ELSEVIER

Surface Science 419 (1999) 89–96

surface science

Structure determination of Ag(111) by low-energy electron diffraction

E.A. Soares [a,*], V.B. Nascimento [a], V.E. de Carvalho [a], C.M.C. de Castilho [b], A.V. de Carvalho [a], R. Toomes [c], D.P. Woodruff [c]

[a] *Depto. de Física, ICEx-UFMG, CP 702, Belo Horizonte, MG, Brazil, CEP 30123-970*
[b] *Instituto de Física-UFBA, Salvador, BA, Brazil CEP 40210-340*
[c] *Department of Physics, University of Warwick, Coventry CV4 7AL, UK*

Received 26 May 1998; accepted for publication 13 September 1998

Abstract

A quantitative structure determination of the Ag(111) clean surface has been performed using low-energy electron diffraction. Optimisation of the outermost layer spacings and vibrational amplitudes was achieved using two different dynamical scattering computational methods, one using the LEEDFIT code and the second exploiting a Simulated Annealing algorithm implemented on the conventional Van Hove/Tong code. The results obtained show that a bulk-terminated structural model describes the data best ($\Delta d_{12} = 0.00 \pm 0.02$ Å and $\Delta d_{23} = 0.00 \pm 0.03$ Å), and in particular, the analysis excludes a 2.5% contraction of the outermost layer spacing, which was recently reported on the basis of ion-scattering measurements. The LEED result of no contraction is consistent with prior results for the (111) face of several other fcc metals. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Silver; Low-energy electron diffraction (LEED); Low-index single crystal surfaces; Surface relaxation and reconstruction; Surface structure, morphology, roughness, and topography

1. Introduction

Although the structure of low-index faces of metallic single crystals is generally well-understood, especially from prior studies using quantitative low-energy electron diffraction (LEED), studies of their surface crystallography remain of interest. They are, for example, good initial candidates for testing new structural methods, including new computational approachs for simulating LEED intensity–voltage [$I(V)$] curves. A good description of the clean surface is also an important starting point to any LEED study of adsorbate-covered surfaces. One class of adsorbates of current interest is species that may be used as surfactants to allow layer-by-layer homoepitaxial growth of metals and semiconductors [1–5], such as the role of Sb in the growth of Ag on Ag(111) [6,7], and our own interest in Ag(111) is related to this problem.

Deviations of surface atomic positions from those expected for an ideal termination of the bulk structure are due to the reduced coordination of the surface atoms and can involve major reconstructions, but for most metal surfaces, only changes in the outermost layer spacings are found.

Early theoretical work [8] predicted that these

* Corresponding author. Fax: +55 31 499 5600; e-mail: edmar@fisica.ufmg.br

PII: S0039-6028(98)00744-4

surface layer spacings should increase. However, the current view (supported by experiments) is that in an ideally bulk-terminated surface, the surface layer of atoms is in a lower average valence charge density than in the bulk, and typically, the outermost layer spacing contracts to reduce this effect. This energy-lowering structural modification is commonly refered to as surface relaxation. Careful studies indicate that there is commonly an associated slight expansion of the second-layer spacing, and indeed a damped oscillatory relaxation occurs in the outermost few layers. Investigations show that there is a correlation between the magnitude of these relaxations and atomic layer density [9], the effect being more pronounced for the more "open-packed" the surface. For example, for the relatively open fcc(210) and bcc(210) surfaces, the contraction of the top layer distance can be approximately 20%, whereas much more close-packed surfaces like Ni(111), Ru(0001) or Fe(110) are essentially bulk-terminated [10]. The (111) surface of fcc metals is generally regarded as being of the second type, and these surfaces have been considered to be bulk-terminated due to the small relaxations observed [9,11]. In fact, a survey of experimental quantitative surface-structure determinations of fcc(111) surfaces [12] shows scattered values, with expansion actually being reported more frequently than contraction. The specific values of the change in the outermost layer spacing are: Al(111), +1.3% [13,14]; Cu(111), +0.8% [15] and −0.3% [16]; Ir(111), −2.6% [17]; Ni(111), 0% [18]; Pb(111), −3.5% [19]; Pd(111), +2.4% [20] and +1.0% [21]; Pt(111), +1.1% [22]; Rh(111), −2.7% [23].

In the case of Ag(111), an early high-energy ion scattering investigation [24] showed that the best agreement between calculated and experimental data was achieved assuming a bulk-like surface. However, in a recent investigation of Ag(111) by Statiris et al. [25], the results of a medium-energy ion scattering (MEIS) study at different sample temperatures led to the conclusion that, at room temperature, this surface has a first-layer contraction of 2.5% (with respect to bulk interlayer spacing), whereas the second layer undergoes an expansion of 0.6%. They also observed an increase in vibrational amplitudes of the outermost layers. For room temperature, they found a first-layer rms vibrational amplitude about 45% larger than that of the bulk. They associate these simultaneous changes in the vibrational behavior and the structural parameters to anharmonic effects that become stronger as the temperature is increased.

In contrast to the early theoretical work, more recent theoretical calculations for Ag(111) have generally yielded surface layer contractions (e.g. of about 1.4% [26]), although Kara et al. [27] showed recently that, depending on the methods used (ranging from a fully anharmonic method using molecular dynamics to a more approximate method based on calculated free energy in a quasi-hamonic treatment provided), the predicted surface layer spacing at room temperature may be either a contraction of about 2% or expansion of about 1%.

The Ag(111) surface has been investigated by LEED during the early development of the technique, notably in a study of an iodine adsorption structure [28], but whereas a "good agreement" was stated to have been achieved for the clean surface, no details of this work appear to have been published, and it is unlikely that any modification from ideal bulk termination was considered. Certainly, there has been no quantitative LEED study since the development of modern *R*-factor (reliability-factor) methodology, and we have, therefore, undertaken such a study to provide a test of this somewhat surprising MEIS result, and present the results herein. Our analysis includes a search of all possible surface relaxations, but specifically includes three models: ideal bulk termination ("bulk"), the contracted layer model found in the MEIS study ("MEIS"), and an early theoretical prediction [8] of a structure involving an expansion of 1.5% in the first layer and 0.2% in the second layer ("early theory"). We stress that this last structure is simply used as a specific model that includes outer-layer expansion, and is not intended to imply that the theoretical treatment used in its derivation in any way represents the current state of the art.

2. Experimental

The experimental data used in this work were collected at the University of Warwick using a

UHV chamber equipped with a range of facilities for sample preparation and surface characterization and fitted with a computer-controlled TV camera system combined with a rear-view LEED optics. The base pressure of the chamber was typically $1–2\times10^{-10}$ Torr. The Ag crystal was cut using spark erosion and the orientation of the (111) face checked using Laue X-ray diffraction. The crystal was then polished using progressively finer grades of diamond paste to produce a mirror finish. After insertion in the vacuum, the sample was cleaned using cycles of sputtering (Ar^+ ions with 3 keV) and annealing (500°C for 10 min). The temperature was monitored using a chromel–alumel thermocouple in contact with the sample. The cleaning cycles were repeated until no carbon, oxygen or sulphur were detectable using XPS and the LEED indicated a sharp (1×1) pattern. LEED patterns from 90 to 300 eV were digitised using an Omicron LEEDStar video system at nominal normal incidence. Problems with the sample manipulator design precluded setting the incidence angle sufficiently close to normal to obtain a fully symmetric LEED pattern, but this problem was satisfactorily overcome for this simple structural problem in the data analysis as decribed below. The $I(V)$ curves for eight diffracted beams [(0,−1), (0,1), (−1,0), (1,0), (−1,−1), (−1,1), (1,1), (−2,1)] were then obtained from the digitised LEED patterns and smoothed using a five-point least-square cubic polynomial algorithm. Each of these $I(V)$ curves was used as a separate data set in the subsequent structure determination.

3. Computational details

The theoretical analysis was performed assuming the muffin-tin potential model for the crystal. A muffin-tin radius of 1.4460 Å was used for the Ag atoms. Clementi atomic wave functions [29] were used as the starting point for determining the scattering potential, and a Slater exchange parameter of 2/3 was assumed. The scattering phase shifts needed for the LEED calculations were evaluated by numerical integration of the radial part of the Schrödinger equation in the muffin-tin spheres.

The full dynamical LEED calculations were performed on an AlphaDec Station using the LEEDFIT code [30–34]. In addition to the automatic optimization of the structural parameters, this code allows optimization of non-structural parameters such as the Debye temperature and the atomic vibrational amplitudes for each atom in each layer. This code comes from an extended LEED multiple scattering theory, including anisotropic vibrations. The method is based on a multipole expansion of the probability density function. This treatment of anisotropic vibrations leads to thermally averaged atomic scattering t-matrices with off-diagonal terms that are inserted into the previous multiple scattering formalism [34]. The Marquardt procedure [35], which combines the steepest descent and expansion methods, was used to locate the structures corresponding to the lowest values of the R-factor. A set of 10 phase shifts and a sample temperature of 293 K were assumed. The three outermost layers were treated as being surface layers with potentially different structural parameters to those of the underlying bulk. A value of $V=(-10+4i)$ eV was assumed for the optical potential.

As a further check to ensure that the optimization method used in the LEED calculation had no influence on the results, the Simulated Annealing (SA) algorithm was also used in this LEED analysis. The SA was implemented with the conventional Van Hove/Tong LEED computational package [36,37]. This algorithm mimics the process of crystallization through annealing with gradual cooling. Its main feature is that it allows large random changes in the trial structures being investigated. By random jumps, SA can, in principle, find the global minimum, at least in a finite region of parameter space. The adapted code was first tested exhaustively on data from the Ni(100) surface (the application of this Simulated Annealing Algorithm in LEED analysis will be published elsewhere), and the algorithm was found to perform well.

As the experimental $I(V)$ curves were collected near to, but not at, normal incidence, we ran calculations aimed at establishing the exact incidence geometry. In order to achieve this, the full dynamical theory intensities were calculated for a

range of polar and azimuthal incidence angles for each of the three principle structural models considered. At each angle, the level of agreement between experiment and theory was quantified using the Pendry R-factor R_P. The structural parameters were analysed using both the grid method and an automatic optimization in order to obtain the best-fit structural model for the Ag(111) surface. The non-structural parameters, such the Debye temperature and thermal vibrational amplitudes, were then optimised for the best-fit structural model in the final stage of refinement.

4. Results and discussion

As summarised above, the first stage of this LEED determination of the clean Ag(111) surface was to calculate the $I(V)$ curves for several different incidence geometries (polar angle, θ, from 0 to 13° in 1° steps and azimuthal angle, ϕ, from 0 to 360° in 10° steps) for the three initial structural models; these were then compared with the experimental data. During these calculations, the Debye temperatures of both surface and bulk layers were kept constant and equal to the bulk value ($\Theta_D = 225$ K [9]). The results are summarised in Table 1. Note that all three models show the minimum R-factor at the same value of θ, whereas the values for the angle ϕ differ only slightly. Table 1 also shows that the bulk terminated surface model exhibits the lowest R_P factor value.

A more complete search of possible structures was then conducted using the incidence angles obtained in this initial stage. The specific values used ($\theta = 1.75°$ and $\phi = 40°$) are those obtained for the bulk termination model, which showed the lowest value of R_P in Table 1, but it is clear that for such a small value of θ, the exact choice of ϕ is not crucial. In this new structural search, both the first (d_{12}) and second (d_{23}) interlayer distances were varied using the conventional grid method but the third interlayer distance (d_{34}) was kept constant and equal to the bulk value. This seems to be a reasonable constraint in view of the very small relaxations found in previous studies of fcc(111) surfaces, even for the outermost layer. Note also that even the larger relaxations deduced for Ag(111) from MEIS show the second-layer spacing change to be less than 1%, so any changes in d_{34} can be expected to be negligible. Contractions and expansions from 0 up to 7% (with respect to the bulk interlayer spacing) were allowed for each layer. The dependence of R_P on the interlayer spacings obtained from this investigation is shown in Fig. 1. Note, in particular, that R_P shows a single well-defined minimum ($R_P = 0.213$) corresponding to $d_{12} = 2.359$ Å and $d_{23} = 2.359$ Å. These values are identical to the bulk-layer spacing. No minimum was found corresponding to the values of the other two models,

Table 1
R_P factor as a function of the incidence angles for the three models

	"Bulk"	"MEIS" [25]	"Early theory" [8]
First-layer relaxation (%)	0	−2.5	+1.9
Second-layer relaxation (%)	0	+0.6	+0.2
θ (degrees)	1.75	1.75	1.75
ϕ (degrees)	40	45	50
R_P factor	0.213	0.330	0.429

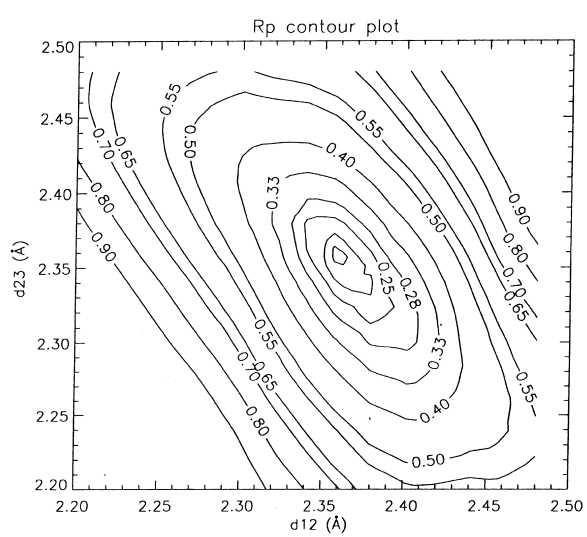

Fig. 1. R_P factor as a function of the first two interlayer spacings with $\theta = 1.75°$ and $\phi = 40°$.

as summarised in Table 1. An automated optimization (again using R_P minimization) of the first three interlayer distances was also performed in order to check that the minimum obtained using the grid method was not a local minimum, but was, indeed, the global minimum. Several different starting points in the parameter space, including each of the three models found in the literature, were used. All of these optimizations converged on the bulk values of the interlayer distances. The possibility of "registry changes", i.e. lateral displacements of the surface atoms, was also explored, but with no reduction in R_P being obtained. The inclusion of more layers (up to six) to define the surface selvedge used in the optimization also failed to give any improvement in R_P.

A more quantitative view of the minimum seen in Fig. 1 is provided in Fig. 2 which shows two orthogonal projections of the parameter space, chosen to pass through the minimum. Fig. 2a shows the variations of R_P respect to d_{23}, keeping d_{12} fixed at its optimum (bulk) value, and Fig. 2b shows R_P as a function of d_{12} while keeping d_{23} fixed at its optimum value. Fig. 2 also provided the basis for estimating the precision of our structure determination. The standard error (refered to by Pendry [38] as the variance) in the minimum value of R_P was calculated to be ± 0.04, leading to corresponding uncertainties in the structural parameters of 0.02 Å for the first interlayer spacing (d_{12}) and 0.03 Å for the second (d_{23}). The total energy range used in the analysis was 1034.0 eV.

For the Simulated Annealing algorithm, the bulk model was chosen as the initial structure, and a constant value of the Debye temperature of 225 K was assumed for all layers. The first three interlayer spacings were allowed to relax, and R_P was again the R-factor that was minimized. The random search was confined to a volume of $(0.4 \times 0.4 \times 0.4)$ Å^3 in the parameter space. This means that each interlayer distance was confined in a range of $\pm 9\%$, i.e. the maximum value for

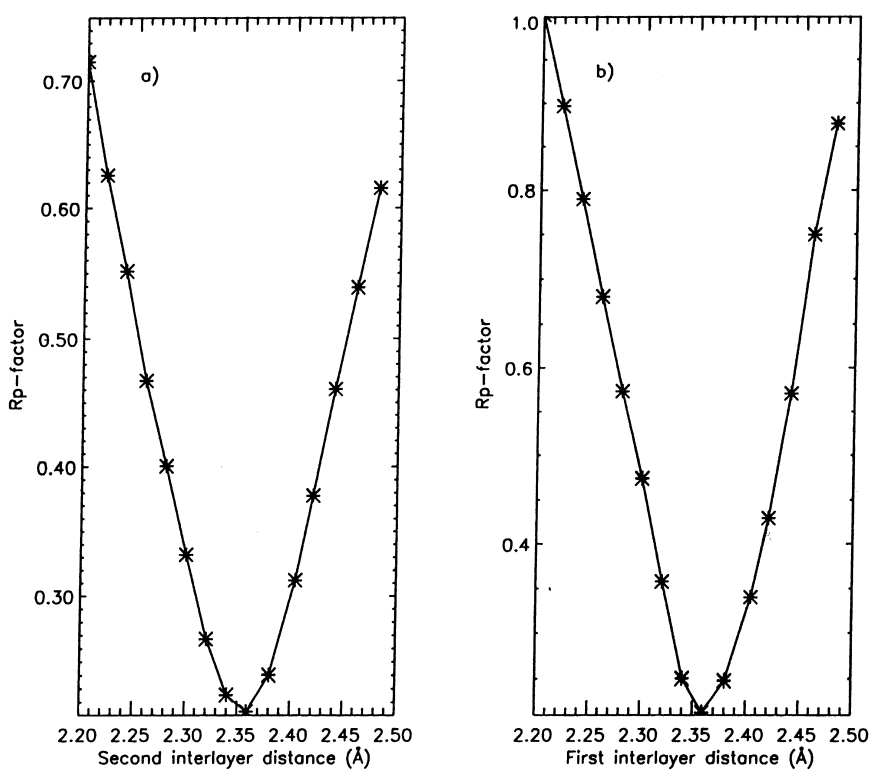

Fig. 2. (a) R_P as a function of the d_{23} for $d_{12}=2.359$ Å. (b) R_P as a function of the d_{12} (d_{23} value fixed at 2.359 Å).

contractions and expansions allowed was 9% with respect to the bulk value. After 600 trial structures, the algorithm converged to the bulk values in agreement with the results obtained with the LEEDFIT code. We conclude, therefore, that the model corresponding to a bulk-terminated surface gives the best structural fit to the experimental data. Fig. 3 shows a comparison of four of the experimental $I(V)$ curves used in this work with the theoretical curves obtained from the LEEDFIT code for the best structural model. Clearly, there is a very good agreement between the experimental and theoretical data.

In addition to this determination of the structural parameters, we have also investigated the optimum value of the surface Debye temperature for the clean Ag(111) surface. Again, the LEEDFIT code was used, but in this case, not only R_P, but also two other R-factors, R_{DE} and R_2 (as defined in Refs. [30,31]) were tested. We first varied the Debye temperature of both suface and bulk layers, keeping the structural parameters fixed to the bulk-terminated model. Similar calculations were performed on a second structural model, including the layer spacing values obtained from the MEIS study. Initially, the surface and bulk Debye temperatures were assumed to be equal. Fig. 4 shows the resulting dependence of the R-factors on the Debye temperature. R_P shows clear minima at $\Theta_D = 225$ K (bulk value) for both

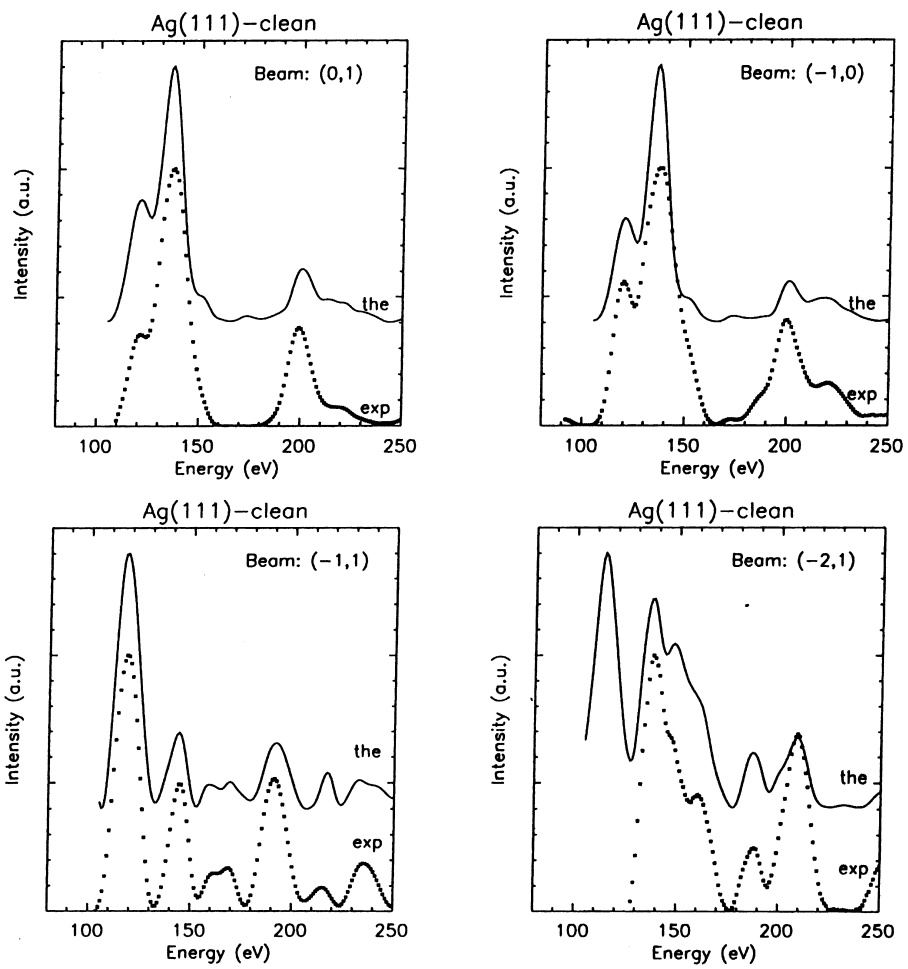

Fig. 3. Representative Ag(111) experimental and theoretical $I(V)$ curves for the best structural model.

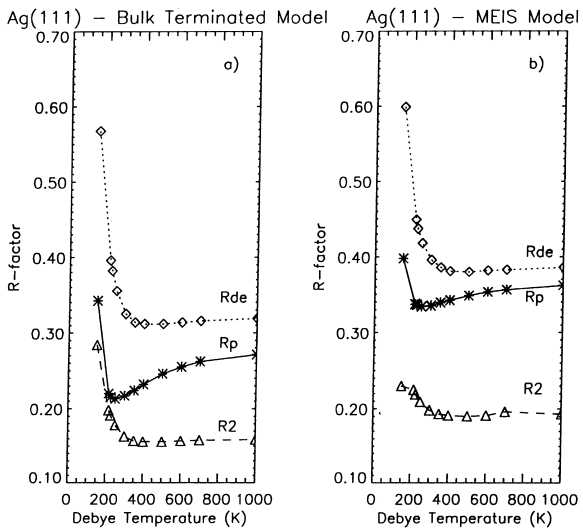

Fig. 4. Behavior of the r-factors as a function of the Debye temperature, Θ_D, for (a) the bulk-terminated model, and (b) the MEIS model.

models, but only very weak broad minima are seen for the other two R-factors. Notice that all the R-factors show lower values for the bulk-terminated structural model than for the MEIS relaxed surface model. This is, of course, consistent with our structural findings described above. Using the Θ_D corresponding to the minimum in R_P as a starting point, an automatic optimization of Θ_D for the first three layers was then carried out. This optimization was perfomed minimizing both R_P and R_{DE} independently. Surprisingly, no improvement in the R-factors was achieved, and the surface layers seemed to have the same Debye temperature as the bulk layers. We also tried to optimize the surface thermal vibrational amplitudes using, as a starting point, the thermal vibrations corresponding to a surface Debye temperature of 225 K. Again, no significant improvement in the R-factors was observed.

5. Conclusion

From the results presented here, we are able to conclude that, of the three models of the clean Ag(111) surface initially considered (bulk termination, a model involving outermost layer contraction found by MEIS, and a model having outermost layer expansion obtained in an early theoretical calculation), the bulk-terminated surface gives the best experiment–theory agreement. More complete searches of the possible structural parameter space revealed a single well-defined R-factor minimum corresponding to this bulk-terminated structure using two different simulation codes, specifically LEEDFIT using the Marquardt algorithm for the minimization procedure and the conventional Van Hove/Tong program adapted for use with a Simulated Annealing algorithm. The precision estimates for the structural parameter values found are very good: about 0.9% for the first interlayer distance, $\Delta d_{12} = (0.00 \pm 0.02)$ Å and 1.3% for the second interlayer distance, $\Delta d_{23} = (0.00 \pm 0.03)$ Å. The result is consistent with other evidence that the close-packed (111) faces of other fcc metals exhibit very small relaxations.

More surprising are our results concerning the thermal vibrations of the surface layers, which favour these having the same associated Debye temperature as the bulk layers. In this case, a lower Debye temperature would be expected for the surface layers. This conclusion warrants further study, but is most likely to be resolved by the use of new data sets collected at several different temperatures.

Acknowledgements

The authors are grateful to Prof. W. Moritz for suppling the LEEDFIT code and the useful discussions and Prof. M.A. Van Hove for suppling the conventional Van Hove/Tong codes. We also would like to thank CNPq and FAPEMIG (Brazilian research agencies) and the European Community (grant number CI1*CT940-0063 supporting the Warwick/UFMG collaboration) for financial support.

References

[1] M. Copel, M.C. Reuter, E. Kaxiras, R.M. Tromp, Phys. Rev. Lett. 63 (1989) 632.
[2] B. Voigtländer, A. Zinner, Surf. Sci. 292 (1993) L775.

[3] M. Copel, M.C. Reuter, M. Horn von Hoegen, R.M. Tromp, Phys. Rev. B 42 (1990) 11682.
[4] M. Horn von Hoegen, M. Pook, A. Al Falou, B.H. Müller, M. Henzler, Surf. Sci. 24 (1993) 53.
[5] S. Esch, M. Hohage, T. Michely, G. Comsa, Phys. Rev. Lett. 72 (1994) 518.
[6] H.A. van der Vegt, H.M. van Pinxteren, M. Lohmeier, E. Vlieg, J.M.C. Thornton, Phys. Rev. Lett. 68 (1992) 3335.
[7] J. Vrijmoeth, H.A. van der Vegt, J.A. Meyer, E. Vlieg, R.J. Behm, Phys. Rev. Lett. 72 (1994) 3843.
[8] J.J. Burton, G. Jura, J. Phys. Chem. 71 (1967) 1937.
[9] M.A. Van Hove, Low Energy Electron Diffraction. Experiments, Theory and Surface Structure Determination, Springer, Berlin, 1986.
[10] K. Heinz, Rep. Prog. Phys. 58 (1995) 637.
[11] M. Prutton, Introduction to Surface Physics, Oxford Science Publications, Oxford, 1994.
[12] P.R. Watson, M.A. Van Hove, K. Hermann, NIST Surface Structure Database Ver. 2.0, NIST Standard Reference Data Program, Gaithersburg, MD
[13] C. Stampfl, M. Scheffler, H. Over, J. Burchhardt, M. Nielsen, D.L. Adams, Phys. Rev. B 49 (1994) 4959.
[14] J. Burchhardt, M.M. Nielsen, D.L. Adams, E. Lundgren, J.N. Andersen, Phys. Rev. B 50 (1994) 4718.
[15] I. Bartos, P. Jaros, A. Barbieri, M.A. Van Hove, W.F. Chung, Q. Cai, M. Altman, Surf. Rev. Lett. 2 (1995) 477.
[16] S.P. Tear, K. Roll, M. Prutton, J. Phys. C. Solid. State. Phys 14 (1981) 3297.
[17] C.M. Chan, S.L. Cunningham, M.A. Van Hove, W.H. Weinberg, S.P. Withrow, Surf. Sci. 66 (1977) 394.
[18] P. Kaukasiona, M. Lindroos, R.D. Diehl, D. Fisher, S. Chandavarkar, J. Phys.: Condens. Matter 5 (1993) 2875.
[19] Y.S. Li, F. Jona, P.M. Marcus, Phys. Rev. B 43 (1991) 63337.
[20] M.E. Grillo, C. Stampfl, W. Berndt, Surf. Sci. 317 (1994) 84.
[21] A. Barbieri, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 306 (1994) 261.
[22] N. Materer, A. Barbieri, D. Gardin, U. Starke, J.D. Bateas, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 303 (1994) 319.
[23] A. Wander, C.J. Barnes, L.D. Mapledoram, D.A. King, Surf. Sci. 281 (1993) 42.
[24] R.J. Culbertson, L.C. Feldman, P.J. Silverman, H. Boehm, Phys. Rev. Lett. 47 (1981) 657.
[25] P. Statiris, H.C. Lu, T. Gustafsson, Phys. Rev. Lett. 72 (1994) 3574.
[26] L.J. Lewis, Phys. Rev. B 50 (1994) 17693.
[27] A. Kara, P. Staikov, A.N. Al-Rawi, T.S. Rahman, Phys. Rev. B 55 (1997) R13440.
[28] F. Forstmann, W. Berndt, P. Büttner, Phys. Rev. Lett. 30 (1973) 17.
[29] E. Clementi, C. Roetti, Atomic Data Nucl. Data Tables 14 (1974) 177.
[30] G. Kleinle, W. Moritz, D.L. Adams, G. Ertl, Surf. Sci. 219 (1989) L637.
[31] G. Kleinle, W. Moritz, G. Ertl, Surf. Sci. 238 (1990) 119.
[32] H. Over, U. Ketterl, W. Moritz, B. Ertl, Phys. Rev. B 46 (1992) 15438.
[33] H. Over, W. Moritz, G. Ertl, Phys. Rev. Lett. 70 (1993) 315.
[34] W. Moritz, J. Landskron, Surf. Sci. 337 (1995) 278.
[35] D.W. Marquardt, J. Soc. Industr. Appl. Math. 11 (1963) 431.
[36] P.J. Rous, Surf. Sci 296 (1993) 358.
[37] M.A. Van Hove, S.Y. Tong, Surface Crystallography by LEED. Theory, Computation and Structural Results, Springer, Berlin, 1979.
[38] J.B. Pendry, J. Phys. C. Solid State Phys. 13 (1980) 937.