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Characterization of Leakage Current Mechanisms for Aerosol-deposited $BaTiO_3$ Thin Films at Room Temperature

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$BaTiO_3$ thin films having different thickness of 0.2-2.2 μm were fabricated on flat Cu and stainless-steel (SUS) substrates by using aerosol deposition (AD) at room temperature. The dependence of the leakage current on the thickness of the $BaTiO_3$ thin films was measured, and the leakage current mechanisms were investigated to clarify the origins of the leakage currents. As a result of the measurements and examination, the leakage currents are highest for the thinnest $BaTiO_3$ films, and by decreasing the thickness of the films, the leakage current mechanism was changed from Poole-Frenkel emission to a modified-Schottky (M-S) emission. In particular, in the case of $BaTiO_3$ thin films with 0.2 μm-thick which is minimum thickness on SUS substrates, the dominant leakage current mechanism was M-S emission at low electric fields, the Fowler-Nordheim tunneling appeared as the primary leakage current mechanism at high electric fields due to electric-field concentration. Consequently, the origins of leakage current are suggested to be microscopic defects, such as oxygen vacancies, acting as donors in the $BaTiO_3$ films and the ununiform electric-field concentration at the rough interfaces between the $BaTiO_3$ films and the metal substrates at high electric fields.

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I. INTRODUCTION

Recently, embedded passive technology (EPT) has been actively studied to achieve miniaturization and high frequencies for electronic devices such as personal digital assistants and mobile phones and to reduce electromagnetic problems such as electromagnetic interfere (EMI) and simultaneous switching noise (SSN) resulting from parasitic inductance in wires [1,2]. In particular, embedded planar decoupling capacitors have received more attention than other passive components because ceramics with good electrical properties require high sintering temperatures over 1000 °C, which is an important problem in realizing the EPT. Also, if capacitors are to be used at higher frequency bands for wide applications, high capacitance density and Cu substrates are required [3].

If the above processing problem in the fabrication of the embedded decoupling capacitors is to be overcome, a new approach for a low temperature process is urgently needed. Thus, we focused on an aerosol deposition (AD), which has many advantages such as room temperature process, very high deposition rates and wide thickness ranges [4]. Also, for high capacitance density, a thin film process is needed. In other words, the thickness of the thin films should be controlled with utmost care to achieve the required capacitance. However, studies on dielectric thin films deposited by AD leave something to be desired because this deposition process was originally invented by Akedo for the growth of ceramic thick films [5].

Moreover, for applications of embedded decoupling capacitors in electric circuits, the leakage current is a critical issue in high-k (relative permittivity) dielectric films such as $BaTiO_3$, $(Ba_x, Sr_{1-x})TiO_3$ and HfO_2 because these films have smaller band gaps and shallower trap levels compared to the conventional SiO_2 or Si_3N_4 insulator films [6]. Thus, one of the key parameters that should be considered is the level of the leakage current. Accordingly, considerable progress has been made in understanding the leakage current mechanisms in dielectric films.

In previous research, we attempted to apply AD as a thin-film process to obtain a high capacitance density and low leakage current [7]. A comparison of the dielectric properties and the microstructures of $BaTiO_3$ thin films grown on Cu substrates having a critical thickness of 0.5 μm with those of $BaTiO_3$ thin films on stainless-steel (SUS) substrates having critical thickness of 0.2 μm suggested that the surface hardness of the substrates is one of solutions to fabricating thin film to obtain a high capacitance density of over 100 nF/cm^2 [7,8]. However, the level of the leakage current is higher than the required leakage current in $BaTiO_3$ thin films. It is therefore necessary to investigate leakage current mechanisms in the

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thin films must be investigated as a function of the film thickness to confirm the origins of the leakage current.

In this study, we investigated the thickness dependence of the leakage current mechanisms in $BaTiO_3$ thin films on Cu and SUS substrates to decrease the leakage current in thin films by clarifying the factors causing the leakage currents in films fabricated by using AD. Then, we examined the leakage currents mechanisms in $BaTiO_3$ thin films on Cu and SUS substrates by using the optical dielectric constant calculated from various equations of leakage current mechanism models, and we analyzed through the leakage current measured as a function of the temperature and the electric field.

II. EXPERIMENTS

AD is based on shock loading solidification due to the impact of ceramic particles. The details of the AD apparatus can be found elsewhere [4,5,7-10]. $BaTiO_3$ particles with an average diameter of 0.45 μm were used as starting powders. $BaTiO_3$ powders became a state of aerosol in the aerosol chamber by means of a vibration and mixing system; then, the aerosol was carried to the deposition chamber by He gas a flow rate of 3 L/min and was vaccelerated through a nozzle. Finally, the $BaTiO_3$ powders were continuously ejected through the nozzle and deposited onto the Cu substrates. The size of nozzle orifice was 10×0.4 mm^2, and deposited area was 5×10 mm^2. The distance between the substrate and the nozzle was 10 mm, and the working pressure was 40 Torr. The vibration speeds were 200 - 400 rpm, and deposition time were 1 - 20 min.

Under the above deposition conditions, $BaTiO_3$ thin films with thickness from 0.2 to 2.2 μm were fabricated on Cu and SUS substrates at room temperature by using AD. For the measurement of the leakage current of the films, Au upper electrodes of 330 μm in diameter were coated on $BaTiO_3$ thin films by sputtering using a shadow mask. The thickness dependence of the leakage current in $BaTiO_3$ thin films were measured at room temperature to obtain the optical dielectric constant for confirming the leakage current mechanisms associated with various thickness of film. Next, to measure the temperature dependence of the leakage current of the films, an electrometer, a high-resistance meter and a temperature controller were used. The measured temperature range was from 25 to 85 °C in step intervals of 20 °C. Finally, to confirm the leakage current mechanisms of $BaTiO_3$ thin films on Cu and SUS substrates from the measured leakage current data, the corresponding optical dielectric constants were obtained to compare with the experimental optical dielectric constants. In order to obtain the optical dielectric constant, we transferred the leakage current mechanism formulae into linear functions by using a natural logarithm functions. In these linear functions, the slopes have the optical dielectric constants as variables. Thus, the slopes of the curves of $\ln(J)$ and $\ln(J/E)$ as functions of $E^{1/2}$ were calculated by using the extrapolation method. After the slopes had been calculated, we could obtain the optical dielectric constant by using already known constants such as T the absolute temperature, q the electronic charge and ϵ_o the dielectric constant in vacuum.

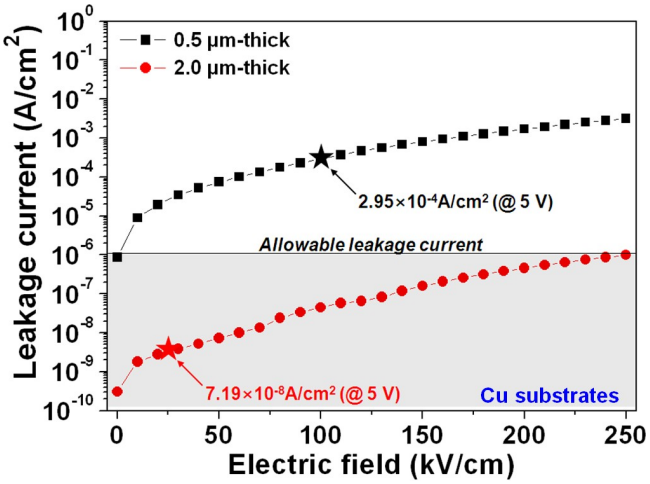

Fig. 1. Current density (J) vs applied electric field (E) measured for films having different thicknesses of 2.0 and 0.5 μm on Cu substrates.

III. RESULTS AND DISCUSSION

First, in order to examine the thickness dependence of the leakage current in $BaTiO_3$ thin films grown at room temperature by using AD, the $BaTiO_3$ thin films with different thicknesses of 2.0 and 0.5 μm were prepared on polished flat Cu substrates and measured their leakage current density. The leakage current density, J, is plotted versus the applied electrical field, E, for the $BaTiO_3$ samples as shown in Fig. 1. The leakage current density of $BaTiO_3$ films with 0.5 μm-thick is much higher than that with 2.0 μm-thick for all electric field region. In addition, at a voltage of 5 V, leakage current density was about 7.19×10^{-8} A/cm^2 for the 2.0 μm-thick $BaTiO_3$ samples and 2.95×10^{-4} A/cm^2 for the 0.5 μm-thick $BaTiO_3$ samples. Clearly, the leakage currents are highest for the thinnest $BaTiO_3$ films and lowest for the thickest films at the voltage. However, if the $BaTiO_3$ thin films with 0.5 μm-thick are to be used as decoupling capacitors, the leakage currents should be decreased down to 10^{-6} A/cm^2 even though the capacitance density of the films is enough for commercialization. So, in order to decrease the increased leakage current at 0.5 μm-thick which is the critical thickness, it is necessary to clarify the causes of the leakage currents by investigating the leakage current mechanism in aerosol-deposited $BaTiO_3$ films.

The optical dielectric constant K is a very important parameter that most previous research regarded as a criterion for the identification of the leakage current mechanisms in ceramic films where the optical dielectric constant is different from the static dielectric constant [11]. If during the emission process, the electron transit time from the interfaces between the metal electrodes and the ceramic films to the barrier maximum is shorter than the dielectric relaxation time, the ceramic medium does not have enough time to be polarized, and smaller dielectric constant than the static value is expected [12]. For $BaTiO_3$ thin films, the reasonable optical dielectric constant range has been reported to be 3 to 7 [13,14]. Based on this optical dielectric constant range, the corresponding optical dielectric constants at 25 °C of $BaTiO_3$ thin films for leakage current mechanisms such as Shottky emission (SE), Modified-Schottky emission (M-S) and Poole-Frenkel emission (PF) can be calculated using the following equations [15–17]:

$$J_{SE} = A^* T^2 \exp\left[\frac{-q(\Phi_B - \sqrt{qE/4\pi\varepsilon_O K})}{kT}\right], \quad (1)$$

$$J_{PF} = BE \exp\left[\frac{-q(\Phi_B - \sqrt{qE/\pi\varepsilon_O K})}{kT}\right], \quad (2)$$

$$J_{M\text{-}S} = \alpha T^{3/2} \mu E \left(\frac{m^*}{m_0}\right)^{3/2} \times \exp\left[\frac{-q(\Phi_B - \sqrt{qE/4\pi\varepsilon_O K})}{kT}\right], \quad (3)$$

where J is the current density, A^* the Richardson constant, B a constant, $\alpha = 3 \times 10^{-4}$ As/cm^{3}K$^{3/2}$, m_o free electron mass, m^* effective electron mass, T the absolute temperature, q the electronic charge, Φ_B the potential barrier at the metal/dielectric interface, μ electron mobility, E the electric field in the dielectric, ϵ_o the dielectric constant in vacuum, K the optical dielectric constant, and k the Boltzmann constant.

In the case of $BaTiO_3$ films with 2.0 μm and 0.5 μm-thick on Cu substrates, the linearized curves of ln(J) and ln(J/E) as functions of $E^{1/2}$ yield straight lines as shown in Fig. 2. The calculated optical dielectric constants were $K_{SE} = 0.66$, $K_{M\text{-}S} = 1.23$ and $K_{PF} = 4.92$ for 2.0 μm-thick $BaTiO_3$ samples, as shown in Figs. 2(a) and 2(b), and $K_{SE} = 1.39$, $K_{M\text{-}S} = 3.61$ and $K_{PF} = 14.09$ for 0.5 μm-thick $BaTiO_3$ samples, as shown in Figs. 3(c) and 3(d). From examinations of the corresponding optical dielectric constants, the leakage current mechanism of the $BaTiO_3$ films with 2.0 μm-thick was deduced to be PF, which is bulk limited because the optical dielectric constant of the films, which is $K_{PF} = 4.92$, is reasonable. By contrast, for $BaTiO_3$ films with 0.5 μm-thick, it was confirmed that dominant leakage current mechanism was M-S which is a combination (of interface and bulk) limited because $K_{M\text{-}S} = 3.61$ for 0.5 μm-thick $BaTiO_3$ samples is a reasonable optical dielectric constant. From these investigations of the optical dielectric constant, it

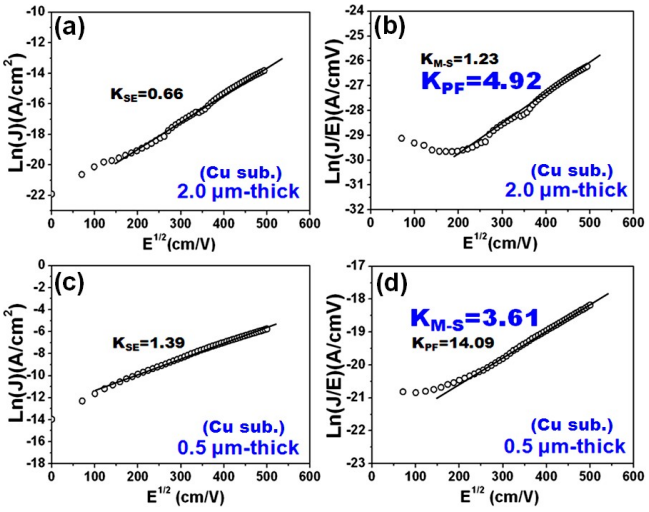

Fig. 2. Dependence of the current density Ln(J) on $E^{1/2}$ to be fit by Schottky emission for $BaTiO_3$ films with (a) 2.0 and (c) 0.5 μm-thick on Cu substrates and Ln(J/E) - $E^{1/2}$ curves to be fit by modified-Schottky emission and Poole-Frenkel emission for $BaTiO_3$ films with (b) 2.0 and (d) 0.5 μm-thick on Cu substrates. The optical dielectric constants of K_{SE}, K_{PF}, and $K_{M\text{-}S}$ calculated from the slopes are indicated.

was considered that the interfaces between $BaTiO_3$ thin films and Cu substrates strongly affect the leakage current transport for decreasing film thickness.

Besides, in order to confirm the Schottky barrier height of $BaTiO_3$ thin films with 0.5 μm-thick which is the critical thickness, showing the M-S mechanism and to confirm the influence of electric-field concentration at the very rough $BaTiO_3$/Cu interfaces having curvatures of approximately 0.1 $\sim$ 0.2 μm observed in previous research [6], we measured temperature dependence of leakage current at temperatures from 25 to 85 °C. As a result of the calculation of the Schottky barrier height from the logarithm of J/T^2 plotted as a function of reciprocal temperature, we obtained 0.41 eV for the value of the zero-voltage Schottky barrier Φ_B for 0.5 μm-thick Cu/$BaTiO_3$ interfaces. Then, the graphs were plotted as a Fowler-Nordheim tunneling (FN) plot of (Ln(J/E^2) vs. $1/E$) for $BaTiO_3$ films with 2.0 and 0.5 μm-thick on Cu substrates at various temperatures as shown in Fig. 3. If the FN mechanism is dominant at certain regions, the temperature independency and large electric field dependency due to pre-exponential term of following FN mechanism equation can be confirmed [18]:

$$J_{FN} = AE^2 \exp\left(\frac{B}{E}\right), \quad (4)$$

$$A = \frac{m_0}{m^*}\frac{q^3}{8\pi h\phi_B}, \quad (5)$$

$$B = \frac{8\pi}{3}\left(2\frac{m^*}{h^2}\right)^{1/2}\frac{\phi_B^{3/2}}{q}, \quad (6)$$

where h is Planck constant, B slope at high electric field,

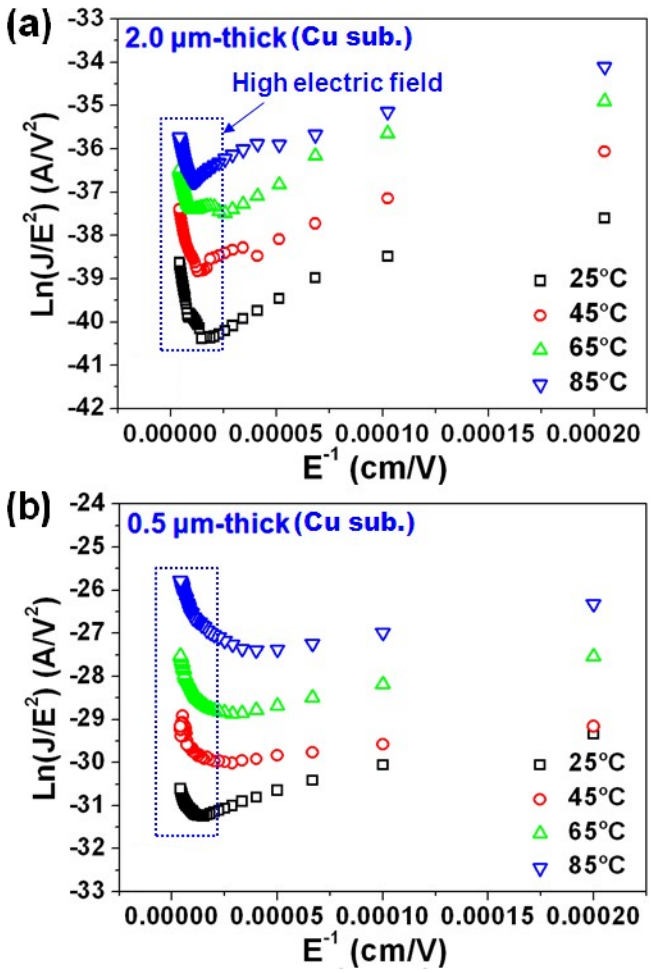

Fig. 3. (Color online) Ln(J/E) - E^{-1} graphs for $BaTiO_3$ films with (a) 2.0 μm-thick and (b) 0.5 μm-thick on Cu substrates at various temperatures from 25 to 85 °C.

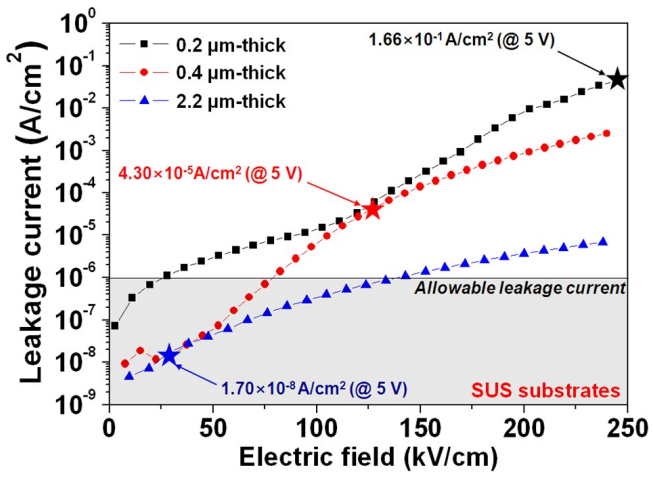

Fig. 4. (Color online) Current density (J) vs applied electric field (E) measured for films having different thicknesses of 2.2, 0.4, and 0.2 μm on SUS substrates.

m_o free electron mass, m^* effective electron mass, q the electronic charge, ϕ_B the potential barrier height at the metal/dielectric interface and E the electric field in the dielectric.

As a result of examination using the FN plot, the temperature dependency of the current density at high electric fields and a small electric field dependency was observed for all $BaTiO_3$ films; thus, FN was not dominant at high electric fields for $BaTiO_3$ films with 2.0 and 0.5 μm-thick on Cu substrates. From these results, we considered that the thickness of $BaTiO_3$ films with 2.0 and 0.5 μm-thick on Cu substrates is thick, which is enough to stand ununiform electric-field concentration at sharp tips of rough interfaces between $BaTiO_3$ films and Cu substrates. Therefore, the cause of leakage current in $BaTiO_3$ films is thought to be microscopic defects such as oxygen vacancies acting as donors creating shallower trap levels under the conduction band and forming a Schottky potential barrier.

Next, in order to confirm the influence of the above mentioned ununiform electric-field concentration in $BaTiO_3$ thin films with below 0.5 μm-thick, thickness dependence of leakage current mechanisms of $BaTiO_3$ thin films on SUS substrates were examined because in the case of $BaTiO_3$ thin films on SUS substrates, the thickness of the films can be decreased to 0.2 μm-thick due to the hard surfaces of the SUS substrates [6]. First, we measured the thickness dependence of the leakage current density of the $BaTiO_3$ thin films having difference thicknesses of 2.2 to 0.2 μm at 25 °C. The results of the measurements show that the leakage current density is clearly much higher for $BaTiO_3$ films of smaller thickness on Cu substrates and at below 0.4 μm, we could confirm increased leakage currents as shown in Fig. 4. Especially, a sudden increase was observed in the case of 0.2 μm-thick films at high electric fields.

To confirm the thickness dependence of the leakage current mechanisms in the films and origin of leakage current and highly increased leakage currents at $BaTiO_3$ films with 0.2 μm-thick on SUS substrates, we calculated the optical dielectric constants and we examined the calculated value to determine if they were reasonable.

As a result of the examination, in the case of $BaTiO_3$ films with 2.2 - 0.2 μm-thick on SUS substrates, the linearized curves of $\ln(J)$ and $\ln(J/E)$ as functions of $E^{1/2}$ yield straight lines, as shown in Fig. 5. From the linearized curves, the calculated optical dielectric constants of $BaTiO_3$ films with 2.2 μm-thick at the lines were K_{SE} = 0.52, $K_{M\text{-}S}$ = 1.12 and K_{PF}= 4.43 as shown in Figs. 5(a) and 5(b), indicating that the PF mechanism was dominant at all electric field region. In the case of the films with 0.2 μm-thick, on the other hand, there are three linear regions and the corresponding calculated optical dielectric constants were K_{SE} = 0.19, $K_{M\text{-}S}$ = 4.02 and K_{PF} = 12.15 at slope 1, K_{SE} = 0.08, $K_{M\text{-}S}$ = 0.09 and K_{PF} = 0.95 at slope 2 and K_{SE} = 0.83, $K_{M\text{-}S}$ = 0.24 and K_{PF} = 0.35 at slope 3 as shown in Figs. 5(c) and 5(d). Only slope 1 yielded a reasonable optical dielec-

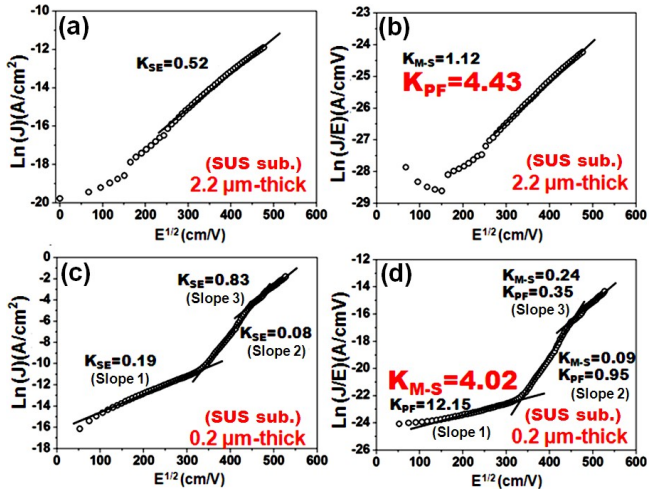

Fig. 5. Dependence of the current density Ln(J) on $E^{1/2}$ to be fit by Schottky emission for $BaTiO_3$ films with (a) 2.2 and (c) 0.2 μm-thick on SUS substrates and Ln(J/E) - $E^{1/2}$ curves to be fit by modified-Schottky emission and Poole-Frenkel emission for $BaTiO_3$ films with (b) 2.2 and (d) 0.2 μm-thick on SUS substrates. The optical dielectric constants of K_{SE}, K_{PF}, and $K_{M\text{-}S}$ calculated from the slopes are indicated.

tric constant, indicating that the M-S mechanism was dominant at low electric fields. From the fitting to the M-S mechanism by using Eq. (2.3) and measurement at various temperatures from 25 to 85 °C, we also obtained 0.37 eV for the value of the zero-voltage Schottky barrier Φ_B for SUS/$BaTiO_3$ interfaces for $BaTiO_3$ films with 0.2 μm-thick which is the critical thickness.

In addition, the graphs were plotted as a FN plots (Ln(J/E^2) vs. $1/E$), as shown in Fig. 6. In Fig. 6, a temperature dependency of the current density is observed at high electric fields in the case of $BaTiO_3$ films with 2.2 μm-thick. So, in the films with 2.2 μm-thick on SUS substrates, it was considered that the ununiform electric-field concentration is not an important factor. On the other hand, in the case of 0.2 μm-thick films, two regions can be distinguished more clearly, as shown in Fig. 6(b). At low electric fields, a temperature dependency of the current density was observed, but at higher electric fields the current density was almost temperature independent. When the applied DC field was larger than 1.15 V/μm (DC bias: ∼2.3 V), the current density increased significantly. Based on this FN data, it is reasonable to assume that the mechanism for electron injection changed from thermionic emission to tunneling in $BaTiO_3$ films with 0.2 μm-thick at high electric fields [19]. This can be explained by ununiform electric-field concentration at the rough interfaces between the $BaTiO_3$ films and the SUS substrates [20], which was also observed in our previous research although the roughness of the $BaTiO_3$/SUS interfaces were lower than those of $BaTiO_3$/Cu interfaces [5]. We also assumed that the M-S and PF mechanisms existed at the high electric fields, but the leakage currents

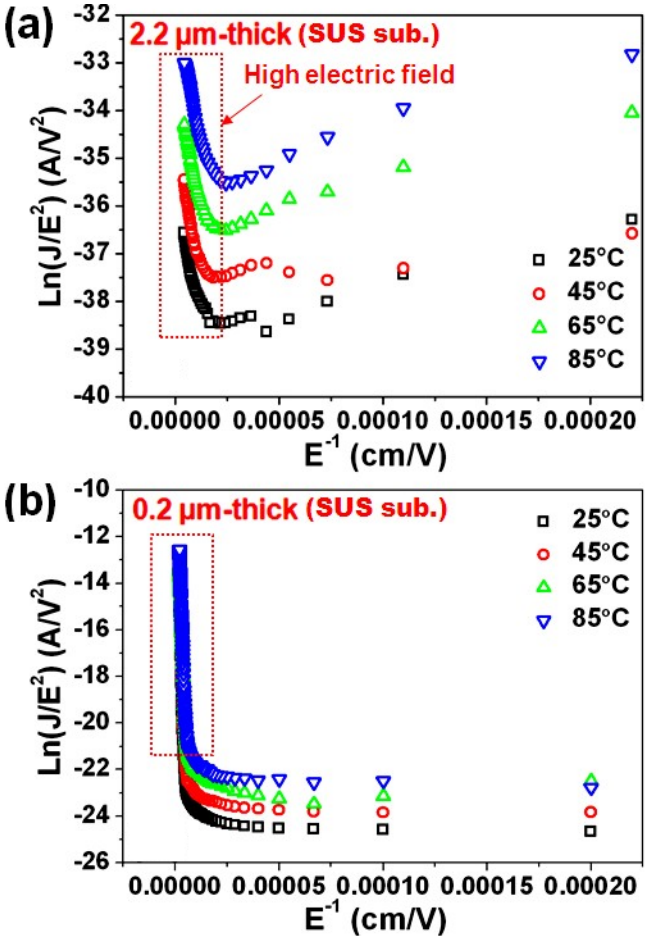

Fig. 6. (Color online) Ln(J/E^2) - E^{-1} graphs for $BaTiO_3$ films with (a) 2.2 μm-thick and (b) 0.2 μm-thick on SUS substrates at various temperatures from 25 to 85 °C.

based on the M-S and PF mechanisms were very small compare to those based on FN mechanism so that they did not contribute to the total leakage current. Consequently, in order to apply AD as a thin film process and fabricate embedded decoupling capacitors with high capacitance and low leakage currents, it is important to reduce interface roughness between films and substrates and decrease microscopic defects, such as oxygen vacancies acting as donors in the films creating shallower trap levels under the conduction band and forming Schottky potential barrier.

IV. CONCLUSION

To clarify the origins of the leakage currents by investigating the leakage current mechanisms in $BaTiO_3$ films for applying AD to a thin film process, $BaTiO_3$ thin films were fabricated on Cu and SUS substrates by using AD at room temperature in the thickness range from 0.2 to 2.2 μm, and we investigated the dependence of leakage

current mechanisms on the thickness of the $BaTiO_3$ thin films. As a result of the examinations, with decreasing thickness of the films, the mechanism changed from PF emission to M-S emission regardless of substrates. In particular, in the case of $BaTiO_3$ thin films with 0.2 μm-thick which is critical thickness on SUS substrates, the dominant leakage current mechanism was M-S emission at low electric fields, but the Fowler-Nordheim tunneling appeared as the primary leakage current mechanism at high electric fields due to the electric-field concentration. Consequently, the origins of the leakage currents are suggested to be microscopic defects, such as oxygen vacancies acting as donors in the $BaTiO_3$ films, and the ununiform electric-field concentration at sharp tips of rough interfaces between the $BaTiO_3$ films and the metal substrates at high electric fields.

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