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A thermodynamic study of gas transport in the growth of antimony telluride thin films

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Abstract

In order to determine the growing conditions of thin films of Sb_2Te_3 in the hot wall epitaxy (HWE) technique, a thermodynamic model for the sublimation of the Sb_2Te_3 phase was studied. The equilibrium constant was calculated, and the expressions for the fluxes and pressures of the components were determined. From these results, equations for the sticking coefficient and the deposition rate, expressed as functions of the source and substrate temperatures only, were formulated.

INTRODUCTION

Owing to their high figures of merit, the V_2VI_3 semiconductors have always been of interest as thermoelectric materials [1]. They have narrow band gaps and can be used in IR or far-IR optoelectronic devices [2].

For such applications, it is necessary that epitaxial p–n heterostructures have been achieved. The very high crystallographic quality required implies that the thin-layer growing techniques involved permit easy control of the epitaxial parameters, as with molecular beam epitaxy (MBE) or hot wall epitaxy (HWE).

With the hot wall epitaxy technique, thermodynamic equilibrium is preserved and the growing conditions can be determined from a theoretical study. Two such studies involving vapor–solid equilibria have already been published for lead and bismuth chalcogenides [3, 4].

This publication concerns the preparation of thin films of Sb_2Te_3 by HWE with reference to the previously described thermodynamic model. The equilibrium constant of evaporation, as well as the partial pressures

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and total pressures of the gases, are calculated. From the results, a representation of the principal deposition parameters can be inferred, using the Hertz–Knudsen kinetic theory.

THE THERMODYNAMIC MODEL

It is well known that bismuth and antimony chalcogenides do not dissociate into atomic species [5]. Sublimation of Sb_2Te_3 leads to a mixture of molecular species. According to refs. 6 and 7, the vaporization of Sb_2Te_3 can be described by the equations

A $Sb_2Te_3(s) \rightleftharpoons \frac{1}{2}Sb_4(g) + \frac{3}{2}Te_2(g)$ $\Delta H = 404.2\ \mathrm{J\ mol^{-1}}$

B $Sb_2Te_3(s) \rightleftharpoons SbTe(g) + Te_2(g) + \frac{1}{4}Sb_4(g)$ $\Delta H = 458.9\ \mathrm{kJ\ mol^{-1}}$

From the mass spectroscopy results [5], the vaporization equations were established

C $Sb_2Te_3(s) \rightleftharpoons 2SbTe(g) + \frac{1}{2}Te_2(g)$ $\Delta H = 501\ \mathrm{kJ\ mol^{-1}}$

D $Sb_2Te_3(s) \rightleftharpoons 2Sb(s) + \frac{3}{2}Te_2(g)$

Boncheva-Mladenova et al. [6] compared these equations and calculated the standard formation enthalpy of $Sb_2Te_3(\Delta H_f^\ominus)$ in each case. By comparison with the experimental value measured by Howlett and Bevet [8], they concluded that scheme **A** predominates in the vaporization of the phase. In addition, by measuring the saturated vapor pressure and the rate of vaporization, using the Knudsen–Langmuir method in the range 700–820 K, they obtained the following relationship for the total pressure

$$\log p_T = -\frac{10021.8}{T} + 10.929 \qquad (1)$$

Our results will be compared with this expression.

Equilibrium constant determination

From the results of Boncheva-Mladenova et al. [6], the equation **A** was selected for the chemical equilibria at the growing surface.

The equilibrium constant can be obtained by substituting the free energy function $\Delta G_T^\ominus(\mathbf{A})$ in eqn. (2)

$$\Delta G_T^\ominus(\mathbf{A}) = -RT \ln K \qquad (2)$$

One obtains

$$\log K = -\frac{\Delta H_T^\ominus(\mathbf{A})}{19.12T} + \frac{\Delta S_T^\ominus(\mathbf{A})}{19.12} \qquad (3)$$

with

$$\Delta H_T^\ominus(\mathbf{A}) = \Delta H_{298.15}^\ominus(\mathbf{A}) + \int_{298.15}^{T} \Delta C_p^\ominus(\mathbf{A})\,\mathrm{d}T \tag{4}$$

and

$$\Delta S_T^\ominus(\mathbf{A}) = \Delta S_{298.15}^\ominus(\mathbf{A}) + \int_{298.15}^{T} \frac{\Delta C_p^\ominus(\mathbf{A})}{T}\,\mathrm{d}T$$

Expression (3) becomes

$$\log K = \frac{1}{19.12}\left[-\frac{\Delta H_{298.15}^\ominus(\mathbf{A})}{T} + \Delta S_{298.15}^\ominus(\mathbf{A}) - 1/T\int_{298.15}^{T} \Delta C_p^\ominus(\mathbf{A})\,\mathrm{d}T + \int_{298.15}^{T} \frac{\Delta C_p^\ominus(\mathbf{A})}{T}\,\mathrm{d}T\right] \tag{5}$$

Standard entropies and $C_p^\ominus$ values were obtained from refs. 6 and 9–11.

After calculation, one obtains

$$\log K = -\frac{21880}{T} + 35.46 - 6.03\log T \tag{6}$$

Expressions for the fluxes of the materials

Calculations of the fluxes were made using the Hertz–Kundsen–Langmuir expression were

$$J = 3.51 \times 10^{22} p[MT]^{-1/2} \tag{7}$$

with J the fictive flux expressed in mol cm^{-1} s^{-1} and p in torr. For the gaseous species, relationship (7) can be written

$$J_{\mathrm{Sb_4}} = 3.51 \times 10^{22} p_{\mathrm{Sb_4}}[M_{\mathrm{Sb_4}}T]^{-1/2} \tag{8}$$

$$J_{\mathrm{Te_2}} = 3.51 \times 10^{22} p_{\mathrm{Te_2}}[M_{\mathrm{Te_2}}T]^{1/2} \tag{9}$$

Conditions of congruent evaporation lead to the expressions

$$J_{\mathrm{Sb_2Te_3}} = 2J_{\mathrm{Sb_4}} \tag{10}$$

$$J_{\mathrm{Sb_2Te_3}} = \tfrac{2}{3}J_{\mathrm{Te_2}} \tag{11}$$

where $J_{\mathrm{Sb_2Te_3}}$ is the fictive flux of $\mathrm{Sb_2Te_3}$.

Pressure calculations

Using the partial pressure of the gaseous species, the equilibrium constant of equation **A** is

$$K = [p_{\mathrm{Sb_4}}^{1/2} p_{\mathrm{Te_2}}^{3/2}] \times 760^{-2} \tag{12}$$

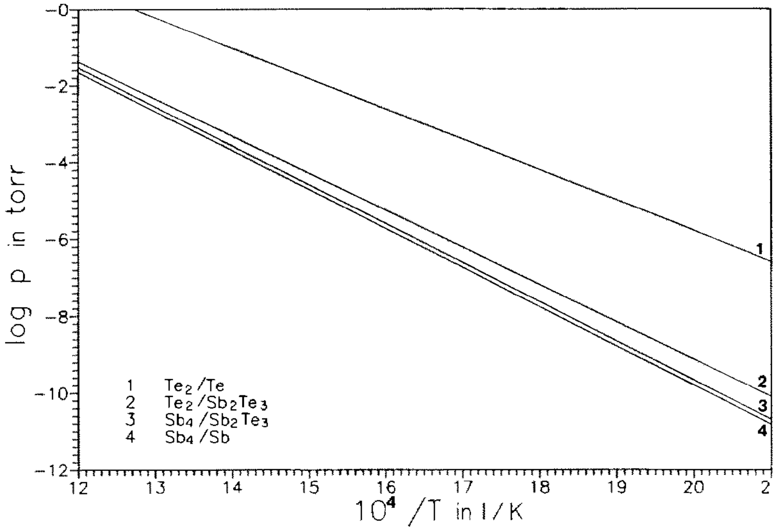

Fig. 1. Plot of log$p$ versus $10^4/T$ for Sb_4(g) and Te_2(g) over Sb_2Te_3(s) and over the condensed phases.

with the pressure expressed in torr. By association of eqns. (6) and (8)–(11), the pressures can be expressed

$$\log p_{Sb_4} = -\frac{10940}{T} + 20.358 - 3.015 \log T \tag{13}$$

$$\log p_{Te_2} = -\frac{10940}{T} + 20.694 - 3.015 \log T \tag{14}$$

$$\log p_{tot} = -\frac{10940}{T} + 20.859 - 3.015 \log T \tag{15}$$

The plot of log$p$ versus $1/T$ for Sb_4(g) and Te_2(g) over Sb_2Te_3(s) and over the condensed phases [12] is shown in Fig. 1.

Table 1 compares our total pressure calculations with the experimental

TABLE 1

Theoretical and experimental total gas pressures

$T/(K)$	Theoretical total gas pressure in torr	Experimental total gas pressure in torr
500	6.9×10^{-10}	7.7×10^{-10}
550	5.1×10^{-8}	5.1×10^{-8}
580	4.6×10^{-7}	4.5×10^{-7}
600	1.8×10^{-6}	1.7×10^{-6}
630	1.1×10^{-5}	1.1×10^{-5}

values obtained by Boncheva-Mladenova et al. [6]. There is good agreement between the two sets of results and we can conclude that our calculations are reliable.

The rate of deposition and the sticking coefficient

The sticking coefficient, which represents the ability of a material to grow on a given substrate, is given by the expression

$$\beta = \frac{J^{\mathrm{so}}_{\mathrm{Sb_2Te_3}} - J^{\mathrm{su}}_{\mathrm{Sb_2Te_3}}}{J^{\mathrm{so}}_{\mathrm{Sb_2Te_3}}} = 1 - \frac{J^{\mathrm{su}}_{\mathrm{Sb_2Te_3}}}{J^{\mathrm{so}}_{\mathrm{Sb_2Te_3}}} \tag{16}$$

with $J^{\mathrm{so}}_{\mathrm{Sb_2Te_3}}$ being the flux of evaporated species from the source and $J^{\mathrm{su}}_{\mathrm{Sb_2Te_3}}$ the flux of reevaporated species from the substrate.

Equations (8)–(12) and (16) provide a means to calculate the β value

$$\beta_{\mathrm{Sb_2Te_3}} = 1 - \left[10^{-10940(1/T_{\mathrm{su}} - 1/T_{\mathrm{so}})}\left(\frac{T_{\mathrm{su}}}{T_{\mathrm{so}}}\right)^{-3.515}\right] \tag{17}$$

This equation is similar to that obtained by Garcia et al. [3] in the $\mathrm{Bi_2Te_3}$ study

$$\beta_{\mathrm{Bi_2Te_3}} = 1 - \left[10^{-11752(1/T_{\mathrm{su}} - 1/T_{\mathrm{so}})}\left(\frac{T_{\mathrm{su}}}{T_{\mathrm{so}}}\right)^{-3.25}\right] \tag{18}$$

Figure 2 shows the curves of T_s versus $f(T)$ for various sticking coefficients. These curves are used to optimize the source and substrate temperatures in order to achieve a sticking coefficient near to 1. The related

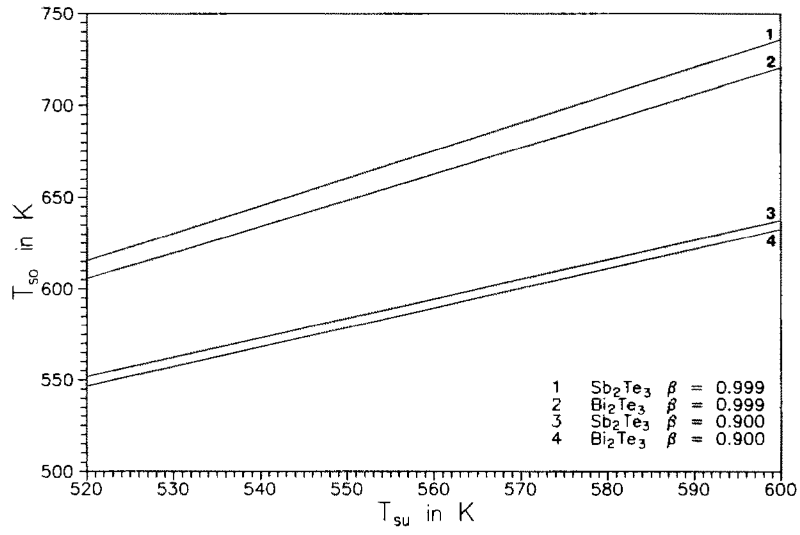

Fig. 2. Plot of T_{so} versus T_{su} for various sticking coefficients β of $\mathrm{Sb_2Te_3}$ and $\mathrm{Bi_2Te_3}$.

Bi_2Te_3 curves are also shown on the figure. For a sticking coefficient near to 0.9, the same conditions are required for both Sb_2Te_3 and Bi_2Te_3. For a sticking coefficient near to 1 ($\beta = 0.999$), a slightly higher substrate temperature is needed for Sb_2Te_3.

The deposition rate is given by the relation

$$v_d = \beta[J^{so}_{Sb_2Te_3}] \tag{19}$$

From eqns. (9), (11), (14) and (17) it follows that

$$\begin{aligned} v_d = {} & 1.465 \times 10^{41.694} \times 10^{-10940/T_{so}} T_{so}^{-3.515} \\ & \times [1 - 10^{-10940[1/T_{su} - 1/T_{so}]}(T_{su}/T_{so})^{-3.515}] \end{aligned} \tag{20}$$

This expression is very similar to the one for Bi_2Te_3. In both cases the linear dependence is verified, the logarithmic terms being neglected in this temperature range.

CONCLUSIONS

This thermodynamic approach to the HWE growing technique of Sb_2Te_3 thin layers has provided some equations for the sticking coefficient and the deposition rate, expressed as functions of the source and substrate temperatures alone.

Comparable results are obtained for Bi_2Te_3 and Sb_2Te_3, provided that the experimental conditions are the same.

The application of this approach to experimental work involving a hot-wall technique of CVD is in progress and will be published later.

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