

we know that:

$$G_m = \gamma_e \gamma_c \dot{G}_{e:c} + \gamma_u \gamma_c \dot{G}_{u:c} + \gamma_e \gamma_{va} \dot{G}_{e:va} + \gamma_u \gamma_{va} \dot{G}_{u:va} + RT (\gamma_e \ln \gamma_e + \gamma_u \ln \gamma_u) \\ + RT (\gamma_c \ln \gamma_c + \gamma_{va} \ln \gamma_{va}) + \gamma_e \gamma_u \gamma_c L_{e:u:c} + \gamma_e \gamma_u \gamma_{va} L_{e:u:va} \\ + \gamma_e \gamma_c \gamma_{va} L_{e:c:va} + \gamma_u \gamma_c \gamma_{va} L_{u:c:va} \quad (I) \\ (1 - \gamma_c) = \gamma_{va} \quad (II)$$

↳ plugging II in I:

$$G_m = \gamma_e \gamma_c \dot{G}_{e:c} + \gamma_u \gamma_c \dot{G}_{u:c} + \gamma_e (1 - \gamma_c) \dot{G}_{e:va} + \gamma_u (1 - \gamma_c) \dot{G}_{u:va} \\ + RT (\gamma_e \ln \gamma_e + \gamma_u \ln \gamma_u) + RT (\gamma_c \ln \gamma_c + (1 - \gamma_c) \ln (1 - \gamma_c)) \\ + \gamma_e \gamma_u \gamma_c L_{e:u:c} + \gamma_e \gamma_u (1 - \gamma_c) L_{e:u:va} \\ + \gamma_e (\gamma_c - \gamma_c^2) L_{e:c:va} + (\gamma_c - \gamma_c^2) \gamma_u L_{u:c:va} \quad (III)$$

$$\text{now } \frac{\partial G_m}{\partial \gamma_c} = \mu_c \quad (IV)$$

by plugging III in (IV) we have

$$\mu_c = \gamma_e \dot{G}_{e:c} + \gamma_u \dot{G}_{u:c} - \gamma_e \dot{G}_{e:va} - \gamma_u \dot{G}_{u:va} \\ + RT \ln \gamma_c + RT - RT - RT \ln (1 - \gamma_c) \\ + \gamma_e \gamma_u L_{e:u:c} - \gamma_e \gamma_u L_{e:u:va} \rightarrow \text{Correct expression} \\ + \gamma_e (1 - 2\gamma_c) L_{e:c:va} + (1 - 2\gamma_c) \gamma_u L_{u:c:va} \quad \checkmark$$

“Thermodynamic analysis for the size-dependence of Si_{1-x}Ge_x nanowire composition grown by a vapor–liquid–solid method”

Introduction:

Si_{1-x}Ge_x nanowires are among the promising candidates for optoelectronics. Since their electronic characteristics are dictated by the composition, it is important to control the composition of this category of materials to reach their true potential. It is discovered that the wire size of nanowires (diameter) has an impact on the composition independent of process conditions. Zhang et al. tried to explain it in terms of the Gibbs–Thompson effect. Based on the size dependence of the growth rate of nanowires and this presumption that the alloy wire composition is determined by the relative growth rate of individual pure component nanowires, their model achieved a reasonable agreement with experimental data. Nonetheless, the result is not able to establish that Gibbs–Thompson effect causes the size dependence of wire composition because they used empirical fitting. In the present work by using fundamental thermodynamic analysis it is shown that size dependency of alloy nanowire is indeed due to the Gibbs–Thompson effect on the thermodynamics of the Au droplet catalyst and the Si_{1-x}Ge_x nanowire.

Thermodynamic approach:

VLS growth is assumed to be composed of two interfacial reactions. One is the reaction between vapor and liquid droplets on the surface of the liquid droplet. The other is the reaction between liquid droplets and solid nanowires on the interface between the two. The vapor is a combination of SiH₄ and/or GeH₄, H₂ gases, and decomposed Si and/or Ge atoms. The liquid droplet composition can be estimated from the equilibrium activity of Si and/or Ge in the vapor phase since Gibbs energy of formation of SiH₄ and/or GeH₄ is readily available in thermodynamic data handbooks. This Gibbs free energy can be used to calculate equilibrium activity values of Si and/or Ge. The size effect is evaluated by the Gibbs–Thompson equation and thermodynamic calculations were performed for Si_{1-x}Ge_x nanowires with various diameters. It was uncovered that the vapor phase cannot reach equilibrium since the calculated equilibrium chemical activities of Si and Ge for a typical process condition are several orders of magnitude bigger than the expected value. Thus, a supersaturated initial liquid composition was assigned and an imaginary vapor phase that is in equilibrium with the liquid was assumed. Further, the rule of mixture for liquid and solid and surface energy was used. Probable error due to the difference in molar value is calculated as well. Finally, by all these assumptions, an expression for the Gibbs–Thompson effect was represented and explored.

Results:

Assuming the rule of mixture indeed size dependence is anticipated in good accordance with the experiments in all composition ranges. By employing the molar volume of pure Si or pure Ge used for the molar volume of solid alloy it is proved that the selected value of solid molar volume has a negligible effect on results. Furthermore, a condition similar to the full segregation of Ge atoms is assumed and calculations are performed to estimate probable error due to the rule of mixture. Size dependence appears to be stronger with this assumption. Hence, it is expected that the real situation corresponds to a condition between surface energy equal to a value between $\gamma_{\text{alloy}} = \gamma_{\text{Ge}}$ and $\gamma_{\text{alloy}} = \gamma$ from the rule of mixture. Finally, the capillarity effect can successfully explain the shift of droplet composition to the Au-rich side which results in the further shift into the Si-rich side. This can be justified by calculation of the Gibbs free energy of the formation of Au–Si and Au–Ge binary liquid alloys.