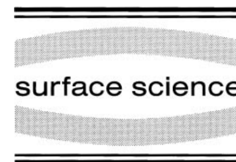
ELSEVIER

Surface Science 405 (1998) L542–L548



Surface Science Letters

Low-temperature deposition of Co on Cu(111): effects on step etching

S. Speller [a,*], S. Degroote [a], J. Dekoster [a], G. Langouche [a], J.E. Ortega [b], A. Närmann [b]

[a] Instituut voor Kern- en Stralingsfysica, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

[b] Universidad del País Vasco, Facultad de Química, Apdo.1072, E-20080 San Sebastián, Spain

Received 15 December 1997; accepted for publication 10 February 1998

Abstract

During growth of submonolayer films of Co on Cu(111) at 280 K, the surface is damaged by etching, leading to an increase in the interfacial mixing and roughness. By means of a quantitative STM study, we analyze the influence of the temperature of the substrate on this etching. Our results for 1/8 ML of Co indicate that the etching rate is considerably reduced by lowering the substrate temperature to 140 K during Co deposition only. The total etched area observed after annealing the film to 300 K can be reduced by a factor of five, although the etching process continues at a much lower rate. From the quantification of both the etched area and the Cu content within terrace islands, we argue that the etching is basically due to the diffusion of Cu atoms out of the step-edges. Such a diffusion process, which is significantly diminished at low temperature, takes place at the early stages of the growth, i.e. during Co aggregation and island formation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Copper; Growth; Scanning tunneling microscopy; Vicinal single crystal surfaces

Low-dimensional systems are increasingly attracting fundamental and technological interest [1,2]. One important representative of the 2D class is the thin film, which usually needs to be supported by a kind of substrate. Mostly – especially for ultra-thin magnetic films – smooth and abrupt interfaces are required, but the lattice and surface energy mismatch generally drive the systems into an irregular structure and/or composition. Intermixing represents the major limitation to obtain a sharp interface. It is often outside the range of standard thermodynamic data, i.e. unexpected and non-predictable, though it is very frequent in metal-on-metal systems. Systems such as Co/Cu(111) [3], Cu/Pb(111) [4–6], Cr/Au(100) [7] or Cr/Fe(100) [8] display some kind of intermixing. As shown recently for Rh/Ag(100) [9], the tendency of the two different species to intermix is also the driving force for another kind of interfacial reactivity, i.e. the etching of the substrate induced by the adsorption of foreign atoms. This effect was also observed in Co/Cu(111) [10], Fe/Cu(100) [11], and Fe/Cu(111) [12]. The surface etching represents an additional source of interface roughness since it increases the number of surface steps [13]. In general, the chemical activity at the surface can be reduced by lowering the temperature of the substrate during growth. However, films obtained in

* Corresponding author. Fax: (+49) 541 9692670; sspeller@rz.uni-osnabrueck.de

0039-6028/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII: S0039-6028(98)00148-4

this way usually require a brief anneal to achieve a good crystallinity. For Cu/Co(100), it has been shown very recently that, in order to prevent interfacial reactivity, it is sufficient to lower the temperature during the deposition of the first layer of adatoms [14]. Further layers can be deposited at room temperature, where layer-by-layer growth is ensured. In this paper, we test the low-temperature (LT) deposition method in the prevention of etching in Co/Cu(111) by means of a quantitative STM analysis. For 1/8 ML of Co, the step-etching is largely suppressed for LT deposition, where we observe a reduction of the etched area by a factor of five, although etching continues at 280 K but at a minor rate. Part of the etched Cu appears incorporated within terrace islands. Our results suggest that the etching is probably due to a sort of "gettering" of the Cu adatoms evaporated from the steps. Thereby, step-edges are "pumped", and etch-pits are formed.

The experiments were carried out in situ in a UHV chamber equipped with Scanning Tunneling Microscopy (Omicron Large Sample STM) and standard surface analytical techniques. The pressure was $<1\times10^{-10}$ Torr. The Cu samples were polished mechanically and electrochemically. Three cycles of 3 keV Ne^{+} sputtering and annealing were necessary in order to achieve a perfect LEED and RHEED pattern. By AES, no contaminations were detected. The sample holder block could be brought in contact with a hollow body of Cu that was cooled by liquid nitrogen. A thermocouple measures the temperature close to the crystal. In radiation equilibrium, the temperature on the surface and at the place of the thermocouple are identical within 5°C. Co is evaporated by an electron beam from a crucible. The flux is regulated via the mass spectrometer signal. The film thickness is measured by a quartz microbalance, which was calibrated by comparison with X-ray diffraction measurements of thick Co films. The error in the film thickness is less than 5%. We use a computer-controlled shutter and a high flux of Co of 0.1 Å s^{-1}. One monolayer of Co is assumed to correspond to a height of 2.035 Å. The clean substrate shows monoatomic (2.1 Å high) and a few double steps between terraces of 400 Å average size, although it does not show step-pinning. By local fluctuations, a spectrum of step densities between 1/200 Å and 1/1000 Å is accessible on the surface. All the images are taken with the sample held at 300 K. In the case of RT-growth (280 K), the STM images are recorded from 15 to 120 min after deposition. For LT-deposited (140 K) films, a break of 110 min was necessary to achieve thermal equilibrium at 300 K in the STM. In this case, the images are taken from 110 to 190 min after LT deposition.

In the left panel of Figs. 1 and 2, we show typical STM pictures for 0.123 ML of Co deposited at LT (Fig. 1) and RT (Fig. 2), respectively. In the right panel, the images show the topography of the same film after a subsequent annealing to 350 K. The growth is characterized by the presence of islands, step decoration and etching of the surface, the latter mainly found close to the surface steps. The basic features are coincident with previous STM work for RT deposition [10,15,16]. The Co has mainly grown at the steps, about 50 Å in the direction perpendicular to the step but on the upper terrace. The occupation of the lower terrace sites at the steps only develops at a higher coverage (0.4 ML with our step density). As observed previously, there is no smooth transition between step-decorating islands. Only a few islands exist on the terraces. The values for separation between these islands and their minimum distance to the steps are listed in Table 1. The morphology of submonolayer films at RT does not depend on the deposition temperature of the Co. Neither the average distance between islands nor the island-step separation is basically affected by the deposition temperature. The similarity of the morphology suggests that the diffusion length of individual Co atoms has not changed dramatically by going to 140 K. Thereby, the islands and the step decoration basically develop at LT. This result was already predicted for Co/Cu(111) from the similar mode of growth observed for thicker films at 80 K and 300 K [17].

The islands' height and shape do not change significantly with deposition temperature. Only after LT deposition do the islands appear slightly more irregular. At this coverage, the small clusters

SURFACE SCIENCE LETTERS

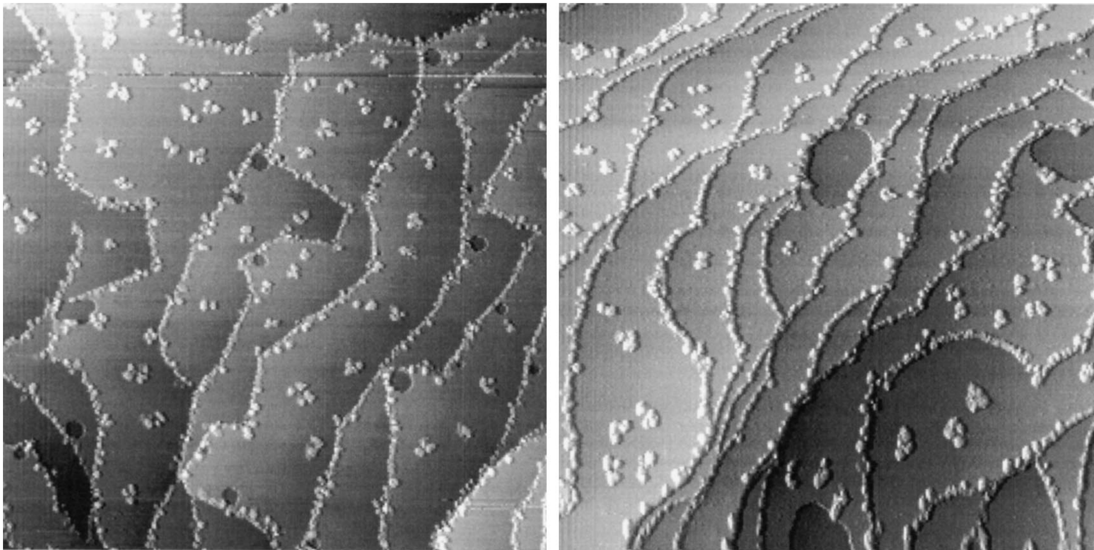


Fig. 1. STM topographs, 0.123 ML Co on Cu(111), deposited at LT, (4000 Å)^2; left, without annealing; right, annealed to 350 K.

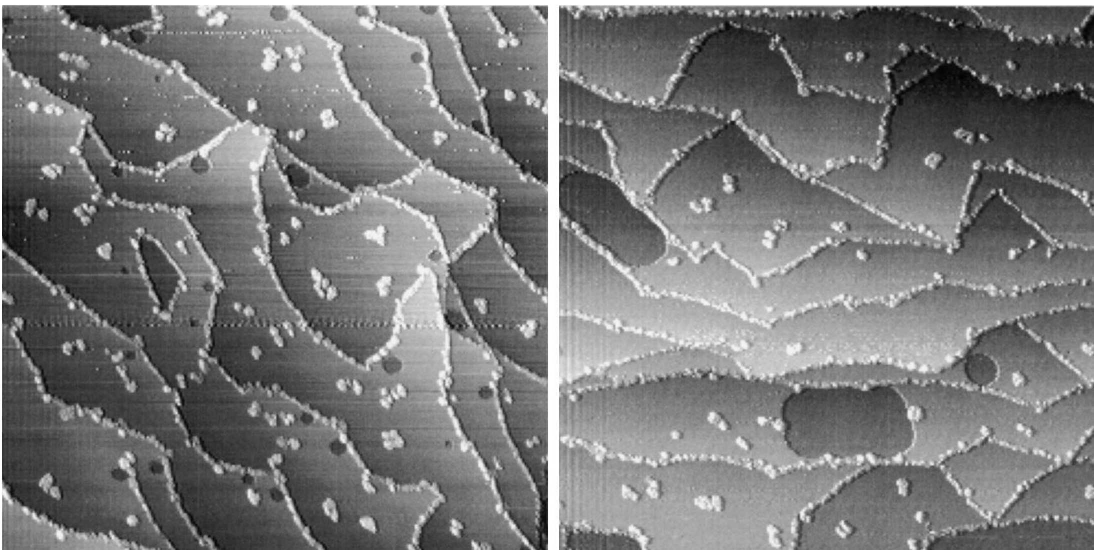


Fig. 2. STM topographs, 0.123 ML Co on Cu(111), deposited at RT, (4000 Å)^2; left, without annealing; right, annealed to 350 K.

do not show any hint of interior lateral symmetry, but they rather resemble liquid droplets. Triangles are found only when the size of a single island exceeds 100 Å [15,16]. Most of the islands reveal a variable height from monolayer (2 Å) to bilayer (4 Å) and even further, up to 5.5 Å, as shown in the histogram of Fig. 3. This is also valid for the islands located at the steps. The height distribution shown in Fig. 3 corresponds to the center of a large terrace, i.e. away from the steps. In the following, we will focuss only on such areas. There is a smooth variation from the lower peak (that marks the position of the terrace plane) up to a maximum intensity close to the bilayer height of

SURFACE SCIENCE LETTERS

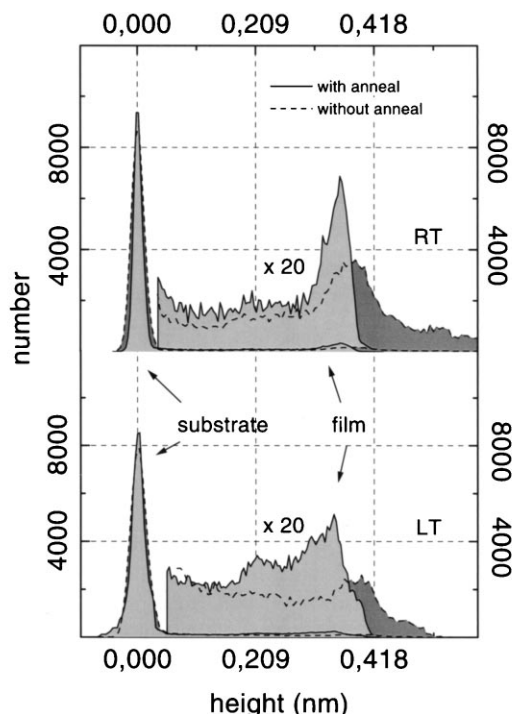


Fig. 3. Height histograms of on-terrace islands, after deposition of 0.123 ML Co on Cu(111).

Table 1
Separations of islands and steps[a]

T_{dep}	d_{isl} (Å)	*Dev* (Å)	*s* (Å)	*Dev* (Å)
140 K	347	115	262	112
280 K	338	172	268	120

[a] T_{dep}, deposition temperature; d_{isl}, mean value of the distance between two neighbouring islands; *Dev*, rms deviation; *s*, average separation of islands from steps.

4 Å. This peaking intensity is more pronounced for RT-deposited films or after the annealing. The smooth histogram actually reveals an irregular height within the island, which is in turn related to the presence of Cu, either segregated on top of the Co or in between close islands [10]. The major effect of the annealing on these terrace islands seems to be a sort of smoothing by moving material from the third level to the second one, as also observed in Fig. 3. The apparent coverage at the center of large terraces is obtained from a numerical analysis of several of these histograms. This varies from 0.15 ± 0.04 ML with LT deposition to 0.2 ± 0.05 ML with RT deposition. The error margins are defined by the maximum variation among different terraces. The local coverage in the middle of a terrace thus always exceeds the nominal Co coverage. Therefore, an additional amount of Cu has necessarily migrated to the Co islands from other parts of the surface, most likely from surface steps.

Fig. 4 (left) shows a place that contains the two typical etching damages after deposition (A and B). These are, respectively, indentations near the steps with some tens of ångstroms of lateral extension and (much less abundant) vacancy islands close to an accumulation of typically three or four cloverleaf-shaped islands. The area of the etched surface increased as a function of the Co coverage at least in the submonolayer regime [10], but it also increased during annealing (right panel of Figs. 1 and 2). The holes always grow behind the Co islands at the higher terrace, indicating that there is no transport of Co towards the inner border of the indentation. Most of them display a small entrance to the lower terrace between two Co islands (see Fig. 4, right), suggesting the transport of Cu to the lower terrace side of the Co island. All the etching holes have ML depth and round shape. Only the smaller ones (<100 Å) reveal a hexagonal shape. They are not from residual sputter damage since they were not observed on the clean, annealed surface. Therefore, the strong decoration observed at the surface steps is never present within the indentations. Etch pits like those displayed in Figs. 1 and 2 were also observed close to the step edges in other systems (Fe/Cu(100) [11] and Fe/Cu(111) [12]. In Rh/Ag(100), the etching of the steps provides the additional amount of Ag needed to encapsulate the foreign Rh atoms, since the exchange place of the first Rh layer does not seem to be complete [9]. We believe that a similar process is taking place in our system. At submonolayer coverages, the additional Cu detected within the islands is probably needed to encapsulate Co atoms in the first layer. This Cu can be provided from the steps at minimal energy cost, either from inside the

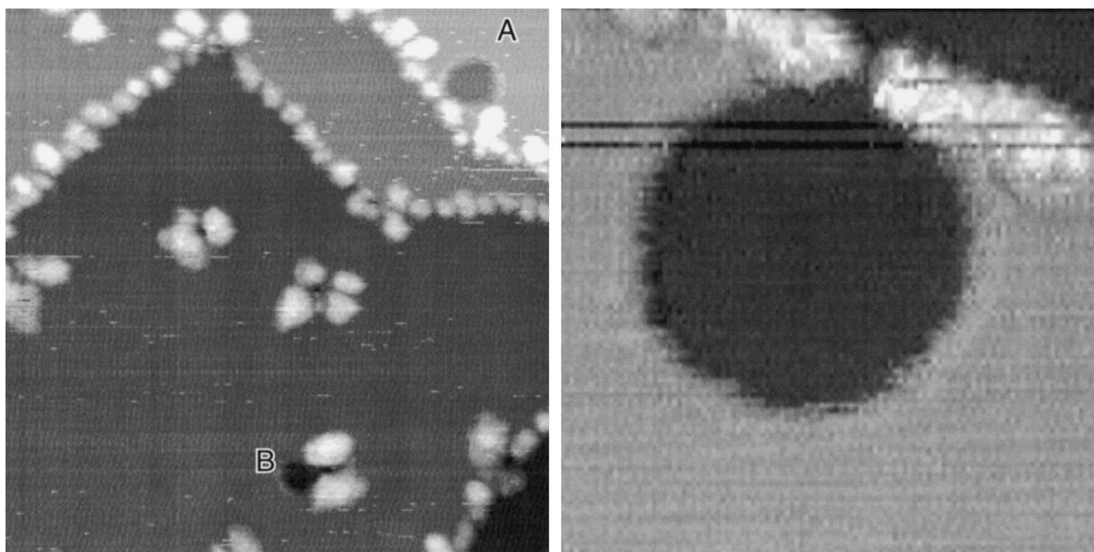


Fig. 4. STM topographs, 0.123 ML Co on Cu(111), deposited at LT; left, (1000 Å)^2; right, (250 Å)^2.

Table 2
Substrate etching with $\theta=0.123$ ML of Co at different deposition temperatures and film annealing temperatures[a]

T_{dep}	T_{ann}	a (μm^2)	ρ (1 μm^{-2})	$\overline{Ø_{ind}}$	Dev (Å)	e (%)
140 K	No	1.226	62.0	62	32	0.24 (1:50)
140 K	350 K	2.800	23.2	382	131	2.98 (1:4)
280 K	No	0.919	222.0	79	36	1.32 (1:10)
280 K	350 K	2.640	23.5	422	152	3.71 (1:3)

[a] T_{dep}, deposition temperature; T_{ann}, annealing temperature; a, sum of evaluated area; ρ, density of indentations; $\overline{Ø_{ind}}$, average diameter of indentations; *Dev*, rms deviation; e, etching (the e/θ ratio is given in parentheses).

etching holes or from point sources that later collapse, forming bigger indentations. The latter process is indeed taking place, as deduced from the hole size and distribution after annealing. In Table 2, we show a numerical analysis of the etching damage observed on the Cu(111) surface for LT- and RT-deposited Co and after annealing both films to 350 K. For LT deposition, the density of the indentations is strongly reduced while their average size decreases only little. The total etching damage is given as the relative number of Cu atoms etched away. At LT, 50 Co atoms attract only one Cu atom from the substrate compared to the 10:1 etching rate during RT deposition. Such small numbers contrast with the noticeable excess of Cu in the islands within the terrace in both cases, thus suggesting a preferential diffusion of the etched Cu to these islands. The lower etching observed with LT deposition is also consistent with a minor concentration of Cu within the islands in the middle of the terrace, although it is not proportional. However, the strong reduction of the etching with the LT deposited film indicates that incorporation of Cu within the Co islands takes place during the early stages of the growth, i.e. during Co diffusion and island formation. It is probably a sort of trapping of the Cu adatoms that are continuously evaporated from the steps by the isolated Co adatoms or small Co nucleation centers, i.e. surface steps are being "pumped" by the Co "getters" leading to the observed step-etching. However, Co nucleation centers quickly develop, forming islands already at LT, whereas the density of Cu adatoms within a terrace is

SURFACE SCIENCE LETTERS

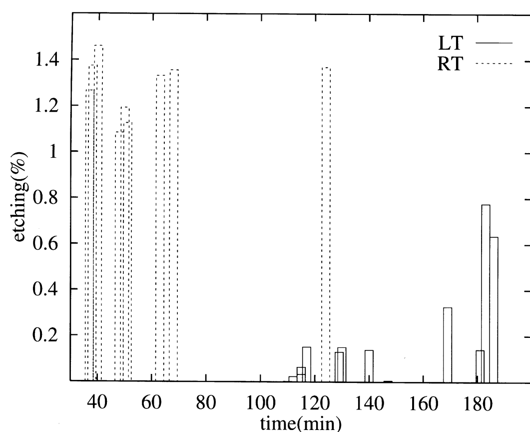


Fig. 5. Time evolution of the etching after deposition of 0.123 ML Co on Cu(111).

expected to be much lower at 140 K [18,19][1]. As a consequence, at LT, the etching is largely supressed.

As shown in Fig. 5, the etching with the RT-grown film is already in saturation after 15 min. This seems to be in contradiction with Ref. [3], where Cu and Co ion scattering signals from 1 ML thick films have not reached saturation even 120 min after growth. Here, we note that thinner films will need less time to intermix with the substrate. However, intermixing can also be partly ion-beam-assisted, since energies put into the surface by ion analysis beams are usually clearly above thermal energies [20]. In contrast to the early saturation at RT, the etching in the case of the LT-grown film still shows a time dependence 180 min after deposition, though the saturation level cannot be determined within a reasonable measuring time. Therefore, etching is also taking place after the system has reached its equilibrium shape at RT, although it is produced at a much slower rate. This supports the idea of Cu adatoms being trapped by the Co. With large nucleation centers already developed, the "gettering" effect is diminished, although the system is not saturated.

In order to accelerate the kinetics of the etching process, both films were annealed to 350 K (Figs. 1 and 2, right). The numerous indentations have coalesced to a few large ones, and the etching damage has increased dramatically, as deduced from the numerical analysis in Table 2. Now, the etching amounts to one Cu atom per three (four) Co atoms at RT (LT) deposition. This additional Cu probably migrated to step-decorating islands since the apparent coverage at the center of the terraces did not change upon annealing for RT deposition and only increases by 15% for LT-deposited films. These numbers also indicate that there is a strong contribution of the step etching to the absolute Cu–Co mixing at the interface. Such an intermixing has already saturated at RT for terrace islands. However the increase in etching rate after annealing indicates that both LT- and RT-deposited films held at RT only reach a delicate equilibrium. The high thermal instability around 300 K is also typical for Cu segregation on top of submonolayer films of Fe/Cu(100) [21], whereas thicker, fully wetting Fe films are more stable. This indicates that submonolayer films are accessible to additional Cu atoms, i.e. those evaporated from the etch pits and diffusing laterally across the clean Cu(111) patches. Therefore, we suggest that by wetting the Cu(111) surface at LT with thicker Co films, one can also diminish the etching induced by the annealing [14]. However, thicker films are out of reach for a quantitative surface etching analysis with STM.

Acknowledgements

This work has been supported by "HCM Institutional Grants" (S.S., ERB4050PL940896), "Belgian Concerted Action", "Fund for Scientifique Research Flanders" (S.D. and J.D.), UPV057.240-EA184/96 research project (A.N. and J.E.O.) and European Commission (A.N., Marie Curie Fellowship, ERBFMBICT950038).

[1] A rough estimate of the relative number of available Cu atoms provided by the step edges can be made, considering the adatom concentration on a lattice-gas model [18]. This is n_{ad}-n_0 exp $(-W_s/kT)$, where W_s is the evaporation energy from the step to the terrace. Assuming W_s to be similar to the kink formation energy in Cu(100) (see Ref. [19]), the adatom density decreases at least by a factor of 50.

SURFACE SCIENCE LETTERS

References

[1] B. Heinrich, J.F. Cochran, Adv. Phys. 42 (1993) 523.
[2] F.J. Himpsel, J.E. Ortega, G.J. Mankey, R.F. Willis, Adv. Phys. in press.
[3] A. Rabe, N. Memmel, A. Steltenpohl, Th. Fauster, Phys. Rev. Lett. 73 (1994) 2728.
[4] C. Nagl, E. Platzgummer, M. Schmid, P. Varga, S. Speller, W. Heiland, Phys. Rev. Lett. 75 (1995) 2976.
[5] C. Nagl, E. Platzgummer, M. Schmid, P. Varga, S. Speller, W. Heiland, Phys. Rev. Lett. 76 (1996) (E) 3240.
[6] C. Nagl, E. Platzgummer, M. Schmid, P. Varga, S. Speller, W. Heiland, Surf. Sci. 352–354 (1996) 540.
[7] M.C. Hanf, C. Pirri, J.C. Peruchetti, D. Bolmont, G. Gewinner, Phys. Rev. B 39 (1989) 3021.
[8] R. Pfandzelter, T. Igel, H. Winter, Phys. Rev. B 54 (1996) 4496.
[9] S.-L. Chang, J.-M. Wen, P.A. Thiel, S. Günther, J.A. Meyer, R.J. Behm, Phys. Rev. B 53 (1996) 13747.
[10] J. de la Figuera, J.E. Prieto, C. Ocal, R. Miranda, Surf. Sci. 307–309 (1994) 538.
[11] A. Brodde, H. Neddermeyer, Surf. Sci. 287/288 (1993) 988.
[12] A. Brodde, K. Dreps, J. Binder, Ch. Lunau, H. Neddermeyer, Phys. Rev. B 47 (1993) 6609.
[13] J.E. Ortega, F.J. Himpsel, Appl. Phys. Lett. 64 (1994) 121.
[14] P. Segovia, E.G. Michel, J.E. Ortega, Phys. Rev. Lett. 77 (1996) 3455.
[15] J. de la Figuera, J.E. Prieto, G. Kostka, S. Müller, C. Ocal, R. Miranda, K. Heinz, Surf. Sci. 349 (1996) L139.
[16] S. Müller, G. Kostka, T. Schäfer, J. de la Figuera, J.E. Prieto, C. Ocal, R. Miranda, K. Heinz, K. Müller, Surf. Sci. 352 (1996) 46.
[17] M.T. Kief, W.F. Egelhoff Jr., Phys. Rev. B 47 (1993) 10785.
[18] W.K. Burton et al., Phil. Trans. R. Soc. Lond. Ser. A 243 (1951) 299.
[19] Poengsen et al., Surf. Sci. 274 (1992) 430.
[20] H. Niehus, W. Heiland, E. Taglauer, Surf. Sci. Rep. 17 (1993)
[21] Th. Detzel, N. Memmel, Phys. Rev. B 49 (1994) 5599.