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Dynamical behaviour and size dependence of 2D copper islands on the Cu(111) surface: a molecular dynamics study

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Abstract

Using molecular dynamics simulations based on an effective potential, in analogy to the tight binding theory in the second-moment approximation, we studied the vibrational behaviour of Cu islands of various sizes on the Cu(111) surface. We found that small clusters are contracted by as much 10% (for a dimer) from the relative positions of the relaxed interlayers of the island's atoms; the effect is less important with increasing cluster size, N , attaining the same value as for the surface atoms for islands with more than $N_c = 33$ atoms. In addition, from the calculated mean-square displacements, we found that in the direction normal to the surface the vibrational amplitudes of the island's atoms do not depend on the size of the cluster, while they are increased by a factor of five in the in-plane directions. These findings are compatible with the behaviour of the cluster phonon modes. Indeed, we found that small islands introduce new vibrational modes that diminish with increasing cluster size, regaining the surface vibrational behaviour. These results suggest that small 2D islands (containing up to 10 atoms) formed on the Cu(111) face are strained; for larger islands this compressive stress is released and the islands exhibit the vibrational behaviour of the substrate for $N > N_c$. This characteristic cluster size, N_c , coincides with the characteristic island size above which the migration energy of the island's atoms saturates to the value of the step-energy barrier.

1. Introduction

One of the most exciting subjects in epitaxial growth is the switching from layer-by-layer to 3D growth observed in the deposition of adsorbates on the fcc(111) surface. There is an abundant literature on this subject, both experimentally [1–4] and theoretically [5–10]. It is concluded that adsorbate kinetics and surface diffusion play a key role in the morphology of clusters

formed on the surface. In addition it is now established that the islands on the substrate are subject to compressive or tensile strain and that this surface stress is a decisive factor in the growth process [11, 12]. This conclusion stems from the measured and calculated vibrational properties of various surfaces in the presence of islands and surfactants. From these studies it is also found that certain phonon modes in the middle of the Brillouin zone are sensitive to the surface stress [13, 14], while the presence of coadsorbed atoms affects both the phonon density of states (DOS) of the substrate and the surface morphology [15, 16]. It is therefore conceivable that an understanding of the dynamical properties of islands at the microscopic level can provide valuable information concerning the structure and the elementary processes involved in epitaxial growth. It is the aim of the present study to substantiate the role of the vibrational properties of small 2D islands (which are vital participants in the early stages of the growth process [17]) in the case of homoepitaxy on the Cu(111) surface.

2. Computational details

We performed simulations in the constant temperature canonical ensemble using the Nose thermostat [18] and a system made up of 7680 atoms arranged on an fcc lattice. Periodic boundary conditions were applied in the three space directions to mimic an infinite system. The free surfaces were produced by fixing the dimensions of the simulation box at a value twice as large as the thickness of the crystal along the z -direction. An infinite slab of 24 atomic layers parallel to the (111) plane is thus produced with 320 atoms in each layer, delimited by two free surfaces. For the atomic interactions we used an effective potential in analogy to the tight binding theory in the second-moment approximation (TBSMA). This model has been employed successfully in the past to describe the vibrational and diffusive properties of copper surfaces [19, 20]. We have to note that a correct description of surface and adatom properties, where it is known that the electronic environment is seriously modified, requires more accurate methods incorporating electronic structure calculations. However, the many-body type contributions as described in the TBSMA model seem to reproduce rather well the main structural and vibrational features of the transition and noble metals [21–23].

The equations of motion were integrated by means of Verlet's algorithm and a time step of 5 fs, ensuring Hamiltonian conservation within 10^{-5} . We performed simulations at 300 K using the lattice constant that resulted in zero pressure for the bulk system. We studied several systems by putting islands with a size that varied from 2 to 138 atoms (0.4 ML) on each surface. We chose the shape of the islands to have an aspect ratio close to unity, corresponding to compact islands. These islands are the most stable, as postulated by Breeman *et al* [24] and Fallis *et al* [25]. Indeed, we verified that the initial shape of the islands did not change significantly during the course of our simulation (1 ns). In figure 1 we give some representative examples of islands of different sizes equilibrated at $T = 300$ K. In all cases the system was initially thermalized for 200 ps, while the statistics for the various quantities we calculated were taken over trajectories that lasted 1 ns.

We calculated the phonon DOS, $g(w)_N^p$, for the island's atoms and for the clean surface atoms by Fourier transforming the corresponding velocity autocorrelation functions [26]:

$$A^p(t) = \frac{1}{N} \sum_{i=1}^N \frac{\langle u_i^p(0)u_i^p(t) \rangle}{\langle u_i^p(0)u_i^p(0) \rangle}. \quad (1)$$

All calculated DOSs have been normalized to unity by

$$\int_0^{w_{\max}} g(w)_N^p dw = 1 \quad (2)$$

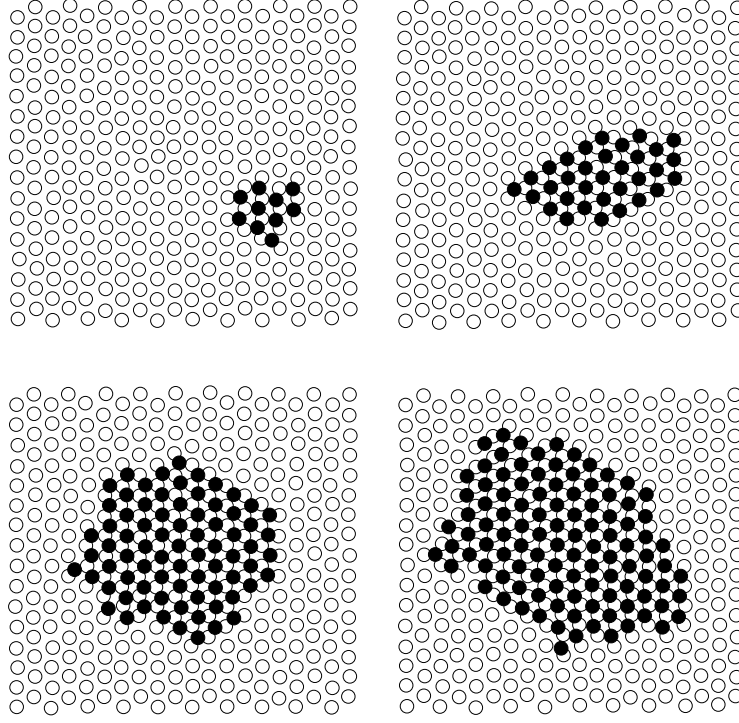


Figure 1. Representative equilibrium configuration for a coverage of 0.03, 0.1, 0.24, 0.33 ML respectively at $T = 300$ K.

where N is the number of atoms making up the island, $u(t)_i^p$ stands for the velocity of atom i at time t , p is the polarization and w_{\max} is the maximum phonon frequency of the system. The brackets denote time averages.

In order to quantify the contribution of the various phonon modes to the total phonon DOS, we calculated the second moment of the DOS (SMDOS) of the island atoms, with respect to that referring to the clean surface:

$$\overline{w_N^{2p}} = \frac{\int_0^{w_{\max}} w^2 g(w)_N^p dw}{\int_0^{w_{\max}} w^2 g(w)_{\text{cleansurface}}^p dw}. \quad (3)$$

In addition, for island atoms along the $[111]$ direction, we calculated the positions of the relaxed interlayers with respect to the bulk interlayer spacing from the local density profile using the relation

$$\frac{\overline{d_{\text{island}}} - \overline{d_{\text{bulk}}}}{\overline{d_{\text{bulk}}}} \times 100\% \quad (4)$$

where $\overline{d_{\text{island}}}$ denotes the average interlayer spacing between the island layer and the surface layer and $\overline{d_{\text{bulk}}}$ stands for the bulk interlayer spacing. The same quantity was also calculated for the surface atoms.

We also calculated the corresponding quantities in the in-plane directions using the following procedure: we calculated the probability $P(r)$ of finding a pair of atoms at a

distance r , using the distribution function:

$$P(r) = \left\langle \sum_{i=1}^{N-1} \sum_{j>i}^N \delta(r - r_{ij}(t)) \right\rangle \quad (5)$$

where

$$r_{ij} = \sqrt{(x_i(t) - x_j(t))^2 + (y_i(t) - y_j(t))^2}. \quad (6)$$

The relaxed first-neighbour distance with respect to the corresponding quantity for the clean surface was then calculated by

$$\bar{R} = \frac{\int_{r_1}^{r_2} r P(r) dr}{\int_{r_1}^{r_2} P(r) dr}. \quad (7)$$

Consequently, the relaxed first-neighbour distance in the in-plane direction can be estimated by

$$\frac{\bar{R}_{\text{island}} - \bar{R}_{\text{surface}}}{\bar{R}_{\text{surface}}} \times 100\% \quad (8)$$

where \bar{R}_{island} is the mean in-plane first-neighbour distance for the island atoms and \bar{R}_{surface} is the mean in-plane first-neighbour distance for the atoms of the clean surface.

The mean-square displacements (\bar{u}_z^2) were calculated in the [111] direction (normal to the surface) from the local density profile using

$$\bar{u}_z^2 = \frac{\int_{z_1}^{z_2} (z - \bar{z})^2 \rho(z) dz}{\int_{z_1}^{z_2} \rho(z) dz} \quad (9)$$

where $\bar{z} = \int_{z_1}^{z_2} z \rho(z) dz$ is the mean value of the atomic layer lying between the limits z_1 , z_2 defining the atomic layer. A similar procedure was followed for the calculation of the mean-square displacements in the in-plane directions.

3. Results and discussion

In figure 2 we present the DOS for a dimer (full curves) along with the corresponding quantities for the clean Cu(111) surface (dotted curves) at $T = 300$ K, for the in-plane [110], [211] and the [111] polarizations (normal to the surface) respectively. We observe that the dimer introduces a new phonon mode situated at 0.5 THz in the in-plane polarization, while in the direction normal to the surface we find a shift of the 3.1 THz surface mode to 2.8 THz and the appearance of a high-energy mode at 7.5 THz. It turns out that this low-frequency mode exhibits shear horizontal character, it is characteristic for the dimer, and it reflects the loose bonding between the atoms forming the dimer. It is interesting to note that from the calculation of the corresponding quantities referring to the single adatom case, it was found that the adatom is responsible for a new mode at 1.1 THz in the in-plane polarization and another one at 7.5 THz in the normal polarization [19]. This latter mode is recovered in the case of the dimer with a smaller intensity in the [111] polarization.

For bigger islands and in the in-plane polarization we found a new peak around 1.0 THz. This mode attenuates, increasing the size of the island, while the characteristic surface mode at 6.5 THz is gradually regained. This phenomenon of regaining the surface modes while increasing the size of the island is more pronounced in the direction normal to the surface. In addition, the surface mode at 3.1 THz (in the same direction) is regained more quickly than in the other two polarizations. In figure 3 we present some representative DOSs for the cases

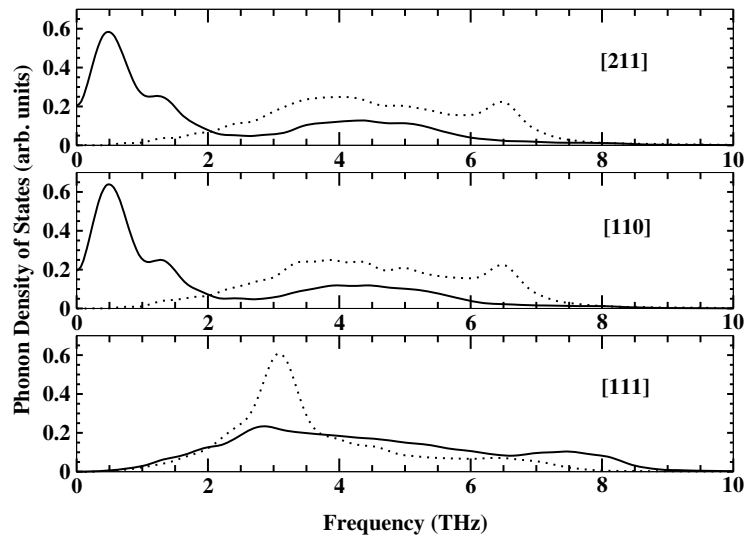


Figure 2. Phonon DOS for a dimer (full curves); the dotted curves represent the clean surface.

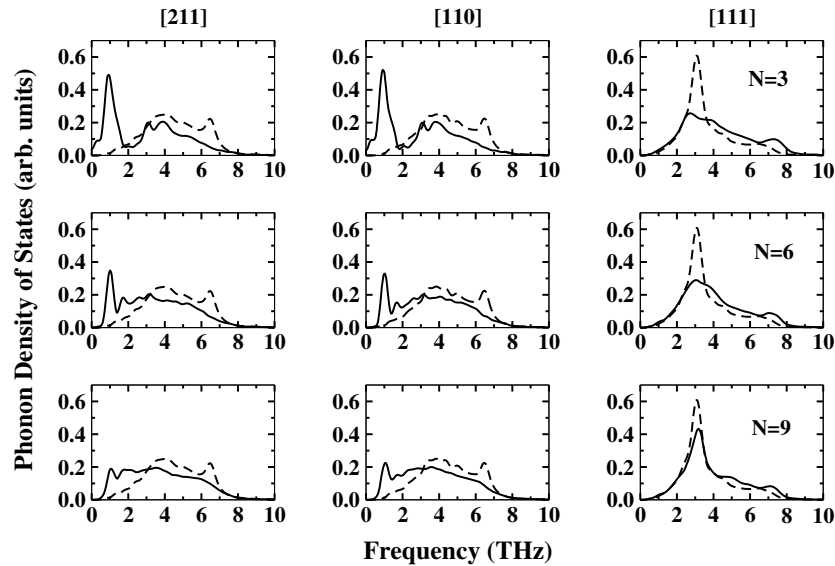


Figure 3. Phonon DOS at 300 K, for islands having sizes of three, six or nine atoms (full curves); the broken curves represent the clean surface.

of islands having sizes of three, six and nine atoms. The systematic shift, mentioned before, persists up to islands with sizes of $N_s = 10$ atoms, above which the new mode disappears and the surface character is almost completely regained (figure 4). This attenuation of the low-frequency mode can be explained by considering that when the size of the island increases its atoms make looser bonds but in an increasing number, resulting overall in stronger binding between them [27]. These effects can be quantified by the second moment of the total phonon DOS, $\overline{w_N^{2p}}$, for the three polarizations as a function of island size (figure 5). For the in-plane

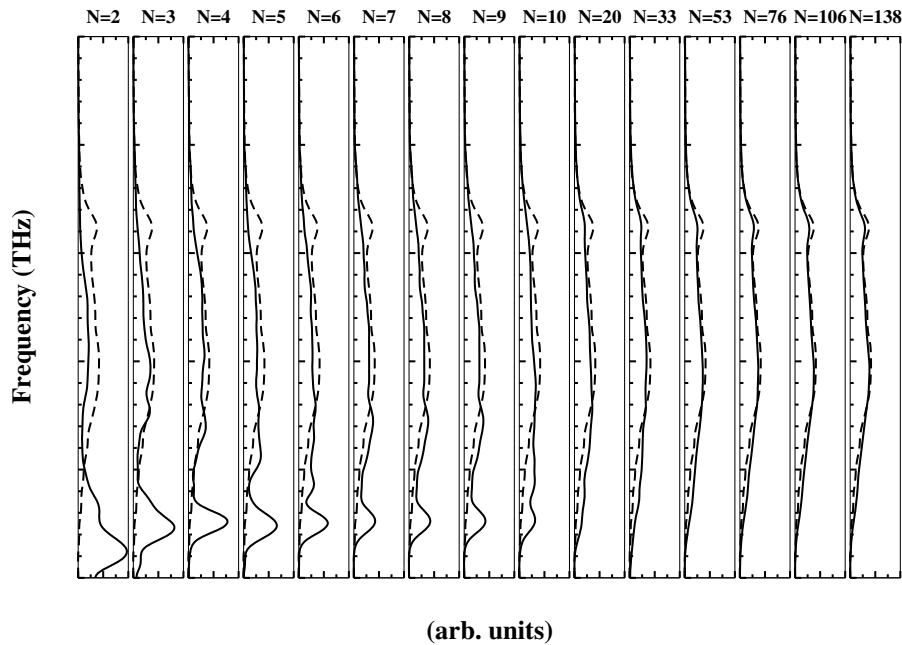


Figure 4. Phonon DOS at 300 K for islands containing (2, 3, 4, ..., 138) atoms (full curves) in the [211] polarization direction; broken curves represent the clean surface.

polarization we observe that the dimer makes a smaller contribution to the second moment than do the larger islands. This is to be expected, since the dimer exhibits the lower phonon mode (0.5 THz). The value of the second moment increases with increasing island size since higher frequencies, corresponding to the surface vibrational modes, start to contribute as well. Actually the second moment of the DOS changes slope for islands having a size greater than N_s to attain a saturated value for islands with a size greater than $N_c = 33$.

From these results, and considering the harmonic approximation according to which the second moment can be related to an effective force constant [28], we can deduce that in the in-plane directions the island's atoms are loosely coupled and that their bonding becomes stronger on increasing the island size. The effect is particularly pronounced for small islands (fewer than 10 atoms) and it is reflected in the behaviour of the second moment by the small oscillations we observe for islands between five and eight atoms in size (figure 6). This finding can be understood by considering simple bond counting arguments. Indeed, although such an approximation is an oversimplification [29] it seems to work rather well in this case, since for small islands the number of bonds per atom is strongly affected by adding even only one additional particle, while for larger islands the same operation has a much smaller effect.

In the direction normal to the surface the situation is totally different: the local environment is the same for all atoms of the island, and since they are deposited on a compact substrate the island reverberates the characteristic surface modes [30]. This can be seen in the calculated second moments even for the case of a dimer (figure 5). These contributions decrease as the size of the island increases, due to the augmenting interactions between the adatoms at the expense of the coupling strength with the substrate. We can conclude, therefore, that the presence of islands having size up to N_s significantly modifies the phonon DOS by introducing new modes and altering existing ones.

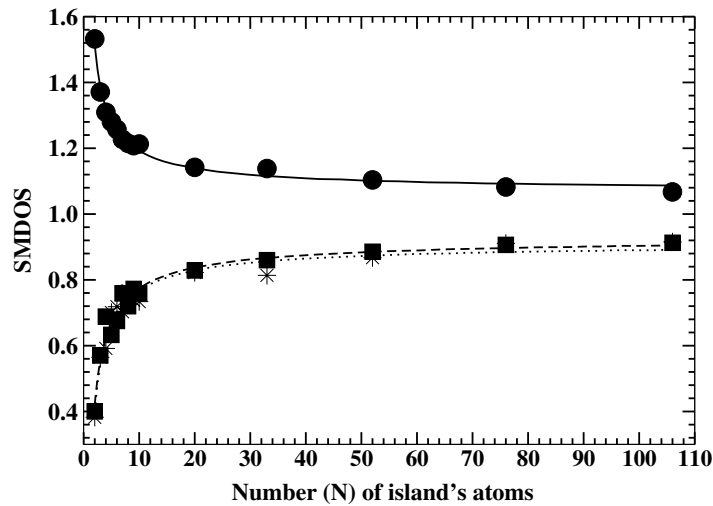


Figure 5. Second moment of the phonon density of states (SMDOS) as a function of island size. Circles stand for the [111] polarization direction normal to the surface; squares and stars stand for in-plane polarization in the [211] and [110] directions respectively. Lines serve as a guide for the eye.

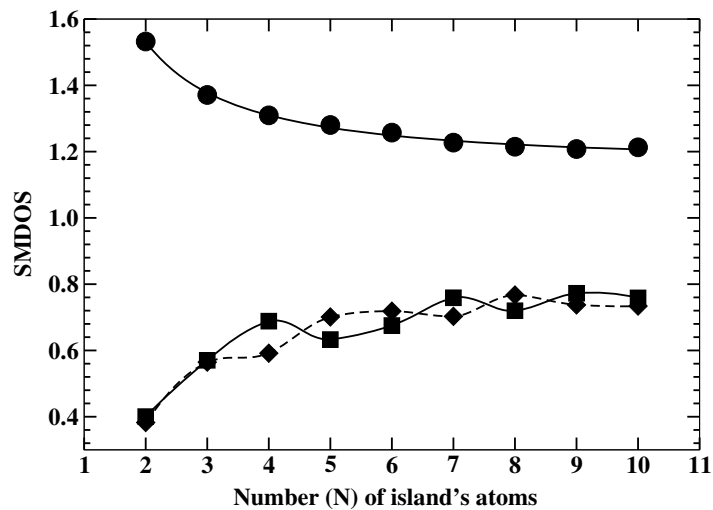


Figure 6. Second moment of the phonon density of states (SMDOS) as a function of island size for small islands. Circles stand for the [111] polarization direction normal to the surface; squares and diamonds stand for the in-plane polarization in the [211] and [110] directions respectively. Lines serve as guides for the eye.

The calculated mean-square displacements lead to similar conclusions. Despite the fact that the two in-plane directions are not geometrically equivalent, the mean-square displacements along the [110] and the [211] directions are practically the same; the small differences between these two components are within the statistical accuracy of our calculations. In figure 7 we present the mean-square displacements of the island atoms as a function of island size. In the in-plane directions we observe that the vibrational amplitudes

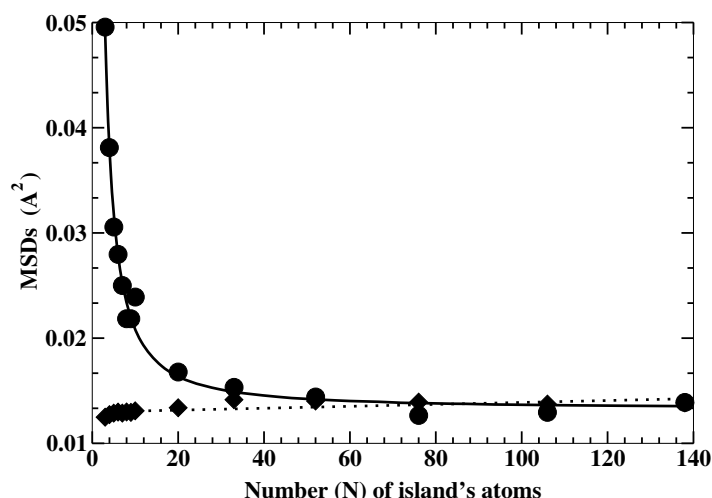


Figure 7. Mean-square displacements (MSDs) of the island atoms as a function of island size in the in-plane direction at 300 K (circles); diamonds stand for the mean-square displacements in the direction normal to the surface.

decrease as the island size increases to attain a value of 0.012 \AA^2 for islands (again) greater than $N_c = 33$ atoms. This finding can be understood taking into account that the mean-square displacements are proportional to the w^{-2} moment of the DOS and it is therefore more influenced by the low-frequency modes. This behaviour suggests that in the in-plane directions the atoms of big islands are more tightly bound. In the $[111]$ direction, the mean-square displacements do not depend on the magnitude of the island, in agreement with the conclusions obtained from the phonon behaviour of the adsorbates in the direction normal to the surface.

The vibrational behaviour of these islands is also characterized by the positions of the relaxed interlayer with respect to the bulk interlayer spacing in the perpendicular direction. In figure 8 we present the relative positions of the relaxed interlayer for the island and the surface atoms as a function of island size. We find that, similarly to the single adatom case, the dimer is contracted by as much as -10% [29], while as the islands become larger their atoms expand to attain a value of -3.0% for islands greater than N_c atoms. These rather large contributions, persisting even in the cases of large islands, are to be compared with the corresponding quantity referring to the clean surface (-0.8%) and second-layer case (-0.01%), the lower layer exhibiting practically no contraction in agreement with first-principle calculations [31, 32]. Interestingly, similar behaviour is also found in the in-plane directions. This can be seen in figure 9, where we show the relaxed first-neighbour distance of the island's atoms as a function of island size. This quantity for the atoms forming a dimer is shorter than the corresponding distance of the surface atoms by -3.3% . This difference is reduced on increasing the island size, to reach the normal lattice spacing for islands greater than N_c atoms.

From these results we can deduce that 2D islands smaller than N_c are contracted and are subject to compressive strain that affects their vibrational properties. Although to our knowledge experimental data referring to a similar homoepitaxial case are lacking, our results are in agreement with helium scattering experiments on strained Cu surfaces [13] and also with the results obtained in the cases of heteroepitaxy of the Co/Au(111) system [14] and the coadsorption of CO in the K-precovered Ni(111) surface [33], from which it was concluded that the stressed surface and the strained adlayer alter the measured phonon spectra. It also has to be pointed out that the number N_c coincides with the characteristic island size above

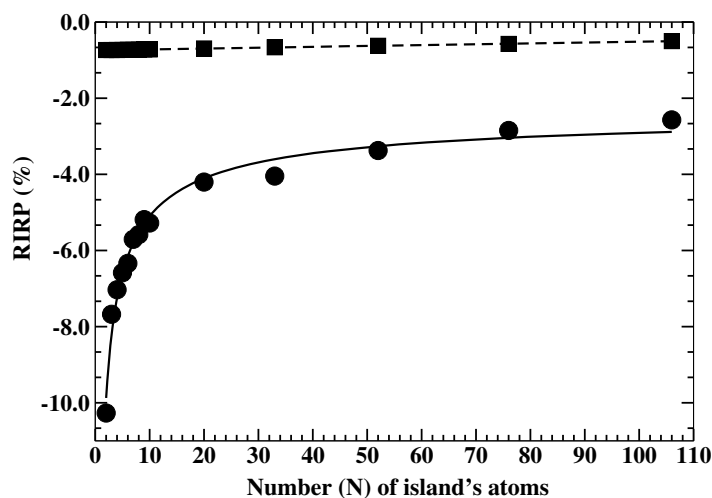


Figure 8. Relative positions of relaxed interlayers (RIRP) (%) for islands as a function of island size, at $T = 300$ K (circles); squares represent the RIRP of surface atoms.

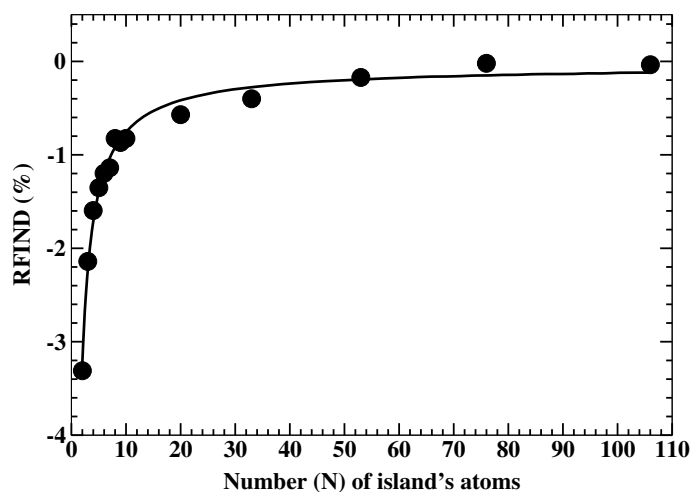


Figure 9. Relaxed first-neighbour distance (RFIND) (%) for islands as a function of island size at $T = 300$ K.

which the migration energy of the island's atoms saturates to the value of 0.37 eV [34], a value which compares very well with the step migration barrier [35,36]. This result indicates that the step-energy barrier and the elastic condition of the islands are correlated; diffusion-driven layer-by-layer or 3D growth can therefore be tuned by controlling the strain of the substrate–adlayer system.

4. Conclusions

In the present study we give results concerning the vibrational properties of 2D islands on the Cu(111) surface. We found that small islands introduce new phonon modes, which gradually reduce to regain the surface characteristics for islands with more than N_s atoms. In addition, we found that the small islands are contracted by as much -10% (dimer). This relaxation

is released for islands having greater size than N_c . Furthermore, the small 2D islands are subject to compressive strain, by as much as -3.3% , due to shortening of their interatomic distance in the in-plane directions, while they are contracted in the direction normal to the surface. Moreover, we found that the mean-square-displacements of the island atoms in the in-plane directions are up to five times greater than the corresponding quantities in the direction normal to the surface. In addition, the in-plane mean-square displacements decrease as the size of the island increases, to attain a constant value for islands greater than N_c , while in the direction normal to the surface they are independent of the size of the island. Interestingly, this characteristic number, N_c , coincides with the value found for the energetic requirements for diffusion of the island atoms on the same surface. Therefore it appears that the elastic properties and the diffusive behaviour of the small islands are correlated, and could be the origin of the morphology and structure of the adlayers on this surface.

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