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Transition from One- to Two-Dimensional Growth of Cu on Pd(110) Promoted by Cross-Exchange Migration.

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Abstract. – A transition from one- to two-dimensional structures is observed in the growth of Cu islands on Pd(110). When Cu is deposited at substrate temperatures below 300 K, the adatoms move along the easy $[1\bar{1}0]$ direction forming 1D Cu chains. At higher temperatures transverse diffusion of adatoms is activated and 2D islands start to grow. Migration barriers are found to be (0.51 ± 0.05) eV and (0.75 ± 0.07) eV along and across the $[1\bar{1}0]$ directions, respectively. In the two-component driven diffusion regime, the shape of the 2D Cu islands is determined by the energy difference of the two orthogonal diffusion barriers.

Physical and chemical properties of a heteroepitaxial structure are ultimately determined by the growth process. Conceptually, heteroepitaxial growth has been widely studied by means of the thermodynamic approach which is essentially based on the idea that the surface free energy must be minimized [1]. The conditions for this to happen in practice are only fulfilled at sufficiently high substrate temperature. In many experiments, however, metastable structures that reflect the kinetic behaviour are the rule. Thus it has been shown that the morphology of the islands grown epitaxially on a substrate can be tailored to a large extent by a careful control of the deposition rates and deposition temperatures [2-7]. This suggests that far from equilibrium a wide variety of new structures can be created by playing with the symmetry of the substrate, the temperature and the atomic nature of the adlayer-substrate system. In this respect, the Cu/Pd(110) system is an interesting example in which anisotropic growth mechanisms come into play. Any unreconstructed f.c.c. (110) surface consists of close-packed atomic rows along the $[1\bar{1}0]$ direction separated by deep channels in which preferential diffusion of incoming adatoms takes place. At not too high temperatures, adatom diffusion occurs exclusively along the $[1\bar{1}0]$ channels allowing linear 1D chains to grow [7]. The one-dimensional growth regime is found to be limited to substrate temperatures not exceeding 300 K. Above this temperature cross-channel migration is activated and 2D islands start to grow kinetically.

In the present work we evaluate quantitatively for the first time the kinetic mechanism that leads to one-dimensional or two-dimensional growth patterns on a metal surface with

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diffusion anisotropy. We extract the relevant information on the anisotropic-diffusion process (diffusion barriers) from a detailed analysis of the densities of the islands formed during deposition of Cu on Pd(110) as a function of temperature. In doing so, we follow a well-known electron-microscopy–based approach [3, 6]. Our findings are corroborated by our Embedded-Atom Method (EAM) calculations, which allow to disentangle the elementary diffusion steps leading to migration of Cu adatoms across the $[1\bar{1}0]$ direction.

The experiment was carried out in a multipurpose UHV chamber (base pressure $1 \cdot 10^{-10}$ mbar) with a home-built variable-temperature, «beetle»-type STM which operates in the temperature range from 150 K to 600 K. A full description of the equipment has been given elsewhere [8]. The Pd(110) crystal was cleaned by repeated cycles of Ar ion bombardment (0.7 kV) at 720 K and subsequent flash annealing at 950 K. After the sample was cooled down to working temperature, it was exposed to a Cu flux evaporated from a Knudsen cell at a constant deposition rate of 10^{-3} ML/s; the time between flash cleaning and completion of 1/10 of a Cu monolayer was below 400 s ensuring a negligible influence of impurities. The STM images were acquired in the constant-current mode with positive tip voltages from 0.1 to 1.0 V and tunnelling currents from 0.5 to 1.0 nA.

Figure 1 shows STM images of submonolayer Cu islands grown on Pd(110) at various temperatures T and low Cu coverages ($\Theta_{\text{Cu}} \leqslant 0.1$ ML). Cu islands have high aspect ratios and are oriented along the $[1\bar{1}0]$ direction. At $T < 300$ K (fig. 1*a*)), linear chains *monatomic* in width are formed. This has been inferred from the distribution of chain spacings which shows discrete peaks at multiples of an elementary distance $\boldsymbol{a} = (4.0 \pm 0.2)$ Å (corresponding to the interrow spacing of two neighbouring Pd close-packed rows). The fact that we were able to measure the lateral island separation down to *two* elementary distances indicates that the chains could not be made of double rows. At $T = 300$ K (fig. 1*b*)) the monatomic Cu wires can reach lengths up to 1000 Å ($\Theta_{\text{Cu}} = 0.07$ ML) corresponding to aspect ratios as large as $\boldsymbol{A} \approx \approx 300$. Above about 300 K, 2D islands that are still elongated in the $[1\bar{1}0]$ direction start to form (see fig. 1*b*) and 1*c*)). As is clear from fig. 1, the surface density of islands drops as a function of temperature. This illustrates that a set of images taken at different deposition temperatures contains information on the adatom diffusion lengths on the surface.

The interpretation of our data has been done by analysing the density of islands as a function of substrate temperature as outlined in two recent papers [3, 4]. This approach is based on the existence of an average «lifetime» τ_{A} for adatoms, which is governed by two different collision rates: ω_{AA}, the collisions between two adatoms and ω_{AI}, the adatom-island collisions. If we assume that two meeting adatoms form a stable nucleus and that an adatom arriving at an existing nucleus sticks to it, the island density N (at constant deposition rate

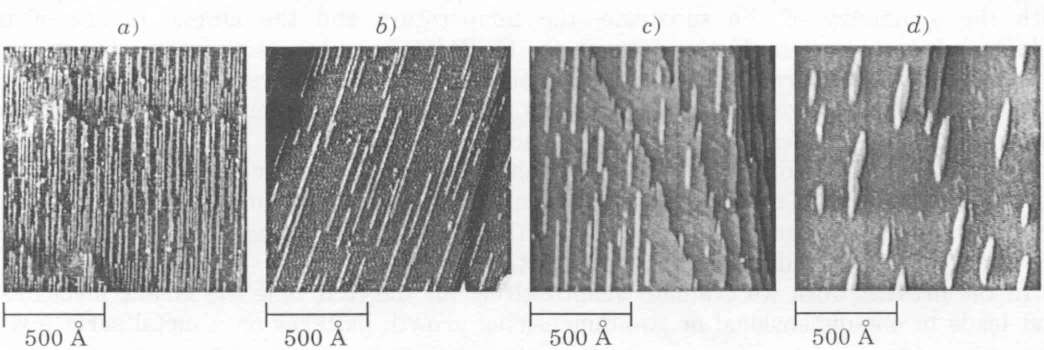

Fig. 1. – STM images of Cu islands grown and imaged on Pd(110) at four different substrate temperatures and nearly the same Cu coverage $\Theta_{\text{Cu}} = 0.1$ ML, except for *b*) where $\Theta_{\text{Cu}} = 0.07$ ML. Temperatures are: *a*) 265 K, *b*) 300 K, *c*) 320 K, *d*) 350 K.

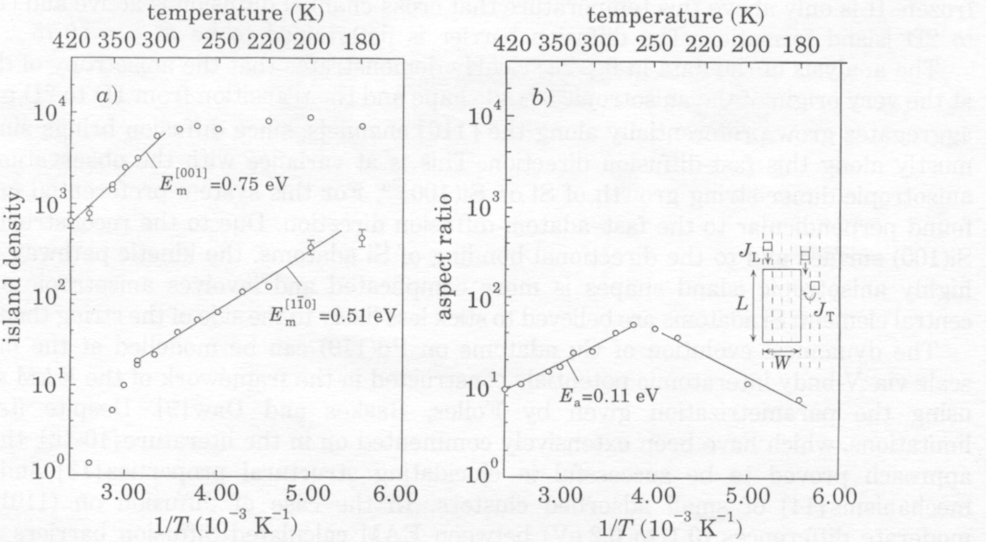

Fig. 2. – *a*) Arrhenius plot of the one-dimensional transverse density of islands (upper curve, $N = 10^0$ corresponds to 420 islands / cm) and of the overall density of islands (lower curve, $N = 10^0$ corresponds to $1.7 \cdot 10^{10}$ islands / cm^2) as a function of $1/T$. *b*) Arrhenius plot of the measured island aspect ratio A as a function of $1/T$; the island aspect ratio $A = L/W$ reflects the ratio of the growth rates of islands in the [110] (dotted lines) and [001] direction. J_L and J_T are the jump rates in the corresponding directions.

and coverage) is found to be proportional to $D^{-d/2(d+1)}$, where D is the diffusion coefficient of adatoms. In the case of isotropic 2D diffusion $d = 2$, while in the case of 1D diffusion $d = 1$. The diffusion coefficient is simply related to the diffusion prefactor D^* and the diffusion energy barrier E_m by $D/a^2 = D^* \exp[-E_m/kT]$, with a being the lattice constant. In the case of one-dimensional diffusion the island density is given by $N^{-4} = (D^* a^4/4R\Theta) \cdot \exp[-E_m/kT]$, here Θ is the adlayer coverage and R the deposition flux. For two-dimensional diffusion we have $N^{-3} = (D^* a^2/3R\Theta) \exp[-E_m/kT]$.

The island counting from the STM images was only performed on large terraces (> 500 Å) to ensure minimal interferences with step regions. Figure 2*a*) shows semi-log plots of the overall surface density of islands (lower curve) and of the one-dimensional density of islands in the [001] direction (upper curve) as a function of $1/T$. As long as the transverse diffusion is not activated, the overall density of islands determines the diffusion barrier in the easy direction, while the one-dimensional density of islands perpendicular to the channel walls essentially determines the diffusion barrier in the [001] direction. In order to avoid coalescence and / or coarsening, the experimental results reported here focus on the low-coverage ($\Theta_{Cu} \leqslant 0.1$ ML) and low-temperature regime ($T < 400$ K). The island densities in fig. 2*a*) nicely reflect the transition from 1D to 2D growth. The overall density shows Arrhenius behaviour in the entire range from 350 K to 180 K, demonstrating that the longitudinal diffusion is active in the entire range down to the lowest measured temperatures. The atoms move along the $[1\bar{1}0]$ channels without any transverse migrations and the island formation is a true one-dimensional problem ($N \sim D^{-1/4}$). The diffusion barrier that can be obtained from the truly 1D regime through the overall density is $E_{m,L} = (0.51 \pm 0.05)$ eV. On the other hand, the linear island density along [001] (determining the cross-channel barrier), shows Arrhenius behaviour only above 300 K and is constant at temperatures below. This indicates that below 300 K transverse diffusion of Cu atoms is frozen. It is only above this temperature that cross-channel diffusion is active and contributes to 2D island formation. The diffusion barrier is determined to be $E_{\mathrm{m},T} = (0.75 \pm 0.07)$ eV.

The analysis of the data in fig. 2*a*) clearly demonstrates that the anisotropy of diffusion is at the very origin of the anisotropic island shape and the transition from 1D to 2D growth. Cu aggregates grow preferentially along the $[1\bar{1}0]$ channels, since diffusion brings single atoms mostly along this fast-diffusion direction. This is at variance with the observations for the anisotropic dimer-string growth of Si on Si(100)[3a]. For this system preferential growth was found perpendicular to the fast–adatom-diffusion direction. Due to the reconstruction of the Si(100) surface and to the directional bonding of Si adatoms, the kinetic pathway leading to highly anisotropic island shapes is more complicated and involves anisotropic sticking as central element; Si adatoms are believed to stick less likely to the side of the string than to its end.

The dynamical evolution of Cu adatoms on Pd(110) can be modelled at the microscopic scale via N-body interatomic potentials constructed in the framework of the EAM scheme by using the parametrization given by Foiles, Baskes and Daw [9]. Despite its intrinsic limitations, which have been extensively commented on in the literature [10-12], this original approach proved to be successful in elucidating structural properties [13] and diffusion mechanisms [14] of small adsorbed clusters. In the case of diffusion on (110) surfaces, moderate differences (0.1 to 0.2 eV) between EAM calculated diffusion barriers along and across the $[1\bar{1}0]$ rows are found upon inclusion of a cross-exchange mechanism in the [001] direction [14], thereby supporting experimental observation of adatom diffusion involving exchanges on f.c.c. (110) substrates [15, 16]. In the computations reported here, energy barriers for migration, denoted by E_m, and related to either adatom hopping or exchange, are calculated by constraining the motion of the adatom (or the centre of mass of the two atoms involved in the exchange) to specific locations in the (X, Y)-plane along a given diffusion path, with the rest of the system relaxing at $T = 0$ K. The value of E_m is then simply the difference in total energy between the saddle point configuration and the equilibrium configuration of the adatom.

Our EAM computations for simple hopping of Cu adatoms yield migration barriers in the longitudinal $[1\bar{1}0]$ and transverse [001] directions equal to $E_{\mathrm{m,L}} = 0.32$ eV and $E_{\mathrm{m,T}} = 1.25$ eV, respectively. This gives rise to an unrealistically large diffusion anisotropy, thereby stimulating the search for a more conceivable diffusion path promoting transverse diffusion. This diffusion path has also to account for the phase separation of Cu and Pd experimentally observed at the surface. In a bimetallic system and in the kinetic-growth regime, the simple atomic-exchange mechanism produces alloying followed by self-diffusion of the displaced substrate atom rather than transverse diffusion of the heteroatom. Cu-Pd surface alloying is however excluded from CO-adsorption infrared spectroscopy and photoemission experiments for temperatures below 700 K [17] (in the temperature range of concern here, an upper limit $\leqslant 3\%$ of Pd incorporated in the Cu islands could be estimated), thereby requiring a more elaborate transverse-diffusion mechanism to explain the data. According to the mechanism we propose in fig. 3, a Cu-Pd exchange can take place leaving one of the Pd atoms on the top while the Cu adatom, originally stable on an adsorption site, is incorporated in the substrate. Such a process is characterized by a migration barrier $E_\mathrm{m}(a \rightarrow b) = 0.57$ eV, the *b*) configuration being 0.15 eV higher in energy than the initial one, *a*), consistently with the Cu-Pd phase separation expected on Pd(110). At this point, to ensure effective migration, the Cu original adatom has to move down across the close-packed rows. This can be triggered by an exchange between two Pd atoms along the $[1\bar{1}2]$ direction leading to the *c*) configuration ($E_\mathrm{m}(b \rightarrow c) = 0.57$ eV), followed by simple hopping of the Pd adatom in the $[1\bar{1}0]$ direction (*d*) configuration, $E_\mathrm{m}(c \rightarrow d) = 0.33$ eV). Finally, to recover the original chemical order and achieve transverse diffusion, the Cu atom can migrate along the [001] direction via a further Pd-Cu exchange, with $E_\mathrm{m}(d \rightarrow e) = 0.42$ eV. We find this combination of steps, which models the migration process in the hypothesis of a *single* Cu adatom moving on the slab, the most effect-

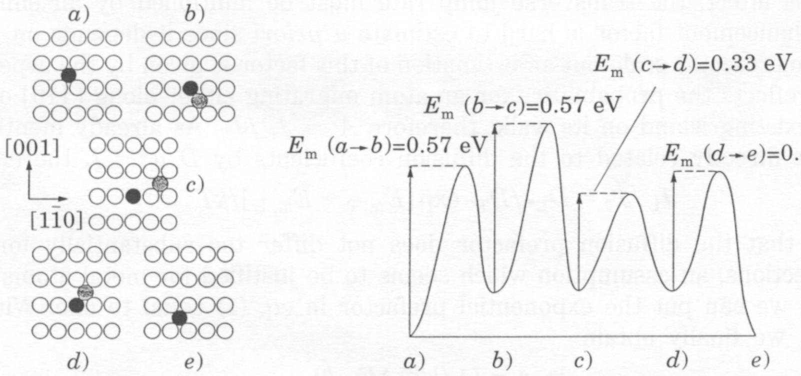

Fig. 3. – Diffusion scenario for a *single* Cu adatom on a Pd(110) surface. Left: mechanism for migration of the Cu adatom along the [001] direction. Open circles: Pd substrate atoms in the uppermost layer. Grey circles: Pd atom moved up to occupy an adsorption site. Dark circles: Cu adatom. Right: energy profile corresponding to the elementary diffusion steps displayed in the upper part. E_{m}'s are the migration barriers. During growth the mechanism simplifies because steps $(b \to c)$ and $(c \to d)$ are not required (see text).

ive way of allowing for Cu diffusion along the hard [001] direction, as opposed to any mechanism requiring vacancy creation in the substrate, characterized by barriers as large as 0.9 eV.

We want to stress, however, that during growth mobile Pd atoms are continuosly generated by Cu-Pd exchanges $(a \to b)$ and then reincorporated in the substrate via Pd-Cu exchanges of the $(d \to e)$ kind, so that two successive exchanges do not necessarily need to involve the same atoms. As a consequence, steps $(b \to c)$ and $(c \to d)$ are not necessarily required, since the transition from *d*) to *e*) can be promoted by a Pd atom different from the one that moved up in *b*). On the basis of these considerations our proposed mechanism results in a moderate diffusion anisotropy, given by $\Delta E_{\mathrm{m}}(\mathrm{cal}) = E_{\mathrm{m}}(a \to b) - E_{\mathrm{m,\,L}} = 0.25$ eV, in full agreement with our experimental observations $(\Delta E_{\mathrm{m}}(\mathrm{exp}) = 0.24\ \mathrm{eV})$.

We would like to conclude by giving an intuitive description of the kinetic, 2D-island growth shapes. In the modelling we neglect any mass-conserving changes in the island shape associated with atom migration along the perimeter. Such a process would require in particular diffusion along the open transverse island edge, the barrier for which is expected to be even higher than the barrier for simple cross-channel migration on terraces, and is thus likely to be not activated at the temperatures studied here ($T < 400$ K). In the following we suppose that atoms land on the surface in a random way and that the neighbourhood of the islands is continuously popopulated with «fresh» adatoms arriving from the gas phase. The aspect ratio A of the islands (island length over island width) then reflects the ratio of the growth rates in the longitudinal and transverse directions (inset fig. 2*b*)). While the growth rate of an island along $[1\bar{1}0]$ is proportional to the jump rate J_{L}, the growth rate across $[1\bar{1}0]$ is less trivially related to the transverse jump rate J_{T}. As a matter of fact, it is faster than would be expected just from the jump rate J_{T}. This comes about because every time a cross-channel migrating atom attaches to the lateral edge of an island, it forms instantaneously a critical (immobile) nucleus with another atom migrating along the corresponding $[1\bar{1}0]$ channel. From our energy barriers, we find that at $T = 300$ K the jump rate in the easy direction is 2×10^4 times higher than that across the channel walls. Thus every time a cross-channel–migrating atom attaches to the lateral edge of an island, it forms instantaneously an immobile nucleus with another atom diffusing in the corresponding $[1\bar{1}0]$ channel. Then, the row is immediately filled up with atoms moving along this channel. To account for this effect, the transverse jump rate must be multiplied by an enhancement factor. This enhancement factor is hard to estimate *a priori* since it depends on particular events on the microscopic scale but an estimation of this factor is given by the aspect ratio A itself, since it reflects the probabilities for an atom migrating either along $[1\bar{1}0]$ or [001] to encounter an existing island on its walk; therefore $A^2 = J_{\mathrm{L}}/J_{\mathrm{T}}$. As already mentioned, the jump rates are directly related to the diffusion coefficients by $D/a^2 = J$, therefore

$$J_{\mathrm{L}}/J_{\mathrm{T}} = D_{\mathrm{L}^*}/D_{\mathrm{T}^*} \exp[E_{\mathrm{m,\,T}} - E_{\mathrm{m,\,L}}]/kT\,. \tag{1}$$

If we assume that the diffusion prefactor does not differ too substantially for the two orthogonal directions, an assumption which seems to be justified for metal atoms on metal substrates [18], we can put the exponential prefactor in eq. (1) equal to one. With $\Delta E_{\mathrm{m}} = E_{\mathrm{m},\,T} - E_{\mathrm{m},\,L}$ we finally obtain

$$\ln A = (1/kT)\,\Delta E_{\mathrm{m}}/2\,. \tag{2}$$

The experimental measurements of the aspect ratio $\boldsymbol{A}$ in the two-component driven diffusion regime shown in fig. 2*b*) do indeed exhibit the exponential variation as a function of $1/T$. The slope of fig. 2*b*) delivers an activation energy of 0.11 eV which within our model is in very good agreement with the difference in energy barriers obtained from island density analysis $(E_{\mathrm{m,\,T}} - E_{\mathrm{m,\,L}})/2 = 0.12$ eV.

Starting at low temperatures (in the 1D regime) the aspect ratio is increasing as a function of T (*i.e.* with increasing diffusion of adatoms within the channels). Here $\boldsymbol{A}$ is a direct measure of the Cu chain length. By extrapolation to low temperatures ($\boldsymbol{A} = 1$), we can estimate a stability temperature of 140 K for the Cu adatom. The break in the aspect ratio as a function of T refers to the onset of 2D growth. From this temperature upwards, $\boldsymbol{A}$ decreases, because both orthogonal diffusion channels contribute to the growth.

In summary, we have observed for the first time a transition from 1D to 2D growth at surfaces. It has been demonstrated that the Cu adatom diffusion anisotropy on Pd(110) is at the very origin of this crossover.

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