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Rate-limiting processes in the fast SET operation of a gapless-type Cu-Ta_2O_5 atomic switch

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The speed of the SET operation of a Cu/Ta_2O_5/Pt atomic switch from a high-resistance state to a low-resistance state was measured by transient current measurements under the application of a short voltage pulse. The SET time decreased exponentially with increasing pulse amplitude, reaching as low as 1 ns using moderate pulse voltages. This observation shows that oxide-based atomic switches hold potential for fast-switching memory applications. From a comparison with atomistic nucleation theory, Cu nucleation on the Pt electrode was found to be the likely rate-limiting process determining the SET time. *Copyright 2013 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License*. [http://dx.doi.org/10.1063/1.4795140]

I. INTRODUCTION

In recent years, resistive-switching random access memory (RRAM) has been recognized as one of the most promising next-generation memory technologies because of its simple structure, high scalability, and ease of operation.[1–3] The basic structure of RRAM is composed of a metal-insulator-metal (MIM) cell featuring an active transport layer with a thickness of less than a few tens of nanometers. Of the various types of RRAM available, the cells whose resistive switching is based on the migration of cations in a thin metal oxide layer are very attractive for practical applications, because metal oxides are highly compatible with current complementary metal-oxide-semiconductor processes.[4] In these devices, an electrochemically active metal (usually Ag or Cu) is used as one electrode. The mechanism of their operation is essentially identical to that of an "atomic switch", whose resistance across a nanometer gap is controlled by the formation and annihilation of a metal bridge under an electrical bias;[5] we call this MIM-structured cell a "gapless-type atomic switch".[6] Because it is constructed by electrochemical deposition and dissolution of a metal on an inert electrode, this type of cell is also referred to as an electrochemical metallization (ECM) cell.[7] It has been demonstrated that the oxide-based atomic switches exhibit an effect analogous to the long-term potentiation of biological synapses, suggesting their potential for use in neural computing systems.[8]

Among the various properties of a RRAM operation, switching speed is one of the most important. Although many research groups have reported the switching time of their RRAM cells,[9–11] it is difficult to measure on or below the order of nanoseconds due to the broadening and ringing of voltage pulses arising from impedance mismatching in the measurement systems featuring RRAM cells. Recently, Torrezan *et al.* reported the observation of a switching time of ~0.1 ns by fabricating a Pt/Ta_2O_5/Pt cell integrated into a coplanar waveguide (CPW) structure, in which the migration of oxygen vacancies is responsible for resistive switching.[12] The integration into a CPW structure

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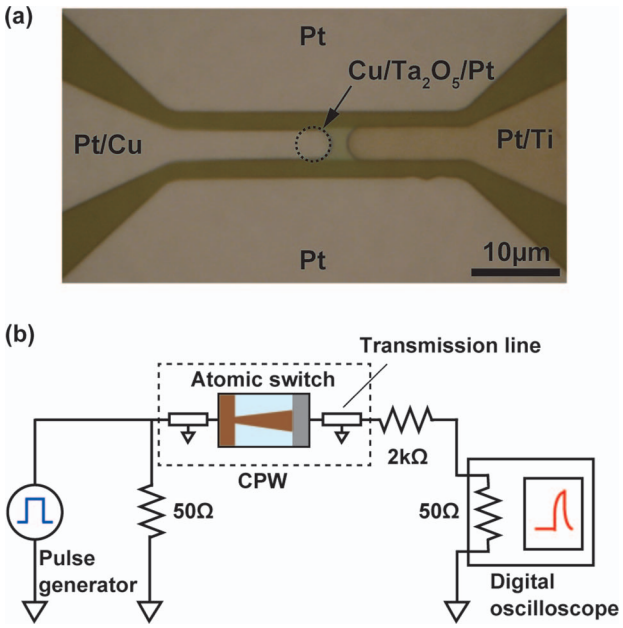

FIG. 1. (a) SEM image of a $Cu/Ta_2O_5/Pt$ cell integrated into a coplanar waveguide, whose junction size is approximately 4 μm in diameter. (b) Schematic of the experimental setup used for transient current measurements.

enables impedance matching between the measurement system and the cell. The switching-time measurement is very important not only in demonstrating the fast switching speed of the cell, but also in understanding the high-speed dynamics of the switching mechanism.[13–15] Here, we report transient current measurements of a Cu-Ta_2O_5 atomic switch under the application of fast voltage pulses used to study the switching dynamics in the SET operation of oxide-based atomic switches from a high-resistance (OFF) state to a low-resistance (ON) state. Measuring the transient current for the atomic switch and ECM cells are difficult due to their high ON/OFF ratio, which leads to a large impedance mismatch. We overcame this problem by integrating the cell into the CPW structure and constructing a specially designed measurement system. The experimental results reveal that a SET time as low as 1 ns is achievable using moderate pulse voltages. Possible rate-limiting processes that determine the SET time are discussed.

II. EXPERIMENTS

A $Cu/Ta_2O_5/Pt$ atomic switch cell (see scanning-electron-microscope (SEM) image of Fig. 1(a)) was fabricated in a tapered CPW structure using photolithographic processes. The tapered CPW structure acts as a transmission line with a nearly characteristic impedance of $\sim$50 Ω from transient current measurements.[12] The cell consists of a top electrode (TE) of Pt(100 nm)/Cu(30 nm), a Ta_2O_5 layer with a thickness of 15 nm, and a bottom electrode (BE) of Pt(20 nm)/Ti(5 nm) on a Si substrate covered with a 200-nm-thick SiO_2 layer. The Ta_2O_5 layer was sputter-deposited from a polycrystalline Ta_2O_5 target with an Ar and O_2 gas mixture. The cell was formed by the overlap between the TE and BE, with a width of 2 or 4 μm at the center of the CPW. The SEM image shows a junction size of approximately 4 μm in diameter, as indicated by the dotted circle. Ground pads of Pt (100 nm thick) were formed outside of the cell to reduce losses associated with the tapered structure at high frequency.

Transient current measurements were carried out at room temperature in ambient atmosphere. Figure 1(b) illustrates the experimental setup in which the cell was connected in series to a fast pulse generator with a rise time of 2 ns (Agilent 81110A) and a single-shot 2.5-GHz bandwidth digital oscilloscope (Lecroy WavePro 725i). The digital oscilloscope monitored the voltage transmitted through the cell and the input voltage from the pulse generator. The voltage pulse was delivered

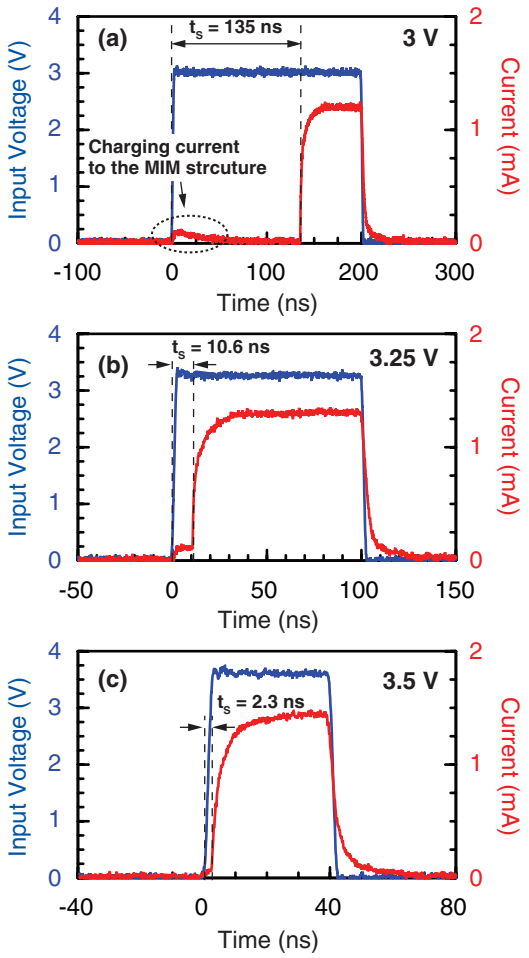

FIG. 2. Typical transient current of the cell under different applied pulse voltages: 3 (a), 3.25 (b), and 3.5 V (c). The OFF resistance before the pulse application was ∼10 MΩ for all data.

to the cell through the transmission lines of the CPW structure in addition to impedance-matched source and scope loads, resulting in a significant reduction in pulse broadening and ringing. Two resistors with resistance of 50 Ω and 2 kΩ were also connected to the cell (Fig. 1(b)); the former was used to minimize the reflected voltage from the cell and to enable a constant input voltage to be applied when the cell was SET, whereas the latter was used to limit the ON current as a current-limiting resistor. These resistors were integrated into specially designed CPW probes.

III. RESULTS AND DISCUSSION

The Cu/Ta_2O_5/Pt cell exhibited bipolar resistive switching when a bias voltage was swept: the cell was SET from the OFF state to the ON state at positive bias relative to the Cu electrode and RESET from the ON state to the OFF state at negative bias. The SET and RESET operations correspond to the formation and dissolution of a nano-scale metal filament between the TE and BE, respectively.[16] The SET and RESET voltages were higher in magnitude for the first voltage sweep, which correspond to the forming and subsequent dissolution processes of the metal filament, and then decreased to nearly constant voltages upon switching cycles.[16,17] The SET voltage ranged from 1 to 1.5 V, whereas the RESET voltage was approximately 0.5 V at a voltage sweep rate of 0.1 V/s.

Figure 2(a) shows a typical result for the transient current response (red curve) under the application of a voltage pulse of 3 V (blue curve), measured for the cell with a junction size of 4 μm.

The pulse was applied after the SET/RESET voltage characteristics became nearly constant during cycling in the voltage sweep mode. The current was calculated from the measured voltage drop across the oscilloscope load (50 Ω). The time delay between the input voltage and the current signals due to different cable lengths was calibrated. As the voltage pulse was applied to the cell, a small current peak rose sharply and then gradually decreased within the first several tens of nanoseconds, as indicated by the dotted circle. This behavior corresponds to a charging current in the parasitic capacitance of the MIM structure with the Ta_2O_5 layer. The capacitance estimated by integrating the charging current agreed with that evaluated from a capacitance-voltage (C-V) measurement.[18] After the charging current flowed, the current suddenly jumped at a certain time and reached a compliance level within a few tens of nanoseconds, which was determined by the pulse amplitude and the total resistance, including the resistance of the current-limiting resistor (2 kΩ), the ON resistance of the cell (a few hundred Ω), and the oscilloscope load (50 Ω).

The cell was seen to be already SET even if the application of the input pulse was finished before the current reached the compliance level, indicating that the cell is SET on the leading edge of the current signal and not when the current reaches the compliance level.[18] This effect occurs because the shape (time constant) of the current signal is mainly determined by the *RC* component of the whole measurement system, where *R* is the total resistance and *C* the cell capacitance plus an additional parasitic capacitance associated with the CPW structure and probe. If we measured a cell with a junction area of 25 μm × 25 μm, the signal shape would be significantly broadened due to the higher capacitance of the cell (not shown here). Thus, the SET time t_s is defined as the time shift between the leading edges of the input voltage signal and the current response (SET current), as indicated by the dashed lines. The rise time of the SET current should not be included in the SET time.

If the pulse amplitude increased, the SET time would be drastically reduced. Figures 2(b) and 2(c) show a typical transient current response for pulse voltages of 3.25 and 3.5 V, respectively. The SET current rose overlapping with the charging current for these higher pulse amplitudes. This observation means that the cell was SET before the charging of the capacitance of the MIM structure was completed. The SET time decreased by approximately two orders of magnitude with an increase in the pulse amplitude of 0.5 V.

Figure 3 plots the measured SET times as a function of the pulse amplitude, which were collected from several cells per point. The data obtained from different junction sizes exhibited almost the same transient current responses, although the shape of the current signal was slightly broadened for the cells with the junction size of 4 μm due to the higher capacitance. Hence, in Fig. 3, we plot all the data for both junction sizes. There is some uncertainty in determining SET times faster than 2 ns because the SET time becomes comparable to the rise time of the pulse generator. Nevertheless, we demonstrated that a SET time as low as 1 ns can be achieved using moderate pulse amplitudes. In the present study, the cell was RESET by sweeping a negative bias voltage after each SET operation with a voltage pulse. Note that the results shown here were obtained for OFF resistances kept in the range from 8 to 13 MΩ. This aspect is very important in the discussion of the SET time because the SET time depends not only on the pulse amplitude but also on the OFF resistance. The OFF resistance value is determined by various parameters of the OFF state, such as the concentration of Cu ions dissolved in the Ta_2O_5 layer and the actual distance between the Cu TE and the remaining metal filament on the Pt BE.[12] Although it is difficult to account for all these parameters alone from the OFF resistance value, we assume that the same OFF resistances indicate almost the same OFF state cell properties. A focused discussion on the correlation between the SET time and the OFF resistance will be reported in a separate paper.[19]

The SET operation of gapless-type atomic switches and ECM cells can involve the following steps:[20] (i) anodic dissolution, (ii) migration of cations in the active layer, (ii) nucleation on the cathode, and (iv) growth of the nucleus to form a filament, as illustrated in Fig. 4. In our experiment, the SET times were measured after repeating switching cycles until the operation voltages become nearly constant. Under these circumstances, it is expected that some Cu ions remain in the Ta_2O_5 layer even in the OFF state,[16] which can contribute to the reformation of the metal filament under applied electrical pulses. Hence, we believe that the anodic dissolution (i) is not the rate-limiting process with respect to the SET time. The rise time of the SET current, as shown in Fig. 2, does not

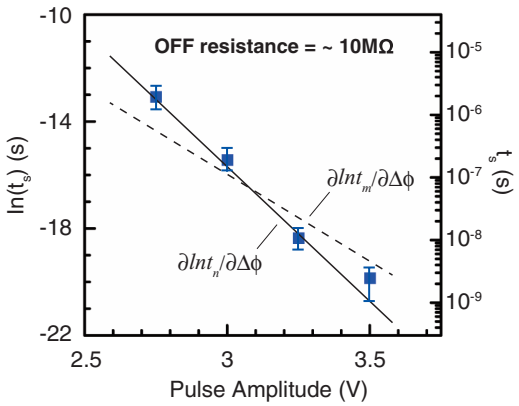

FIG. 3. SET time plotted as a function of the pulse amplitude. All data were obtained for OFF resistances ranging from 8 to 13 MΩ before the application of a voltage pulse. The solid and dashed lines represent slopes fitted to the experimental data using Eqs. (1) and (2), respectively.

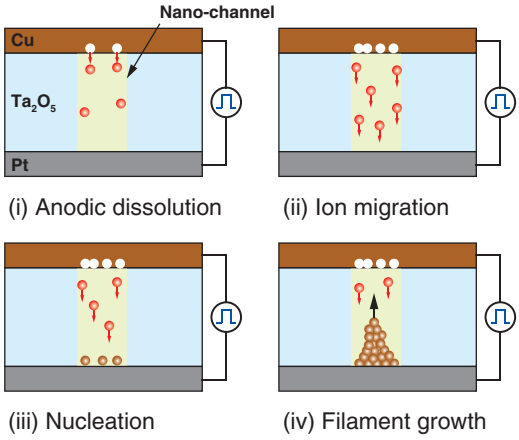

FIG. 4. Possible mechanisms that determine the SET time: (i) anodic dissolution at the Cu electrode, (ii) migration of Cu ions in the Ta_2O_5 film, (iii) nucleation of Cu on the Pt electrode, and (iv) growth of Cu nucleus to form a metal filament between the electrodes.

correspond to the growth time of the metal filament. Because the observed rise time is determined by the *RC* component of the whole system, as mentioned above, the actual growth time is much faster than the observed rise time. Thus, the growth of the filament is also not the rate-limiting process.

From the above discussion, the SET time appears to be determined by the migration of Cu ions in the Ta_2O_5 layer and/or Cu nucleation on the Pt BE. When a positive voltage is initially applied to the cell, the forming (the first SET operation) can be considered a stochastic process because the large Pt electrode can offer many sites for nucleation. However, once a metal filament is formed, the subsequent SET and RESET processes should be site-invariant, due to the existence of a nano-channel that aids the fast migration of Cu ions and nucleation, as illustrated in Fig. 4.[2,7,16] The subsequent reformation and dissolution of the metal filament take place at the same location on the Pt electrode. This situation is quite similar to that observed for a gap-type atomic switch, in which a metal bridge is formed between the tip of a scanning tunneling microscope (STM) and a sample.[4,21]

Atomistic nucleation theory predicts that the nucleation time depends exponentially on the applied voltage:[22]

$$t_n = t_0(Z_0, N_{ion})exp\left[\frac{(N_c + \alpha)e\Delta\phi}{kT}\right], \quad (1)$$

where the pre-exponential term $t_0(Z_0, N_{ion})$ depends on the number density Z_0 of the nucleation sites and on the number (concentration) N_{ion} of ions, N_c is the number of atoms constituting the critical nucleus, α the cathodic transfer coefficient, e the electron charge, $\Delta\phi$ the applied cathodic potential (takes negative values), k the Boltzmann constant, and T the absolute temperature.[2,23] The solid line in Fig. 3 represents the slope $\partial \ln t_n/\partial\Delta\phi$ according to Eq. (1). The slope is well fitted to the experimental results, indicating that nucleation (iii) could be the rate-limiting process. The corresponding slope coefficient $(N_c + \alpha)/kT$ is estimated to be -10 V^{-1} and is comparable to that of the Ag/Ag-GeS$_x$/W system;[24] α generally ranges from 0 to 1 and can depend on the applied cathodic potential. It represents the change in the activation energy of the forward (backward) process normalized by the total energy applied and the geometrical position of the potential energy barrier maximum in the dense part of the electrical double layer. Recently, Valov *et al.* determined α to be 0.2 in a gap-type atomic switch using $RbAg_4I_5$.[21] Although it is difficult to know the exact value of α, we expect a smaller α for our cell because the distance between the TE and BE (15 nm) is much larger than the tunnel gap of an STM (1 nm). N_c is then estimated to be between 0 and 0.26. This value suggests that an empty nucleation site acts as a critical nucleus. Every deposited metal atom can then be regarded as a supercritical cluster of the new phase.

According to hopping conduction theory,[25] the ion migration step (ii) involves thermally activated jumps between adjacent sites, and under high electric fields, the migration velocity of Cu ions v_m has a non-linear dependence on the electric field:

$$v_m = Aaexp\left(-\frac{\Delta H}{kT}\right) exp\left(\frac{aeE}{2kT}\right) \tag{2}$$

for one-dimensional adjacent sites with an asymmetric energy barrier ΔH, where A is a constant that includes the entropy change due to the ion jump, a the jump distance of the ions, and E the applied electric field. Then, the migration time t_m for a fixed traveling distance exhibits an exponential dependence $\exp(-aeE/2kT)$. The dashed line in Fig. 3 represents the slope $\partial \ln t_m/\partial\Delta\phi$ according to Eq. (2). The slope is in accord with the experimental results. However, the jump distance a was estimated to be ~4.2 nm assuming a traveling distance of 15 nm (thickness of the Ta_2O_5 layer), which is much larger than inter-atomic distances. Because such a large value has no real physical meaning, the contribution of non-linear ion migration would be less probable.

In the present measurement, an input oscilloscope load of 50 Ω was used to ensure a broad frequency band up to 2.5 GHz. Under these conditions, the minimum detectable current is approximately 10 μA (=0.5 mV/50 Ω). Because the current level due to the migration of Cu ions is expected to be smaller than this detection limit, it is difficult to directly determine the contribution of the migration step to the SET time. To clarify the exact partial contributions of the nucleation and migration steps, broadband measurements with much better current resolutions are required; these are still challenging to achieve.

IV. SUMMARY

In summary, we investigated fast switching dynamics in a Cu/Ta_2O_5/Pt atomic switch under the application of short voltage pulses. The experimental results demonstrated that the SET time decreased exponentially with increasing pulse amplitude, and switching times as low as 1 ns were achieved using moderate pulse voltages, suggesting that oxide-based atomic switches are promising candidates for fast switching memory devices. Atomistic nucleation theory was able to explain well the non-linear dependence of the SET time on the pulse amplitude, and the nucleation of Cu on the Pt electrode is likely to be the rate-limiting process. However, the migration of Cu ions in the oxide layer cannot be completely excluded in considering the contributions to the SET time.

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