also obtained in the same manner.

X-ray diffraction (XRD, D/Max-2500; Rigaku, Tokyo, Japan) investigation was performed with CuKα radiation at 40 kV and 30 mA. Polarization versus electric field (*P–E*) hysteresis loops were obtained at a probing frequency of 2 kHz with the FE module of a Thin Film Analyzer (Model 2000; aixACCT Systems, Germany) which is a computer-based measurement tool used to characterize ferroelectric thin films. The dielectric properties of the films were obtained using an impedance analyzer (Model HP 4194A; Agilent Technologies, USA).

3. Results and discussion

Fig. 2(a) shows the XRD patterns of KNMN films with various total irradiation doses. The XRD patterns of KNMN film before and after irradiation reveal that the films have a polycrystalline structure and consist of perovskite phases without pyrochlore phases. The splitting of the (220) and (002) peaks at approximately $2\theta = 46°$ indicates that the crystal structure of the film is orthorhombic (space group: *Amm*2), which was indexed using the Joint Committee on Powder Diffraction Standards card No. 32-0822. In order to observe the change in crystal structure in KNMN films after irradiation, the full-widths at half-maximum (FWHM) and the ratio of the (220) and (002) peaks were obtained by Gaussian fitting of the XRD patterns. The variation of the FWHM and ratio of the peaks is plotted as a function of total doses in Fig. 2(b) and it shows that the FWHM and the ratio of peaks are changed after irradiation. However, the variations in the FWHM of each peak and the ratio of the peaks do not exhibit a systematic decrease or increase in response to an increase in the total dose, and they were changed in the range of less than 0.1% and 4% respectively. Because this change value is very small compared to those used to record changing crystal structure in other papers [19,20], it can be assumed that the variation in the crystal structure is very small after irradiation.