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Journal:	*2011 MRS Spring Meeting*
Manuscript ID:	Draft
Manuscript Type:	Symposium K
Date Submitted by the Author:	n/a
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Keywords:	ionic conductor, memory, Ag

Probing of Ag-based Resistive Switching on the Nanoscale

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ABSTRACT

We study the switching characteristics of nanoscale junctions between a metallic tip and a silver film covered by a thin Ag_2S ionic conductor layer. Resistive switching phenomena are studied on samples of various Ag_2S layer thicknesses. Metallic and semiconductor behavior are distinguished by current-voltage characteristics measured at room temperature and at 4.2 K.

INTRODUCTION

Memristive systems based on solid state ionic conductors are good candidates for the next generation of nonvolatile computer memory elements [1-3]. Pushing the limits of device fabrication to further increase the speed and integration, electrical characterization becomes important in order to ensure the control of the device parameters.

The ionic conductor Ag_2S has already proven to be a promising compound for novel nanoelectronic circuits [4,5]. The operation is based on the electrochemical reaction $Ag^+_{(Ag_2S)} + e^- \Leftrightarrow Ag_{(metal)}$ controlled by the bias voltage, i.e. metallic silver is dissolved or retracted from the Ag_2S. Depending on the polarity, Ag metallic filaments are built up or destructed thus the resistance of the junction can be tuned in a reversible manner [6-8]. The Ag^+ ionic migration is effectively stopped at zero bias even at room temperature resulting in a nonvolatile operation. Due to the bipolar switching of this system, memory elements based on Ag_2S are often presented as a realization of the memristor, the circuit element first proposed by L. Chua [9].

EXPERIMENTAL DETAILS AND SAMPLE CHARACTERIZATION

Sample preparation and characterization

Ag thin films with a nominal thickness of 80 nm were vacuum evaporated onto a Si substrate. The thin Ag_2S layer was grown by depositing sulfur onto the Ag surface in a clean environment. First, analytic grade sulfur powder was loaded in a quartz tube, melted and cooled back in order to ensure a homogenous source. The thin film sample was then loaded in the tube to a distance of 2 cm from the sulfur. After loading both the sulfur and the sample, the tube was evacuated to 10^{-5} mbar. Then the temperature was ramped up to T=60°C and the sublimation of the sulfur was performed in a static vacuum for a designated time t_S. Finally, the temperature was rapidly ramped down.

The samples were characterized by He-RBS (Rutherford Backscattering Spectrometry) and ERDA (Elastic Recoil Detection Analysis). The RBS and ERDA experiments were performed using an ion beam of 1620 keV $^4He^+$ simultaneously at a tilt, recoil and scattering angles of 80°, 20° and 165°, respectively. An ion current of typically 4-8 nA was measured by a transmission Faraday cup [10].

The concentration profiles determined from the acquired spectra by the RBX code [11] are presented in figure 1 for three samples containing various sulfur content. In case of the sample prepared with t_S=20 min exposure time the sulfur penetrated the entire Ag thin film resulting in a stoichiometric Ag_2S compound [figure 1 (a)]. Samples with shorter sulfur exposure (t_S=10 min and 2.5 min) exhibit inhomogeneous profiles which is consistent with the presence of a surface layer of Ag_2S. The blurred Ag-Si boundary which clearly exceeds the uncertainties of the RBS analysis is attributed to the textured surface of the Ag_2S layer on top, often observed in earlier experimental works [8,12].

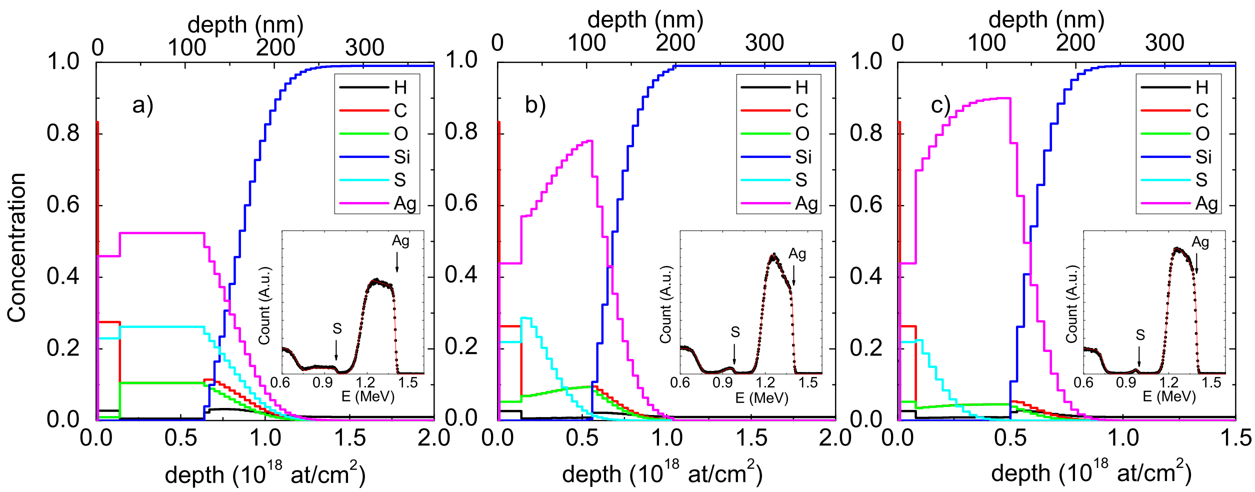

Figure 1. Concentration profiles of the samples of various sulfur exposure times, t_S, based on the RBS and ERD measurements. Note that the penetration depth in nm is calculated assuming a homogeneous Ag_2S layer with a atomic density of 5.27×10^{22} cm^{-3}. Inset shows the corresponding RBS spectra (circle) and simulation (line) at a tilt angle of 60°. The exposure times are t_S=20 min (a), t_S=10 min (b), t_S=2.5 min (c), respectively.

Experimental setup

Nanoscale contacts were created by gently touching the sample surface with a mechanically sharpened PtIr tip. For coarse adjustment a screw thread mechanism was used, whereas for the fine positioning a 3D piezo actuator was applied. Numerous contacts were created and the features of the I-V curves shown later were well reproducible. Measurements were performed both at T=4.2 K and at T=300 K in order to demonstrate operation at low temperature and room temperature environments as well.

All of the contacts were characterized by I-V curve measurements. The bias voltage was applied to the junctions utilizing a National Instruments data acquisition card. The output voltage is divided and filtered in order to ensure low noise on the contact. The current was measured using a variable range I-V converter and then processed by the data acquisition card. The current-voltage characteristics of the junctions were taken by a linearly ramped voltage. A full cycle was recorded in 400 ms. The on- and off-state resistances R_{ON} and R_{OFF} were measured in a narrow voltage window of 50 mV around zero bias.

RESULTS

By tuning the sulfurization parameters, the transport through the thin film junction dramatically varies, which is apparent both at low bias voltage (i.e. well below the switching threshold voltage) and also in the high bias switching characteristics.

The samples prepared with the longest sulfurization time were not conducting. For t_S=10 min the junctions showed a Schottky barrier character, which is attributed to the intrinsic semiconducting behavior of the Ag_2S layer on the top of the Ag thin film. For samples of shorter exposure t_S=2.5 min, however, a reproducible metallic character was found with a linear I-V curves of the junctions at low bias.

First we present measurements performed on a sample exposed to the sulfur atmosphere for a t_S=10 min and then turn to the characterization of the sample with an exposure time of 2.5 min.

Semiconducting regime

Typical I-V curves acquired at room temperature are shown in figure 2. A highly nonlinear steady state behavior is found when the amplitude of the bias voltage is kept below about 100 mV [figure 2 (a)]. This resembles a Schottky diode behavior, which is consistent with earlier reports on semiconducting junctions [7,12]. The nonlinearity has been attributed to the Ag^+ ionic migration causing a dynamic doping of the Ag_2S layer, which is reflected in an opposite curvature compared to the conventional Schottky diode behavior for a metal – n type semiconductor junction [12].

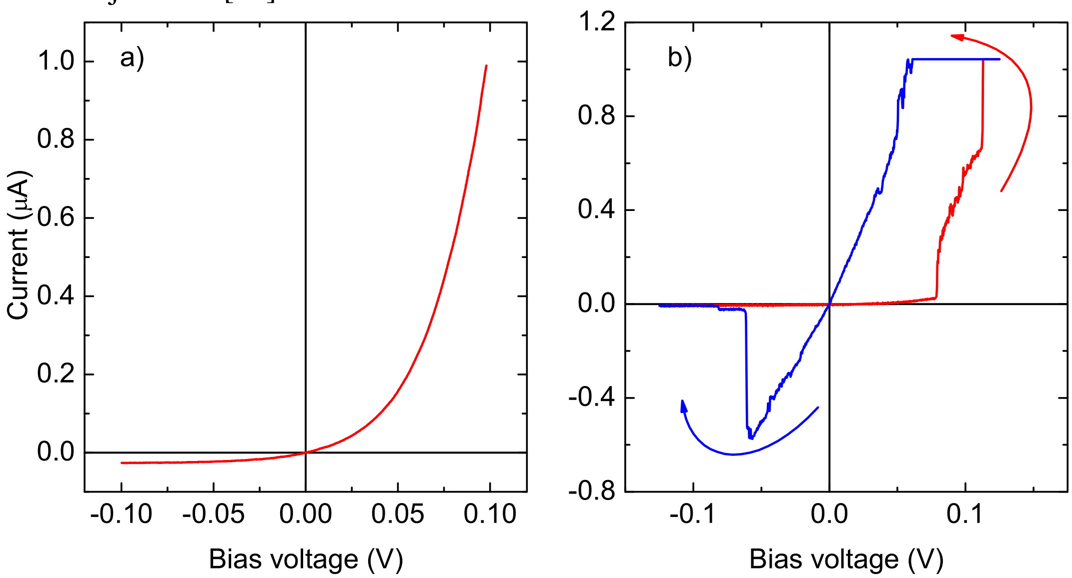

Figure 2. Typical I-V curves measured at room temperature on the sample of t_S=10 min sulfur exposure time. a) The nonlinear I-V curve recorded below the switching threshold. b) Bipolar switching curve recorded after numerous switching cycles. The OFF-ON transition is limited by the current compliance set to 1 μA.

For voltage ramps exceeding V_{max}=100 mV resistive switching was observed appearing abruptly while the bias amplitude is tuned [figure 2 (b)]. This type of junction became insulating at liquid helium temperature. All the above observations are in good agreement with the results of earlier studies [7,8,12].

Metallic regime

Samples of thinner Ag_2S layer exhibited linear I-V characteristics at low bias. For these samples the ohmic conductance of the junctions provides the possibility to estimate the junction diameter from the on-state conductance using the Wexler equation [13]. The typical lateral size of the junctions is between 10 nm and 100 nm.

The metallic character of these junctions is well demonstrated by the same switching character observed at room temperature and at liquid helium temperature (figure 3). Such superior temperature stability has not been found in earlier studies on Ag_2S-based resistive switches.

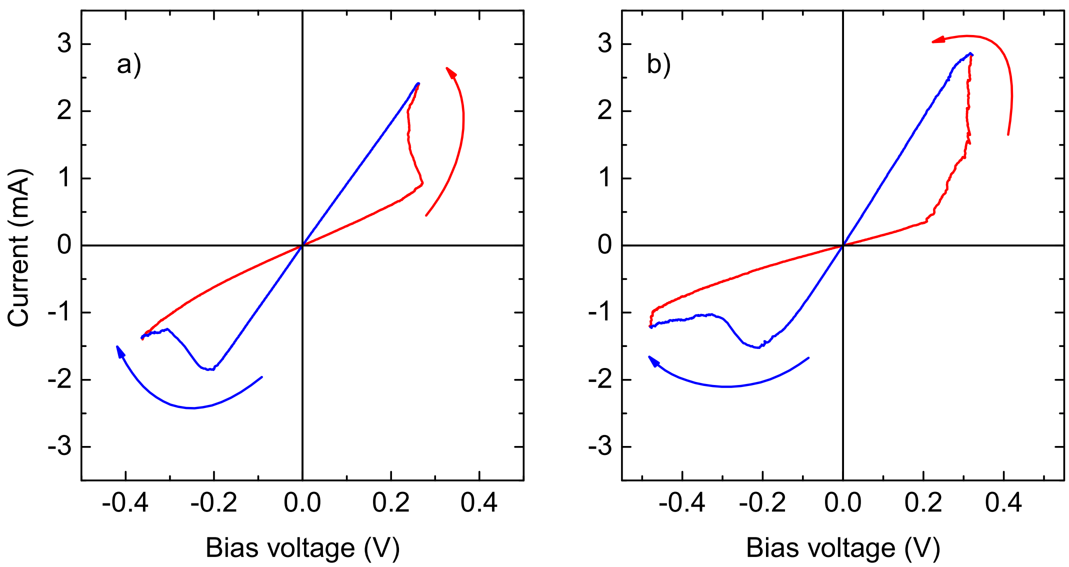

Figure 3. Typical I-V curves for the sample of t_S=2.5 min sulfur exposure time taken at T=4.2 K (a) and T=300 K (b), respectively.

We have also investigated the smooth tuning of the on- and off-state resistance [14]. The results are shown in figure 4. Consistently with the migration of the Ag^+ ions in the ionic conductor layer, both R_{ON} and R_{OFF} were altered considerably by the amplitude of the bias voltage [figure 4 (a)]. The ratio R_{OFF}/R_{ON} increases up to 16 at bias ramp amplitude of about 0.5 V [figure 4(b)], which is feasible for technical applications.

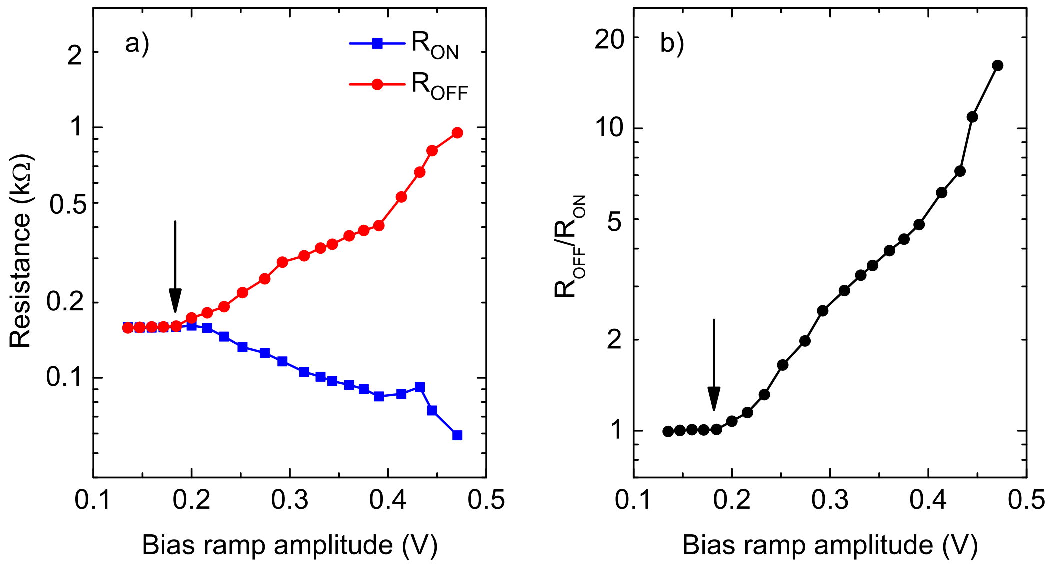

Figure 4. a) Evolution of the on- and off-state resistance as a function of the bias ramp amplitude for the sample of t_S=2.5 min sulfur exposure time. b) The on-off resistance ratio as a function of the amplitude on the same junction. The arrows show the onset of the resistive switching at 0.18V.

CONCLUSIONS

In conclusion we investigated the switching characteristics of nanoscale junctions created between a thin Ag_2S mixed conductor layer and a PtIr tip. By separating the metallic and semiconductor behavior, we demonstrated the impact of the sulfur deposition time on the device parameters. In contrast to the strong temperature dependence of the semiconducting Ag_2S layer, for metallic junctions no apparent variation of the switching character was found between room temperature and 4.2 K. For these junctions the smooth tuning of the on and off states was demonstrated as opposed to the abrupt change for the semiconducting sample. The temperature stability and the ohmic behavior of the metallic junctions make them feasible for technical applications.

ACKNOWLEDGMENTS

This work was supported by the New Hungary Development Plan under project ID: TAMOP-4.2.1/B-09/1/KMR-2010-0002 and by the Hungarian Research Funds OTKA under grants No. 72916 and No. 76010. RBS and ERDA experiments were supported by the Hungarian Ion-beam Physics Platform. A. H. is a grantee of the Bolyai Janos scholarship.

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