

A New Model for the Critical Thickness of Metallic Amorphous Thin Films

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Abstract – A new model for the critical thickness of amorphous metallic thin films is proposed in which the surface free energy difference, $\Delta\gamma$, equals $\gamma_{CV} + \gamma_{CA} - \gamma_{AV}$, where γ_{CV} is the crystalline-vapor, γ_{CA} the crystalline-amorphous, and γ_{AV} the amorphous-vapor interface free energy. It is predicated upon experimental evidence that non-epitaxial film growth due to large atomic-size difference dictates one or two *amorphous atomic layers* in contact with the substrate phase. Consequently, the model does not require hardly-accessible film-substrate interface free energies in predicting the critical thickness for amorphous-crystalline transition.

Certain nano-crystalline films such as Fe or Co have attracted much attention because of their interesting magnetic properties. When their thickness is greater than a critical value, h , they become crystalline and ferromagnetic, otherwise they remain amorphous and paramagnetic. Typically, balancing between the volume free energy and the surface free energy [1,2] yields h :

$$h = \frac{\Delta\gamma}{\Delta G} = \frac{(\gamma_{CV} + \gamma_{CS}) - (\gamma_{AV} + \gamma_{AS})}{G_A - G_C}, \quad (1)$$

where γ_{CV} is the interface free energy between crystalline and vapor phase, and G_A and G_C are the volume free energies of amorphous and crystalline phase, respectively. Other γ 's are similarly defined with subscript A for amorphous and S for substrate. Eq. (1) appears qualitatively sound. But its validity is indeterminate, as numerical values of both γ_{AS} and γ_{CS} are either unknown or hardly accessible, and prediction of $h = 2\sim 3$ nm leads to unusually high values of $\Delta\gamma$ in the range of $2\sim 2.5$ J/m² [1]. Since the typical surface free energy, γ_{CV} , of transition metals is about 2 J/m² [3], Eq. (1) needs reexamination. It is based on the assumption that all the amorphous atoms become crystalline. Therefore it ignores the basic nature of non-epitaxial growth due to a large difference in atomic size. Detailed experiments, however, showed that there remain one or two *amorphous atomic layers* in contact with the substrate phase. **Figure (b)** below displays, in green, the residual amorphous layers sandwiched between crystalline and substrate phase. Since only the blue atoms in the region of $h-d$ undergo transition, h should be given by:

$$h = d + \frac{\Delta\gamma}{\Delta G} = d + \frac{(\gamma_{CV} + \gamma_{CA}) - \gamma_{AV}}{G_A - G_C} \cong \Omega^{1/3} + \frac{(\gamma_{CV} + \gamma_{CL}) - \gamma_{LV}}{G_A - G_C}. \quad (2)$$

Note that both γ_{AS} and γ_{CS} are irrelevant for predicting h . Furthermore, since amorphous is a quenched liquid state, $\gamma_{CA} \approx \gamma_{CL}$ (crystalline-liquid interface free energy) and $\gamma_{AV} \approx \gamma_{LV}$ (liquid surface free energy). With d in terms of atomic volume, Ω , the critical thickness, h , can be expressed with easily-accessible thermodynamic quantities, as shown in Eq. (2). Typically, $\gamma_{CL} \approx 0.1\sim 0.3 \gamma_{CV}$ and $\gamma_{LV} \approx 0.7\sim 0.9 \gamma_{CV}$ [3]. Thus, $\Delta\gamma \approx 0.2\sim 0.6 \gamma_{CV} \approx 0.4\sim 1.2$ J/m², which seems quite reasonable.

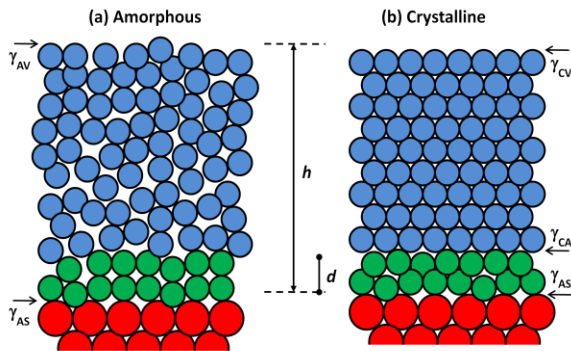


Figure: (a) Amorphous film of height, h , on a substrate and (b) crystalline film of height, $h-d$. Both blue and green balls indicate metallic film atoms, while red balls are for the substrate atoms. γ_{AV} is the interface free energy between amorphous and vapor phase, and γ_{AS} is for between amorphous and substrate. Other γ 's are defined likewise with "c" for crystalline.

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[2] T. Shinjo, Struct. Chem., 2 (1991) 281.

[3] J. M. Howe, *Interface in Materials*, Wiley, New York, NY (1997).