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Effects of temperature and ambient pressure on the resistive switching behaviour of polymer-based atomic switches

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Current-voltage measurements demonstrated the effects of temperature on the resistive switching behavior of a gapless-type atomic switch based on a silver-ion-conductive solid polymer electrolyte (SPE) consisting of a mixture of polyethylene oxide (PEO) and AgClO₄. The operation voltages decreased in magnitude with increased ambient temperature. The reduction of the operation voltages can be explained by the increased conductivity of silver ions in the amorphous PEO-salt complex region of the SPE film. This situation is completely different from a cell with a pure PEO film, in which the increased crystallinity of the PEO film may hinder ionic conductivity, although similar switching behavior was observed. It was also found that cells based on SPE and PEO show different behaviors under air and vacuum conditions. This is probably associated with different water uptakes from the ambient surrounding by the SPE and PEO films. The results suggest the importance of the crystallinity and water uptake ability of matrix polymer film on the resistive switching characteristics.

1. Introduction

Resistive random access memories (RRAM) based on organic materials have recently become an attractive research topic due to their superior characteristics, such as excellent mechanical strength, compatibility with flexible substrates, and the possibility of low-cost fabrication using printing and coating techniques.^{1,2} Of the various types of organic RRAMs, electrochemical switching memory cells, based on the formation and dissolution of a metal filament in an organic thin film, possess unique advantages in the areas of ON/OFF resistance ratios, retention times, and write/erase speeds, which makes them attractive for practical applications.³⁻⁵ These cells consist of a simple metal/ionic conductor/metal (MIM) structure, in which a thin organic film is sandwiched between an electrochemically active metal electrode (usually Ag or Cu) and an inert metal electrode (such as Pt, Au, or W). When an alternative bias voltage is applied, a metal filament is formed and dissolved in the organic film between the two electrodes, resulting in a transition between a low-resistance (ON) state and a high-resistance (OFF) state. Due to its similarity to the switching mechanism of a 'gap-type atomic switch', in which resistance across a nanometer gap is controlled by the formation and annihilation of a metal bridge between an electrolyte electrode and an inert metal electrode,⁶ the MIM-structured cell can itself be referred to as a 'gapless-type

atomic switch'.⁷ So far, gapless-type atomic switches have mostly been realized with inorganic materials such as chalcogenides (Ag₂S, Cu₂S),^{8,9} metal oxides (SiO₂, Ta₂O₅),^{10,11} and super ionic conductors (AgI).¹²

Several years ago, we demonstrated that an atomic switch can be realized in a MIM structure using a silver-ion-conductive solid polymer electrolyte (SPE).¹³ An Ag/SPE/Pt cell, fabricated with a mixture of poly(ethylene oxide) (PEO) and Ag salt (AgClO₄), showed bipolar resistive switching under bias voltage sweeping. The cell was SET from the OFF state to the ON state in positive bias relative to the Ag electrode, and RESET from the ON state to the OFF state in negative bias.¹⁴ The observed switching was attributed to the formation and dissolution of a metal filament formed in the SPE film. We also successfully fabricated cross-point structured cells, with a junction size of 50 μm, on a plastic substrate using an inkjet-printed SPE film.^{15,16} The fabricated cells showed stable switching behaviour under substrate bending, which indicates their great potential for flexible switch/memory applications.

Since switching behaviour is based on electrochemical reactions and ion transport, one can expect that the switching parameters, such as the SET and RESET voltages, should be ambient temperature-dependent. In this paper, the current-voltage (*I-V*) measurements of an Ag/SPE/Pt atomic switch, at varying ambient temperatures, are reported to determine the validity of our switching model and to obtain deeper insights into the switching mechanism. For comparison, the *I-V* characteristics of an Ag/PEO/Pt cell, fabricated by the same method, were examined and compared with the results of the Ag/SPE/Pt cell. It is well known that the ionic conductivity of SPE is enhanced by water absorption from the ambient surroundings.^{17,18} Here, measurements were performed under air

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and vacuum conditions in order to investigate the effect on the switching behaviour of water uptake by the polymer film.

II. Experimental section

Ag/SPE/Pt and Ag/PEO/Pt cells were fabricated on polyethylene naphthalate (PEN) substrates. First, 5-nm-thick Ti and 30-nm-thick Pt were deposited as the adhesion layer and bottom electrode (BE) on a PEN substrate by electron beam (EB) deposition with a metal mask. Then, a film of SPE or PEO was formed on the Pt BE using an inkjet printing method. PEO with a molecular weight of 20,000 was dissolved in an acetonitrile solution, with the SPE solution including 3 wt% of AgClO_4 relative to the PEO. Finally, 80-nm-thick Ag was deposited onto the SPE or PEO film as the top electrode (TE) using EB deposition with another metal mask with a different pattern. Details of the cell fabrication process were described in a previous report.¹⁵ Each cell had a cross-point structure, with a junction area of $50 \mu\text{m} \times 50 \mu\text{m}$. Figure 1a shows an optical microscope image of the fabricated cell. From atomic force microscopy (AFM) measurements, the thickness of the SPE and PEO films was estimated to be 200 ~ 400 nm,¹⁵ as illustrated schematically by a cross section of the cell in Fig. 1b.

I - V measurements of the cells were performed in air (with a relative humidity of 30 ~ 40 %) and in vacuum ($\sim 10^{-3}$ Pa) conditions over a certain temperature range. A home-made prober was used for the measurements in air. The prober has a heater stage that can operate over a range of temperatures between room temperature and 70 °C, and was equipped with a source/measure unit (Agilent 2901B). The measurements in vacuum were carried out using a high-vacuum prober, which can operate over a wider temperature range (-60 ~ 70 °C) and which was equipped with a semiconductor characterization system (Keithley 4200SCS). A bias voltage was applied to the Ag TE, and the Pt BE was electrically grounded in all of the measurements. To regulate the ON-state current, the current

compliance was set to 10 ~ 100 μA for the positive bias polarity. In all the measurements, the forming process (the first SET operation from the initial state to the ON state) was made at room temperature, and the I - V measurements were then performed from the lowest temperature to higher temperature.

To investigate the thermal properties of PEO and SPE films, differential scanning calorimetry (DSC) measurements were carried out using a Hitachi HT-Seiko Instrument SII Exster X-DSC7000. Al_2O_3 was used as a reference material. The DSC curves were obtained in a cooling and heating cycle (from room temperature to -100 °C and then -100 to 200 °C) with a constant cooling/heating rate of 10 °C/min.

III. Results

Figure 2 shows typical I - V curves of the Ag/SPE/Pt cell at temperature ranges of -40 to 0 °C (a) and 20 to 60 °C (b) in increments of 20 °C, which were measured in a $\sim 10^{-3}$ Pa vacuum. The current compliance was set at 10 μA . Here, we show the results obtained in vacuum to discuss the variation of the switching behaviour in a wider temperature range, but almost the same switching characteristics were observed in both air and vacuum.^{15,16} The cell exhibited bipolar switching behaviour at all the temperatures used (except for 70 °C). According to our previous work,¹³ the SET and RESET processes are attributed to the formation and dissolution of a metal filament between the electrodes due to the transport of Ag^+ ions through the SPE film and nucleation of Ag on the Pt BE, as schematically illustrated in Fig. 2b. Below -40 °C, the cell required a higher bias voltage for the SET operation,

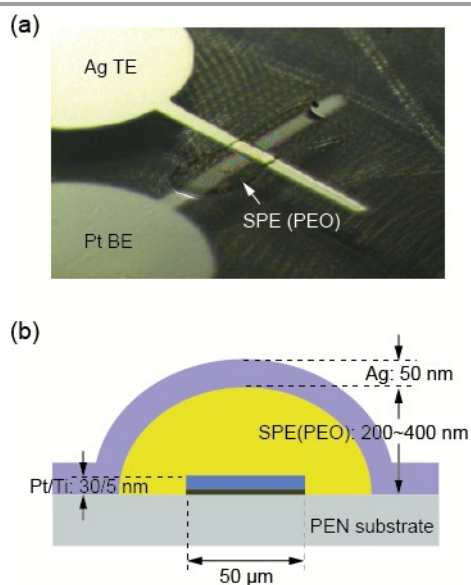


Fig. 1 Optical microphotographs of an Ag/SPE/Pt cell fabricated on a PEN substrate (a) and a schematic illustration of a cross-section of the cell (b).

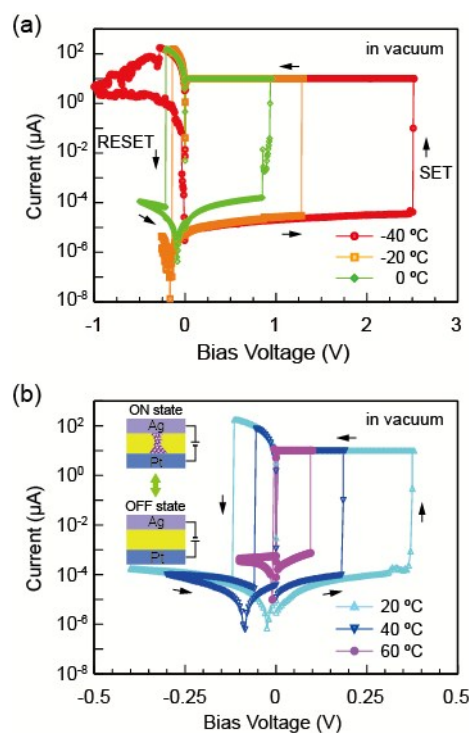


Fig. 2 Typical I - V curves of an Ag/SPE/Pt cell measured in temperature ranges of -40 to 0 °C (a) 20 to 60 °C (b). All the curves were taken in vacuum.

while it was difficult to RESET the cell sharply, as shown by the red curve in Fig. 2a. As the ambient temperature increased, the SET and RESET voltages required decreased in magnitude. Up to 60 °C, the cell showed very stable switching behaviour with lowering of the SET and RESET voltages. Finally, at 70 °C, the SET voltage became very small and the cell was RESET before the bias voltage was swept back to 0 V, showing volatile switching behaviour.

Figure 3a plots the SET (red squares) and RESET (blue squares) voltages of the Ag/SPE/Pt cell for the temperature range observed. The data were collected from ten cells at each temperature. It is clearly observed that the SET and RESET voltages decreased in magnitude with increasing ambient temperature. This temperature behaviour is almost identical to that observed for a Cu/Ta₂O₅/Pt atomic switch,¹⁹ indicating that the switching mechanism of SPE-based cells is almost the same as in oxide-based atomic switches. The corresponding ON (red squares) and OFF (blue squares) resistances are plotted in Fig. 3b. The ON resistance was in a range of between a few hundred Ω to several kΩ, while the OFF resistance was around 10⁹ Ω. The resultant ON/OFF resistance ratio was ~10⁶ up to 40 °C. Above 40 °C, the OFF resistance decreased by more than one order of magnitude but the ON resistance was not changed, giving rise to a decrease of the ON/OFF resistance ratio.

We also measured the cell with a pure PEO film to investigate the impact of Ag salt on the switching behaviour. Figures 4a and 4b show typical *I-V* curves of the Ag/PEO/Pt cell for various ambient temperatures, measured in air and vacuum, respectively. Because the ON state could not be maintained with a compliance current of 10 μA, the *I-V* curves in Fig. 4a were obtained using a higher compliance current of 100 μA. Under these circumstances, bipolar

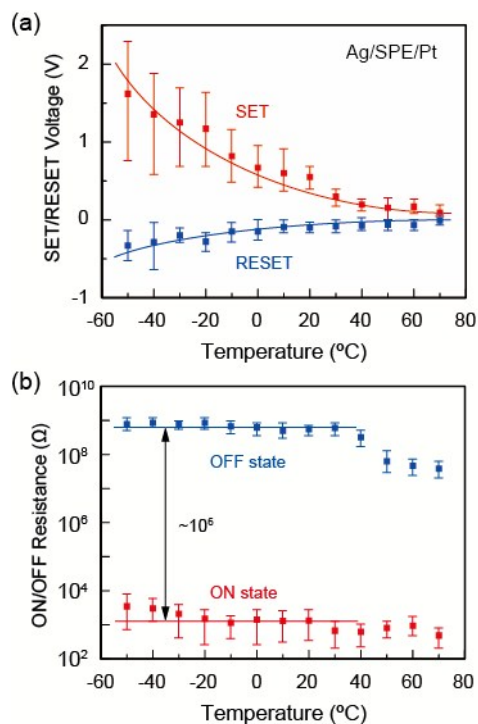


Fig. 3 (a) Temperature variations of the SET/RESET voltages (a) and the ON/OFF resistances (b) measured for the Ag/SPE/Pt cell.

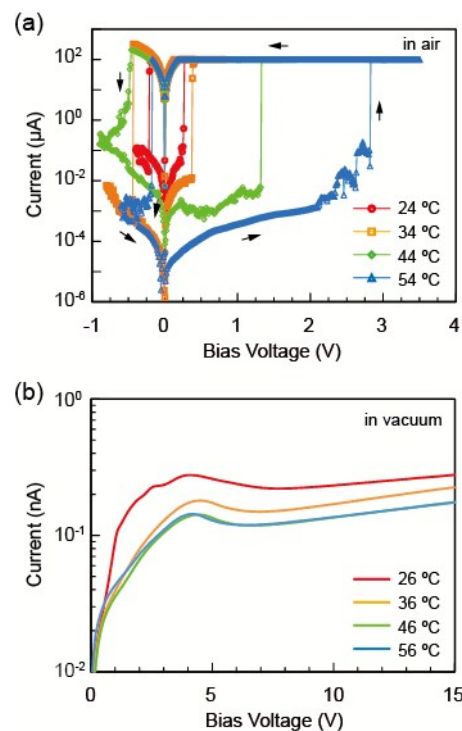


Fig. 4 Typical *I-V* curves of an Ag/PEO/Pt cell measured in a temperature range of 24 to 54 °C in air (a) and in vacuum (b).

switching was observed in a temperature range of from 24 to 54 °C, which shows that atomic switch operation is also possible in an Ag/PEO/Pt cell. Figure 5a plots the SET and RESET voltages of the Ag/PEO/Pt cell for the temperature range observed. Although the RESET voltage was almost independent of temperature, the SET voltage increased for higher temperatures. This temperature variation of the SET voltage is opposite to the tendency in Ag/SPE/Pt cells. The different temperature behaviours of the Ag/SPE/Pt and Ag/PEO/Pt cells suggest that an additional mechanism may be involved. The ON and OFF resistances were almost constant at 10³ ~ 10⁴ and 10⁷ ~ 10⁸ Ω, respectively, as shown in Fig. 5b. The ON/OFF resistance ratio was kept to around 10⁵ in the temperature range observed. The switching behaviour became unstable above 60 °C (not shown here). No resistive switching phenomenon occurred in vacuum, even if a bias voltage up to 15 V was applied, as shown in Fig. 4b.

IV. Discussion

PEO is a highly crystalline polymer, most of which is a crystalline phase, with a small amount in an amorphous phase.²⁰ When salt is dissolved in PEO, the resultant electrolyte has a rich phase behaviour that depends on temperature, salt concentration, and thermal history.²¹ Such SPEs generally contain more than one phase, such as the crystalline and amorphous pure PEO phases plus an amorphous PEO-salt complex phase.²² The thermal properties, such as T_g and the melting temperature (T_m), are determined by the phase state of the polymer. Figure 6 shows DSC curves measured for a pure PEO film and an SPE film with an AgClO₄ concentration of 3 wt%. Their 5 - 8 mg films were formed by drop casting into a petri dish

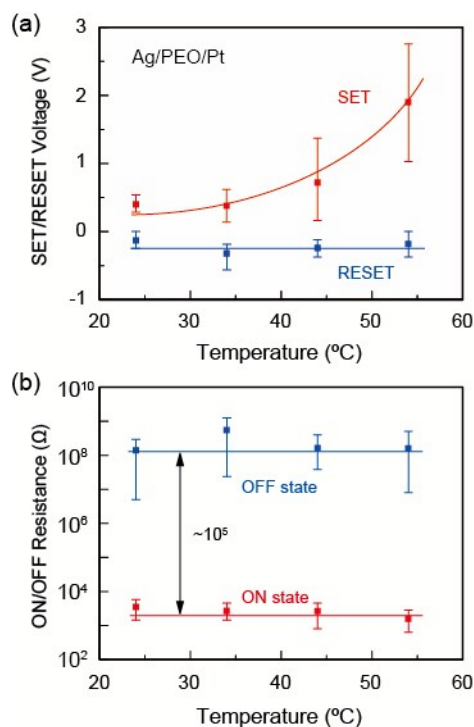


Fig. 5 Temperature variations of the SET/RESET voltages (a) and the ON/OFF resistances (b) measured for the Ag/PEO/Pt cell.

and drying in air, which were the same preparation conditions as used for the measured cells. The sharp endothermic peak observed at 67.5 °C corresponds to T_m of pure PEO. This peak shifted slightly to a lower temperature (65.4 °C) with the addition of 3 wt% Ag salt. The degree of crystallinity (X_c) of the polymer can be estimated by

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100, \quad (1)$$

where ΔH_m is the melting enthalpy of polymer calculated from the area of the endothermic peak, and ΔH_m^0 is the reference melting enthalpy of 100 % crystalline PEO (213.7 J/g).^{23,24} From the DSC curves, shown in Fig. 6, X_c was calculated to be 85.4 and 77.9 % for pure PEO and Ag salt incorporated PEO, respectively. Although the exact values of X_c may differ for thin films deposited onto Pt BE by the inkjet printing, it can be concluded that the film's crystallinity decreases with salt concentration, thus enhancing its amorphous nature.

The ionic conductivity in polymer electrolytes depends strongly on their crystallinity at a given temperature. At room temperature, the conductivity of pure PEO was found to be $\sim 10^{-9}$ S/cm, which increased by about two orders of magnitude with the introduction of 3 wt% Ag salt.¹³ As mentioned above, the crystallinity of the film is reduced to only 7.5 % with the inclusion of Ag salt, but the conductivity drastically changes with the phase variation of the polymer. For Ag/SPE/Pt cells, two kinds of Ag^+ ions can participate in the formation of a metal filament. One already exists in the SPE film, and the other is oxidized from the TE under positive bias. The transport of these Ag^+ ions preferentially occurs in the amorphous PEO-salt complex region, based on segmental polymer motion.²⁰ As the ambient temperature increases, the segmental polymer motions

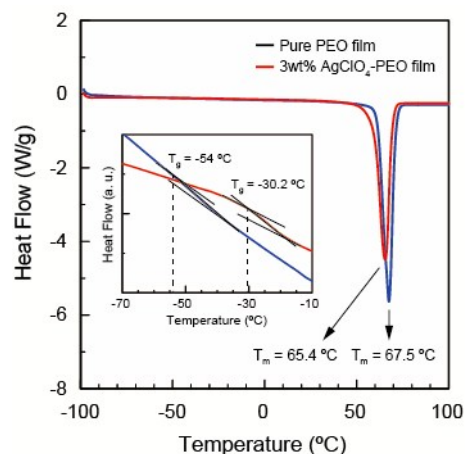


Fig. 6 DSC plots of pure PEO and 3 wt% AgClO_4 incorporated PEO films. The inset depicts a magnified view in the temperature range of between -70 and -10 °C, showing that T_g is determined by the onset of the transition.

are less affected by the structural relaxation around the melting temperature, due to the higher amorphous nature of the polymer electrolyte.²⁵ As a result, the ionic conductivity increases continuously with increased temperature, which was reported for a PEO- AgNO_3 SPE.²⁶ Thus, the reduction of the SET voltage at higher temperatures, as seen in Fig. 2, can be attributed to the increased conductivity of the Ag^+ ions in the amorphous PEO-salt complex region. The RESET voltage also decreases in magnitude, because the precipitated Ag atoms in the metal filament are easily dissolved at higher temperatures.¹⁹ Figure 2b shows that the OFF resistance decreased by about one order of magnitude above 40 °C. This may be due to an increased concentration of Ag^+ ions in the SPE film.

For the Ag/PEO/Pt cell, no Ag^+ ion exists in the matrix PEO film in the initial state. Ag^+ ions are injected from the TE into the amorphous region of the PEO film by anodic dissolution when positive bias is applied. Therefore, a higher compliance current is needed to inject more Ag^+ ions for the stable formation of a metal filament. The SET and RESET voltages were observed in almost the same range as in the Ag/SPE/Pt cell at room temperature. This result implies that the Ag^+ ions can transport through the amorphous region of PEO film in the same way as in the amorphous complex region of SPE film, and the switching mechanism seems to be identical to that shown in an Ag/SPE/Pt cell. However, the SET voltage increased with increased temperature, which is opposite to the tendency in the Ag/SPE/Pt cell. Recently, Money *et al.* reported that dc conductivity of a PEO film decreases dramatically below the melting temperature due to the formation of lamellar crystallites.²⁶ Growth of such spherulites increases the amount of the crystalline phase in PEO and severely restricts long-range ion diffusion, resulting in a decoupling of dc conductivity and structural relaxation. Figure 7 shows a typical AFM image measured for a PEO film deposited onto a Pt BE by inkjet printing. Lamella structures can be observed on the film surface, which indicates its highly crystalline nature. Thus, the increase in the SET voltages of the Ag/PEO/Pt cell can be attributed to the increased crystallinity induced by the formation of spherulitic structures. As the temperature approaches to T_m , the crystalline

portion of the PEO film starts to melt, resulting in the unstable switching behavior at temperatures above 60 °C. Note that SPE film deposited by the same method also exhibited lamella structures, which is due to its slightly decreased crystallinity (as shown in Fig. 1 of Ref. [15]). However, our results suggest that the existence of a PEO-salt complex phase plays a crucial role in the ionic conductivity and its temperature dependence of the polymer. Further investigation is needed to clarify the correlation between the structural relaxation of the polymer film and the switching behaviour.

The inset of Fig. 6 shows that T_g of pure PEO was observed at -54 °C and that it increased to -30.2 °C with the addition of 3 wt% Ag salt. The increase in T_g indicates a reduction in the flexibility of the polymer chains due to interaction between the ether oxygens and the Ag^+ ions, which decreases the ionic conductivity. The higher T_g of Ag salt incorporated PEO can explain the larger SET and RESET voltages of the Ag/SPE/Pt cell at -40 °C, as seen in Fig. 2a. As this temperature is lower than that for the T_g of SPE film, the matrix polymer loses mechanical flexibility and the conductivity of the Ag^+ ions significantly decreases, giving rise to larger SET and RESET voltages. Indeed, the cell no longer exhibited any switching behaviour at -60 °C, which is well below T_g .

To some extent, pure PEO absorbs water from the ambient atmosphere.¹⁷ It is also well known that as salts are dissolved in the polymer, its ability to take up water increases dramatically.²⁸ In general, water is absorbed in the amorphous phase but not in the crystalline phase. The ionic conductivity in the amorphous region increases significantly with water uptake, because water molecules reduce interaction between metal cations and ether groups in polymer chains, which results in faster diffusion and higher conductivity of metal cations in the polymer matrix.¹⁸ In the case of the Ag/SPE/Pt cell, the switching behaviour was observed both in air and in vacuum, but the SET voltage was lower in air (as shown in Fig. 3 of Ref. [15]). This can be attributed to the enhanced conductivity of Ag^+ ions in the amorphous PEO-salt complex region of the SPE film as a result of water uptake. In contrast, the Ag/PEO/Pt cell exhibited no resistive switching under vacuum conditions, as seen in Fig. 4b. This result suggests that water uptake in the PEO film affects the switching behaviour more significantly.

Water molecules absorbed in the amorphous region of pure PEO may desorb easily in vacuum, thus retarding the transport of Ag^+ ions and the anodic dissolution reaction at the Ag/PEO interface. Therefore, it is difficult for resistive switching of the Ag/PEO/Pt cell to take place under vacuum conditions. A similar phenomenon was observed in cells with inorganic oxide films, such as SiO_2 .²⁹ We are currently carrying out $I-V$ measurements under controlled humidity so as to elucidate the impact of water uptake by the polymer film on the switching characteristics.

V. Conclusions

The effects of temperature on the switching behaviour of Ag/SPE/Pt cells were investigated in comparison to Ag/PEO/Pt cells. Bipolar switching behaviour could be observed in both types of cell, which indicates that the atomic switch operation is possible with both SPE and PEO films. The SET and RESET processes are attributed to the formation and dissolution of a metal filament between the electrodes, based on the transport of Ag^+ ions and the nucleation of Ag in the amorphous region of the polymer film. The SET and RESET voltages of the Ag/SPE/Pt cell decreased in magnitude, while the SET voltage of the Ag/PEO/Pt cell increased with increased ambient temperature. The reduction in the SET and RESET voltages of the Ag/SPE/Pt cell can be explained by the increased conductivity of Ag^+ ions in the amorphous PEO-salt complex region of the SPE film at higher temperatures. In contrast, the increased SET voltage observed in the Ag/PEO/Pt cell may be attributed to the increased crystallinity of the PEO film below the melting temperature, which hinders Ag ion transport. The Ag/SPE/Pt cell exhibited stable switching, both in air and in vacuum, but no switching behaviour was observed for the Ag/PEO/Pt cell in vacuum. This can be explained by the different water uptakes of the SPE and PEO films. The results suggest the importance of the crystallinity and water uptake ability of the matrix polymer film on the switching behaviour.

Acknowledgements

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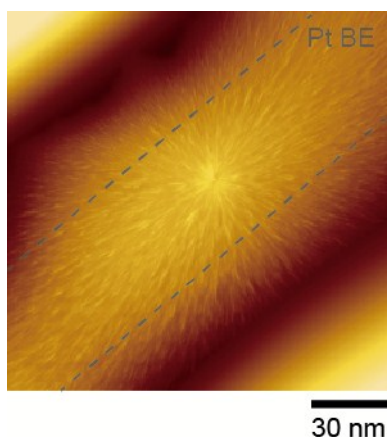


Fig. 7 Typical AFM image of a PEO film, deposited onto a Pt BE (indicated by the dashed lines) by inkjet printing, showing lamella structures.

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Effects of temperature and ambient pressure on the resistive switching behavior of electrochemical 'atomic switches' based on pure PEO and Ag-doped PEO were investigated.

