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Model for Dopant and Impurity Segregation During Vapor Phase Growth

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ABSTRACT

We propose a new kinetic model for surface segregation during vapor phase growth that takes into account multiple mechanisms for segregation, including mechanisms for inter-layer exchange and surface diffusion. The resulting behavior of the segregation length shows temperature and velocity dependence, both of which have been observed in experiments. We compare our analytic model to experimental measurements for segregation of Phosphorus in Si(001), and we find an excellent agreement using realistic energies and pre-exponential factors for kinetic rate constants.

INTRODUCTION

The growth of extremely sharp interfaces in materials has become increasingly important in the devices we build. For example, the device quality for delta doping in semiconductors [1, 2] or certain multi-layered metallic systems [3, 4] is sensitive to the redistribution of atomic species on the monolayer scale. The main physical problem to overcome is the tendency for atoms of one species or another to segregate to the free surface during film growth. Growth of such structures is experimentally challenging, and although there are some exceptions [5], high quality crystal growth with completely suppressed segregation is not generally possible. The physical, chemical, and kinetic principles underlying segregation are not entirely understood in these systems. Several models have been presented in the literature, but none of them have been successful in describing the segregation behavior under a wide variety of conditions. Our objective is to develop a more robust model for surface segregation during vapor phase growth. The approach starts with successful models for liquid phase growth which enables us to include multiple mechanisms for segregation which are missing in earlier models.

PREVIOUS MODELS

Previous models for segregation can be divided into three major categories based on the type of mechanism used. The first and earliest type of models were phenomenological in nature [6, 7]. Their important conclusion was that at sufficiently low temperatures, there exists a kinetically limited regime in which the impurity atoms cannot move quickly enough to avoid becoming trapped in the bulk.

Phenomenological models were followed by a class of models invoking an interlayer exchange pathway for segregation [8, 9]. In these models, an atom is first buried by the incident deposition flux and subsequently may exchange positions with an adjacent atom above or below, provided both are within the first two layers of the free surface. An atom is considered incorporated once it is buried three layers below the surface and unable to make any further exchanges. As did the earlier models, these models display a transition temperature from equilibrium segregation to a kinetically limited segregation regime. However, the main problem with these models is that they are unsuccessful at reproducing the experimentally measured results at low deposition temperatures [10, 11].
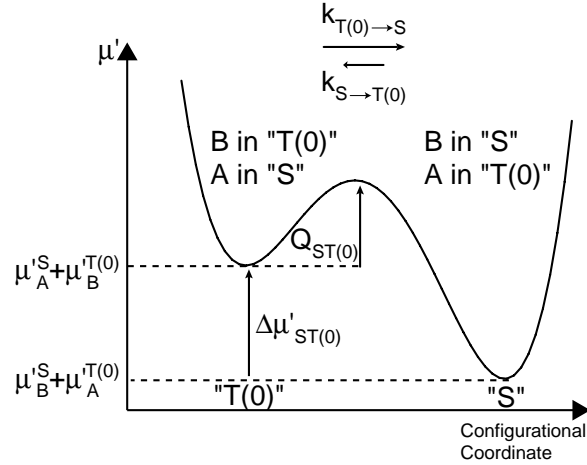
Figure 1. Simplified version of exchange mechanisms for segregation on a surface. There are four distinct regions: (S) step edge, (D) adatoms, (T) terrace, and Bulk. The terrace extends from step edge to step edge with an average length L. An atom is considered incorporated once it reaches the bulk region. Exchange events are denoted with double ended arrows.

A more recently developed class of models invoke a surface diffusion mechanism for segregation behavior [12, 13]. In these models, an atom can avoid incorporation by remaining on the free surface either by climbing over a step edge or by riding at the step edge. An atom is considered incorporated once it is completely surrounded by other atoms in the plane. These models better described the experimental behavior at low temperatures, but did not predict a transition temperature from equilibrium segregation to kinetically limited segregation.

NEW MODEL

Our new model for surface segregation combines both interlayer and surface diffusion processes based on earlier models developed for liquid-solid segregation [14, 15]. The first step is to reduce the multitude of atomistic processes that may be occurring on the surface to a tractable few as shown in figure 1. Here, our model is not concerned with the detailed kinetic pathway for a given exchange event, but rather the effective result of an atom moving from one location (S,D,T) to another. Hence we consider direct interchange events between atoms on different sites on the surface. We label solute as "B" and solvent as "A" and a solute atom is not completely incorporated until it reaches the region labeled "bulk" in the figure.

For the purposes of developing this model, we consider only two types of transitions. Refinement to include other transitions is currently in progress. The first transition is similar to the surface diffusion mechanism in which we take a B atom from the first terrace position $(T(0))$ and exchange it with an A atom at the step edge $((T(0) \leftrightarrow S))$. The second transition takes a B atom from the final terrace position $(T(L))$ and exchanges it with an A atom at the step edge (denoted $(T(L) \leftrightarrow S)$). This transition can be associated with the previously described interlayer mechanism.

If a B atom is sitting at (S), then once another atom attaches to the step, it will "bury" the B atom laterally by changing it into a $(T(0))$. This B atom can then undergo a $(T(0) \leftrightarrow S)$ exchange event to return it to (S). In the reference frame that is moving laterally with the step edge, the atomic fraction of B atoms at $(T(0))$ evolves in time as

$$\frac{dX^{T(0)}}{dt} = J_{S \to T(0)} - J_{T(0) \to S} + J^c_{S \to T(0)} - J^c_{T(0) \to T(x)}. \tag{1}$$

The $J_{\alpha \to \beta}$ terms represent the number of B atoms diffusing into state β per unit time. $J^c_{\alpha \to \beta}$ is the convective flux of B atoms from state α to state β. This is the number of B atoms that move into state β from α due to the motion of the coordinate system. The convective term is not an activated

Figure 2. Energy diagram for the $(T(0) \leftrightarrow S)$ transition.

process, so it depends only on the velocity of the moving step edge v and the fraction of B atoms in the initial state:

$$J^c_{\alpha \to \beta} = X^\alpha \frac{v}{\lambda}. \tag{2}$$

The diffusive flux terms depend on the chemical potential of the A and B atoms at their particular locations. Consider the energy diagram in figure 2 which represents the barrier between states (S) and $(T(0))$. We are interested in the motion of B atoms, but because in this model all transitions require direct interchange events, we also need to consider the energetics of A atoms.

Then we can write the diffusive fluxes in the form

$$J_{S \to T(0)} = X^S(1 - X^{T(0)})\nu \exp\left(-\frac{Q_{ST(0)} + \Delta\mu'_{ST(0)}}{k_B T}\right) \tag{3}$$

$$J_{T(0) \to S} = X^{T(0)}(1 - X^S)\nu \exp\left(-\frac{Q_{ST(0)}}{k_B T}\right) \tag{4}$$

Here we have accounted for the ideal entropy of mixing by multiplying our transition rates by the number fraction of occupation in the appropriate states.

We bring the second transition into the model by considering a similar dependence for the atomic fraction of B atoms in the $(T(L))$ state. In this case, there is an analogous set of equations (1-4), with the important difference that the convective flux (equation 2) depends on $X^{T(0)}$ because we are not allowing any exchanges along the terrace.

Next, we assume the transitions are able to reach steady state, thereby allowing us to set equation 1 and the analogous equation for $(T(L) \leftrightarrow S)$ to 0. We solve these equations in the dilute limit for the ratio,

$$\kappa^{ST(0)} \equiv \frac{X^{T(0)}}{X^S} = \frac{\kappa_e^{ST(0)} + \dfrac{v}{v_d^{ST(0)}}}{\dfrac{v}{v_d^{ST(0)}} + 1} \tag{5}$$

$$\kappa^{ST(L)} \equiv \frac{X^{T(L)}}{X^S} = \frac{\kappa_e^{ST(L)} + \kappa^{ST(0)}\frac{v}{v_d^{ST(L)}}}{\frac{v}{v_d^{ST(L)}} + 1}. \tag{6}$$

Here we have made the substitutions

$$\kappa_e^{ST(0)} \equiv \exp\left(-\frac{\Delta\mu'_{ST(0)}}{k_B T}\right) \tag{7}$$

$$v_d^{ST(0)} \equiv \nu\lambda \exp\left(-\frac{Q_{ST(0)}}{k_B T}\right), \tag{8}$$

with similar equations for $\kappa_e^{ST(L)}$ and $v_d^{ST(L)}$.

The final step in the development of this model is to extract a measurable quantity from these atomic fractions. There are a variety of measures used in the literature, but for convenience, we will use the segregation ratio r as defined by Jorke [9]:

$$r \equiv \frac{\text{Surface Areal Concentration of Impurity}}{\text{Bulk Volume Concentration}}. \tag{9}$$

Then by simply adding up the total number of B atoms in the surface and normalizing by the surface area, we obtain

$$r = \frac{\lambda^2}{\kappa^{ST(L)}}\left[\rho + \left(\frac{1}{\lambda} - \rho\right)\kappa^{ST(0)}\right], \tag{10}$$

where ρ is the density of steps on the surface and λ is the atomic spacing.

One of the main results of our model is the prediction of transition between kinetically limited and equilibrium segregation. For different combinations of energies for the two transitions, we can observe multiple transition temperatures corresponding to the segregation regime of each individual transition. Furthermore, the transition temperature will have a velocity dependence as well as a miscut dependence for the case of step flow growth. The apparent activation enthalpy of the segregation length will depend on the growth temperature relative to these transition temperatures. A complete discussion of these behaviors is beyond the scope of this letter and is discussed elsewhere[16].

COMPARISON TO EXPERIMENTS

In order to compare our model results to experimental data, we make some further assumptions about the step density. For the experimental data of Phosphorus in Si(001), it is suggested that films grow in a layer by layer fashion [13]. Therefore, we assume the validity of scaling theories which relate the step density to the surface diffusion rate $\tilde{D}$ (surface diffusivity divided by λ^2) to deposition flux ($\frac{monolayers}{sec}$) [17],

$$\rho = \rho_0\left(\frac{\tilde{D}}{F}\right)^{-\frac{1}{3}} = \rho_0\left(\frac{\nu\exp\left(\frac{-E_{diff}}{k_B T}\right)}{F}\right)^{-\frac{1}{3}}. \tag{11}$$
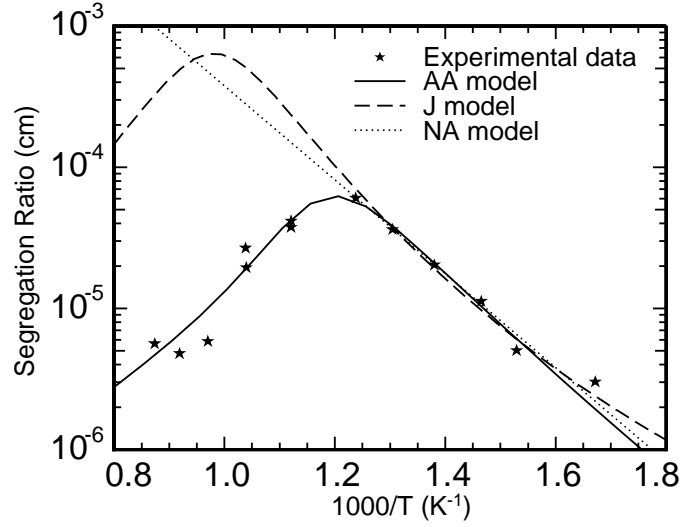
Figure 3. Segregation ratio vs. inverse temperature for the segregation of P in Si(001). Symbols: data of Nutzel and Abstreiter [19]. The solid line shows the fit to our model (AA model) using a temperature dependent step density (equation 11). The dashed line shows the fit to the Jorke model [9] (J model) and the dotted line shows the fit to the model of Nutzel and Abstreiter [13](NA model) All the relevant parameters are given in table I.

For the purpose of comparing our model to experiment, we use the value of E_{diff}=1.1eV for the diffusing species in Si(001)[18].

Figure 3 shows the experimental measurement (symbols) of the segregation ratio for phosphorus in Si(001) grown at 0.1 nm s^{-1} [19]. The experimental data show a transition between the equilibrium segregation regime and the kinetically limited regime at approximately 800 K. As we can see from the figure, our model is superior at fitting the experimental data over the entire range of temperatures. We accurately reproduce the transition between kinetically limited and equilibrium segregation using energies and prefactors that are quite typical for segregating species.

Table I. Table of the parameters used in our model to fit the data in figure 3. The variables in parentheses represent the analogous parameters in our model. ν was not used as fitting parameter in either our model or the NA model. Δ_0 is a free parameter in the NA model with no direct analog in our model.

	AA model		J model		NA model
$Q_{ST(0)}$	1.00 eV	$E_A \rightsquigarrow (Q_{ST(L)})$	0.1 eV	$E_s \rightsquigarrow (\frac{1}{2}E_{diff}-\Delta\mu'_{ST(0)})$	0.66 eV
$\Delta\mu'_{ST(0)}$	1.65 eV	$E_I \rightsquigarrow (\Delta\mu'_{ST(L)})$	1.0 eV	Δ_0	0.8 cm
$Q_{ST(L)}$	1.00 eV	ν	26.5 s^{-1}	$\underline{\nu}$	1.6x10^{14} s^{-1}
$\Delta\mu'_{ST(L)}$	1.22 eV				
ρ_0	3.2x10^6 cm^{-1}				
$\underline{\nu}$	1x10^{13} s^{-1}				

In contrast, the interlayer exchange model of Jorke [9] and the surface diffusion model of Nutzel and Abstreiter [13] are not sufficient to describe the experimental data fully. In the NA model, the model fits the low temperature data, but is unable to produce a transition temperature. In the J model, we can find a fit to the low temperature data only after applying clearly non-physical parameters to the model, and even then we are unable to predict the transition temperature accurately.

SUMMARY

We have developed a new kinetic model for segregation that can reproduce the experimental observations of the segregation process. Our model overcomes some of the shortcomings of previous models by incorporating both surface diffusion mechanisms and interlayer exchange mechanisms. We obtain a velocity and miscut angle dependent transition temperature between an equilibrium segregation regime and a kinetically limited regime. In the kinetically limited regime, the segregation length increases with increasing temperature, increasing miscut angle, or decreasing deposition flux. The model assumes a particular scaling behavior for the temperature dependence of the step density and contains a number of parameters. In principle, some of these can be determined by independent experimental measurements. We find better agreement with previous experimental measurements of the temperature dependence of the segregation ratio of P in Si(001) than is possible with earlier models.

References

1. E. Schubert, *Delta-Doping of Semiconductors* (Cambridge University Press, Cambridge, 1996), p. 604.

2. H. Gossmann and E. Schubert, Critical Reviews in Solid State and Materials Sciences **18**, 1 (1993).

3. P. Allen, Solid State Comm. **102**, 127 (1997).

4. R. Farrow, IBM J. of Res. and Dev. **42**, 43 (1998).

5. H. Gossmann, E. Schubert, D. Eaglesham, and M. Cerullo, Appl. Phys. Lett. **57**, 2440 (1990).

6. S. Iyer, R. Metzger, and F. Allen, J. Appl. Phys. **52**, 5608 (1981).

7. S. Barnett and J. Greene, Surf. Sci. **151**, 67 (1985).

8. J. Harris, D. Ashenford, C. Foxon, P. Dobson, and B. Joyce, Appl. Phys. A **33**, 87 (1984).

9. H. Jorke, Surf. Sci. **193**, 569 (1988).

10. H. Jorke, H. Herzog, and H. Kibbel, Fresenius J. Anal. Chem. **341**, 176 (1991).

11. Z. Jiang, C. Pei, L. Liao, X. Zhou, X. Zhang, X. Wang, T. Smith, and I. Sou, Thin Solid Films **336**, 236 (1998).

12. S. Andrieu, F. A. d'Avitaya, and J. Pfister, J. Appl. Phys. **65**, 2681 (1989).

13. J. Nutzel and G. Abstreiter, Phys. Rev. B **53**, 13551 (1996).

14. M. Aziz, J. Appl. Phys. **53**, 1158 (1982).

15. L. Goldman and M. Aziz, J. Mater. Res. **2**, 524 (1987).

16. C. B. Arnold, Ph.D. thesis, Harvard University, Cambridge, MA, 2000.

17. A. L. Barabasi and H. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, UK, 1995).

18. M. Krueger, B. Borovsky, and E. Ganz, Surf. Sci **385**, 146 (1997).

19. J. Nutzel and G. Abstreiter, J. Appl. Phys. **78**, 937 (1995).