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Competition of Resistive-Switching Mechanisms in Nickel-Rich Nickel Oxide Thin Films

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Resistive-switching behaviors of Ni-rich nickel oxide thin films during the set and reset processes have been examined. In the switching from a low-resistance state (LRS) to a high-resistance state (HRS), a preferable reset voltage is observed. In addition, resistance fluctuations can be also observed in a successful or unsuccessful reset switching. These observations suggest that both the formation and deformation of conductive filaments could be involved and compete in the reset process. On the other hand, the switching from the HRS to the LRS in the set process is easier to occur with a higher pulse voltage, showing that the voltage promotes the formation of the filaments.
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Resistive switching in metal oxide or semiconductor oxide in a metal-insulator-metal (MIM) structure has attracted much research interest due to its possible application in nonvolatile memory.[1–12] Mechanisms including thermal effect,[1,2] trapping of charge carriers,[3,4] insulator-metal transition,[5,6] and model associated with ferroelectricity[7,8] have been proposed to interpret the phenomena. NiO thin film has been extensively reported as a promising material in resistive random access memory (RRAM) application.[9–12] Thermal effect is considered as the main mechanism in NiO film that let the resistive switching occurs.[11,12] Fuse-antifuse type is believed to be the reason to form and deform the filament. In the present work, Ni-rich NiO thin film is synthesized by radio-frequency (rf) magnetron sputtering to form MIM structure. Electrical pulses are used to set and reset the device. A preferable reset pulse voltage of 0.5 V is observed to be most sensitive in the reset switching from low-resistance to high-resistance, suggesting that both the formation and deformation of conductive filaments are involved and competing in the reset process.

A 200 nm SiO_2 thin film was thermally grown on p-type silicon substrate. A 10 nm Ti layer and a 200 nm Au layer were deposited on the SiO_2/Si substrate with electron-beam evaporation, subsequently. Polycrystalline NiO thin film with ~ 60 nm in thickness was then deposited onto the Au/Ti/SiO_2/Si substrate by rf magnetron sputtering of a NiO target ($> 99.99\%$ in purity) with Ar flow at 75 sccm. The rf power and frequency used in the sputtering were 250 W and 13.6 MHz, respectively. 120 nm Au/10 nm Ni layer was finally deposited onto the NiO film by electron-beam evaporation through a shadow mask to form the top electrodes with 200 μm in diameter. The chemical states of the synthesized NiO thin film were analyzed by a Kratos AXIS Ultra x-ray photoelectron spectroscopy (XPS) equipped with monochromatic Al $K\alpha$ (1486.71 eV) x-ray radiation (12 kV and 15 mA). As shown in Fig. 1a, the Ni 2*p* core level XPS spectra can be deconvoluted into two bands, i.e., Ni $2p_{1/2}$ and Ni $2p_{3/2}$ bands, respectively. There is a Ni^0 peak located at ~ 853.5 eV within the Ni $2p_{3/2}$ signal band, indicating that the as-deposited NiO thin film is Ni-rich. Electrical characterizations were carried out with a Keithley-4200 semiconductor characterization system. The compliance current was set to 0.01 and 0.1 A for set and reset process, respectively, in order to avoid hard breakdown.

Typical current-voltage (*I-V*) characteristics for the device are presented in Fig. 1b. By sweeping the voltage applied to the top electrode, a bistable resistive switching was observed. As the biasing voltage was increased to a level of ~ 1.4 V with a current compliance of 0.01 A (a smaller compliance current was used in the set process to avoid the hard breakdown in the oxide layer.), a sudden increase of current appeared (the current increased from $\sim 10^{-4}$ A to $\sim 10^{-2}$ A), i.e., the so-called "set" process occurred, without any prior forming process. In the set process the resistance was switched from a high-resistance state (HRS) to a low-resistance state (LRS), and then the sample maintained at the LRS. In the second voltage sweeping starting from 0 V with a current compliance of 0.1 A, the LRS was maintained until the voltage was increased to a value of

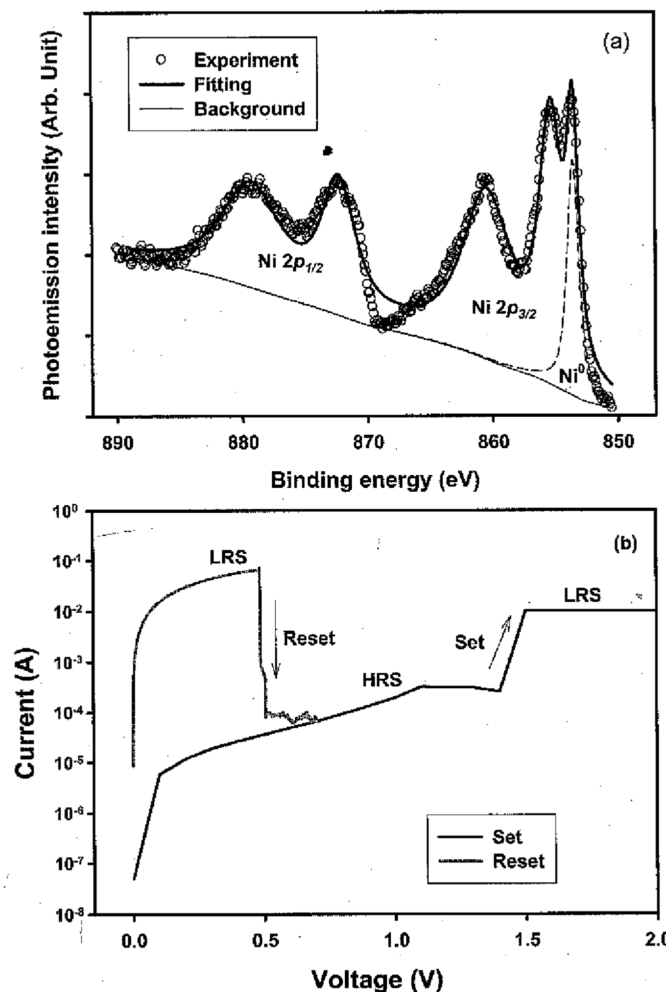

Figure 1. (Color online) (a) Ni 2*p* core levels of the Ni-rich NiO thin film; and (b) *I-V* characteristics measured with voltage sweeping.

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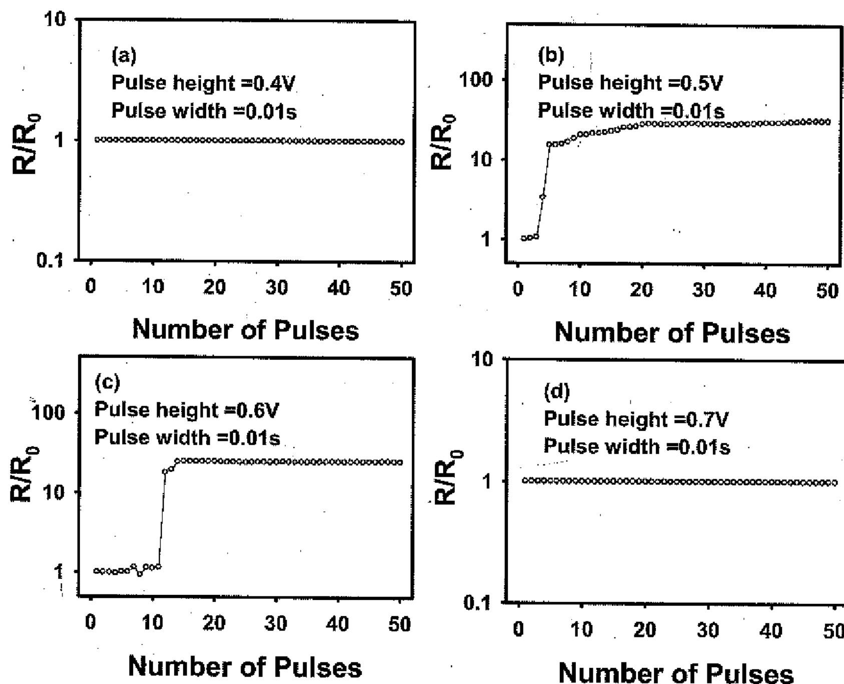

Figure 2. Change in the resistance of the device in reset process with number of pulses for different pulse voltages. The pulse width is fixed at 0.01 s. The device is set to LRS in advance.

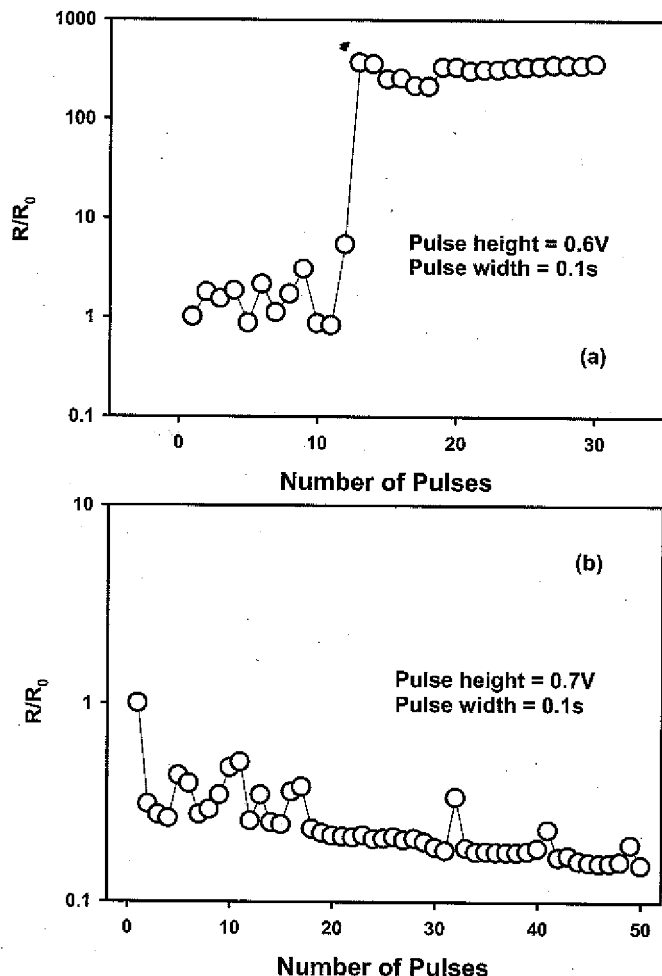

Figure 3. Resistance fluctuations in a successful reset switching (a) and an unsuccessful reset switching (b).

$\sim$0.5 V at which an abrupt decrease of current appeared. This process is known as the "reset" process and it is defined as the resistive transition from the LRS to the HRS. The reset and set processes were highly reproducible. The formation and deformation of conductive filament(s) are considered as the origin of the resistance switching in the NiO_x film. Thermal effect plays an important role in the formation and deformation of filament(s).[11,12] In the set process material in ruptured filament is modified by voltage-induced Joule heating, leading to formation of conductive filament. In the reset process, conductive filament is deformed thermally due to the high power density of the order of 10^{12} W cm^{-3} locally.[11,12] However, as discussed later, the results reported in this work indicate that both the formation and deformation processes occur simultaneously and compete with each other during the reset or set process.

For memory application, electrical pulses are used to set and reset the device for changing the memory states. Here a state transition is considered as occurring when the resistance is changed for at least one order. Continuous pulses with various voltages and a fixed pulse width of 0.01 s were applied on the device and the resistance of the device after each pulse was recorded. As shown in Fig. 2, the pulses with voltages of 0.4 V or below cannot reset the device from the LRS to the HRS. The device can be reset by 0.5 or 0.6 V. Five and 12 pulses were required to reset the device for the pulse voltages

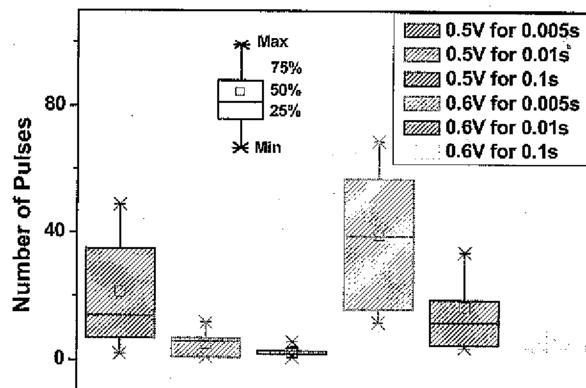

Figure 4. (Color online) Statistics of number of pulses required for state transition from the LRS to the HRS for different pulse voltages/pulse widths.

of 0.5 and 0.6 V, respectively. For the pulse voltage of 0.7 V, no switching could be observed even after 50 pulses. A preferable reset pulse voltage of 0.5 V is observed. For the voltage of 0.8 V or higher, the current compliance is approached for all the devices under test and thus no switching can be observed. The above result suggests that both the two mechanisms, i.e. the formation and deformation of conductive filaments are involved and competing in the reset process. If the pulse voltage is below 0.4 V, there is no sufficient energy to modify the material to form or deform the filaments. At 0.5 V, the conductive filaments deform thermally due to the locally generated high power density, and at the same time the voltage-induced Joule heating also modifies the material, causing reconnection of a ruptured filament. However, the deformation process is dominant, and thus after five pulses the device is switched from the LRS to the HRS. At 0.6 V, the deformation is also the dominant process, but the formation process is stronger than that at 0.5 V. This

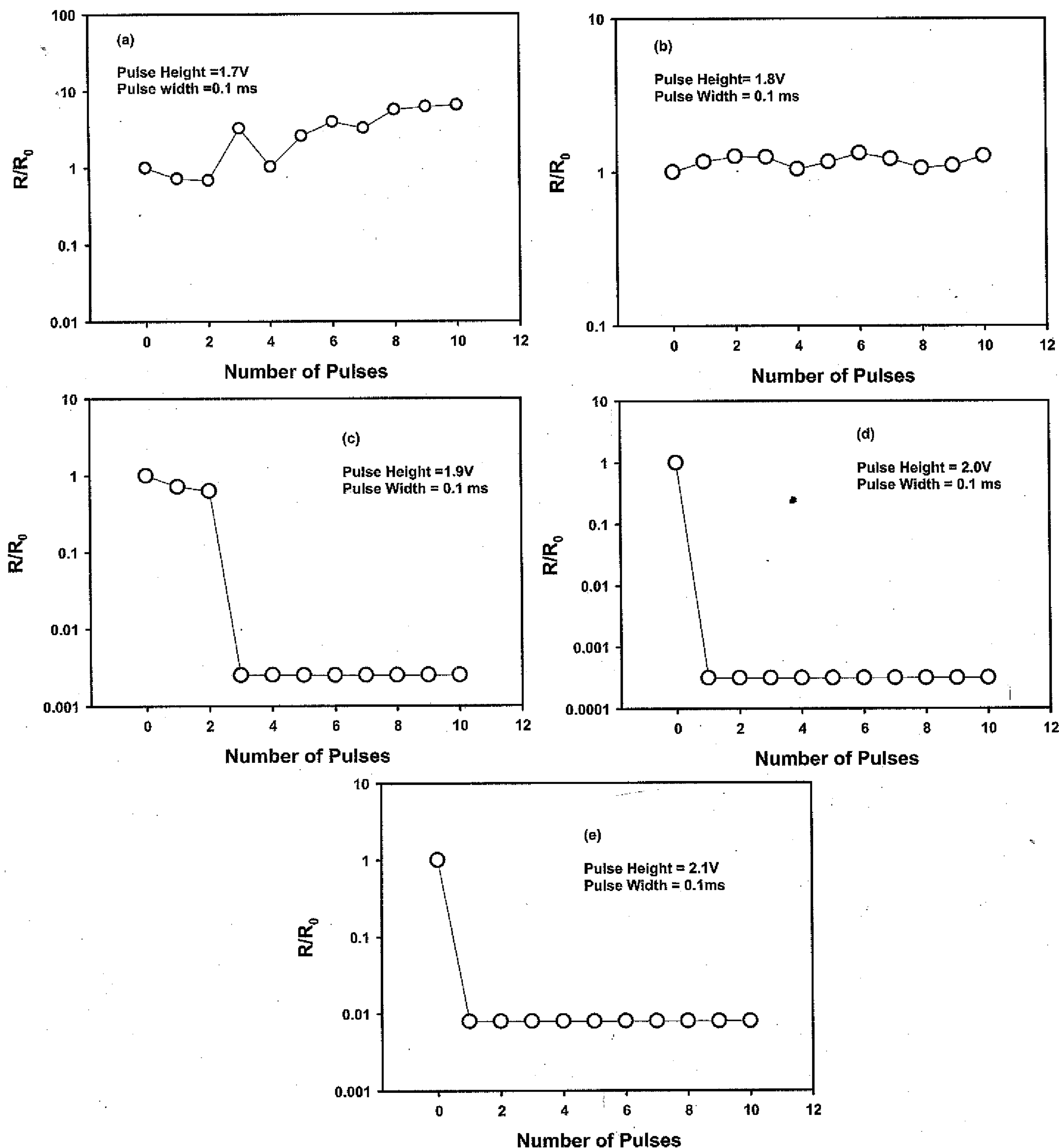

Figure 5. Change in the resistance of the device in set process with number of pulses for different pulse voltages. The pulse width is fixed at 0.1 ms. The device is set to the HRS in advance.

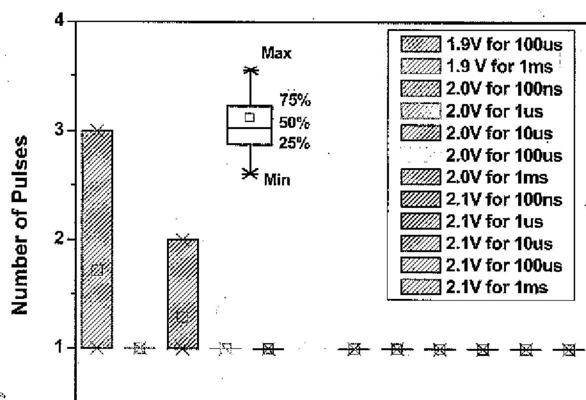

Figure 6. (Color online) Statistics of number of pulses required for state transition from the HRS to the LRS for different pulse voltages/pulse widths.

explains why more pulses are needed to make the state transition from the LRS to the HRS at 0.6 V than at 0.5 V. At 0.7 V, the formation and deformation of filament reach a balance and thus there is no state transition observed even after 50 pulses. It should be noted that in many cases for the non-switching situation, the resistance is actually not constant, i.e., the resistance can increase or decrease with the pulse number.

On the other hand, as shown in Figs. 2b and 2c, for both the pulse voltages of 0.5 and 0.6 V, the resistance may change with each voltage pulse before and after the reset switching. In some devices, we can observe a significant resistance fluctuation; one example is shown in Fig. 3a. Even in the case of an unsuccessful reset switching at 0.7 V, there are large resistance fluctuations, as shown in Fig. 3b. These results support the argument that both the formation and deformation of conductive filaments could be involved and compete in the reset process.

Figure 4 shows statistics of the number of pulses when state transition from the LRS to the HRS occurs for various pulse widths. Here the occurrence of state transition is defined as when the resistance is changed for one order or more. For each pulse voltage, at least eight devices at different locations on the wafer were measured. Pulse voltage of 0.4 V or below cannot lead to a state transition due to the insufficient thermal effect required to modify the material. At 0.5 and 0.6 V, state transition can be obtained. At 0.5 V, the device can be switched from the LRS to the HRS with a smaller number of pulses on average. However, at 0.6 V, a larger number of pulses on average are required to switch the device from the LRS to the HRS. This is attributed to the competition between the formation and deformation of filaments as above discussed. At 0.7 V, the two mechanisms reach balanced and thus no well-defined state transition can be observed even after 50 pulses. On the other hand, at a fixed pulse voltage such as 0.5 or 0.6 V, with pulse width increasing, the state transition is easier to occur.

A series of pulses with various voltages and a fixed pulse width of 0.01 s were applied to set the device from the HRS to the LRS and the resistance of the device after each pulse was recorded. As shown in Fig. 5, the pulses with voltages of 1.8 V or below cannot set the device from the HRS to the LRS. It should be noted that a set process can occur at 1.4 V or even below 1.4 V in continuous *I-V* sweeping. In the pulse experiment, a set process can be only observed at a higher pulse voltage such as 1.9 V or above. Above 1.9 V, with pulse voltage increasing, fewer pulses are needed to set the device. The result indicates that a pulse voltage of 1.9 V or higher is able to generate sufficient Joule heating to modify the material, causing the formation of conductive filament from ruptured filament during the set process.

Figure 6 shows statistics of the number of pulses when the state transition from the HRS to the LRS occurs for various pulse widths. For a fixed pulse voltage and width, seven devices at different locations on the wafer were measured. State transition does not occur at a pulse voltage of 1.8 V or below. For a fixed pulse width, a smaller number of pulses on average are needed for a higher pulse voltage to make the state transition. For example, for the pulse width of 100 μs, an average number of 1.75 pulses are needed to switch the device from the HRS to the LRS at 1.9 V, while only one pulse is used at 2.0 or 2.1 V. On the other hand, at a fixed pulse voltage, the state transition is easier to occur with a larger pulse width. At the voltage of 1.9 V and above, the formation of filament as a result of the voltage-induced Joule heating plays the dominant role. It is worth to mention that the interval between the pulses for the above experiment is set to 0.1 s. We have also examined different intervals such as 0.01, 0.1 and 1 s. It is found that more pulses are needed for a larger interval to realize the state transition due to the heat dissipation in between the pulses.

In conclusion, a preferable reset voltage is observed in the reset process, and resistance fluctuations can be also observed in a successful or unsuccessful reset switching. These observations suggest that both the formation and deformation of conductive filaments could be involved and compete in the reset process. In the set process, the device is easier to switch with a higher pulse voltage, indicating that a higher pulse voltage promotes the formation of filament.

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