

Dry etching of new phase-change material $\text{Al}_{1.3}\text{Sb}_3\text{Te}$ in CF_4/Ar plasma*

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Abstract: The dry etching characteristic of $\text{Al}_{1.3}\text{Sb}_3\text{Te}$ film was investigated by using a CF_4/Ar gas mixture. The experimental control parameters were gas flow rate into the chamber, CF_4/Ar ratio, the O_2 addition, the chamber background pressure, and the incident RF power applied to the lower electrode. The total flow rate was 50 sccm and the behavior of etch rate of $\text{Al}_{1.3}\text{Sb}_3\text{Te}$ thin films was investigated as a function of the CF_4/Ar ratio, the O_2 addition, the chamber background pressure, and the incident RF power. Then the parameters were optimized. The fast etch rate was up to 70.8 nm/min and a smooth surface was achieved using optimized etching parameters of CF_4 concentration of 4%, power of 300 W and pressure of 80 mTorr.

Key words: $\text{Al}_{1.3}\text{Sb}_3\text{Te}$; dry etching; CF_4/Ar gas mixture; etch rate

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1. Introduction

Phase change random access memory (PCRAM) based on the rapid phase change effect in the phase change material film has been considered as one of the most promising candidates for the next generation of nonvolatile memory. The chalcogenide compounds such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) have been widely used in the phase change memory. Recently a new chalcogenide compound $\text{Al}_{1.3}\text{Sb}_3\text{Te}$ (AST) has been proposed. Compared to GST, AST is proved to be better for the phase change memory use because of its higher crystallization temperature ($\sim 210^\circ\text{C}$), larger crystallization activation energy (3.32 eV), better data retention ability (124°C for 10 years), and faster phase change speed^[1].

In the memory fabrication procedures, the etching process of the phase change memory is very essential. However, compared to many studies on how to etch GST, there is no study on how to etch AST^[2-4].

Etching using Cl-based plasma can be done with a high etching rate by forming volatile product AlCl_3 at high temperature ($>180^\circ\text{C}$) or Al_2Cl_6 at room temperature^[5]. However, there are some disadvantages using Cl-based plasma, as reported in Ref. [6]. Firstly, the etching process in pure Cl-based plasma is usually isotropic as a result of its chemical mechanism. In order to solve the problem, some available methods were reported including adding C, H, or O in the plasma to form an etch-inhibiting layer on vertical sidewalls^[5,7]. Secondly, the reaction products have to be carefully disposed of to avoid pollution and corrosion damage. In this paper we introduce F-based plasma to etch the phase change material AST.

The reaction products of F-based plasma are usually low corrosives and environmentally safe. The etching of Al compounds using F-based plasma was found to leave the film surface almost unaffected since F reacts with Al to form AlF_3 , which has a low volatility and may block further etching^[8]. However, if the low volatile products on the surface can be efficiently removed by ion bombardment, the etching of an Al compound with a reasonable rate may also be realized by using F-based plasma. Furthermore, AlF_3 formed on the pattern sidewalls may be accumulated to inhibit lateral etching. In the present study, this issue has been handled by adding Ar in plasma and increasing the bias voltage during the etching process.

In this paper, for the first time the reactive-ion etching (RIE) of AST in CF_4/Ar plasma at different proportions is investigated. The etch rate is examined systematically as a function of pressure, power, and the CF_4 concentration in the CF_4/Ar mixture gas. An etch rate of up to 70.8 nm/min has been achieved.

2. Experimental details

AST films (100 nm) were fabricated on Si substrates by using the radio frequency (RF)-magnetron sputtering method using Al, Sb, and Sb_2Te_3 targets at room temperature with a base pressure of 2.1×10^{-4} Pa. Composition of $\text{Al}_{1.3}\text{Sb}_3\text{Te}$ film was determined by means of energy dispersive spectroscopy (EDS). A Shipley 6809 photo-resist was used for pattern definition. An Oxford 80plus RIE system with a maximum RF power of 600 W was used for etching the AST film. The etch

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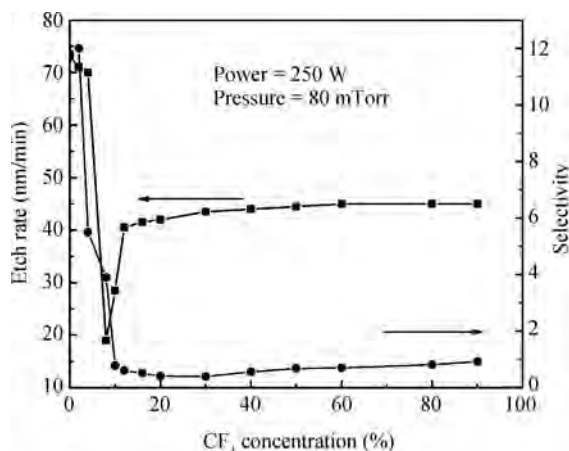


Fig. 1. Etch rate of AST and the selectivity of AST/SiO₂ as a function of oxygen concentration under the constant pressure of 80 mTorr and power of 300 W.

Table 1. Boiling points of the Al, Sb, Te-fluoride^[10].

Material	Bonding	Boiling point (°C)
Sb	SbF ₅	141
Sb	SbF ₃	345
Te	TeF ₄	195
Te	TeF ₆	-39
Al	AlF ₃	1275

gas ratio was controlled by mass flow controllers, and the gas pressure in the chamber was adjusted by using a clapper valve. The temperature of the sample holder was controlled by heat transfer fluid (Hexid) and held at 30 °C. The total flow rate of CF₄ + Ar was 50 sccm throughout the experiment, while the CF₄/Ar ratio was varied as an optimizable parameter. Etch depths were measured by using a surface profile meter. The surface morphology and patterning of mesa structure were examined using scanning electron microscopy (SEM, Hitachi S-4700). The chemical states of the etched surfaces compared with the as-grown ones were examined by X-ray photoelectron spectroscopy (XPS).

3. Results

3.1. Effect of gas mixing ratio

Figure 1 shows the etch rate as a function of the CF₄/Ar gas mixture ratio. The etchings are carried out at a constant pressure of 80 mTorr and an applied power of 300 W. When there is very little CF₄ in the etchant gas (the content of CF₄ from 0 to 4%), the etch rate is very high. Ion Ar⁺ bombardment plays an important role in this etching process^[9]. In this process, the etching volatile products GeF₂ (boiling point: 130 °C) can be removed easily at high temperature. The etching products TeF₄ (boiling point: 195 °C), SbF₃ (boiling point: 345 °C) and AlF₃ shown in Table 1, which have a low volatility and may block further etching. However, there is only a small amount of low volatile products on the surface, which can be efficiently removed by ion bombardment, so the etch rate of AST using F-based plasma is not reduced too much in this process.

It is evident that the etch rate decreases rapidly along with

the content of CF₄ increasing from 4% to 10% in the gas mixture. As the F⁻ ions in the plasma further increase, poor Ar ion sputtering leads to the accumulation of AlF₃^[8], which may inhibit further reaction on the etching surface and, therefore, the etching rate decreases. All the F⁻ ions are in the chemical reaction with the weakest ion bombardment and the amount of nonvolatile products is the greatest when the content of Ar⁺ ions is 8%. So the etch rate reaches its the lowest value.

It is clear that the etch rate increases along with the content of CF₄ increasing from 8% to 16% in the gas mixture shown in Fig. 1. After the amount of nonvolatile products reaches its highest value, some CF₄ ions are left behind. F atoms in the fluorine-based plasma can etch the nonvolatile products and take those away^[11]. That compensates the reduction of ion Ar⁺ bombardment so the etch rate is increasing slightly as the content of CF₄ increases. The etch rate of SiO₂ is very sensitive to the concentration of CF₄. When the CF₄ gas content increases, the intensity of F radicals increases and it increases the etch rate of SiO₂. As a result, the selectivity of AST to SiO₂ decreases.

As the content of CF₄ increases in the range from 0 to 10%, the etch slopes of AST are improved, as shown in Fig. 2. The AST films are all 100 nm thick and deposited on the Si substrates in the same conditions and are all etched for 2 min. The etch power is 300 W and the chamber pressure is 80 mTorr. When we use pure Ar to etch the AST film, there is no non-volatile products so the etching process is isotropic and the etch slopes are not vertical at all, as shown in Fig. 2(a). When there is some CF₄ in the gas mixture, some nonvolatile products such as Al₂O₃ and AlF₃ are formed on the pattern sidewalls, which can accumulate to inhibit lateral etching. So, with the amount of CF₄ gas increasing, the etch slopes of AST are improved. The AST film etched at CF₄ concentration of 4% shows an almost vertical etch slope, as shown in Fig. 2(c). In this way, the high anisotropic pattern can be obtained in F-based plasma. The etch rate of AST is reduced greatly, as shown in Fig. 2(d).

3.2. Effect of RF power

Figure 3 shows the etch rate of AST thin films as a function of the power, while the process pressure is 80 mTorr and the flow rates of CF₄ and Ar are fixed at 2 and 48 sccm, respectively. Figure 3 illustrates the monotonic increase trend of etch rate upon increasing of power. According to this trend, the high etch rate of AST thin films 70.8 nm/min is obtained under 300 W. With the power increasing, the plasma density increases and the bombardment energy also increases. So the etch rate of AST thin films is enhanced.

3.3. Effect of process pressure

Figure 4 shows the etch rate of the AST film as a function of pressure, while the power is 300 W and the flow rates of CF₄ and Ar are fixed at 2 and 48 sccm, respectively. The rate increases approximately linearly with pressure below 80 mTorr. The increase of the etch rate is most likely due to an increase in the concentration of radicals resulting from the increase of gas pressure. Therefore the pressure dependence of the etch rate should be dominated by the active abundance of neutral etchant species. On the other hand, as the pressure increases, the mean

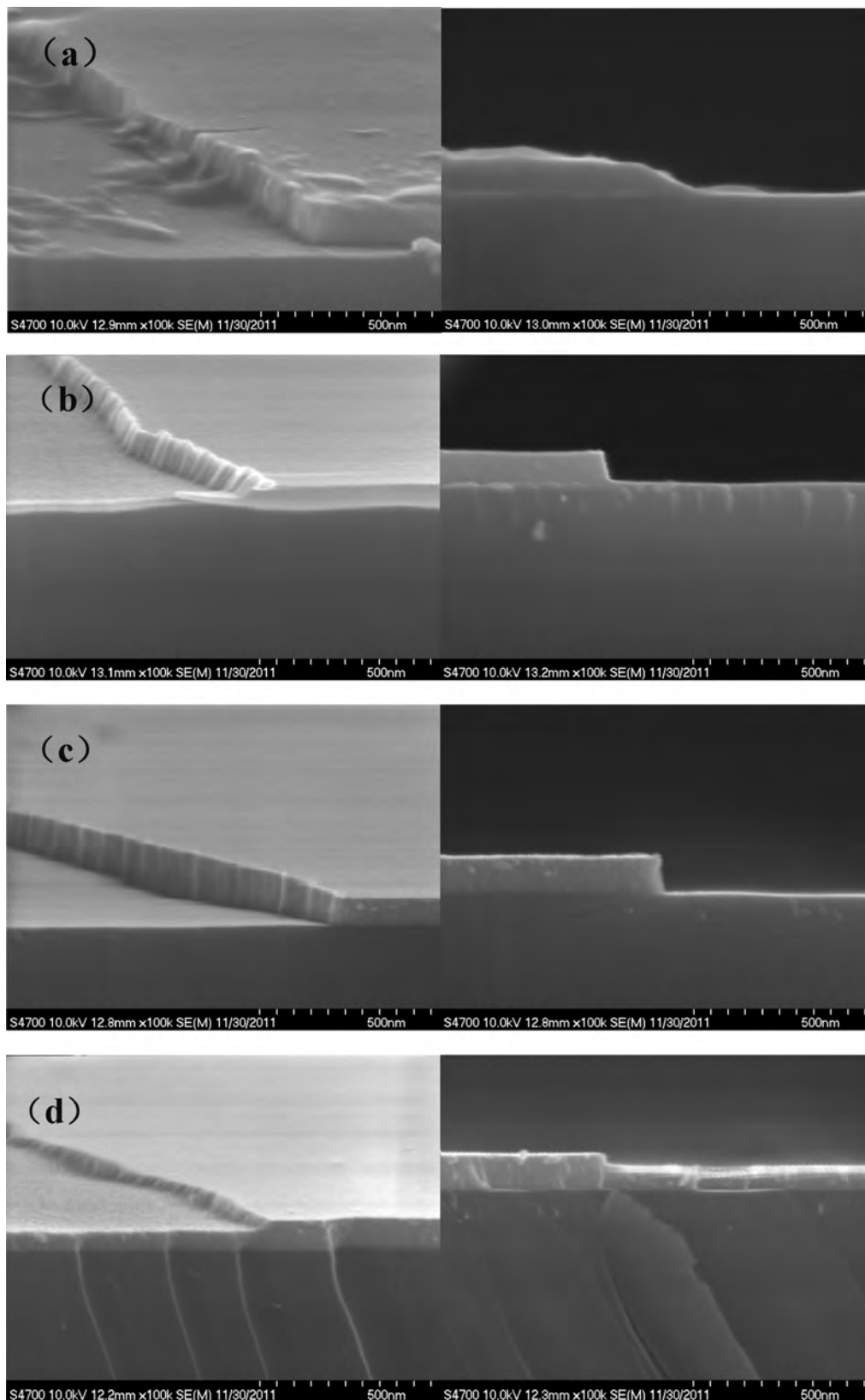


Fig. 2. Scanning electron micrographs (SEMs) of surfaces and cross-sections of AST features after etching with CF_4/Ar ratios of (a) 0, (b) 2%, (c) 4%, (d) 10%. The etchings are carried out at a constant pressure of 80 mTorr and an applied power of 300 W.

free path of the charged particles decreases and hence the effect of dc bias is lower^[12]. As the DC bias decreases, physical bombardment of the substrate by positive ions becomes weaker. So the etch rate seems to decrease above 80 mTorr.

3.4. Effect of O_2

Figure 5 shows the etch rate of AST as a function of O_2 percentage in the $\text{CF}_4/\text{Ar}/\text{O}_2$ gas mixture. The flow rates of

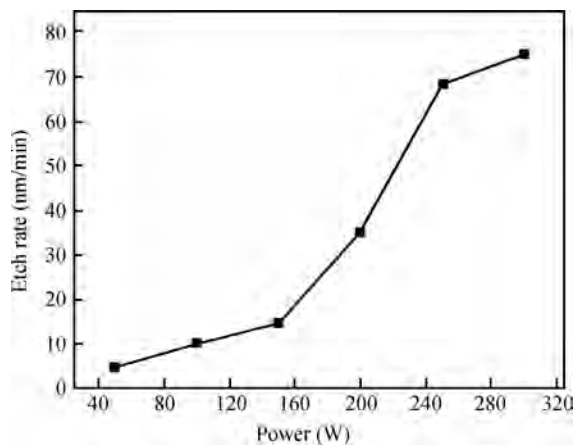


Fig. 3. Etch rate of the AST film as a function of power.

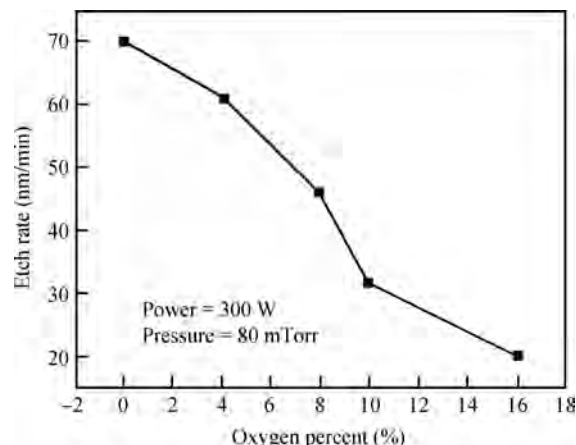


Fig. 5. Etch rate of the AST film as a function of O₂ percent in the CF₄/Ar/O₂ gas mixture.

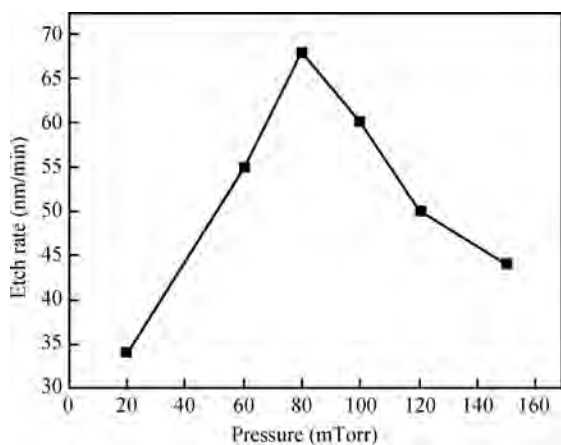


Fig. 4. Etch rate of the AST film as a function of pressure.

CF₄ and Ar are fixed at 2 and 48 sccm, respectively. The etch rate of AST decreases with increasing O₂ flow rate monotonically. This indicates that a film that is more etch resistive than AST is formed on the sample surface in an oxygen ambient. This was proved by the Al–O bonds, which have larger bonding energy, being present in the XPS experiment^[13]. That is to say, once the oxide layers are formed on the surface, the etch rate is limited by the surface oxide because the bond strengths of the oxides are larger. The formation of surface oxide leads to a more etch-resistive surface.

3.5. Analysis using XPS

In order to clarify chemical states of etched surfaces, the chemical bonding states of the AST surface etched by the CF₄/Ar (25/25 sccm) plasma were investigated by XPS. The etchings were carried out at a constant pressure of 80 mTorr and an applied power of 300 W.

In Fig. 6(a), there are no peaks in the spectrum of the as-grown sample surface. It is clear that there are no F elements on the as-grown AST surface. After the sample is etched by CF₄/Ar, there are some new peaks in the spectrum. Each XPS peak could be deconvoluted to fluoride (fluorinated AST portion) at 685.8 eV and free F at 684.5 eV. The two peaks also exist in the spectrum after the sample is sputtered for 10 s subsequently but the intensities decrease.

Figure 6(b) shows that the peak at 74.9 eV in the spectrum of the as-grown sample surface shifts to the right peak at 75.9 eV after the sample is etched. This is because some F atoms substitute O in Al–O bonds and Sb in Al–Sb bonds and the electronegativity of Sb and O elements is smaller than that of F element. After the sample is sputtered for 10 s by the Ar, the peak at 75.9 eV subsequently shifts to the left a little and the intensity decreases a little. The result indicates that there are many nonvolatile Al₂O₃ and AlF_x products on the etched surface and they are not easily removed by sputtering. These nonvolatile products stop the etching process greatly.

Figure 6(c) shows the Te3d XPS narrow scan spectra. The peak at 571.9 eV in the spectrum of the as-grown sample surface shifts to the right after the sample is etched. This is because more F atoms substitute Sb in Sb–Te bonds and the electronegativity of the Sb element is smaller than that of the F element. After the sample is sputtered for 10 s in pure Ar subsequently, the peak locates at 572.0 eV and its intensity decreases dramatically. Figure 6(d) is similar to Fig. 6(c). Both the results indicate that there are very little TeF_x etch products on the etched film surface and they can be very easily removed by subsequently sputtering. So they will not stop the etching greatly.

Figure 6(d) shows Sb3d XPS narrow scan spectra. The peak at 530.1 eV from Sb–O bonding in the spectrum of the as-grown sample surface indicates that the as-grown sample has been oxidized. This peak shifts to the right a little after the sample is etched. This is because some F atoms substitute O in Sb–O bonds and the electro-negativity of O element is smaller than that of the F element. The peak at 528.2 eV from Sb–Te bonding in the spectrum of the as-grown sample surface shifts to the right peak, which is from Sb–F_x bonding and its intensity decreases dramatically after the sample is etched. After the sample is sputtered for 10s by the pure Ar subsequently the peak from Sb–F_x bonding cannot be found. All the results indicate that Sb–Te bonding is easily etched and there are very little SbF_x etch products and they are easily removed by the subsequent sputtering. This corresponds to Table 1.

The SEM micrograph of AST film etched with CF₄/Ar ratio of 2/48, pressure of 80 mTorr, and power of 300 W is shown in Fig. 2(c). It can be seen in Fig. 2(c) that the etched surface is

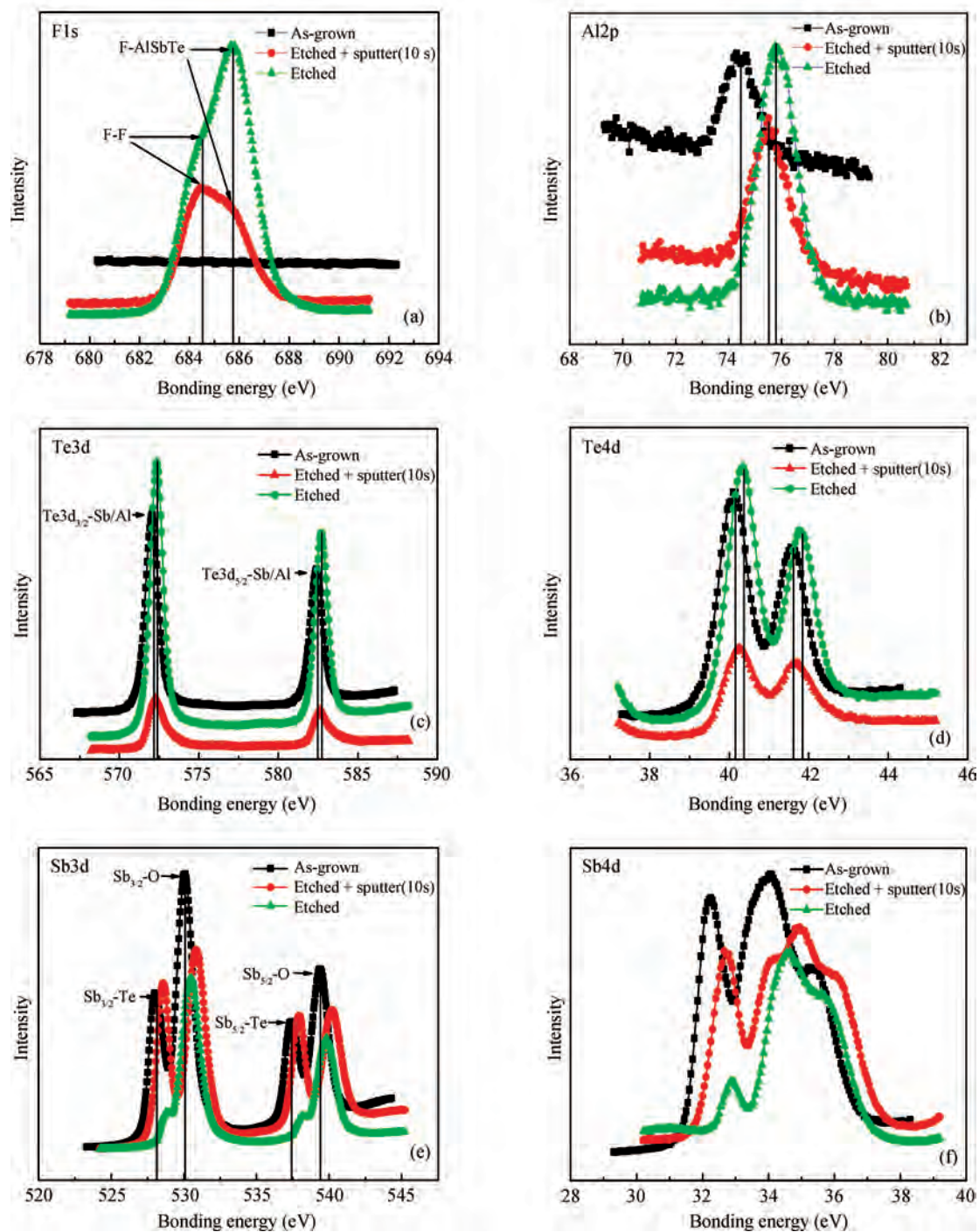


Fig. 6. (a) F1s, (b) Al2p, (c) Te3d, (d) Te4d, (e) Sb3d, (f) Sb4d XPS narrow scan spectra.

very smooth and the sidewall is nearly vertical. The etch rate up to 70.8 nm/min is achieved. These meet all application requirements for high-density phase change memory devices. We have used these optimized parameters in the etch process of phase change memory device fabrication based on AST and the phase change memory devices have a good performance.

4. Conclusion

The etch rate of AST films in a CF_4/Ar plasma decreases with the increase of CF_4 concentration from 0 to 10% at constant background pressure and power. The presence of CF_4 will

lead to nonvolatile product accumulation, which will decrease the etch rate of AST. However, the etch profiles were improved with increasing CF_4 concentration. Adding O_2 to the etch gas will lead to the oxidation of aluminum, which will reduce the etch rate. XPS results indicate that the accumulation of Al_2O_3 and AlF_x nonvolatile products on the surface is the main reason for the decreasing of the AST etch rate. Al and Sb elements are very easily oxidized. The smooth surface, the vertical sidewall, and the fast etch rate were achieved using the following etching parameters: CF_4/Ar mixing ratio of 2/48, base pressure of 80 mTorr, and power of 300 W. We have used these optimized parameters in the etch process of phase change memory device

fabrication based on AST.

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