**Operando** observation of resistive switching in a resistive random-access memory by laser-excited photoemission electron microscope

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We developed a laser-excited photoemission electron microscope (Laser-PEEM) that enables us to perform a non-destructive operando observation for elucidating the changes in the physical properties of electronic devices. By utilizing the Laser-PEEM, the non-volatile resistance change in the resistive random-access memory (ReRAM) was clearly visualized, even though the resistance change occurred under the electrode of the ReRAM, thanks to the deep probing depth. The operando observation of the Laser-PEEM is very promising as an observation method for various kinds of devices because the observation simultaneously provides us with morphological and electrical properties in real time.

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1. Introduction

The resistive random-access memory (ReRAM) is a device recording data as the resistance with a simple structure consisting of an oxide layer with two electrodes at both ends.1,2 The resistance change is considered to be caused by the formation and annihilation of the conductive path generated by oxygen vacancies. The formation occurs by the current-induced redox reaction when a voltage is applied between the electrodes.3–14 However, a bottleneck for the ReRAM developments to improve its stability and performance of the memory operation exists because the formation process and the shape of the oxygen vacancy paths are not clear, and a visual observation is difficult.

From the point of view of ReRAM developments, non-destructive imaging methods are indispensable in comparing the changes in chemical states before and after memory operations. Kumar et al. previously adopted the X-ray absorption microscopy technique for the ReRAM device,15,16 but had to repeat 105 operations to compensate for the small difference in contrast between the low and high resistance states. On the other hand, the transmission electron microscopy (TEM) technique was successfully used to observe the conductive path of metal ions.17,18 However, in this case, the device must be processed for the TEM observation, and it may deteriorate because of multiple operations and electron beam irradiation.

Several reports on ReRAM observations in a photoemission electron microscope (PEEM) have been presented. Yasuhara et al.19 and Baeumer et al.20 performed PEEM measurements with the photon energies of 932.6 and 458.5 eV, respectively, using synchrotron radiation as a light source. At these photon energies, the probing depths of the PEEM, which are calculated from the universal curve between the kinetic energy of the excited electrons, and their inelastic mean free path (IMFP), are estimated to be short.21 Accordingly, ReRAM devices with a special structure or processing must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

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The probing depth of the Laser-PEEM was rigidly studied herein. The PEEM image under a 42 nm thick Pt-TE was even successfully obtained. In addition, the newly developed Laser-PEEM equipped with a pulse–voltage application system was introduced to trace the resistance change of a ReRAM device without processing. With the pulse–voltage application method, in which the timing of the voltage application and image acquisition is different, a video image of the PEEM with a high time resolution and a high spatial resolution was acquired.

2. Experimental methods

2.1. Probing depth estimation

A cross-bar ReRAM sample having five top electrodes (TE) with different film thicknesses was prepared to estimate the probing depth. We reactively sputter-deposited a TiN layer on a thermally oxidized Si substrate. The TiN thin film was patterned into a line shape for use as a bottom electrode (TiN-BE) by conventional photolithography and dry-etching processes with mixed Ar and Cl2 gases. We then deposited a Ta2O5 layer on the TiN-BE by sputtering method. Subsequently, we fabricated five Pt-TE patterns with different film thicknesses via sputtering and liftoff processes. The obtained stacking structure for the cross-bar-type ReRAM device was Pt/Ta2O5/TiN. The film thicknesses of TiN-BE and Ta2O5 were 20 and 4 nm, respectively. Finally, a Pt thin film with a 10 nm thickness was sputter-deposited around the ReRAM devices to stabilize the electric charge of the TE during the PEEM observation. All of the five Pt-TE patterns were connected to this Pt thin film. Figures 1(a) and 1(b) show the optical microscope image of the fabricated five ReRAMs and the scanning electron microscope (SEM) image for one of the five ReRAMs, respectively. The widths of Pt-TE and TiN-BE were 6.26 and 2.53 μm, respectively. The height of the five Pt-TE patterns was estimated by atomic force microscopy as 6, 7, 12, 22, and 42 nm. As schematically shown in Fig. 2, the TE film thickness-dependent PEEM images can be obtained by observing this sample with the Laser-PEEM. The probing depth of the Laser-PEEM can also be estimated.

2.2. Operando observation

The stacking structure of the ReRAM device for the operando observation was Pt/Ta2O5/TiN and prepared through the same abovementioned fabrication process. The film thicknesses for TiN, Ta2O5, and Pt were 20, 4, and 10 nm, respectively. We patterned the Au/Ti electrical contact pads for both BE and TE via the evaporation and liftoff processes prior to the Pt-TE pattern fabrication. The widths of the TE and BE electrodes were designed as 1.5 and 1.0 μm, respectively. Figures 3(a) and 3(b) depict a photograph of the entire device and the microscope image of the cross-bar area observed under magnification, respectively. As shown in Fig. 3(b), two independent TEs shared one common BE. We can choose the ReRAM device to be voltage-biased for the resistance change operation by toggling between the two TEs. Figure 3(c) shows an example of the PEEM image obtained using the present ReRAM device for the operando observation. The geometry of the ReRAM device was clearly observed by our Laser-PEEM despite the complicated cross-bar-type stacking structure consisting of various metal and oxide elements.

Figure 4 depicts a schematic illustration of the measurement setup for the operando Laser-PEEM observation. The electrical connections to a source measure unit (SMU) were introduced into our PEEM chamber; hence, both the PEEM image, and the resistance value of the ReRAM device under test can be simultaneously acquired. Here the low and high terminals of the SMU were connected to the BE and TE, respectively.

Figures 5(a)–5(c) show the PEEM images of the identical ReRAM device under the SMU voltages of 0, 1, and 2 V, respectively. Unlike in Fig. 5(c), the electrode intersections appeared bright in Fig. 5(a). Even though the stacking structure and the constituent material for the devices in the two figures were basically identical to each other, the brightness of the PEEM image was different because of the quite high sensitivity of the Laser-PEEM observation to some other properties of the device, such as the surface contamination, surface roughness, and crystal states of materials in the device. Therefore, in the conventional PEEM observation, especially when the device location on the wafer is different and/or the device is exposed to a different atmosphere or temperature, the abovementioned issue must be considered. However, in the case of the present operando Laser-PEEM observation, it is completely negligible because a number of the PEEM images can be acquired from exactly the same device with changing the SMU voltage values. The PEEM images by operando observation are appropriate for evaluating the impact of the applied voltage. In contrast, the potential of the sample surface caused by the SMU voltage severely distorted the PEEM image in Figs. 5(a)–5(c). Therefore, in the DC voltage sweep measurement, where the external voltage was continuously applied as shown in Fig. 6(a), the acquisition of a clear PEEM image was difficult. To solve this problem, we adopted a measurement method, in which the timing of the voltage application and image acquisition becomes different, by using the pulse voltage for the resistance change [Fig. 6(b)]. Therefore, the I–V characteristic of the device and a clear PEEM image can be simultaneously acquired. The operando Laser-PEEM observation for the electronic state change that causes the ReRAM device resistance change can be conducted by our technique.

In the operando observation herein, the pulse voltage width was fixed to 1 ms, which is the minimum output range.
of the SMU (Keysight B2902A). The PEEM image was acquired with an exposure time of 1.0 s after a delay time of 0.2 s following the pulse output. The next pulse was injected after 0.2 s from the PEEM image acquisition.

3. Results and discussion

3.1. Probing depth estimation

Figure 7(a) shows the Laser-PEEM images of the five ReRAM devices with different Pt-TE thickness values. Five bright Pt-TEs in the vertical direction and dark TiN-BEs in the horizontal direction were visible. Figure 7(b) presents an enlarged PEEM image for the ReRAM device with a Pt-TE thickness of 42 nm. Although the contrast for the BE gradually became faint with an increase in the Pt-TE thickness, the BE pattern buried beneath the 46 nm thick films (the 42 nm thick Pt-TE and 4 nm thick Ta2O5) was successfully observed.

We estimated the probing depth of the present Laser-PEEM from the Pt-TE thickness dependence of the TiN-BE signal intensity. Figure 8 illustrates the signal intensity across
the TiN-BE along each Pt-TE. The signal intensity was normalized such that the signal intensity from the Pt-TE pattern having no overlap with TiN-BE in the longitudinal location was 100%. The relative signal intensity decreased in the area inside the cross-bar structure where an overlap existed between the TE and the BE. The signal intensity decreased as the TE film thickness increased because the TiN-BE was reduced. The signal intensity for the Pt-TE with 42 nm thickness was not used for the present probing depth estimation because some speckles on the surface were probably and unintentionally produced in the device fabrication process. The signal intensity from the buried part beneath Pt-TE and Ta$_2$O$_5$ decreased in accordance with the formula, exp ($-t/\lambda$), where, $t$ is the transmission distance (film thickness), and $\lambda$ is the probing depth of the Laser-PEEM (inelastic mean free process). Figure 9 shows the signal intensity from the buried BE estimated from Fig. 8 as a function of the thickness of Pt-TE while keeping the Ta$_2$O$_5$ thickness 4 nm and the fitted curve obtained using the

![Fig. 5.](image1) Laser-PEEM images acquired under the SMU voltages of (a)–(c) 0 V, 1 V and 2 V. The PEEM images are distorted because of the surface potential change by the application of voltage voltage.

![Fig. 6.](image2) (Color online) Schematic illustrations for the operand Laser-PEEM observation flow using (a) DC voltage sweep and (b) pulse voltage. The red circles and the green cross marks correspond to the current measurement and the image acquisition timing, respectively.

![Fig. 7.](image3) (Color online) Laser-PEEM images of the (a) five ReRAM devices with different Pt-TE thickness values and the (b) enlarged PEEM image for the ReRAM device with the Pt-TE thickness of 42 nm.

![Fig. 8.](image4) (Color online) Normalized signal intensities measured vertically across the Pt-TE for four ReRAM devices with different Pt-TE thickness from 6 to 22 nm. The signal intensity is normalized such that the signal intensity form the Pt-TE pattern having no overlap with TiN-BE along the normal direction to the substrate is 100%.
change in the present device was non-volatile; therefore, the consecutive measurement similar to the DC $I$–$V$ sweep was realized by the intermittent voltage pulse application shown in Fig. 4.

Figures 11(a) and 11(b) show the PEEM images acquired in Points [A] and [G] of Fig. 10, respectively. The Pt-TE across the TiN-BE is clearly seen in these figures. Although the resistance value of the ReRAM markedly increased (Fig. 10), extracting the difference of the photoelectron intensities in between the raw PEEM images for Points [A] and [G] was not easy. Although these PEEM images were seemingly analogous to each other, an obvious change was detected from the differential image created by using the two images. The differential PEEM image for Point X (X = A, B, ..., and G in Fig. 10) denoted by $\Delta P(X)$ is defined as follows:

$$\Delta P(X) = 100 \times \frac{P(X)}{P(A)},$$

where $P(X)$ represents the photoelectron intensities of the PEEM image observed at Point [X]. $\Delta P(G)$ is displayed in Fig. 11(c) based on this definition. In this figure, the blue and red colors represent the $-25\%$ and $+25\%$ changes in the photoelectron intensities, respectively. Different from the raw PEEM image $P(G)$ in Fig. 11(b), two blue spots were evidently observed near the edge of the device area in the differential image $\Delta P(G)$ in Fig. 11(c). Thus, our Laser-PEEM can visualize such a very small change in the device. These PEEM images were acquired between the pulse voltages; hence, the image was clear, and stable with almost no drift and distortion. This is one of the key points for creating accurate differential images with sufficient spatial resolution.

Figures 12(a)–12(f) show the differential images $\Delta P(X)$ for X = B, C, ..., and G, which provide spatial, and temporal information on the resistance increase procedure in the present ReRAM device. According to $\Delta P(B)$, $\Delta P(C)$, and $\Delta P(D)$ in Figs. 12(a)–12(c), the decrease of the photoelectron intensity was observed at the right-bottom corner of the device (in 3 o’clock direction in the field of view). The blue-colored area in the differential image $\Delta P(C)$ in Fig. 12(b) was beginning to emerge. This color change was considered to correspond to the sudden current decrease just after Point [B] in Fig. 10. When we compared $\Delta P(C)$ and $\Delta P(D)$, the...
size of the blue-colored area expanded along with the increase of the applied voltage pulse height from Points [C] to [D] in Fig. 10. In addition to that, the second blue spot appeared at the lower left part of the device (in 7 o’clock direction in the field of view) in $\Delta P(E)$ in Fig. 12(d). This color change can also be associated with the current decrease observed immediately before Point [E] in Fig. 10. Thus, the decrease in the photoelectron intensity in Fig. 12 was perfectly matched with the decrease in the ReRAM conductivity depicted in Fig. 10. The multiple filament behavior during the RESET process was successfully visualized by our Laser-PEEM, which was difficult to determine only from the electrical measurement. Although this photoelectron intensity change was observed only at the edge of the ReRAM in the present study, we confirmed that the photoelectron intensity also changed in the areas other than the edge of the ReRAM in the past study. Therefore, the operando technique we developed is expected to be a powerful tool for understanding the relationship between the electric properties of the nano-electronic devices and the microscopic changes in chemical states. This technique can also be applied to a variety of devices, such as NAND-flash, phase-change memory, and magneto-ReRAM, because the Laser-PEEM can obtain various information on not only the chemical states, but also on the valence, crystallinity, magnetism, and elements of materials constituting these devices.

4. Conclusions

We developed herein the Laser-PEEM with a pulse–voltage application system for the operando observation. The microscope enabled us to clearly visualize the change in the chemical states of the ReRAM, followed by the electrical change in real time. The probing depth of the Laser-PEEM on the current ReRAM structure reached 16 nm, which elucidated the resistance change under the top electrode. The Laser-PEEM with the pulse–voltage application system makes it possible to observe the fine and dynamic changes in the device, and will help us understand the operation mechanism and the improvement of device operations.

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