

Dynamics of an adsorption-induced roughening transition as a phase transition in a vacancy subsystem

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This letter analyzes the dynamics of a first-order phase transition in the vacancy subsystem in a surface layer of silicon which results in a roughening transition of the silicon surface. Two possible mechanisms for the onset of supersaturation in the vacancy system are proposed. A phase diagram for the transition is found. The distribution of roughness features with respect to height and wave vector is derived. Conditions under which quasiperiodic structures appear on the surface and a stochastic roughness arises are predicted. © 1995 *American Institute of Physics.*

It has recently been observed^{1–3} by scanning tunneling microscopy that the interaction of oxygen with Si(100) gives rise to vacancy voids at the surface, and the surface becomes rough as the exposure time is increased. Analysis of experimental data shows that this effect is observed at gas pressures and temperatures near (below) the threshold for nucleation of the solid oxide SiO₂. For the latter, an adsorption-induced vacancy instability of the crystal determines an abrupt change in the growth rate of the oxide under these conditions. The role of vacancies in the limiting step of the growth of islands of a submonolayer oxide on a crystal surface has been pointed out previously.^{4,5}

In this letter we propose a fundamentally new mechanism for the roughening transition of a crystal surface: a phase transition in a vacancy subsystem in which a supersaturation is created by desorption of volatile molecules of a compound of chemically active particles with crystal atoms (SiO in the case of silicon) from the surface. Another mechanism discussed below for the onset of a supersaturation in the vacancy subsystem is a spontaneous nucleation of vacancies induced by an adsorption of chemically active particles.⁴

The conditions for the occurrence of a roughening transition during adsorption of chemically active particles are quite different from those for the occurrence of this transition for the surfaces of several metals which is observed in ultrahigh vacuum at temperatures $T = (0.5–0.8)T_{\text{melt}}$. The roughening transition has customarily been described as a Kosterlitz–Thouless thermodynamic equilibrium transition in models of the solid-on-solid type.⁶

Below we discuss the dynamics of an adsorption-induced roughening transition in the example of the silicon–oxygen system, for which the literature has experimental data.

According to Refs. 1–3, the kinetic equations for an initially clean silicon surface,

which describe the change in the concentrations of adatoms of oxygen (n_a) vacancies (n_v), and silicon adatoms (n_s) as a function of the time are

$$\begin{aligned} \dot{n}_a &= Q - \alpha n_a n_s, \\ \dot{n}_v &= D_v \nabla \left(\nabla n_v + \frac{1}{T} \nabla u n_v \right) - \gamma n_s n_v + \gamma_1 n_0 n_v^{(0)}, \\ \dot{n}_s &= \alpha n_a n_s - \gamma n_s n_v + \gamma_1 n_0 n_v^{(0)}. \end{aligned} \quad (1)$$

Here Q is the flux of oxygen molecules to the Si surface; α , γ , and γ_1 are the rates of desorption of the oxide SiO, of the “healing” of vacancies, and of the creation of vacancies, respectively; n_0 is the number of lattice sites in a layer $L \approx 10\text{--}30 \text{ \AA}$ thick in which, because the vacancy diffusion coefficient is higher than in the interior,⁷ the average vacancy concentration does not depend on the normal coordinate; and $n_v^{(0)}$ is the equilibrium vacancy concentration. The first term in the equation for n_v describes a diffusion of vacancies for the case in which they interact with each other. In the approximation of a self-consistent field, this interaction is described by

$$u(\mathbf{r}) = \int_0^1 d\lambda \int d\mathbf{r}' V(\mathbf{r}, \mathbf{r}') g_2^{(\lambda)} n_v(\mathbf{r}'),$$

where

$$V(\mathbf{r}, \mathbf{r}') = \begin{cases} \epsilon, & 0 < r \leq a, \\ 0, & r > 0 \end{cases}$$

is the potential of the binary interaction of vacancies, $g_2^{(\lambda)} = e^{-\lambda \epsilon / T}$ is a binary correlation function, and λ is an interaction parameter.⁸

System (1) can be written in the dimensionless form

$$\dot{x} = 1 - \nu x z, \quad \dot{y} = D' \Delta y - \mu (y_0 - z y), \quad \dot{z} = -x y + (y_0 - z y),$$

where $x = \alpha \tau_a n_a$, $y = \gamma \tau_a n_v$, and $z = \gamma \tau_v n_s$ are the dimensionless concentrations of oxygen adatoms, vacancies, and silicon adatoms, respectively; and $\tau_a = (Q\alpha)^{-1/2}$ and $\tau_v = (n_0 \gamma)^{-1}$ are time scales for the changes in the number of adsorbed particles and for the creation of vacancies, respectively. The dimensionless parameters μ and ν are given by

$$\mu = \frac{\tau_a}{\tau_v}, \quad \nu = \frac{\tau_a}{\tau_v} \frac{\tau_\gamma}{\tau_d},$$

where $\tau_\gamma = (n_s^{(0)} \gamma)^{-1}$ is the time scale for the healing of vacancies, and $\tau_d = (\alpha n_s^{(0)})^{-1}$ is a time scale for the desorption of SiO. Estimates based on the data in the review in Ref. 3 show that, for a temperature $T = 1000 \text{ K}$ and an oxygen pressure $P \approx 10^{-6} \text{ torr}$, which are typical of experiments, the parameters μ and ν have the values $\mu = 10^6 \gg 1$ and $\nu \approx 10^{-2} \ll 1$ ($\tau_a \approx 50 \text{ s}$, $\tau_v \approx 10^{-4} \text{ s}$, $\tau_\gamma \approx 10^{-6} \text{ s}$, and $\tau_d \approx 10 \text{ s}$). Under these conditions, with sufficiently wide terraces on the crystal surface ($l \approx 10^{-4} \text{ cm}$)—as is the case

experimentally—diffusion can be ignored in the second equation in system (1) ($l^2/D \approx 10^{-3}$ s $\gg \tau_\gamma$, $D \approx 10^{-5}$ cm²/s at $T = 1000$ K), and a spatially uniform solution of system (1) can be written

$$\begin{aligned} n_a^s(t) &= Qt, \\ n_v^s(t) &= n_v^{(0)} \tau_\gamma \tau_a^{-1} e^{t^2/2\tau_a^2}, \\ n_s^s(t) &= n_s^{(0)} e^{-t^2/2\tau_a^2}. \end{aligned} \quad (2)$$

It follows from (2) that the first step is a linear accumulation of adsorbed particles. The number of vacancies on the surface increases more rapidly than exponentially over a time t on the order of the time scale τ_a . The number of adsorbed crystal atoms tends toward zero by the same law, and over the same time.

The time scale for the onset of the instability in this system is, as we show below, on the order of 10^{-6} s. This time is considerably shorter than the time scale for increases in the concentrations n_a and n_v (which is ~ 10 s in order of magnitude). Accordingly, to analyze the stability, we can write small deviations δn_a and δn_v from quasisteady solution (2) in the form $\delta n_a \sim e^{\lambda_1 t}$, and $\delta n_v \sim e^{\lambda_2 t}$. Going over to the Fourier representation, we find

$$\begin{aligned} (\lambda_1 + \alpha n_s^s) \delta n_a &= 0, \\ [\lambda_2 + \tilde{D}_v(k) + \gamma n_s^s] \delta n_v &= 0, \end{aligned} \quad (3)$$

where

$$\tilde{D}_v(k) = D_v k^2 \left[1 + \frac{2}{3} \pi a^3 n_v^s (1 - e^{\epsilon/T}) f(k) \right], \quad (4)$$

$$f(k) = 3 \left[\frac{\sin ka}{(ka)^3} - \frac{\cos ka}{(ka)^2} \right], \quad (5)$$

and a is the lattice constant.

It follows from Ref. 3 that the natural modes of the linearized system are

$$\lambda_1 = -\alpha n_s^s, \quad \lambda_2 = -[\tilde{D}_v(k) + \gamma n_s^s]. \quad (6)$$

According to (2) we have $n_s^s \rightarrow 0$ at $t \gg \tau_a$, so an instability occurs ($\lambda_2 > 0$) only in the vacancy subsystem, under the condition

$$\tilde{D}_v(k) < 0. \quad (7)$$

In the limit of small wave vectors ($ka \rightarrow 0$), according to (4) and (5), this inequality holds when the vacancy concentration reaches

$$n_v^c = \frac{3}{2\pi a^3 (e^{\epsilon/T} - 1)} \approx 10^{19} \text{ cm}^{-3}, \quad (8)$$

($\epsilon \approx 1$ eV, $a \approx 3$ Å, $T \approx 1100$ K).

Using the density-functional method,⁹ we can derive an equation for the amplitude of an unstable mode, $\xi = \delta n_v$. This equation describes the onset of the vacancy instability and is an equation for the order parameter of the vacancy subsystem:

$$\dot{\xi}_k = -\tilde{D}_v(k)\xi_k + \frac{\partial \tilde{D}_v}{\partial n_v} \xi_k^2 + \frac{2}{n_0} \frac{\partial \tilde{D}_v}{\partial n_v} \xi_k^3. \quad (9)$$

Using (4) and (8), we see that in the limit $ka \rightarrow 0$ this equation reduces to a Landau–Ginzburg equation for the order parameter, which describes the case of void formation:

$$\dot{\xi} = -D_v \Delta (\mu \xi + b \xi^2 + \Gamma \xi^3), \quad (10)$$

where

$$\mu = \frac{2}{3} \pi a^3 n_v^s (e^{\xi/T} - 1), \quad b = \frac{2}{3} \pi a^3 (1 - e^{\xi/T}), \quad \Gamma = \frac{4}{3} \frac{\pi a^3}{n_0} (1 - e^{\xi/T}).$$

We know¹⁰ that Eq. (10) describes the kinetics of the nucleation and growth of vacancy voids at low supersaturation levels. The coefficients in (10) are calculated in terms of the kinetic parameters of Eqs. (1). It is thus possible to describe the formation of vacancy voids observed in Ref. 3 in an interaction of silicon with oxygen.

The onset of the vacancy instability at a high supersaturation level, $n_v > n_v^c$, is described by an equation which follows from (9) and (5):

$$\dot{\xi}_k = \tilde{D}_v k^2 \left\{ \left[\frac{n_v}{n_v^c} f(k) - 1 \right] \xi_k + \frac{1}{n_0} e^{\xi/T} \xi_k^2 - \frac{1}{n_0^2} e^{\xi/T} f(k) \xi_k^3 \right\}. \quad (11)$$

In the linear approximation in ξ we have

$$\dot{\xi}_k = -R(k) \xi_k \quad (12)$$

and $R(k) = D_v k^2 [1 - \eta f(k)]$.

The quantity $\eta = n_v/n_v^c$ represents the supersaturation of the vacancy subsystem. We write a solution of Eq. (12) in the form

$$\xi_k(t) = A(k) e^{-R(k)t}. \quad (13)$$

By analogy with a concept introduced in the theory of spinodal theory,¹¹ we can thus call the function $R(k)$ the “gain” of the instability, and the onset of an instability at $R(k) < 0$ (Fig. 1) can be treated as spinodal decay in a vacancy subsystem.

Figure 1 shows the functional dependence $R(k)$ for $\eta = 1.3$. We see that all modes with k values satisfying the inequality $0 < k < k_c$, where $k_c a = 1.66$, become unstable. The critical wave vector k_c depends on η and can be found from the equation $\eta^{-1} = f(k_c a)$. It follows from (13) that the instability of the mode ξ_{k_m} develops most rapidly. This mode corresponds to a minimum of $R(k_m a)$ at $k_m \approx k_c / \sqrt{2}$. Estimates show that as the supersaturation is increased from 1.1 to 1.5 the length scale of the irregularities which arise in the vacancy system, $\lambda_m = 2\pi/k_m$, falls off from $\lambda_m = 9.1a$, to $4.8a$.

According to (2) and (8), the supersaturation η depends on the gas pressure, the exposure time, and the temperature. For any given values of k_c , it is thus possible to construct a surface which forms a lower bound on the region of values of the variables P, T , and t for which an instability of the vacancy subsystem occurs (this is a phase diagram of the system). That surface is determined by the equation

$$\eta(P, T, t) f(k_c) = 1. \quad (14)$$

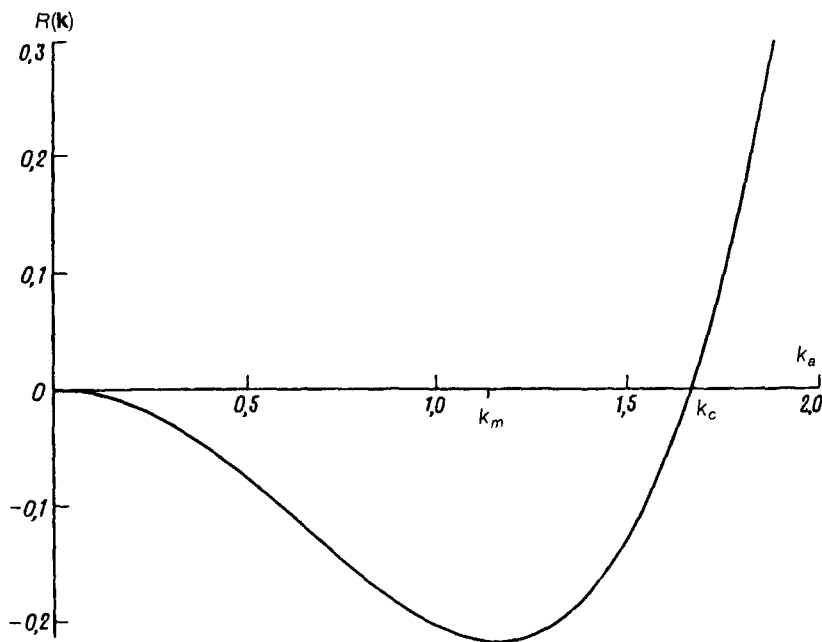


FIG. 1. The gain R versus the wave vector k for a supersaturation level $\eta=1.3$.

According to (2) and (8), this equation can be written

$$Pt^2e^{-E/T} + \epsilon/T = C(k_c a). \quad (15)$$

Here $C(k_c a)$ is a function which can easily be determined through the use of expressions (2), (5), and (8). The quantity E is the activation energy for the formation and desorption of molecules of volatile products. In writing (15) we assumed that the activation energies for the healing and formation of vacancies are approximately the same.

Figure 2 shows a phase diagram of the system constructed from (15) for the values $k_m = 4 \times 10^7 \text{ cm}^{-1}$ and $\eta = 1.3$. The minima on the plots of $P(T)$ and $t(T)$ at $t = \text{const}$ and $P = \text{const}$, respectively, stem from a competition between two processes: the accumulation of vacancies as molecules of volatile products form and desorb and the decay of vacancy complexes. Accordingly, in order to achieve a given value of η at both low and high temperatures, we need either higher gas pressures or a longer exposure time. According to (14), surfaces which correspond to smaller values of k_m lie above that in Fig. 2.

Our estimates show that the inequality $R^{-1}(k_m a) \ll \tau_a$ holds for the time scales for the onset of the instability in silicon as it interacts with oxygen for the region of P and T values corresponding to Fig. 2. The activation energy for vacancy diffusion, for example, is¹² $E_v \approx 1 \text{ eV}$; at $T = 900 \text{ K}$, $P = 10^{-7} \text{ torr}$, and $k_m = 4 \times 10^7 \text{ cm}^{-1}$, we have

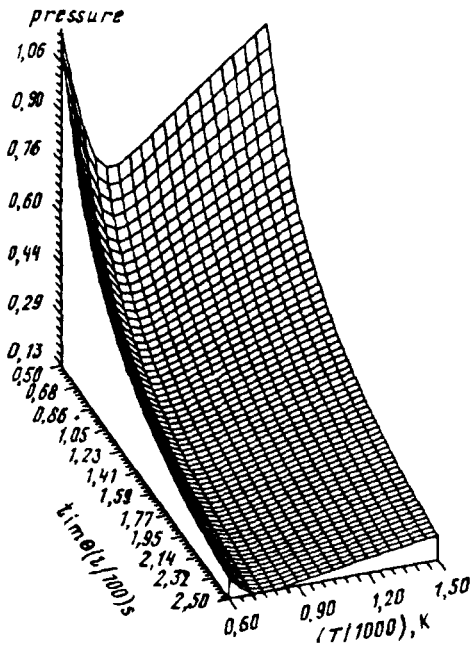


FIG. 2. P, T, t phase diagram for $k_m \approx 4 \times 10^7 \text{ cm}^{-1}$ and $\eta = 1.3$.

$R^{-1}(k_m a) \approx 10^{-6} \text{ s}$ and $\tau_a \approx 50 \text{ s}$. It is thus interesting to analyze the formation of the surface of the crystal as it interacts with chemically active particles near values of P , T , and t such that the relation $n_v \approx n_v^c$ holds.

We introduce a roughness height referred to a unit surface area: $h = aL\xi$. An equation describing the dynamics of the onset and development of a surface roughness according to (11) can be written as follows:

$$\dot{h} = -D_v k^2 \frac{\partial F_k}{\partial h}, \tag{16}$$

where

$$F_k + k = \frac{1}{2} \lambda(k) h^2 - \frac{1}{a n_0} \exp(\epsilon/T) h^3 + \frac{1}{a^2 n_0^2} \exp(\epsilon/T) h^4, \text{ and } \lambda(k) = 1 - \eta f(k).$$

The quantity F_k is the “free energy” of the rough surface. We see that F_k has the same form as the free energy which is analyzed in the theory of first-order phase transitions. Analysis of the dynamics of behavior of this system thus reduces to a known procedure.

The solution of the equation $\partial F_k / \partial h = 0$ has three roots:

$$h_1 = 0, \quad h_{2,3} = \frac{3}{8} a n_0 \left(1 \mp \sqrt{1 - \frac{16}{9} \lambda(k) e^{-\epsilon/T}} \right).$$

They describe the states of a smooth surface ($h=h_1$) and of a rough surface ($h=h_3$). The smooth-surface state ($h=h_1$) is metastable during adsorption of oxygen; the height of the barrier for the nucleation of voids, $F(h=h_2)$, tends toward zero as $n \times f(k) \rightarrow n_c$.

The correlation function for the heights of the roughness features is

$$\langle \delta h |^2 \rangle = \left(\frac{\partial^2 F_k}{\partial h^2} \right)^{-1} = \begin{cases} \approx 1/\lambda, & h=h_1, \\ \approx e^{-\epsilon/T}, & h=h_3. \end{cases} \quad (17)$$

As $nf(k) \rightarrow n_c f(\mathbf{k})^{-1}$, the correlation function at the point $h=h_1$ diverges; it is finite at the point $h=h_3$.

The distribution (W) of roughness features with respect to height h can be found as a function of \mathbf{k} as a steady-state solution of the Fokker-Planck equation corresponding to a Langevin equation for h . In the Gaussian approximation, W is

$$W(h, \mathbf{k}) = \sqrt{\frac{\beta}{\pi}} e^{-\beta(h-h_3)}, \quad (18)$$

where $\beta(\mathbf{k}) = -2\lambda(\mathbf{k}) + 3e^{-\epsilon/T}h_3$.

At a supersaturation level $\eta \approx 1$ ($n_v \approx 10^{-4}$ and $T=969$ K), the probability $W(h, k)$ has a narrow peak, which indicates the formation of quasiperiodic structures with a period close to $\lambda_m \approx 2\pi/k_m \approx 20 \text{ \AA}$ and a relief height $h \approx 20 \text{ \AA}$ on the surface. As the temperature is lowered and as η is thus increased, according to (14), all modes with $0 < k < k_c$ become unstable, and the probability distribution $W(h, k)$ describes an irregular surface relief. It apparently corresponds to the irregular structure of the silicon surface which was found in Ref. 3 and which arises in the interaction of Si with oxygen.

Finally, we note that, according to Ref. 4, the vacancy instability can be induced by an adsorption of oxygen on Si. Calculations show that the expression for $n_v^s(t)$ in (4) should be replaced in this case by

$$n_v^s(t) = n_v^{(0)} \tau_v^{-1} \exp \left[\frac{V_{av} n_0}{T} \frac{\tau_p t}{\tau_a^2} + \frac{t^2}{2\tau_a^2} \right], \quad (19)$$

where V_{av} is the adatom-vacancy interaction potential, and $\tau_p = (\epsilon n_0)^{-1}$ is the time scale for the creation of vacancies due to the escape of SiO. For this mechanism, only the $n_v(t)$ dependence in the stage of vacancy accumulation changes. However, the results found above on the dynamics of the formation of rough surfaces and on the characteristics of these surfaces remain the same. One can distinguish between these two mechanisms by examining the diagram for the roughening transition.

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