Iron trichloride as oxidizer in acid slurry for chemical mechanical polishing of $Ge_2Sb_2Te_5$*

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The effect of iron trichloride ($FeCl_3$) on chemical mechanical polishing (CMP) of $Ge_2Sb_2Te_5$ (GST) film is investigated in this paper. The polishing rate of GST increases from 38 nm/min to 144 nm/min when the $FeCl_3$ concentration changes from 0.01 wt% to 0.15 wt%, which is much faster than 20 nm/min for the 1 wt% H_2O_2-based slurry. This polishing rate trends are inversely correlated with the contact angle data of $FeCl_3$-based slurry on the GST film surface. Thus, it is hypothesized that the hydrophilicity of the GST film surface is associated with the polishing rate during CMP. Atomic force microscope (AFM) and optical microscope (OM) are used to characterize the surface quality after CMP. The chemical mechanism is studied by potentiodynamic measurements such as E_{corr} and I_{corr} to analyze chemical reaction between $FeCl_3$ and GST surface. Finally, it is verified that slurry with $FeCl_3$ has no influence on the electrical property of the post-CMP GST film by the resistivity–temperature (RT) tests.

Keywords: chemical mechanical polishing, iron trichloride, $Ge_2Sb_2Te_5$

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1. Introduction

With the release of phase change memory (PCM) products by Samsung and Numonyx,[1] and as flash technologies face major scaling issues at 32-nm node,[2] PCM is taken as one of the best performing candidates for scaled non-volatile memories of the next generation due to its advantages of high write/read speed, bit alterability, erase-free operation, good data retention, high cycling endurance, and scalability.[3] Although many chalcogenide materials have been investigated for the application of PCM, $Ge_2Sb_2Te_5$ (GST) is one of the best.[4] As a unique global planarization method used in the semiconductor manufacturing process, chemical mechanical planarization (CMP) has been introduced to planarize the GST film surface after gap filling of GST in the confined structure.[5–7] At the same time, polishing of a ternary material such as GST also faces new challenges for the CMP process like composition control, thickness control of small device region, imperfections (e.g., scratches, defects, and corrosions) minimization, etc.[8,9]

An oxidizer is usually the necessary composition of the slurry. The function of the oxidizer is to accelerate the removal rate, and a suitable oxidizer will form a passive oxide layer which is mechanically polished during CMP. This mechanism could obtain a good quality CMP performance including surface and scratches. In previous studies, H_2O_2 was usually chosen as an oxidizer added in the slurry. Cui *et al.*[10] investigated the effect of hydrogen peroxide (H_2O_2) on CMP of nitrogen-doped polycrystalline GST using nitric acidic slurry. He *et al.*[11] studied the mechanism of the amorphous $Ge_2Sb_2Te_5$ during chemical mechanical planarization in acid H_2O_2 slurry. Cho *et al.*[12] mentioned the effect of H_2O_2 in alkaline slurry on the polishing rate of polycrystalline GST. However, the corrosion process of GST film with H_2O_2 is likely to cause a high density of scratches and corrosion-induced pits on the GST film surface during CMP.[6] Cui *et al.*[6] studied potassium permanganate as the oxidizer in alkaline slurry for chemical mechanical planarization of nitrogen-doped polycrystalline GST film. On the basis of the above situation, we choose iron trichloride ($FeCl_3$) as an oxidizer in acid slurry.

In this study, we develop acidic CMP slurry with $FeCl_3$ added as an oxidizer to improve CMP performance on GST film, obtaining a faster polishing rate and better surface quality than those in the situation with commonly used H_2O_2-based slurry. In addition, the mechanism of how $FeCl_3$ improves CMP performance on GST film is investigated by electrochemical measurements such as corrosion potential and current density. Finally, the electrical property of GST is studied by resistivity–temperature (RT) test.

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2. Experiment

GST-thin films were deposited onto 800-nm SiO_2/Si substrates using a Unaxis LLS EVO tool (produced by Oerlikon-Balzers Ltd., Liechtenstein). Deposition conditions were as follows: target GST, 127 mm×381 mm (99.999 wt%); substrate, 1400-nm SiO_2/Si; radio-frequency power, 0.2 kW; argon pressure, 0.27 Pa; and deposition temperature was ambient temperature. Oxide wafers prepared by plasma enhanced tetraethyl orthosilicate (TEOS) method were available from Semiconductor Manufacturing International Corporation (SMIC). All theses wafers were cut into 2.5 cm×3 cm pieces for polishing.

The 430-nm thick GST films with an area of 2.5 cm×3 cm were polished using a CMP tester (CETR CP-4), with an IC 1010/Suba IV stacked pad (Dow). The composition of GST was 26:22:52 (Ge:Sb:Te) and tested in atomic percentage by the top-view scanning electron microscope (SEM) energy dispersive spectrometer (EDS) analysis. The analysis results are listed in Table 1.

Table 1. Results of EDS analysis of composition of the GST film.

Element	Weight percentage	Atomic percentage
Ge(K)	18.47	25.20
Sb(L)	24.08	24.92
Te (L)	57.45	50.98
Totals	100.00	100.00

The polishing process parameters were set as follows: pad rotation speed, 100 rpm; wafer rotation speed, 100 rpm; down force, 3 psi; feed rate of the slurry, 100 mL/min; polishing time, 1 min. All experiments were conducted at room temperature.

The thickness values of the GST films were measured with a thin-film mapper (FILMETRICS, F50, China) before and after the polishing tests. Atomic force microscope (AFM) and optical microscope were used to examine the surface qualities, microscopic and macroscopic. Potentiodynamic measurements were conducted by a potentiostat (PASTAT2273, Princeton Applied Research, TN). This cell allows a 1 cm^2 exposure area of the working electrode with crystalline GST film. The counter electrode uses a built-in Pt-coated sheet and its effective area was 1 cm^2, and the reference electrode was Ag/AgCl. All potentials were measured with respect to an Ag/AgCl electrode. The polarization curves were obtained with a voltage scan rate of 1 mV/s.

The particle mean size and distribution were analyzed by dynamic light scattering (DLS) particle size analyzer (PSS, USA).

3. Results and discussion

The composition of approximately 26:22:52 (Ge:Sb:Te) by atomic percentage, as shown by the top-view SEM EDS analysis is listed in Table 1.

Figure 1 shows the shapes and morphologies of the colloidal silica abrasives used in the alkaline slurry. The silica particles each exhibit a cocoon-shaped appearance.

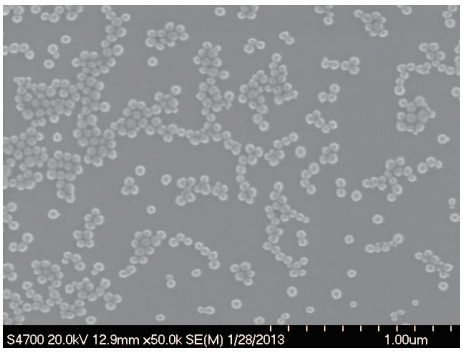


Fig. 1. The SEM image of the silica.

The particle concentration of slurry is 2 wt% and pH of the slurry is 2.1. To investigate the effect of particle size on GST removal rate, DLS is used to analyze the particle mean size and distribution as shown in Fig. 2. The mean particle diameter of abrasive is 40.3 nm. When 1% H_2O_2 is added in the acid slurry, the mean particle diameter reaches 55 nm, which is almost the same as that when $FeCl_3$ was added in the acid slurry. As a function of $FeCl_3$ concentration, the particle mean size is slightly different, so we take 0.15 wt% $FeCl_3$ as representative.

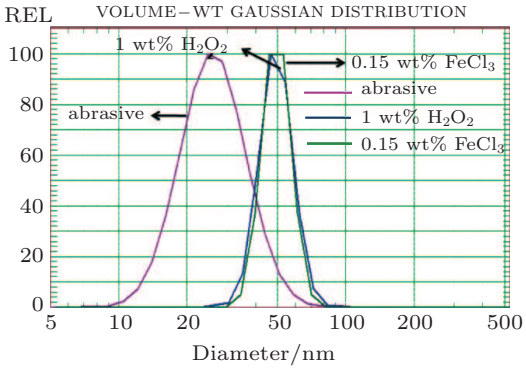


Fig. 2. (color online) Size distributions of silica particles.

The polishing rate of GST films as a function of an oxidizer ($FeCl_3$ and H_2O_2) in the acid slurry is shown in Fig. 3(a). With 1 wt% H_2O_2 in the acid slurry, the polishing rate is 18 nm/min. However, the GST polishing rate drastically and linearly increases from 38 nm/min to 144 nm/min when $FeCl_3$ concentration increases from 0.01 wt% to 0.15 wt%. This striking difference in the polishing rates between the cases of using $FeCl_3$ and H_2O_2 resulted from the chemical reactions between GST film and $FeCl_3$. This behavior may be related to the effect that $FeCl_3$ has on the chemical reaction with GST film surface, such as hydrophobic or hydrophilic interactions.

The characteristics of the reaction between $FeCl_3$ and GST film surface can be estimated from the surface tension by measuring the contact angle. In general, wettability can be quantitatively evaluated in terms of the spreading coefficient, which is the energy difference between the solid substrate and the contacting liquid phase. The interaction between the interfacial tensions at the liquid–vapor–solid junction is described by the Yong equation as follows:

$$\cos\theta = \frac{r_{SV} - r_{SL}}{r_{LV}},$$

where θ is the contact angle ($\theta > 0^\circ$), and r_{SV}, r_{SL}, and r_{LV} are the thermodynamic properties of the liquid, solid, and vapor. The value of θ indicates the extent of the wettability between solid phase and liquid phase, and when the value is zero, it means absolute wettability between solid phase and liquid phase. The contact angles of the GST film surface range from 39.4° to 27.4°, which are shown as a function of $FeCl_3$ concentration in Fig. 3(b). With the increase of $FeCl_3$ concentration, the contact angle decreases linearly. Comparing Fig. 3(a) with Fig. 3(b), we find that the contact angle changes in opposition to the GST film polishing rate curve. Slurry with added $FeCl_3$ improves the hydrophilicity indicated by a smaller contact angle. It enhances the absorption of slurry and then accelerates the chemical reaction between the slurry and the GST film. As a result, slurry with enhanced hydrophilicity initially produces a higher polishing rate.

Figure 4 shows the AFM images and root-mean-square (RMS) values of roughness of GST films after polishing using slurries with or without $FeCl_3$. In Fig. 4(a), the RMS value of roughness in the case with 1 wt% H_2O_2 is relatively high (4.62 nm). In the presence of the additive $FeCl_3$, the roughness decreases, and it becomes smaller with more $FeCl_3$. When the $FeCl_3$ concentration is 0.01 wt%, the RMS value of roughness is 2.68 nm as shown in Fig. 4(b). The roughness decreases as $FeCl_3$ concentration increases. RMS value is lowest at 0.15-wt% $FeCl_3$, namely, 0.73 nm shown in Fig. 4(e). The results may be explained as the fact that as an oxidizer, $FeCl_3$ accelerates the GST oxidation and forms the passive oxide layer.

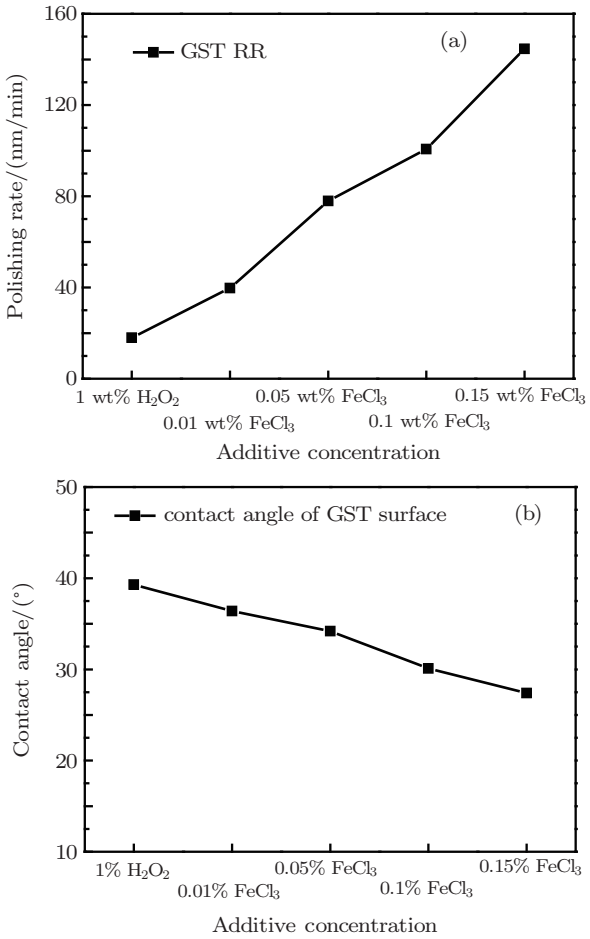


Fig. 3. Dependencies of the polishing rate (a) and contact angle (b) on the $FeCl_3$ concentration of GST film surface.

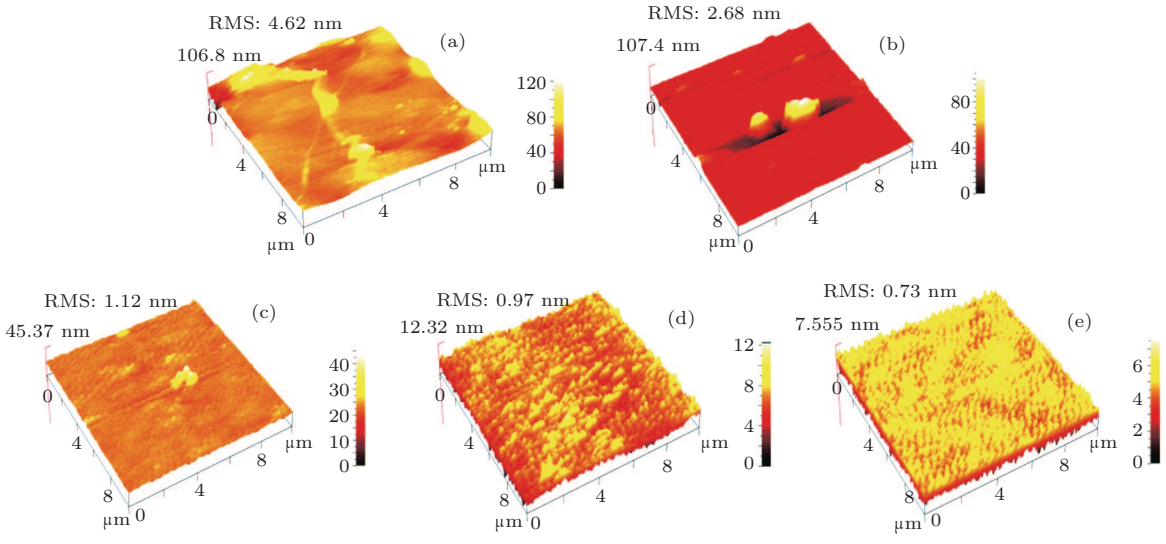


Fig. 4. (color online) The RMS values and the three-dimensional images of the GST film surface after being polished with (a) 1-wt% H_2O_2, (b) 0.01-wt% $FeCl_3$, (c) 0.05-wt% $FeCl_3$, (d) 0.1-wt% $FeCl_3$, and (e) 0.15-wt% $FeCl_3$.

Optical microscopic images of the GST surface post-CMP are shown in Fig. 5. As shown in Fig. 5(a), after CMP, the GST surface has a great quantity of residual which may be Te hillock. The increase in Te aggregation on the surface affects the increase in the surface roughness of the specimen, which is the main cause of the increasing surface roughness.[13] While adding $FeCl_3$ in the acid slurry, we obtain good quality CMP performance as shown in Fig. 5. There is no residual on the GST surface, which reduces the roughness of the GST. Based on the above results, it may be suggested that the $FeCl_3$ oxidizes the Te, which makes Te-oxide easier to remove than Te. So, $FeCl_3$ forms a uniform passive oxide layer compared with H_2O_2-based slurry.

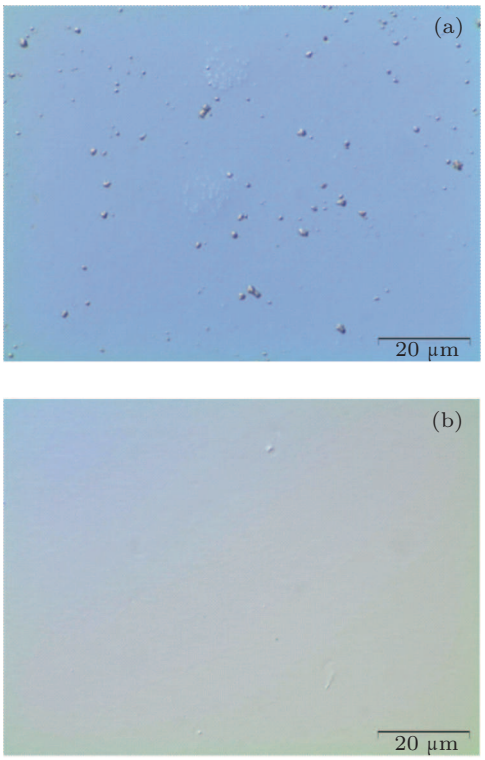


Fig. 5. (color online) Optical microscopic images of the GST film after CMP with (a) 1-wt% H_2O_2 and with (b) 0.15-wt% $FeCl_3$

To further confirm the passive oxide layer formed on the GST surface, electrochemical characteristics of the GST film surface were analyzed to investigate the chemical reaction between $FeCl_3$ and the GST film surface. Figure 6(a) shows potentiodynamic polarization curves for the GST films each as a function of H_2O_2 and $FeCl_3$ concentration. The polarization curves are shifted toward a higher potential as $FeCl_3$ concentration increases. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are calculated by the Tafel method.[14] With 1 wt% H_2O_2, the E_{corr} is 162.4 mV. While the $FeCl_3$ concentration ranges from 0.01 wt% to 0.05 wt%, E_{corr} increases sharply from 180.1 mV to 220.7 mV and then increases slightly up to 245.8 mV with $FeCl_3$ concentration at 0.15 wt% $FeCl_3$ as shown in Fig. 6(b). Generally, the E_{corr} increases when there is an oxidizer in the solution and becomes larger as the concentration increases.[14] However, the I_{corr} decreases slightly and linearly from 4.3 μA/cm^2 (with 1 wt% H_2O_2) to 3.7 μA/cm^2 (at 0.15 wt% $FeCl_3$) as shown in Fig. 5(b). I_{corr} of 1 wt% H_2O_2 is larger than that of $FeCl_3$, which suggests that $FeCl_3$ accelerates the formation of the passive oxide layer. The oxidized Te product of the H_2O_2 is Te, while it is in the form of TeO_2 for $FeCl_3$.[15] Thus, $FeCl_3$ oxidizes all elements, which could lead to better CMP performance and higher GST-RR than H_2O_2 does. Comparing Fig. 3(a) with Fig. 6(b), the trend of E_{corr} is consistent with that of the GST film polishing rate which depends on the $FeCl_3$ concentration. On the other hand, the curve of the I_{corr} changes in opposition to that of the GST film polishing rate. Adding an oxidizer generally leads to two main results. One is that the corrosion process of the corresponding anodic material is enhanced by the corrosion potential shifting into the corrosion domain; the other is that the corrosion process is suppressed by a passive oxide layer forming on the surface.[16] Based on the I_{corr} decrease as a function of $FeCl_3$ concentration, those results can be explained by the fact that as an oxidizer, $FeCl_3$ enhances the passive oxide layer. We know that the products of the $FeCl_3$ are GeO_2, Sb_2O_5, and TeO_2.[15] Thus, the resulting passivated layer by chemical oxide is mechanically polished via direct

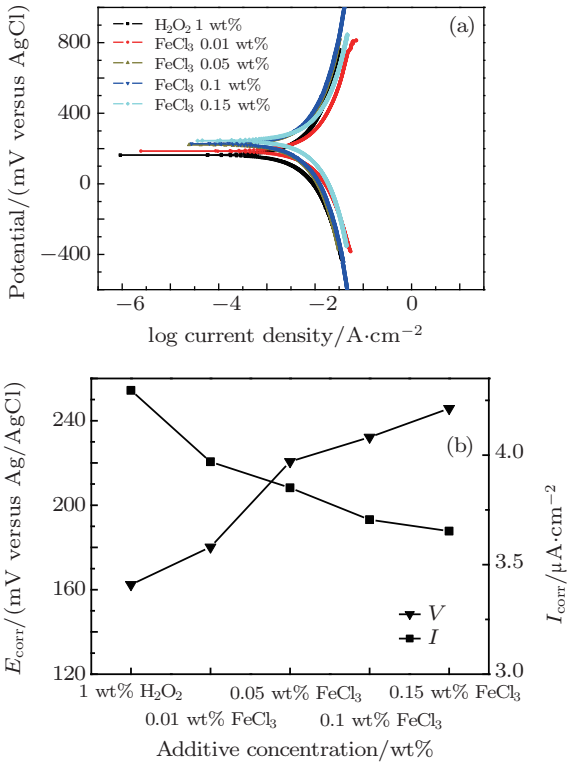


Fig. 6. (color online) Dependences of potentiodynamic behavior of GST film surface on $FeCl_3$ concentration in the acid slurries: (a) Potentiodynamic polarization curves of GST film surface in solutions containing 1 wt% H_2O_2 and $FeCl_3$ of 0.01 wt%, 0.05 wt%, 0.1 wt%, 0.15 wt% respectively, and (b) corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of GST film surface each as a function of H_2O_2 and $FeCl_3$ concentrations.

touching between the colloidal silica and the passivated layer on the GST film surface, called a cyclic reaction polishing mechanism.

GST stores date by rapidly heating and quenching to either amorphous or crystalline phase. To investigate the phase-change properties of post-CMPGST film with and without $FeCl_3$, we carry out the experiment of sheet resistance–temperature tests, which are shown in Fig. 7. The results show that the GST film polished with $FeCl_3$ reveals no difference from the pre-CMP film. The two of them have almost the same curves. With the increase of temperature, the sheet resistance of GST film slowly declines. There appears a sudden decrease at 150 °C for the GST film, which is due to the transformation from amorphous state to a face-center cubic (FCC) state. Then, the sheet resistance of the GST film slowly decreases to 100 Ω at 400 °C. This indicates that slurry with $FeCl_3$ would not change the electrical properties of the GST films with pre-CMP and post-CMP.

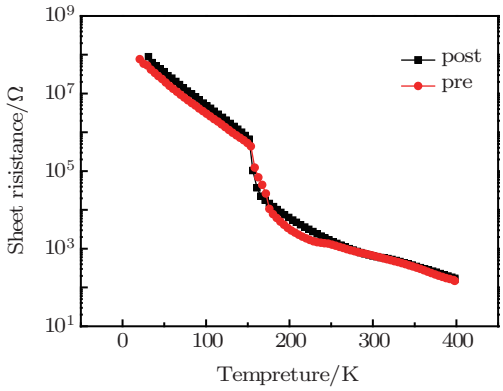


Fig. 7. (color online) Plots of sheet resistance versus temperature of GST films.

4. Conclusion

In this paper, we systematically investigated the effect of $FeCl_3$ on the polishing rate of GST during CMP with slurry based on colloidal silica abrasives. The polishing rate increases with $FeCl_3$ concentration increasing up to 0.15 wt%, which is associated with hydrophilicity. Enhancing hydrophilicity with the increase of concentration of $FeCl_3$ strengthens the absorption of slurry on the GST film surface and then accelerates the chemical reaction between slurry and GST film. The RMS value of the roughness of GST film becomes lower with the increase of $FeCl_3$ concentration. Slurry with $FeCl_3$ improves the surface quality during CMP. In addition, the polishing mechanism is analyzed by the potentiodynamic measurements such as E_{corr} and I_{corr}. The increasing E_{corr} and reducing I_{corr} each as a function of $FeCl_3$ concentration demonstrate that $FeCl_3$ tends to chemically oxidize the GST film surface. Thus, the resulting passivated layer by chemical oxide is mechanically polished via direct touching between the colloidal silica and the passivated layer on polycrystalline GST film surface, called a cyclic reaction polishing mechanism. Therefore, $FeCl_3$ can be a promising oxidizer for GST CMP.

References

[1] Wang L Y, Song Z T, Zhong M, Liu W L, Yan W X, Qin F, He A D and Liu B 2012 *Appl. Surf. Sci.* **258** 5185
[2] Castro D T, Goux L, Hurkx G A M, Attenborough K, Delhougne R, Lisoni J, Edema F J, Zandt M A A, Wolters R A M, Gravesteijn D J, Verheijen M A, Kaiser M, Weemaes R G R and Wouters D J 2007 *Electron Devices Meeting*, December 10–12, 2007, Washington, DC, p. 315
[3] Bez R 2009 *Chalcogenide PCM: A Memory Technology for Next Decade IEEE IEDM Technology*, December 7–9, 2009, Baltimore, MD, p. 1
[4] Sun Z M, Zhou J and Ahuja R 2006 *Phys. Rev. Lett.* **96** 055507
[5] Zhang Z F, Liu W L and Song Z T 2011 *J. Vac. Sci. Technol. B* **29** 011020
[6] Cui H, Cho J Y, Hwang H S, Lim J H, Park J H, Park H S, Hong K and Park J G 2010 *J. Electrochem. Soc.* **157** H1036
[7] Zhong M, Song Z T, Liu B, Feng S L and Chen B 2008 *J. Electrochem. Soc.* **155** H929
[8] Krishnan M, Nalaskowski J W and Cook L M 2010 *Chem. Rev.* **110** 178
[9] Lee T Y, Lee I K, Choi B H and Park Y S 2007 US Patent Application 11967446 1–4
[10] Cui H, Cho J Y, Hwang H S, Lin J H, Park J H, Park H S, Hong K and Park J G 2011 *J. Electrochem. Soc.* **158** H666
[11] He A D, Song Z T, Liu B, Zhong M, Wang L Y, Lü Y G and Feng S L 2012 *Chin. Phys. B* **22** 018503
[12] Cho Y J, Cui H, Park J H, Yi S H and Park J G 2010 *Electrochem. Solid-State Lett.* **13** H155
[13] Shin D H, Lee D H, Jeong M G, Park H S and Lim D S 2012 *J. Electrochem. Soc.* **159** H349
[14] Barr T L and Seal S 1995 *J. Vac. Sci. Technol. A* **13** 1239
[15] Yan W X, Wang L Y, Zhang Z F, He A D, Zhong M, Liu W L, Wu L C and Song Z T 2012 *Chin. Phys. Lett.* **29** 038301
[16] Bardal E 2003 *Corrosion and Protection* (New York: Springer) p. 65