Resistive Switching in $Ge_{0.3}Se_{0.7}$ Films by Means of Copper Ion Migration

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Dedicated to Prof. Dr. Konrad G. Weil on the occasion of his 80th birthday

Resistive Switching / Non-Volatile Memory / Chalcogenide Films / Ion Migration

$Cu/Ge_{0.3}Se_{0.7}/Pt$ cells were prepared and bipolar resistive switching in $Ge_{0.3}Se_{0.7}$ films by means of copper ion migration was examined. The cell was switched from the high to the low resistance state at about -50 mV, and it was switched back to the high resistance state at about 100 mV. The resistance ratio between the high and the low state was up to 200. Up to approximately 10^4 switching cycles were achieved. Pulse measurements showed that the two resistance states were tuneable by varying the applied voltage and the pulse length. Therefore, it is possible to store more than one bit per cell. The current density is independent of the electrode diameter, indicating that the cell can be scaled down to the range of nanometers. Due to the low switching voltages, non-destructive read out operation, high storage density, and scalability, such cells are promising for future memory applications.

1. Introduction

Chalcogenide materials are widely used in phase change memory devices [1, 2], two- and three-terminal switches [3–5] and electrochemical metallization memory devices [6]. Contrary to resistive switching in oxides such as NiO [7] or TiO_2 [8, 9], the switching in an electrochemical cell, consisting of an oxidizable electrode (Cu or Ag), an inert electrode (Pt), and a chalcogenide layer, altogether forming an electrochemical metallization memory, is known to be

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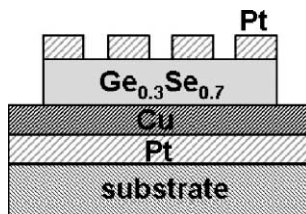* Corresponding author. E-mail: c.schindler@fz-juelich.de

Fig. 1. Schematic of the cell structure.

due to the migration of cations [6]. The migration of cations such as copper or silver ions in chalcogenide materials, such as Ge_xS_{1-x} [10], Ag_2S [11], CuS [3], and Ge_xSe_{1-x} [12], is sufficiently fast even at room temperature. A metallic conductive path connecting the oxidizable and the inert electrode can be established by applying a positive voltage to the oxidizable electrode. Due to the electric field, metal ions move through the chalcogenide layer and are reduced at the inert electrode. Therefore, a metallic path grows continuously from the inert electrode to the oxidizable electrode until a conductive connection is established. The conductive path can be dissolved by reversing the voltage polarity. Kozicki and co-workers [6] demonstrated that a Ag/Ag-Ge-Se/Pt cell can be switched on/off in less than 100 ns. Scalability down to the atomic level was demonstrated by Aono and co-workers [11]. Electrochemical metallization memory devices show excellent retention, true non-volatility, and high scalability. Such memories would merge the advantages of today's DRAM and mass storage devices, while removing the drawbacks.

Until now, mainly silver was used as mobile ion species in Ge_xSe_{1-x}. In this work cells consisting of an oxidizable copper electrode, $Ge_{0.3}Se_{0.7}$, and an inert platinum electrode were examined. Different $Ge_{0.3}Se_{0.7}$ deposition processes were tested and the cells showed promising results; even for large electrode areas, they allowed resistive switching for approximately 10^4 cycles with switching voltages as low as ± 100 mV and currents in the µA range.

2. Experimental

$Cu/Ge_{0.3}Se_{0.7}/Pt$ cells as shown in Fig. 1 were prepared according to the following procedure. Firstly, a 13 nm thick Cu bottom electrode was deposited on a platinized Si/SiO_2 wafer by radio frequency (rf) magnetron sputtering at a rate of 2.3 nm/s. Then, a 160 nm thick $Ge_{0.3}Se_{0.7}$ film was deposited onto the bottom electrode by rf magnetron sputtering at a rate of 0.37 nm/s. Afterwards, a 50 nm thick Pt top electrode was deposited by e-beam evaporation at a rate of 0.5 nm/s. The circular top electrodes with a diameter of 1130 µm, 500 µm, 250 µm, and 150 µm were structured by optical lithography (Karl Suess Maskaligner MA 6, photo resist AZ5214, Allresist) and a lift-off process
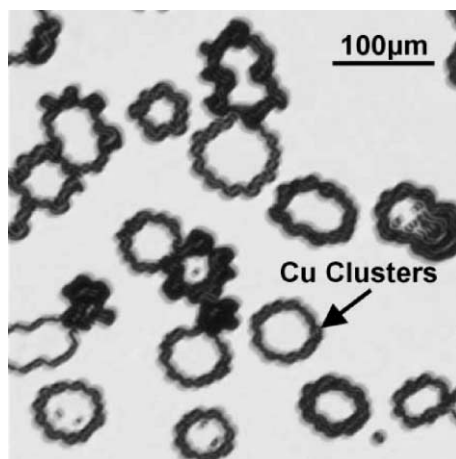
Fig. 2. Cu clusters on the surface of a 160 nm thick Ge$_{0.3}$Se$_{0.7}$ film under an optical microscope. The Ge$_{0.3}$Se$_{0.7}$ film was deposited on a 50 nm Cu layer.

in acetone and isopropanol. Current–voltage (I–V) measurements were performed by a Keithley 617 electrometer. In this work, a positive voltage when applied to the Pt electrode is defined as positive.

Ge$_{0.3}$Se$_{0.7}$ films usually allow easy diffusion of Cu^{2+} and Ag^{+} [15]. As shown in Fig. 2, after the Ge$_{0.3}$Se$_{0.7}$ deposition, Cu diffused in large amounts to the Ge$_{0.3}$Se$_{0.7}$ film surface even without further heat treatment or exposure to UV light. Kawaguchi and Maruno [16] observed similar Ag clusters in the case of Ag-As-S glasses, and assigned this cluster formation to a photoelectro-ionic reaction occurring in thermodynamically unstable glasses. In order to prevent the Cu diffusion, a diffusion barrier inside the Ge$_{0.3}$Se$_{0.7}$ film is necessary; therefore, a two-stage deposition process was used. Initially, a 50 nm thick Ge$_{0.3}$Se$_{0.7}$ layer was deposited, then the chalcogenide film was left to ambient atmosphere, allowing the formation of a GeO$_2$ layer. The oxide layer serves as diffusion barrier layer. Afterwards, another 110 nm thick Ge$_{0.3}$Se$_{0.7}$ layer was sputtered on top. The Ge$_{0.3}$Se$_{0.7}$ film thus prepared was amorphous, as demonstrated by X-ray diffraction analysis. The mean surface roughness was measured by atomic force microscopy (PicoStation, *Surface Imaging Systems*) to be $\sim$ 1 nm.

The formation of an oxide layer was verified by X-ray photoelectron spectroscopy (XPS) (Fig. 3). XPS measurements were performed on a fresh and an exposed Ge$_{0.3}$Se$_{0.7}$ sample using a PE XPS 5600 (Physical Electronics, USA) equipped with a monochromatic Alkα radiation source. Spectra were corrected for charging by shifting the Se 3d5/2 peak to the reference value of GeSe (54.5 eV). Figure 3a shows the Se3d peak for both samples. The exposed surface induces a slightly broader peak for Se, which is due to different charging
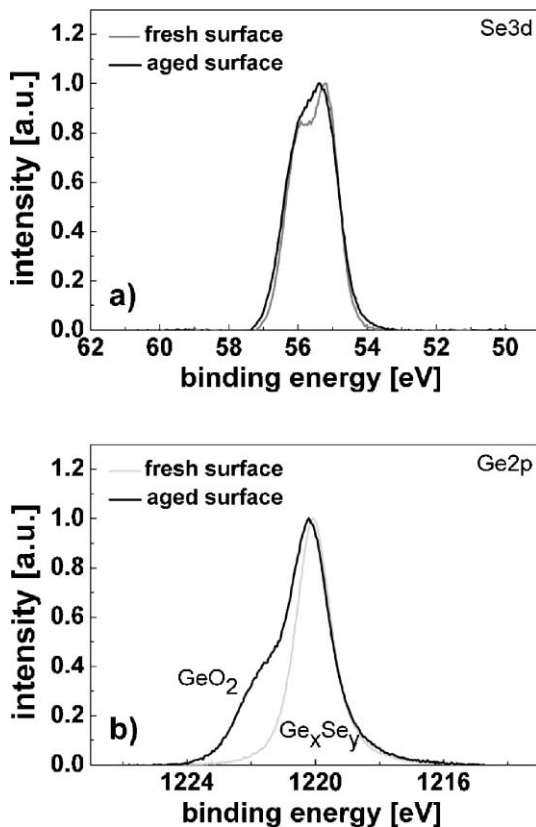
Fig. 3. XPS spectra of a Ge$_{0.3}$Se$_{0.7}$ film before and after exposure to ambient atmosphere. a) Se 3d peak, no obvious difference between both samples; b) Ge 2p peak, GeO$_2$ was formed on the film surface.

conditions and therefore a broader energy distribution of the emitted photo-electrons. A clear difference is detected for the Ge 2p peak, which is shown in Fig. 3b. Exposure to ambient atmosphere results in the formation of GeO$_2$; this is evident from the additional peak at 1220.7 eV.

3. Results and discussion

An as-deposited cell was initially in a high resistance state. By applying a nega-tive bias voltage to the cell (*i.e.* a positive bias to the Cu electrode), the cell was switched to a low resistance state. By reversing the bias polarity, the cell was switched back to the high resistance state. To determine the switching voltage, the applied voltage was increased stepwise at a rate of 10 mV/0.3 s between
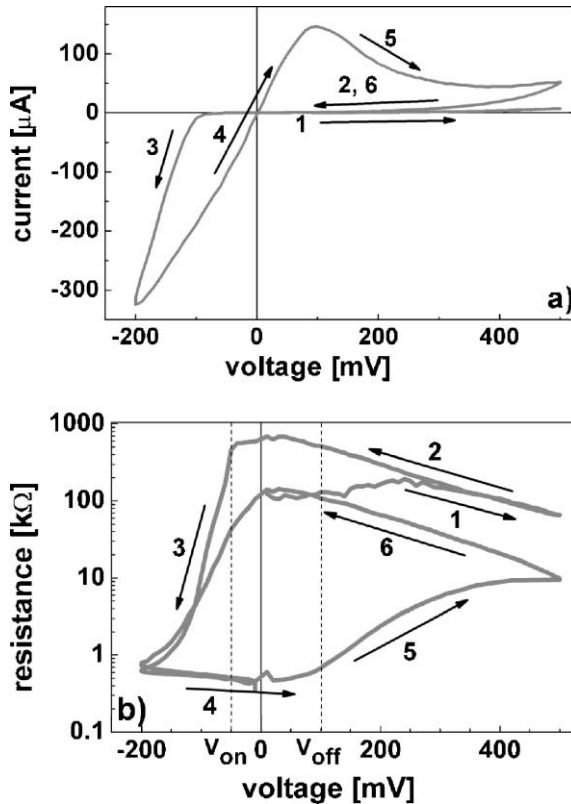
Fig. 4. a) *I–V* curve measured on a Pt top electrode with a diameter of 500 μm. The voltage was increased stepwise at a rate of 10 mV/0.3 s starting from 0V; and b) the corresponding *R–V* curve and the difference between the initial film resistance (arrow 1/2) and the OFF-resistance (arrow 6).

−200 mV and 500 mV. As can be seen in Fig. 4, the cell was switched from the high to the low resistance state (OFF to ON) at about −50 mV, and from the low to the high resistance state (ON to OFF) at about 100 mV. Resistive switching was achieved for approximately 10^4 cycles. A resistance ratio between the high and low resistance state of ∼ 200 was obtained at a read-out voltage of 10 mV. It has to be noted that the OFF-resistance is lower than the initial film resistance, as indicated in Fig. 4b, suggesting that Cu had diffused into the Ge$_{0.3}$Se$_{0.7}$ film and remained there even after switching to the OFF-state.

The resistance states did not change abruptly but a gradual transition between the ON- and OFF-state was observed. This behaviour is different from what is reported in literature where a sudden transition between the two resistive states is described [6, 12]. The gradual transition between ON- and OFF-state might be due to more impurity incorporation during the deposi-
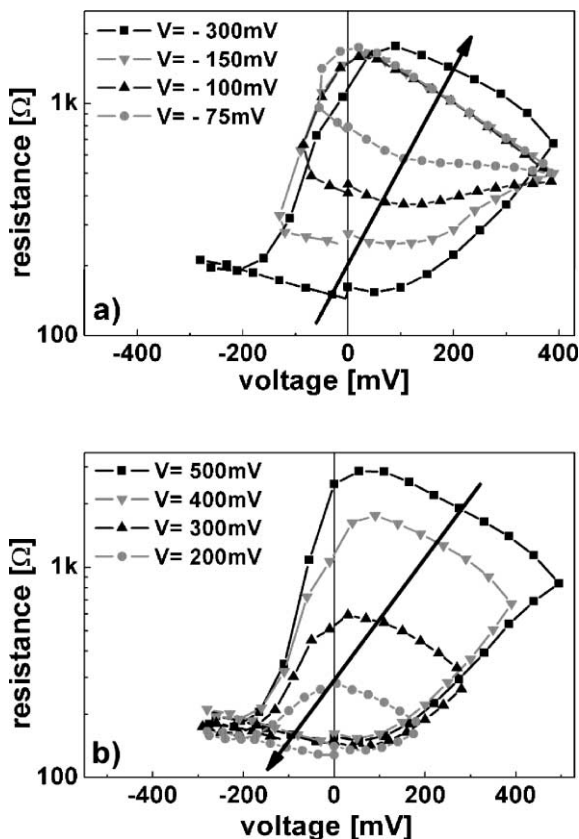
Fig. 5. a) Tunable ON-resistance and b) tunable OFF-resistance. The voltage, applied to a Pt top electrode with a diameter of 500 μm, is increased stepwise at a rate of 5 mV/0.3 s.

tion process and therefore a higher leakage. Figure 5 shows that the ON- and OFF-resistances are tuneable, as long as the switching voltage is varied within this gradual transition region between the ON- and OFF-states. By varying the maximum negative voltage, the ON-resistance decreased with increasing negative voltage, while the OFF-resistance remained almost constant (Fig. 5a). The OFF-resistance could also be tuned by varying the positive voltage applied to the Pt electrode (Fig. 5b). The tuneable ON- and OFF-resistances demonstrate that multiple bits can be stored in one cell. However, above a certain threshold voltage, *i.e.* as soon as the ON- or the OFF-resistance reached saturation, the resistances were not tuneable anymore.

If the voltage is increased gradually at a constant ramping time, it is not clear whether the tuneable ON- and OFF-resistances are due to the bias voltage or due to the time of the voltage application. Therefore, pulse meas-
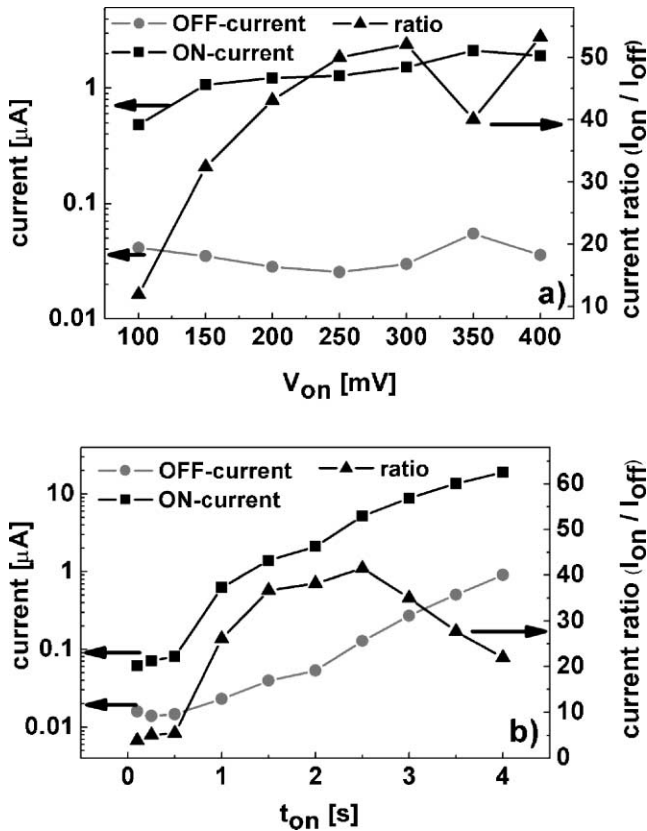
Fig. 6. Influence of a) V_{on} when $t_{on} = 1\,s$, and b) t_{on} when $V_{on} = -400\,mV$ on ON- and OFF-current and the corresponding current ratio. The fixed parameters are $V_{off} = 400\,mV$, $t_{off} = 5\,s$.

urements were performed with variable writing and erasing voltage (V_{on}, V_{off}) and variable writing and erasing time (t_{on}, t_{off}). The states were read out non-destructively at 10 mV for 5 s. It was shown that both factors, voltage and time, influence the ON- and OFF-currents as well as the current ratio or the corresponding resistance ratio. A higher V_{on} and a longer t_{on} result in a higher ON-current (I_{on}). The OFF-current (I_{off}) though stays nearly constant; hence the I_{on}/I_{off} ratio increases as shown in Fig. 6. In contrast, a higher V_{off} as well as a longer t_{off} leads to a decreased I_{off}. Now I_{on} remains constant, therefore the I_{on}/I_{off} ratio increases, as can be seen in Fig. 7.

It is believed that the formation and dissolution of metallic Cu paths between an oxidizable Cu and an inert Pt electrode are responsible for the switching behaviour shown in Figs. 4 to 7. Since switching to the OFF-state was not reflected by a steep but a gradual decrease in current, it is reasonably to assume
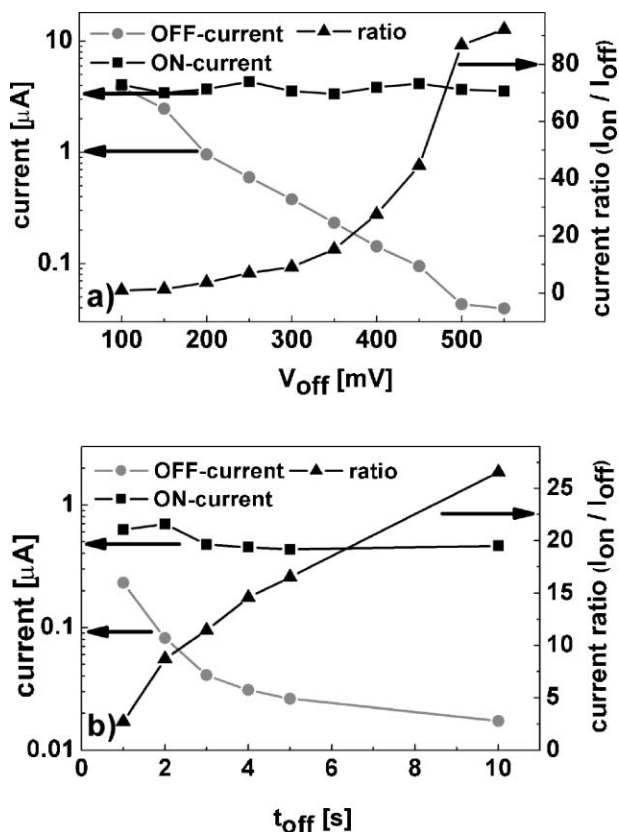
Fig. 7. Influence of a) V_{off} when $t_{off} = 5\,s$, and b) t_{off} when $V_{off} = 400\,mV$ on ON- and OFF-current and the corresponding current ratio. The fixed parameters are $V_{on} = -400\,mV$, $t_{on} = 1\,s$.

that the metallic paths between the electrodes are not completely dissolved but weakened, and some of the metallic Cu paths remain in the $Ge_{0.3}Se_{0.7}$ film. One sign confirming this assumption is that the OFF-resistance is lower than the high resistance of the as-deposited film. $Ge_{0.3}Se_{0.7}$ was deposited on a thin Cu layer, but since no special doping step such as heat treatment or UV exposure was performed, the film was not saturated with Cu. This is evident from the different initial and following OFF-resistance and by the tuneable ON- and OFF-resistances. The longer V_{on} is applied, the more Cu can diffuse into the $Ge_{0.3}Se_{0.7}$ film and strengthen the conductive paths. The following I_{on} is therefore dependent on t_{on}. It becomes independent of t_{on} after Cu saturation in the $Ge_{0.3}Se_{0.7}$ film is reached. Equivalently, I_{off} depends on t_{off} as long as Cu remains in the $Ge_{0.3}Se_{0.7}$ film and the weakened conductive paths can be tuned.
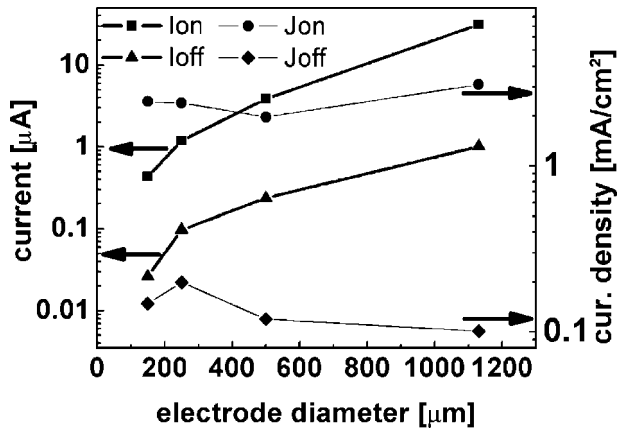
Fig. 8. Electrode size-dependence of the ON- and OFF-current. The switching parameters were set to $V_{on} = -400\,\mathrm{mV}$, $V_{off} = 400\,\mathrm{mV}$, $t_{on} = 1\,\mathrm{s}$, $t_{off} = 5\,\mathrm{s}$, $V_{read} = 10\,\mathrm{mV}$, $t_{read} = 5\,\mathrm{s}$.

The currents I_{on} and I_{off} are electrode size-dependent. The larger the electrode is, the higher are I_{on} and I_{off}, as illustrated in Fig. 8. As the resistance switching in Ge$_{0.3}$Se$_{0.7}$ can be explained by the formation and dissolution of metallic paths between the electrodes, a larger electrode area might allow the formation of more conductive paths, which, when connected in parallel, decreases the overall resistance. Another explanation for the electrode size dependence of I_{on} and I_{off} might be the leakage current, which contributes to the current in both states. Even in case of only one metallic path between bottom and top electrode, an electrode size dependence of I_{on} and I_{off} could be observed, because the leakage current scales with the electrode area. However, the current densities in the ON- an OFF-state, J_{on} and J_{off}, are almost independent of the electrode diameter. This feature is very promising for down-scaling the switching device to the nano-scale, because it implies that resistive switching in Ge$_{0.3}$Se$_{0.7}$ thin films will be possible even for very small electrode areas.

4. Conclusion

Bipolar resistive switching in Ge$_{0.3}$Se$_{0.7}$ films by means of copper ion migration between Pt and Cu electrodes was demonstrated. To prevent Cu diffusion from the bottom electrode to the film surface, Ge$_{0.3}$Se$_{0.7}$ was deposited in two runs with an oxide layer in between. Initially, the Ge$_{0.3}$Se$_{0.7}$ film was in a high resistance state. By applying a negative voltage to the Pt electrode, the Ge$_{0.3}$Se$_{0.7}$ film was switched to a low resistance state (ON). The film was switched back to a high resistance state (OFF) by reversing the voltage polarity. Resistance ratios up to 200 were obtained, and non-destructive read-out was achieved by

applying a voltage smaller than the switching voltage, *e.g.* 10 mV. Tuning the ON-resistance whilst keeping a constant OFF-resistance was realized by varying the negative voltage pulse applied to the Pt electrode. The OFF-resistance was tuned by varying the positive voltage pulse applied to the inert electrode.

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