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Basic Wet-Etching Solutions for $Ge_2Sb_2Te_5$ Phase Change Material

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We report on basic wet-etching solutions for $Ge_2Sb_2Te_5$ (GST) phase change material. A scanning electronic microscope was used to observe the surface morphology and measure the etching rate. On the basis of the etching results, it was found that the aqueous solutions of 10 vol % H_2O_2 plus 25 wt % bases, such as KOH, $NH_3 \cdot H_2O$, and tetramethylammonium hydroxide, resulted in lower etching rates but a much smoother surface than that of common acid solutions. In addition, the etching process could be well controlled. Further X-ray photoelectron spectroscopy study of the etched samples showed that GST, etched by KOH, possessed higher oxidized states than that by HNO_3, which revealed that the etching process was milder in basic solutions, while the dissolution of GST was more favored in acid environments due to the protonation effect.
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In recent years, there has been increasing interest in chalcogenide $Ge_2Sb_2Te_5$ (GST) for phase change memory (PCM), which is taken as the best performing candidate for scaled nonvolatile memories, as Flash technologies face major scaling issues at the 32 nm node and beyond.[1,2] GST can be rapidly heated and quenched to either amorphous or crystalline phases that strongly differ in resistivity, which especially fits the requirements of PCM.[3]

A key requirement for the application of GST in PCM is the development of controlled wet and dry etching techniques for cleaning and patterning of device structures. Compared with dry etching, wet etching is cheaper, more convenient, and not restricted by precious equipment. Some attempts have been done on GST wet etching. Cheng et al.[4] found that GST could be control-etched by an aqueous solution of 20% nitric acid. They further studied the possible mechanisms by an inductively coupled plasma method and X-ray photoelectron spectroscopy (XPS).[5] However, research on GST wet etching is still scarce. More studies are still necessary to find better wet-etching solutions and further understand the chemical properties of GST in aqueous environments. In this study, we developed basic wet-etching solutions for the GST film. We found that the etching process could be smooth and well controlled in aqueous solutions of 10 vol % H_2O_2 plus 25 wt % bases, such as KOH, $NH_3 \cdot H_2O$, and tetramethylammonium hydroxide (TMAH). Possible mechanisms were further studied by XPS.

Experimental

The deposition of amorphous GST was performed with Φ 200 mm SiO_2/Si substrates using a Unaxis LLS EVO tool (produced by Oerlikon Balzers Ltd., Liechtenstein). Deposition conditions were as follows: target GST of 127 × 381 mm (99.999 wt %), substrate of 1400 nm SiO_2/Si, radio-frequency power of 0.2 kW, argon pressure of 0.27 Pa, and deposition temperature at room temperature.

Aqueous solutions of 10 vol % H_2O_2 plus 25 wt % bases, such as KOH, NaOH, $NH_3 \cdot H_2O$, and TMAH, respectively, were prepared as etchants. Acid solutions of citric acid, HNO_3, H_2SO_4, H_3PO_4, tartaric acid, and HCl were used for reference. The surface morphology and etching rate were observed with a field-emission-scanning electron microscope (s-4700 type, Hitachi). The chemical bonding characteristics of amorphous GST after etching was examined by XPS.

Results and Discussion

Preliminary wet-etching results in acid solutions.— Figure 1 shows the etch rate of amorphous GST as a function of acids with/without H_2O_2. When there was no H_2O_2 in the acid wet-etching solutions, only HNO_3 could be the effective etchant for GST. However, when 10 vol % H_2O_2 was added, almost all the acid solutions could etch GST. Especially, strong inorganic acids such as HNO_3, H_2SO_4, H_3PO_4, and HCl could rapidly remove GST with the etch rates of 4.02, 3.26, 2.96, and 2.11 nm/s for HNO_3, H_2SO_4, H_3PO_4 and HCl, respectively. Although the etch rates for citric acid and tartaric acid were much lower, they could still reach as high as 0.74 and 0.60 nm/s, respectively.

Figure 2 further shows the typical scanning electron microscope (SEM) images of the GST surface after etching in HNO_3 + 10 vol % H_2O_2 solutions for 2 min (results were almost the same with/without H_2O_2). As can be seen from Fig. 2a, GST was islandlike after etching, and there were obvious voids among the etched GST islands. This trend was also reflected from the cross section view of Fig. 2b. The recess and the prude of the etched GST surface were about 30 and 69 nm, respectively.

It seems that acid solutions (especially with H_2O_2) could rapidly remove GST but result in a very rough surface, which would badly deteriorate the reliability of the device when acid solutions are used to fabricate PCM structures. Thus, it is necessary to find other solutions for GST wet etching to get better results with respect to a suitable etch rate and a smooth surface.

Basic wet-etching solutions.— Figure 3 shows the etch rate of amorphous GST as a function of bases with 10 vol % H_2O_2. There was no etch rate for $NH_3 \cdot H_2O$, while the etch rates could reach 8.87, 13.2, and 17.83 nm/min for NaOH, TMAH, and KOH, respectively. The corresponding etched GST surface for the KOH solution is further shown in Fig. 4. After 15 min of etching, both surface view and cross section view show that the etched GST surface is still quite smooth. In general, the basic wet-etching solutions led to a slower etch rate but a much smoother surface compared to acid wet-etching solutions.

To confirm whether this etching process could be controlled, we carried out the experiments of etch depth vs etch time test, the results of which are shown in Fig. 5. The etched depth was 247.5 nm after 3 min of etching, while it was 302.5 and 354.5 nm after 6 and 9 min, respectively. There is a nice linearity between etch depth and etch time, which indicated that the etching process for the KOH basic solution could be well controlled.

Possible wet-etching mechanisms.— Because there were so much differences between the basic solutions and the acid solutions for GST wet etching, XPS tests were conducted to assess the chemical binding characteristics of the etched films, which aimed to further explore the possible wet-etching mechanisms for different so-

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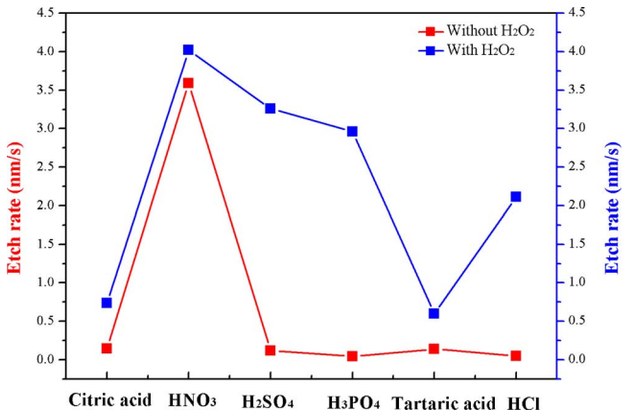

Figure 1. (Color online) Etch rate of amorphous GST as a function of acids with/without H_2O_2.

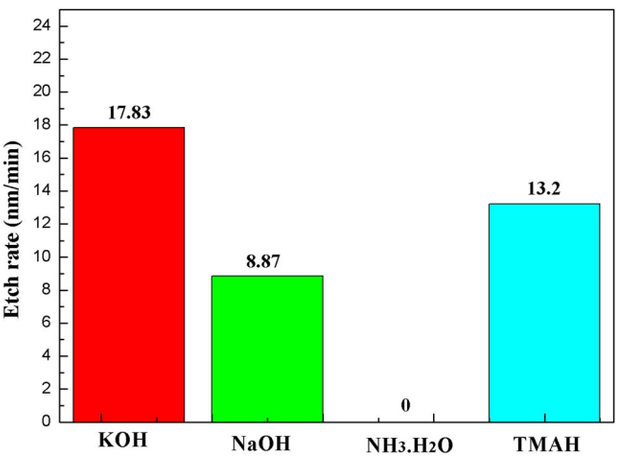

Figure 3. (Color online) Etch rate of amorphous GST as a function of bases with 10 vol % H_2O_2.

lutions. Two typical GST samples were chosen for the XPS tests: one is dipped in HNO_3 + 10 vol % H_2O_2 for 2 min, while the other one is etched in KOH + 10 vol % H_2O_2 for 15 min.

Figure 6 shows the XPS spectra of Ge 2p for samples after etching in HNO_3 and KOH solutions. The peak position for the sample after etching in HNO_3 is at 1218.4 eV, while it is at 1223.8 eV for the sample after etching in KOH solution. The peak positions of Ge $2p^{3/2}$ of homopolar Ge, GeO_2, and GeO are 1217, 1219.8, and

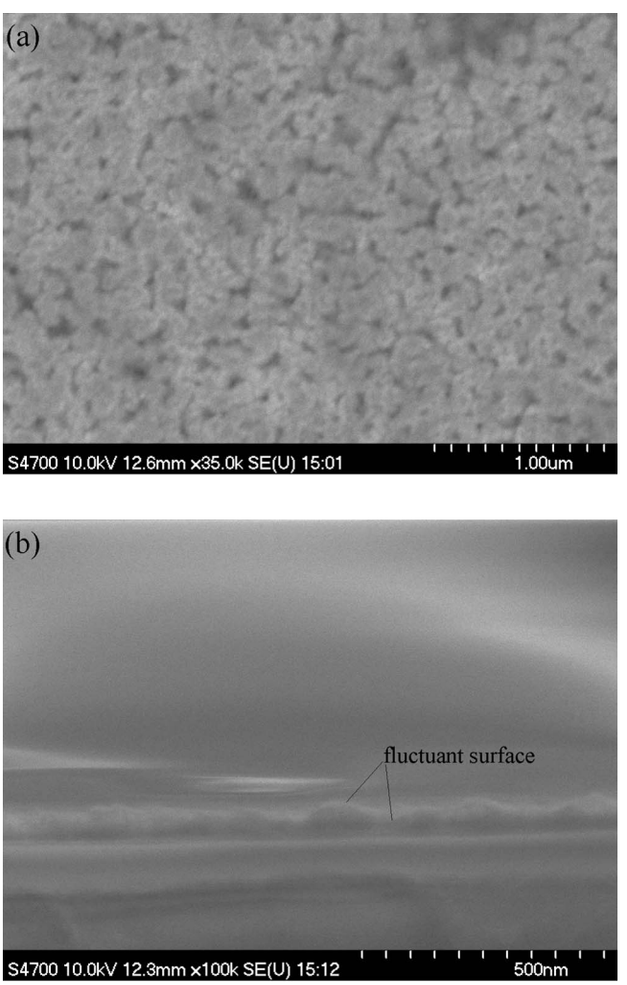

Figure 2. Typical SEM images of GST surface after etching in HNO_3 + 10 vol % H_2O_2 for 2 min. (a) Surface view. (b) Cross section.

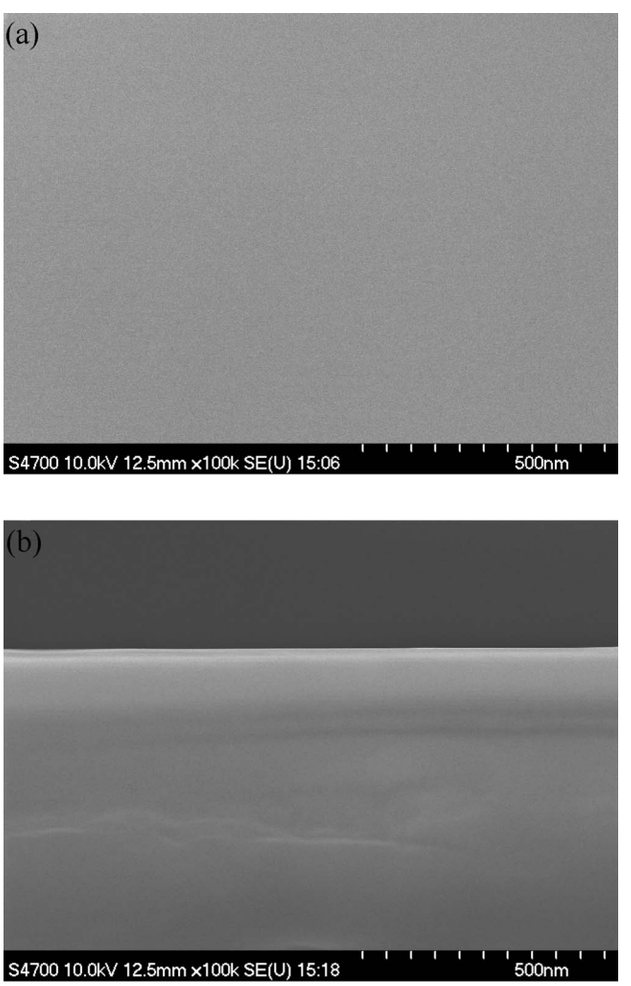

Figure 4. Typical SEM images of GST surface after etching in KOH + 10 vol % H_2O_2 for 15 min. (a) Surface view. (b) Cross section.

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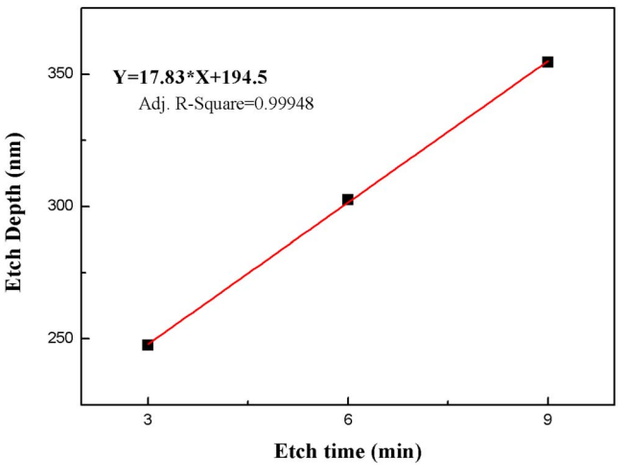

Figure 5. (Color online) Etch depths of amorphous GST vs etch time in KOH + 10 vol % H_2O_2 solution.

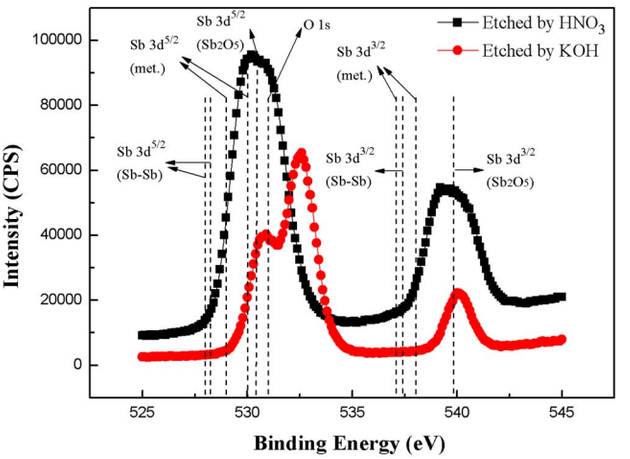

Figure 7. (Color online) XPS spectra of Sb 3d for GST samples after etching in HNO_3 and KOH solutions.

1221.2 eV, respectively.[5] Therefore, the Ge chemical state for the sample after etching in HNO_3 is mainly Ge–Te or Ge–Sb, while it is GeO for the sample after dipping in KOH.

The XPS spectra of Sb 3d for the two samples are shown in Fig. 7. According to the literature, the Sb $3d^{3/2}$ of Sb_2O_5 and the Sb metallic bondings are at 539.8 and 537–538 eV, respectively.[5] The Sb $3d^{5/2}$ of Sb_2O_5 and the Sb metallic bondings are at 530.4 and 529–530 eV, respectively.[5] The Sb homopolar (Sb–Sb) bonding is at 537.4 and 527.9 eV or 528.2 eV for Sb $3d^{3/2}$ and Sb $3d^{5/2}$, respectively.[5] As can be seen from Fig. 7, the peak positions for the sample after etching in HNO_3 are at 530.2 and 539.2 eV, which can be ascribed to Sb–Te or Sb–Ge bonds because they are both located between the peaks of Sb metallic bonding and Sb_2O_5. As for the sample after etching in KOH solution, there are three peaks at 530.9, 532.6, and 540 eV, respectively. The position of 530.9 eV is the O 1s peak. The peak 532.6 eV is located between the positions of Sb metallic bonds and Sb_2O_5, which means that Sb atoms do not bond with Sb atoms but with Te and Ge atoms. As far as the peak at 540 eV is concerned, it reflects the existence of Sb_2O_5.

Figure 8 shows the XPS spectra of Te 3d for the selected GST samples after etching. Te $3d^{5/2}$ of Te metallic bonding and Te oxide bonding is located at 572.5–574 and 576–577 eV, respectively.[5] Te $3d^{3/2}$ of Te metallic bonding and Te oxide bonding is located at 583–584 and 586–587 eV, respectively.[5] The Te homopolar peak is at 573.1 and 583 eV for Te $3d^{5/2}$ and Te $3d^{3/2}$, respectively.[5] As can be seen from Fig. 8, the peak positions for the sample after etching in HNO_3 are at 575.8 and 586.3 eV. The peak at 575.8 eV can be ascribed to Te–Sb or Te–Ge because it is located between the positions of Te metallic bonding and Te oxide bonding for Te $3d^{5/2}$. The peak at 586.3 eV is Te $3d^{3/2}$ peak for Te oxide bonding. The spectrum is much simpler for the GST sample after being dipped in KOH solution. There are two weak peaks located at 576.5 and 586.9 eV, both of which can be ascribed to Te oxide bonding.

In general, the XPS spectra show that the chemical bondings for the GST sample after etching in HNO_3 are mainly Ge–Sb, Ge–Te, and Sb–Te, while they are Ge–O, Sb_2O_5, and Te–O for the sample after dipping in KOH solution. It is strange that the GST etched by KOH possessed higher oxidized states than that by HNO_3 because the oxidation ability for H_2O_2 is much stronger in acid environments than in basic solutions. One possible explanation could be that, in a strong acid environment, the GST film is rapidly oxidized. The corresponding oxidized states for Ge, Sb, and Te were Ge (IV), Sb (V), and Te (IV), respectively.[6] However, the oxidized GST film could quickly dissolve in the acid solution because there is a strong protonation effect because of H^+, hence promoting the wet-etching process and leaving the fresh GST surface with low oxidized states

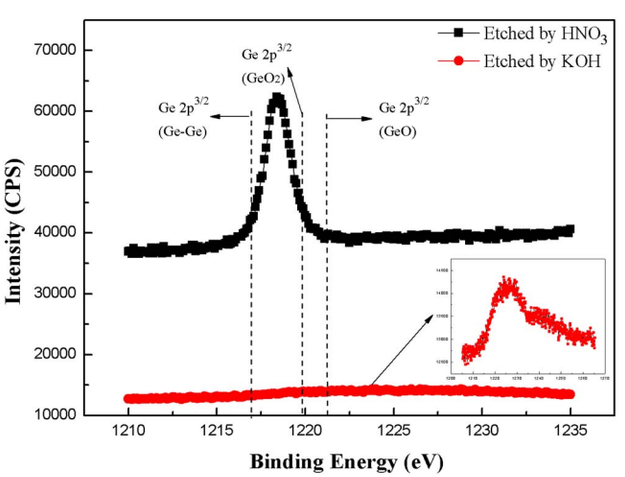

Figure 6. (Color online) XPS spectra of Ge 2p for GST samples after etching in HNO_3 and KOH solutions.

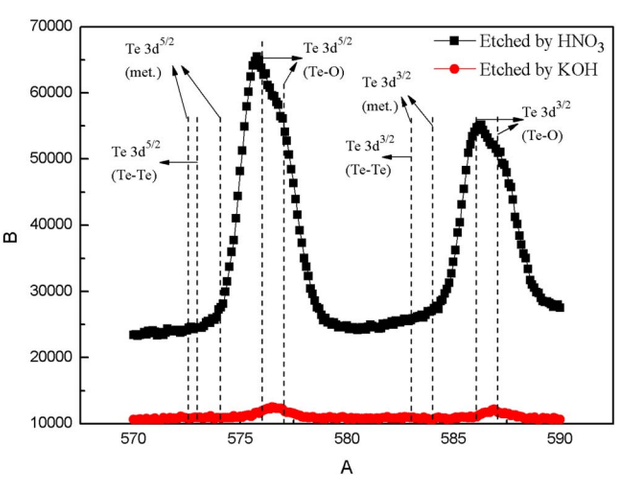

Figure 8. (Color online) XPS spectra of Te 3d for GST samples after etching in HNO_3 and KOH solutions.

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(Ge–Sb, Ge–Te, and Sb–Te). As for strong basic solutions, oxidation could occur in a milder way. Then the oxidized GST film could be etched slowly in bases, which would lead to a low etch rate and a smooth surface.

Conclusions

We show that etching GST thin films can be smooth and well controlled by using 25 wt % bases (such as KOH, $NH_3 \cdot H_2O$, and TMAH) plus 10 vol % H_2O_2. The basic wet-etching solutions can result in lower GST etching rates but with a much smoother surface than common acid solutions (such as HNO_3) do. GST samples, after dipping in KOH and HNO_3 solutions, were selected for XPS measurements to obtain insights into the wet-etching behaviors under different aqueous environments. Results showed that the chemical bondings for the GST sample after etching in HNO_3 are mainly Ge–Sb, Ge–Te, and Sb–Te, while they are Ge–O, Sb_2O_5, and Te–O for the sample after dipping in KOH solution. It was hypothesized that GST was first oxidized by H_2O_2 both in basic and acid solutions. The etching process was milder in basic solutions, while the dissolution of GST was more favored in acid environments due to the protonation effect, leaving a fresh GST surface.

Acknowledgments

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