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Boundary effects on universal growth of islands driven by ion-beam irradiation

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This paper considers the boundary conditions imposed by step edge sinks on an assembly of thermal point defects in which reactions among antidefects may dominate defect lifetimes. A model of sink behavior is described that incorporates the concepts of effective chemical potential μ^* and effective defect temperature T^* into the action of defect sinks. The law of mass action exactly couples the defect concentrations when $T^*=T$. An application of the results to a problem of current interest is described. Specifically, an earlier demonstration of universality in island growth driven by ion-beam irradiation is reanalyzed to determine the extent to which universality is sensitive to the boundary conditions imposed by the step edges on the diffusion field of reacting thermal defects.

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I. INTRODUCTION

It was clearly recognized in early research that step edges on crystal surfaces act as sites where excess atoms may incorporate into the crystal structure.[1] For excess atoms (adatoms) or surface vacancies (advacancies) created by external driving forces, step edges act as "sinks" that tend to restore the defect population to equilibrium values.[2,3] Typical driving forces that create defects and displace step edges on surfaces may be ion-beam irradiation,[4–7] sublimation of surface atoms at elevated temperatures,[1,8] or deposition of atoms from the vapor.[9–11] These are the surface analog of similar processes with vacancies and interstitials in the bulk crystal, where edge dislocations, voids or surfaces structures such as grain boundaries act as sinks.[12,13] In both bulk and surface cases, the transport of thermal defects to sinks is a diffusion problem subject to boundary conditions at the sinks. As the sinks cause the defect distribution to thermalize, the usual boundary condition is a requirement that defects take thermal equilibrium concentrations at each sink.[9,12]

The appropriate conditions have not yet been clearly identified for the case in which antidefects (i.e., adatoms and advacancies on terraces or vacancies and interstitials in the bulk) react strongly. A useful criterion is whether a defect life cycle typically begins and ends with pair processes of spontaneous creation and annihilation or is instead typically defined by independent events at sinks for the separate defects.[14] The former case occurs when sinks are widely spaced or when the system is driven sufficiently strongly by external creation processes. In the presence of strong coupling among antidefects, two collective variables, the effective defect temperature T^* and chemical potential μ^*, take the place of independent concentration as descriptors for the defect configuration,[14] somewhat like carriers in semiconductor[15–17] driven by pair creation processes such as interband light absorption. A careful discussion of the boundary conditions at sinks satisfied by strongly reacting thermal antidefects is, as yet, lacking.

Here we emphasize surface processes and merely recognize that the extension to bulk processes is possible. It is believed that reaction conditions prevail for sufficiently wide terraces on many close-packed metal surfaces at high temperatures and methods are being developed to grow terraces many microns in size,[18,19] easily sufficient for this purpose. One may therefore anticipate that the conditions of defects at sinks will become open to experimental assessment in future research. One such possibility springs from the recent observation that islands, when nucleated by ion-beam irradiation on large terraces,[20] undergo a universal evolution of radius $a(t)$ relative to the terrace radius R.[21] A beam of self-ions with low ion energy resembles molecular beam epitaxy as ions land gently in favored sites to create, by definition, excess adatoms. Higher impact energy creates added adatom-advacancy pairs, from which adatoms may then sputter off into vacuum. Above a neutral energy' ε more than one atom is lost per incident ion so a net excess of advacancies occurs. With sufficient intensity, for $E<\varepsilon$, the beam causes adatom islands to nucleate and grow, while for $E>\varepsilon$ advacancy islands nucleate and grow. It is observed that the universal behavior is the same for adatom and advacancy islands, and this offers unanticipated symmetry in the process of island nucleation and growth.[22] The observed $a(t)$ conforms well to the predictions of a theory for strongly reacting antidefects constrained to equilibrium concentrations (so $T^*=T$) at the step edge that forms the perimeter of the growing island.[22] In the present paper this problem of island growth offers a test case for the development of more general boundary conditions for reacting assemblies. We enquire whether or not the evolution remains universal when the boundary conditions at sinks are relaxed from earlier requirements, specifically when defect densities no longer take thermal equilibrium values there.

For completeness we remark that a large literature concerns flow to steps from adatom and advacancy populations, even including driving forces such as currents in metals[23] treated on the basis of work mentioned above.[10] For references the reader should consult reviews.[3,5,24] For flow by adatoms alone, continuum models have been used to discuss flow including processes internal to steps[25,26] in part on the basis of much earlier work by Mullins.[27] The present work focuses instead on adatom-advacancy reactions, and the way contact with step edges establishes the chemical potential μ^* and the effective temperature T^* of the defect populations on neighboring terraces. This facilitates a discussion of universality in the consequent evolution.

In the text below, the question of universality is deferred to Sec. III. In Sec. II, the nature of boundary conditions in a reacting assembly is discussed and a simplified model is developed to trace the behavior when the boundary conditions at sinks are relaxed. Since some introduction to defect processes may be helpful, an Appendix collects elementary facts about notation, for the occupation probabilities $\bar{c}_1$ and $\bar{c}_2$ at equilibrium, for adatoms and advacancies, respectively, and for the collective parameters T^* and μ^* that describe reacting defect assemblies. What follows in the remainder of this introduction is an outline of the equations that determine driven transport to sinks.

To track the transport in driven systems we need diffusion equations for the hydrodynamic evolutions of the locally averaged concentrations, c_1 and c_2, of adatoms and advacancies. For this purpose their random walk diffusion coefficients are written D_1 and D_2. The normal (linear) diffusion equations must be augmented by two further terms. The first is the creation rates per site K_1 (K_2) of adatoms (advacancies) by the ion-beam; and the second is the balance $K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2)$ of antidefect pair creation and pair-annihilation processes. Here the first term in parentheses represents the rate at which pairs are spontaneously created, per surface site, on the open, perfect terrace, and the second term is the corresponding rate at which existing pairs react to leave locally perfect terrace. The equations for the two species are thus

$$\partial c_i/\partial t = D_i\nabla^2(c_i - \bar{c}_i) + K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2) + K_i, \quad (i = 1,2). \tag{1}$$

In treating the time evolution of driven reacting systems, these two simultaneous, nonlinear partial differential equations are to be solved together, subject to boundary conditions that are imposed on the reacting assembly at defect sinks. Up to the present time there has been no complete discussion of the appropriate boundary conditions and their effects on the time evolution of the distributions. It is the purpose of Sec. II to examine the boundary conditions and to identify models of sufficient simplicity that the time development of irradiated systems can be discussed with some degree of generality. The results of Sec. II then feed into the discussion in Sec. III of the extent to which the time evolution of driven islands remains universal in the face of various alternative boundary conditions at sinks.

II. REACTIONS, THE LAW OF MASS ACTION, AND BOUNDARY CONDITIONS

It is not apparent that the evolution of Eq. (1) from arbitrary initial distributions of μ^* and T^* is of any particular use or interest; distributions of practical concern profit from the entropy increase associated with locally smooth variations in T^* and μ^*. Here we focus on the roles of pair processes, diffusion, and defect sinks in establishing the smooth steady state of a driven, reacting system. It may be noted in Eq. (1) that the pair generation rate $K_{12}\bar{c}_1\bar{c}_2$, the defect generation rates at fixed sinks, and the diffusion coefficients D_i, are determined entirely by the lattice temperature T. Together with the imposed defect creation rates K_i, they determine the concentrations $c_i(r)$ through Eq. (1), and hence T^* and μ^* also, using Eq. (A4). By these means the actual lattice temperature T enters into T^* and μ^*, and their behavior at sinks.

A. Bulk reactions

Equations (1) present a balance among four processes of driven defect creation, defect reaction, and defect elimination by diffusion to sinks of adatoms and of advacancies. Our focus is on the driven steady state and on evolution that is quasistatic. In a quasistatic process the flow of defects through the system is much larger than the flow that arises from evolution, for example by the motion of sinks caused by the defect flow. Solutions may thus be obtained conveniently by setting $\partial c/\partial t \rightarrow 0$ in Eq. (1) and then calculating the sink motion using the flow $J_i = -D_i\nabla c_i$ obtained from the solution $c_i(r)$. In this process, the detailed geometry of the diffusive flow is of less interest than the balance among the competing processes, which are relatively subtle and give rise to three distinct regimes of linear response. To explore the latter factors with ease we simplify Eq. (1) by writing

$$D_i\nabla^2(c_i - \bar{c}_i) \rightarrow -\lambda^2 D_i(c_i - \bar{c}_i), \tag{2}$$

thereby eliminating geometry entirely and leaving the nonlinear simultaneous equations

$$\lambda^2 D_1(c_1 - \bar{c}_1) = K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2) + K_1;$$

$$\lambda^2 D_2(c_2 - \bar{c}_2) = K_{12}(\bar{c}_1\bar{c}_2 - c_1c_2) + K_2. \tag{3}$$

Here, λ^2 is an effective inverse square diffusion length to sinks. The diffusive flows in Eq. (3) correctly remain linear in the concentrations, and in proportion the transport coefficients D_i, while the nonlinear balance among the four processes is unchanged. Note that $\lambda^2 D_i\bar{c}_i$ represents the creation rate at a sink in equilibrium, and $\lambda^2 D_i c_i$ is the rate of loss, with the two in balance at equilibrium when $c_i = \bar{c}_i$. We now use the simplified Eq. (3) to identify general regimes of behavior.

The behavior is defined entirely by the effect of the perturbing rates K_1 and K_2 on the three rates d_1, d_2, and k that describe the kinetics at equilibrium, specifically

$$d_1 = \lambda^2 D_1\bar{c}_1; \quad d_2 = \lambda^2 D_2\bar{c}_2; \quad k = K_{12}\bar{c}_1\bar{c}_2, \tag{4}$$

for diffusion to sinks of adatoms, d_1, and advacancies, d_2, and for equilibrium antidefect pair creation on the perfect terrace, namely, k, respectively. In terms of more convenient variables

$$\sigma_1 = (c_1 - \bar{c}_1)/\bar{c}_1 = s_1/\bar{c}_1; \quad \sigma_2 = (c_2 - \bar{c}_2)/\bar{c}_2 = s_2/\bar{c}_2, \tag{5}$$

one obtains by subtracting the second of Eq. (3) from the first

$$d_1\sigma_1 - d_2\sigma_2 = K_1 - K_2. \tag{6}$$

Using this value of σ_2 in the first of Eq. (3) one now finds

$${\sigma_1}^2 + b\sigma_1 + c = 0, \tag{7}$$

so that

$$\sigma_1 = -\tfrac{1}{2}b[1 \pm (1 + 4c/b^2)^{1/2}], \tag{8}$$

in which

$$b = [d_1 + d_2 + d_1 d_2/k + K_2 - K_1]/d_1;$$

$$c = [K_1(1 + d_2/k) - K_2]/d_1. \tag{9}$$

Values of σ_2 are obtained by similar means or directly from Eq. (6) with σ_1 from Eq. (8).

The simplicity of solution notwithstanding, the results of the calculation are not lacking in complication. The solutions contain three separate regimes in which the changes of concentrations σ_1 and σ_2, respond linearly to the driving forces K_1 and K_2, as described immediately in what follows.

(i) The K_i small. In this regime of true linear response the perturbing force of defect creation is resisted both by diffusion to sinks and by rebalanced recombination. We must select the $-$ sign of $\pm$ in Eq. (8), because, with c small in Eq. (8), σ_1 must take the sign of K_1 (i.e., +) or K_2 (i.e., −) in c, whichever perturbation is stronger. Then

$$\sigma_1 \to c/b = \frac{K_1(1 + d_2/k) - K_2}{d_1 + d_2 + d_1 d_2/k + K_2 - K_1}, \tag{10}$$

from which, for the linear response alone, $K_2 - K_1$ in the denominator must be dropped.

(ii) $K_1 - K_2 < d_1 + d_2 + d_1 d_2/k$. Here, the negative choice from $\pm$ is again required. As K_2 becomes large in Eq. (10), evidently $\sigma_1 \to -1$, which corresponds to the adatom concentration $c_1 \to 0$, as expected in the presence of the excess advacancies from K_2.

(iii) $K_1 - K_2 > d_1 + d_2 + d_1 d_2/k$. The physical choice here is the positive root, so that

$$\sigma_1 \to -b = -(d_1 + d_2 + d_1 d_1/k + K_2 - K_1)/d_1. \tag{11}$$

As K_1 becomes large, $\sigma_1 \to K_1/d_1 = K_1/\lambda^2 D_1 \bar{c}_1$, which is evident from Eq. (3) for the case when the term in K_{12} may be neglected. Thus at large K_1 the response becomes linear once more, resisted by diffusion alone. Here $c_2 \to 0$ just as for c_1 with K_2 large (above). Note that the term c/b from the expansion of the root is needed to obtain the lowest order correction to $\sigma_1 \to -b$ for K_1 large.

(iv) $K_1 - K_2 \approx d_1 + d_2 + d_1 d_2/k$. In this regime the value of c/b^2 becomes large and the solution takes the form

$$\sigma_1 \to \sqrt{c} = \{[K_1(1 + d_2/k) - K_2]/d_1\}^{1/2}. \tag{12}$$

The appearance that the form of c in Eq. (9) allows c to become negative, and hence σ_1 imaginary is, of course, misleading. As $K_1 - K_2 \approx d_1 + d_2 + d_1 d_2/k$ for this regime, it follows that $c \sim d_1 + d_2 + d_1 d_2/k + K_1 d_2/k$, in which all terms are, in fact, positive.

B. Mass action

The product $c_1 c_2$ is of special interest for our focus on sink action. At the same time it evidently bears a close connection to the concept of effective defect temperature T^* introduced through Eq. (A4). In reacting assemblies the product of concentrations for reactants in equilibrium follows the law of mass action which, for the reacting antidefects of concern here, reads

$$c_1 c_2 = C(T), \tag{13}$$

with $C = \bar{c}_1 \bar{c}_2$ a temperature-dependent constant. In the present case, however, the concentrations obtained in the above discussion are steady-state values for a driven system rather than equilibrium values pertinent to mass action. The extent to which the concentrations and the effective temperatures to which they correspond, conform to mass action is clearly of concern in the present discussion of sink behavior.

A simple measure of the reaction behavior is given by the quantity

$$m = \frac{c_1 c_2}{\bar{c}_1 \bar{c}_2}. \tag{14}$$

If mass action holds, $m = 1$. In practice m is obtained from σ_1 in Eqs. (3), (4), (8), and (9) as

$$m = 1 + (K_1 - d_1 \sigma_1)/k. \tag{15}$$

For K_1 and c_1 large the limiting value of m may be traced as

$$m \to 1 + d_1/k, \quad (K_1 \text{ large}), \tag{16a}$$

With σ_1 from Eq. (10) instead, for the regime of linear response, we now find

$$m \to 1 + \frac{K_1/D_1\bar{c}_1 + K_2/D_2\bar{c}_2}{\kappa^2 + \lambda^2}, \quad (K_1 \text{ and } K_2 \text{ small}), \tag{16b}$$

in which, as in earlier studies,[14]

$$\kappa^2 = K_{12}(D_1\bar{c}_1 + D_2\bar{c}_2)/D_1 D_2. \tag{17}$$

In linear response, the correction to the law of mass action ($m = 1$) is evidently the sum of creation rates, each divided by the mobility $D_\mathrm{i}\bar{c}_\mathrm{i}$ of the species, multiplied by a squared wave vector. The latter is the sum of two terms one, λ^2, relating to the length of random walk to sinks, and the other κ^2, fixing the distance over which reactions are completed.[14]

In a related development, we may obtain the effective defect temperature T^* as

$$T^* = T\frac{\ln \bar{c}_1\bar{c}_2}{\ln c_1 c_2} = T\frac{\ln \bar{c}_1\bar{c}_2}{\ln m\bar{c}_1\bar{c}_2} = \frac{T}{1 + (\ln \bar{c}_1\bar{c}_2)^{-1}\ln m}. \tag{18}$$

In these equations $\ln \bar{c}_1\bar{c}_2 \sim -10$ typically, for defects on surfaces (a value ~ -1 would require $c_1, c_2, \sim 1$, which is much too large, while a value $\sim -10^2$ would require $c_1, c_2, \sim 10^{-20}$, which is much too small). The equations reveal that $T^* = T$ exactly when the law of mass action is valid, and that T^* may remain very close to T even in the presence of small deviations from mass action.

We take particular interest in the behavior for the regime of linear response. From Eqs. (7)–(9) this regime occupies the range

$$|c|/b^2 \sim |\sigma_1|/b \ll 1. \tag{19}$$

For strongly reacting systems, with k large, this criterion becomes

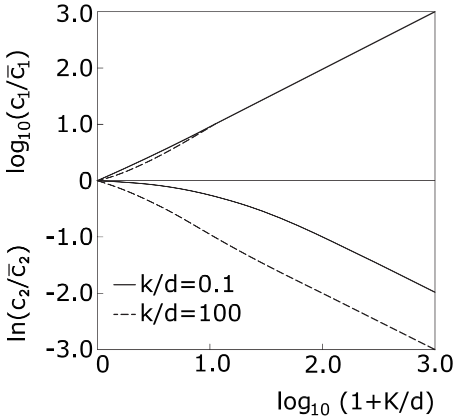

FIG. 1. Graphs showing the defect concentration c_1 and c_2, as functions of driving irradiation K for two cases in which, first, recombination is weaker than diffusion, $k/d=0.1$ and second, is much stronger than diffusion, $k/d=100$. In the figure, the ion-beam creates defect at rates up to $K/d=1000$ times diffusion. The perturbed c_1 is not very sensitive to k/d but c_2 is suppressed more when recombination is dominant.

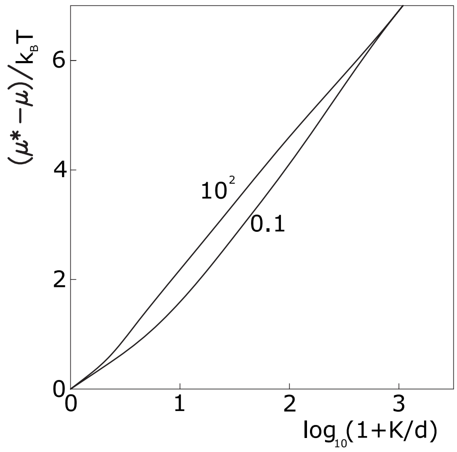

FIG. 2. Graphs showing the effective chemical potential μ^* as a function of driving irradiation K for two cases in which recombination is weaker than diffusion, $k/d=0.1$, and much stronger than diffusion, $k/d=100$. The ion-beam creates defect at rates up to $K/d=1000$ times diffusion. The resulting defect chemical potential μ^* does not change strongly with scaled recombination rate k/d.

$$\frac{d_1|\Delta K|}{(d_1+d_2)^2} \ll 1, \quad (k \gg d_1, d_2) \tag{20}$$

in which $\Delta K=K_1-K_2$. With $\kappa^2 \gg \lambda^2$ we now find from Eq. (16) that $m \approx 1$, and thus from Eq. (18), $T^* \approx T$, through the entire domain of linear response. In the regime of weak reactions, however, with k/d small the range of linear response is smaller, namely

$$\frac{k|K_1|}{d_1 d_2} \ll 1, \tag{21}$$

and the deviations of m from 1 in Eq. (15) and T^* from T in Eq. (18) may possibly be more substantial. It is an important conclusion that the law of mass action is closely followed, and that T^* consequently remains close to T, throughout the domain of linear response for strongly reacting systems, with $k \gg d_1, d_2$.

The precise behavior of T^* in reacting assemblies may evidently be accessed by the present methods and it is to a simple example of general interest that we now turn. It will suffice for the present purposes to examine the case of a terrace driven by either adatom creation $K_1=K$ with $K_2=0$ or advacancy creation $K_2=K$ with $K_1=0$. To avoid complication we make the two species of defect equally mobile (i.e., $d_1=d_2=d$), although generally they must differ, and for metals d_1 is usually thought to be the larger. Given our model choice we can determine by direct calculation the variation in σ_1 (and hence c_2) and $m=c_1c_2/\bar{c}_1\bar{c}_2$ with scaled driving force K/d and scaled reaction rate k/d, using Eqs. (8) and (15), above. Figure 1 shows how c_1 and c_2 vary with irradiation rate over a wide range of driving forces for two strongly differing reaction rates. The irradiation level is shown as $\log_{10}(1+K/d)$ for values of K from 0 to 10^3 times the equilibrium diffusion rate d. In the two sets of data c_1 and c_2 are given for $k=10^2 d$, so reactions are dominant, and $k=0.1d$, when diffusion is dominant. Even these large differences cause only small deviations between the two values of c_1, mainly for K small. However, the values of c_2 differ by an order of magnitude, as advacancies are more strongly suppressed when the reaction rate is large. Variations in $\mu^*-\mu$ in the driven systems, which depend mainly on c_1/c_2, likewise depend only weakly on k, as shown in Fig. 2 for the case $\bar{c}_1=\bar{c}_2$.

The differences are much more striking for $m=c_1c_2/\bar{c}_1\bar{c}_2$ in the driven systems. This is illustrated in Fig. 3 by graphs showing $\log_{10} m$ as a function of $\log_{10}(c_1/\bar{c}_1)$ for reaction rates k of $10^{-1}d$, d, $10d$, and $100d$. The lower half of the figure shows analogous results when the irradiation created advacancies rather than adatoms. In all cases m rises linearly

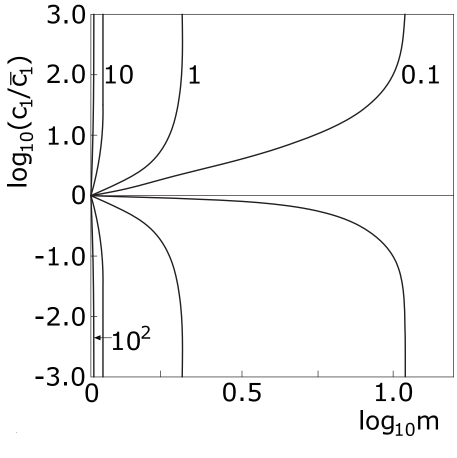

FIG. 3. Law of mass action, monitored by $\log_{10} m$, with $m=c_1c_2/\bar{c}_1\bar{c}_2$, shown as a function of c_1 over a factor 10^3 in the driven system, for four values of k/d. The upper half of the figure represents irradiation by adatoms and the lower half advacancies. In agreement with Eq. (21), m increases linearly with c_1 but then saturates. As a result, the law of mass action $c_1c_2=\bar{c}_1\bar{c}_2$ holds with increasing precision for $k/d>1$. Under these conditions, also, $T^* \cong T$.

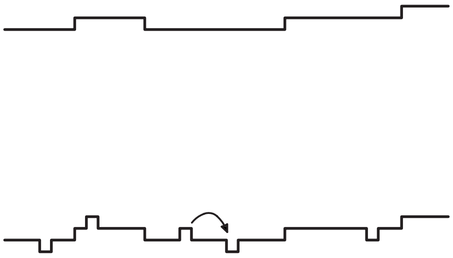

FIG. 4. Cartoon showing a step profile with spaced kinks (top). The step traps adatoms and advacancies (bottom) that can recombine (arrow) or annihilate at kinks.

with c_1 for c_1 small, in accordance with Eq. (16b). An important point is that this increase quickly saturates to leave m independent of c_1, as given by Eq. (16a). It is of central interest in this paper that m never exceeds ~ 2 even for $k = d$, and for $k \gg d$ we find $m \cong 1$ with increasing precision as k is increased. Under these conditions, then, the law of mass action is obeyed accurately. The fractional deviations of T^* from T are much smaller still, depending on $\bar{c}_1 \bar{c}_2$, in keeping with the predictions of Eq. (18).

In general summary of these observations, the response c_1 remains linear in driving force K_1 and is not very sensitive to the magnitude of recombination relative to diffusion. However, c_2 is suppressed more strongly for large k/d. The law of mass action $m=1$ is obeyed with accuracy for all K_1 when $k \gg d$ and the kinetics are thus dominated by pair reactions. A consequence of the law of mass action is that the effective temperature of the reacting assembly is pinned at $T^* \approx T$. In this case the local configuration at steady state is almost entirely fixed by μ^* through the equations

$$c_1(\mathbf{r}) = \bar{c}_1 \exp[(\mu^*(\mathbf{r}) - \mu)/k_B T];$$

$$c_2(\mathbf{r}) = \bar{c}_2 \exp[-(\mu^*(\mathbf{r}) - \mu)/k_B T]. \tag{22}$$

These results are sufficiently simple as to suggest useful models for determining boundary conditions on a reacting assembly. We return to this topic after first examining models for sink action.

C. Reactions at step edge sinks

Just as a driven terrace relaxes in part by recombination and in part by diffusion of defects to step edge sinks, the driven sinks themselves function by a combination of reaction by defects trapped from the terrace, and their diffusion to kinks at various locations along the step profile. Figure 4 is a cartoon in which the upper drawing shows a step profile with spaced kinks and the lower drawing includes trapped adatoms and advacancies. The latter are free to annihilate by pair reaction (arrow) or at kinks. We assume here that kinks provide sinks at which defects annihilate (or form) with no further consequence for the free energy of the system caused by the modified sink configuration. The creation energies f_{1s} and f_{2s} for defects bound to steps near kinks must therefore generally differ from those, f_1 and f_2, on the open terrace, by the defect binding free energies b_1 and b_2 to the step edge:

$$b_i = f_i - f_{is}; \quad (i = 1,2). \tag{23}$$

This modifies the equilibrium concentrations of defects bound on steps to:

$$\bar{c}_{1s} = \bar{c}_1 \exp(b_1/k_B T); \quad \bar{c}_{2s} = \bar{c}_2 \exp(b_2/k_B T) \tag{24}$$

In general the hopping diffusion coefficients also change so we use D_{1s} and D_{2s} for diffusion along a step to a kink. General expectations are that the free energies b are positive and that $D_{is} > D_i$ for diffusion along step edges.

A point of considerable interest here is that the kinetics of a step edge sink driven by trapping rates (per site) of K_{1s} and K_{2s}, of defects from the nearby terraces very much resembles a one-dimensional analog of the two-dimensional case discussed in Sec. II B of a terrace driven by rates K_1 and K_2 by ion-beam irradiation. The attractive possibility emerges for simply adapting the terrace results to the step sink, using a defined effective temperature T_s^* and chemical potential μ_s^* to describe the sink configuration. This is particularly appealing when both the sink and the terrace exist in regimes where the law of mass action holds such that

$$T_s^* = T^* = T, \quad (m_s = m = 1). \tag{25}$$

Then the entire operation of the combined terrace and sink must be described by the effective chemical potentials μ_s^* and $\mu^*(r)$ of the sink and terrace, respectively. The characteristics of boundaries between sink and terrace are discussed in what follows.

It bears comment that the connection between effective temperature and mass action has been discussed using the simplified form of Eq. (3). However, the definition in Eq. (A4) of T^*, combined with the explicit term $K_{12} c_1 c_2$ in the full Eq. (1), lends confidence that the same insights for effective temperatures hold also for the full solutions.

D. Reaction boundary conditions at sinks

In what follows we develop a model of boundary conditions for a case in which the law of mass action is accurately valid everywhere. The result is that the effective temperatures everywhere coalesce upon the lattice temperature T. Flow of defects over the terrace then responds solely to the gradient $\nabla \mu^*(r)$ of effective defect potential. Flow from the terrace to the sink is responsive to the actual values of the chemical potentials μ^* and μ_s^* at the sink, by arguments discussed below. Upon adapting Eq. (3) to the case of sink kinetics, we characterize the sink by a single value of μ_s^*, and thereby avoid the description of sinks with position-dependent properties. This is not, of course, a faithful description, but it is difficult to see that errors of principle are thereby introduced. The resulting approximation has the merit of leading directly to a clear and physically appealing model of reaction boundary conditions at sinks.

Consider then the excess flow of K_{1s}, K_{2s} defects per second (per sink site) from the terrace to trapped locations at the sink. There result excess occupancies σ_{1s} and σ_{2s}, per site of defects. These are obtained from Eqs. (22) and (24) as

$$\sigma_{1s} = \exp[(\mu_s{}^* - \mu)/k_B T]; \quad \sigma_{2s} = \exp[-(\mu_s{}^* - \mu)/k_B T], \tag{26}$$

given that the law of mass action holds. Kink sites have $\mu^* = \mu$ and the difference from other edge sites causes excess defects to flow to the kinks. Given n_s step edge sites per kink, the net currents of atoms are

$$J_1 = n_s \lambda_s{}^2 D_{1s} \bar{c}_{1s} \sigma_1 \approx n_s \lambda_s{}^2 D_{1s} \bar{c}_{1s} (\mu_s{}^* - \mu)/k_B T;$$

$$J_2 = -n_s \lambda_s{}^2 D_{2s} \bar{c}_{2s} \sigma_2 \approx n_s \lambda_s{}^2 D_{2s} \bar{c}_{2s} (\mu_s{}^* - \mu)/k_B T, \tag{27}$$

and by adding these contributions we find the total sink current to a kink as

$$J_s = J_1 + J_2 = n_s \lambda_s{}^2 (D_{1s} \bar{c}_{1s} + D_{2s} \bar{c}_{2s})(\mu_s{}^* - \mu)/k_B T, \tag{28}$$

$$\text{or,} \quad J_s = \alpha(\mu_s{}^* - \mu); \quad \alpha = n_s \lambda_s{}^2 (D_{1s} \bar{c}_{1s} + D_{2s} \bar{c}_{2s})/k_B T. \tag{29}$$

This flux of atoms to kinks is of course driven by a flux of atoms over the terrace to trapped sites on the step edge. From the Nernst-Einstein equation the current from the terrace per kink, passing to a length $n_s l$ of step, with l the site spacing, is

$$J_t = -n_s l [(D_1 \bar{c}_1 + D_2 \bar{c}_2)/A k_B T][\nabla \mu^*]_s, \tag{30}$$

in which the area A per site converts occupation probabilities c into concentrations C, and the gradient is evaluated next to the sink. Note, for typical cases in which reactions are dominant because sinks are widely spaced, that the changes of μ^* from one site to the next that drive this flux are very small, perhaps $\sim 10^{-4}$ μ^* for terraces 10^4 atoms wide. As transitions taking defects into sink sites are not in any way impeded, there is no reason to suppose that larger driving potentials are needed to promote transitions into the sink. For this reason, the actual chemical potential $[\mu^*]_s$ on the terrace next to the sink can be taken as almost identical to that, $\mu_s{}^*$, of trapped defects actually in the sink specifically

$$[\mu^*]_s \approx \mu_s{}^*, \tag{31}$$

with an error typically $\sim 10^{-4}$ that is negligible. A cartoon depicting the consequent behavior of μ^* near sinks is provided as Fig. 5. With the replacement of Eq. (31) in Eq. (29), we find by equating the currents J_s and J_t per kink in Eqs. (28) and (30) that

$$\gamma[\nabla(\mu^* - \mu)]_s = [\mu^* - \mu]_s; \quad \gamma = -\frac{l(D_1 \bar{c}_1 + D_2 \bar{c}_2)}{\lambda_s{}^2 A (D_{1s} \bar{c}_{1s} + D_{2s} \bar{c}_{2s})}. \tag{32}$$

Equation (32) is the principal result of Sec. II. For systems in which the law of mass action holds for both sinks and terraces, $T^* = T$ throughout, and the boundary condition on the terrace diffusion field is evidently that the effective chemical potential μ^* on the terrace near the sink has a fixed ratio, γ, of amplitude to derivative, given explicitly in Eq. (32). Note that when transport in a sink is much more rapid than on the terrace, $\gamma \to 0$, so then $[\mu^*]_s \to \mu$, and one thus recovers the conventional boundary condition for diffusion fields at equilibrium sinks.[14] Section III considers the consequences of the more general boundary conditions for the universality of growth for islands nucleated on terraces.

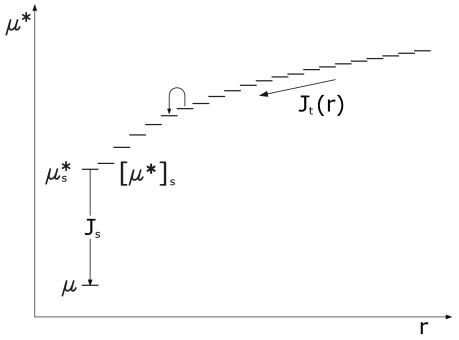

FIG. 5. Defect flow over surface to a sink. Short horizontal lines indicate chemical potentials μ^* at successive sites. Hopping among sites (e.g., inverted U with arrow) causes net downhill flow $J_t(r)$ of defects over the terrace terminating at $[\mu^*]_s$ adjacent to the sink. From there defects can hop to potential $\mu_s{}^*$ at sink sites and eventually annihilate at chemical potential μ through processes internal to the sink. Local mixing causes the effective defect chemical potential μ^* to vary smoothly from site to site on terraces, driving defect flow to or from the sinks. On terraces microns wide, the change of μ^* between neighboring sites is $\sim 10^{-4}(\mu^* - \mu)$. Consequently $\mu_s{}^*$ in the sink is almost equal to $[\mu^*]_s$ on the neighboring terrace, as shown.

III. EFFECT OF BOUNDARY CONDITIONS ON DRIVEN ISLAND GROWTH

We can illustrate the approach to boundary conditions outlined above by application to the significant problem of the growth of islands on terraces driven by an ion-beam. Several researchers have found evidence that boundary conditions for diffusing defects at step edge sinks may be more elaborate than the simple requirement of an equilibrium defect density. In step fluctuation studies of step stiffness on Si(001), for example[28] evidence for an "attachment" model in which reaction at steps is so slow that the flow from the terrace requires negligible gradients. This is the limit $\gamma \to \infty$ of Eq. (32), which extends readily to cover this physical behavior. A second example comes from the study of relaxation by step flow during annealing of TiN (001) at elevated temperature,[29] to suggest that thermal defects may cross steps without attaching,[30] so that the steps are in part transparent to defect flow. The resulting excess of defect density immediately next to the step may once more be modeled by boundary conditions with a fixed ratio of derivative to amplitude in defect occupancy. These considerations open the possibility that step edges may act as reactive sinks and in this way modify the universality of driven island growth identified when sinks locally maintain thermal equilibrium conditions. This is the topic addressed below.

A. Boundary conditions on defect concentrations

It is convenient to obtain boundary conditions in terms of defect occupation probabilities written alternatively as c_i, $s_i = c_i - \bar{c}_i$, or $\sigma_i = s_i / \bar{c}_1$, [Eq. (5)] rather than chemical potentials

μ^*. For linear response in the case of interest here, for which the law of mass action is closely valid, this is accomplished as follows.

First, from Eq. (26) we find the connection between the σ_i and μ^* as

$$\sigma_1 = (c_1 - \bar{c}_1)/\bar{c}_1 = \exp[(\mu^* - \mu)/k_B T] - 1$$
$$\approx (\mu^* - \mu)/k_B T = -\sigma_2, \tag{33}$$

so that

$$[(\mu^* - \mu)/\nabla(\mu^* - \mu)]_s = [\sigma_1/\nabla\sigma_1]_s = [\sigma_2/\nabla\sigma_2]_s = \gamma, \tag{34}$$

with γ constant; the same result for σ_2 follows much as that for σ_1. The approximation in Eq. (33) assumes that the exponent is small, consistent with the linear regime discussed here. The first boundary condition on the concentration changes is therefore that the departures from equilibrium values obey the same amplitude to derivative constraint demonstrated in Sec. II for $\mu^* - \mu$. This condition requires the steady-state diffusive flow to the boundary to equal the steady-state transfer from the terrace to the sink.

A second boundary condition constrains the time evolution of concentration, at all points, but most particularly at the boundaries. For sinks to thermalize the defect distribution, the concentrations must obey the law of mass action at the sink. With $\partial/\partial t \to 0$ in Eq. (1), and $c_1 c_2 \equiv \bar{c}_1 \bar{c}_2$, we obtain for sink sites the conditions

$$[\nabla^2 \sigma_1]_s = -K_1 D_1 \bar{c}_1; \quad [\nabla^2 \sigma_2]_s = -K_2 D_2 \bar{c}_2, \tag{35}$$

on the driven, steady state concentrations. Some comment on the results is desirable.

Equations (33) applied at sinks gives $c_1 c_2 \approx \bar{c}_1 \bar{c}_2$ just as does the requirement $c_1 = \bar{c}_1$, $c_2 = \bar{c}_2$ of thermal equilibrium employed in earlier research. The effect is nevertheless different, in that the concentrations are now permitted to depart from equilibrium values in accordance with Eq. (34). These are properties of sinks at which reactions are fast enough that the lattice temperature is imposed on the defect system by sinks, but not so rapid that the defect system is constrained to the chemical potential μ of the lattice at equilibrium, even at fixed sinks. The effect of these boundary conditions on the driven flow of defects to islands is the subject to which we turn in what follows.

B. Driven island growth

In the problem to be solved here, an island of radius a grows at the center of a pan or mesa of radius R, under the influence of ion-beam creation rates K_1 and K_2. We now assume that the same boundary conditions $[s_i/\nabla s_i]_s = \gamma$ and $i = 1, 2$, apply both at a and at R. The quantity of interest is the rate $a(t)$ at which growth of the island is driven by the beam and whether the evolution takes a universal form independent of γ.

Elsewhere it is shown[22] how the desired a(t) may be obtained from quasistatic solutions of the linearized simultaneous Eq. (1), when subject to the appropriate boundary conditions, in the present case Eqs. (34) and (35). As in the earlier work, the general solutions, including Eq. (35) take the form

$$\sigma_1 = \frac{K_2 - K_1}{D_1 \bar{c}_1 + D_2 \bar{c}_2} f(\mathbf{r}) + \frac{A}{\kappa^2}\left[\frac{g_\kappa(\mathbf{r})}{g_\kappa(\rho)} - 1\right];$$

$$\sigma_2 = \frac{K_1 - K_2}{D_1 \bar{c}_1 + D_2 \bar{c}_2} f(r) + \frac{A}{\kappa^2}\left[\frac{g_\kappa(r)}{g_\kappa(\rho)} - 1\right], \tag{36}$$

$$\text{in which} \quad A = -\frac{D_1 \bar{c}_1 K_2 + D_2 \bar{c}_2 K_1}{D_1 \bar{c}_1 + D_2 \bar{c}_2};$$

$$\kappa^2 = \frac{K_{12}(D_1 \bar{c}_1 + D_2 \bar{c}_2)}{D_1 D_2}. \tag{37}$$

Here $g_\kappa(r)$ is the solution of $(\nabla^2 + \kappa^2) g_\kappa(r) = 1$ with $g(r) = 1$ at fixed sinks $\mathbf{r} = \rho$, and $f(r)$ is the solution of Poisson's equation $\nabla^2 f(r) = 1$, now chosen to satisfy reaction boundary conditions [Eq. (34)] at the step edge sinks.

Previous research[22] was carried through for the limit of strong reactions with $\kappa^2 R^2 \gg 1$, when the second terms in Eq. (37) may be neglected, leaving the first (Poisson) term in $f(r)$ alone. To determine the sensitivity of universality to the boundary constant γ it will suffice to study the solutions in this same limit for reaction conditions. The solution $f(r) = r^2/4$, and solutions of Laplace's equation $\nabla^2 f = 0$ with circular symmetry may be added to satisfy the boundary conditions at $r = a$ and $r = R$. Thus

$$f_<(r) = B + r^2/4, \quad (0 < r < a);$$

$$f_>(r) = C + D \ln r + r^2/4, \quad (a < r < R). \tag{38}$$

with B, C, and D constants. The amplitude to derivative ratios in the two functions are

$$\left[\frac{f_<}{df_</dr}\right]_a = \frac{B + a^2/4}{a/2} = \gamma;$$

$$\left[\frac{f_>}{df_>/dr}\right]_a = \frac{C + D \ln a + a^2/4}{D/a + a/2} = \gamma;$$

$$\left[\frac{f_>}{df_>/dr}\right]_R = \frac{C + D \ln R + R^2/4}{D/R + R/2} = \gamma. \tag{39}$$

One thus obtains

$$B = (a\gamma - a^2/2)/2; \quad D = \frac{(R - a)(R + a - 2\gamma)}{\gamma(R - a)/aR - \ln(a/R)}, \tag{40}$$

and C may likewise be found from Eq. (38).

It is now easy to determine that the boundary conditions modify the universality found earlier for $\gamma = 0$. From the derivatives above we find that the ratio J_a/J_R of atom current J_a to the step at a to the current J_R to the peripheral step at R is given by

$$\frac{J_a}{J_R} = \frac{1}{1 + R^2/2D}. \tag{41}$$

Here, the current to a includes contributions from both inside and outside the step. We see that the apportionment between a and R of precipitating defects created by irradiation is a function of both γ and a/R, so that the universal evolution of a/R with time is in general lost. When $\gamma=0$ in Eq. (40), however, D/R^2 once more becomes a function only of a/R, and the universality discovered earlier[21,22] for the thermal equilibrium boundary condition is recovered in Eq. (41) also. This is the desired result. From Eq. (40) it is clear, starting from a small, that deviations from universality first occur for $a/R \sim \exp(\gamma/a)$.

IV. SUMMARY

This paper treats the boundary conditions to which thermal defects created by irradiation are subject. The focus is on the steady-state response of surfaces to irradiation, under conditions of elevated temperatures where the life cycle of defects is strongly influenced by pair processes of antidefect formation and annihilation on the perfect terrace. The boundary conditions obeyed at step edges by the evolving defect system have not previously been discussed in detail. Some work has gone forward with the assumption that the step edge sinks impose on the defect system near the step concentrations that locally take thermal equilibrium values.[22]

In this paper we present a more general, but still well-defined type of sink that brings the defect system locally to the same temperature $T^*=T$ as the lattice and establishes a defect chemical potential $\mu^*(r)$ appropriate to the local state of steady flow. In this regime the law of mass action $c_1c_2 = \bar{c}_1\bar{c}_2$ is closely valid, and for the equilibrium lattice temperature, although the two concentrations both depart from equilibrium values. In a linearly responding system, the excess defect concentrations both obey boundary conditions of the same fixed derivative-to-amplitude ratio, determined by the relative mobilities for flow over the terrace and into the sink.

As an illustrative exercise, the defect flow from ion-beam irradiation to a growing island on a circular terrace is calculated for a case in which step edges act as reactive sinks rather that as points at which defect concentrations locally take equilibrium values. The universality of evolution determined for the latter case is found to hold no longer with the more general boundary conditions.

It will be important in future research to incorporate the Gibbs Thompson potential at precipitates into the description of defect flow at step edges, in order that island nucleation, growth and subcritical fluctuations may be treated more completely for reacting assemblies.

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APPENDIX: SURFACE DEFECT PROCESSES

The discussion in the text requires a brief introduction here to defect processes on surfaces. Suppose then that work F_2 is needed to remove an atom from a perfect terrace, and work F_1 is needed to place a host atom onto an available site of a perfect terrace. The net work in the two cases of adatoms and advacancy formation, respectively, is:

$$f_1 = F_1 - \mu; \quad f_2 = F_2 + \mu; \tag{A1}$$

in which μ is the chemical potential of host atoms; in Eq. (1) the terms in μ allow for the acquisition of a host atom to replace as the adatom, and the disposal of the atom removed in creating the advacancy. It is a simple matter to show that the (dilute) equilibrium concentrations, $\bar{c}_1, \bar{c}_2$ on the terrace, of the antidefects thus created, are

$$\bar{c}_1 = e^{-f_1/k_BT} = e^{-(F_1-\mu)/k_BT}; \quad \bar{c}_2 = e^{-f_2/k_BT} = e^{-(F_2+\mu)/k_BT}. \tag{A2}$$

In the paper we deal with processes by which adatoms and advacancies are, in addition, created by the action of imposed ion-beam irradiation, leading to actual defect concentrations $c_1(r)$ and $c_2(r)$, that are generally dependent on location r. We may write

$$c_1 = e^{-f_1^*/k_BT^*} = e^{-(F_1-\mu^*)/k_BT^*}; \quad c_2 = e^{-f_2^*/k_BT^*} = e^{-(F_2+\mu^*)/k_BT^*}. \tag{A3}$$

to define the "effective chemical potential" μ^* and "effective antidefect temperature" T^* as

$$\mu^* - \mu = (k_B/2)[T^* \ln(c_1/c_2) - T^* \ln(\bar{c}_1/\bar{c}_2)]; \quad T^* = T\frac{\ln c_1c_2}{\ln \bar{c}_1\bar{c}_2}. \tag{A4}$$

In what follows we take particular interest in cases where $T^*=T$, when evidently

$$c_1 = \bar{c}_1 e^{(\mu^*-\mu)/k_BT}; \quad c_2 = \bar{c}_2 e^{-(\mu^*-\mu)/k_BT}; \quad (T^* = T). \tag{A5}$$

Note that the law of mass action $c_1c_2=\bar{c}_1\bar{c}_2$ is exactly valid in this case alone, when spontaneous creation and annihilation of pairs are in exact local balance. The chemical potential μ^* is determined by the relative proportions of the two species, just as is the Fermi energy in the analogous case of carriers in semiconductors.[15–17]

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