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Improvement of the electrical properties of TiO_2-doped $Bi_5Nb_3O_{15}$ thin films by the addition of MnO_2

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The leakage current density of a 1.0 mol% TiO_2-doped $Bi_5Nb_3O_{15}$ (TB_5N_3) film was high, and the breakdown electric field was low. This could be attributed to the presence of intrinsic oxygen vacancies and free electrons. The electrical properties of the TB_5N_3 film improved upon the addition of MnO_2 because of the formation of extrinsic oxygen vacancies, which caused the number of intrinsic oxygen vacancies to decrease in order to maintain the equilibrium concentration of oxygen vacancies in the film. However, the electric properties degraded when the MnO_2 content exceeded 15.0 mol% because of the formation of interstitial oxygen ions and holes. The dielectric constant (ε_r) of the TB_5N_3 film slightly decreased upon the addition of a small amount of MnO_2. The TB_5N_3 film with 15.0 mol% MnO_2, which exhibited a small leakage current density of 2.5×10^{-11} A/cm^2 at 0.15 MV/cm and a high breakdown electric field of 0.47 MV/cm, still maintained a large ε_r of 118 with a small loss tangent of 2.0% at 100.0 kHz.

1. Introduction

There has been increasing interest in dielectric thin films that can be grown at low temperatures (≤300 °C). They can be utilized as embedded capacitors formed inside printed circuit boards (PCB) [1] and as gate insulators of the thin film transistor of an organic light emitting diode. Moreover, they also can be used in radio-frequency (RF) or analog/mixed metal–insulator–metal capacitors. These dielectric thin films should have high dielectric constants (ε_r) in order to obtain the required high capacitance [2].

Recently, bi-based thin films such as $Bi_3Zn_2Nb_3O_{14}$ [3–5], $Bi_4Ti_3O_{12}$ [6], $Bi_6Ti_5TeO_{22}$ [7], and $Bi_5Nb_3O_{15}$ (B_5N_3) [8–10] films have been extensively investigated because of their low growth temperature and high ε_r. In particular, even though the B_5N_3 film grown at 200–300 °C using RF magnetron sputtering had an amorphous phase, it had a relatively high ε_r of 70 [9,10]. Therefore, many investigations into procedures such as doping with an additive or crystallization of the amorphous B_5N_3 have been conducted with the goal of increasing the ε_r values of B_5N_3 films grown at low temperature [11,12]. Furthermore, it was reported that TiO_2 doping increased the ε_r value of the B_5N_3 phase, and a B_5N_3 film grown at 300 °C using a pulsed laser deposition (PLD) method crystallized as the beam energy density increased. As a result, the 1.0 mol% TiO_2-doped B_5N_3 (TB_5N_3) films grown at 300 °C by PLD with a beam energy density of 3.0 J/cm^2 exhibited a very high ε_r value of 135.5 with a relatively low loss of 3.0% at 100 kHz [11]. However, their leakage current density was high and the breakdown field was low because of the presence of intrinsic oxygen vacancies and free electrons. Post-annealing under various oxygen pressures was conducted to improve the electrical properties of the TB_5N_3 film by decreasing the number of intrinsic oxygen vacancies [11]. The TB_5N_3 films annealed under 50.0 Torr exhibited improved electrical properties [11]. However, their ε_r values and dissipation factors were not satisfactory [12]. Therefore, it is necessary to develop another method to improve the electrical properties while maintaining good dielectric properties.

In this work, Mn_2O doping was used to improve the electrical properties of the TB_5N_3 film. This approach was chosen because Mn ions have been used previously to improve the electrical properties of thin films and multilayer capacitors in which intrinsic oxygen vacancies are the major defects causing the degradation of the electric properties of the devices [13–15]. The effects of Mn ions on

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the ε_r value and the dissipation loss of the TB_5N_3 film were also studied.

2. Experimental procedure

All the films were grown at 300 °C on a Pt/Ti/SiO_2/Si(100) substrate using PLD, and these films were then annealed at 300 °C after deposition of the Pt top electrode under 5.0 Torr oxygen partial pressure. PLD targets with nominal compositions of TB_5N_3 + x mol% MnO_2 (x = 0.0, 5.0, 10.0, 15.0 and 20.0) were produced using the conventional solid-state sintering method. An Nd-YAG laser beam (NL303HT, EKSPLA, Lithuania) with a wavelength of 266 nm (the fourth harmonic generation), a repetition rate of 10 Hz, and an energy density of 4.0 J/cm^2 was focused onto the sintered MnO_2-doped TB_5N_3 ceramic targets while they were being rotated in a vacuum chamber under an oxygen pressure of 200 mTorr. The film structure was examined using scanning electron microscopy (SEM: Hitachi S-4300, Japan), atomic force microscopy (AFM: JPK Nano Wizard, Germany), and X-ray diffraction (XRD: Rigaku D/max-RC). To measure the dielectric properties in the frequency range from 75.0 kHz to 1.0 MHz, Pt was deposited on the films using conventional DC sputtering to form the top electrode of the metal–insulator–metal (MIM) capacitor. The top electrode was patterned using a shadow mask to form a 300 μm-diameter disk. The capacitance and the dissipation factor were measured using a precision LCR meter (Agilent 4285A, USA). The leakage current was measured using a programmable electrometer (Keithley 617, USA).

3. Results and discussion

Fig. 1(a) shows a cross-sectional SEM image of the 15.0 mol% Mn-doped TB_5N_3 film grown by PLD at 300 °C under a beam energy density of 4.0 J/cm^2. The 84 nm thick film was well formed, and the interface between the film and the Pt substrate was very continuous and sharp. The AES depth profile of this film is illustrated in Fig. 1(b). No diffusion of Pt ions into the film or of Bi or Nb ions into the bottom Pt electrode was detected, indicating a chemically sharp interface between the film and the Pt substrate. These results confirm that even though MnO_2 was added into the TB_5N_3 film, this film was well developed with a chemically homogeneous and physically sharp interface between the film and the Pt electrode.

The leakage current densities of the x mol% Mn-doped TB_5N_3 films with $0.0 \le x \le 20.0$ mol% are illustrated in Fig. 2a. The leakage current density of the TB_5N_3 film was a relatively high 1.5×10^{-7} A/cm^2 at 0.15 MV/cm, and breakdown occurred at a low electric field of 0.2 MV/cm. The TB_5N_3 film is considered to contain intrinsic oxygen vacancies which were formed during the growing process of the film [11]. These intrinsic oxygen vacancies produce the free electrons in the TB_5N_3 film. Therefore, the large leakage current density observed in the TB_5N_3 film could be explained by the presence of these intrinsic oxygen vacancies. Furthermore, decreased numbers of intrinsic oxygen vacancies and free electrons are required to improve the electrical properties.

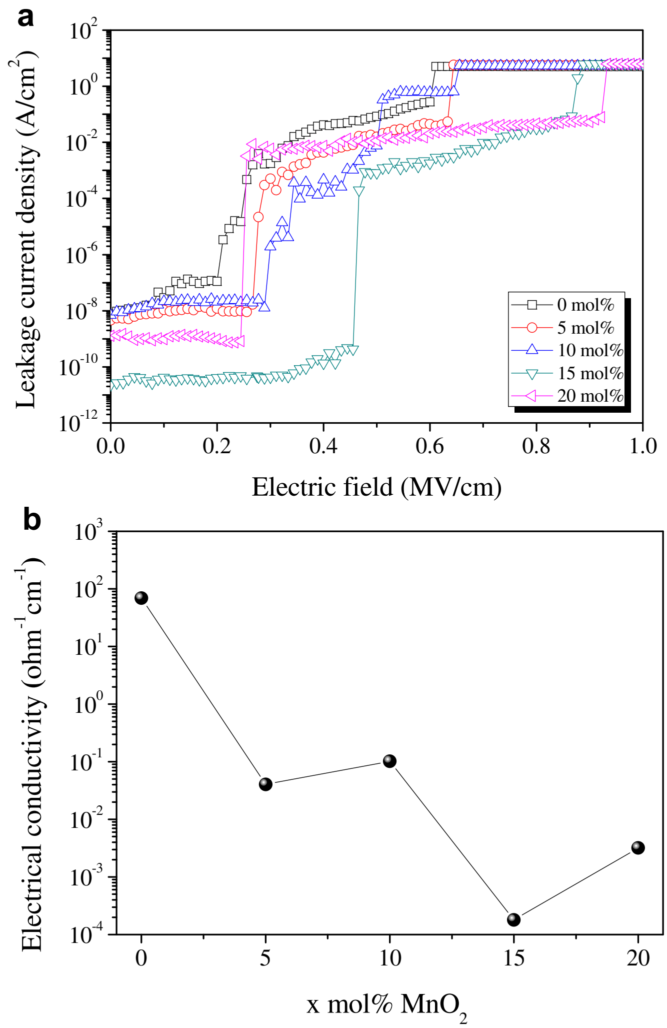

Fig. 2. (a) Leakage current densities and (b) variation of the conductivity measured at 0.23 MV/cm of the x mol% Mn-doped TB_5N_3 films with $0.0 \le x \le 20.0$ mol%.

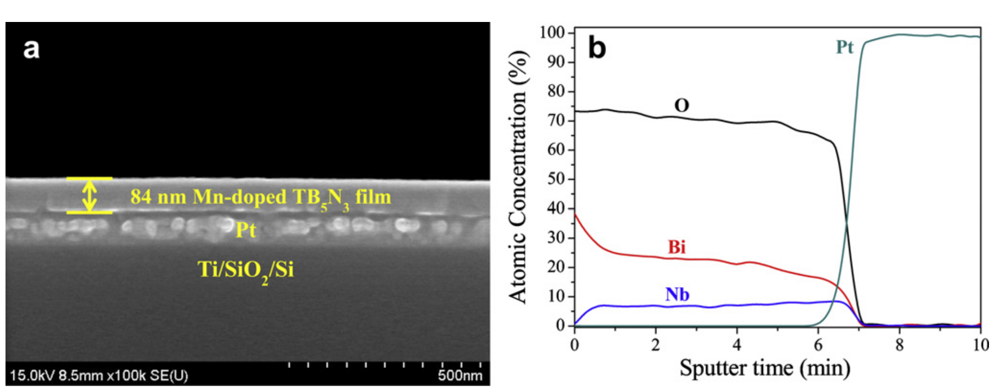

Fig. 1. (a) Cross-sectional SEM image and (b) AES depth profile of the 15.0 mol% Mn-doped TB_5N_3 film grown by PLD at 300 °C under a beam energy density of 4.0 J/cm^2.