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Characterization of Hybrid Copper/Oxygen Vacancy Nanofilaments

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Evidence for existence of hybrid Cu/oxygen vacancy (V_O) nanofilaments is presented. The composite conductive nanofilment (CF) is a serial connection of Cu and V_O CFs forming a hybrid V_O/Cu CF where the Cu filament segment is formed first and Vo filament segment completes the hybrid CF. A hybrid CF can be formed also in reverse order Cu/V_O displaying different properties than V_O/Cu CF. The hybrid CF displays V_{form} at considerable lower voltage than a monolithic CF and V_{form} and V_{set} distributions are much tighter than the distributions of monolithic Cu and V_O CFs. The resistive Cu/Ta_2O_5/Pt devices have been fabricated in a crossbar array on a thermally oxidized Si wafer. Metal electrodes were deposited by e-beam evaporation and patterned by lift-off technology. The Ta_2O_5 thin film is deposited by atomic layer deposition. The thickness of Ta_2O_5 is 16nm.

We characterize V_{form} of V_O CF in two different circumstances. In each case, a fresh (unstressed) cell is being used. Here, Pt electrode is grounded and the bias is applied to the Cu electrode. In the first case of characterization, a negative voltage sweep begins at 0; at $V_{form}(V_O\text{-}1)= -6.70$ V a forming operation is observed when the cell changes from high resistive state (HRS) to a low resistive state (LRS). Since under negative voltage the migration of Cu^+ ions is suppressed, the LRS is attributed to the formation of a Vo CF in agreement with [1]. Subsequent unipolar rupturing of the V_O CF at $V_{reset}(V_O)= -1.27$V. The temperature coefficient of the monolithic Vo CF is α(Vo-CF)=0.001K-1, i.e a very similar value measured for Vo CF in PVD TaO_x [1]. In the second case, another fresh cell is subjected first to a positive voltage sweep: at $V_{form}(Cu\text{-}1)=3.49$V the cell enters the LRS state when a Cu CF is formed. The Cu bridge is subsequently reset in a bipolar mode at $V_{reset}(Cu)= -1.19$V. The temperature coefficient of the monolithic Cu CF is α(Cu-CF)=0.0025K-1. After the Cu CF has been ruptured, a new negative voltage sweep is applied to the cell and a set event in Fig.1(c) is observed at $V_{form}(V_O\text{-}2)= -2.64$V. Since transition from HRS to LRS state occurs on the negative voltage axis we identify it with the formation of the V_O-CF. One observes a significant voltage difference for Vo-CF of $\Delta V_{form}(V_O)= V_{form}(V_O\text{-}2)-V_{form}(V_O\text{-}1)=4.06$V. To have a broader statistics such operations have been repeated on many fresh cells and the resulting $V_{form}(V_O\text{-}1)$ and $V_{form}(V_O\text{-}2)$ distributions are shown in Fig.1. A clear separation of the two distributions of $V_{form}(V_O)$ of more than 2.3V is observed.

The observed discrepancy between the two forming voltages can be consistently explained with the model shown in Fig.2. In the 1st case (Fig.2(a)) V_O CF is being formed across the entire thickness of Ta_2O_5 dielectric at a rather high electric field of 4.2 10^6 V/cm. In the 2nd case (Fig.2(b)), when V_O CF is formed after the rupturing of the Cu bridge a pedestal of the Cu bridge remains intact in the Ta_2O_5. According to [2], the rupturing of Cu-CF leaves a major portion of the bridge remains intact. The rupturing creates a small gap in the CF near the Cu electrode interface. The Cu pedestal extends thus the voltage of the Pt electrode deep into the Ta_2O_5 dielectric, thus increasing the local electric field at the same applied voltage when compared with a device free of any Cu CF formation. Assuming that the V_O bridge formation occurs in both cases at about the same critical field, we can calculate the height of the partial Cu bridge to be at least 10 nm as indicated in Fig. 2(b) from the difference of forming voltages. From this calculation we can estimate the ruptured gap of Cu CF to be smaller than 6nm.

Analogous experiment has been performed for the formation of Cu CF. In the 1st case a fresh sample was subjected to positive voltage sweep showing $V_{form}(Cu\text{-}1)=3.49$V for Cu CF. In the 2nd case, a fresh sample has been subjected to a negative voltage sweep leading to V_O formation at $V_{form}(V_O)=-6.4$V leading to a difference of 2.70V between the two forming voltages. The respective distributions of the two forming voltages (Fig.1) are separated by at least 2.4V, giving evidence to hybrid Vo/Cu CF formation. In conclusion, the hybrid CF can occur in two manifestations Cu/V_O and V_O/Cu depending on which part of the hybrid bridge has been formed first. The first formed bridge when ruptured serves as a pedestal for the formation of the other part of the bridge. The two hybrid bridges have distinctly different temperature effective coefficients of resistance: $\alpha_{???}(V_O/Cu) \approx \alpha_{VO}=0.001K^{-1}$ and $\alpha_{???}(Cu/VO) \approx \alpha_{Cu}=0.0025K^{-1}$, where α_{eff} for 2 resistors in series is given by $\alpha_{eff}=(R_{Cu}(T_o)\alpha_{Cu}+R_{Vo}(T_o)\alpha_{Vo})/(R_{Cu}(T_o)+R_{Vo}(T_o))$ where R_{Cu} and R_{Vo} are the on-resistances of Cu and V_O CF segments, α_{Cu} and α_{Vo} are the temperature coefficients of resistance of the partial Cu and V_O CFs, respectively. The hybrid CFs display greatly reduced V_{form} and have analogous switching characteristics to monolithic CFs.

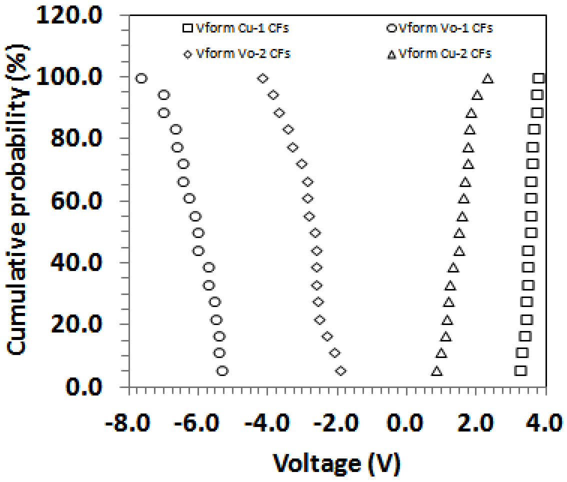

Fig.1 V_{form}(Cu-1), V_{form}(Cu-2), V_{form}(V_O-1), V_{form}(V_O-2) distributions of Cu/TaO_x/Pt devices.

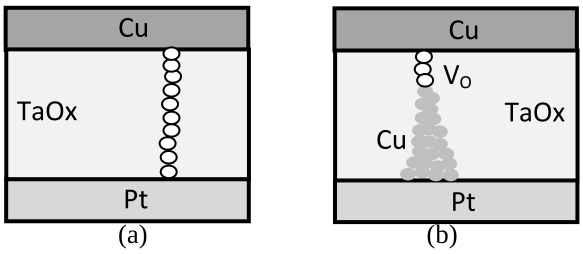

Fig.2 Coexistence of copper and oxygen vacancy conductive CFs in a Cu/TaO_x/Pt device. (a) monolithic Vo CF formed between the electrodes; (b) hybrid V_O/Cu CF comprising Cu-CF in series with Vo-CF.

References

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[2] U. Russo, D. Ielmini, D. Cagli, A.L. Lacaita, IEEE Trans. Electron Dev. 56, 193-200 (2009)