SUBMONOLAYER NUCLEATION AND GROWTH OF COPPER ON Ni(100)

Bert Müller, Lorenz Nedelmann, Bjørn Fischer,
Harald Brune, and Klaus Kern

Institut de Physique Expérimentale
Ecole Polytechnique Féderale de Lausanne
CH-1015 Lausanne, Switzerland

ABSTRACT

Island densities and island sizes can be varied or even tailored by choice of external parameters in molecular beam epitaxy, i. e., by the choice of substrate temperature, deposition rate, and coverage. We present a comprehensive study of the nucleation kinetics of Cu on Ni(100) using variable temperature scanning tunneling microscopy. The analysis of the saturation island density as a function of substrate temperature and deposition rate reveals that the smallest stable island abruptly changes from a dimer to a tetramer. The sizes of the critical nuclei are determined from the rate dependence of the saturation island density using mean-field nucleation theory consistent with results from the island size distribution using scaling theory. From the Arrhenius-plot, the microscopic quantities (migration barrier and dimer bond energy) have been deduced.

INTRODUCTION

The early stages in molecular beam epitaxy determine crucially the physical and chemical properties of epitaxial structures. Therefore, the quantitative understanding of submonolayer film growth – especially in heteroepitaxy – is an important challenge in material science. Besides the choice of substrate and film material, the external growth parameters, i.e., substrate temperature, deposition rate, and coverage, define the film morphology, including the island density, size, and shape. For simulations, such as Monte Carlo and rate equation analysis, however, microscopic parameters are necessary ingredients, which describe, e.g., the adatom diffusion on terraces and at step edges and the stability of nuclei. These physical quantities can be obtained by the quantitative analysis of STM images using mean-field nucleation theory.[1,2] We have investigated one of the most simple heteroepitaxial systems with square symmetry: copper on Ni(100). Both materials have fcc structure and do not show intermixing and reconstruction below 400 K. Moreover, the lattice mismatch is small, $m = +2.6$ %. Thus, Cu/Ni(100) is an ideal model system to investigate the influence of strain on the island density, which is measured as a function of substrate temperature, deposition

Surface Diffusion: Atomistic and Collective Processes
Edited by Michael C. Tringides, Plenum Press, New York, 1997

rate, and coverage. On the basis of these measurements, the barriers of adatom diffusion and dimer breaking are extracted.

The starting point is the deposition of atoms on a surface without defects. The adatoms can migrate, meet further adatoms and form nuclei. These nuclei either dissociate (subcritical size $< i$) or, for the critical ones (size i), grow to stable islands. These islands continue to grow up to a coverage between 0.1 and 0.2 monolayers (ML), then the island density usually saturates, just before coalescence of islands sets in. The saturation island density can be measured by several surface sensitive techniques, such as electron microscopy,[1] electron diffraction,[3] helium atom diffraction,[4] and scanning tunneling microscopy (STM).[2,5–11] With respect to STM, the other methods have certain disadvantages, mainly related to the difficulties in resolving small islands and coverages of less than 0.1 monolayers. Therefore, STM and especially variable temperature STM has gained attraction for investigations of the very early stages in MBE. One of the first systematic nucleation studies by means of STM on metal surfaces has been carried out by Stroscio and Pierce, who investigated the homoepitaxial growth on Fe(100) at substrate temperatures above 300 K.[7] They derived the migration barrier from the temperature dependence of the saturation island density using nucleation theory in assuming a critical nucleus size of 1. Later on, the sizes of the critical nuclei were determined by the scaling behavior of the island size distribution.[12] Brune et al. have determined the critical island size independent from nucleation theory for the heteroepitaxial system Ag/Pt(111) by direct measurement of the mean island sizes in the very initial stages of nucleation[2] and by measuring the temperature threshold for Ostwald ripening of dimers.[13] Therefore, the rate dependence as well as the Arrhenius behavior of the saturation island density at a known critical cluster size of 1 allowed a direct test of nucleation theory.[2]

The particular bond geometry on square lattices leads to characteristic features in the nucleation kinetics on fcc(100) surfaces. These particularities include the stability of islands. To elucidate that, we briefly recall the concept of the critical nucleus. The critical nucleus i corresponds to an island which becomes stable by the incorporation of an extra atom. Here, stable refers to the time scale of deposition, i.e., stable islands have a higher probability to grow than to dissociate during deposition. In the saturation regime, islands are much larger than the critical nucleus and the surface can be reproducible imaged over hours under isothermal conditions without any change. Depending upon the substrate temperature, deposition rate, and binding energies, one may find for very low temperatures that the monomers do not migrate at all (statistic growth with monomers being stable, i.e., $i = 0$). With an increasing temperature, the monomers start to migrate and form dimers which are stable ($i = 1$). Increasing the temperature further, dimers dissociate, and either the trimer becomes the smallest stable island ($i = 2$), or the smallest island corresponds to a tetramer ($i = 3$), and so on. This classic continuum model ignores the adsorption site geometry of the substrate which does not matter for the critical island sizes $i = 0$ and $i = 1$. The adsorption site geometry, however, becomes important on square lattices with $i = 2$. Contrary to triangular or hexagonal surfaces, on square surfaces the dissociation of both dimers ($i = 1$) and trimers ($i = 2$) is characterized by single bond breaking and therefore associated with similar dissociation barriers. Hence, on square lattices, one expects a direct change from $i = 1$ to $i = 3$ due to the transition from single to double bond breaking. The atoms of compact islands which contain 4 atoms have two neighbors in the adlayer. Above $i = 3$, there is no well-defined behavior since all islands on square lattices are characterized by single or double bond breaking. In the present experiment, we intend to verify the well-defined transition from $i = 1$ to $i = 3$ by the systematic investigation of the saturation island density as a function of substrate temperature and flux. The determination of the sizes of the critical nuclei, of the migration barrier, and the dimer bond energy, as well as the related attempt frequencies is based on the comparison of the experimental results to mean-field nucleation theory.[14] In addition, we have analyzed the island size distributions in comparison with scaling theory[15,16] to confirm the size of critical nucleus.

EXPERIMENTAL

The growth of copper on Ni(100) has been investigated by a variable temperature STM at substrate temperatures between 100 and 400 K; analogous instrumentation as used here has been described by Brune et al.[17] The nickel crystal was prepared by argon ion sputtering and subsequent annealing to 1200 K resulting in perfect terraces of several hundred nanometers. Copper was deposited by thermal evaporation from a Knudsen-type MBE source at a background pressure below 5×10^{-10} mbar. The growth rate has varied between 5×10^{-5} and 5×10^{-3} monolayers per second (ML/s). It was calibrated from STM images with monolayer coverage. The STM measurements have been performed in the constant current mode at 0.5–2.0 V positive or negative bias and 0.5–8.0 nA tunneling current.

The island densities were determined by counting the islands on a certain area, where the size of the analyzed area has been corrected for thermal drift by determination of characteristic features at successively obtained images. The influence of structural defects such as steps has been excluded by depicting areas far away from such defects.

RESULTS AND DISCUSSION

The first step of the analysis, according to nucleation theory, is the experimental verification of the saturation island density which is expected at a coverage of about 0.1–0.2 ML. The experimental values for the island density as a function of coverage are shown in Fig. 1 for a substrate temperature of 345 K and two different deposition

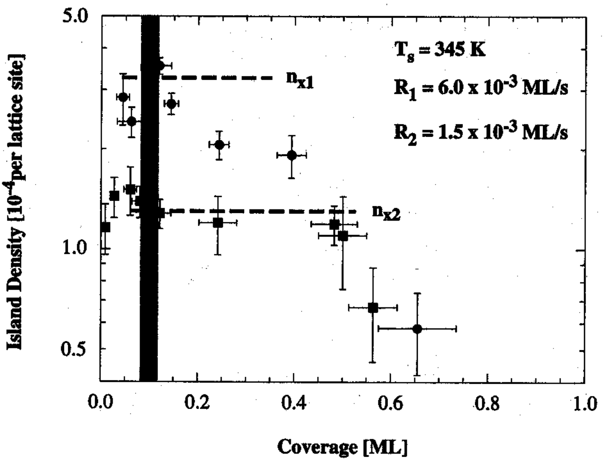

Figure 1. Island densities versus coverage for two different fluxes (1.5×10^{-3} ML/s and 6.0×10^{-3} ML/s) at a substrate temperature of 345 K.

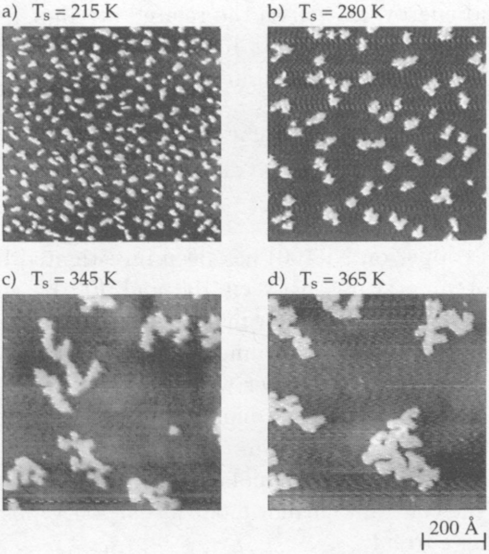

Figure 2. STM images characterizing the saturation island densities for the submonolayer growth of Cu on Ni(100) at different growth temperatures and fixed deposition rate (1.5×10^{-3} ML/s) and coverage (0.1 ML).

rates. For that substrate temperature, the island density stays nearly constant over a wide coverage range (0.01–0.50 ML). Coalescence starts above the expected percolation limit. Therefore, the choice of the coverage to obtain the saturation island density is not crucial. Coverages between 0.08 and 0.12 ML are used for the present study.

The variation of the saturation island density with substrate temperature is characterized in Fig. 2, showing four STM images obtained at fixed deposition rate and coverage. The decrease in island density over orders of magnitudes with substrate temperature is clearly visible. These island densities directly reflect the adatom mobility, which depends exponentially on substrate temperature.

Note, the larger islands in Fig. 2 are not compact at high substrate temperatures (215–370 K). This is surprising since it contradicts the generally accepted picture that on square lattices edge diffusion is always fast enough to produce square shaped islands.[18] The physical reason for the formation of islands with an irregular shape at high substrate temperatures is presumably related to strain accommodation at the step edges of the heteroepitaxial islands as to be discussed in a forthcoming paper.[19]

Fig. 3 shows the measured temperature dependence of the saturation island density as Arrhenius plot at a coverage of about 0.1 ML and a flux of 1.5×10^{-3} ML/s. One can clearly distinguish between three different nucleation regimes which are labeled postnucleation, $i = 1$, and $i = 3$, respectively. Below 160 K, the island density does not vary with temperature indicating statistic growth with $i = 0$. However, the mean island size of 4–5 atoms is too large. For statistic growth a mean island size of 1.25 atoms is obtained on a square lattice at 0.1 ML from percolation theory.[20] Therefore, statistic growth can definitely be excluded. The physical reason for the plateau in the Arrhenius plot is the island formation and the incorporation of monomers into existing islands after deposition, discussed in detail elsewhere.[21]

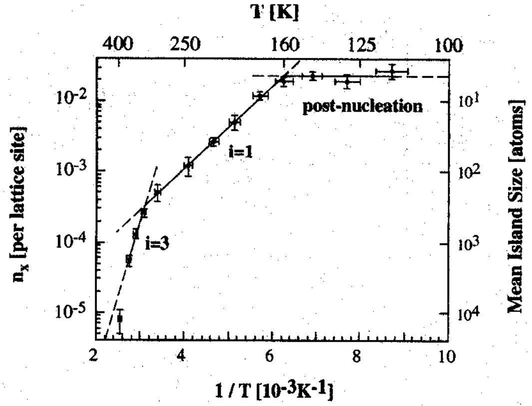

Figure 3. Arrhenius plot of the measured saturation island density of Cu on Ni(100) (flux: 1.5×10^{-3} ML/s; coverage 0.1 ML).

The two regimes entered above 160 K and 320 K, respectively, have been labeled corresponding to the sizes of the critical nuclei. To establish these sizes, we have measured the rate dependence of the island density $n_x(R)$ at three different substrate temperatures – 145, 215, and 345 K – each is located in the center of the labeled regions in the Arrhenius plot. The rate dependency of the island density follows a power law: $n_x \propto (D/R)^{-\chi}$, with χ being $i/(i+2)$ for isotropic 2D migration.[1] The diffusion constant D characterizes the monomer migration at a certain temperature, which is on a square lattice: $D = \frac{1}{4}\nu_0 \exp[-E_m/(kT)]$. For the different critical nuclei, the exponent χ corresponds to 1/3 for $i = 1$,[22] 1/2 for $i = 2$ and raises to 3/5 for $i = 3$. The double-logarithmic plots of the island density versus flux in Fig. 4 show the exponent corresponds to (0.32 ± 0.01) at 215 K and to (0.58 ± 0.02) at 345 K which clearly shows the monomer is the critical nucleus at 215 K ($i = 1$) and the tetramer becomes the smallest stable island at 345 K ($i = 3$). In addition to the rate dependency of the saturation island density, one can use the scaled island size distribution and scaling theory to extract the size of the critical nucleus. These size distributions are presented in Fig. 5 for three substrate temperatures. They exactly show the expected behavior, $i = 0$ for 160 K, $i = 1$ for 215 K, and a distribution closely resembling that of $i = 3$ for 345 K, each at a deposition rate of 1.5×10^{-3} ML/s. The coverage corresponds to 0.1 ML for 160 and 215 K. For 345 K, however, the coverage chosen is much smaller, since for higher coverages the islands become irregular shaped leading to a significant broadening of the size distribution. Because the sizes of the critical nuclei are known, the migration barrier of a single adatom E_m, the dimer bond energy E_b as well as the attempt frequency ν_0 can be determined analyzing the Arrhenius plot of the saturation island density in Fig. 3. Copper is known to grow two-dimensional on Ni(100), and reevaporation of copper atoms from the surface can be neglected in the considered temperature range (100–400 K). On this basis, i.e., for 2D islands and complete condensation, the saturation island density n_x is only a function of deposition rate R and substrate temperature T and given for a square lattice[1] by:

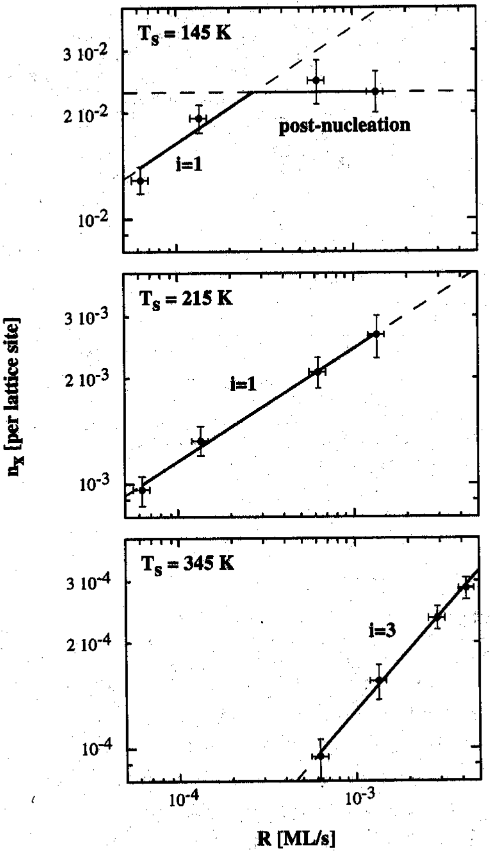

Figure 4. Double-logarithmic plots of saturation island densities versus deposition flux at different growth temperatures and fixed coverage (0.1 ML).

$$n_x \cong 0.2 \left(\frac{4R}{\nu_0}\right)^{\frac{i}{i+2}} \exp\left(\frac{1}{(i+2)kT}\,(iE_m + E_i)\right)$$

In this equation, k is the Boltzmann constant and E_i the binding energy of the critical nucleus i, i.e., $E_0 = E_1 = 0$, $E_2 = E_b$ and $E_3 \cong 2E_b$. The latter value is based upon a bond counting argument, where E_i is given by the number of nearest neighbor adatom bonds in the critical nucleus i times the binding energy per bond E_b. The migration barrier and attempt frequency, E_m and ν_0, for Cu/Ni(100) are obtained in the temperature range where the critical nucleus is one (between 160 and 320 K). The slope of the linear fit results in a migration barrier of E_m = (0.35 ± 0.02) eV. The attempt frequency is found by the intersection of the linear fit with the ordinate and yields $\nu_0 = 4 \times 10^{(11\pm1)}$ Hz. The slope of the second linear fit, where $i = 3$, then unambiguously determines the dimer bond energy, for which we obtain E_b = (0.46 ± 0.19) eV. As an additional check for the consistency of the foregoing analysis, one

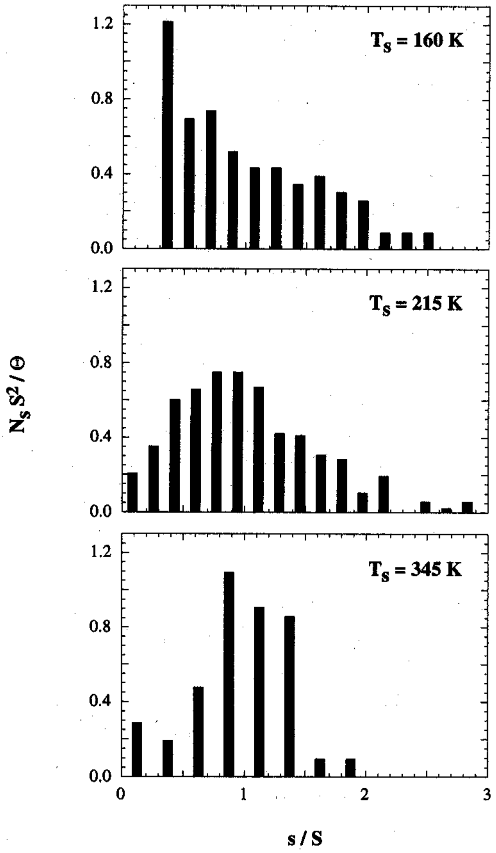

Figure 5. Scaled island size distributions deduced from STM images at different substrate temperatures (deposition flux 1.5 × 10^{-3} ML/s). The temperatures are indicated.

can extract the attempt frequency for single bond breaking from the intersection of the ordinate and the fit to the $i = 3$ data. The value, $\nu_0^* = 5 \times 10^{(12\pm2)}$ Hz, agrees within the error bars with the attempt frequency of monomer migration. If one would ignore the result from the flux dependency and the scaling behavior ($i = 3$) and assumes $i = 2$ for substrate temperatures above 320 K, one obtains an attempt frequency of $\nu_0^* = 5 \times 10^{(15\pm2)}$ Hz, which is far too high, since the attempt frequencies for the different processes are of the same order of magnitude. The value for the migration barrier compares well with the experimental data for Cu/Cu(100). For example, Dürr et al. found from a LEED analysis of island separations as a function of temperature $E_m = (0.36 \pm 0.03)$ eV[3] which is very close to our value.

From Field Ion Microscopy (FIM) measurements, it is known that migration of single adatoms on fcc(100) surfaces can involve exchange processes (see e.g., Pt/Pt(100)[23]). This implies the question whether surface migration of Cu/Ni(100) takes place by exchange or hopping. Since Cu/Ni(100) is a heteroepitaxial system, one should find indications for exchange processes, either upon different imaging of Cu and Ni atoms, or from a particular nucleation behavior. Below 400 K, there is no evidence for a second species besides Cu in the islands and the nucleation behavior is in full agreement with migration by hopping on fcc(100). At 450 K, however, one can clearly distinguish two different species at step and island edges, indicative for the onset of alloying. Therefore, we conclude, in agreement with a theoretical study[24] that for Cu/Ni(100) surface migration takes place by hopping in the temperature range up to 400 K.

Our experimental value for the dimer bond energy $E_b = (0.46 \pm 0.19)$ eV is large in relation to the migration barrier. This explains the sharp transition from $i = 1$ to $i = 3$ and the well-defined $i = 3$ regime, which is not generally expected for nucleation on square lattices.[25] It is interesting to compare our experimental results to calculations performed with Effective Medium Theory (EMT).[26,27] For hopping migration of Cu on Ni(100), we calculate $E_m = 0.47$ eV, which is slightly higher than our experimental value; it compares well to the value of 0.45 eV calculated by Perkins and DePristo.[24] For the activation barrier of dimer dissociation we calculate 0.74 eV yielding a dimer bond energy of $E_b = 0.27$ eV, which is somewhat smaller than the experimental value. Seen the approximate character of EMT and the large error bar of E_b in the experiment, there is reasonable agreement.

CONCLUSION

The quantitative analysis of STM images obtained at variable temperature from Cu nucleation on Ni(100) – a simple heteroepitaxial system with square symmetry – and the comparison with mean-field nucleation theory yields a precise value for the migration barrier and reasonable values for the dimer bond energy as well as for the related attempt frequencies. Copper on Ni(100) shows a direct transition from $i = 1$ to a well defined $i = 3$ regime. Strain effects seem to play a minor role in the nucleation kinetics at low coverages (< 0.1 ML), although island size distributions are sensitive to changes of the island shapes giving rise to a significant broadening of the size distribution for Cu/Ni(100) at higher coverages.

ACKNOWLEDGEMENTS

Financial support of the Alexander von Humboldt-Stiftung (B.M.) and the Deutscher Akademischer Austauschdienst (L.N.) is gratefully acknowledged.

REFERENCES

1. J. A. Venables, G. D. T. Spiller, and M. Hanbücken. "Nucleation and growth of thin films". *Rep. Prog. Phys.*, **47**, 399 (1984).
2. H. Brune, H. Röder, C. Boragno, and K. Kern. "Microscopic view of nucleation on surfaces". *Phys. Rev. Lett.*, **73**, 1955 (1994).
3. H. Dürr, J. F. Wendelken, and J. K. Zuo. "Island morphology and adatom energy barriers during homoepitaxy on Cu(001)". *Surf. Sci.*, **328**, L527 (1995).
4. H. J. Ernst, F. Fabre, and J. Lapujoulade. "Nucleation and diffusion of Cu adatoms on Cu(001): A helium-atom-beam scattering study". *Phys. Rev. B*, **46**, 1929 (1992).
5. M. Bott, T. Michely, and G. Comsa. "The homoepitaxial growth of Pt on Pt(111) studied with STM". *Surf. Sci.*, **272**, 161 (1992).
6. H. Röder, H. Brune, J. P. Bucher, and K. Kern. "Changing morphology of metallic monolayers via temperature controlled heteroepitaxial growth". *Surf. Sci.*, **298**, 121 (1993).

7. J. A. Stroscio, D. T. Pierce, and R. A. Dragoset. "Homoepitaxial growth of iron and a real space view of reflection-high-energy-electron diffraction". *Phys. Rev. Lett.*, **70**, 3615 (1993).
8. J.-P. Bucher, E. Hahn, P. Fernandez, C. Massobrio, and K. Kern. "Transition from one- to two-dimensional growth of Cu on Pd(110) promoted by cross-exchange migration". *Europhys. Lett.*, **27**, 473 (1994).
9. S. Günther, E. Kopatzki, M. C. Bartelt, J. W. Evans, and R. J. Behm. "Anisotropy in nucleation and growth of two-dimensional islands during homoepitaxy on 'hex' reconstructed Au(100)". *Phys. Rev. Lett.*, **73**, 553 (1994).
10. Michael Bott, Michael Hohage, Markus Morgenstern, Thomas Michely, and George Comsa. "New approach for determination of diffusion parameters of adatoms". *Phys. Rev. Lett.*, **76**, 1304 (1996).
11. T. R. Linderoth, J. J. Mortensen, K. W. Jacobsen, E. Laegsgaard, I. Stensgaard, and F. Besenbacher. "Homoepitaxial growth of Pt on Pt(001)-hex: Effects of strongly anisotropic diffusion and finite island sizes". *Phys. Rev. Lett.*, **77**, 87 (1996).
12. J. A. Stroscio and D. T. Pierce. "Scaling of diffusion-mediated island growth in iron-on-iron homoepitaxy". *Phys. Rev. B*, **49**, 8522 (1994).
13. Holger Röder, Elmar Hahn, Harald Brune, Jean-Pierre Bucher, and Klaus Kern. "Building one- and two-dimensional nanostructures by diffusion-controlled aggregation at surfaces". *Nature*, **366**, 141 (1993).
14. J. A. Venables. "Rate equation approaches to thin film nucleation kinetics". *Philos. Mag.*, **17**, 697 (1973).
15. M. C. Bartelt and J. W. Evans. "Scaling analysis of diffusion-mediated island growth in surface adsorption processes". *Phys. Rev. B*, **46**, 12675 (1992).
16. J. G. Amar and F. Family. "Critical cluster size: Island morphology and size distribution in submonolayer epitaxial growth". *Phys. Rev. Lett.*, **74**, 2066 (1995).
17. Harald Brune, Holger Röder, Karsten Bromann, and Klaus Kern. "Kinetic processes in metal epitaxy studied with variable temperature STM: Ag/Pt(111)". *Thin Solid Films*, **264**, 230 (1995).
18. Z. Zhang, X. Chen, and M. G. Lagally. "Bonding-geometry dependence of fractal growth on metal surfaces". *Phys. Rev. Lett.*, **73**, 1829 (1994).
19. B. Müller, L. Nedelmann, B. Fischer, J. Barth, H. Brune, and K. Kern. "Irregular island shapes on square lattices". to be published.
20. M. F. Sykes and M. Glen. "Percolation processes in two dimensions I. low density series expansions". *J. Phys. A. Math. Gen.*, **9**, 87 (1976).
21. B. Müller, L. Nedelmann, B. Fischer, H. Brune, and K. Kern. "Initial stages of Cu epitaxy on Ni(100): Post-nucleation and a well defined transition in critical island size". Phys. Rev. B, accepted.
22. Strictly speaking $\chi = 1/3$ is only exact for compact islands. For ramified islands slightly higher values have been reported. G. S. Bales and D. C. Chrzan. "Dynamic of irreversible island growth during submonolayer epitaxy". *Phys. Rev. B*, **50**, 6057 (1994).
23. G. L. Kellogg. "Field ion microscopy studies of single-atom surface diffusion and cluster nucleation on metal surfaces". *Surf. Sci. Rep.*, **21**, 1 (1994).
24. L. S. Perkins and A. E. DePristo. "Heterogeneous adatom diffusion on fcc(100) surfaces: Ni, Cu, Rh, Pd, and Ag". *Surf. Sci.*, **319**, 225 (1994).
25. M. C. Bartelt, L. S. Perkins, and J. W. Evans. "Transitions in critical size for metal (100) homoepitaxy". *Surf. Sci.*, **344**, L1193 (1995).
26. K. W. Jacobsen. "Bonding in metallic systems: An effective-medium approach". *Comments Cond. Mat. Phys.*, **14**, 129 (1988).
27. P. Stoltze. "Simulations of surface defects". *J. Phys. Condens. Matter*, **6**, 9495 (1994).