Flexible conductive-bridging random-access-memory cell vertically stacked with top Ag electrode, PEO, PVK, and bottom Pt electrode

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Abstract
Flexible conductive-bridging random-access-memory (RAM) cells were fabricated with a cross-bar memory cell stacked with a top Ag electrode, conductive polymer (poly(n-vinylcarbazole): PVK), electrolyte (polyethylene oxide: PEO), bottom Pt electrode, and flexible substrate (polyethersulfone: PES), exhibiting the bipolar switching behavior of resistive random access memory (ReRAM). The cell also exhibited bending-fatigue-free nonvolatile memory characteristics: i.e., a set voltage of 1.0 V, a reset voltage of \(-1.6\) V, retention time of \(>1 \times 10^5\) s with a memory margin of \(9.2 \times 10^5\), program/erase endurance cycles of \(>10^2\) with a memory margin of \(8.4 \times 10^5\), and bending-fatigue-free cycles of \(\sim 1 \times 10^3\) with a memory margin \((I_{on}/I_{off})\) of \(3.3 \times 10^5\).

Keywords: flexible memory, CBRAM, nonvolatile, polymer memory, organic memory, conductive-bridging

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, extensive research on flexible nonvolatile memory cells has been conducted since information technology (IT) mobile devices have been rapidly transitioning from solid mobile devices to flexible mobile devices. Four types of flexible nonvolatile memory cells such as ReRAM \cite{1,2}, polymer random-access-memory (PoRAM) \cite{3,4}, conductive-bridging random-access-memory (CBRAM) \cite{5,6}, and nano-floating-gate-memory (NFGM) have been reported \cite{7,8}. Among them, ReRAM, PoRAM, and CBRAM are fabricated with a 4F\^2 cross-bar memory-cell structure, which enables the stacking of three-dimensional (3D) memory cells for achieving terra-bit-level integration. Although flexible ReRAMs using binary oxide material have demonstrated nonvolatile memory characteristics, their retention time and write/erase endurance cycles make it difficult to satisfy bending-fatigue-free criteria since they fundamentally use inorganic materials. Otherwise, PoRAM \cite{9,10} or CBRAM \cite{11} probably exhibits bending-fatigue-free nonvolatile memory characteristics since they use a polymer or polymer electrolyte. Although a CBRAM using a polymer electrolyte (PEO) fabricated on a flexible substrate (PES) exhibits the feasibility of 180 bending degrees, it does not exhibit flexible nonvolatile memory characteristics such as retention time, write/erase endurance cycles, and bending...
fatigue cycles [6]. Thus, we developed flexible CBRAM cells that use a double-layered structure (PEO/PVK) and have a crossbar memory-cell structure vertically sandwiched with a reactive Ag electrode, polymer electrolyte (PEO) layer, conductive polymer (PVK) layer, and inert Pt electrode. First, we investigated the dependency of the current-voltage (I–V) curve on the concentration (weight percentage) of PEO and PVK for flexible CBRAM cells fabricated on a solid substrate (SiO₂ on Si substrate) to optimize the thickness ratio of the PEO to PVK layer. We also estimated the nonvolatile memory characteristics of flexible CBRAM cells, such as set voltage, reset voltage, retention time, program/erase endurance cycles, and bending-fatigue-free cycles, for optimizing the thickness ratio of the PEO to PVK layer. Finally, we reviewed the current conduction mechanism by which our flexible CBRAM cells exhibit nonvolatile memory characteristics.

2. Experimental procedure

To investigate the dependency of the bi-stable I–V curve on the weight percentage (wt%) of PEO and PVK, arrays of 20 × 20 CBRAM cells were fabricated on SiO₂ film grown on a Si wafer, as shown in figures 1(a) and 2(a). Arrays of 20 × 20 250 nm-diameter nano-holes were patterned on the bottom 50 nm thick Pt-electrode by using lithography and etching, where the thickness of the SiO₂ film isolating the holes was ~50 nm. Then, PEO or PVK were spin-coated on the hole arrays at 2000 rpm for 120 s and baked at 120 °C for 5 min and 60 °C for 5 min, respectively. Note that the PEO was mixed with a co-solvent of acetonitrile and ethanol at 30 °C for 1 h. Afterward, 300 μm-diameter 200 nm-thick top Ag electrodes were thermally evaporated at a rate of 1.0 Å s⁻¹ under 10⁻⁵ Pa by using a shadow mask. Thus, the CBRAM cells have a sandwich structure consisting of a bottom Pt electrode, PEO, and top Ag electrode on the SiO₂ film grown on a Si wafer. To investigate the bending fatigue of flexible CBREM cells, 2 × 6 cross-bar memory-cell arrays sandwiched with a bottom Pt electrode, PVK, PEO, and top Ag electrode were fabricated on a flexible substrate (PES), as shown in figure 3(a). The 150 μm wide bottom Pt electrode was patterned on the PES substrate by evaporation using a shadow mask. The PVK was spin-coated under 2000 rpm for 120 s and baked at 120 °C for 5 min. Then, PEO was spin-coated under 2000 rpm for 120 s and baked at 60 °C for 5 min. Finally, the 150 μm-wide top Ag electrode was patterned on the PEO film. Thus, these flexible CBRAM cells have a sandwich structure consisting of a bottom Pt electrode, PVK, PEO, and top Ag electrode on a flexible PES substrate.

3. Results and discussion

3.1. Dependency of PEO-based CBRAM cell characteristics on electrolyte thickness

A cross-sectional transmission-electron-microscopy (x-TEM) image of a CBRAM cell using a solid electrolyte PEO layer showed that the thicknesses of the bottom electrode (Pt/TiN), polymer electrolyte (PEO 1.0 wt%), and top passivation (Al) layer were 92.6/50.0, 78.7, and 103.6 nm, respectively, and the hole diameter of the memory was 250 nm, as shown in figure 1(b). Note that the top Al layer was evaporated on the PEO layer to prepare an x-TEM sample and measure the PEO layer thickness. The thickness of the polymer electrolyte (PEO) layer was strongly dependent on the weight percentage (wt%) of the PEO solution, i.e., the PEO thickness linearly increased from 13 to 73 nm when the wt% of the PEO solution increased from 0.4 to 1.0 wt%, as shown in figure 1(c). In a CBRAM, the low resistance state (LRS) is achieved when conductive bridging filaments in the PEO layer are produced by Ag ion migration and stacking from the Pt to Ag electrodes in the polymer electrolyte (PEO) layer, which determines a set voltage (V_{set}). Otherwise, the high resistance state (HRS) is achieved when conductive bridging filaments in the polymer electrolyte (PEO) are broken by Ag ion migration and stacking from the Pt to Ag electrodes in the polymer electrolyte (PEO) layer, which determines the reset voltage (V_{reset}). In addition, the conical-shaped conductive-bridging filaments grow radially and vertically between the Ag and Pt electrodes so that the conical shape depends on the thickness of the PEO layer thickness, which determines V_{set} or V_{reset}. The nonvolatile memory characteristics of CBRAM cells depended on the PEO layer thickness (wt%), as shown in figure 1(c). All CBRAM cells showed a typical bi-stable I–V curve demonstrating the bipolar switching behavior of resistive RAM. When the PEO layer thickness increased from 13 to 73 nm, the set current decreases with increasing PEO layer thickness and V_{set} decreases from 3.1 × 10⁻⁶ to 5.6 × 10⁻¹¹ A. In addition, when the PEO thickness increased from 13 to 73 nm, V_{set} increased from 0.3 to 1.7 V while V_{reset} decreased from −3.4 to −0.85 V. The dependencies of the set current, reset current, V_{set}, and V_{reset} on the PEO layer thickness are related to the shape of the filaments in the PEO layer. The filaments in the PEO layer become longer when the PEO layer thickness increases, so that both set and reset current decrease with increasing PEO layer thickness and V_{set} increases with the PEO layer thickness. The mechanism of set and reset current decreases with increasing PEO layer thickness, which was discovered by fitting the HRS of J–V curves with the current conduction mechanism of the Poole–Frenkel emission, as shown figure 1(d). The current mechanism of the Poole–Frenkel emission is defined by Ln(J/V) ∝ (2√(q/4πε)d) ∝ V·ΦB/kT, where q, ε, d, V, k, T, and ΦB are elementary charge, PEO permittivity, PEO thickness, the applied voltage, Boltzmann’s constant, temperature, and barrier height, respectively [12, 13]. The slope of Ln(J/V)–√V curves includes the PEO thickness so that a lower slope leads to a greater PEO thickness. As expected, the thicker PEO layer showed a lower slope of Ln(J/V)–√V, as shown figure 1(d). This result indicates that the Ag ion migration distance for forming the conductive-bridging filaments would increase with the PEO thickness. Otherwise, the diameter of the filaments in the PEO layer becomes smaller.
when the PEO layer thickness increases, so that $V_{\text{reset}}$ decreases with increasing PEO layer thickness. Furthermore, the PEO-based CBRAM (Ag/50 nm thick PEO/Pt) demonstrated a retention time of $\sim 10^5$ s at room temperature by sustaining a memory margin ($I_{\text{on}}/I_{\text{off}}$) of $10^4$ and program and erase cycles of $10^3$ by sustaining a memory margin ($I_{\text{on}}/I_{\text{off}}$) of $1.31 \times 10^5$, as shown in figure 1(e).

3.2. Dependency of PVK-based ReRAM cell characteristics on conductive polymer thickness

Next, the dependency of the bi-stable $I$-$V$ curves on conduction polymer (PVK) layer thickness was investigated in detail, as shown in figure 2. An x-TEM image of a ReRAM cell with a 250 nm diameter hole using a PVK layer showed that the thicknesses of the bottom electrode (Pt/TiN), polymer...
electrolyte (PVK 0.36 wt%), and top passivation (Al) layer were 100.6/50.5, 35.3, and 99.6 nm, respectively, as shown in figure 2(b). The thickness of the PVK layer was strongly dependent on the weight percentage (wt%) of the PVK solution, i.e., the PVK layer thickness linearly increased from 13 to 100 nm when the wt% of the PVK solution increased from 0.18 to 0.74 wt%, as shown in figure 2(c). All samples showed a typical bi-stable I-V curve demonstrating the bipolar switching behavior of ReRAM. However, there was no dependency of the nonvolatile characteristics on PVK layer thickness between 13 nm and 100 nm; i.e., the set current ($10^{-3}$ A), reset current ($\sim 3.2 \times 10^{-8}$ A), $V_{\text{set}}$ (0.3 V), and $V_{\text{reset}}$ ($-3.95$ V) were independent of the PVK layer thickness. This result indicates that the current conduction for the ReRAM using a conductive polymer (PVK) layer is probably not associated with charged defects that exist in a solid electrolyte layer.

3.3. Flexible CBRAM fabricated with double polymer layers

To fabricate a flexible CBRAM cell, cross-bar (150 μm long × 150 μm wide) memory-cell arrays were fabricated with a cross-bar structure; top Ag electrode/polymer electrolyte layer (PEO)/conductive polymer (PVK) layer/bottom Pt electrode/flexible substrate (PES), as shown in figures 3(a) and (b). The CBRAM fabricated with the device structure of Ag/PEO/Pt performed with a quite low set voltage and ON-state current, as shown in figure 1(c). Thus, to overcome this issue, we developed a double-stacked polymer (PEO/PVK) based CBRAM since the PEO layer was used for a polymer electrolyte layer, while the PVK layer was used for a conductive polymer (or insulator), as shown in figure 3(a). The insertion of the thin PVK layer between the PEO layer and bottom Pt electrode may control the conduction current level and the shape of filaments in the PEO layer. A strain of $\sim 0.4\%$ was applied to the CBRAM cells to estimate bending fatigue, where the diameter of the bended flexible CBRAM cells was 25 mm, as shown in figure 3(g) [14, 15]. An x-TEM image of a flexible CBRAM cell using double polymer layers (PEO/PVK) showed that the thicknesses of the bottom Pt electrode, polymer electrolyte (PEO 0.8 wt%) layer, conductive polymer (PVK 0.3 wt%) layer, and top Ag electrode were 109.9, 20.8, 49.1, and 40.6 nm, respectively, as shown in figure 3(c). This flexible CBRAM cell showed a typical bi-stable I-V curve having a $V_{\text{set}}$ of 1.0 V, LRS of $9.5 \times 10^{-4}$ A, $V_{\text{reset}}$ of $-1.6$ V, and HRS of $8.8 \times 10^{-9}$ A when the bias was scanned from 0, 3, 0, $-3$, and 0 V, as shown in figure 3(d). In particular, the flexible CBRAM cell exhibited an asymmetrical I-V curve, where the absolute $V_{\text{set}}$ (1.0 V) was less than the absolute $V_{\text{reset}}$ ($-1.6$ V), implying that the shape of the conical conductive-bridging filament may be asymmetrical. A retention time of $\sim 10^5$ s of the memory cell at room temperature was obtained by sustaining a memory margin ($I_{\text{on}}/I_{\text{off}}$) of $9.2 \times 10^3$, indicating a probable extension to 10 years, as shown in figure 3(e). In addition, program and erase cycles of more than $10^4$ was obtained by sustaining a memory margin ($I_{\text{on}}/I_{\text{off}}$) of $8.4 \times 10^3$, as shown in figure 3(f). Furthermore, bending-fatigue-free cycles of $\sim 1 \times 10^3$ were obtained by sustaining a memory margin ($I_{\text{on}}/I_{\text{off}}$) of $3.3 \times 10^3$, as shown in figure 3(h). In addition, bending-
fatigue-free time of \( \sim 170 \) h was obtained by sustaining a memory margin \((I_{\text{on}}/I_{\text{off}})\) of \(2.34 \times 10^6\), as shown in figure 3(i). These results indicate that a flexible CBRAM cell using a double polymer layer exhibits good bending-fatigue-free cycles, which suggests the possibility of commercially viable nonvolatile memory cells.

3.4. The current conduction mechanism of flexible CBRAM

The current conduction mechanism of a flexible CBRAM cell using a double polymer layer was reviewed by fitting the \( I-V \) curve in figure 3(e) when the applied bias was scanned from 0, 3, 0, –3, and 0 V, as shown in figure 4. The current conduction of the HRS between 0 V and \( V_{\text{set}} \) (1.0 V) fitted well with the conduction mechanism of the Poole-Frenkel emission, having a slope of 0.02, as shown in figure 4(a), which is defined by \( J \propto q^2 \sqrt{\frac{q}{kT}} \exp \left[ \frac{qV - \Phi_B}{kT} \right] \), where \( q \), \( \varepsilon_i \), \( d \), \( V \), \( k \), \( T \), and \( \Phi_B \) are elementary charge, insulator permittivity, insulator thickness, the applied voltage, Boltzmann’s constant, temperature, and barrier height, respectively. This result indicates that the conical-shaped filaments in the double
polymer layer are formed due to the drift of Ag ions from the top Ag electrode to the bottom Pt electrode via the Poole–Frenkel emission process. After forming the conical-shaped filaments and sustaining the compliance level of the conduction current, the current conduction from V_{set} to 0 V was fitted with the Ohmic conduction mechanism, as shown in figure 4(b), \( J/V \propto e^{-c/V} \) where \( c, V, \) and \( T \) are a constant, the applied voltage, and temperature, respectively [16]. In addition, the current conduction between 0 and \( V_{reset} \) exhibited typical I-V behavior of negative-differential resistance (NDR), which implied the breaking process of the conical-shaped filaments in the double polymer layer, as shown in figure 4(c). After breaking the conical-shaped filaments, the current conduction from \( V_{reset} \) to 0 V was fitted with the current conduction mechanism of the Poole–Frenkel emission, drifting back Ag ions from the Pt electrode to Ag electrode, as shown in figure 4(d). Therefore, the current conduction mechanism for a flexible CBRAM cell is well described by the forming and breaking process of the conical-shaped filaments in the double polymer layer between the Pt and Ag electrodes.

4. Conclusion

The nonvolatile memory characteristics of CBRAM cells are dependent on the cross-bar memory-cell size since nano-scale conical-shaped filaments are randomly distributed in the polymer electrolyte layer after the forming process; i.e., a larger cross-bar memory-cell size leads to a higher number of conical-shaped filaments. In general, a thinner polymer electrolyte layer in CBRAM cells results in a smaller distribution of nonvolatile memory characteristics since the length and diameter of such filament becomes smaller and more uniform as the polymer electrolyte layer thickness becomes thinner. However, a thinner polymer electrolyte layer in CBRAM cells produces a higher conduction current, which easily approaches the compliance current level. The insertion of a conductive polymer layer between the polymer electrolyte layer (PEO) and bottom Pt electrode in CBRAM cells could control the length and diameter of the conical-shaped filaments in the polymer electrolyte layer and adjust the conduction current level. Thus, the thickness ratio control of the polymer electrolyte layer to the inserted conductive polymer layer enable control of nonvolatile memory characteristics such as the
compliance current level, $V_{set}$, $V_{reset}$, memory margin ($I_{on}/I_{off}$), retention time, write/erase endurance cycles, and bending fatigue behavior. It was confirmed that the thickness ratio of the electrolyte polymer layer to the conductive polymer layer strongly affects nonvolatile memory characteristics; i.e., there is a specific thickness ratio exhibiting the best nonvolatile memory characteristics since the drift velocity and solubility of Ag ions in the polymer electrolyte (PEO) layer is different from that of the conductive polymer (PVK) layer. In addition, since the interface between the conductive polymer layer and proper metal electrode is able to produce a Schottky barrier, investigating the design of a selecting diode using a Schottky barrier at the interface between the bottom inert electrode and inserted conductive polymer is key to engineering flexible 3D stacked cross-bar CBRAM-cell arrays for terra-bit-level nonvolatile flexible memory cells.

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References

[1] Zheng Z W, Cheng C H, Chou K I, Liu M and Chin A 2013 Current uniformity improvement in flexible resistive memory \textit{EDSSC: IEEE Int. Conf. on Electron Devices and Solid-State Circuits} 1–2
[2] Jung S J, Kong J M, Song S H, Lee K H, Lee T H, Hwang H S and Jeon S H 2011 Resistive switching characteristics of solution-processed TiOx for next-generation non-volatile memory application; transparency, flexibility, and nano-scale memory feasibility \textit{Microelectron. Eng.} \textbf{88} 1143–7
[3] Lai Y C, Wang Y X, Huang Y C, Lin T Y, Hsieh Y P, Yang Y J and Chen Y F 2014 Rewritable, moldable, and flexible sticker-type organic memory on arbitrary substrates \textit{Adv. Funct. Mater.} \textbf{24} 1430–8
[4] Son D I, Shim J H, Park D H, Jung J H, Lee J M, Park W I, Kim T W and Choi W K 2011 Polymer–ultrathin graphite sheet–polymer composite structured flexible nonvolatile bistable organic memory devices \textit{Nanotechnology} \textbf{22} 295203
[5] Tada M, Okamoto K, Sakamoto T, Miyamura M, Banno N and Hada H 2011 Polymer solid-electrolyte switch embedded on CMOS for nonvolatile crossbar switch \textit{IEEE Trans. Electron Devices} \textbf{58} 4398–406
[6] Mohapatra S R, Tsuruoka T, Hasegawa T, Terabe K and Aono M 2012 Flexible resistive switching memory using inkjet printing of a solid polymer electrolyte \textit{AIP Adv.} \textbf{2} 022144
[7] Kim C W, Song J M, Lee J S and Lee M J 2014 All-solution-processed nonvolatile flexible Nano-floating gate memory devices \textit{Nanotechnology} \textbf{25} 014016
[8] Han S T, Zhou Y and Roy V A L 2013 Towards the development of flexible non-volatile memories \textit{Adv. Mater.} \textbf{25} 5425–49
[9] Seung H M, Lee J D, Lee J S, Song M J, Hong J P and Park J G 2012 Self-rectifying flexible nonvolatile small-molecule memory-cell embedded with Ni nanocrystals surrounded by NiO tunneling barrier \textit{Ext. Abstr.} \#2840, 222th ECS Meeting 231
[10] Kwon K C, Seung H M, Yang D H, Park D H, Hong J P and Park J G 2012 Flexible polymer memory-cell with au nanocrystals embedded in poly styrene \textit{Ext. Abstr.} \#2841, 222th ECS Meeting 231
[11] Song M J, Seung H M, Kwon K C, Lee J S, Park D H and Park J G 2013 Flexible conductive-bridging random-access memory cell fabricated with stacked polymer electrolyte and conductive polymer \textit{Ext. Abstr.} \#1997, 224th ECS Meeting 205
[12] Frenkel J 1938 On pre-breakdown phenomena in insulators and electronic semi-conductors \textit{Tech. Phys.} \textbf{54} 647–8
[13] Kim S J et al 2011 Characteristics and the model of resistive random access memory switching of the Ti/TiO$_2$ resistive material depending on the thickness of Ti \textit{Japan J. Appl. Phys.} \textbf{50} 04DD14
[14] Grego S, Lewis J, Vick E and Temple D 2005 Development and evaluation of bend-testing techniques for flexible-display applications \textit{J. Soc. Inf. Display} \textbf{13} 575–81
[15] Park S K, Han J L, Moon D G and Kim W K 2003 Mechanical stability of externally deformed indium–In-oxide films on polymer substrates \textit{Japan. J. Appl. Phys.} \textbf{42} 623–9
[16] Su Y T et al 2013 Characteristics of hafnium oxide resistance random access memory with different setting compliance current \textit{Appl. Phys. Lett.} \textbf{103} 163502