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Nucleation and diffusion of Cu adatoms on Cu(100): A helium-atom-beam scattering study

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We have determined the diffusion coefficient of a Cu adatom on Cu(100) by using helium-atom-beam scattering as a probe. Our approach relies on measuring *in situ* and in real time the separation between islands nucleated on individual terraces during a submonolayer deposition of Cu. The method can be applied with other surface-sensitive diffraction techniques as well.

The migration of adatoms on surfaces in a fundamental problem in surface science and has attracted attention for many years and still does.[1-7] However, despite its importance, techniques for determining the pure migration coefficient in a reliable way are rare. Field ion microscopy (FIM) experiments[1,2] have provided most of our insights into how diffusion of individual atoms on surfaces occur, but this technique is restricted in the number of appropriate materials due to the high field used for imaging. The energies inferred from a Boltzmann Matano analysis,[4] based on the spreading of an initially well-defined mass-density profile, contain in general more than just the activation energy for diffusion, but also a detachment energy. The close relation between diffusion and growth in order to determine the diffusion coefficient has been explored as well. A huge body of valuable data has been obtained by measuring number densities of islands formed after deposition, mostly with scanning electron or Auger electron microscopy.[5] However, in general only "effective" values for migration coefficients are reported, because diffusion distances in these experiments are typically of the order of micrometers. Therefore, residual steps might influence the diffusion and nucleation process. Very recently with this procedure, information on surface diffusion on a local scale has been obtained using the scanning tunneling microscope (STM).[6] However, as long as the actual measurements are done only at room temperature, this method is restricted to materials with low diffusivity in order to freeze mobility at 300 K. STM investigations at variable temperatures are only just beginning and are still very difficult to perform.[7]

Our approach to explore the close relation between diffusion, nucleation, and growth is to use helium-atom-beam scattering as a probe. He scattering has been shown in the past to be a very useful tool for investigations on the structure and the dynamics on surfaces.[8] Applications to the kinetics are rare and often rather indirect. In the time-of-flight mode, diffusion has been investigated by measuring the energy transferred to scattered particles through mobile surface atoms.[9] To date, these experiments are restricted to systems with extremely high diffusion coefficients because of limitations in the energy resolution. A different but rather indirect way to obtain information on diffusion is to monitor the disappearance of intensity oscillations of the specularly reflected beam in multilayer deposition experiments at high temperatures under step flow condition.[10]

Here, we focus on the nucleation of adatoms to islands on individual terraces between residual steps. Little can be said in that case by just measuring the intensity of the specular beam. Therefore, we explore the whole diffraction pattern made up by the arrangement of islands. In this way, information on the number density of islands is obtained. Nucleation theory[5,6] relates this quantity to the migration coefficient. The measurements are performed *in situ* and in real time for a homogeneous system. Therefore, possible distortions due to sample transfers, temperature quenches, or replica techniques can be avoided. Because the island formation process is investigated at a submonolayer level and on individual terraces, disturbing influences due to coalescence or residual steps can be kept negligibly small. We feel that this approach has a potential for general application. We demonstrate here its performance for the migration of Cu on Cu(100).

Random deposition of adatoms drives the system into nonequilibrium, because the number of defects created this way does not correspond to the equilibrium concentration. The system tries to restore equilibrium. This is done by forming islands. Rate equation theories, which are currently in use and believed to give a rather detailed picture of the nucleation process, predict the following scenario:[5] Adatoms arriving on the surface make random walks. Due to encounters of adatoms, stable nuclei are formed, which subsequently grow to islands. The number density of stable nuclei N_x at a given time depends essentially on the arrival rate of adatoms R, the mobility of adatoms at a given temperature, and the size of the critical nucleus. At the very beginning of the nucleation process, in the transient regime, the number density N of adatoms increases steeply with deposition time, and so does the density of stable nuclei N_x. Thereafter, in the steady-state regime, adatoms are predominantly captured by already existing nuclei, which in turn drastically reduces the adatom number density N. At this stage, new nuclei are formed only at a low rate, and N_x increases slowly before it decreases due to coalescence.

In both regimes the parameter dependence on N_x is expressed as[5]

$$N_x(1,2) = f(\Theta,i)(R)^p \exp(E_n/kT) ,$$

with $p=(i+1)/(i+3)$ and $E_n=[E_i+(i+1)E_d]/(i+3)$

at the end of the transient regime [$N_x(1)$], but $p = i/i+2$ and $E_n = (E_i + iE_d)/(i+2)$ at the end of the steady-state regime [$N_x(2)$]. i is the number of atoms in the critical nucleus, E_i the binding energy of the critical nucleus, and E_d the activation energy for migration. The function $f(\Theta,i)$ depends on the coverage Θ and on specific material parameters.[5,6] It can be seen that the preexponential factor (from the limit $1/T = 0$) and the activation energy for migration can be deduced without relying on in general unfamiliar binding energies of nuclei, when $i = 1$, i.e., if the size of the critical nucleus is 1 and a dimer forms a stable nucleus. For strongly bonded materials, such as metals, the dimer is expected to be stable at only low enough temperatures.[11]

Our experiments were performed in a Campargue-type source Helium-atom-beam spectrometer. The Cu sample, oriented within 0.1° to (001) direction, was desulphurized for 2 months in a hydrogen atmosphere at 1200 K before being mounted into the apparatus. Cu was evaporated from a high-purity, desulphurized Cu disk heated by a W filament. The average terrace length of our sample is estimated from helium-atom-beam scattering experiments to at least 700 Å.

Figure 1 shows a series of angular distributions obtained in the out-of-phase condition during deposition of Cu at a rate of 2700 sec/monolayer (ML). As expected, the specular intensity decreases continuously with increasing coverage up to 0.5 ML. For coverages larger than about 0.1 ML, additional diffraction peaks are detected, whose intensities increase with increasing coverage. The angular position of the diffraction peaks reflects a characteristic length L that is associated with the nucleation and growth of islands.

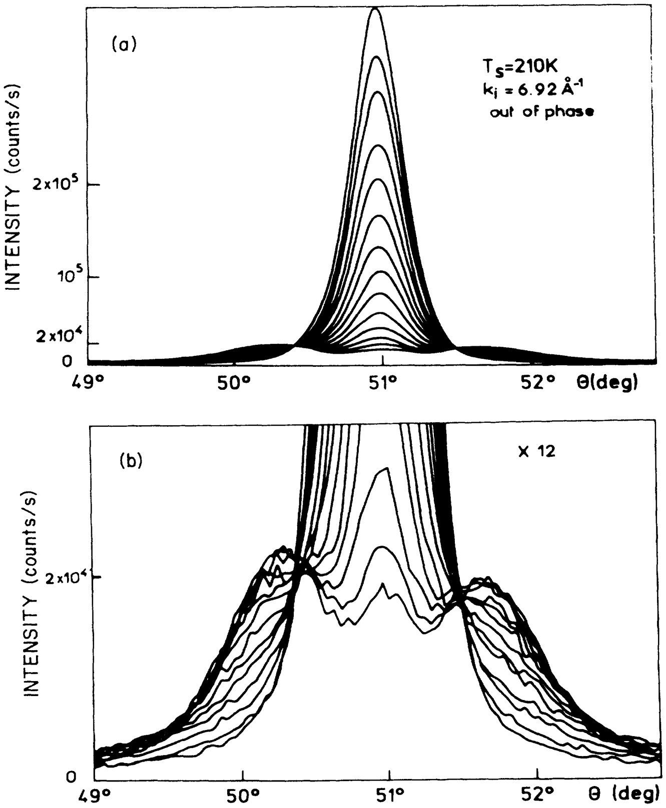

FIG. 1. Series of angular distributions, taken in the out-of-phase condition, as a function of time during deposition of Cu at a rate of 2700 sec/ML. Each scan takes 104 sec. The specular intensity ($\Theta = 51°$) decreases, while additional diffraction peaks appear. The diffraction peaks reflect the separation between islands formed during deposition.

Generally, the diffraction pattern contains information on both the island separation and the island size distribution. The spatial distribution of islands in growth processes typically is not random, because nucleation is less likely in the immediate vicinity of existing islands.[5] Island size distributions show a relatively sharp maximum that is associated with the largest islands.[12] In order to elucidate what information is associated with the position of the experimentally observed diffraction peak, we have performed a simple simulation of the diffraction pattern within the kinematic approximation.[13] A narrow distribution of island center separations and sizes produces a series of diffraction peaks in the simulation. Their position reflects the mean separation between islands. The addition of smaller island center separations and sizes suppresses higher-order diffraction peaks, without, however, affecting the *position* of the first-order diffraction peaks. We therefore identify the experimentally determined characteristic length L with the periodicity imposed by *large* islands formed during the growth process. According to Zinsmeister and others,[12] these islands were nucleated in the very beginning of the growth process. L is therefore not related to the total density of islands $N_x(2)$ formed after deposition, but only to $N_x(1)$ via $L = 1/[N_x(1)]^{1/2}$.[14] This assignment explains the experimental observation that the position of the diffraction peak is independent of coverage up to 0.7 ML. Although the diffraction pattern is recorded under steady-state conditions, it contains stored information from the transient regime. Under the condition of this experiment the crossover from the transient to the steady-state regime takes place at a coverage in the range of 10^{-3} ML.[5] Therefore, the migration coefficient determined this way corresponds to those inferred from FIM experiments.

Figure 2 shows the characteristic length L versus inverse temperature between 130 and 250 K. For an accurate quantitative analysis of the peak positions the diffraction pattern was fitted with three Gaussians at a coverage of $\Theta = 0.5$ ML. We found that the separation of the diffraction peaks increases with decreasing temperature, while their intensities decrease. Below 160 K, only a broad base below the specular peak is observed. Between 250 and 160 K, L follows an Arrhenius-type law. The deviation from the Arrhenius behavior at the lowest temperatures is a consequence of reduced thermally activated mobility. Our multilayer deposition experiments[15] show that the number of observed oscillations in the specularly reflected intensity decreases rapidly for temperatures below about 160 K, indicating that the width of the interface becomes increasingly larger. In this case we probe the island separation function on many different levels at the same time. Moreover, islands formed in this tempera-

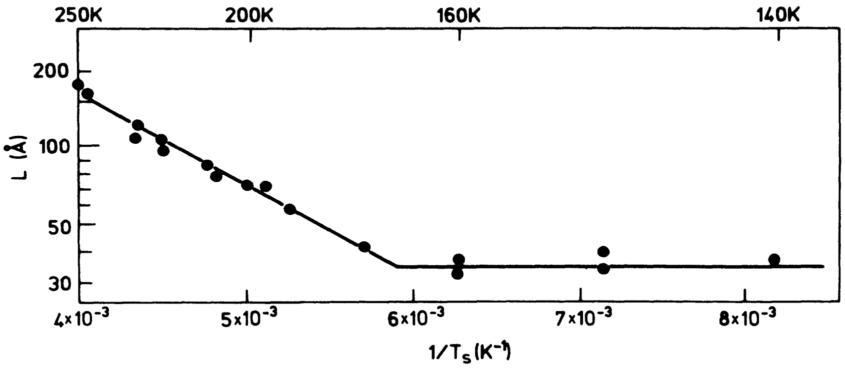

FIG. 2. Mean separation L between islands as a function of inverse temperature. The data were taken with an incident flux of 1270 sec/ML. L follows an Arrhenius-type law for $T_s > 160$ K. The migration coefficient has been determined from this part of the data. L appears to be nearly constant below 160 K. This is due to reduced thermally activated mobility in this temperature range (see text).

ture range might have a noncompact structure due to negligible island edge diffusion. It is conceivable that both effects tend to suppress the well-defined diffraction "sidebands" observed at higher temperatures.

For the determination of the migration coefficient only the temperature dependent part in Fig. 2 is of interest. The slope corresponds to an energy of $E_n = 70$ meV, and the intercept at $1/T = 0$ is 5×10^3 Å. In addition to these values the size i of the critical nucleus is needed, because it determines the functional relationship between the characteristic length L and the migration coefficient. This quantity is experimentally accessible by measuring L as a function of deposition rate R at fixed temperature. Figure 3 shows that within experimental error the characteristic length L varies as $R^{-1/4}$, which means that in the temperature range covered by this experiment i is indeed 1. With

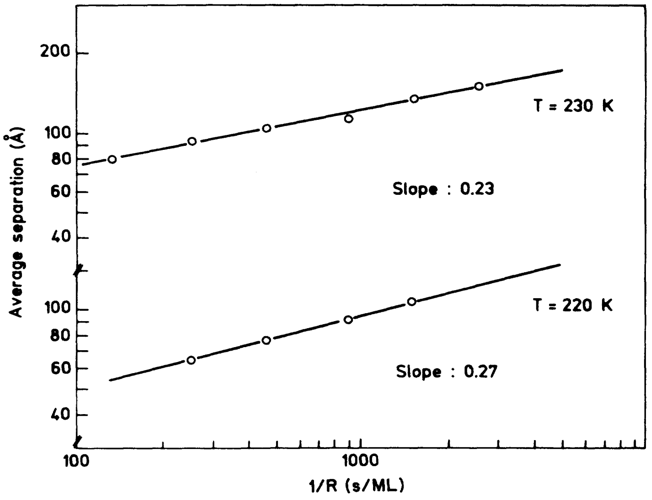

FIG. 3. Mean separation between islands L vs $1/R$ (here in sec/ML) at fixed deposition temperature. The flux has been calibrated from intensity oscillations in the layer-by-layer growth regime. Within experimental error, the relationship can be expressed as $L \approx (R)^{-1/4}$.

Eq. (1) (Ref. 16) it is now straightforward to determine the migration coefficient. We find 0.28 eV ± 0.06 eV for the activation energy and $\approx 10^{-5}$ cm^2/sec for the preexponential factor.

There are several possible processes that might demand a modification of the analytical procedure the evaluation of the migration coefficient is based on. The characteristic length L varies between 40 and 150 Å. These values must be compared with the average terrace width w of at least 700 Å in order to judge the influence of residual steps on the nucleation process. Steps act to sink adatoms and reduce the number of islands formed.[5,17] The influence of steps should be largely negligible if $2L/w < 1$.[17] This condition is certainly represented at lower temperatures. If there were an influence at higher temperatures, it would show up in deviations from the Arrhenius behavior, which is not the case. Coarsening due to coalescence or Ostwald ripening will have the same effect on the Arrhenius plot. The coarsening due to mobile clusters has recently been treated by Villain.[18] For a given temperature, the dependence of the characteristic length L on the incident flux is $L \approx R^{-[1/4(1+1/2M)]}$, where M is the number of atoms in the largest mobile cluster. This expression is compatible with our experimental finding of $-\frac{1}{4}$ only in the limit of very large M. We consider it unlikely that such large clusters have significant mobility for a homoepitaxial system in the temperature range covered by our experiment.

Recent theoretical studies give values for the migration energy very close to ours. The effective-medium theory of Hansen *et al.*[19] gives a value of 0.23 eV. Hansen *et al.* show that this energy corresponds to an exchange diffusion mechanism. A bridge hopping process needs nearly double the energy. By comparison with this theory, our data provide an experimental indication for the exchange diffusion path. The same mechanism has been predicted and experimentally verified with FIM for other fcc (100) surfaces as well.[2,3]

FIM data for diffusion on Cu surfaces are not available. However, our value for the activation energy of 0.28 eV differs substantially from the value of 0.4 eV reported by de Miguel *et al.*, deduced from the appearance of diffraction peak oscillations in multilayer deposition experiments at around 400 K.[10] This procedure to determine the migration coefficient has recently been criticized.[17] However, a possible explanation for at least part of this discrepancy might be that at higher temperatures the bridge hopping diffusion channel opens, while at lower temperatures the exchange diffusion path dominates.

We feel that this technique gives reliable values for the migration coefficient, and might have a potential for general application. In fact, we believe that this method is not even restricted to helium-atom-beam scattering as a probe, but may also be applied with other surface sensitive techniques. Indeed, various low-energy electron-diffraction investigations on growth in metal systems reported in the literature[13,20] show the appearance of sidebands in the diffraction pattern as well, but have not yet been explored in connection with the migration coefficient so far. Although atomistic nucleation theory[5,6] is able to take into account the influences of steps, large critical nuclei, coalescence, or even desorption at the cost of a huge set of fitting parameters, we consider it as a major advantage of our approach that the experiments can be performed *in situ* and in real time at low deposition temperature, so that the dimer forms a stable nucleus and the number of active processes is reduced to migration of adatoms on individual terraces only. In that case the migration coefficient can be obtained directly.

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