Crystallographic Analysis of Sn_xTe_{100-x}/Sb₂Te₃ Superlattice and Proposal of its Low Switching Power Mechanism

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We performed XRD measurements on previously discovered Sn_XTe_{100-X}/Sb_2Te_3 superlattice (SL) with ultra-low switching power (X=10, 20, 35, and 50 at.%), and then analyzed its crystalline structure for proposal of the ultra-low switching power mechanism. XRD showed that only a little $SnTe/Sb_2Te_3$ SL and major NaCl-type SnSbTe phases coexist for X=50, and that only a little $SnTe/Sb_2Te_3$ SL, major Bi₂Te₃-type SnSbTe, and Te phases coexist for X=10, 20, and 35. The detailed crystallographic analysis showed as follows. There was a high possibility that both the NaCl-type and Bi₂Te₃-type SnSbTe-alloy phases have SL structures themself: "Self-assembly SL", with the vacancy layer in the specific (Sn, Sb) and Te layer, and that something new phenomenon such as Sn switching in the SnSbTe self-assembly SL leads to the ultra-low switching power.

I. INTRODUCTION

Recently, our group discovered Sn_XTe_{100-X}/Sb_2Te_3 diluted SL device which showed the ultra-low switching power.¹⁻³ The consumed power was approximately 1/2250th (X=10 at.%)~ 1/15th (X=50 at.%) that of the GST225 device.¹⁻³ The XRD results showed that only a little SnTe/Sb₂Te₃ SL and major NaCl-type SnSbTe-alloy (only a little SnTe/Sb₂Te₃ SL, major Bi₂Te₃-type SnSbTe-alloy, and Te) phases coexist for X=50 (X=10, 20, and 35) (later Figs. 1 and 3 references). Since the SnTe/Sb₂Te₃ SL phase was only a little, the cause of the ultra-low switching power may be so-called Sn switching in the SL phase¹ seemed to be unreasonable.

The purpose of this current study is, therefore, to carry out the crystallographic analysis of the SnSbTe phase, and afterward to propose the ultra-low switching power mechanism.

I. EXPERIMENTAL

Sb₂Te₃ (10 nm)/[Sn_XTe_{100-X} (1 nm)/Sb₂Te₃ (4 nm)]₉ SL film (X = 10, 20, 35, and 50 at.%) was deposited at substrate temperature of 200°C by using a dc magnetron sputtering apparatus. XRD measurement (Cu K α) was carried out to analyze the crystalline structure of the SnSbTe phase.

The structure of the SnSbTe phase with NaCl-type for X=50 (Bi_2Te_3 -type for X=10, 20, and 35) was examined by using the following procedure (a)–(d): ⁶

(a) Experimental integral peak-intensity ratio of $(I_{111}/I_{222})_{Obs.}$ ($(I_{006}/I_{009})_{Obs.}$) was estimated from the SnSbTe(111) and (222) peaks (SnSbTe(006) and (009) peaks) obtained in the XRD experiments. (I_{111} and I_{222} (I_{006} and I_{009}): integral peak-intensity of SnSbTe(111) and (222) peaks (SnSbTe (006) and (009) peaks)).

(b) Conceivable vacancies were taken in the SnSbTe structure, and modeled.

(c) Theoretical integral peak-intensity ratios of $(I_{111}/I_{222})_{\text{Cal.}}$ ($(I_{006}/I_{009})_{\text{Cal.}}$) were estimated for all the modeled SnSbTe structures by using Eqs. (1) and (2).

$$I_{hkl} \approx \left|F_{hkl}\right|^2 \times LZ \times P = \left|F_{hkl}\right|^2 \times \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \times P \tag{1}$$

$$F_{hkl} = \sum_{n}^{N} f_n e^{2\pi i (hx(n) + ky(n) + lz(n))}$$
(2).

 F_{hkl} , P, and LZ are the structure factor, multiplicity factor, Lorenz polarization factor, respectively. θ is the Bragg angle, f_n is the atomic scattering factor for atomic sort n, and hkl and xyz are the mirror index and the fractional coordinates, respectively.⁴

(d) From the obtained $(I_{111}/I_{222})_{\text{Obs.}}$ and $(I_{111}/I_{222})_{\text{Cal.}}$ $((I_{006}/I_{009})_{\text{Obs.}}$ and $(I_{006}/I_{009})_{\text{Cal.}})$, the order parameter S was estimated using the following equation.⁵

$$S^{2} = \frac{[I_{111}/I_{222}]_{obs}}{[I_{111}/I_{222}]_{cal}}$$
 for X=50 (3).
$$S^{2} = \frac{[I_{006}/I_{009}]_{obs}}{[I_{006}/I_{009}]_{obs}}$$
 for X=10, 20, and 35 (4).

$$\left(S^{2} = \frac{\left[I_{006}/I_{009}\right]_{obs}}{\left[I_{006}/I_{009}\right]_{cal}}\right) \qquad (\text{for X=10, 20, and 35} \quad (4).$$

The vacancy layer and/or site which satisfy 0.7 $(\pm 0.1) \leq S \leq 1.0 \ (\pm 0.1)$ "as a judgment whether the SnSbTe phase is ordered or not" were searched.⁶ The resultant vacancy configuration is judged to be the most likely.⁶

III. RESULTS

A. Crystalline structure of X=50 at.%

Figure 1 shows an XRD profile for the $SnTe/Sb_2Te_3$ SL film. Only a little $SnTe(111)/Sb_2Te_3(001)$ SL phase and a major SnSbTe phase with the NaCl-type structure coexisted.

The theoretical relatively integral peak-intensity ($I_{111, Cal.}$) of the SnSbTe phase is expressed as follows: ⁴

$$I_{111, Cal.} \approx \left| 4f_{(Sn,Sb)} - 4f_{Te} \right|^{2} \times LZ \times P$$

$$f_{Sn} \approx f_{Sb} \approx f_{Te}$$

$$\therefore I_{111} \approx 0$$
(5).

So, the SnSbTe(111) peak of Fig. 1 should not be observed. The structure that can allow this peak was thus searched according to the aforementioned procedure (a)-(d).

The resultant configuration: crystalline structure, was shown in Fig. 2 (a). In Fig. 2 (b), that of GeTe layer in GeTe(111)/Sb₂Te₃(001) SL film was also shown for comparison.⁶⁻⁹ The -(Sn, Sb) (layer)-Te-Vacancy-Te-(Sn, Sb)- stacks in order along the SnSbTe[111] for Fig. 2 (a) well corresponded to the –Ge-Te-Vacancy-Te-Ge- stacks for Fig. 2 (b). The structure of the SnSbTe phase was all the same as the GeTe layer in the GeTe(111)/Sb₂Te₃(001) SL film.



Fig.1 XRD profile of SnTe/Sb₂Te₃ SL film.



Fig.2 The most likely structure for (a) the SnSbTe-alloy phase in the SnTe/Sb₂Te₃ SL film and (b) the GeTe layer in the GeTe/Sb₂Te₃ SL film.



Fig. 6 XRD profile of SnSbTe-alloy film prepared by co-sputtering.

B. Crystalline structure of X= 10, 20, and 35 at.%

Figure 3 shows an XRD profile of Sn_XTe_{100-X}/Sb_2Te_3 SL film when X=10, representatively. Only a little $SnTe(111)/Sb_2Te_3(00l)$ SL phase, a major Sb_2Te_3 phase with Sn: Bi_2Te_3 -type SnSbTe phase, and a Te phase coexisted. The strong SnSbTe(00l) peaks mean that this phase mainly exists the SL film.

The structure of SnSbTe phase was thus searched according to the aforementioned procedure (a) – (d). The resultant configuration: crystalline structure, was shown in Fig. 4. The configuration was as follows: -Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-Stacks, in order along the SnSbTe[001] per its one lattice.

Ⅳ. DISCUSSION

A. Switching mechanism in case of X=50 at.%

The mechanism on the low switching power was still unclear.¹ But, figure 2 (a) offered the key to consider it.

We stacked up two SnSbTe lattices of Fig. 2 (a) in its [111] (Fig. 5). Figuratively speaking, it was possible that the upper (lower) lattice corresponds to the GeTe (Sb₂Te₃) layer in the GeTe(111)/Sb₂Te₃(001) SL. And that the vacancy layer of the upper (lower) lattice corresponds to a vacancy layer (a Te – Te weak bond layer) of the GeTe (Sb₂Te₃) layer.^{7–9} Therefore, it was possible that the SnSbTe phase has a SL structure itself, i.e., *"self-assembly SL structure"*. And that something new phenomenon such as Sn switching occurs in such a self-assembly SL phase, which leads to the low switching power.¹ (Consumed power: ~1/15th that of GST225 device.)

Figure 6 shows an XRD profile of SnSbTe film prepared by co-sputtering using the SnTe and Sb₂Te₃ targets. The SnSbTe(111) peak was hallow pattern, which means that the NaCl-type SnSbTe lattice has no vacancy layer. Only when the layer by layer sputtering between the SnTe and Sb₂Te₃ layers was performed, the SnSbTe can have the self-assembly SL structure.

B. Switching mechanism in case of X= 10, 20, and 35 at.%

The mechanism on the ultra-low switching power was also unclear. Figure 4, however, offered the key to consider it.

The vacancy layer of GeTe layer in the GeTe(111)/Sb₂Te₃(001) SL is the essence of Ge switching.^{7, 9} The Refs. 7 and 9 also mentioned that the Te – Te weak bond layer of Sb₂Te₃ layer in that SL is also essential. And that the following partial arrangement along the GeTe[111]/Sb₂Te₃[001] SL, for example, is also essential:^{7,9}

-Te-Sb-Te-Sb-Te-Sb-Te-Ge-Te-Vacancy-Te-Ge-Te-Sb-Te-.

As shown in Fig.4, the SnSbTe phase had the vacancy and the Te – Te weak bond layers. And its phase also had the following partial arrangement along the SnSbTe[001]: -Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-(Sn, Sb)-Te-(Sn, Sb)-Te-(Sn, Sb)-Te-(Sn, Sb)-Te-Te-(Sn, Sb)-Te-

Something new phenomenon concerning the numbers of Sn atoms such as Sn switching¹ occurs in the its self-assembly SL, the Sn atoms ought to operate for the resistance switching is decreased with decreasing X, as it turned out, the maximum conservation of electric power, $\sim 1/2250$ th that of GST225 device (X=10 at.%), is considered to be obtained.³

In the Sn_XTe_{100-X}/Sb_2Te_3 diluted SL also, the SnSbTe can have the self-assembly SL structure only when the layer by layer sputtering between the Sn_XTe_{100-X} and Sb_2Te_3 layers was performed.

V. CONCLUSION

In summary, it was possible that the SnSbTe-alloy phase mainly existed the Sn_XTe_{100-X}/Sb_2Te_3 SL film has a self-assembly SL structure, and that something new phenomenon in its self-assembly SL leads to the ultra-low switching power.

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APPENDIX

Thinning of SnTe/Sb₂Te₃ superlattice

Figure 7 shows the electrical properties of one unit SL composed of Sb₂Te₃(4 nm)/[SnTe(1 nm)/Sb₂Te₃(4 nm)]₁. The set (reset) voltage was $\sim 0.2 \text{ V} (0.39 \text{ V})$, and the set (reset) current was $\sim 1.0 \mu \text{ A} (\sim 2.27 \mu \text{ A})$. Multiplying the reset voltage by the reset current yields switching power of $\sim 0.89 \mu$ W. Since the switching power of GST225 device with the same prober was $\sim 6080 \mu$ W, this power is $\sim 1/6800$ th that of GST225. As a result of crystallographic analysis by using the aforementioned procedure (a) – (d), the one unit SL also had the self-assembly SL structure shown in Fig. 5. Therefore, thinning down to 5nm might thus be possible.



Figure 7 Electrical properties of one unit SL composed of Sb₂Te₃(4 nm)/[SnTe(1 nm)/Sb₂Te₃(4 nm)]₁.