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Redox processes in silicon dioxide thin films using copper microelectrodes

S. Tappertzhofen,^{1,3} S. Menzel,^{1,3} I. Valov,^{1,2,3,a)} and R. Waser^{1,2,3}

¹Institut für Werkstoffe der Elektrotechnik 2, RWTH Aachen University, Sommerfeldstraße 24, D-52074 Aachen, Germany

²Peter Grünberg Institut 7, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

³JARA-Fundamentals of Future Information Technology, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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Although SiO₂ is a typical insulator, we demonstrate an electrochemical characteristic of the Cu/Cu⁺ oxidation at the interface with 30 nm thick silicon dioxide thin films studied by cyclic voltammetry. This study reveals the process of anodic oxidation and subsequent reduction of oxidized Cu ions injected in the SiO₂ layer with special attention to the kinetics of the redox process. We estimated the diffusion coefficient and the mobility of Cu ions in SiO₂. The results gain deeper insight in the processes involved during resistive switching of Cu/SiO₂ based nonvolatile memory devices. © 2011 American Institute of Physics. [doi:10.1063/1.3662013]

Recently, redox processes on the nanoscale attracted high attention in the context of resistive switching random access memories (RRAM). RRAMs have the prospect of high scalability and low power consumption.¹ In general, the simple structure of a RRAM cell consists of an ion conducting thin film (e.g., SiO₂) sandwiched between an electrochemically working electrode (WE, e.g., Cu) and an inert counter electrode (CE, e.g., Pt). By applying a sufficiently high voltage an anodic oxidation of the WE and a simultaneous electrochemical formation of a metallic filament at the CE take place, short circuiting both electrodes.² This resistance transition can be reversed by applying a voltage in the opposite direction dissolving the filament. SiO₂ based RRAM cells have been studied in respect to switching endurance,³ power consumption,⁴ and switching (reduction) kinetics.⁵ It has been also demonstrated that at higher temperatures (above 560 °C) the initial switching voltage decreases by thermal diffusion of Cu.⁶ Nevertheless, a detailed investigation on the WE kinetics and the transport of mass and charge in very thin SiO₂ films are still missing. In contrast to ion conductors such as Cu₂S and Cu-GeS_x used for RRAM cells, SiO₂ is initially free from Cu⁺ ions, and one needs first to dissolve electrochemically ions in order to be possible to operate the cell at all. Therefore, the kinetics of the oxidation process is even more important to understand than the reduction process.

This study reveals the anodic oxidation of Cu and subsequent reduction of Cu ions at the WE by cyclic voltammetry (CV) using microelectrodes. Although CV is a widely used method in electrochemistry, insulating thin films which do not initially contain mobile ions were not investigated yet. Based on our measurements we found that the charge transfer kinetics are rate determining and derived the diffusion coefficient and mobility of Cu ions in SiO₂ which are significantly higher compared to values extrapolated for room temperature diffusion of Cu ions in SiO₂ reported in literature.⁷

Platinized silicon substrates were used for the sample fabrication. A 30 nm thick SiO₂ thin film was deposited by electron-beam (e-beam) evaporation. Top Cu microelectro-

des with an area of 0.008–0.2 mm² and 30 nm thickness were prepared by UV-lithography and e-beam evaporation. The electrodes were finally encapsulated by a 100 nm thick Pt film to prevent chemical oxidation of the Cu electrode. CV sweeps were performed in a voltage range between –2 V and 2 V using a Keithley 6430 Sub-Femtoamp Remote Source Meter.¹² The sweep rates were varied between 16 mV/s and 2 V/s. Details on the method can be found in Ref. 8.

Fig. 1 shows a CV measurement of a Cu/SiO₂/Pt cell. We observed a dependence of the electrode area on the current, and therefore the current density is plotted in the following figures. During the kinetic experiments we intentionally avoided the formation of a metallic filament short circuiting the top and bottom electrode by limitation of the voltage amplitude. If the applied voltage is further increased above 2 V, resistive switching of the cell is observed.¹² In this context, the Cu oxidation appears to be the preceding process enabling the first resistive switching.

We associate the observed current peaks to a redox reaction of the Cu electrode. The charge number z of the Cu^{z+} ion is yet unknown,⁹ and thus redox reactions of both Cu⁺ and Cu²⁺ may take place. Cu is firstly oxidized by applying a positive voltage between the Cu and Pt electrode (A). Further increase of the voltage results in increased rate of anodic oxidation of Cu and, thus, an increase of the current (B). Simultaneously, oxidized Cu ions are injected into the SiO₂ thin film under the concentration and electrical field gradients. After the vertex potential is achieved, the current decreases because the driving force of the oxidation process is reduced (C). At $V \approx 0.85$ V a reduction of the oxidized Cu is starting to take place (D). By further decrease of the applied voltage a reduction current density peak j_p at $V_p \approx -0.72$ V is observed. Here, the concentration of Cu ions close to the Cu electrode is strongly decreased, and the current is limited by the diffusion of Cu ions (injected into the SiO₂ thin film during oxidation). In this case the reduction cannot take place at the Pt electrode due to the voltage polarity. In contrast, injected Cu ions may be reduced at the working electrode. We associate the second peak (G) $V \approx -1.6$ V to a direct Cu²⁺ to Cu reduction or to a partial

^{a)}Electronic mail: i.valov@fz-juelich.de.

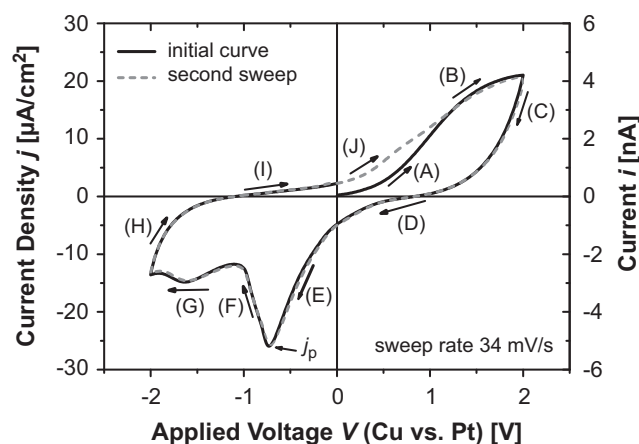


FIG. 1. Initial curve (black) and subsequent sweep (grey, dashed) of a cyclic voltammogram of a Cu/SiO₂/Pt cell. Arrows indicate the direction of the sweep.

Cu²⁺ to Cu⁺ reaction. As soon as the driving force of the reduction is diminished, the absolute current decreases (H) while a second current zero crossing is observed at -1.1 V (I). During the reverse sweeping Cu may be oxidized at the anode although a voltage of less than 0 V is applied (J). Hence, the initial curve and second curve do not overlap for $V=0$. Without an initial sweep in the positive direction current peaks in the negative voltage regime have not been observed because there are no Cu ions which can be reduced.

In general, an oxidation current peak in the positive sweep direction can be expected for a typical redox system. However, in this particular case the oxidation takes place directly at the electrode and its thickness is similar to the SiO₂ thickness. The Cu electrode is acting as a nearly endless source for Cu²⁺ which is directly injected into the SiO₂ thin film. Hence, an oxidation peak may not be necessarily observed below 2 V. By increase of the voltage amplitude oxidation peak(s) may be overlaid by the current after the switching event.

Typical CV measurements with variable sweep rates are shown in Fig. 2. As expected for a redox system the current peaks increase by increase of the sweep rate. The peak potential V_p shifts to more negative values by increasing the sweep rate indicating an inhibited charge transfer controlled

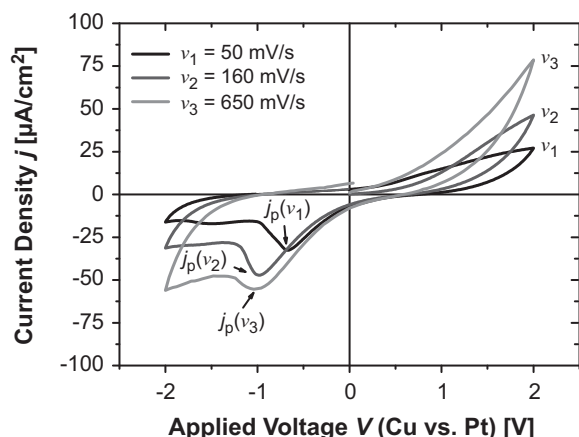


FIG. 2. Typical electrochemical kinetics of the Cu/SiO₂/Pt system analyzed by variation of the sweep rate between 50 and 650 mV/s.

electrode reaction.⁸ The reduction peak current density j_p in case of an inhibited charge transfer can be estimated at room temperature based on the Randles-Sevcik equation⁸:

$$j_p = 2.99 \cdot 10^5 \cdot z^{3/2} \cdot c_{\text{ox}} \cdot \sqrt{\alpha D_{\text{ox}} v}. \quad (1)$$

Here, D_{ox} is the diffusion coefficient of the Cu ions in cm²/s, c_{ox} the concentration in mol/cm³, z the number of electrons transferred in the redox reaction, $\alpha \approx 0.5$ the charge transfer coefficient, and v the sweep rate in V/s. Thus, a linear relation of j_p versus $v^{1/2}$ is expected which is shown in Fig. 3. With $v = 160$ mV/s and $j_p = 47$ μA/cm² extracted from Fig. 2 we estimated a generated charge of Cu ions of $Q_{\text{ox}} \approx 6 \cdot 10^{-8}$ C by integration of the current in the positive voltage regime with $z = 1$. With Q_{ox} and the cell geometry we calculated $c_{\text{ox}} \approx 1.2 \cdot 10^{-3}$ mol/cm³. Here, we estimated a mean value of the ion concentration since c_{ox} decreases by increase of the sweep rate within the same order of magnitude, indicating that the SiO₂ film close to the Cu electrode behaves as a concentrated solution. Note, the capacitively stored charge $Q_C \approx 10^{-10}$ C for $V = 2$ V and $C_{\text{cell}} \approx 100$ pF is insignificant compared to Q_{ox} . Using Eq. (1) we calculated a diffusion coefficient $D_{\text{ox}} \approx 2 \cdot 10^{-13}$ cm²/s at room temperature. The mobility of Cu²⁺ can now be estimated using the Nernst-Einstein relation

$$\mu = \frac{D_{\text{ox}} z e}{k_B T} \approx 7.8 \cdot 10^{-12} \text{ cm}^2/\text{Vs}. \quad (2)$$

Compared to extrapolated diffusion coefficients of Cu ions in SiO₂ at room temperature which are too small to explain resistive switching in μs range or below, the values found in this study are significantly higher.^{7,10} In general, this may be contributed to a higher diffusion coefficient of oxidized Cu in the amorphous matrix of SiO₂ thin films as well as electrical field enhanced diffusion. A potential nano porous structure of our SiO₂ thin film may also increase Cu²⁺ mobility. However, the estimated ion mobility is still too small to explain fast switching below 10 μs. Hence, the existence of high ion conducting paths with small cross-section areas proposed in literature⁵ could be investigated by CV measurements using nanoscaled electrodes. Since we used the overall electrode area for estimation of the ion mobility these paths would drastically increase the mobility measured in our work. Moreover, further experiments are needed to

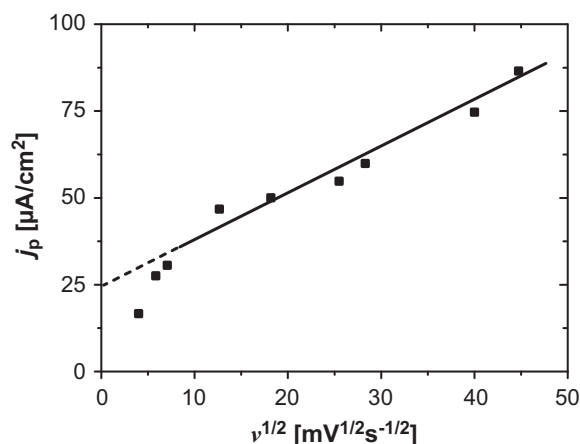


FIG. 3. Negative peak current j_p versus $v^{1/2}$. A linear relation of $j_p \sim v^{1/2}$ is observed which can be derived from the Randles-Sevcik equation.

elucidate the accompanying redox reaction at the Pt electrode^{9,11} as well as potential oxidation peaks at higher voltages or after special electrode pretreatment.

In conclusion, we report on the electrochemical kinetics of Cu oxidation at the Cu/SiO₂ interface. This observed oxidation is the initial stage of the resistive switching process.¹² Based on the analysis of the potentiodynamic experiments we estimated the diffusion coefficient and the Cu ion mobility which were found to be significantly higher than the values expected from literature. The results contribute to the understanding of the phenomena of resistive switching using very thin insulating materials as solid electrolytes.

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