Alloy Nanostructure Evolution Via Surface Diffusion

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Summary

The dynamics of a solid evolving exclusively by surface diffusion is a classic problem in materials physics. However, when the material is an alloy, a new nanoscale lengthscale is introduced. The resulting new continuum equations for alloys exhibit novel behavior not seen for single-component systems. In particular, the evolution of nanoscale structures can be dramatically affected.

Introduction

The dynamics of a solid evolving exclusively by surface diffusion is a classic problem in materials physics. However, when the material is an alloy, the classic continuum equations are not directly applicable. Instead, it is necessary to consider a distinct surface layer [1]. In general, the properties of this layer may be discontinuous from the bulk, leading to new continuum equations for the surface evolution [2]. In particular, the thickness of the surface layer (typically a few atomic layers) introduces a new lengthscale, so that even within a continuum treatment the physical problem has an inherent multi-scale character.

In general, the evolution near the surface can involve atomic-scale effects, giving a complex kinetic problem. However, there is evidence that there is layer at the surface with diffusivity greatly enhanced relative to the bulk [3,4]. If this layer is in internal equilibrium over its (atomically thin) vertical extent, one obtains a relative simple behavior, independent of the atomic details of the surface [2].

Then, neglecting certain higher-order terms, the evolution equations may be written

$$v_n = \sum_{\nu}\left[F_{\nu} + \nabla \cdot \left(D_{\nu}\nabla\mu_{\nu}\right)\right]$$

$$w_s \frac{d\xi_{\nu}}{dt} = F_{\nu} + \nabla \cdot \left(D_{\nu}\nabla\mu_{\nu}\right) - c_{\nu}v \tag{1}$$

Here v_n is the normal velocity of the surface, t is time, D is the surface diffusivity, F is the incident growth flux and μ is the chemical potential. The subscript ν is an index running over the two components of the alloy. The composition is c, except that there is a layer of thickness w_s at the surface (the region of enhanced diffusivity) which may

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have different composition ξ (averaged over the thickness w_s). This thickness may be of order 2-4 atomic layers [3].

These equations exhibit novel behavior not seen for single-component systems. Even in the simplest case, the decay of a non-planar surface profile, the system exhibits "kinetic surface segregation". This arises because the two alloy components typically have radically different diffusivities. The effect of this is best understood by comparison with classic treatment for a pure material.

For a pure material, a sinusoidal perturbation decays exponentially with time, as $\exp\left(-\gamma D q^4 t\right)$, where q is the wavevector [5,6]. For a nonplanar alloy, beginning with perfectly uniform composition, there is a brief transient period where the same behavior occurs, but with the single-component diffusivity replaced by the weighted average of the two alloy components. However, as the low points on the surface fill in by surface diffusion, they fill preferentially with the fast-diffusing species. This leads to an accumulation of the slow-diffusing species in the surface layer. As a result, after the transient period, the system re-establishes an exponential decay, but with a much slower decay constant, determined by the slower-diffusing of the two species [2]. (Because diffusion is an activated process, in general it is expected that the two species will have very different diffusivities, possibly differing by orders of magnitude.)

In the case of a macroscopic structure, the resulting behavior is simple but surprising. The initial transient is very brief, and the degree of alloy decomposition is very small after the transient. Thus, for all practical purposes, the behavior appears to follow the classic behavior predicted for a single-component material [5,6]. However, the decay rate is controlled strictly by the slower of the two diffusivities, even if this is the minority species.

For a nanoscale structure, the behavior is more complex. The transient period, when evolution is much faster, can represent a substantial portion of the total evolution. Moreover, the degree of alloy decomposition can be rather large, with important implications for electronic devices.

More complex behavior occurs during strained-layer heteroepitaxy. A particularly interesting case is capping of self-assembled quantum dots. If e.g. a few atomic layers of InAs are deposited on GaAs (001), the InAs forms nanoscale strained islands that are free of dislocations. These can be overgrown ("capped") with more GaAs, for use in opto-electronic applications, such as quantum-dot lasers.

However, the evolution equations above predict that there can be substantial intermixing and shape change of the quantum dot during capping, despite the assumed absence of bulk diffusion. Although results so far are preliminary, these changes are consistent with what is observed experimentally.

Reference

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