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To understand electrical/dielectric phenomena and the origins of bistable resistive switching, impedance spectroscopy was applied to NiO thin films prepared through atomic layer deposition. The dc current-voltage characteristics of the NiO thin films were also determined. Frequency-dependent characterizations indicated that the switching and memory phenomena in NiO thin films did not originate from the non-Ohmic effect at the electrode/NiO interfaces but from the bulk-related responses, i.e., from an electrocomposite where highly conducting components are distributed in the insulating NiO matrix. Low dielectric constants and bias-independent capacitance appeared to corroborate the bulk-based responses in resistive switching in NiO thin films. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2392991]

High speeds and large amounts of digital data in global information and communication products have brought the continuous scaling down of the current dynamic random access memory, in which 1 bit is made up of one capacitor in series with one switching transistor. This requires a refreshing function that impedes high speed and low power consumption. With nonvolatile characteristics and a simplified device structure, resistive random access memories provide a simultaneous solution to the need for high speed, low power consumption, and high-density integration, as one of the next-generation nonvolatile memory candidates. Switching phenomena are found in transition metal oxides and perovskite oxides, e.g., in NiO,[1,2] TiO_2,[3] Nb_2O_5,[4] Cr-doped $SrZrO_3$,[5] $SrTiO_x$,[6] and $(PrCa)MnO_3$.[7] Various mechanisms have been proposed to explain the reversible switching between high and low resistance states, but detailed origins remain unsolved, i.e., Schottky barriers with trapped charges in the interface states,[8] space-charge-limited current,[9] phonon-assisted tunneling,[10] formation and rupture of filaments,[1,11] etc.

ac impedance spectroscopy is a highly powerful technique used to investigate electrical/dielectric properties in electroceramic materials, such as ferroelectric materials, ionic conductors, positive-temperature coefficient resistors, and voltage-dependent resistors.[12–14] Frequency-dependent impedance provides valuable information on the physical origins of electrical/dielectric properties, e.g., separation of bulk-based responses from electrode-related contributions, along with the simultaneous measurement of materials constants such as resistivity and dielectric constants. The estimation of arc depression is attributed to the spatial distribution of the microstructural components governing the corresponding electrical responses.

The resistive switching mechanism remains controversial over whether the memory characteristics originate from bulk-related effects or from electrode-related phenomena. Papagianni *et al.* claimed two bulk contributions and one interfacial effect, only from impedance spectra of $Pr_{0.7}Ca_{0.3}MnO_3$ with no detailed analysis on capacitance.[7] In our study, ac impedance spectroscopy was employed to determine the electrical/dielectric properties in NiO thin films and the possible origins of resistive switching, in addition to the dc current-voltage characterizations.

NiO thin films were deposited using atomic layer deposition (ALD) which used $Ni(dmamb)_2$ as a Ni precursor, where dmamb is described as 1-dimethylamino-2-methyl-2-butanolate ($–OCMeEtCH_2NMe_2$) and water as an oxygen source.[15] Two amorphous NiO thin films, 40 and 190 nm, were deposited onto commercial Pt-coated wafers (Inostek Inc., Ansan, Korea) at 140 °C. To perform ac impedance spectroscopy and determine dc current-voltage characteristics in a two-point configuration, top Pt electrodes of 100 nm thickness were sputtered into disk-shaped pads using metal shadow masks. Impedance characterizations were performed using a low-frequency impedance analyzer (Hewlett-Packard, 4192A, Palo Alto, CA): the oscillating amplitude was fixed at 25 mV and impedance spectra were collected between 1 MHz and 100 Hz in the logarithmic manner, ten points per decade. dc current-voltage measurements were made using a source-meter unit (Keithley 236, Cleveland, OH) in combination with the controlled compliance in the "current" mode.

Figure 1 displays the current-voltage characteristics in ALD-deposited NiO thin films. Despite the amorphous state of NiO thin films, resistance switching was noticeable and comparable to resistance switching in polycrystalline NiO thin films.[2] Under the compliance of 100 mA, the 190 nm NiO thin film was converted to the on state. The forming state was achieved within the NiO thin films at a voltage of 8.1 V, equivalent to 0.43 MV/cm, without causing catastrophic breakdown. In successive voltage sweeping modes, the current decreased abruptly near 1.0 V, shifting to the off state, leading to an abrupt increase of three orders of magnitude in resistance. Another voltage sweep caused the current

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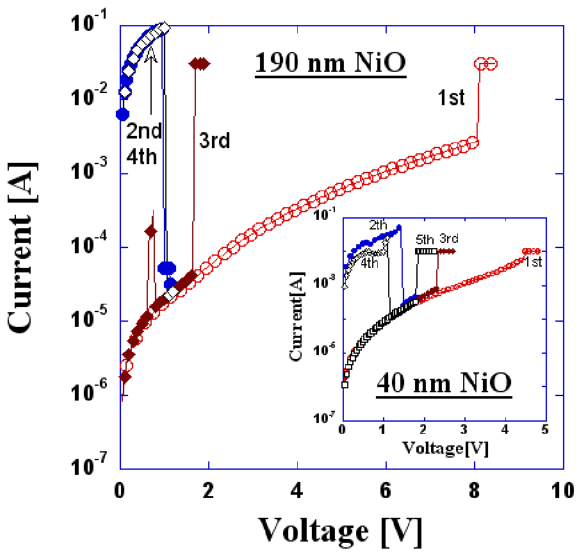

FIG. 1. (Color online) Current-voltage characteristics in the NiO thin films (40 and 190 nm) prepared through atomic layer deposition.

TABLE I. Summary of the equivalent circuit parameters obtained using impedance spectra of Figs. 2(a) and 2(b) at the on and off states.

Parameter	Value
R(lead)	4.43 Ω
L(lead)	3.54×10^{-6} H
R(on)	3.20 Ω
R(off)	5.49×10^{4} Ω
CPE(off)	7.75×10^{-10} F and $n=0.8206$

level to increase rapidly at approximately 1.7 V. The current-voltage responses and the corresponding "reset" and "set" voltages were reproducible even in amorphous NiO thin films. The results of Fig. 1 show that the derivation of voltage versus current, dV/dI, defined as dynamic resistance was not constant with respect to the applied voltage, implying that the current-voltage characteristics were not linearly correlated in the on or off states. However, the 40 nm NiO thin film exhibited higher off-state current, lower on-state current, and lower forming voltage than those of the 190 nm NiO film. The reset and set voltages approached those of the thicker NiO film after two consecutive sweeping.

Three electronic states, such as forming, off, and on were monitored using impedance spectroscopy, based on Fig. 1. In Fig. 2(a), the initial state before electrical forming and the off state exhibit impedance spectra of highly resistive materials, whose equivalent circuit can be described by the parallel connection of a resistor and a capacitor, or more precisely a constant phase element. The off state can simulate a parallel combination of a highly resistive component, R(off), and a constant phase element, CPE(off), as shown in Fig. 2(a). The on state induced very low impedance, as can be seen in Fig. 2(b). The equivalent circuit is modeled by a serial connection of two contributions from lead wires and NiO-based responses. The effect of lead wires is described by a serial connection of an inductor, i.e., L(lead), and a resistor, i.e., R(lead), and the NiO-related response can be explained by a parallel combination of three components from the on and off states, specifically R(on), R(off), and CPE(off). Through the equivalent circuit modeling, the presence of a highly conducting path, R(on), that formed across NiO thin films is believed to produce the Cole-Cole plot of Fig. 2(b). Detailed circuit parameters are summarized in Table I. Initial resistances with no bias voltage were in agreement with those of the low-frequency impedance in Figs. 2(a) and 2(b).

Corrected for the contribution of lead wires to the measuring apparatus, the apparent resistance was approximately 3.20 Ω, equivalently 131.9 Ω cm [see Fig. 2(b)]. However, it should be noted that the arc depression is not negligible with regard to the real impedance axis, as shown in Fig. 2(a) where the center of a simulated impedance arc is located below the real axis of a complex plane. Depression analysis in Nyquist plots ($-Z_{\mathrm{imaginary}}$ vs Z_{real}) provides information concerning homogeneity in the electrical/dielectric origins governing the corresponding impedance responses. The impedance information of Fig. 2(a) reflects an assemblage of a variety of time constants and leads to the hypothesis that the corresponding electrical components are distributed with regard to the average value. This feature appears to be due to the amorphous quality of the NiO thin films, i.e., possibly due to the lack in long-range order.

The impedance information can incorporate, if present, the contribution of non-Ohmic contacts between electrodes and NiO thin films. Seo *et al.* tested a variety of electrodes onto NiO thin films prepared through sputtering and found that platinum and gold form Ohmic contacts.[16] The relevant impedance data can eliminate spurious contributions originating from Schottky effects due to the high values in work

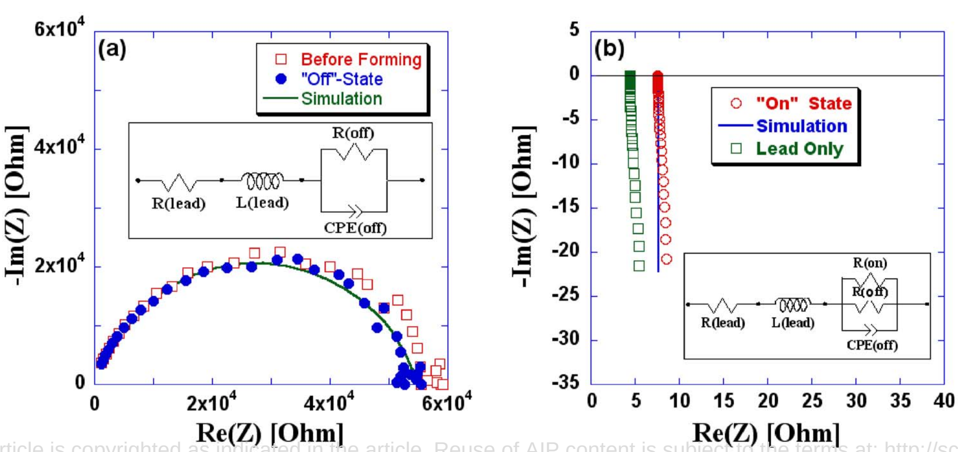

FIG. 2. (Color online) Impedance spectra at each step in the current-voltage characteristics (a) before forming and after forming (off state) and (b) after forming (on state) along with the lead contributions occurring in the measuring apparatus. (a) and (b) incorporate simulated impedance spectra and the corresponding equivalent circuit models for off and on states, respectively. (Thickness of NiO thin film: 190 nm).

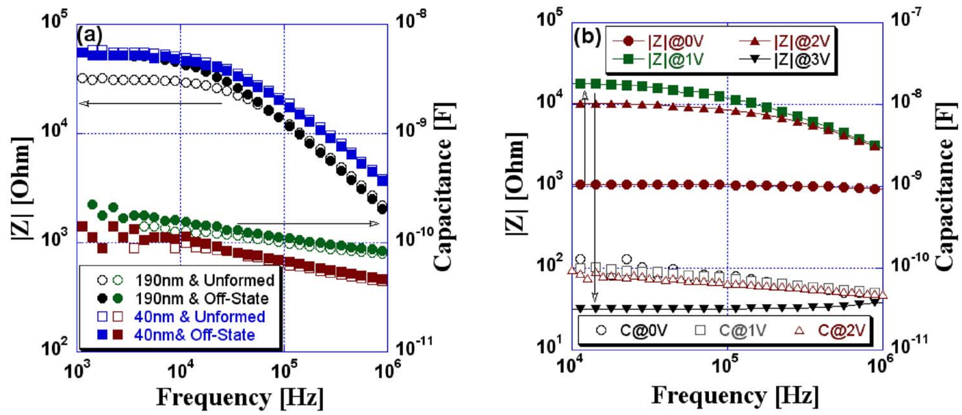

FIG. 3. (Color online) Bode plots of absolute impedance $|Z|$ and capacitance as a function of frequency: (a) thickness dependence (190 and 40 nm) and (b) bias dependence in NiO thin films between 0 and 3 V. (Thickness of NiO thin film: 190 nm).

functions. Therefore, the impedance spectra reflect the contributions of the bulk-related responses, but not from the interfacial contributions between NiO and the Pt electrode. Bode plots of absolute impedance and capacitance are shown as a function of frequency in Fig. 3(a) for two different thicknesses, 40 and 190 nm. The corresponding capacitances at 1 MHz were calculated to be 7.9×10^{-11} and 4.4×10^{-11} F. Corrected for the geometric factors, the effective dielectric constants for the 40 and 190 nm films were estimated to be approximately 8.86 and 11.51, respectively. The dielectric constant is quite close to the reported value of bulk NiO materials, i.e., 15: the switching behavior cannot be explained in terms of the interfacial responses originating from the Pt/NiO contacts, since the non-Ohmic effects lead to much higher capacitance, e.g., in the range of nanofarads.

The impedance information obtained during the off state was similar to that before forming. The two impedance spectra show almost identical capacitance as a function of frequency, indicating that both states have the same origin. The impedance of Fig. 2(b) suggests percolated interconnections of the highly conducting components between the two electrodes embedded into the pseudoinsulating NiO matrix. During the bias sweeping from 0 to 3 V, the impedance arc decreased in magnitude after a maximum at 1 V [see Fig. 3(b)]. The bias sweeping showed a gradual decrease in impedance unlike the rapid changes in the current-voltage characteristics. The low-frequency capacitance was independent of the applied bias. In the retention test, impedance at 100 Hz continued to retain the initial values without any significant changes up to 1000 s.

As shown in Fig. 1, the initial "electroforming" can generate highly defective components, such as vacancies, metallic clusters, phase separation, dislocations, etc., in the insulating NiO matrix, leading to the interconnected filaments between electrodes. In the on state, the resistance increases with the applied voltage, probably in combination with local Joule heating. Since NiO thin films are highly sensitive to applied voltage, more precisely to power as mentioned above, the Joule heating at local domains drives the defective states to the oxidized ones, isolated into NiO matrix. The formation and rupture of a conducting filament were used to explain the NiO thin films deposited by sputtering.[2,17] Taking into account the power dependence of resistive switching systems in transition metal oxides,[3] impedance spectroscopy is preferred because the uncontrolled dc probing technique involves unexpected prolonged power accumulation and can unpredictably modify the electronic state in switching devices.

In summary, the use of impedance spectroscopy allows for the separation of the bulk responses from the interfacial effects between the electrode and thin films. ac impedance measurements for ALD NiO thin films indicated several unique features: (i) low dielectric constant, (ii) bias-independent capacitance, and (iii) the capability of impedance to monitor data retention. The low dielectric constant and bias-independent capacitance indicate that the switching behavior in NiO thin films originates from the filament-controlled NiO matrix.

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