Submonolayer Growth with Repulsive Impurities: Island Density Scaling with Anomalous Diffusion

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We examine the island density during submonolayer growth on a surface with randomly distributed repulsive impurities. Rate-equation analysis suggests a scaling relation which is tested by simulations. This relation can be used in conjunction with experiments to determine the exponent characterizing "anomalous" diffusion.

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Numerous experiments have shown that the shape of a solid surface or the properties of a film grown on it can be appreciably altered by the presence of small amounts of impurities. Smooth Ge films can be grown on the Si(100) surface covered by a monolayer of Sb, Bi, Te, or Ga [1–7], while films grown on the clean surface are rough. The presence of a little oxygen on a Pt(111) surface changes the growth of a Pt film so that two-dimensional islands are formed in preference to the three-dimensional structures obtained on the pure Pt surface [8]. A small amount of Pt deposited on Pt(111) will cause a massive surface reconstruction [9]. A monolayer of Pd, Pt, Ir, Rh, or Au on W(111) [10–13] leads, upon annealing, to the spontaneous formation of large pyramids, while Ti, Co, Ni, Cu, and Ag cause no such faceting. The three-dimensional growth of Ag/Ag(111) becomes two dimensional if a submonolayer of Sb is deposited on the surface before the growth begins [14,15].

From these examples it should become clear that various impurities are likely to act through very different mechanisms. One, in which the impurities facilitate intralayer transport, has already been examined theoretically by Zhang and Lagally [16]. Here we consider a different model, in which randomly distributed impurities repel the atoms deposited on the surface and affect their migration, nucleation, and aggregation. A possible example is provided by the growth of Ag on Ag(111) precovered with a small amount of Sb [14]. According to the density functional calculations [17], the Sb atoms burrow into the top surface layer and exert a long-range (i.e., several lattice sites) repulsion on the Ag atoms diffusing on the surface. Another example is a surface on which small holes have been created by sputtering [18,19]. The probability that an adsorbed atom descends in a hole is smaller than the probability that the atom will move away from the hole's border; the holes act as centers exerting a short-range repulsion on the migrating atom. Many other examples are provided by the chemical kinetics of bimolecular reactions taking place on a surface, where various additives diminish the ability of reactants to meet. Similarly, various ligands used in metalorganic chemical-vapor deposition (e.g., hydrogen or alkali radicals) can block surface sites and affect, as described here, the migration of the atoms forming the film.

We propose here that the changes observed in a system for which Sb/Ag(111) is a typical representative are due to the anomalous [20] diffusion of the Ag atoms on the surface having repulsive centers (such as Sb). This differs from previous interpretations which have assumed that the effect of Sb is to increase the activation energy for diffusion.

It is well known [20] that the presence of repulsive centers diminishes the mean-square displacement of a particle performing a random walk among them. A smaller displacement will result in increased island density and will favor two-dimensional growth [21] in the earlier stages of deposition. In the later stages the ability of an atom deposited on top of an existing island to descend from it becomes an additional parameter [21,22] which, in our model, is not affected by the impurities.

We will show, by analysis and by simulations, that one of the more dramatic manifestations of the presence of repulsive impurities (e.g., Sb on Ag) is a modification of the scaling laws for island density. It is well known that in the early stages of growth (i.e., low submonolayer coverage) on a clean surface, the island density N satisfies the scaling relation [23–29]

$$N \sim (h/r)^{-\lambda}, \tag{1}$$

where h is the site-to-site hopping rate for the single atoms and r is the deposition rate. In two dimensions $\lambda = \frac{1}{3}$, and in one dimension $\lambda = \frac{1}{4}$. This scaling relation has been confirmed by simulations [23] and, in part, by experiment [30], and was used [31] to analyze data. Mo *et al.* [32] have employed it to determine the activation energy of a single atom diffusion. We show that the density of the islands grown on a surface having randomly distributed repulsive centers satisfies a new scaling law. This can be used to analyze the data and establish the growth mechanism and also to determine the manner in which single atoms move through the repulsive network.

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To define the rate equations for island growth on a surface with impurities on it, we need to know the dependence of the mean-square displacement on time. We find it by performing simulations. We use a square lattice having a fraction of the sites occupied by repulsive impurities. We then place randomly a walker on a lattice site and follow its motion. The rate of a jump to a neighboring site, in the absence of the impurities, is given by $h = 10^{13}\exp[-\beta E_0]\ \mathrm{s}^{-1}$, where E_0 is the activation energy. We assume that the walker-impurity interaction energy is equal to $(0.5/\rho^3)$ eV if the walker-impurity distance ρ is at most three lattice sites away, and is zero otherwise. The unit length here is the lattice constant of the surface. The qualitative results depend on the existence of long-range repulsion, but are insensitive to the specific form of the interaction energy. To simulate the effect of impurities on the walker's migration, we calculate the difference $E_s = E_f - E_i$, where E_i (E_f) is the interaction energy of the walker with all the impurities when the walker is at its location before (after) a jump. If E_s is negative, we perform the jump. If E_s is positive, we perform the jump with probability equal to $\exp[-\beta E_s]$. This procedure generates a kinetic scheme in which the random walker tends to avoid the impurity.

The mean-square displacement (for a large number of such walkers) has an interesting time dependence. At early times

$$\langle R^2\rangle \sim t \quad \text{for } t < \tau_1\,. \tag{2}$$

Here τ_1 is the time in which most of the walkers in the ensemble did not travel far enough to interact with the impurities. At a longer time

$$\langle R^2\rangle \sim t^{\alpha} \quad \text{for } \tau_1 < t < \tau_2\,, \tag{3}$$

and α depends on impurity coverage and temperature (see Fig. 1). At even longer times ($\tau_2 < t$) we expect $\langle R^2\rangle \sim t$ [20]. In what follows we assume that the deposition conditions are such that the time τ in which a deposited particle meets an island or another particle satisfies $\tau_1 < t < \tau_2$. This condition and Eq. (3) are always satisfied in our simulations.

We note that Eq. (3) is satisfied by many random-walk models on lattices with random static disorder [20]. The purpose of the above simulations was not to establish Eq. (3), which we expected, but to determine how α depends on the temperature T and the impurity concentration c. We need this information in our study of island formation. We also note that a change in the walker-impurity interaction affects the dependence of α on T and c, but does not change Eq. (3).

We can now turn to the main question: Is there a scaling equation for the number of islands formed by atoms walking through this impurity network? If so, what is the form of the scaling law? To "derive" it we need to modify the rate equations [23,26] to take into account the presence of the impurity. Let H_d be the number of distinct sites a random walker visits during its lifetime τ (i.e., the time between its deposition and its joining an island or another single atom), then on average we have [23,26] $H_d \sim 1/(n + N)$, where n is the free adatom density and N is the island density. Through simulations of a single walker in the presence of impurities, we find that $H_d \sim H^{\alpha}$, where H is the number of random hops. This is in agreement with Eq. (3). Since $H = h\tau$, then one finds that

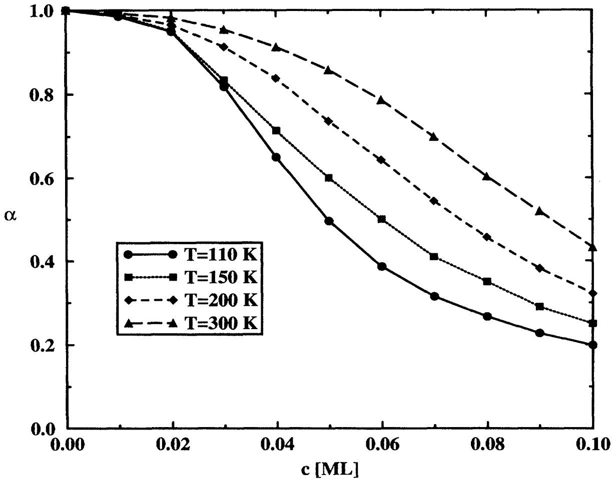

FIG. 1. Single particle diffusion exponent α as a function of coverage of impurity c at four different surface temperatures.

$$(h\tau)^{\alpha} \sim 1/(n + N)\,. \tag{4}$$

It is interesting to note that the above equation recovers the cases of diffusion in two dimensions and one dimension when $\alpha = 1$ and $\frac{1}{2}$, respectively [29,33]. Applying Eq. (4) to the rate equations [23]

$$dn/dt = r - n/\tau\,, \tag{5a}$$

$$dN/dt = (n/\tau)(n/n + N)\,, \tag{5b}$$

one obtains a new scaling relation of island density

$$N = B(T,c)\,(rt)^{\chi_1}(h/r)^{-\chi_2} \tag{6}$$

with

$$\chi_1 = \chi_2 = \alpha/(1 + 2\alpha) \equiv \chi\,. \tag{7}$$

While deriving Eq. (6), we have made the steady-state approximation $dn/dt \approx 0$ and have assumed that the monomer density n is much smaller then the island density N. Both assumptions have been tested by solving numerically Eqs. (4) and (5). Equation (7) is valid only for two-dimensional systems. The factor $B(T,c)$ is a function of the temperature T and the impurity coverage c. In our simulations we find that $B(T,c)$ is close to 1. The calculation of $B(T,c)$ from information on the diffusion of a *single* random walker will be explained elsewhere. For a clean surface, B is a constant. We have written

Eq. (6) in this form to display the role of the adatom coverage $\theta = rt$. In the absence of impurities, $\alpha = 1$ and $\chi_1 = \chi_2 = 1/3$, as obtained previously [23,26]. Note that α depends on both impurity coverage and temperature (see Fig. 1) and can differ substantially from 1.

The same scaling law [Eq. (6)] can also be derived [34] from the first two equations in Ref. [24] by using an effective diffusion constant [20] $D \sim hL^{2(1-1/\alpha)} \sim hN^{-(1-1/\alpha)}$. Here L is the mean distance between the islands.

This new scaling law is next tested by computer simulations. We use a 500×500 square lattice with the impurities distributed randomly on it. Since we are interested in the number of islands and this is established in the early deposition time, we treat each island as if it occupies one lattice site. This procedure worked well in the case of a clean (i.e., no impurities) surface [23].

In Fig. 2 we plot the results of the simulations in a form convenient for the analysis of scaling with respect to h/r. All points were determined for $E_0 = 0.2$ eV, an impurity coverage of 5%, and a temperature of 110 K. For example, the data shown by circles were obtained by counting how many islands were present on the surface at the time t when the atoms deposited on the surface (i.e., rt) occupied 5% of the lattice sites. In these simulations we have varied r between 10^{-2} and 3.3×10^{-6} ML/s. We see from Fig. 2 that $\ln N$ vs $\ln(h/r)$ is linear (at constant $\theta = rt$), as predicted by Eq. (6). The graph gives $\chi_2 = 0.21 \pm 0.02$. The mean number of jumps $h\tau$ performed by a single walker during its lifetime is between 10^2 and 10^5, while $h\tau_1 \leq 10^2$ and $h\tau_2 \geq 10^6$. This confirms that Eq. (3) holds. The value of α for the impurity coverage and the temperature used in the simulations is $\alpha = 0.48$, which leads to $\chi_2 = 0.245$ [see Eq. (7)].

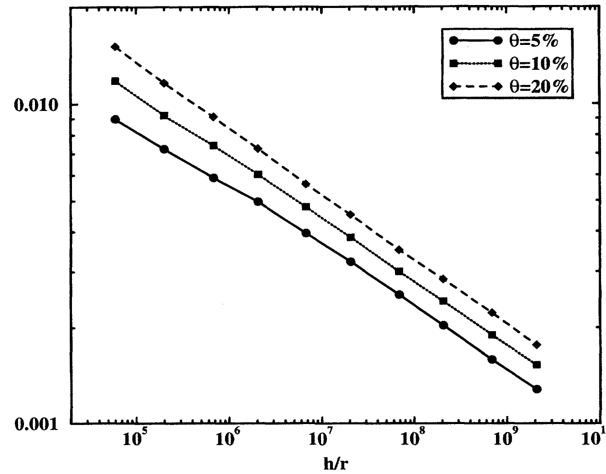

FIG. 2. Island density N as a function of the ratio h/r at three different adatom coverages $\theta = rt$. The coverage of impurity is 5% and the temperature is $T = 110$ K. The points are averages over at least 40 runs on a 500×500 square lattice.

The agreement between the rate-equation predictions and the simulations can be improved by making a small "logarithmic correction" [23] to the rate equations. The "corrected" equations cannot be solved analytically. However, the numerical solutions agree with the results of the simulations within the statistical error. The logarithmic correction is negligible if a walker makes an infinite number of hops before joining an island. The error caused by a finite number of hops is small.

We note that for a surface with impurities there is no temperature scaling because both the factor B and the exponent χ depend on temperature. The absence of temperature scaling is not very surprising since the presence of the impurities introduces a second energy scale (the walker-impurity interaction) in the problem, besides the activation energy of single atom diffusion.

We conclude with a few remarks regarding the implications of these results. The presence of randomly distributed repulsive centers on the surface diminishes the distance traveled by the walkers in a given time and therefore delays the moment when the walkers meet to form islands; as a result, island formation occurs at a higher walker coverage. This increases the island density, in agreement with the observations of Vrijmoeth *et al.* [15] who noted that the number of islands formed when Ag is deposited on a Sb-covered Ag(111) surface is dramatically higher than the number formed when Sb is absent. This happens when the surface is annealed, after Sb deposition and prior to Ag deposition. The Sb atoms are embedded in the top layer [15] and, according to Oppo, Fiorentini, and Scheffler [17], repel the adsorbed Ag atoms. It is found [15] that with 8% of Sb on Ag(111), the island density increases by a factor of 6 as compared to the clean surface. With 30% of Sb precoverage, the island density increases by a factor of 10^3. Since the experiments were carried out at a value of h/r for which a kinetic Monte Carlo simulation of the growth requires more computer power than is available to us, we use the rate-equation result [Eq. (6)] to estimate the island densities $N(c)$ at different Sb coverage c. Simulation for a *single* random walker at $T = 300$ K gives us $\alpha = 0.60$ at $c = 8\%$ (as shown in Fig. 1) and $\alpha = 0.10$ at $c = 30\%$ (not shown in Fig. 1). The factors $B(T,c)$ are found to be $B(T = 300\text{ K}, c = 0\%) = 0.98$, $B(T = 300\text{ K}, c = 8\%) = 0.71$, and $B(T = 300\text{ K}, c = 30\%) = 1.0$. The dominant term in Eq. (6) is $(h/r)^{-\chi_2}$, whose value depends on E_0, the activation energy for Ag diffusion on the clean Ag(111) surface. If $E_0 = 0.20$ eV, we get $N(c = 8\%)/N(c = 0\%) = 4.2$ and $N(c = 30\%)/N(c = 0\%) = 1.2 \times 10^3$. If $E_0 = 0.15$ eV, we have $N(c = 8\%)/N(c = 0\%) = 4.7$ and $N(c = 30\%)/N(c = 0\%) = 1.8 \times 10^3$. These results are in satisfactory agreement with the experimental values. Moreover, an increase of island density is known [21] to favor two-dimensional growth, and this is in agreement with the earlier observations of van der Vegt *et al.* [14].

Our main conclusion is that the assumption that the role of Sb is to create randomly distributed repulsive centers on the surface is consistent with the experimental data. The main role of the repulsive network is to change the character of the diffusion and slow it down. The diminished mobility leads to an increased island density. The changed character of diffusion leads to new scaling relations in which the island density has a strong dependence on the impurity concentration.

The new scaling relations can be used to extract from the island-density data the value of α and its dependence on impurity coverage c and temperature T. This can be done by plotting the island density N (measured at fixed T, c, and rt) as a function of $1/r$. The functional dependence of island density on coverage obtained here is an artifact of the point-island model [23,35] and should not be used to examine data. But finite island size has little effect on the flux scaling as long as the island sizes are much smaller than the interisland distances. Thus detailed information about the "percolation properties" of a network of repelling centers can be obtained experimentally. Such measurements are very difficult by other methods.

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