

## Macrovacancy Nucleation on Evaporating Si(001)

Alberto Pimpinelli<sup>1</sup> and Jean-Jacques Métois<sup>2</sup>

<sup>1</sup>Commissariat à l'Energie Atomique/Département de Recherche Fondamentale sur la Matière Condensée, Service de Physique Statistique, Magnétisme et Supraconductivité Groupe de Magnétisme et Diffraction Neutronique, Centre d'Etudes Nucléaires de Grenoble, 17, rue des Martyrs, F-38054 Grenoble Cedex 9, France

<sup>2</sup>Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Centre National de la Recherche Scientifique, Campus de Luminy, case 913, F-13288 Marseille Cedex 09, France

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Measurements of the nucleation rate of macrovacancies ("Lochkeim" formation) on Si(001) during high-temperature sublimation are presented. A theoretical description of macrovacancy nucleation on evaporating surfaces is also given. The nucleation rate is shown to follow a non-Arrhenius behavior as a function of temperature. The experiment is seen to compare favorably with the theory.

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Because of their technological importance, semiconductors in general, and silicon in particular, are extensively studied. The main current interest is on surface properties, whose understanding is fundamental for controlling epitaxial growth techniques. While progress in scanning tunneling microscopy (STM) now allows study of surface phenomena such as step fluctuations on vicinal surfaces and adatom motion at moderately high temperature [1-3], electron microscopy still remains the method most applied for investigating crystal surface dynamics in real time at high temperatures (even in the sublimation range). Reflection electron microscopy (REM) [4-7] and low-energy electron microscopy (LEEM) [8], have been used in particular for studying the behavior of high-temperature silicon surfaces, either at equilibrium—that is, at temperatures where adatom desorption is still negligible—or during evaporation. This behavior can be summarized as follows: At intermediate temperature [ $T \approx 1100$  K for Si(001)] a vicinal surface consists of an array of steps which undergo thermal fluctuations about a fixed direction [6,9,10]. With increasing temperatures, surface adatoms desorb and the train of steps starts to move in a step flow fashion. The evaporation rate is independent of the miscut angle (or, equivalently, of the interstep separation  $l$ ) and of the surface orientation [4,5,7,11]. This is in agreement with Burton, Cabrera, and Frank's theory (BCF) [12], which gives the sublimation rate of a vicinal surface with average step density  $1/l$  as

$$\dot{z} = 2(\kappa/l)D\rho_0 \tanh(\kappa l/2), \quad (1)$$

where  $D\rho_0$  is the adatom mass diffusion constant. If  $\tau_e$ , the adatom lifetime before evaporation, is large, the adatom diffusion length before desorption,  $x_s = \sqrt{D\tau_e} = l/\kappa$ , may be larger than the average terrace size  $l$ . In this case  $\dot{z}$  reduces to  $\rho_0/\tau_e$ , the mass desorption rate, independent of  $l$ . At higher temperature,  $x_s$  shortens and formula (1) predicts an  $l$ -dependent behavior of  $\dot{z}$ . This behavior, however, is never observed on {111} and {001} silicon faces. The former maintains a step flow mode of sublimation with an  $l$ -independent sublimation rate, although

steps show a tendency to bunch in certain temperature ranges, depending on the heating current direction [4,13]; on the latter, one rather observes nucleation and growth of surface vacancies, eventually disrupting any step flow motion [7,8].

In this Letter we present a detailed experimental and theoretical investigation of macrovacancy nucleation ("Lochkeim" formation). We report measurements of the nucleation rate of macroscopic vacancies on Si(001) between 1400 and 1430 K. Our results suggest that Lochkeim formation is not described by a simple thermally activated process, even though an Arrhenius plot of the nucleation rate is well fitted by a straight line. In fact, the corresponding (apparent) activation energy is too high ( $\approx 20$  eV), and a good linear fit on a temperature range of only 30 K is to be taken with care anyway. We interpret these findings within the frame of a recently proposed [14] modified BCF theory which includes adatom-advacancy pair formation, coupled to the classical Becker and Döring nucleation theory [15]. The theory is able to reproduce the experimental observations using activation energies for elementary surface processes as found in literature.

Silicon is certainly one of the most studied systems, and a very good testing ground for theory. We will review here some of the relevant surface physical parameter. Note that we use units where the interatomic spacing  $a$  is 1. Evaporation experiments under different conditions [4,5,7,11] have shown that the evaporation rate  $1/\tau_{ev}$  is orientation independent; given a thermally activated rate, one can write  $1/\tau_{ev} = \rho_0/\tau_e = 1/\tau_e^0 \exp[-\beta(W_a + W_e)]$ , where  $1/\tau_e^0$  is an atomic frequency of the order  $10^{13}$ - $10^{14}$  s<sup>-1</sup>,  $W_e$  is the desorption barrier for adatoms, and  $W_a$  is the adatom formation free energy defined by the Gibbs formula  $\rho_0 = \exp[-\beta W_a]$  for the equilibrium adatom density  $\rho_0$ . The measurements then give  $W_a + W_e \approx 4.3 \pm 0.3$  eV. Surface relaxation [16] and reflection high energy electron diffraction intensity recovery [17] experiments have provided the activation energy for the mass surface diffusion coefficient  $\rho_0 D$ ; again this quantity has an activated form,  $\rho_0 D$

$= D_0 \exp[-\beta(W_a + W_{sd})]$ , where  $D_0$  is an atomic frequency of the order  $10^{13}$ – $10^{14}$  s $^{-1}$ , and  $W_{sd}$  the surface diffusion barrier for adatoms. It has been found [16,17]  $W_a + W_{sd} \approx 2.2 \pm 0.2$  eV. These measurements provide the activation energy for the surface diffusion length  $x_s = \sqrt{D\tau_c}$ ; since  $D_0 \approx 1/\tau_c^0$ , we have  $x_s^2 = \exp[\beta(W_c - W_{sd})]$ , with  $W_c - W_{sd} \approx 2.3 \pm 0.3$  eV. Note that the activation energy  $W_{sd}$  for the surface diffusion coefficient of single adatoms (i.e.,  $D$ ) has been separately measured [18],  $W_{sd} \approx 0.7$  eV, but we will not need it here. The step free energy  $\gamma$  has also been investigated: due to the diamond structure, a vicinal (001) silicon face contains two alternating types of steps, of low and high energy, respectively. Chadi [19] has numerically computed the respective values 10 and 150 meV/atom. STM measurements around 300°C [20] have given 28 and 90 meV/atom, respectively. At approximately the same temperature, the observation of the equilibrium shape of bulk voids has given a step free energy of 23 meV/atom on Si(001) [21]. At the much higher temperatures we will consider, the difference in the step free energy is expected to be severely reduced [16]. The *Lochkeime* observed in this temperature range show very little anisotropy (they have a slightly elliptical shape with ratio of minor to major axis of  $\approx 0.8$  [4,7]) which confirms this expectation. Numerical estimates [16] point to very similar values for both steps, of the order of 35 meV/atom. Last but not least is the surface single vacancy (“advacancy”) density  $\sigma$ ; very little is known about it. A numerical estimation [22] of the energy barrier  $\bar{W}_{adv}$  which opposes advacancy formation on Si(001) gives  $\bar{W}_{adv} \approx 2.4$  eV. As for adatoms, we define the advacancy formation energy  $W_{adv}$  through the equilibrium relation  $\sigma_0 = \exp[-\beta W_{adv}]$ . Broken-bond considerations suggest for  $W_{adv}$  a value near the Si-Si bond energy,  $\approx 2.2$  eV; anyway,  $W_{adv}$  is treated as a fitting parameter. We summarize the above values in Table I. We turn now to the measure of the macrovacancy nucleation rate  $J$  (number of macrovacancies observed per unit surface and time) on Si(001).

*In situ* experiments were performed with an ultrahigh

TABLE I. Surface quantities for Si(001) as reported in literature. In the first column is the crystal evaporation energy, in the second one the mass diffusion activation energy. The third column gives the average value of the difference of the first two. In the fourth one we give the numerical estimation of the barrier for advacancy formation, and in the last one, computed and measured values of the step free energies. Respective sources are also indicated.

$W_a + W_c$ (eV)	$W_a + W_{sd}$ (eV)	$W_c - W_{sd}$ (eV)	$\bar{W}_{adv}$ (eV)	$\gamma$ (meV/atom)
$4.2 \pm 0.2$ [4]	$2.2 \pm 0.2$ [16]	$2.3 \pm 0.3$	2.4 [22]	10; 150 [19]
$4.3 \pm 0.3$ [5]	$2.4 \pm 0.2$ [17]			28; 90 [20]
4.1 [10]				23 [21]
$4.1 \pm 0.5$ [11]				

vacuum electron microscope in reflection mode [23]. Details of the cleaning procedures of the sample and of the experimental technique are given elsewhere [7]. Regular step flow is observed up to  $\approx 1400$  K. The step velocity is proportional to the step-step separation  $l$  until this temperature, where the density of surface vacancies becomes large enough to form clusters—*Lochkeime*—of atomic depth. The edges of these *Lochkeime* are additional steps which appear at random positions near the center of the terrace, thus breaking the regular step flow. Large surface vacancies are seen to form between 1400 and 1455 K, depending on the terrace size (a typical macrovacancy is shown in Fig. 1 of Ref. [7]). We tape recorded in real time the nucleation of macrovacancies and we counted the number of macrovacancies which formed per second on a terrace of size  $l = 1.9$   $\mu\text{m}$  in an area  $\Omega = 2.2 \times 10^{-7}$  cm $^2$ , at three temperatures,  $T = 1410, 1420$  and  $1430$  K. The logarithms of the measured  $J\Omega$  values are shown as full circles in Fig. 1, where they are plotted vs  $1/T$  (Arrhenius plot). We notice that a decent straight-line fit (solid line) is obtained, whose slope, however, gives an activation energy of  $23 \pm 3$  eV. This number is meaningless, as the following argument shows. A simple way of looking at nucleation of macrovacancies is to consider a circular surface cavity with competing edge energy  $\gamma$  and surface chemical potential  $\delta\mu$ . The free energy of a *Lochkeim* of radius  $R$  is thus

$$F(R) = 2\pi\gamma R - \pi\delta\mu R^2. \quad (2)$$

$F(R)$  has a maximum which occurs at  $R$  equal to  $R_c = \gamma/\delta\mu$ , where it takes the value  $F(R_c) = \pi\gamma^2/\delta\mu$ . This maximum means that macrovacancies with radius smaller than  $R_c$  will shrink, while larger ones will grow.  $F(R_c)$  plays then the role of activation energy for macrovacancy nucleation. One expects that the concentration of macrovacancies of radius approximately  $R_c$  (“critical clusters”) is given by  $\exp[-\beta F(R_c)]$ , which gives a

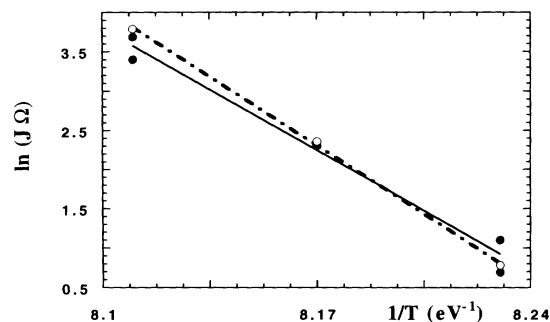


FIG. 1. Arrhenius plot of the measured (full circles) nucleation frequency  $\Omega J$ , for a terrace of size  $l = 1.9$   $\mu\text{m}$  and in an area  $\Omega = 2.2 \times 10^{-7}$  cm $^2$ . Same plot of formula (12) (empty circles) with the parameters in Table II. The solid and dash-dotted straight lines are the respective linear fits. As we discuss in the body of the paper, this plot is in fact misleading, and  $J$  does not follow an Arrhenius behavior.

rough estimate of the nucleation rate. An activation energy of 23 eV implies a concentration of critical clusters of approximately  $10^{-83}$  at 1400 K. A better theoretical evaluation of  $J$  is clearly needed. As we previously mentioned, silicon evaporation occurs *via* step flow until *Lochkeime* form. We will therefore use Burton, Cabrera, and Frank's (BCF) diffusion-desorption equation for the adatom density  $\rho(x)$ , allowing for adatom-advacancy pair formation and annihilation at a rate  $k(\rho_0\sigma_0 - \rho\sigma)$ , where  $\rho_0$  and  $\sigma_0$  are the adatom and advacancy equilibrium densities, respectively. An analogous equation is used for the advacancy density  $\sigma(x)$  [24]. As usual, surface diffusion of adatoms is assumed sufficiently fast to allow making a quasistationary approximation—that is, we neglect the time dependence of both  $\rho$  and  $\sigma$ . The gradient of  $\rho(x)$  and  $\sigma(x)$  near a step edge gives then the current of adatoms and advacancies impinging onto the step, which is easily related to the velocity of step advancement. The resulting equations neglect clustering of adatoms. This is certainly an excellent approximation in the case of evaporation, since the temperatures involved are so high that pairs and even triplets of adatoms are unstable. Clustering of advacancies will be treated next in the spirit of classical nucleation theory. We skip all details, which have already been published in Ref. [14]. Even as they are, the BCF equations are nonlinear and quite complicated to treat. Since evaporation is very slow ( $1/\tau_{ev} \approx 10^{-2}$  layer per second at 1400 K),  $\rho$  and  $\sigma$  cannot be very different from their equilibrium values,  $\rho_0$  and  $\sigma_0$ . We introduce therefore small deviation from equilibrium  $\delta\rho = \rho - \rho_0$  and  $\delta\sigma = \sigma - \sigma_0$  and linearize the equations. Assuming local equilibrium  $\delta\rho = \delta\sigma = 0$  at the step positions  $x = \pm l/2$  (the origin is chosen at the center of the terrace), and limiting ourselves to first order in the small parameter  $\rho/\tau_v$ , after some tedious algebra we obtain [14] the solutions

$$\rho(x) = \rho_0 \frac{\cosh(\kappa x)}{\cosh(\kappa l/2)}, \quad (3)$$

$$\sigma(x) = \sigma_0 \left[ 2 - \frac{\cosh(\kappa x)}{\cosh(\kappa l/2)} \right], \quad (4)$$

where

$$\kappa^2 = \frac{\rho_0/\tau_v}{D\rho_0 + \Lambda\sigma_0}, \quad (5)$$

where  $\Lambda$  is the diffusion coefficient of advacancies. Note that reasonably one has  $\Lambda\sigma_0 \leq D\rho_0$ , so that one can take

$$\kappa^2 \approx 1/(D\tau_v) = \exp[-\beta(W_v - W_{sd})]. \quad (6)$$

Since  $\kappa$  is small, we can write  $\rho$  and  $\sigma$  in (3) and (4) in the approximate but convenient exponential form

$$\rho(x) = \rho_0 \exp[-\beta\delta\mu(x)], \quad (7)$$

$$\sigma(x) = \sigma_0 \exp[\beta\delta\mu(x)],$$

which define by comparison with (3) and (4) the (small) chemical potential difference  $\delta\mu$ . We approximate  $\delta\mu(x)$  by its value at the center of the terrace,  $x=0$ ,

$$\beta\delta\mu(0) \approx \frac{\sigma(0)}{\sigma_0} - 1 = 1 - \frac{1}{\cosh(\kappa l/2)} \approx \frac{(\kappa l)^2}{8}. \quad (8)$$

We already see here a way out to the paradox of the enormous experimental activation energy:  $\delta\mu$  is not constant with varying temperature, as needed for Eq. (2) to give an Arrhenius behavior. On the contrary, since  $\kappa$  itself is an Arrhenius exponential [see Eq. (6) above]  $\delta\mu$  varies strongly with temperature [see Eq. (13) below], and this can explain the high apparent activation energy (slope of the solid line in Fig. 1). We assume now that the clustering of advacancies can be described through nucleation theory [15]. Therefore, we write a set of rate equations for the concentrations  $\sigma_n$  of  $n$ -vacancy clusters, and seek for a stationary, nonequilibrium solution. The rate equations can be cast in the form [14]  $\dot{\sigma}_n = J_n - J_{n+1}$ , where  $J_n = a_{n-1}\sigma_{n-1} - b_n\sigma_n$  and the coefficients  $a_n$ ,  $b_n$  are appropriate functions of  $D\rho_0 + \Lambda\sigma_0$ ,  $\sigma$  and  $l$ , describing birth and death of the clusters  $\sigma_n$  of  $n$  vacancies. We see that the stationary solutions are found for  $J_n = J = \text{const} \forall n$ , where  $J$  is a continuous parameter, representing the stationary "current" in the abstract space of the indices  $n$ . The special value  $J=0$  (no current) corresponds to the equilibrium solution. The coefficients  $a_n$  and  $b_n$  are fixed by the requirement of satisfying detailed balance at equilibrium. Solving iteratively for  $\sigma_n$  and defining  $f_p = \exp[\beta\gamma\sqrt{\pi p} - \beta\pi\delta\mu p]$ , we obtain [14]

$$\sigma_n f_{n-1} = \sigma - \frac{J}{D\rho_0 + \Lambda\sigma_0} \sum_{p=1}^{n-1} f_p. \quad (9)$$

Letting  $n \rightarrow \infty$ , the left-hand side vanishes and one finds

$$J = \sigma(D\rho_0 + \Lambda\sigma_0) \left( \sum_{p=1}^{\infty} f_p \right)^{-1}. \quad (10)$$

Approximating the summation in Eq. (10) by a Gaussian integration and using  $\sigma \approx \sigma_0$ , the difference being of order  $\beta\delta\mu$ , which is small, we obtain [14]

$$J \approx \sigma_0(D\rho_0 + \Lambda\sigma_0) \left( \frac{\beta\delta\mu^3}{4\pi\gamma^2} \right)^{1/2} \exp\left[-\frac{\beta\pi\gamma^2}{\delta\mu}\right], \quad (11)$$

where  $\gamma$  is the line stiffness of a monatomic step averaged on the orientations  $n$  of the step, and the order of magnitude of  $\delta\mu$  is given by Eq. (8). We stress that, due to the strong temperature dependence of  $\delta\mu$ , the nucleation rate  $J$  does not have a simple Arrhenius form.

We are now in a position of comparing Eq. (11) to the measured  $J$  (Fig. 1). First of all, since we have little information on the advacancy mobility [22,25], we make the simplifying reasonable assumption  $\rho_0 D \geq \sigma_0 \Lambda$  [22], and neglect the latter in Eq. (11). We then rewrite formula (11) in a form which makes explicit the temperature dependence,

TABLE II. Parameters in Eqs. (12) and (13) which give the values shown in the third column and the curve in Fig. 1. Symbols are the same as in Table I,  $D_0$  is the prefactor of the adatom surface diffusion coefficient  $D$ .

$W_a + W_{sd}$ (eV)	$W_c - W_{sd}$ (eV)	$W_{adv}$ (eV)	$\gamma$ (meV/atom)	$D_0$ ( $s^{-1}$ )
2.2	2.3	2.4	33	$10^{14}$

$$J = \frac{D_0}{\gamma} \left( \frac{\delta\mu^3(T)}{4\pi k_B T} \right)^{1/2} \times \exp \left[ - \frac{W_{sd} + W_a + W_{adv} + \pi\gamma^2/\delta\mu(T)}{k_B T} \right], \quad (12)$$

$$\delta\mu(T) = \frac{k_B T l^2}{8} \exp \left[ - \frac{W_c - W_{sd}}{k_B T} \right]. \quad (13)$$

Because of the large number of parameters, we have not attempted a real best fit. Nonetheless, we have found a set of parameters, shown in Table II, which reproduces well the experimental result. The theoretical expression is most sensitive to one parameter, the energy difference  $W_c - W_{sd}$  which enters exponentially in determining the chemical potential  $\delta\mu$ , which in turn appears in the argument of an exponential [see Eqs. (12) and (13)]. A 10% variation of this energy difference causes  $J$  to vary over several orders of magnitude, while a similar variation of  $\gamma$  (which also enter an exponential) only causes a variation of a factor 10, that can be easily compensated by slightly changing  $W_{adv}$ . It is therefore comforting to see that our value of  $W_c - W_{sd}$  is in good accord with independent experimental estimates (see Table I). The comparison to the experimental data is shown in an Arrhenius-plot fashion in Fig. 1. There, we plot as empty circles the log of Eq. (12) vs  $1/T$  on the experimental temperature range. The agreement with the experiment is remarkable. We fitted then the empty circles with a straight line (dash-dotted line). The slope of the dash-dotted line would imply an "activation energy" of 25 eV (to be compared with the experimental figure  $23 \pm 3$ ). This number, however, is not an activation energy; the role of the latter is rather played by the exponent  $\pi\gamma^2/\delta\mu$  in formula (12), which is of order 1 eV, but it is not, as it is apparent from Eq. (13), a constant with varying  $T$  as it would be required to give an Arrhenius behavior. It is therefore clear that the puzzling observation of an unphysically large activation energy for *Lochkeim* formation (Fig. 1) is only the result of a misleading logarithmic plot on a too small  $1/T$  range. A direct test of the  $l$  dependence of formulas (12) and (13) was attempted, but no reliable measurements were possible on terraces narrower than 1.9  $\mu\text{m}$ , the largest value at our disposal. However, *Lochkeim* formation is reported in Ref. [8] at 1300 K on terraces of  $\approx 6 \mu\text{m}$ . Equations (12) and (13) with the same parameters as in Table II give  $Jl^2 \approx 1 \text{ s}^{-1}$  at 1300 K for  $l \approx 5.2 \mu\text{m}$ , and at 1285 K for  $l \approx 6 \mu\text{m}$ .

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