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A Possible Bipolar HfO_x Resistive Memory Device with Self-Rectification – Observations from STM Study

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Abstract – The conduction property of the filamentary path in the HfO_x dielectric subjected to different levels of forming hardness is examined by scanning tunneling microscopy (STM). An asymmetrical current conduction property is consistently revealed for the case of *intermediate* forming hardness. The current under reverse polarity is found to be much smaller than that under forward polarity (same polarity as forming), pointing to the formation of a rectifying filamentary path. Such a behavior is, however, not seen for cases of softer and harder forming. The reduced current under reverse polarity may be ascribed to space-charge limited conduction as opposed to Poole-Frenkel conduction under forward polarity, suggesting the role of different dielectric compositions near the two electrode interfaces. The finding points to the prospects of an extremely compact cross-point bipolar resistive memory with *built-in* rectification.

Introduction – The resistive memory device has attracted a lot of interest by virtue of its superior scalability[1,2] and the potential for ultra-high-density on-chip integration via the simple crossbar architecture. However, the fundamental problem of a crossbar memory array is the sneak-path current, which can severely compromise the integrity of data readout[3]. To overcome the problem, a typical approach would be to connect a selection device, e.g. diode or transistor in series with each memory element[4], at the expense of a lower integration density and greater processing complexity. In this paper, we show, via STM study, that the filamentary path in the HfOx dielectric could exhibit a highly asymmetrical conduction property when the forming hardness is appropriately controlled. The finding suggests possible exploitation for extremely compact cross-point bipolar resistive memory with built-in rectification.

Experimental Details – A 10-nm Ti layer was first sputter-deposited on a HF-last p-Si substrate at a temperature of 300 °C and a chamber pressure of 8.2×10^{-4} mbar. This was followed by sputter deposition of a 50-nm TiN (Ti:N ~1.1) layer as the bottom electrode. Subsequently, a 4-nm HfO_x layer was grown via atomic layer deposition at a temperature of 300 °C and a chamber pressure of 1.0×10^{-1} Torr. The device structure and the STM measurement setup are depicted in Fig. 1.

Results and Discussion – During forming, a voltage ramp was applied to the substrate until an abrupt jump in the current was observed (Fig. 1). The current through the filamentary path at the instant of forming was self-limited by the vacuum gap between the STM tip and the HfO_x surface. Three levels of forming-hardness (soft, intermediate, hard), as indicated by the varying degrees of lateral shift in the I-V curve towards smaller voltage values, were achieved by extending the voltage sweep to increasingly larger values after the abrupt current jump.

Fig. 2 shows the current-voltage (I-V) curves for the case of soft forming. An almost symmetrical I-V plot, i.e. nearly equal currents for both voltage polarities, is evident. A good fit to the Poole-Frenkel (PF) conduction model can be achieved for the I-V curve in the negative voltage regime, implying that electron hopping is the dominant conduction mechanism. The fit for the I-V curve in the positive voltage regime is, however, less satisfactory, especially at the low current region. The mismatch is due to the vacuum gap, which affects electronic transport at low voltages. When a positive bias voltage is applied to the substrate, electron injection occurs from the STM tip. When the voltage is small, the current is limited by tunneling through the vacuum gap, resulting in a lower current than that predicted by the PF model. The good fit achieved with the I-V curve measured by CAFM (for which no vacuum gap exists between the tip and HfO_x), supports the above explanation.

Interestingly, a highly asymmetrical I-V plot, with a much smaller current in the negative voltage regime, is obtained for the case of intermediate forming (Fig. 3). Unlike the soft forming case, the I-V curve in the negative voltage regime can no longer be fitted by the PF model. Instead, a good fit is obtained using the space-charge limited conduction (SCLC) model. On the other hand, the PF model can still fit the I-V curve in the positive voltage regime (except for the mismatch at low currents caused by the vacuum gap). Since electron injection occurs from the tip and from the bottom TiN electrode under positive and negative voltage biasing, respectively, the distinct conduction mechanisms as inferred from the I-V fitting imply that the nature of the HfO_x dielectric near two electrode interfaces are different. Such an asymmetrical I-V behavior is consistently observed regardless of the forming voltage polarity, provided the forming hardness is controlled at the intermediate level. Fig. 4 shows the results for negative forming. In this case, the positive current is much smaller than the negative current. A good fit to the SCLC model is now obtained for the I-V curve in the positive voltage regime. As for the negative voltage regime, the I-V curve can be fitted by the PF model. Fig. 5 shows the statistical distribution for the ratio between the positive and negative currents for the case of positive forming. The average ratio at 1.5 V is ~50. The decrease at lower voltages may be ascribed to the suppression of positive current by the influence of the vacuum gap. Consistent resistive switching with an average memory window of ~100 can be observed (Fig. 6). With a further increase of forming hardness, near-symmetrical I-V curves are again observed (Fig. 7).

A proposed explanation for the asymmetrical I-V behavior is illustrated in Fig. 8 for the positive forming case. When the applied electric field approaches the critical value for forming to occur, oxygen vacancy defects are rapidly formed in the HfO_x region underneath the STM tip, when the migration of oxygen ions towards the bottom TiN starts to occur. As a result of the decrease in the local resistance of the HfO_x under the STM tip due to defect generation, the bulk of the applied voltage will be transferred from the HfO_x to the vacuum gap. This in turn reduces the electric field in the HfO_x and self-limits the forming process through slowing down the oxygen-ion migration process. As the defect distribution across the HfO_x is expected to be relatively uniform under soft forming where the oxygen ions are slightly displaced from the vacancy sites, the I-V curves are symmetrical and the current conduction under both polarities follow the Poole-Frenkel mechanism. Extending the voltage to higher values during forming may lead to a non-uniform defect distribution (with the density near the anode being higher than that near the cathode) when oxygen ions from the top of the HfO_x recombine with the vacancy sites generated at the bottom part. When a positive voltage polarity is applied during the post-forming measurement, electron injection occurs from the STM tip into an HfO_x region of high defect density. Thus, the current will be large and electronic transport is "hopping-like". On the other hand, electrons are injected from the bottom TiN into a relatively 'intact' HfO_2 region under a negative voltage bias. As a consequence, the current is smaller and electronic transport is determined by the space charge effect[5]. A further increase of the voltage during forming would result in most of the oxygen ions being moved out of the HfO_x, into the bottom TiN. The defect distribution across the HfO_x is expected to become more uniform, giving rise again to symmetrical I-V curves for both voltage polarities.

Summary – STM study reveals an asymmetrical conduction property of the filamentary path in the HfO_x dielectric in the case of intermediate forming hardness. Such a behavior is believed to have resulted from a non-uniform defect density profile along the filamentary path, which in turn gives rise to different mechanisms limiting the transport of electronic charge at the injecting electrodes.

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References: [1] Waser *et al.*, Nature Mater., 6, 833–840, 2007. [2] Yang *et al.*, Nature Nanotech., 8, 13–24, 2012. [3] Flocke *et al.*, in Proc. 33rd ESSCIRC, 328–331, 2007. [4] Kim *et al.*, Adv. Funct. Mater., 1440–1449, 23, 2013. [5] Wang *et al.*, Appl. Phys. Lett. 93, 202904, 2008.

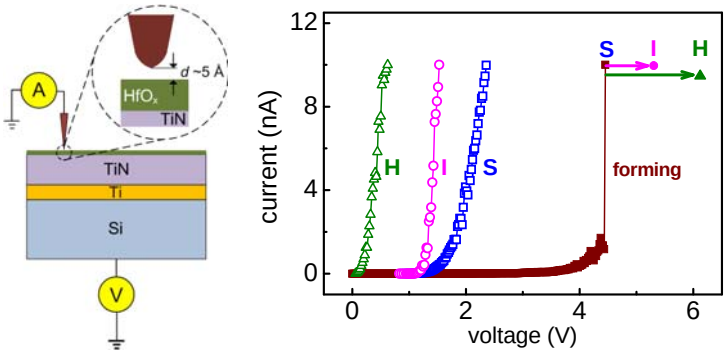

Fig. 1. Left: Schematic illustration (not to scale) of the test sample and STM measurement set-up. The voltage bias is applied to the Si substrate and the STM tip is grounded. The vacuum gap between the STM tip and the HfO_x surface is denoted as *d*. Right: Current-voltage curves during forming and post-forming voltage sweeps for three levels of forming hardness: S(soft), I(intermediate), and H(hard). Soft forming is achieved by interrupting the voltage sweep immediately upon the abrupt jump of current. Harder forming is realized by extending the voltage sweep to higher voltage values following the current jump, as shown by the arrows.

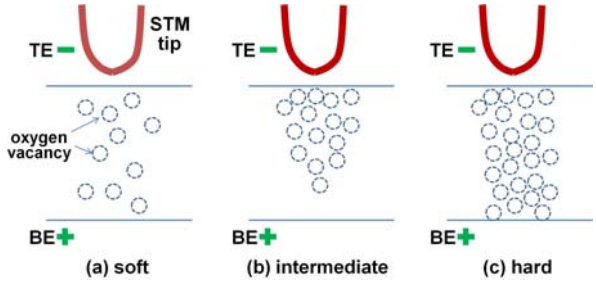

Fig. 8. Schematic illustration of possible oxide trap density profile along the filamentary path in the HfO_x dielectric, for different degrees of forming hardness. (a) Soft forming – Traps are sparely distributed, with no distinct difference in concentration along the HfO_x thickness. (b) Intermediate forming – A 'tapered' trap density profile along the HfO_x thickness may be expected, with a higher trap density near the cathode. The non-uniform distribution may have arisen from oxygen ions displaced from the cathode region recombining with vacancies near the anode region. (c) Hard forming – Trap density become uniform again when most of the oxygen ions are drawn out of the filamentary path into the bottom electrode (BE).

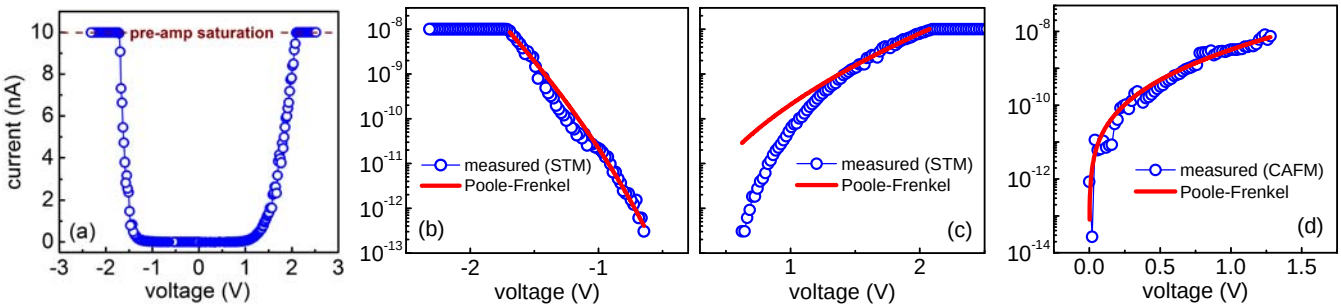

Fig. 2. (a) For the case of soft positive forming (cf. Fig. 1, S), the current-voltage (I-V) curves (in the low resistance state) of both voltage polarities are nearly symmetrical. (b) A good match between the Poole-Frenkel (PF) model and the I-V curve in the negative voltage regime. (c) Mismatch, due to the vacuum gap between the tip and HfO_x surface, can be observed in the low current region of the positive voltage regime. (d) A good match between the PF model and the positive I-V curve measured via CAFM (for which no vacuum gap exists).

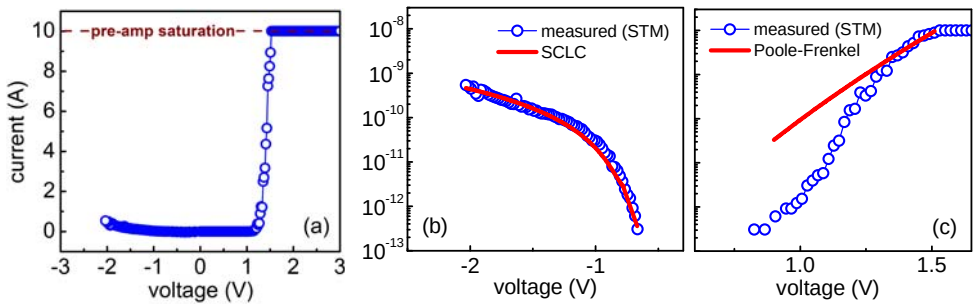

Fig. 3. (a) Asymmetrical I-V curves, with significantly lower current in the negative voltage regime, are observed for intermediate positive forming. (b) The I-V curve in the negative voltage regime cannot be matched with the Poole-Frenkel (PF) model, unlike in the case of soft forming (Fig. 2(b)). Instead, a good fit is obtained using the space-charge limited conduction (SCLC) model. (c) Similar to the soft forming case, the positive I-V curve only matches the PF model in the high current region; mismatch at the low current region is caused by the vacuum gap.

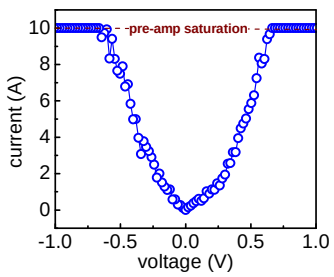

Fig. 7. For hard positive forming (cf. Fig. 1), symmetrical I-V curves are again observed. It should be mentioned that the probability of observing subsequent resistive switching after hard forming is relatively low.

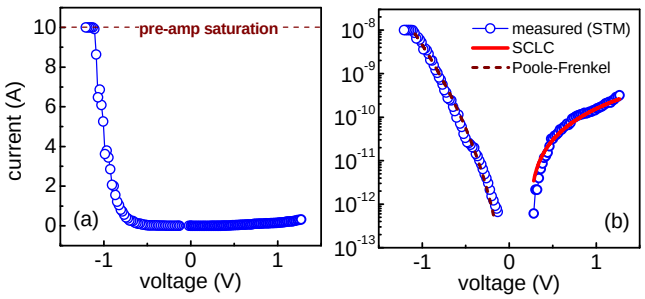

Fig. 4. (a) Asymmetrical I-V curves are also consistently observed under negative forming, as long as the hardness is controlled at the intermediate level. (b) Good agreement between the Poole-Frenkel model and the I-V curve in the negative voltage regime. The positive I-V curve can only be fit by the SCLC model. Mismatch is also seen at the low current region due to the vacuum gap.

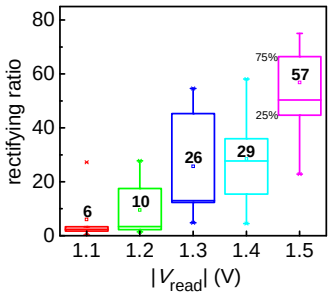

Fig. 5. Ratio of the positive to negative current, defined as the rectifying ratio, as a function of the 'read' voltage V_{read}. Mean values are as indicated. Data shown are for positive forming.

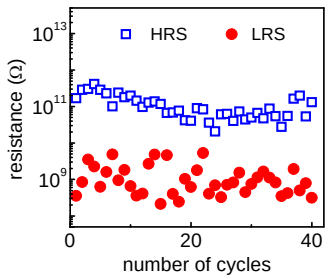

Fig. 6. Resistance as a function of the number of set/reset cycles for the high and low resistance states (HRS and LRS, respectively). Data shown are for positive forming.