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High rate dry etching of $(BiSb)_2Te_3$ film by CH_4/H_2-based plasma

Junqiang Song*, Xun Shi, Lidong Chen

CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, PR China

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ABSTRACT

Etching characteristics of p-type $(BiSb)_2Te_3$ films were studied with $CH_4/H_2/Ar$ gas mixture using an inductively coupled plasma (ICP)-reactive ion etching (RIE) system. The effects of gas mixing ratio, working pressure and gas flow rate on the etch rate and the surface morphology were investigated. The vertical etched profile with the etch rate of 600 nm/min was achieved at the optimized processing parameters. X-ray photoelectron spectroscopy (XPS) analysis revealed the non-uniform etching of $(BiSb)_2Te_3$ films due to disparate volatility of the etching products. Micro-masking effects caused by polymer deposition and Bi-rich residues resulted in roughly etched surfaces. Smooth surfaces can be obtained by optimizing the $CH_4/H_2/Ar$ mixing ratio.

1. Introduction

Thermoelectric (TE) micro-devices such as thermoelectric micro-coolers (μ-TECs) [1–4], thermoelectric micro-generators (μ-TEGs) [5–7], and micro-thermoelectric gas sensors [8] have received a great deal of attention recently. Among the various thermoelectric materials, bismuth telluride-based compounds are viewed as one of the best candidates to be used in thermoelectric micro devices due to their excellent thermoelectric properties near room temperature [9]. One important technology for integrating TE micro-devices is the patterning of thermoelectric materials, and various methods have been reported to pattern bismuth telluride-based materials such as lift-off [2], wet-chemical etching [3], shadow-masking [5], dry-plasma etching [6,10], and the combined process of lithography and electrochemical deposition [1]. Among them, dry-plasma etching can provide significant benefits for the fabrication of the micrometer/nanometer sized patterns with anisotropic profiles, improved dimensional control and greater uniformity. However, there are only few reports focusing on the dry etching behavior of bismuth telluride-based materials. Böttner et al. have used reactive dry etching to pattern n-type Bi_2Te_3 and p-type $(BiSb)_2Te_3$, but the etched pattern showed a large sidewall angle [6]. Recently Boniche et al. reported reactive plasma etching of p-type Bi_2Te_3 with the etch rates of 0.6 μm/min by using CH_4/H_2-based gases, but the etched profiles showed lateral undercut [10].

In this paper, we report dry etching of p-type $(BiSb)_2Te_3$ films using $CH_4/H_2/Ar$ process gases in an ICP-RIE system. The primary principle of CH_4/H_2-based plasma etching is to form volatile methyl and hydride compounds, which have been used widely in reactive etching for a range of semiconducting compounds such as groups III–V [11,12] and II–VI [13,14]. The combinations of bismuth telluride-based compounds such as p-type $(BiSb)_2Te_3$ and n-type $Bi_2(TeSe)_3$ with highly reactive hydrogen and methane radicals or ions can form all volatile methyl and hydride compounds. Table 1 lists the boiling temperatures of several possible methyl and hydride compounds [15]. On the other hand, there are also polymerization reactions of hydrocarbon compounds originated from methane. The deposition of hydrocarbon polymers on the etched surface can slow or stop the etching process and roughen the etched surface [16,17]. Therefore, it is possible to achieve both the high etch rate and the smooth etched surface through adjusting the mixing ratio of CH_4/H_2 gases. Furthermore, the other processing parameters such as Ar ratio in mixture, working pressure and total gas flow rate could also affect the etch rate and the etched profile, which also were investigated.

2. Experimental

P-type $(BiSb)_2Te_3$ films were deposited on silicon wafers with a thermally grown 300 nm oxide layer by a magnetron co-sputtering system. See the details in Ref. [18]. The sample wafer was masked by the photoresist (AZ 4620) which was patterned by the lithography technology and baked in an oven at 100 °C for about 30 min, and then diced to small pieces for etching. Dry etching of p-type

* Corresponding author. Tel.: +86 2152412522.
E-mail address: jqsong@mail.sic.ac.cn (J. Song).

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Table 1
Boiling temperature of several possible etching byproducts of p-type $(BiSb)_2Te_3$ and n-type $Bi_2(TeSe)_3$ materials in CH_4/H_2-based plasma chemistry.

Byproducts	$Bi(CH_3)_3$[a]	$Sb(CH_3)_3$[a]	SbH_3[a]	H_2Te[a]	H_2Se[a]
Boiling temp (°C)	110	81	−17	−2	−41

[a] Ref. [15].

$(BiSb)_2Te_3$ films was performed in an ICP-RIE system(Oxford ICP 180) with two separate RF sources, an ICP source and a biased RF source. The ICP source is used to generate high-density plasma and the biased RF source is connected to the substrate electrode to control the energy of the ions. The ICP power and the biased RF power were fixed at 1500 W and 50 W, respectively. The substrate temperature was maintained at 20 °C by using He cooling. The etch depth was measured using a surface profilometer (Veeco Dektak150) after removal of the photoresist from the etched samples. The surface morphology was measured using scanning electronic microscopy (SEM; JSM-6360LV). The sample surface was analyzed with an X-ray photoelectron spectroscopy (XPS; Thermo Scientific ESCALAB 250).

3. Results and discussions

3.1. The influence of CH_4 ratio in the gas mixture

Etching characteristics of $(BiSb)_2Te_3$ films were investigated firstly as a function of CH_4 ratio in the gas mixture. CH_4 ratio was adjusted by gradually increasing H_2 flow rate with 0, 5, 10, 15, 20, and 25 sccm while the flow rate of CH_4 and Ar gas was fixed at 15 sccm and 10 sccm, respectively. Fig. 1 shows the etch rate of $(BiSb)_2Te_3$ film at the different CH_4 ratio. The etch rate firstly increases and then decreases with gradually increasing CH_4 ratio. The maximum etch rate is about 600 nm/min at CH_4 ratio of 0.38. The non-monotonic dependence of the etch rate on CH_4 ratio could be explained by the conflicting influence of methane gas on etching characteristics of $(BiSb)_2Te_3$. A low CH_4 ratio means a low concentration of the reactive CH_3 radical in plasma at a constant chamber pressure, which reduces the generation of the volatile methyl compounds and results in a low etch rate. Increasing CH_4 ratio tends to improve the etch rate due to the increase of the reactive CH_3 radicals. However, there are also polymerization reactions of hydrocarbon compounds originated from methane. The generation of hydrocarbon polymer was reported to be proportional to CH_4 ratio, and the deposition of hydrocarbon polymer on the etched surfaces could slow down or stop the etching process [17]. So a

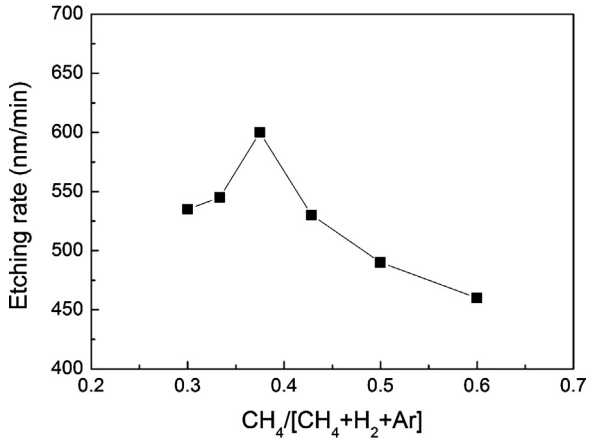

Fig. 1. The etch rates as a function of CH_4 ratio in mixture. The working pressure is 20 mTorr.

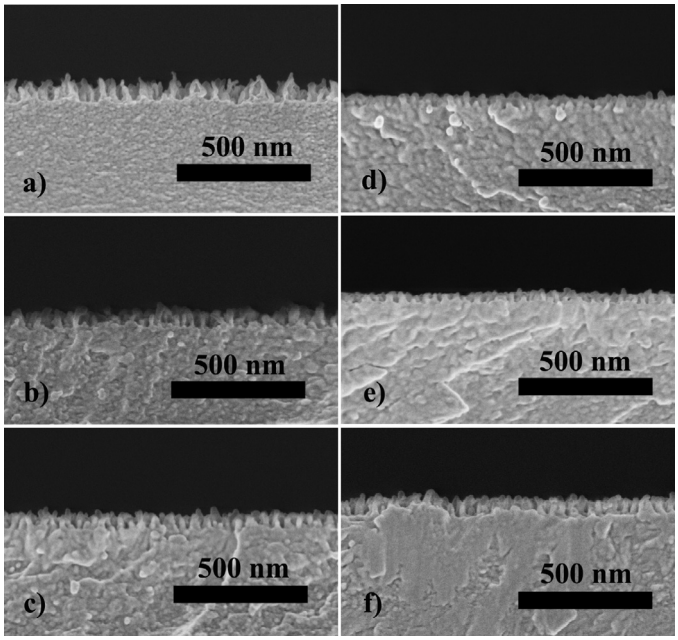

Fig. 2. Cross-sectional SEM micrographs of the etched samples with different CH_4 ratio: (a) 0.6; (b) 0.5; (c) 0.43; (d) 0.38; (e) 0.33; and (f) 0.3.

high CH_4 ratio could decrease the etch rate due to the effect of polymer deposition. The competition of etching and polymer deposition results in the non-monotonic relation between the etch rate and CH_4 ratio.

On the other hand, the deposition of hydrocarbon polymer also roughens the etched surface due to the micro-masking effect [19,20]. Fig. 2 shows the cross-sectional SEM images of the etched samples at different CH_4 ratio. As shown in Fig. 2(a)–(e), the etched surface with the absence of H_2 gas is very rough and the surface roughness obviously decreases with gradually decreasing CH_4 ratio. This can contribute to the decreasing influence of polymer deposition with decreasing CH_4 ratio. However, further decreasing the CH_4 ratio resulted in an obvious increase of the surface roughness shown in Fig. 2(f), which may be mainly caused by the non-uniform etching of $(BiSb)_2Te_3$ in CH_4/H_2-based plasma etching process. A similar observation was also reported in HgCdTe etching experiments, in which the formation of Cd-rich residues due to the non-uniform etching in H_2-based RIE process produced the rough etched surface [19]. The detailed discussion of non-uniform etching of $(BiSb)_2Te_3$ is given below.

Fig. 3(a) displays the surface XPS spectrum of the $(BiSb)_2Te_3$ samples etched with the different CH_4 ratio. For comparison, the surface XPS spectrum of the un-etched sample is also shown. All samples display C1s peak with insignificant difference in peak intensity. The residue polymer on the etched surfaces cannot be distinguished quantitatively because of the natural absorption of atmospheric carbon on all sample surfaces. However, the peak intensity of Bi, Sb and Te XPS spectrum shows significant change before and after etching. As shown in Fig. 3(a), the intensity of Bi5d, Bi4d and Bi4f peaks increases significantly after etching, while the intensity of Te4d and Te3d peaks decreases significantly after etching. But the intensity of Sb4d and Sb3d peaks shows no obvious change before and after etching. The relative atomic percentages of Bi, Sb and Te components of the un-etched and etched surfaces from the XPS results are calculated and displayed in Fig. 3(b). Compared to the un-etched surface, all etched surfaces display the much higher Bi atomic percentage and the much lower Te atomic percentage while the Sb atomic percentage of the etched surfaces shows a slight decrease. The significant deviation of surface composition of