Effect of Top Electrode Materials on the Nonvolatile Resistive Switching Characteristics of CCTO Films

Chun-Chieh Lin[1], Yi-Peng Chang[1], Chia-Cheng Ho[2], Yu-Shu Shen[3], and Bi-Shiou Chiou[3]

[1]Department of Electrical Engineering, National Dong Hwa University, Hualien 974, Taiwan
[2]R&D Department, Taiwan Semiconductor Manufacturing Company, Hsinchu 300, Taiwan
[3]Institute of Electronics, National Chiao Tung University, Hsinchu 300, Taiwan

A novel material $CaCu_3Ti_4O_{12}$ (CCTO) for resistive random access memory (RRAM) application was prepared by sol-gel spin-coating method. Our previous studies indicated that the CCTO possesses stable resistive switching behavior. In this work, the effects of the top electrode (TE) material on the resistive switching characteristics of CCTO films are investigated. It indicates the work function of the TE is an important factor on the resistive switching properties. Successive resistive switching was observed for electrode materials of Ni, Pd, and Pt. Furthermore, optimized consideration of the electrode material for RRAM is also studied.

***Index Terms*—Electrodes, nonvolatile memory, resistive random access memory, work function.**

I. Introduction

NEW technologies for making next-generation nonvolatile memory (NVM) have attracted extensive attention due to the conventional memory approaching its scaling limits. The requirements for the next-generation NVM include high speed, high-density integration, and low power consumption [1]–[6]. In recent years, more attention has been paid to the development of resistive random access memory (RRAM), which is one of the promising candidates for the next-generation NVM application due to its superior properties, such as reversible resistive switching, simple structure, small size, low power consumption, high operation speed, and low cost [7].

Recently, research efforts have been focused on the effects of the electrode materials on the resistive switching properties [8], [9]. These studies indicate that contacts between the electrode material and resistive film are related to the resistive switching behavior. In the case of the p-type oxide, electrode material with large work function causes an Ohmic contact or a low Schottky barrier to induce the resistive switching behavior. However, how to optimize the RRAM properties such as memory window, endurance, and currents for ON and OFF states has not been clarified extensively.

Our previous work on $CaCu_3Ti_4O_{12}$ (CCTO) deposited by sol-gel spin-coating method shows crystallinity and uniform microstructure [10]–[12]. The CCTO also has excellent resistive switching properties and a small degradation of current ratio between the ON and OFF states. In this work, electrode material dependence on resistive switching properties of the CCTO films are investigated, and optimized consideration for RRAM applications has also been explored.

II. Experimental Procedure

The precursor solution of the CCTO was prepared by dissolving the appropriate ratio of calcium and cupric acetates in acetic acid, and then a stoichiometric amount of titanium (IV) isopropoxide was added into the solution. In order to increase the solution stability, ethylene glycol was also added into the precursor solution. After that, the formamide was selected as an additive to adjust the solution viscosity to prevent from cracking of the CCTO films during drying and baking. The precursor solution was then heated at 100°C for 1.5 h to ensure a complete reaction [12].

Metal-resistor-metal structure with the top electrode (TE)/CCTO/Pt/Ti/SiO_2/Si was employed in this work. Initially, the boron-doped p-type (100) Si wafer was adopted as a substrate for device fabrication. After performing the standard Radio Corporation of America (RCA) cleaning process, a 100-nm-thick SiO_2 was grown on the Si substrate by oxidation furnace. 5-nm-thick Ti and 50-nm-thick Pt, serving as the adhesion layer and bottom electrode (BE), respectively, were continuously deposited on the SiO_2 by dc sputtering without breaking a vacuum. The CCTO film was deposited on the Pt/Ti/SiO_2/Si substrate by a two-stage spin-coating process. The first spin-coated layer was baked at 160°C for 20 min for drying the gel; then it was baked at 300°C for 20 min for removing the residual organic compounds. The sample was then annealed at 700°C for 5 min in atmosphere. The second CCTO layer was also deposited by spin-coating method on the first CCTO layer directly. The baking and annealing processes of the second CCTO layer were performed as those of the first one. Two layers of CCTO film were spin-coated sequentially in order to avoid through pin-holes [10]. Fig. 1(a) and (b) show the fabrication flow chart of the CCTO film by the sol-gel spin-coating method, and the schematic structure of the CCTO-based RRAM device, respectively. The total thickness of two CCTO layers was about 250 nm [12]. Finally, the TEs of Al, Cu, Ni, Pd, and Pt were deposited on the samples by dc sputtering at room temperature (RT) through a shadow mask. A semiconductor parameter analyzer (HP-4155B) was used to measure the current-voltage (I-V) characteristics of the CCTO-based RRAM devices. During the measurement, the bias voltage was applied on TE with grounded Pt BE. In addition, all the measurements were performed at RT.

III. Results and Discussion

Fig. 2 depicts the typical resistive switching I-V curves of the CCTO-based RRAM devices with various TEs, including Al, Cu, Ni, Pd, and Pt. Before the resistive switching is performed,

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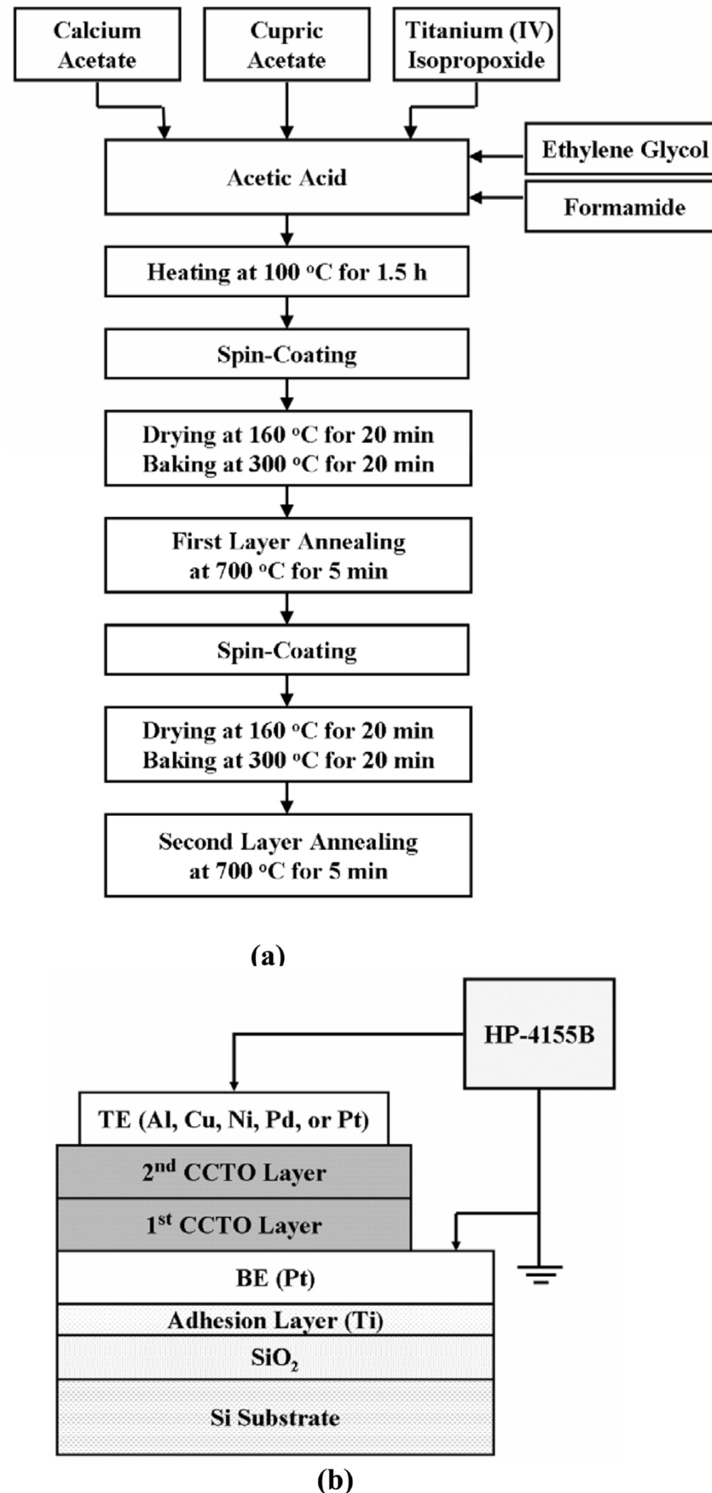

Fig. 1. (a) Fabrication flow chart of the CCTO film by the sol-gel spin-coating method. (b) The schematic structure of the CCTO-based RRAM device [12].

a forming process achieved by applying dc voltage is necessary. After the forming process, a high conductive state (ON state) is obtained, and then the device holds on the ON state. By applying the voltage bias to V_{RESET}, the device is switched from the ON state to an OFF state, called as turn-off process. Then, the device can keep at the OFF state until V_{SET} is applied on TE. The current abruptly increases, and the device is switched back to the ON state, called as turn-on process. A current compliance is set at 10 mA during the forming and turn-on processes to prevent the permanent damage on the CCTO film. However, no current compliance is used during the turn-off process; therefore, the ON state current (I_{ON}) could be over 10 mA. As shown in Fig. 2, two distinct resistance states, i.e., resistive switching, are observed in the TEs of Pt, Pd, and Ni, but no resistive switching is exhibited for the TEs of Cu and Al.

As the CCTO-based RRAM devices went through many resistive switching cycles, the memory window (current ratio between the ON and OFF states) indicates the endurance characteristics. In this work, the endurance of the CCTO-based RRAM devices is measured in terms of the number of resistive

TABLE I
RESISTIVE SWITCHING PROPERTIES OF THE CCTO-BASED RRAM DEVICES AND THE WORK FUNCTIONS OF VARIOUS TEs

TE	Resistive Switching	Ratio of the 1st Cycle (I_{ON} / I_{OFF} at 0.3 V)	Ratio of the 100th Cycle (I_{ON} / I_{OFF} at 0.3 V)	Work Function (eV) [15]
Al	X	N.A.[a]	N.A.[a]	4.2
Cu	X	N.A.[a]	N.A.[a]	4.5
Ni	O	51140	5193	4.7
Pd	O	1085	619	5.0
Pt	O	620	110	5.3

[a] No resistive switching for the TEs of Al and Cu.

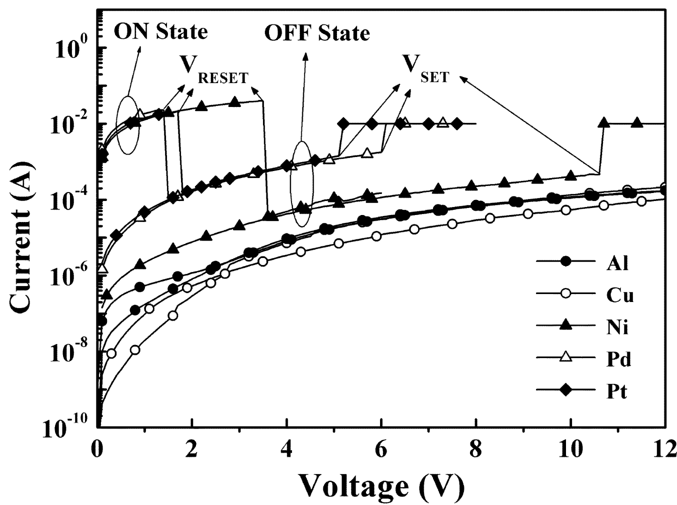

Fig. 2. Typical resistive switching I-V curves of the CCTO-based RRAM devices with various TEs.

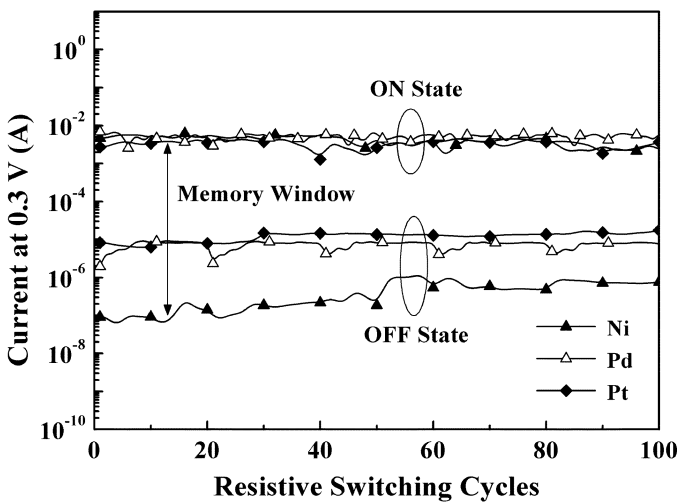

Fig. 3. The currents versus the resistive switching cycles of the CCTO-based RRAM devices. Difference between the I_{ON} and I_{OFF} is referred to as the memory window.

switching cycles, and the memory window is maintained above 10 times to avoid readout errors and noise effects [13]. Fig. 3 exhibits the currents at 0.3 V of both ON and OFF states. The specimens of TEs of Pt, Pd, and Ni are entirely reversible and reproducible during the successfully resistive switching cycles. The CCTO-based RRAM device with a TE of Ni shows the largest ratio between the I_{ON} and the OFF state current (I_{OFF}). The ratios of the CCTO-based RRAM device with the Ni TE at the 1st and 100th resistive switching cycles are 51140 and 5190, respectively. Table I summarizes the current ratios between the ON and OFF states for all specimens. All the CCTO-based RRAM devices show a large memory window, and the ratios between I_{ON} and I_{OFF} remain above 100 times, which is feasible to distinguish between the ON and OFF states to avoid the readout errors and noise effects. The drastic resistance change from the OFF state to the ON state is attributed, according to our previous report [12], to the establishment of the conductive paths. Many conductive paths are connected in parallel between the TE and BE in the ON state. I_{ON} is dependent on the amount of conductive paths between the TE and BE. Hence, similar I_{ON} is obtained for the specimens of TEs of Ni, Pd, and Pt, as shown in Fig. 3.

Fig. 4 shows the currents and current ratios between I_{ON} and I_{OFF} of the 1st switching cycle, while a read voltage of 0.3 V is applied. Regarding the specimens of TEs of Pt, Pd, and Ni, the currents at the OFF state are higher than the leakage current of TEs of Cu and Al. According to the Schottky contact model, the characteristics of the metal-semiconductor junction are determined by the metal work function and the Fermi level in the semiconductor. Joanni *et al.* indicated that CCTO thin films exhibit p-type semiconductor behavior [14]. Therefore, the junction made from TE with large work function contacting the CCTO film exhibits an Ohmic contact. The work functions of TE materials are also summarized in Table I. Pt, Pd, or Ni with larger work functions form an Ohmic contact or a low Schottky barrier with the CCTO film. Consequently, higher voltages across the CCTO film are required to induce enough current at the OFF state to establish the conductive paths. Then, the CCTO film can be switched from the OFF state to the ON state. For the specimen with TE of Al or Cu with the smaller work function, a high Schottky barrier is formed at the interface between the TE and the CCTO. The leakage current through CCTO film in this case is not enough to establish the conductive paths and to induce the resistive switching. Therefore, no resistive switching is observed in the specimen with TEs of Al and Cu. It is reasonable to conclude that the resistive switching

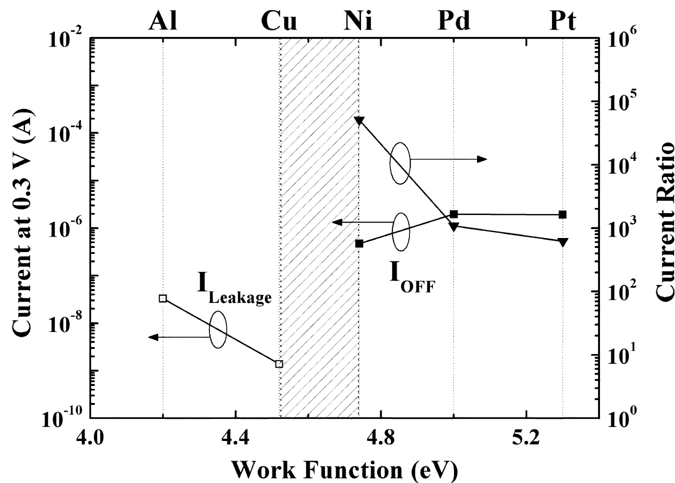

Fig. 4. The I_{OFF} and the ratio between I_{ON} and I_{OFF} at 0.3 V as a function of the work function of TE. No resistive switching is observed for the specimens of TEs of Al and Cu. Therefore, no current ratio is obtained, and the leakage currents are only indicated.

of the CCTO film is obtained only with the electrode material with larger work function.

However, even though the electrode with the larger work function induces the resistive switching in CCTO, it also causes a decrease in the current ratio and degrades the memory window between I_{ON} and I_{OFF} of the CCTO-based RRAM, as shown in Fig. 4. It leads us into further consideration of the optimum electrode work function. First of all, the work function plays a key role in determining I_{OFF}, and is also important to maximize the ratio between I_{ON} and I_{OFF}, i.e., the ratio must be appreciable to distinguish between the I_{ON} and I_{OFF} to avoid readout errors and noise effects. For the TE materials investigated in this study, Ni appears to be the optimized TE for the CCTO film. It provides the appropriate work function to achieve the resistive switching characteristics with about 51140 times memory window between the I_{ON} and I_{OFF}.

As mentioned above, the TE material with the larger work function can induce more current through the CCTO film and cause the resistive switching. Subjected to stability and compatibility requirements for TE materials, it is possible to conclude that to induce an enough current for the resistive switching behavior to occur, a TE with work function greater than 4.5 eV is needed. Thus, for copper with work function of 4.5 eV, no resistive switching was exhibited on the Cu/CCTO/Pt structured device. In addition, when the work function of TE material is smaller, lower I_{OFF} is also obtained. On the other hand, higher ratio between I_{ON} and I_{OFF} than that of the Ni/CCTO/Pt structured device is suggested, as the work function is smaller than 4.7 eV. Judged from the above, we suggest that a work function of the optimized TE material probably exists within the shaded area shown in Fig. 4.

IV. Conclusion

In summary, the effects of TE materials on the resistive switching characteristics of CCTO films are investigated in this work. It is found that the devices with Pt/CCTO/Pt, Pd/CCTO/Pt, and Ni/CCTO/Pt structures exhibit the resistive switching behavior. It is believed that the main reason is that low Schottky or Ohmic contact between the TE and CCTO film induces an effective voltage drop inside the CCTO film, and then leads to the formation of conductive paths. Among the TE materials of Pt, Pd, and Ni, the work function of Ni is the lowest one. Consequently, Ni/CCTO/Pt structured device exhibits the lowest I_{OFF}, and has the largest ratio between I_{ON} and I_{OFF}. Regarding the Ni/CCTO/Pt structured device, not only the resistive switching characteristics are obtained, but the excellent memory window is exhibited. Given that the stability and compatibility requirements for the CCTO process, the optimized work function of the TE material was also indicated. Finally, the points of optimized TE materials made in this study can also apply in principle to other RRAM materials.

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References

[1] M. Fujimoto, H. Koyama, S. Kobayashi, Y. Tamai, N. Awaya, Y. Nishi, and T. Suzuki, "Resistivity and resistive switching properties of $Pr_{0.7}Ca_{0.3}MnO_3$ thin films," *Appl. Phys. Lett.*, vol. 89, 2006, # 243504.

[2] C.-C. Lin, C.-Y. Lin, M.-H. Lin, C.-H. Lin, and T.-Y. Tseng, "Voltage-polarity-independent and high-speed resistive switching properties of V-doped $SrZrO_3$ thin films," *IEEE Trans. Electron Devices*, vol. 54, no. 12, pp. 3146–3151, Dec. 2007.

[3] C.-Y. Lin, C.-Y. Wu, C.-Y. Wu, and T.-Y. Tseng, "Modified resistive switching behavior of ZrO_2 memory films based on the interface layer formed by using Ti top electrode," *J. Appl. Phys.*, vol. 102, 2007, # 094101.

[4] C.-Y. Lin, S.-Y. Wang, D.-Y. Lee, and T.-Y. Tseng, "Electrical properties and fatigue behaviors of ZrO_2 resistive switching thin films," *J. Electrochem. Soc.*, vol. 155, no. 8, pp. H615–H619, 2008.

[5] W. Zhao, E. Belhaire, C. Chappert, and P. Mazoyer, "Power and area optimization for run-time reconfiguration system on programmable chip based on magnetic random access memory," *IEEE Trans. Magn.*, vol. 45, no. 2, pp. 776–780, Feb. 2009.

[6] W. Wang, "Magnetic random accessible memory based magnetic content addressable memory cell design," *IEEE Trans. Magn.*, vol. 46, no. 6, pp. 1967–1970, Jun. 2010.

[7] I. G. Baek, M. S. Lee, S. Seo, M. J. Lee, D. H. Seo, D.-S. Suh, J. C. Park, S. O. Park, H. S. Kim, I. K. Yoo, U.-I. Chung, and J. T. Moon, "Highly scalable non-volatile resistive memory using simple binary oxide driven by asymmetric unipolar voltage pulses," in *IEDM Tech. Dig.*, 2004, pp. 587–590.

[8] W.-Y. Yang and S.-W. Rhee, "Effect of electrode material on the resistance switching of Cu_2O film," *Appl. Phys. Lett.*, vol. 91, 2007, # 232907.

[9] W.-G. Kim and S.-W. Rhee, "Effect of the top electrode material on the resistive switching of TiO_2 thin film," *Microelectron. Eng.*, vol. 87, pp. 98–103, 2010.

[10] L.-C. Chang, D.-Y. Lee, C.-C. Ho, and B.-S. Chiou, "Thickness-dependent microstructures and electrical properties of $CaCu_3Ti_4O_{12}$ films derived from sol-gel process," *Thin Solid Films*, vol. 516, pp. 454–459, 2007.

[11] Y.-S. Shen, B.-S. Chiou, and C.-C. Ho, "Effect of annealing temperature on the resistance switching behavior of $CaCu_3Ti_4O_{12}$," *Thin Solid Films*, vol. 517, pp. 1209–1213, 2008.

[12] Y.-S. Shen, C.-C. Ho, and B.-S. Chiou, "Impedance spectroscopy of $CaCu_3Ti_4O_{12}$ films showing resistive switching," *J. Electrochem. Soc.*, vol. 156, no. 6, pp. H466–H470, 2009.

[13] K. P. Biju, X. Liu, E. M. Bourim, I. Kim, S. Jung, M. Siddik, J. Lee, and H. Hwang, "Asymmetric bipolar resistive switching in solution-processed $Pt/TiO_2/W$ devices," *J. Phys. D-Appl. Phys.*, vol. 43, 2010, # 495104.

[14] E. Joanni, R. Savu, P. R. Bueno, E. Longo, and J. A. Varela, "P-type semiconductor gas sensing behavior of nanoporous rf sputtered $CaCu_3Ti_4O_{12}$ thin films," *Appl. Phys. Lett.*, vol. 92, 2008, # 132110.

[15] B. Pellegrini, "Properties of silicon-metal contacts versus metal work-function silicon impurity concentration and bias voltage," *J. Phys. D-Appl. Phys.*, vol. 9, pp. 55–68, 1976.