A multi-layer interface partition model for nonequilibrium solidification

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Abstract

The disadvantages of Aziz’s interface partition model are summarized in this paper. Using transition state theory and the Maxwell–Boltzmann distribution law, a multi-layer interface solute partition model (MLIPM) for dilute solution is advanced. It is shown that interface structure and roughening characteristics have significant effects on solute partitioning. Based upon an academic speculation of interface roughening behavior, both the partition processes of semiconductors and metals can be explained rationally by MLIPM. Comparisons with experimental results in Si(As, Ge, Bi, Sn) and Al(Cu, Sn, Ge, In) show quite good agreement; provided that the proper roughening law is given. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the introduction of rapid solidification, solid/liquid interface non-equilibrium has been studied for almost 40 years. In the 1970s, Baker and Cahn [1] gave the detailed thermal dynamics for non-equilibrium solidification. Many kinetic models for so-called solute trapping have also been constructed [2–10]. However it was only until the 1980s, with strictly controlled laser surface remelting, that these models were able to be examined for their validity. Among these models, that put forward by Aziz [4,5] gained fame for its clear physical picture and concise expression, in which the partition coefficient $k$ is given by:

$$k = \frac{V/V_D + k_0}{V/V_D + 1},$$

where $V$ is the interface velocity, $V_D$ is the diffusive speed, which is defined as the ratio of interface diffusivity $D_I$ to the interatomic distance $\lambda$, and $k_0$ is the equilibrium partition coefficient. By proper choice of the only adjustable parameter $V_D$, the Aziz model can fit quite well experimental results up to the present date and has gained popularity [11].

Nevertheless, beyond the success achieved, in the Aziz model, a sharp solid/liquid interface is assumed for continuous growth. One will be perplexed to try to correlate this with the two different interface structures, facettted (sharp and smooth) and non-facettted (diffuse and rough). As a result, if the reader looks into the interface diffusivities derived from the Aziz model, which are listed in Table 1, it is found that $D_I$, thus obtained is unreasonable larger than the bulk liquid diffusivity in metallic systems. Smith and Aziz [12] suggested that for a diffuse interface composed of $n$ layers, the partition coefficient should be $k^n$. For $k < 1$ (if not declared, $k < 1$ in this context), this correction requires even larger interface diffusivity for a same trapping level. Therefore, the continuous mode of the Aziz model implies that it should apply for metallic systems, but it indeed fails to quantify solute trapping in metallic systems. Moreover, interface diffusivity can by no means determined a priori in the Aziz model, so it can only describe, but not predict, the trapping behavior in all systems.

With this in mind, the authors deem that the S/L interface must be considered on a mesoscopic scale, which suggests that the interface is a nano-scale transition region as indicated by the theories and molecular simulations of many investigators [13–20]. From this point of view, in this paper we will build a solute partition model accounting for both semiconductors and metals.

2. Theoretical model

Suppose the S/L interface is composed of $n_i$ layers, the structure element in each layer is isotropic, and the $j$th layer has a constant influence on the $(j + 1)$th layer [21,22]. The
transition barrier of atoms in the interface should decrease from solid to liquid for alloy systems with \( k < 1 \). Namely, \( Q_1 > Q_2 > \cdots > Q_j > \cdots > Q_n \) where \( Q_1 \) and \( Q_n \) is activation energy of solid and liquid, respectively. For dilute alloys, Henry’s law can be applied:

\[
\mu_i^L = \mu_i^0 + R_g T_i \ln \gamma_i C_i^L
\]

\[
\mu_i^S = \mu_i^0 + R_g T_i \ln \gamma_i C_i^S,
\]

where \( \mu \) is the chemical potential; superscripts \( i \) refer to the interface region; \( S \) and \( L \) to solid and liquid, \( A \) and \( B \) to solvent and solute, respectively. \( \mu_i^L \) and \( \mu_i^S \) are the standard solute chemical potential of liquid and solid, respectively.

Comparison of \( \Delta \mu_B \) at equilibrium and complete solute trapping shows smaller \( \Delta \mu_B \) for complete solute trapping. This implies that \( \Delta \mu_B \) is a decreasing function of interface velocity, which is contradictory to the viewpoint of Wood [6,7]. The neighboring interactions are determined by atom separation rather than by interface velocity, hence the only reason for barrier decrease is the change in many-body interactions, say, the change of interface layers. It is known that kinetic roughening occurs for large interface velocity [13,14,19,20], so from the Bragg–Williams approximation:

\[
\Delta U = \frac{n_s}{n_i} \Delta \mu_B^0 + Q_B.
\]

According to chemical reaction rate theory, the image of atom diffusion can be described as follows: A solute atom \( B \) in the first layer with energy higher than \( Q_1 \) might jump over the energy barrier to the second layer, where \( B \) either makes an elastic collision with another atom \( B' \) making \( B' \) activated, or encounters a vacancy and jumps across to the next layer successively. This domino-like chain diffusion continues until a solute atom reaches the liquid. On the other hand, a solute atom in the \( n \)th layer (liquid edge) must have an energy higher than \( Q_m \) to jump to the \((n-1)\)th layer. No matter if it collides with another atom solute in its neighboring layer or jumps into a vacancy, the energy needed to jump uphill over the \((n-1)\)th layer is decreased by \( Q_m \). Correspondingly, the activation energy required for the \( j \)th layer would be \( (U_j - Q_j) \) (Fig. 1).

The energy of solute atoms is by no means unique but rather a distribution. For dilute alloys, solute atoms can be regarded as independent. Therefore the most probable energy distribution of solute atoms must obey the Maxwell–Boltzmann’s distribution law. As for the jumping distance, although it is interatomic for a particular atom, mesoscopic diffusion flux seems to be the result of solute atoms jumping a distance of the interface width, since solute atoms are indistinguishable. Hence the diffusion flux in molar fraction can be written as:

\[
J_{S-L} = d_i P_{S} \gamma_S \int_{Q_{m}}^{\infty} C_S \exp \left( -\frac{\varepsilon}{k_B T_i} \right) \frac{d\varepsilon}{k_B T_i}
\]

\[
= d_i P_{S} \gamma_S C_S \exp \left( -\frac{Q_B}{k_B T_i} \right)
\]  

(3a)

Fig. 1. Multi-layer transition model.
\[ J_{L-S} = dPf n_i n_j \int_{U_s - Q_s}^{\infty} \cdots \]

\[
\int_{U_s - Q_{s,n-1}}^{\infty} \prod_{j=1}^{n} \frac{C^j_L \left[ \exp \left( -\frac{\epsilon_j}{k_BT_i} \right) \right]}{k_BT_i} \, \text{d}\epsilon_j \hspace{1cm} (3b)
\]

\[ = dPf n_i n_j C^j_L \exp \left( -\frac{\Delta U_B}{k_BT_i} \right) \]

where \( P \) is the direction probability of atomic jumping and \( f \), \( n \) and \( \gamma \) are the jumping fraction, jumping frequency and activity coefficient, respectively. \( T_i \) is the interface temperature, and \( \epsilon_j \) energy of the \( j \)th level. \( k_B \) Boltzmann’s constant.

Fick’s law says that \( \partial J_x / \partial x = V \partial C / \partial z \), i.e. \( J_{S-L} = V(C^L_1 - C^S_3) \) for the S/L interface, so that substitution of Eqs. (3a) and (3b) results in:

\[ V(C^L_1 - C^S_3) = Pf \nu d \exp \left( -\frac{Q_B}{k_BT_i} \right) \]

\[ \times \left[ \gamma_s C^L_3 - \gamma_l C^L_1 \exp \left( -\frac{n_0}{n_1} \frac{\Delta U_B}{k_BT_i} \right) \right] \quad (4) \]

From Henry’s law, \( k_0 = \gamma_l / \gamma_s \exp(-\Delta U_B / k_BT_i) \). Noting that \( \gamma_L = \gamma_S \) for dilute alloys, defined interface diffusivity \( D_i = \frac{PAf}{\nu} \gamma_s \exp(-\frac{Q_B}{k_BT_i}) \), and interface Peclet number \( P_i = V\lambda / D_i \), finally:

\[ k = \frac{P_i/n_1 + k_0/n_1}{P_i/n_1 + 1} \quad (5) \]

3. Discussion

In the multi-layer interface partition model (MLIPM) as derived above, two important parameters, \( n_i \) and \( D_i \), need to be determined. Variation of interface layers occurs due to kinetic roughening, thus the roughening law determines \( n_i \). Although the physical nature has been explained for kinetic roughening [19,20], and numerical simulations have been done in many systems [15,17,18], no explicit roughening law has been given so far. Here the authors explore the roughening law from the equilibrium structure and limiting kinetic growth behavior of two different interface types.

As indicated by Cahn [13,14], there is a critical interface undercooling, \( \Delta T^* \), or velocity, \( V_c \), at which the growth behavior turn from step-wise growth into continuous growth. For semiconductors with a sharp interface, \( V_c \) is generally large, some meters per second; while for metals with a diffuse interface, \( V_c \) is quite small, causing no appreciable transition under normal solidification conditions. It is believed that a sharp interface can be several layers thick [11,19,20], while a diffuse interface can compose tens layers [15–18], thus it should not roughen significantly further. Thus a roughening law can be given as:

\[ n_i = n_0 \left[ 1 + \zeta \exp \left( -\frac{V_c}{V} \right) \right] \]

Fig. 2. Experimental data from Aziz et al. of arsenic in silicon and comparison of MLIPM with Aziz model.

Around \( V_c \), apparent roughening occurs. As \( V \) tends to infinity, \( n_i = n_0(1 + \zeta) \), so \( \zeta \) can be taken as around 5–10 for semiconductors, and 0.01–0.1 for metals. Applying the roughening law suggested here, experimental results can be fitted by varying the interface diffusivity. Considering silicon, only face (111) is faceted, MLIPM can also apply for all other directions. Results obtained are shown in Figs. 2–5. One may question that no determined values have been given for \( \zeta \) and \( V_c \), but they only have slight influences on \( D_i \), not exceeding an order of magnitude, also for \( n_0 \).

From Figs. 2–5, it is found that several combinations of \( n_0 \) and \( D_i \) can all fit experimental data [12,23–31] quite well. This raises some uncertainty in the determination of \( D_i \), but such uncertainty is not larger than an order of magnitude. Moreover, with further study of interface structure, the uncertainty may be eliminated. Comparing MLIPM with the Aziz model, it can be seen that MLIPM fits the experimental results better. For semiconductors, the Aziz model is precise enough to describe the partition behavior, but MLIPM provides a more rational physical picture. For metals, the Aziz model can to some extent reflect solute trapping, but unreasonable interface diffusivities are

Fig. 3. Experimental data from Aziz et al. of bismuth in silicon and comparison of MLIPM with Aziz model.
required. On the contrary, MLIPM gives reasonable interface diffusivity for both semiconductors and metals (see Table 1). $D_i$ so obtained is larger than the geometric mean of solid and liquid diffusivity, and strongly correlated with interface structure. For sharp interface, $D_i$ is close to liquid diffusivity, but for diffuse interface, $D_i$ is intermediate between solid and liquid diffusivity. If kinetic roughening occurs, the interface diffusivity will be lowered. Although exact value of $D_i$ cannot so far be predicted MLIPM, it can be determined by a few trapping experiments once the precise roughening behavior is found.

4. Conclusion

Based upon mesoscopic structure of solid/liquid interface and energy distribution of solute atoms, a multi-layer interface partition model is advanced. An academic roughening law is suggested to fit MLIPM with experimental results in both semiconductors and metals. Compared with the acknowledged Aziz model, MLIPM is more accurate in describing trapping behavior: especially it gives reasonable interface diffusivity $D_i$. It is for the first time that $D_i$ has been indicated to be determined by interface structure. For a sharp interface, $D_i$ is close to that of the bulk liquid; while for a diffuse interface, it lies between that of bulk liquid and that of the solid, but much greater than their geometric mean.

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References

[1] J.C. Baker, J.W. Cahn, Solidification, ASM Metals Park, Ohio, 1971, p. 23.
[2] J.W. Cahn, S.R. Coriell, W.J. Boettinger, Laser and Electron Beam Processing of Materials, Academic Press, New York, 1980, p. 89.
[3] K.A. Jackson, G.H. Gilmer, H.J. Leamy, Laser and Electron Beam Processing of Materials, Academic Press, New York, 1980, p. 104.
[4] M.J. Aziz, J. Appl. Phys. 53 (1982) 1158.
[5] M.J. Aziz, T. Kaplan, Acta Metall. 36 (1988) 2335.
[6] R.F. Wood, Appl. Phys. Lett. 37 (1980) 302.
[7] R.F. Wood, Phys. Rev. 25 (1982) 2786.
[8] G.H. Gilmer, Mater. Sci. Engng. 65 (1984) 15.
[9] W.J. Boettinger, M.J. Aziz, Acta Metall. 37 (1989) 3379.
[10] W.J. Boettinger, Mater. Sci. Engng. A178 (1994) 217.
[11] W. Kurz, D.J. Fisher, Fundamentals of Solidification, 3rd ed., Trans. Tech. Publications, Lausanne, Switzerland, 1989.
[12] P.M. Smith, M.J. Aziz, Acta Metall. Mater. 42 (1994) 3515–3525.
[13] J.W. Cahn, Acta Metall. 8 (1960) 554.
[14] J.W. Cahn, W.B. Hilling, G.W. Sears, Acta Metall. 12 (1964) 1421.
[15] D.E. Temkin, Crystallization Process, Consultants Bureau, Pittsburgh, USA, 1966, p. 15.
[16] J.H. Bilgram, H. Güttinger, W.J. Kanzig, Phys. Rev. Lett. 40 (1978) 1394.
[17] L.V. Mkheev, A.A. Chernov, J. Cryst. Grow. 112 (1991) 591–596.
[18] D.W. Octoby, A.D.J. Haynet, J. Chem. Phys. 76 (1982) 6262–6292.
[19] H. Müller-Krumbharr, in: E. Kaldes (Ed.), Current Topics in Materials Science, vol. 1, North-Holland, Amsterdam, 1978.
[20] W.A. Tiller, The Science of Crystallization: Microscopic Interfacial Phenomena, Cambridge University Press, Cambridge, 1991.
[21] Cai Yingwen, Mesoscopic Response of SE Interface during Non-equilibrium Solidification — Behavior from Near-rapid to Rapid Solidification (in Chinese). PhD Thesis, Northwestern Polytechnical University, 1996.
[22] Yingwen Cai, Xiemin Mao, Jianguo Li, Hengzhi Fu, Acta Metall. Sinica 7 (1994) 84.
[23] M.J. Aziz, Phys. Rev. Lett. 56 (1986) 2489.
[24] M.J. Aziz, Mater. Sci. Engng. 98 (1988) 39,369.
[25] T. Kaplan, M.J. Aziz, L.J. Gray, J. Chem. Phys. 99 (1993) 8031.
[26] M.J. Aziz, Mater. Sci. Engng. A178 (1994) 217.
[27] J.A. Kitte, M.J. Aziz, D.P. Buruco, M.O. Thompson, Appl. Phys. Lett. 64 (1994) 2359.
[28] M.J. Aziz, W.J. Boettinger, Acta Metall. 42 (1994) 527.
[29] M.J. Aziz, Metall. Trans. 27A (1996) 671.
[30] D.P. Bruno, M.O. Thompson, D.E. Hoglund, M.J. Aziz, H.J. Grossman, J. Appl. Phys. 78 (1995) 1575–1582.
[31] M.J. Aziz, Mater. Sci. Engng. A226–228 (1997) 255–260.