Microscopic Theory of Electromigration on Semiconductor Surfaces

Daniel Kandel and Efthimios Kaxiras
Department of Physics and Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 14 June 1995; revised manuscript received 22 August 1995)

Electromigration has a dramatic effect on the morphology of semiconductor surfaces, inducing, for example, step bunching instabilities. To explain these phenomena from a microscopic point of view, we study self-diffusion on Si(111) through first principles calculations, and propose a mechanism for diffusion bias induced by external electric fields. A competing, wind-force effect arises from enhanced surface electron density, due to incomplete melting. The competition leads to two transitions in surface kinetics with increasing temperature, in agreement with experimental observations.

PACS numbers: 68.35.Ja, 68.35.Rh, 68.55.Jk, 73.20.–r

Electric current flow through a solid can produce large atomic motion, referred to as electromigration. On the surface of a solid, this phenomenon can even lead to morphological instabilities. Surprisingly, this effect is observed not only on metal surfaces, but also on semiconductor surfaces. Electromigration phenomena are of tremendous practical importance, since they affect growth and annealing of thin films as well as the performance and stability of electronic devices, which typically operate in the presence of electric fields. A well documented case of surface instabilities due to electric currents is the step motion on Si(111) surfaces, observed [1] during annealing of the sample at high temperatures and in the presence of an electric field perpendicular to the step edges.

Stoyanov [2] introduced the idea that the diffusion of surface adatoms may be biased by the electric field, and showed that step bunching instabilities can result from such a model. By proposing a step flow model that takes this biased diffusion into account, Kandel and Weeks [3] were able to achieve excellent agreement with experiment in terms of step patterns and their dynamics. While this theory was very successful in reproducing qualitatively the experimental behavior, it did not address the crucial link between microscopic atomic motion and electromigration effects.

In the case of Si(111), the issue of the microscopic mechanism(s) responsible for electromigration is especially intriguing because of the complicated temperature dependence of the effect. The phenomena of interest take place at temperatures greater than $T_r \approx 830\,^\circ\mathrm{C}$, the $(7 \times 7) \leftrightarrow (1 \times 1)$ phase transition temperature, above which the surface loses its long-range periodic reconstruction. Experiments indicate [1] that there are two transitions at $T_1 \approx 1000\,^\circ\mathrm{C}$ and $T_2 \approx 1175\,^\circ\mathrm{C}$. For $T_r < T < T_1$ and $T > T_2$ the steps are uniformly spaced when the current is in the step-up direction, but when the current is in the step-down direction a kinetic instability occurs that leads to step bunching. In the intermediate temperature regime $T_1 < T < T_2$ the effect is reversed, i.e., the step-bunching instability occurs only when the current is in the step-up direction. In this Letter we propose microscopic explanations of these phenomena.

The effective force $\boldsymbol{F}$ acting on the diffusing atoms is proportional to the electric field $\boldsymbol{E}$. We define an effective charge Z for the atoms (measured in units of the electron charge e) such that

$$\boldsymbol{F} = eZ\boldsymbol{E}\,. \tag{1}$$

The effective charge is a sum of two terms, $Z = Z_d + Z_w$. The "direct term" Z_d is associated with the force due to electrostatic interactions between the atom and the electric field, whereas Z_w is a charge associated with the scattering of atoms produced by the electron current, leading to the so called "wind" force. A comparison of the theories of Stoyanov [2] and Kandel and Weeks [3] to experiments [4] yields an estimate of the effective charge $Z \approx -0.1$ at $T = 1130\,^\circ\mathrm{C}$.

We attribute the instabilities discussed above to *surface* direct and wind force effects which we now analyze. Specifically, we will examine surface effects on both Z_d and Z_w as well as the competition between the two. To understand the direct surface effect we examine the charge distribution around Si adatoms on the (111) surface in configurations which are relevant for adatom diffusion. The stable (T_4) and metastable (H_3) positions of adatoms on the surface are shown in Figs. 1(a) and 1(b), respectively. The adatom diffuses by hopping between the T_4 and H_3 positions. In each such hop it passes through the saddle-point (SP) position shown in Fig. 1(c). A homogeneous electric field $\boldsymbol{E}$ can bias the diffusion in the following way: Consider two configurations that differ from one another by the position of a single adatom, which is at the T_4 position first and then moves to the H_3 position. The charge densities of the two configurations are $\rho(\boldsymbol{r})$ and $\rho'(\boldsymbol{r})$, respectively. The energy difference between the configurations in the absence of a field is denoted by $\Delta \equiv \varepsilon(H_3) - \varepsilon(T_4)$. Treating the electric field effect classically, we obtain for the energy difference $\overline{\Delta}$ between the two configurations in the presence of a field:

$$\overline{\Delta} = \Delta - \boldsymbol{E} \cdot \int \boldsymbol{r}[\rho'(\boldsymbol{r}) - \rho(\boldsymbol{r})]\,d^3r. \tag{2}$$

We ignore the effect of the electric field on the charge distribution itself, because the electric fields involved in

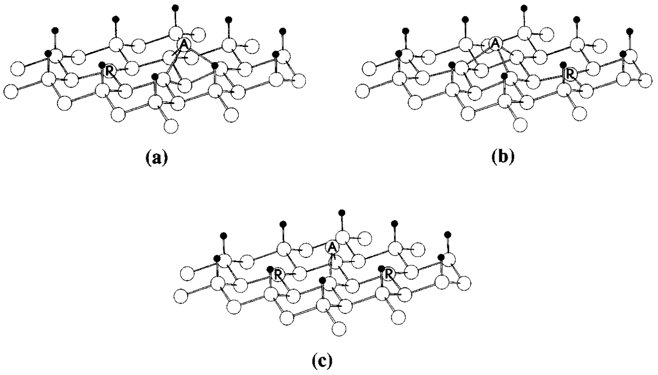

FIG. 1. A portion of the top bilayer of the supercell for three configurations (only ten of the twelve H atoms attached to surface Si atoms are shown): (a) The T_4 configuration, (b) the H_3 configuration, and (c) the SP configuration. Open circles denote Si atoms while H atoms are represented by full circles. Adatoms are marked by A and rest atoms by R.

electromigration are very weak (few V/cm). Z_d can now be calculated as if it originated from the motion of a point charge from the T_4 position to the H_3 position: $eZ_d\boldsymbol{E} \cdot \boldsymbol{a} = \Delta - \overline{\Delta}$, with $\boldsymbol{a}$ being the vector between the T_4 and the H_3 positions. A nonvanishing Z_d leads to a bias in the diffusion, since the energy barrier for hopping from one T_4 position to the next in the direction of the field is smaller than the barrier for hopping against the field by an amount $2(\Delta - \overline{\Delta})$. This is because, for a given geometry, the charge transferred along the path between the H_3 and T_4 positions is identical to the charge transferred in the reverse path. This symmetry is broken only by the electric field, which is too weak to affect the charge distributions (as we assumed above).

The result of this calculation depends, in principle, on the arrangement of other adatoms around the hopping adatom. In order to calculate Z_d one should therefore repeat the calculation for all possible environments and average the results, weighing each configuration with its probability of occurrence. This is a very difficult, if not intractable, task. Instead, we calculate Z_d from a single representative configuration. Our result will therefore be an estimate of the order of magnitude of Z_d rather than an exact value.

To calculate the charge densities involved in Eq. (2), we performed first principles calculations within local density functional theory. Our supercell consists of a slab of three bilayers of Si atoms with a (4×4) surface unit cell. This supercell is large enough to avoid finite size effects; its borders can be chosen so that no significant charge transfer occurs at the boundaries during the hop of the adatom. This condition must be satisfied in order for the integral in (2) to be well defined. The experimental density of adatoms on the Si(111) surface is about 1/4. Accordingly, in a typical configuration, charge associated with surface Si atoms whose distance to the hopping adatom is two lattice vectors or more is bonded to other adatoms. To mimic this effect, 12 of the 16 dangling bonds of the top layer were passivated by attaching H atoms to them (see Fig. 1). This leaves four unsaturated Si atoms in the top layer, each having one dangling bond. The presence of one Si adatom saturates three of these surface dangling bonds in the T_4 and H_3 positions. The atom with the remaining unsaturated dangling bond is called a rest atom. The bottom layer was fully hydrogenated to terminate the slab. The positions of all atoms except those in the bottom layer were fully relaxed during the calculation. For each relaxed configuration we calculated the charge density, and then used Eq. (2) to calculate Z_d for an electric field in the direction of the adatom hop (the line from the T_4 position to the H_3 position). The result is

$$Z_d = +0.05 \pm 0.006 . \tag{3}$$

We obtain the error estimate by performing the integral in Eq. (2) over different, but equivalent by periodicity, regions. Thus this error is a measure of finite size effects, but does not take into account inaccuracies associated with the approximations made in deriving Eq. (2). The positive effective charge of the adatom can be interpreted as being due to backflow of electronic charge induced by the hop of the adatom [5].

The direct electromigration effect is demonstrated schematically in Fig. 2 for a one-dimensional energy landscape along a diffusion path. The solid line is the energy landscape in the presence of an electric field, and the dashed line in the absence of a field (the difference between the two curves is amplified for illustration purposes). The electric field distorts the energy landscape and most importantly induces a *bias*. The energy barrier for a hop to the right (from a T_4 position to the next) is thus lower than the one for a hop to the left.

Next we consider surface effects on the charge Z_w associated with the wind force. For simplicity, this is

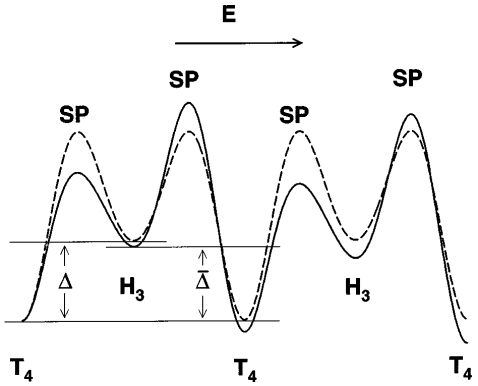

FIG. 2. Schematic representation of a one-dimensional energy landscape along the adatom diffusion path in the presence (solid line) and in the absence (dashed line) of an electric field. The equilibrium, metastable, and saddle-point positions are marked as T_4, H_3, and SP, respectively. Δ and $\overline{\Delta}$ are defined in the text. The arrow at the top corresponds to the direction of the electric field.

estimated using a ballistic model with bulk parameters [6]

$$Z_w = -nl\sigma, \tag{4}$$

where n is the density of free electrons, l is the electron mean free path, and σ is the transport cross section of an atom at the Fermi energy. For bulk Si at $T = 1150\,^\circ\mathrm{C}$, $n \approx 10^{-5}$ Å^{-3} [7], $l \approx 3$ Å (since $l = 76$ Å at 27 °C) and $\sigma \approx 1$ Å^2, a typical atomic cross section. These estimates give $Z_w < 10^{-4}$, which is negligible compared to the surface direct effect calculated above. This estimate raises the question: Is there a surface effect that can enhance the wind force? In certain materials, a surface phase transition occurs at a high temperature above which a few monolayers near the surface melt. This phenomenon, first predicted by Chernov and Mikheev [8] on the basis of thermodynamic arguments, is known as incomplete surface melting. The thickness of the molten layer remains finite as the temperature is further raised until the bulk melting temperature is reached. There exists both theoretical and experimental evidence for such a transition in Ge: On the theoretical side, Takeuchi, Selloni, and Tosatti [9] reported first principles molecular dynamics simulations of Ge(111), showing that only the first surface bilayer melts at T_c, and that the surface starts behaving as a conductor (similar to bulk liquid Ge). On the experimental side, McRae and Malic [10] and Denier van der Gon *et al.* [11] have observed incomplete surface melting in Ge(111), with a $T_c \approx 780\,^\circ\mathrm{C}$, about 150° lower than the bulk melting temperature $T_m = 937\,^\circ\mathrm{C}$. Modesti *et al.* [12] measured the surface conductivity, which is proportional to the surface density of free electrons n_s. Their experiment shows that below the $c(2 \times 8) \leftrightarrow (1 \times 1)$ reconstruction transition temperature ($T_r \approx 325\,^\circ\mathrm{C}$), n_s is negligible and the surface is an insulator. For $T_r < T < T_c$, n_s rises linearly with temperature from zero to 0.13 Å^{-2} just below T_c. At T_c, n_s jumps to 0.58 Å^{-2} and remains constant between T_c and T_m. The surface is metalliclike in this regime.

The structural similarity between Si and Ge, in both their bulk and surface features, leads us to postulate that similar phenomena should occur on the Si(111) surface. Specifically, we assume that the Si(111) surface, just like the Ge(111) surface, has an enhanced density of free surface electrons above the $(7 \times 7) \leftrightarrow (1 \times 1)$ reconstruction transition ($T_r \approx 830\,^\circ\mathrm{C}$). We also assume that the Si(111) surface undergoes incomplete melting at a $T_c^{(111)}$ of a few hundred degrees below $T_m = 1415\,^\circ\mathrm{C}$. Indirect experimental evidence exists to support this assumption. Anomalously fast diffusion has been observed on Si(111) surfaces at high temperatures, which was interpreted as being due to the presence of a 2D fluidlike layer of Si atoms on the surface [13]. Moreover, incomplete melting has been observed on the Si(001) surface with x-ray photoelectron diffraction at $T_c^{(001)} \approx 1125\,^\circ\mathrm{C}$ [14]. Since the surface energy of the Si(111) surface is lower than that of the Si(001) surface, we expect that the (111) surface would exhibit incomplete melting at some $T_c^{(111)}$ bounded by $T_c^{(001)} < T_c^{(111)} < T_m$. We emphasize that even though above T_c the surface is molten, surface steps are still well defined. The reason for this is that only one bilayer melts at the temperature range between T_c and T_m, while the rest of the material retains its crystalline properties and surface features.

The enhanced electron density at the surface, which is a consequence of the loss of an ordered reconstruction (i.e., for $T > T_r$), leads to a pronounced wind force that competes with the direct electromigration effect we calculated above. When the direct effect dominates, the effective charge is positive [cf. Eq. (2)], leading to an instability when the current is in the step-down direction [3]. When the wind force dominates, the effective charge becomes negative and the morphological instability occurs with the current in the step-up direction. Thus this competition can explain the transitions in the behavior of the system as a function of temperature.

To see how these transitions come about, an ansatz on the dependence of Z_d and Z_w on temperature is required. In what follows we make the simplest plausible ansatz, which can explain the origin of the transitions at T_1 and T_2. The ansatz is by no means unique; what actually happens in Si(111) will have to be determined by more involved theories and experiments. First, we use the result from our first principles calculations and assume that $Z_d = 0.05$ below T_c [see Eq. (3)]. Above T_c, however, Z_d should be larger and closer to the actual valence charge of a Si atom, since the surface at these temperatures is molten and metalliclike. We will assume $Z_d = 0.5$ in this regime. This dependence of Z_d on temperature is plotted in Fig. 3 as a dashed line.

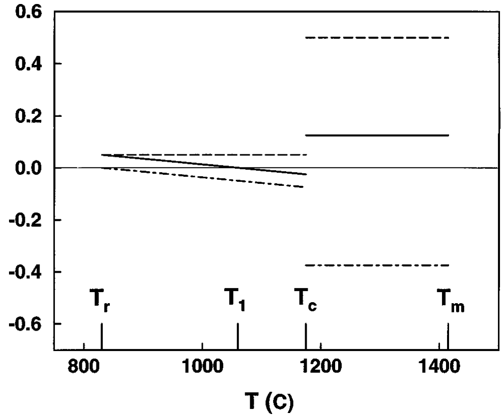

FIG. 3. Effective adatom charge as a function of temperature. Z_d (the charge associated with the direct effect) is shown as a dashed line, and Z_w (the contribution of the wind force) is the dash-dotted line. The solid line corresponds to the total effective charge Z. It crosses zero at two temperatures—T_1 and T_c. T_r and T_m are defined in the text.

To estimate Z_w we use Eq. (4) with $l = 3$ Å and $\sigma = 1$ Å^{-2}, independent of temperature. We assume that the surface electron density n_s rises linearly from zero to $n_s = 0.1$ Å^{-2} at $T_c = 1175\,^\circ$C and jumps to $n_s = 0.5$ Å^{-2} for $T > T_c$, by analogy to what was observed experimentally for Ge(111) [12]. To get n we divide n_s by 4 Å to account for the thickness of the molten layer. The resulting Z_w is plotted in Fig. 3 as a dash-dotted line. The total effective charge Z is the solid line in Fig. 3. As is readily seen from this plot, Z changes sign at two temperatures. The lower one at $1060\,^\circ$C corresponds to the first experimentally observed transition at $T_1 = 1000\,^\circ$C, and the second at T_c corresponds to the experimental transition at $T_2 \approx 1175\,^\circ$C. Note that this value of T_c is between the incomplete melting temperature of Si(001) and the bulk melting temperature, as expected from the surface energy argument. The typical value of Z in the intermediate regime between T_1 and T_2 is $Z \approx -0.02$, not too far from the experimental estimate of $Z \approx -0.1$ [4]. Considering the fact that the approximations we made allow us to estimate only orders of magnitude, the experiment and the theory are certainly in good agreement.

In conclusion, we investigated surface effects on the effective charge of adatoms associated with electromigration phenomena. Our first principles calculations reveal a significant direct effect, which has its origin in electronic charge transfer between different sites as the adatoms diffuse on the surface. Electronic charge transfer is not the only mechanism one may try to invoke in order to address the direct effect. A vast amount of literature exists on diffusion mechanisms in bulk Si [15], some of which may be relevant to surface diffusion and perhaps even to the direct electromigration effect. In this work we have shown that the relatively simple and physically motivated effect of electronic charge transfer arising from adatom motion induces electromigration effects of the right order of magnitude to account for experimental results.

We have also shown that the hypothesis of incomplete surface melting in Si(111) leads to the prediction of an enhanced wind force at higher temperatures. The competition between these two effects induces sign changes of the effective charge as a function of temperature. This explains the two transitions in the morphology of the surface that were observed experimentally. It is hoped that this work will motivate detailed experiments to test the hypothesis of enhanced surface electron density and incomplete melting of Si(111) surfaces.

This work was supported by Office of Naval Research Grant No. N00014-95-1-0350.

[1] See, for example, A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, and S.I. Stenin, Surf. Sci. **213**, 157 (1989); Y. Homma, R.J. McClelland, and H. Hibino, Jpn. J. Appl. Phys. **29**, L2254 (1990); H. Yasunaga and A. Natori, Surf. Sci. Rep. **15**, 205 (1992), and references therein; M. Suzuki, Y. Homma, Y. Kudoh, and R. Kaneko, Ultramicroscopy **42–44**, 940 (1992); H. Tokumoto, K. Miki, Y. Morita, T. Sato, M. Iwatsuki, M. Suzuki, and T. Fukuda, Ultramicroscopy **42–44**, 816 (1992); A.V. Latyshev, A.B. Krasilnikov, and A.L. Aseev, Ultramicroscopy **48**, 377 (1993); M.J. Ramstad, R.J. Birgeneau, K.I. Blum, D.Y. Noh, B.O. Wells, and M.J. Young, Europhys. Lett. **24**, 653 (1993); H. Yamaguchi and K. Yagi, Surf. Sci. **287/288**, 820 (1993); A.V. Latyshev, A.B. Krasilnikov, and A.L. Aseev, Surf. Sci. **311**, 395 (1994).

[2] S. Stoyanov, Jpn. J. Appl. Phys. **30**, 1 (1991); S. Stoyanov, H. Nakahara, and M. Ichikawa, Jpn. J. Appl. Phys. **33**, 254 (1994); see also C. Misbah, O. Pierre-Louise, and A. Pimpinelli, Phys. Rev. B **51**, 17 283 (1995).

[3] D. Kandel and J.D. Weeks, Phys. Rev. Lett. **74**, 3632 (1995).

[4] E.D. Williams, E. Fu, Y.-N. Yang, D. Kandel, and J.D. Weeks, Surf. Sci. Lett. (to be published).

[5] See, for example, Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989); N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. B **49**, 10 757 (1994).

[6] V.B. Fiks, Sov. Phys. Solid State **1**, 14 (1959).

[7] S.M. Sze, *Physics of Semiconductor Devices* (John Wiley & Sons, New York, 1981).

[8] A.A. Chernov and L.V. Mikheev, Phys. Rev. Lett. **60**, 2488 (1988); Physica (Amsterdam) **157A**, 1042 (1989).

[9] N. Takeuchi, A. Selloni, and E. Tosatti, Phys. Rev. Lett. **72**, 2227 (1994).

[10] E.G. McRae and R.A. Malic, Phys. Rev. Lett. **58**, 1437 (1987); Phys. Rev. B **38**, 13 163 (1988).

[11] A.W. Denier van der Gon, J.M. Gay, J.W.M. Frenken, and J.F. van der Veen, Surf. Sci. **241**, 335 (1991).

[12] S. Modesti, V.R. Dhanak, M. Sancrotti, A. Santoni, B.N.J. Persson, and E. Tosatti, Phys. Rev. Lett. **73**, 1951 (1994).

[13] See, for example, C. Alfonso, J.C. Heynard, and J.J. Métois, Surf. Sci. Lett. **291**, L745 (1993).

[14] J. Fraxedas, S. Ferrer, and F. Comin, Europhys. Lett. **25**, 119 (1994).

[15] See, for example, W. Frank, U. Gösele, H. Mehrer, and A. Seeger, in *Diffusion in Crystalline Solids,* edited by G.E. Murch and A.S. Nowick (Academic, Orlando, FL, 1985), p. 64, and references therein.