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Leakage current mechanism and effect of oxygen vacancy on the leakage current of $Bi_5Nb_3O_{15}$ films

Kyung-Hoon Cho[a], Chang-Hak Choi[a], Joo-Young Choi[a], Tae-Geun Seong[a], Sahn Nahm[a,*], Chong-Yun Kang[b], Seok-Jin Yoon[b], Jong-Hee Kim[c]

[a] *Department of Materials Science and Engineering, Korea University, 1-5 Ka, Anam-Dong, Sungbuk-Ku, Seoul 136-701, Republic of Korea*
[b] *Thin Film Materials Research Center Korea Institute of Science and Technology, 39-1, Hawolgok-Dong, Sungbuk-Ku, Seoul 136-791, Republic of Korea*
[c] *Korea Institute of Ceramic Engineering and Technology, 233-5, Gasan-Dong, Guemcheon-Gu, Seoul 153-801, Republic of Korea*

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Abstract

The effect of oxygen partial pressure (OPP) on the leakage current density of $Bi_5Nb_3O_{15}$ (B_5N_3) films grown on Pt electrodes was investigated. The leakage current density was very high for the film grown under a low OPP of 1.7 mTorr, but was significantly reduced by the subsequent annealing under a high oxygen pressure or for the film grown under high OPP of 5.1 mTorr. The variation of the leakage current density with OPP was explained by the number of oxygen vacancies, which produced electron trap sites at the interface between the Pt electrode and the B_5N_3 film. Schottky emission was postulated as the leakage current mechanism of the B_5N_3 films. The barrier height between the Pt electrode and the B_5N_3 film grown under a high OPP of 5.1 mTorr was approximately 1.55 eV, but decreased to 0.81 eV for the film grown under a low OPP of 1.7 mTorr due to the presence of the oxygen vacancy.

Keywords: Films; Capacitors; $Bi_5Nb_3O_{15}$; Leakage current density

1. Introduction

Investigations on dielectric thin films with low growth temperatures (≤300 °C) have increased for the application to embedded decoupling capacitors for printed circuit boards.[1,2] The radio frequency (RF) or analog/mixed metal–insulator–metal (MIM) capacitors in semiconductor devices also require a dielectric thin film with a low processing temperature because of the limitation of the very large scale integration back-end line integration temperature (<400 °C). These capacitors needed a high capacitance density that can be obtained by using a dielectric film with a high dielectric constant (*k*) or by decreasing the film thickness. However, decreasing the film thickness induces a high leakage current with a low breakdown voltage. Therefore, it is important to develop a very thin dielectric film with a low processing temperature and a low leakage current density for application to embedded and RF MIM capacitors.

Recently, $Bi_5Nb_3O_{15}$ (B_5N_3) thin film has been investigated because this film was expected to have a high *k* value with a low growth temperature due to the low sintering temperature of the B_5N_3 ceramics (∼1100 °C), which showed a high *k* value of 200.[3–7] Moreover, the B_5N_3 thin film grown at 300 °C by RF magnetron sputtering showed a high *k* value of 70, confirming that B_5N_3 is a good candidate material for high *k* dielectric films with low processing temperatures.[3] In particular, the 27-nm thick B_5N_3 film showed a very high capacitance of 22.3 fF/μm^2 but suffered from a very high leakage current with a low breakdown field.[5] The leakage current density of this film was considerably improved by controlling the oxygen partial pressure (OPP) during the growth of the film.[5] However, the leakage current mechanism of the B_5N_3 film and the oxygen vacancy effect on the leakage current density have not been investigated systematically. In this work, therefore, the B_5N_3 films were grown on a $Pt/Ti/SiO_2/Si$ (1 0 0) substrate at 300 °C using RF sputtering and their leakage current mechanism was studied in detail. Moreover, the oxygen vacancy effect on the leakage current and the variation of barrier height between the Pt electrode and the B_5N_3 film were also investigated.

* Corresponding author. Tel.: +82 2 3290 3279; fax: +82 2 928 3584.
E-mail address: snahm@korea.ac.kr (S. Nahm).

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2. Experimental procedure

The B_5N_3 films with a thickness ranging from 19.6 to 70 nm were grown on a Pt/Ti/SiO_2/Si (1 0 0) substrate by RF magnetron sputtering using a 3-in. diameter B_5N_3 target, which was synthesized using the conventional solid state method. Deposition was carried out at 300 °C in a mixed oxygen and argon atmosphere with a total pressure of 8.5 mTorr and a sputtering power of 100 W. The oxygen to argon ratio (O_2/Ar) was varied from 20/80 to 70/30 to investigate the effect of OPP on the electrical properties while the total pressure was maintained at 8.5 mTorr. The microstructure of the films was examined by scanning electron microscopy (SEM: Hitachi S-4300, Japan) and atomic force microscopy (AFM: JSPM-5200, JEOL Ltd., Japan). The pseudo-dielectric function spectra were measured at room temperature using a spectroscopic ellipsometer (J.A. Woollam VASE, USA) and the refractive index of the B_5N_3 films was obtained by multilayer analysis. To measure the dielectric properties, Pt was deposited on the B_5N_3 film using conventional DC sputtering to form the top electrode of the MIM capacitor, which was patterned using a shadow mask to form a 380-μm diameter disk. The leakage current density was measured using a programmable electrometer (Keithley 617, USA).

3. Results and discussion

Fig. 1(a) shows a cross-sectional SEM image of the B_5N_3 film grown at 300 °C under an OPP of 5.1 mTorr. A 70-nm thick B_5N_3 film was well developed with a sharp interface between it and the Pt electrode. An AFM image of the surface of this B_5N_3 film is also shown in Fig. 1(b). The average roughness of this film was approximately 0.14 nm, demonstrating the very smooth surface of the B_5N_3 film. These results suggested that the 70-nm thick, homogeneous B_5N_3 film grown under an OPP of 5.1 mTorr was well developed on the Pt/Ti/SiO_2/Si substrate. Similar results were also observed for the B_5N_3 films grown at 300 °C under OPPs of 1.7–5.95 mTorr.

The leakage current density of the B_5N_3 film grown at 300 °C under the various OPPs is shown in Fig. 2(a). At 1.7 mTorr (O_2/Ar = 20/80), the leakage current density was very high but it considerably decreased with increasing OPP to 5.8×10^{-9} A/cm^2 at 1.0 MV/cm for the film grown under 5.1 mTorr (O_2/Ar = 60/40). Numerous oxygen vacancies were considered to exist in the B_5N_3 film grown under low OPP. Therefore, the high leakage current density of the B_5N_3 films grown under the low OPPs was explained by the presence of numerous oxygen vacancies, while the improvement in electrical properties of the B_5N_3 films with increasing OPP was due to the decreased number of oxygen vacancies. To confirm the oxy-

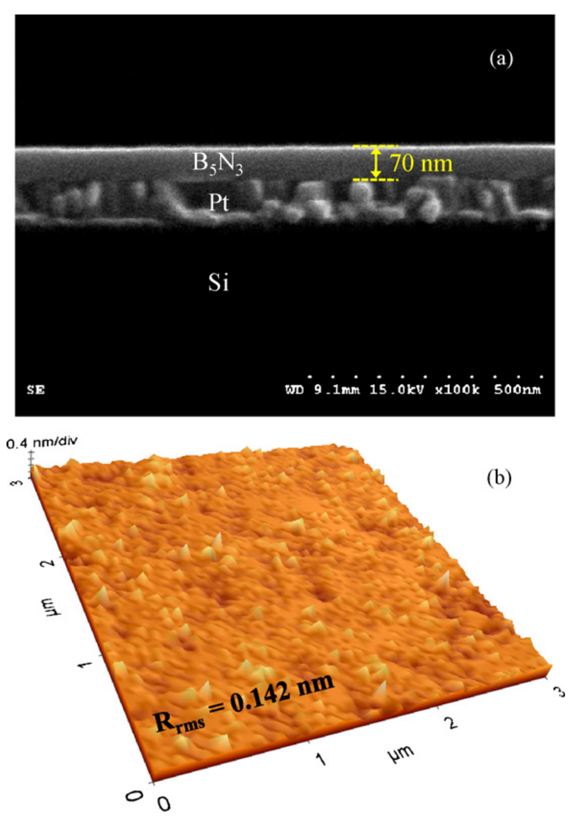

Fig. 1. (a) Cross-sectional SEM and (b) AFM images of the 70-nm thick B_5N_3 film grown at 300 °C.

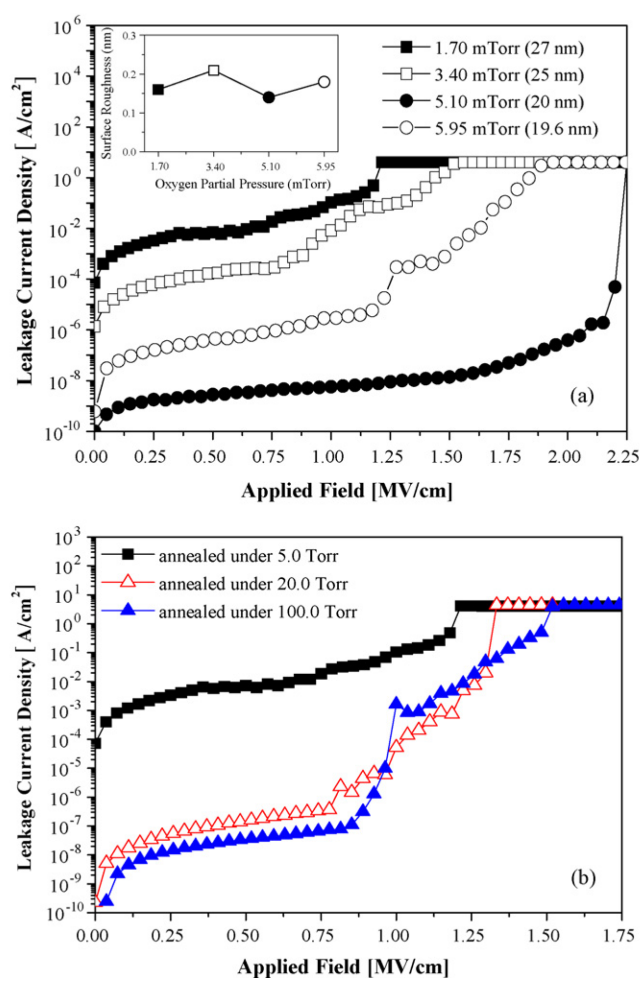

Fig. 2. Leakage current density of the B_5N_3 thin films grown at 300 °C under (a) various OPPs and (b) the OPP of 1.71 mTorr and rapidly thermally annealed at 300 °C for 5 min after metal deposition under various oxygen pressures. The inset of (a) shows the variation of the film surface roughness with OPPs.

gen vacancy effect on the electrical properties of the B_5N_3 film, the films were grown under a low OPP of 1.7 mTorr and subsequently annealed under different oxygen pressure, as shown in Fig. 2(b). The leakage current density of the B_5N_3 film annealed at a low oxygen pressure of 5 Torr was very high but it considerably decreased for the film annealed under a high oxygen pressure of 100 Torr, indicating that the presence of the oxygen vacancy considerably influenced the leakage current density of the film. The oxygen vacancies were also expected to exist in the $Bi_{4-x}La_xTiO_3$ films and they were used to explain the fatigue property of the films.[8,9] In addition, all the films had a very smooth surface and the variation of the surface roughness with OPPs was negligible, ranging between 0.21 and 0.14 nm, as shown in the inset of Fig. 2(a). Therefore, we considered the effect of the surface roughness on the leakage current density to be negligible. In order to clarify the oxygen vacancy effect on the electrical properties of the B_5N_3 films in detail, their leakage current mechanism and the variation of the energy barrier height between the Pt electrode and the B_5N_3 films were investigated.

There are two leakage current mechanisms for a dielectric thin film in a high field: Schottky emission and Poole-Frenkel emission.[10,11] Tunneling is also possible but only in insulating films with a thickness less than 10 nm.[10] Since the B_5N_3 films investigated in this work were thicker than 10 nm, tunneling cannot have been the leakage current mechanism for the B_5N_3 films. A plot of $\ln(J/T^2)$ vs. $E^{1/2}$ produces a straight line for Schottky emission, where J is the current density, T the temperature and E the electric field. Moreover, the dielectric constant in the optical range of frequencies (K_o) was calculated from the slope of this line.[10,11] If this calculated K_o is the same as n^2, where n is the refractive index of the material, the leakage current mechanism is Schottky emission.[10,11] On the other hand, a plot of $\ln(J/E)$ vs. $E^{1/2}$ produces a straight line for Poole-Frenkel emission. If the value of K_o calculated from the slope of this line is the same as n^2, then the leakage current mechanism is a Poole-Frenkel emission.[10,11]

Fig. 3(a) and (b) shows the plots of $\ln(J/T^2)$ vs. $E^{1/2}$ and $\ln(J/E)$ vs. $E^{1/2}$, respectively, for B_5N_3 films grown at 300 °C under the OPPs of 1.7 and 5.1 mTorr. The calculated n values

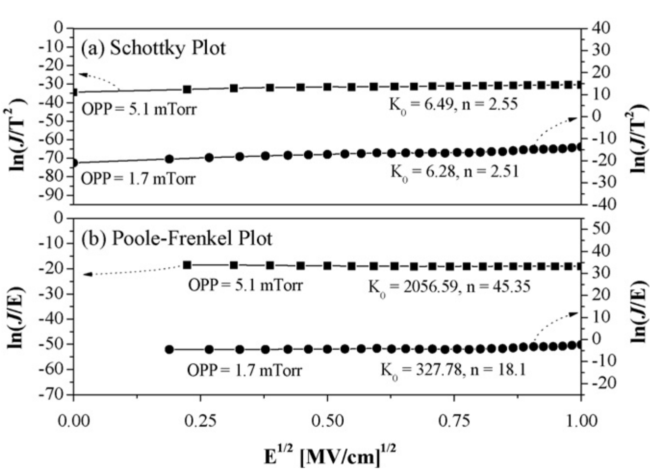

Fig. 3. Plots of (a) $\ln(J/T^2)$ vs. $E^{1/2}$ and (b) $\ln(J/E)$ vs. $E^{1/2}$ for the B_5N_3 films grown at 300 °C under the OPPs of 1.7 and 5.1 mTorr.

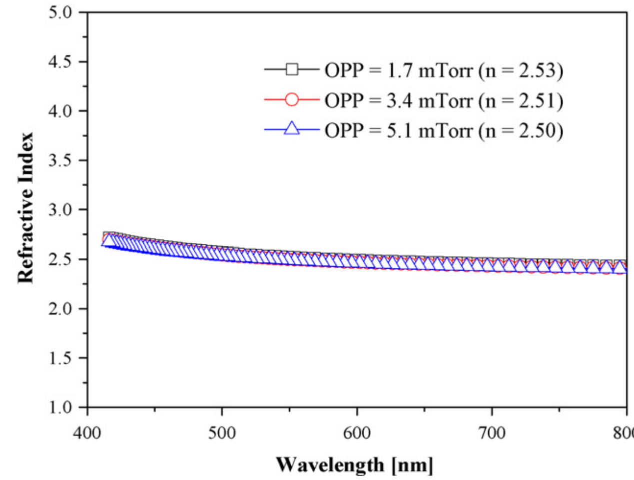

Fig. 4. Refractive index measured by an ellipsometer for the B_5N_3 films grown at 300 °C under various OPPs.

of the B_5N_3 films grown at OPPs of 1.7 and 5.1 mTorr obtained from the plots shown in Fig. 3(a) were 2.51 and 2.55, respectively. On the other hand, their n values obtained from Fig. 3(b) were 18.1 and 45.35, respectively. The refractive index of the B_5N_3 films grown at 300 °C under various OPPs was measured using an ellipsometer, as shown in Fig. 4, and it ranged between 2.50 and 2.53, indicating that the leakage current mechanism of the B_5N_3 film is the Schottky emission.

According to a previous work, the presence of oxygen vacancies in the dielectric film, in which the leakage current is produced by the Schottky emission, increased the leakage current because they acted as the electron trap sites at the interface and decreased the barrier height of the Schottky emission.[12,13] Therefore, it is considered that the oxygen vacancy effect on barrier height can be obtained by calculating the difference of the Schottky barrier height of the B_5N_3 films grown under low (1.7 mTorr) and high (5.1 mTorr) OPPs. The leakage current density (J) due to the Schottky emission is expressed by the following equation:

$$\ln(J) = \ln(AT^2) - \frac{\psi_o}{kT} + \frac{(\beta E)^{1/2}}{kT} \quad (1)$$

where A is the effective Richardson constant, T the temperature, ψ_o the Schottky barrier height, k the Boltzmann constant, E the electric field and β is $e^3/4\pi\varepsilon_o K_o$, in which ε_o is the dielectric constant in a vacuum and K_o the dielectric constant at the optical frequency.[10,11] A plot of $\ln(J)$ vs. $E^{1/2}$ produced a straight line, and its intercept at the y-axis, $\ln(J)$ axis, is $\ln(AT^2) - \psi_o/kT$. Therefore, if J is measured at various temperatures, ψ_o can be obtained from the plots of $\ln(J)$ vs. $E^{1/2}$.

Fig. 5(a) and (b) shows the $\ln(J)$ vs. $E^{1/2}$ plots of the B_5N_3 films grown at 300 °C under the OPPs of 1.7 and 5.1 mTorr, respectively, measured at different temperatures. According to the calculation, the Schottky barrier heights between the Pt electrode and the B_5N_3 film grown under a high OPP of 5.1 mTorr, which showed the lowest leakage current density, and under a low OPP of 1.7 mTorr were approximately 1.55 and 0.81 eV, respectively. This approximate 0.74 eV difference of Schottky

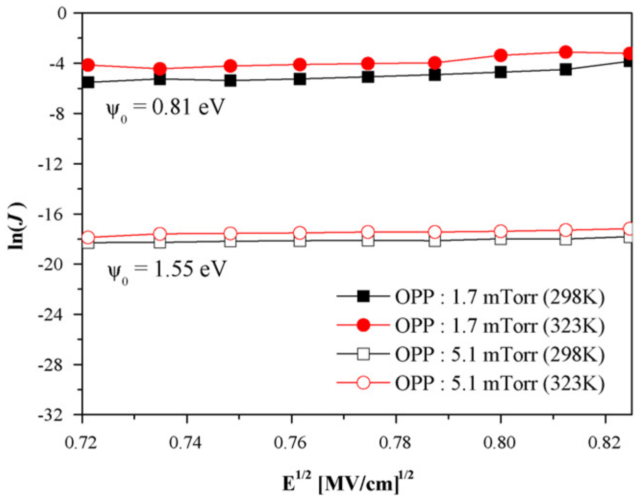

Fig. 5. Plots of ln(*J*) vs. $E^{1/2}$ measured at different temperatures for the B_5N_3 films grown at 300 °C under the OPPs of (a) 1.71 mTorr and (b) 5.1 mTorr.

barrier height indicated that the barrier height was decreased by 0.74 eV due to the presence of the oxygen vacancies.

The leakage current density was deteriorated when the OPP exceeded 5.1 mTorr. Very few oxygen vacancies were considered to exist in the film grown under a high OPP of 5.1 mTorr because of its good electrical properties. Furthermore, it was considered that the oxygen interstitial ions or metal vacancies started to be formed in the films when the OPP exceeded a certain critical value, presumed to be around 5.1 mTorr. Therefore, the degradation of the electrical properties of the B_5N_3 films grown under high OPPs of >5.1 mTorr was attributed to the formation of the oxygen interstitial ions or metal vacancies.

4. Conclusions

The B_5N_3 films grown at 300 °C under various OPPs were well formed on the Pt/Ti/SiO_2/Si substrate. The leakage current of the film grown under a low OPP of 1.7 mTorr was very high with a low breakdown field, due to the presence of numerous oxygen vacancies. However, the leakage current was considerably reduced for the films subsequently annealed under high oxygen pressure or grown under a high OPP of 5.1 mTorr, probably due to the decreased number of oxygen vacancies. The refractive index of the B_5N_3 film was approximately 2.5 and its leakage current mechanism was Schottky emission. The barrier height between the Pt electrode and the B_5N_3 film was 1.55 eV and it was decreased for the film grown under the low OPP, due to the formation of oxygen vacancies which produced trap sites at the interface and decreased the barrier height of the Schottky emission. The barrier height between the Pt electrode and the B_5N_3 film grown under a low OPP of 1.7 mTorr was approximately 0.81 eV.

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