Diffusion in a Single Crystal within a Stressed Environment

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The energetics of point defects and diffusion in a single crystal is analyzed with respect to stress in overlying or encapsulating layers. The resulting theory subsumes previous formulations of pressure and stress effects on diffusion. A key prediction is that stress on the overlayer side of the crystal boundary perturbs point defect concentrations in the underlying crystal. The effect can occur without significant strain in the crystal itself. The theory is compared with available published data on diffusion in silicon under thin strained overlayers.

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Stress is a driving force for atom transport in crystalline solids under circumstances as diverse as nanodevice fabrication and geophysics. A key challenge is the formulation of a robust, approximate continuum theory for the formation and diffusion of point defects and impurity atoms in a single crystal in communication with a stressed environment. Such a theory is now essential for the simulation of diffusion in advanced semiconductor devices, and in future nanotechnologies where devices self-organize as a result of stress. It may also be relevant to certain composite material systems.

Up to now the effects of stress on point defect formation and diffusion in single crystals have only been considered in special cases. While the effect of hydrostatic pressure can be conveniently described in terms of enthalpy [1], specific models have been proposed for other situation. Examples include the effects of stress on diffusion in epitaxial strained layers [2,3], and the Nabarro-Herring creep that occurs as a result of variations in normal stress around the periphery of grains in a stressed matrix [4].

For a general continuum theory of nonuniform stress effects on diffusion in a single crystal, one needs to look at the role of stress in each step of the reaction-diffusion chain. A convenient model system for this discussion is that of self-diffusion.

In the interior of a single crystal, i.e., one which is essentially free of extended defects, diffusion can occur by one of three physical processes—concerted exchange, interstitial-mediated diffusion, and vacancy-mediated diffusion. In concerted exchange, the diffusion step occurs spontaneously as a result of numerous atomic motions within a small (nanometer-sized) region around the moving atom, thus avoiding a prohibitively energetic two-atom direct exchange. Despite the complexity of a concerted exchange, in a continuum formulation it appears as a simple localized event, the effect of stress on diffusion appearing as an interaction between the local stress field and the "migration volume" involved in the event.

In the case of either interstitial- or vacancy-mediated diffusion, the process is more complicated. Point defects in a defect-free crystal generally originate from a reaction at the crystal boundary, while bulk generation or recombination plays a secondary role except under nonequilibrium conditions or in large crystals such as those used in the manufacture of semiconductor wafers. Consequently, although we are considering diffusion at a location inside the crystal, the energy cost of bringing the mediating point defect—an interstitial or vacancy—to this location also depends on the cost of initially forming it at the boundary. We therefore need to consider the effects of stresses at the current diffusion location, *and* at the initial formation point of the mediating defect at the boundary. This situation is illustrated in Fig. 1(a).

The total energy as a function of configuration as the point defect is formed and migrates away into the crystal is illustrated schematically in Fig. 1(b) for the strain-free case. The change in energy as a result of strain in the bulk crystal is illustrated schematically in Fig. 1(c) by considering a stress that varies as a function of position within the crystal. In the example shown, the energy increases owing to interaction between the inward relaxation of the lattice around the vacancy and the tensile strain field.

We now need to include additional effects arising from interactions at the boundary. In the usual picture these are included through the effect of normal stress on the defect formation energy [5]. However, it is argued here that this formulation is not sufficient. In general, defect formation is likely to be a complex extended process involving atoms on both sides of the crystal-overlayer interface. This is of key importance, especially in structures where there is a stress discontinuity at the interface. To take care of this we switch briefly to an atomistic line of thought.

Consider a surface "kink", that is, a one-atom sideways step at a point on a "surface step" of the crystal boundary. This is a convenient point at which to consider the addition or removal of an atom to the crystal boundary, since—on a free crystal surface—it corresponds to motion of the kink by one atomic position along the step, leaving the surface configuration and surface energy unchanged. This single configuration may be taken as representative of an en-

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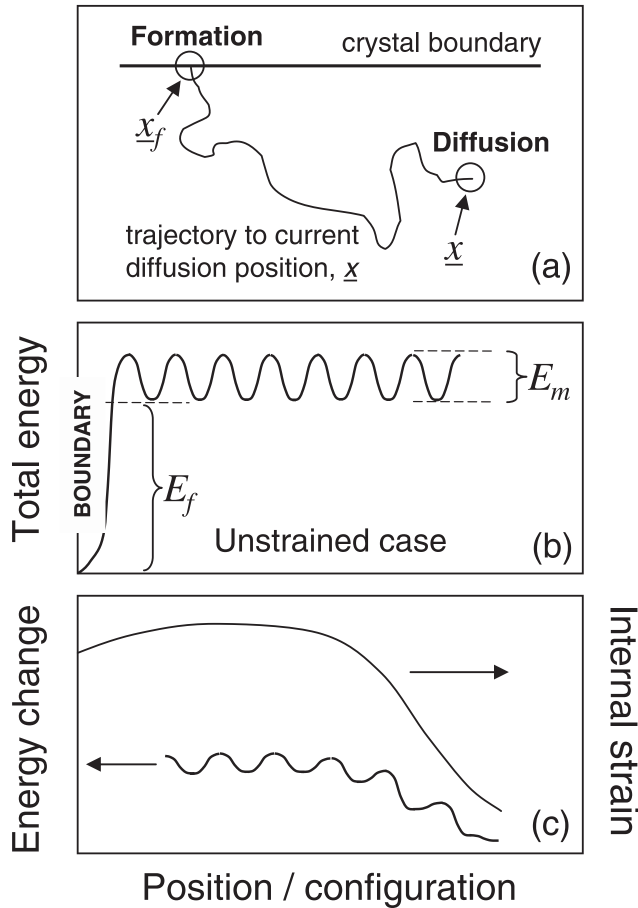

FIG. 1. (a) Illustration of the formation and diffusion of a point defect in a crystal, and the locations where energetic events occur that can be influenced by stress. (b) Total-energy/configuration diagram describing the energies along the formation and diffusion trajectory in the absence of stress. (c) Plot of the change in energy of the defect caused by stress in the interior of the crystal.

semble of surface geometries where generation or recombination takes place with, on average, no change in surface energy.

We now consider a crystal boundary overlaid with an unstrained material that is not epitaxially bonded to the single crystal substrate, and does not react chemically with it. If this exterior material is compliant to the formation or recombination of a point defect at the kink—in other words, if atoms on the exterior of the boundary move in a concerted way as part of the defect reaction—then the generation or recombination process still involves no net work other than the intrinsic formation energy of the point defect. After the step movement—which now includes any atomic displacements on the exterior side of the interface that occur together with this movement—the interfacial energy remains the same, even though there may have been a barrier to the reaction as a result of the energy lent to the concerted atomic movements. The equilibrium populations of point defects in the interior of the crystal are thus unchanged. Figure 2 illustrates this picture for the case of vacancy formation.

If the overlayer is not compliant to formation or recombination of a point defect at the kink, the symmetry between generation and recombination described above no longer applies. However, just as in the case of the concerted-exchange diffusion process, there is a built-in energetic penalty against reactions that are not concerted, and it seems reasonable to take the compliant overlayer as an "ideal" case from which to start our discussion.

Applied stress or built-in stress fields may alter the energy cost of forming a point defect at the crystal boundary. For example, during vacancy formation an atom from the crystal is pushed outward to grow the interface step at the location of the kink. As a result, the crystal grows by one atomic volume, Ω—the vacancy "formation volume"—at this location. It is important to note that, even though the atom pushed up during this process moves perpendicularly to the crystal surface, the associated relaxation motion in the compliant overlayer will generally

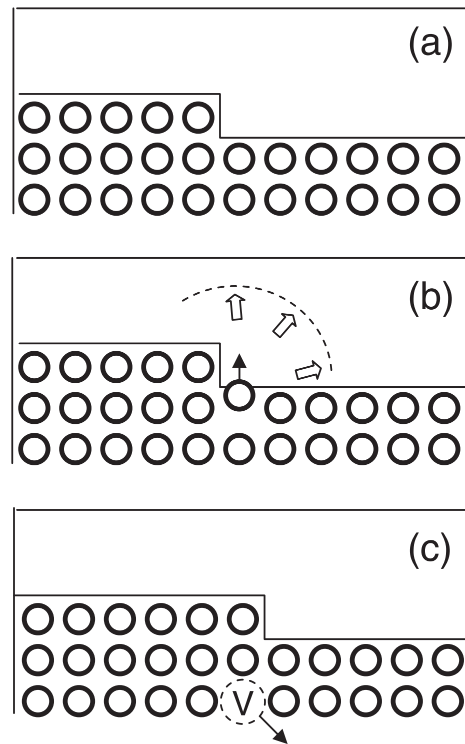

FIG. 2. Schematic outline of steps involved in vacancy formation at the boundary between a compliant overlayer and a single crystal substrate: (a) initial configuration, viewed at a kink on a surface step, (b) upward movement by an atom of the crystal, causing overlayer atoms to rearrange with a net outward relaxation V_f equal to one atomic volume, generating an additional term $\boldsymbol{\sigma}_{\mathrm{ext}} \cdot \mathbf{V}_f$ in the vacancy formation energy, (c) the final interface configuration, unchanged apart from random differences in the overlayer atom distribution (not shown).

take place in three dimensions. For the sake of generality we represent this net movement by a relaxation volume tensor for the overlayer, which depends on the interaction between the adatom and the overlayer material above it under the relevant temperature and stress conditions. Because this tensor is associated with vacancy formation in the underlying crystal, we label it $\mathbf{V}_f$. If the relaxation motion in the compliant overlayer is isotropic in the half-sphere above the interface, then $\mathbf{V}_f = \Omega \mathbf{I}$, where $\mathbf{I}$ is the identity tensor.

The resulting displacement of the overlayer does an amount of work $-\boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f$ against the stress field $\boldsymbol{\sigma}_{\rm ext}$ in the material on the exterior side of the boundary, where we have adopted the convention that tensile stresses and strains are positive. At the same time, the relaxation of the crystal around the resultant vacancy on the interior (crystal) side of the boundary, by an amount $\mathbf{V}_r$, the relaxation volume tensor for the crystal, creates an energy change $-\boldsymbol{\sigma}_{\rm int} \cdot \mathbf{V}_r$ arising from the stress field in that location. For a vacancy in an isotropic crystal, $\mathbf{V}_f = -\alpha\Omega\mathbf{I}$, where α is generally positive and less than unity. A similar argument holds for the formation of an interstitial, in which case the signs of V_f and V_r are reversed. This symmetry takes care of "detailed balance" in the various interfacial and bulk reactions that can create or annihilate vacancies and interstitials in the crystal-overlayer system.

The resultant effect on the point defect formation energy at the interface is

$$\delta E_f = -\boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f - \boldsymbol{\sigma}_{\rm int} \cdot \mathbf{V}_r. \tag{1}$$

This simple equation crucially enables a description of the general case where stresses on either side of a material interface are different. We now consider what Eq. (1) predicts for some special cases.

In a pressure experiment, where a material sample is uniformly stressed, the pressure, P, on each side of the interface is the same. Assuming the external stressor is compliant, this results in an energy change $\delta E_f = P(\Omega + V_r)$ In contrast, in an uncapped epitaxial strained layer, the stresses on either side of the interface (here a solid/air interface) are different. We have $\boldsymbol{\sigma}_{\rm ext} = \mathbf{0}$, and thus $\delta E_f = -\boldsymbol{\sigma}_{\rm int} \cdot \mathbf{V}_r$. These results replicate the conclusions from previously published derivations [1–3] in a simple but general way.

An interesting special case, of particular relevance to nanodevice fabrication, is that of a thin stressed amorphous overlayer on an almost unstrained single-crystal substrate. In this case, neglecting the small stress in the substrate crystal, Eq. (1) reduces to $\delta E_f = -\boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f$. The clear prediction is that point defect formation energies are changed by the presence of a stressed overlayer, even when the crystal itself is not significantly stressed.

We now go on to look at the effects of stress on point defect concentrations and point defect mediated self-diffusion. Consider a crystal region where the point defect concentrations have reached a steady-state in the presence of an overlying stressed layer, and where other sources or sinks are too distant to perturb the situation. The self-diffusion activation energy is given by $Q = E_f + E_m$, where E_m is the migration energy of the mediating point defect. As Fig. 1 shows, we need to consider diffusion at a location $\underline{x}$ which is different from the interfacial location $\underline{x}_f$, where the initial point defect formation event took place. The effect on Q is the sum total of (a) the stress effect on the initial defect formation at $\underline{x}_f$, (b) the energy cost of bringing the point defect from the part of the crystal at location $\underline{x}_f$ with stress value $\boldsymbol{\sigma}_{\rm int}$ to the location $\underline{x}$ with stress value $\boldsymbol{\sigma}(\underline{x})$, and (c) the change in the migration energy at location $\underline{x}$, given by $-\boldsymbol{\sigma}(\underline{x}) \cdot \mathbf{V}_m$, where $\mathbf{V}_m$ is the so-called "migration volume" of the point defect. The resultant stress-dependent energy cost of forming and bringing a point defect to location $\underline{x}$ is then $E_f(\underline{x}) = E_f^* - \boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f - \boldsymbol{\sigma}(\underline{x}) \cdot \mathbf{V}_r$, and the corresponding diffusion activation energy at $\underline{x}$ is $Q(\underline{x}) = Q^* - \boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f - \boldsymbol{\sigma}(\underline{x}) \cdot (\mathbf{V}_r + \mathbf{V}_m)$, where asterisks indicate values in the absence of all stresses.

In terms of the point defect concentration and the associated diffusion via this point defect, we may write $C(\underline{x}) = C_0 S(\underline{x}_f) \exp-\{E_f{}^* - \boldsymbol{\sigma}(\underline{x}) \cdot \mathbf{V}_r\}/kT$ and

$$D(\underline{x}) = D_0 S(\underline{x}_f) \exp-\{Q^* - \boldsymbol{\sigma}(\underline{x}) \cdot (\mathbf{V}_r + \mathbf{V}_m)\}/kT, \tag{2}$$

where the explicitly written exponential terms contain the local effects at the diffusion location, and the term

$$S(\underline{x}_f) = \exp(\boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{V}_f/kT) \tag{3}$$

contains the nonlocal effect of stress on the initial formation event at the interface. In the case of uniform hydrostatic pressure, this can be seen as a PV term in the defect formation enthalpy, but in the more general case this interpretation does not hold.

According to generally accepted convention, the formation energy of a point defect is an inherent property of a crystalline material and should not depend on the presence or absence of overlayers. This viewpoint can be maintained by defining the equilibrium point defect concentration as $C_{\rm eq}(\underline{x}) = C_0 \exp-\{E_f{}^* - \boldsymbol{\sigma}(\underline{x}) \cdot \mathbf{V}_r\}/kT$, and treating any departure from this value, such as the factor $S(\underline{x}_f)$ in Eq. (3), as a supersaturation. This approach is particularly convenient for continuum simulation of semiconductor fabrication processes, where numerous stresses, chemical reactions, and other nonequilibrium phenomena may contribute simultaneously to the perturbation of point defect concentrations [6]. The simultaneous operation of these different effects fits naturally into the multistream rate equation approach with mixed boundary conditions used in continuum process simulation tools [7,8], and the interface effects discussed here form a natural generalization of the boundary conditions.

An interesting special case of our results arises when the interior stress is small and the exterior stress large. Two obvious examples concern the anomalous changes in dopant diffusion observed in the presence of deposited nitride layers on Si wafers, and during thermal oxide growth on Si. In both cases a stressed amorphous overlayer is present while, in the absence of patterning, the substrate is only weakly strained owing to its much greater thickness.

In the case of thermal oxide growth the stress in the growing oxide layer is compressive, i.e., negative, with its highest absolute value close to the interface with the Si. Consequently, Eq. (3) implies that oxide growth will cause a supersaturation of interstitials and an undersaturation of vacancies. The effect increases as a function of oxidant partial pressure, because of the increased generation rate of newly compressed oxide at the interface. This effect may play a partial role, together with known chemical effects, in the well-known phenomenon of "oxidation-enhanced diffusion" [9].

In the case of strained nitride layers on Si, a direct quantitative test of the theory is possible using experimental stress and diffusion results published by Zaitsu *et al.* [10] Layers with stresses in the region of 2 GPa at the annealing temperature gave rise to a retardation of B diffusion by a factor of $\sim 6 \pm 3$ at an anneal temperature of 900 °C. The corresponding stresses in the substrate wafer were ~MPa—too small to influence diffusion. B in Si diffuses by an interstitial-mediated process, so stress effects in its diffusion reflect the response of interstitial defects and the retardation of diffusion is a direct measure of $S(\underline{x}_f)$. Assuming isotropic relaxation of the overlayer and rearranging Eq. (3) we have $V_f = kT \ln S(\underline{x}_f)/\boldsymbol{\sigma}_{\rm ext} \cdot \mathbf{I}$. Substituting the relevant stress value and interstitial undersaturation at 900 °C one extracts an interstitial formation volume $V_{f(I)} - (1.2 \pm 0.2)\ \Omega$, in agreement with the theory's prediction of $-1.0\ \Omega$. The theory provides solid support for earlier speculation that nitride layers on Si absorb interstitials to reduce their internal tensile stress [11]. The generic mechanism outlined in Fig. 2 shows clearly how this can happen.

Over the full temperature range of the experiments by Zaitsu *et al.* [10], ranging from 900–1100 °C, the diffusion retardation weakens somewhat faster than predicted with increasing temperature. One possible explanation is that at high temperature some diffusive rearrangement occurs in the Si-nitride interfacial region, reducing stress locally while the average stress in the nitride layer is unaffected. Nevertheless, even at 1100 °C, the formation volume extracted using our simple model is $\sim 0.9\ \Omega$—still close to the expected value of 1.

Finally, the generation of point defect supersaturations in a crystal embedded in a differently stressed environment has implications for diffusion-assisted creep. Mass transport in the crystal is dependent on both interior and exterior stress, and in the presence of thin stressed overlayers creep can occur without significant stress in the crystal, driven by the reduction in energy as overlayers relax. This has potential consequences for a range of scientific and technological problems, for example, electromigration in the interconnect lines of integrated circuits. In comparison with Nabarro-Herring creep, where transport is driven by variations in the normal stress around the periphery of a crystal or grain, here there is no need for a normal stress to be present.

In summary, a continuum theory of stress effects on point defect formation and diffusion in single crystals has been presented, which includes for the first time a physical description of exterior stress effects at the crystal boundary. The exterior stress term leads to a prediction that stressed overlayers generate point defect supersaturations in the underlying crystal, even when the latter is not significantly stressed.

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