

Evolution of a Reactive Surface via Subsurface Defect Dynamics

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We find that the topography and composition of a reactive surface can evolve during epitaxy via motion of point and line defects within the material. We observe the response of a NiAl surface to an Al atom flux with low-energy electron microscopy. Initially, new NiAl layers grow as Al atoms exchange with bulk Ni atoms. When the surface is critically enriched in Al, condensation occurs at dislocations. They dissociate, move linearly, and leave tracks of altered composition and new atomic steps. We show how these dynamics depend on the identity and quantity of point defects near the surface.

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The topology and composition of a solid surface determine how it functions. An important challenge is to learn how these properties evolve at the atomic scale when one material (an overlayer) is deposited on another (a substrate). Often, the substrate is passive in film growth, and factors relevant to only the topmost atomic layers determine how the surface evolves. Then, the substrate is just a template that guides how deposited atoms organize.

Chemically reactive systems have added complexity because deposited atoms can react preferentially with particular components of the substrate. In this Letter, we investigate how the surface of NiAl, an ordered alloy, responds to deposited Al atoms. We find that Ni is drawn out of the bulk because it binds preferentially to Al. We observe complex surface dynamics that result from the combined motions of point defects (atoms and vacancies) and line defects (dislocations) in the bulk. These defects create atomic steps and chemical inhomogeneities at the surface. Dislocations have been found previously to affect surface morphology, most notably in observations of growth spirals [1] and etch pits. Here we find that dislocations can also affect composition, and that the dynamics of bulk defects must be understood to describe even the most basic aspects of the evolution of the surface.

Upon exposing the β -NiAl(110) surface to an Al atom flux, we see the immediate consequences of subsurface dynamics. In the low-energy electron microscope (LEEM) image in Fig. 1(a), dark, curved lines show the locations of monatomic steps on our slightly Ni-rich substrate [2]. Steps advance and islands nucleate during Al deposition, as seen by comparing step locations in Figs. 1(a) and 1(b). Island nucleation and step flow are well-understood processes commonly seen during epitaxial growth. The behavior here is notable, however, since we find the new layers to be NiAl alloy (see below) even though only Al is deposited. As more Al is added, dark bands appear and elongate. Figures 1(c) and 1(d) capture the formation of a band. The band starts where a surface step ends [point “D” in Fig. 1(b)]. This point is where a bulk dislocation termi-

nates at the surface. The band lengthens to $\sim 2 \mu\text{m}$ [Fig. 1(d)], stops growing, and dissipates. Figures 1(e) and 1(f) show that the dislocation moved from the point where the band originated to the point where the band stopped growing. With time [Fig. 1(e)], more bands move into view. Importantly, new surface layers nucleate and grow along the bands, as evidenced by the new atomic steps that form and advance from them [Figs. 1(e) and 1(f)]. Thus, dislocations move during crystal growth and growth occurs rapidly along bands that they leave behind.

This behavior differs from typical epitaxial growth in two ways. First, the composition of the growing crystal differs from the deposited material—Al is deposited but β -NiAl growth is observed. Thus, the substrate is not simply a passive template for crystal growth, but actively supplies a flux of Ni atoms to its surface. Second, we see localized changes in surface topography and composition associated with motion of dislocations. Below, we determine the microscopic processes by which the motion of point and line defects in the subsurface cause these changes.

We find two distinct stages of behavior when Al atoms impinge onto the NiAl surface [2]. Initially, step-flow growth (stage 1) occurs [Figs. 1(a) and 1(b)]. In this stage, we see no changes in the image intensity or in the surface’s electron diffraction pattern, establishing that new NiAl alloy grows above the original surface. As more Al is added, dislocations begin to move and dark bands form (stage 2), as in Figs. 1(c)–1(f) and 2. We present evidence suggesting that the bands are Al-rich regions of crystal. Depositing Al at low temperature (T) under the same imaging conditions (e.g., using the same electron energy) causes the LEEM images to darken (i.e., the electron reflectivity decreases) [3,4]. Diffraction analysis establishes that a series of increasingly Al-rich phases grow epitaxially on the surface during this low- T deposition [5,6]. Since the dark bands that form during high- T Al deposition show the same imaging characteristics in LEEM as do Al-rich phases, we conclude that the bands are also Al-rich surface regions.

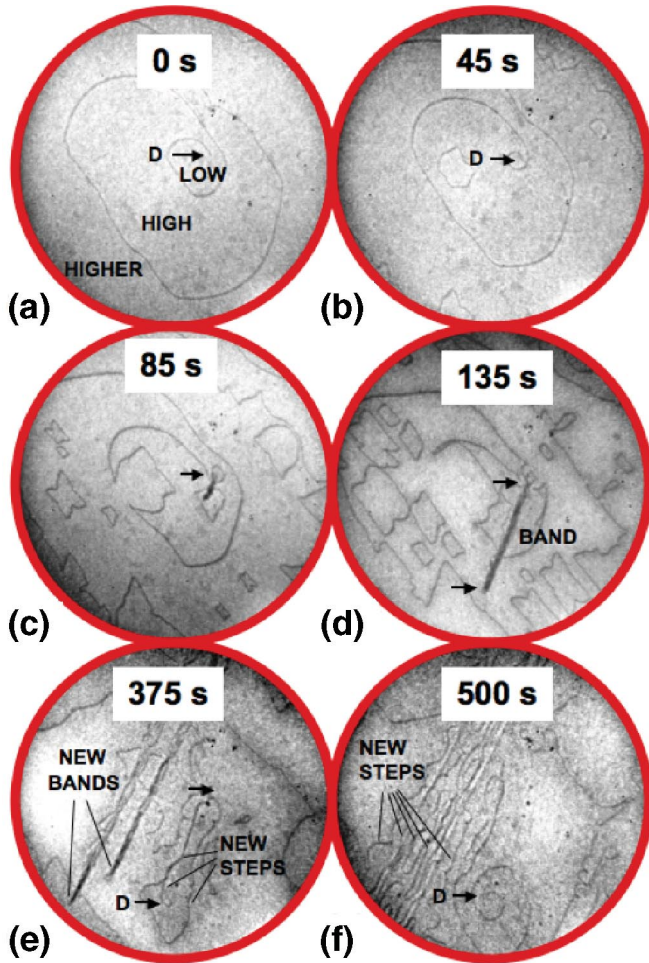


FIG. 1 (color). (a) LEEM image of a $7 \mu\text{m}$ diam area of NiAl(110) at 890 K before exposure to Al flux at $t = 0$ sec. A dislocation emerges from the substrate at point “D.” (b) 45 s: Steps advance as NiAl grows above the original surface. (c) 85 s: A dark band appears at the dislocation. (d) 135 s: The band elongates. (e) 375 s: The band vanishes and the dislocation has moved to the band’s endpoint. Two bands from dislocations outside the field of view move across the surface. (f) 500 s: Rapid, localized growth occurs as new steps advance from the bands.

The mechanism for step-flow growth (stage 1) and the crossover in behavior to dislocation motion (stage 2) is understood by considering the point defects in β -NiAl alloys, which have been extensively studied [7–9]. β -NiAl has the CsCl unit cell, with Al atoms at the four corners of a cube and a Ni atom at the center. Since the substrate is initially Ni rich, excess Ni atoms reside on sites typically occupied by Al atoms, i.e., Ni antisites [8,9]. Here we assume that the surface uses the same defects as the bulk to accommodate nonstoichiometry. During Al deposition, Ni atoms at antisites near the surface exchange with impinging Al atoms. Ejected Ni reacts with incoming Al, fueling NiAl growth and causing surface steps to advance. This picture has quantitative support. Comparing the flux of Al atoms to the growth rate of NiAl reveals that half of the deposited Al atoms replace Ni in the bulk and the other

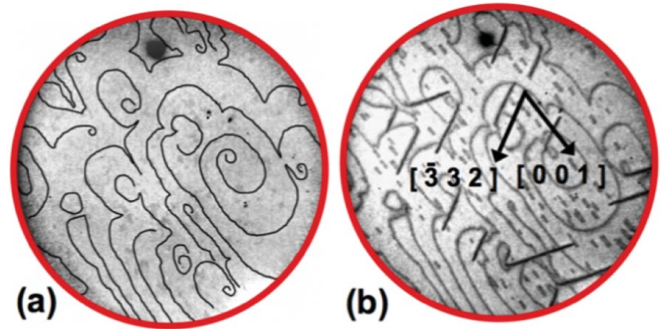


FIG. 2 (color). (a) LEEM image of a $25 \mu\text{m}$ diam area. Many dislocations terminate at the surface. Steps are outlined to enhance contrast. (b) Same area after adding <1 ML of Al at 700 K. Linear bands have grown from dislocations.

half incorporate into new NiAl on the surface [10,11]. One Al atom goes into the bulk for each NiAl unit created at the surface. Initially, the population of Ni antisites and the speed of lattice diffusion suffice to allow the excess Ni to react with the incoming Al atoms to form β -NiAl, the thermodynamically favored compound, instead of an Al overlayer.

However, this mode in which Al from the surface replaces bulk Ni antisite atoms does not continue indefinitely. Here, we show that the second stage of growth, which involves dislocation motion, begins after the surface reaches a critical composition. The time elapsed before dislocations move depends on the Al flux and the substrate temperature. Figure 3 shows that this induction time scales as the inverse square of the deposited Al flux. This is understood by analyzing the time-dependent concentration of the point defects that diffuse to the surface from the bulk. Consider how the bulk concentration of excess Ni, $c(z, t)$, depends on time (t) and depth into the substrate (z). We apply the diffusion equation, $\partial c / \partial t = D \nabla^2 c$, where D is the bulk diffusion constant for Ni antisites. With the substrate uniformly Ni rich at the beginning of each experiment and for the boundary condition that the flux of excess Ni to the surface is half the Al deposition flux F_0 [i.e., $-D \frac{\partial c}{\partial z}(t, z = 0) = -F_0/2$, as measured], the concen-

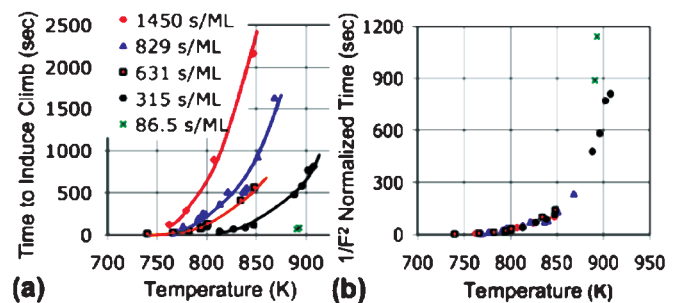


FIG. 3 (color). (a) Temperature and Al flux dependence of the time required to induce dislocation motion. Raising T increased the time to induce dislocation motion. Curves through the data are guides to the eye. (b) Data from (a) overlap when normalized by $1/\text{flux}^2$, as predicted by the diffusion equation.

tration of excess Ni at the surface is $c(0, t) = -F_0\sqrt{t/(\pi D)}$. Then the time for the Ni concentration [12] to reach a critical value, $c = c_N$, is $t_N = \pi D c_N^2 / F_0^2$, the same dependence on Al deposition flux found in Fig. 3(b). So, we conclude that dislocation motion begins when the excess Ni diminishes to a certain critical value [13].

Why do dislocations move only after the surface has been Al enriched to a certain composition? The answer comes from understanding how defects in β -NiAl change with composition. As Al is deposited, the near surface is eventually depleted of Ni antisites but new NiAl continues to grow. NiAl becomes Al rich by making vacancies on the Ni sublattice [8,9]. Thus, as the substrate is enriched in Al, there is an important change in the supply of Ni atoms that fuels Ni-Al growth on the surface—Ni-Al layers must form with Ni drawn from bulk Ni sites instead of from Ni antisites. In this way, Al deposition leads to Ni vacancy accumulation in the near-surface region. We therefore propose that dislocation motion (stage 2) begins after the growth of NiAl layers on the surface consumes available Ni antisites. Then, Ni vacancies form and, when sufficiently abundant, condense on dislocations and cause them to move via climb.

We first propose and then justify a mechanism by which dislocations change the local composition and create Al-rich regions where rapid NiAl alloy growth occurs. We begin by emphasizing that the dark bands nucleate at dislocations, which then move [Figs. 1(b)–1(f) and 2] as the bands elongate. TEM studies [9] have shown that the dislocations in NiAl are perfect dislocations; i.e., their Burgers vectors connect equivalent lattice sites [15,16]. Movement of perfect dislocations cannot change the composition of NiAl to create Al-rich bands. However, these dislocations can dissociate into imperfect, or partial dislocations, whose Burgers vectors connect inequivalent lattice sites. The movement of partials can change local composition [15]. When partials separate, an antiphase boundary (APB) is created on the plane bounded by them, as shown in Fig. 4(a). Since APBs in NiAl can be either Ni or Al rich compared to the surrounding crystal, formation of these planar defects can change the local composition. We propose that the dark bands that we observe to grow from dislocations in our LEEM studies are Al-rich surface regions that form where perfect dislocations dissociate and APBs intersect the surface. We next show observations that support this interpretation.

The directions of dislocation motion allow us to identify which partial dislocations move. After extended Al deposition at high temperature, bands form along the four $[\bar{1}12]$ -type directions [17,18]. Moving a dislocation with line direction l and Burgers vector b a unit of length along a displacement vector s changes the volume (V) of a crystal by [15]:

$$V = \hat{s} \cdot (\vec{b} \times \vec{l}) = \vec{l} \cdot (\hat{s} \times \vec{b}).$$

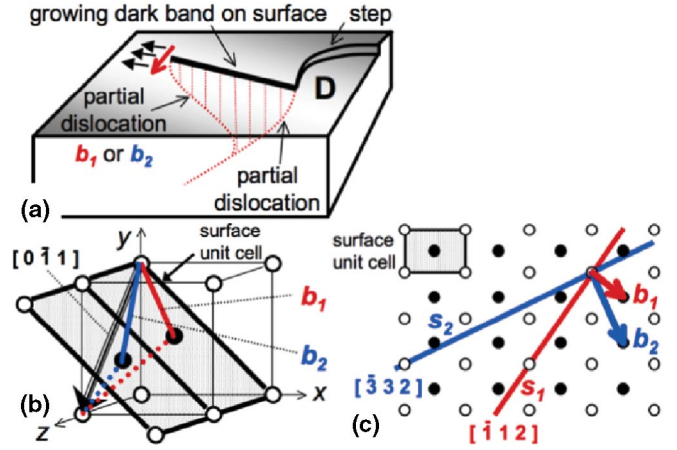


FIG. 4 (color). (a) Schematic of the surface after Al deposition, corresponding to Fig. 1(d). The partials and APB between them extend below the surface. (b) The β -NiAl unit cell. A dislocation with Burgers vector $[011]$ can dissociate to produce $b_1 = [1\bar{1}1]/2$ -type or $b_2 = [1\bar{1}3]/2$ -type partials. (c) Top view of β -NiAl(110). When climbing purely due to diffusion, b_1 partials in the surface plane climb along $[\bar{1}12]$ -type directions, while b_2 partials move along $[\bar{3}32]$ -type directions.

If this volume change is attributed to vacancy flow, then $N = V/\Omega$ vacancies diffuse to the core per unit length of climb, where Ω is an associated atomic volume [19]. A limiting case is pure climb, i.e., when the dislocation moves only by vacancies diffusing to and from its core. Then, the local change in composition (determined by N) is greatest and s , b , and l are mutually perpendicular. Figure 4(c) illustrates this case for the two partial dislocations $b_1 = [1\bar{1}1]/2$ -type and $b_2 = [1\bar{1}3]/2$. We note that $[\bar{1}12]$ -type directions are perpendicular to b_1 , the shortest Burgers vectors that connect occupied lattice sites on β -NiAl(110). Thus, we propose that the bands along $[\bar{1}12]$ -type directions form as b_1 partials climb along the surface plane. Consistently, in a high-resolution TEM study under static conditions [9], Mills and Miracle found that the core structure of $[011]$ -type dislocations contains two dissociated $[1\bar{1}1]/2$ -type partials that bound small areas of APB. So, the dark band is associated with the APB that results from the b_1 partial dislocation climbing away from a trailing partial dislocation. The Burgers vector of the trailing partial, $[1\bar{1}1]/2$, is not in the surface plane and must have an associated surface step. Thus, our data support the picture that the deposition of Al on β -NiAl(110) causes perfect dislocations to decompose into partials, which climb due to vacancy diffusion and leave Al-rich surface bands in their wake. This is shown schematically in Fig. 4(a).

At lower T (600–825 K), bands grow along different surface directions: the four equivalent $[\bar{3}32]$ directions [see Fig. 2(b)] [17,18]. These directions are exactly perpendicular to the partial with the second shortest Burgers vector, b_2 in Figs. 4(b) and 4(c). These directions of dislocation motion are understood by the same mechanism. As Ni

vacancies accumulate, a $[0\bar{1}1]$ -type perfect dislocation dissociates into two partials [16]. The partial with its Burgers vector (\mathbf{b}_2) in the surface plane climbs along its perpendicular ($[\bar{3}32]$) direction. An Al-rich APB forms on the plane bounded by this dislocation and a trailing partial. Because the Burgers vector of the latter, $[\bar{1}\bar{1}\bar{1}]/2$, is out of plane, a surface step is associated.

We now explore how the APBs affect crystal growth. As Figs. 1(e) and 1(f) show, the crystal grows more rapidly along the bands associated with APBs than elsewhere. New surface layers form at the bands and expand outward. One cause of this enhanced growth may be that the APB serves as a preferred site for new-layer nucleation, perhaps because atomic bonding is disrupted where the APB meets the surface. An alternative interpretation is that the APB leads to enhanced mass transport from the bulk to the surface, thereby increasing the local crystal growth rate. During deposition or annealing, the APB can be absorbed, as seen in the disappearance of the dark band between Figs. 1(d) and 1(f). The antiphase boundary was destroyed as the trailing partial moved toward the leading partial. In principle, the leading partial could have retraced its path backward to the trailing partial. This would have had no net effect on the crystal. However, the net result of the observed pathway (e.g., the leading partial climbs and creates the APB, then the trailing partial climbs and destroys it) was to climb the perfect dislocation. This process would require Ni and Al atoms to move away from the plane of the APB. If some flux from the destruction of the APB went to the surface, the local growth rate would be enhanced. Whether via enhanced nucleation or enhanced bulk mass transport, the formation and eventual destruction of APBs enhances local growth.

Dislocations and point defects are ubiquitous in solids and especially important in ordered alloys as they accommodate composition changes. We found that these “bulk” features moved steps, enhanced growth, and changed local composition at the surface. The dynamics related directly to the type and abundance of point defects in the near-surface region. The condensation phenomena we described are reminiscent of Guinier-Preston zone formation [20] and Suzuki segregation [21], which involve dislocation dissociation and precipitation of chemical inhomogeneities in the bulk of supersaturated alloys. Here, we found that such phenomena can also control surface morphology and composition.

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