PHYSICAL REVIEW B VOLUME 61, NUMBER 4 15 JANUARY 2000-II

Surface optical properties of clean Cu(110) and Cu(110)-(2×1)-O

K. Stahrenberg,* Th. Herrmann, N. Esser, and W. Richter
Institut für Festkörperphysik der TU Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

(Received 7 June 1999)

The surface optical and electronical properties of Cu(110) surfaces were studied by using reflectance anisotropy spectroscopy (RAS) together with angle-resolved photoemission spectroscopy (ARUPS). On the clean surface, a structure in the optical spectra at 2.1 eV is assigned to transitions between occupied *p*-type and unoccupied *s*-type surface states occurring at the $\overline{Y}$ point of the surface Brillouin zone. Another structure at 4.2 eV is associated with a transition at the $\overline{X}$ point between a surface resonance (occupied) split off from the bulk *d* bands and a *p*-derived surface state (unoccupied). The oxygen-induced (2×1) surface exhibits a double peak in the reflectance anisotropy which can be explained partly by transitions from oxygen induced *d*- to empty *p*-derived states. Surface modified bulk *d*-states are responsible for parts of the features around 2 eV and features at higher energies.

I. INTRODUCTION

The clean Cu(110)-(1×1) and the Cu(110)-(2×1)-O surfaces have been investigated extensively in recent years. The surface electronic properties[1–5] are well known. The added row reconstruction model for the oxygen induced (2×1) phase was established mainly by STM.[6,7] Experiments using photoelectron diffraction and LEED[8,9] and a recent first principles study[10] confirmed the proposed structure.

On the other hand, there exist few experimental investigations on the surface optical properties of Cu(110), and at present no theoretical studies are available. Optical investigations are important because they can be used in UHV as well as in gaseous environments or liquids, which are not accessable to the normally used UHV-based probes. The power of surface optical investigations was shown in the 1980s by Kolb *et al.*[11] They detected a surface state on Ag(100) using electroreflectance spectroscopy in an electrolyte. We apply here reflectance anisotropy spectroscopy (RAS), which measures the difference of the complex reflectivity along two perpendicular axes in the surface. In case of optically isotropic materials RAS is a surface specific probe since by symmetry arguments a surface anisotropy must be induced by the surface.[12] So far, RAS has mainly been used to study the properties of semiconductors,[13] only recently it was extended to study metal surfaces.[14–18]

The reflectance anisotropy spectra discussed in the following exhibit structures that have mainly two different origins. One is due to electronic transitions between localized surface states. Those transitions are expected to be energetically separated from the critical points of the bulk electronic band structure. Considerations of the dipole selection rules led Jiang *et al.*[19] to the prediction of such transitions. This has been demonstrated in case of Ag(110) and Cu(110).[14,20,21]

Secondly, structures in the reflectance anisotropy are commonly observed close to the bulk critical points and obviously related to the bulk electronic properties. The anisotropy in such a case may be induced by the surface potential modifying lifetime and eigenenergies of bulk states near the surface.[22–24] In case of Cu(110) or Ag(110) *d* states are involved in those transitions, which are termed surface modified bulk states in the following.

On clean Ag(110), both contributions, originating from surface states and modified bulk states, can be identified unambiguously since the the silver *d*-band transitions set in at a photon energy of about 4 eV, energetically well separated from the surface state transition which occurs at 1.7 eV.[20]

On Cu(110) the interpretation of structures is more complicated. A sharp peak in the spectrum of the clean surface at 2.1 eV was assigned to electronic transitions involving surface states at the $\overline{Y}$ point of the surface Brillouin zone.[14] This peak was also found by other groups with RAS[18,21] and with second harmonic generation.[25] However, since in Cu the transition of bulk *d* states to empty states just above the Fermi level are also located in the energy range of the surface state transition, the observed feature in the Cu(110) spectra might as well contain contributions arising from near surface bulk states.

The optical anisotropy of the oxygen-induced Cu(110)-(2×1)-O phase has also been reported.[14,21] The RAS result of the adsorbate covered surfaces were up to now always discussed in terms of quenching the surface electronic states. However, the oxygen-induced reconstruction introduces new surface states[3] which may also contribute to the reflectance anisotropy.

In our paper we report angle resolved photoemission and RAS measurements on clean and oxygen covered Cu(110) crystals in order to clarify surface and bulk related contributions to the optical anisotropy of these surfaces. On the clean surface we find a peak in the RAS spectra whose appearance correlates with the occupied surface state observed simultaneously with photoemission spectroscopy. We consider the appearance of the surface state in the photoemission spectra as the most sensitive check of the surface preparation. The peak in RAS decrases dramatically upon oxygen adsorption. However, careful examination of the results for the oxygen induced (2×1) reconstruction reveals a clear double structure in the RAS spectrum, in which one of the peaks is assigned to a transition between *d*-type antibonding surface

0163-1829/2000/61(4)/3043(5)/$15.00

states and an unoccupied p_y-type orbital. This double structure is not present on the surface under ambient conditions. In the latter case, only near surface bulk *d* bands contribute to the RAS.

II. EXPERIMENTAL

We used single crystal Cu(110) samples for the experiments, which were performed in an ultrahigh-vacuum chamber with a base pressure of 1×10^{-10} mbar. The vacuum chamber was equipped with standard facilities for sample preparation and characterization. The Cu(110) crystal of 12 mm diameter was aligned with Laue x-ray backscattering to 0.1° and mechanically polished before introducing into the chamber. *In situ* cleaning of the surface was done using cycles of argon ion sputtering ($12\,\mu\mathrm{A/cm}^2$, 600 eV, 20 min at 300 K) and subsequent annealing to 670 K. Thereafter, the LEED pattern showed the typical (1×1) structure with sharp spots and a low background intensity. The method of choice to clean the sample may leave the surface more rough than the original one. However, we did not observe any changes of the quality of the LEED pattern even after several sputtering cycles. The oxygen overlayer was prepared by dosing oxygen at room temperature at a partial pressure of about 2×10^{-8} Torr. An amount of 10 Langmuir was sufficient to produce a sharp (2×1) LEED pattern.

For the ARUPS measurements, unpolarized He(I) radiation (21.1 eV) was used. A spherical analyzer (VSW HA 50) with a full-angle resolution of 1° and an energy resolution of about 90 meV was used for photoelectron detection. The sample was aligned using the LEED pattern. The angle between the incident photons and the surface normal was fixed to 45°.

The RAS spectrometer used for the optical investigations is a custom built system which follows the standard design by Aspnes.[12] Using a Xe short arc lamp together with a double grating monochromator, the system covers a spectral range from 1.5 to 5.5 eV. In order to minimize other sources of anisotropy the spectrometer was mounted in front of a low strain quartz window at the UHV chamber. The RAS signal consists of the real and the imaginary part of the reflectance anisotropy:

$$\frac{\Delta r}{r}=2\frac{r_{[1\bar{1}0]}-r_{[001]}}{r_{[1\bar{1}0]}+r_{[001]}}. \tag{1}$$

For a discussion of the surface anisotropies we rather use the surface dielectric anisotropy (SDA) than the RAS. For that purpose we assume a three phase model consisting of an optically anisotropic surface layer (thickness $d\ll\lambda$) with $\Delta\epsilon=\epsilon_{[1\bar{1}0]}-\epsilon_{[001]}$ on top of the homogeneous bulk with an isotropic dielectric function ϵ_b and the surrounding vacuum. The SDA can then be calculated from the measured reflectance anisotropy:[26]

$$\Delta\epsilon\cdot d=\frac{\lambda}{4\pi i}(\epsilon_b-1)\frac{\Delta r}{r}. \tag{2}$$

The data of Johnson and Christy[27] were used for the bulk dielectric function (ϵ_b) of copper.

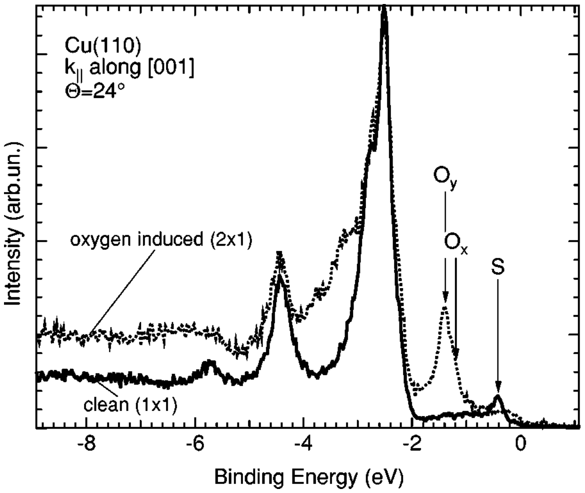

FIG. 1. ARUPS spectra for clean (solid line) Cu(110) and for Cu(110)-$(2\times1)-$O (dotted line). Data were taken along the [001] direction at an azimuthal angle of 24°. The *p*-type surface state of the clean surface is labeled S, the oxygen-induced features are labeled O_x and O_y.

III. RESULTS

The clean as well as the oxygen covered Cu(110) surface exhibits occupied and unoccupied surface bands which are important for the explanation of the surface optical data. Therefore, we shortly summarize the known surface states. Those states have been found experimentally either in ARUPS or inverse photoemission spectroscopy (IPES) (see Fig. 5). On the clean surface at the $\bar{Y}$ point, the Fermi level crosses the $p-s$ band gap and an occupied surface state lies 0.4 eV below the Fermi level.[1] An unoccupied surface state was found 1.8 eV above E_F.[5] The band gap at $\bar{X}$ lies entirely above E_F. Unoccupied bands were found at an energy of 2.2 and 5.5 eV above E_F, respectively.[28] Cord *et al.* reported an occupied surface resonance superimposed on the bulk *d* bands $\sim$2 eV below E_F.[29]

On the Cu(110)-(2×1)-O surface the formerly discussed bands are shifted upwards in energy and new *d*-like oxygen derived surface states are formed. The former occupied *p*-type surface state at $\bar{Y}$ becomes unoccupied due to an upwards shift in binding energy of 0.7 eV.[30] Moreover, at $\bar{Y}$ two oxygen derived states lying 1.2 and 1.4 eV below E_F could be identified.[3]

Two spectra of our ARUPS measurements are shown in Fig. 1. The spectra are recorded at an angle of 24° which corresponds to the $\bar{Y}$ point for small binding energies. The clean surface shows the occupied *p*-type surface state (labeled S) at -0.4 eV. We also followed the dispersion with $k_{||}$ of the surface state along the [001] direction which is in perfect agreement with the curves known from the literature.[1] Also shown is a spectrum of the oxygen covered surface. It exhibits the expected oxygen derived peak at -1.4 eV. Since we used unpolarized light the two surface bands that contribute to this structure are not resolved. The peak, however, exhibits a small shoulder towards E_F that may account for the two surface bands.

RAS spectra (real part) of three different surfaces are shown in Fig. 2: the spectrum of the clean Cu(110)-(1×1)

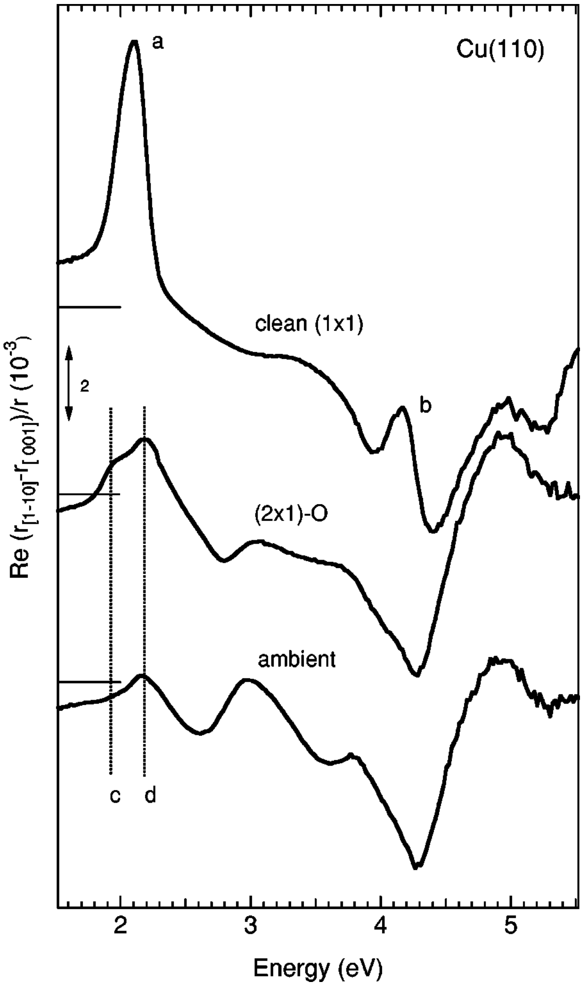

FIG. 2. Real part of the reflectance anisotropy from Cu(110). The first spectrum was recorded on the clean surface. The spectrum denoted (2×1)-O was recorded after exposure of 10 Langmuir O_2, the last spectrum was recorded after venting the UHV chamber. a, b, c denote possible surface state transitions. The zero points on the *y* axis are indicated by the vertical bars.

surface (upper curve in Fig. 2) shows two positive peaks: at 2.1 eV (labeled a) and at 4.2 eV (labeled b). Upon oxygen adsorption the line shape of the RAS changes dramatically. There is still an anisotropy around 2 eV but it has changed into a double peak (1.9 and 2.2 eV), while the high energy feature (b) is absent.

The third spectrum labeled ambient (lower curve in Fig. 2) was recorded shortly after venting the chamber. In this spectrum no surface state contributions are expected. The double peak structure around 2 eV has disappeared, but a small anisotropy remains. An additional anisotropy appears around 3 eV.

These results agree with previous work[14] apart from the sign of the anisotropy, which is caused by a wrong assignment of the crystal axes in Fig. 1 of Ref. 14.

IV. DISCUSSION

The spectrum labeled ambient (Fig. 2) can be described using an expression for surface modified bulk states derived by Aspnes:[24]

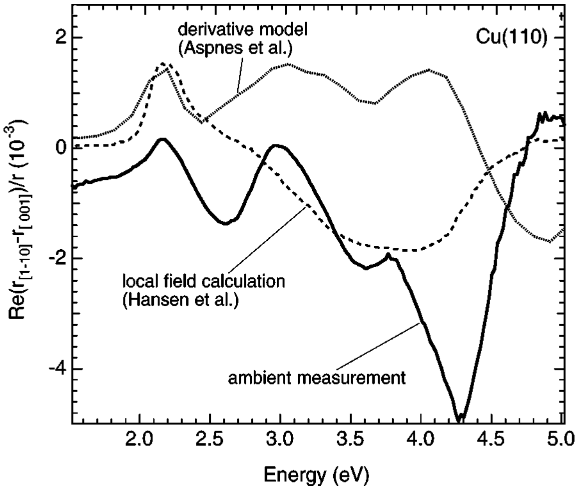

FIG. 3. Contribution of near surface bulk states to the reflectance anisotropy. The line shape of the spectra is energy derivative-like. The model (dotted curve) was calculated using Eq. (3). Also included is the spectrum calculated by Hansen *et al.* (Ref. 21) (dashed curve).

$$\frac{\Delta r}{r}=-\frac{4\pi iEd}{hc}\frac{(-\Delta E_g+i\Delta\Gamma)}{(\epsilon_b-1)}\frac{\partial\epsilon_b}{\partial E}. \tag{3}$$

The anisotropic gap energies and broadening parameters are represented by the constants ΔE_g and $\Delta\Gamma$. The result with the bulk dielectric function of copper (ϵ_b) from[27] is shown in Fig. 3. With the parameters $d=2$ nm, $\Delta E_g=0.1$ eV and $\Delta\Gamma=0$ the calculation fits quite well to the line shape of the measurement in the low energy part.

Hansen *et al.*[21] took another approach to explain the bulk contribution to the RAS. They applied a phenomenological surface local field model originally developed by Mochán and Barrera.[31] In this model the bulk electronic structure and the actual surface geometry is taken into account. The *d* electrons are described by dipoles located in spheres at the lattice points of the fcc lattice, whereas the $s-p$ electrons are described by the Drude model.

Their result resembles the line shape of the spectrum measured under ambient conditions in the low energy region very well, even the amplitude of the peak in the calculation corresponds very good to the experimental data (Fig. 3). These findings show that the spectra measured under ambient conditions contain only contributions from the bulk *d* bands.

In Fig. 4 we plotted the imaginary parts of the surface dielectric anisotropy (SDA) of the clean and oxygen covered Cu(110) surface. The imaginary part of the SDA is related to the anisotropy of the absorption. Two clear negative structures (i.e. adsorption along the [001] direction) arise for the clean surface at 2.1 eV (peak a) and 4.2 eV (peak b). They can be attributed to transitions between the surface electronic states at $\bar{Y}$ and $\bar{X}$ as we will show below by using the selection rules that are well established from photoemission experiments.[1,5,19,29,30] In the following *y* denotes the [001] and *x* the $[1\bar{1}0]$ direction.

We shortly recall the eigenenergies of the surface states for the clean surface summarized earlier (Fig. 5). At $\bar{Y}$ the binding energies are 0.4 eV for the occupied state and 1.8 eV

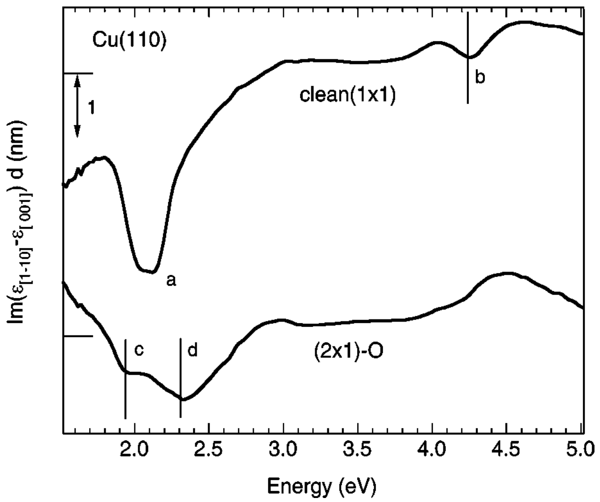

FIG. 4. Imaginary parts of the surface dielectric anisotropy. The real parts are not shown but were checked for Kramers-Kronig consistency. Zero on the y axis is denoted by the lines.

for the unoccupied state, i.e. one would expect a surface transition at 2.2 eV. The occupied surface state at $\overline{Y}$ has p_y character. The unoccupied state of s type character possesses even symmetry in x and y directions. Therefore the transition between both states is only allowed for light polarized along [001]. Since RAS probes the difference for light polarized along [001] and [1$\overline{1}$0], one expects to observe this surface state transition due to the absorption for light polarized along [001]. As a result a minimum in the SDA should appear. This transition occurs at 2.1 eV (peak a). However, there is an uncertainty concerning the binding energy of the unoccupied s-type surface state. The values reported are ranging from 1.8 eV[5] to 2.5 eV.[32] The origin of these differences is not clear.[4] Woll *et al.*[25] argued that the transition occurs near E_F since the p_y derived state disperses faster upwards in energy with $k_{\|}$ than the unoccupied band. Hence the measured transition energy is smaller than the energy difference of the involved states. A recent experiment on the isostructural and isoelectronic Ag(110) surface found the corresponding transition at 1.7 eV,[20] in perfect agreement with the energy difference of the surface states involved.

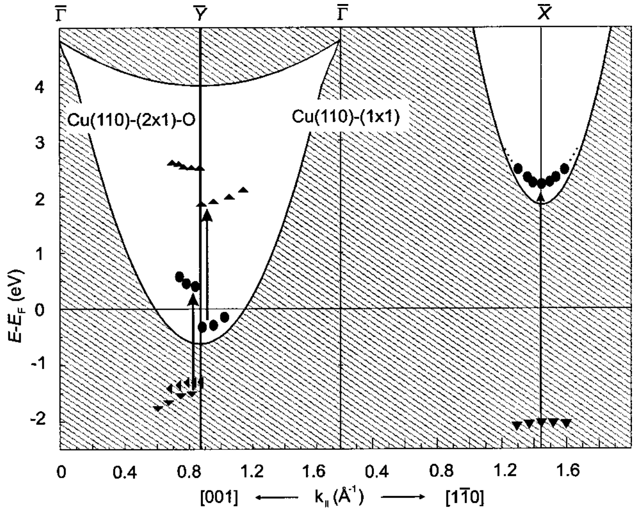

FIG. 5. Surface band structure of Cu(110). Hatched areas denote bulk bands. Data points were taken from ARUPS measurements or from the literature. [1,5,19,29,30] Around $\overline{Y}$ the oxygen induced (2 $\times$1) structure is shown (left part) together with the surface bands of the clean surface (right part). Around $\overline{X}$ only the surface bands of the clean surface are shown. The arrows indicate possible transitions between surface states visible in RAS.

At $\overline{X}$ the lower of the empty surface states has a binding energy of 2.2 eV. The surface resonance lies 2 eV below E_F. A transition should occur at 4.2 eV in the SDA. The empty surface state is of p_x type. The occupied surface resonance posesses d_{xy} symmetry. This state is odd with respect to the x and y direction.[25] Hence the transition can only be excited with light polarized along [001], that means the transition should appear as a negative structure in the SDA just like the resonance at 2.1 eV. The small minimum at 4.2 eV (peak b) in the imaginary part of the SDA in Fig. 4 therefore is assigned to transitions involving surface bands located at $\overline{X}$. Here the energetic difference of the surface bands matches perfectly to our measured data. The possible appearance of this transition was already discussed in Ref. 14.

On the Cu(110)-(2$\times$1)-O surface the p_y-type surface band at $\overline{Y}$ is shifted by 0.7 eV above E_F,[30] i.e., its binding energy is 0.3 eV (left part of Fig. 5). When dosing oxygen the strong resonance in the reflectance anisotropy is reduced. This behavior was formerly interpreted as an effect of quenching the surface state involved in the transition. This, however, is only partly correct, since the interaction of the Cu(3d) with the O(2p) orbitals forms new occupied surface states.[2] The higher-lying antibonding bands are predominately of d character,[3,4] which means that a transition to the p_y-type state at $\overline{Y}$ is dipole allowed. Two states were reported in polarization resolved UPS: One state with even symmetry with respect to y ($E_b = -1.4$ eV) and another state with odd symmetry with respect to y ($E_b = -1.2$ eV).[3] A transition between the oxygen derived band at -1.4 eV to the empty band (0.3 eV above E_F) would match the selection rules. The transition would be expected to occur at 1.7 eV. The low energy shoulder in the SDA, peak c in the spectrum denoted (2$\times$1)-O in Fig. 4, appears at an energy at 1.9 eV. We assign this feature to the transition between the described surface bands. Again the energy difference of the surface states determined by PES and IPES does not match exactly the transition energy found in our experiment. Tjeng *et al.*[4] reported a binding energy of 0.4 eV for the empty surface state rather than 0.3 eV, which would give a value of 1.8 eV for the transition. The difference is most likely the consequence of the limited spectral resolution of IPES (around $\Delta E = 0.4$ eV.[5]) In ARUPS and RAS measurements the energy resolution is typically better than 50 meV.

The remaining structure at 2.3 eV (peak d of the spectrum labeled (2$\times$1)-O in Fig. 4) should be related to the previously discussed bulk contribution, see Figs. 2 and 3.

V. SUMMARY

We have studied the reflectance anisotropy of clean and oxygen covered Cu(110) surfaces. RAS allows the spectroscopic investigation of the surface electronic properties. We have found transitions between surface bands at the $\overline{Y}$ symmetry points of the surface Brillouin zone. At $\overline{X}$ on the clean surface a transition between a surface resonance and an unoccupied surface state is identified. Simultaneously we used angle resolved photoemission spectroscopy for the occupied part of the surface band structure. Oxygen dosage leads to a quenching of surface states which correlates with a disappearance of features in the reflectance anisotropy. On the other hand new adsorbate induced surface bands are formed, which lead to new transitions also visible in RAS. In all spectra there is also a contribution from anisotropic near surface bulk states. These features are the only contribution to the spectrum when the surface is measured under ambient conditions.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) under Ri/208 32-1 and SFB 290. We would like to thank U. Rossow for many critical discussions.

---

*Author to whom correspondence should be addressed. FAX: +49 30 314 21769. Electronic address: knut@gift.physik.tu-berlin.de

[1] S. D. Kevan, Phys. Rev. B **28**, 4882 (1983).

[2] R. A. DiDo, D. M. Zehner, and E. W. Plummer, J. Vac. Sci. Technol. A **2**, 852 (1984).

[3] R. Courths, S. Hüfner, P. Kemkes, and G. Wiesen, Surf. Sci. **376**, 43 (1997).

[4] L. H. Tjeng, M. B. J. Meinders, and G. A. Sawatzky, Surf. Sci. **233**, 163 (1990).

[5] A. Goldmann, V. Dose, and G. Borstel, Phys. Rev. B **32**, 1971 (1985).

[6] D. J. Coulman, J. Wintterlin, R. J. Behm, and G. Ertl, Phys. Rev. Lett. **64**, 1761 (1990).

[7] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. Goerge, and G. Comsa, Phys. Rev. Lett. **67**, 855 (1991).

[8] A. W. Robinson, J. S. Somers, D. E. Ricken, A. M. Bradshaw, A. L. D. Kilcoyne, and D. P. Woodruff, Surf. Sci. **227**, 237 (1990).

[9] S. R. Parkin, H. C. Zeng, M. Y. Zhou, and K. A. R. Mitchell, Phys. Rev. B **41**, 5432 (1990).

[10] S. Y. Liem, G. Kresse, and J. H. R. Clarke, Surf. Sci. **415**, 194 (1998).

[11] D. M. Kolb, W. Boeck, K.-M. Ho, and S. H. Liu, Phys. Rev. Lett. **47**, 1921 (1981).

[12] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A **6**, 1327 (1988).

[13] W. Richter, and J.-T. Zettler, Appl. Surf. Sci. **100**, 465 (1996).

[14] Ph. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, and W. Richter, Phys. Rev. Lett. **75**, 2039 (1995).

[15] A. Borg, O. Hunderi, W. Richter, J. Rumberg, and H. J. Venvik, Phys. Status Solidi A **152**, 77 (1995).

[16] S. M. Scholz, F. Mertens, K. Jacobi, R. Imbihl, and W. Richter, Surf. Sci. **340**, L945 (1995).

[17] V. Fernandez, D. Pahlke, N. Esser, K. Stahrenberg, O. Hunderi, A. M. Bradshaw, and W. Richter, Surf. Sci. **377-379**, 388 (1997).

[18] B. G. Frederick, J. R. Power, R. J. Cole, C. C. Perry, Q. Chen, S. Haq, Th. Bertrams, N. V. Richardson, and P. Weightman, Phys. Rev. Lett. **80**, 4490 (1998).

[19] M. J. Jiang, G. Pajer, and E. Burstein, Surf. Sci. **242**, 306 (1991).

[20] K. Stahrenberg, T. Herrmann, N. Esser, J. Sahm, W. Richter, S. V. Hoffmann, and Ph. Hofmann, Phys. Rev. B **58**, R10207 (1998).

[21] J.-K. Hansen, J. Bremer, and O. Hunderi, Surf. Sci. **418**, L58 (1998).

[22] U. Rossow, L. Mantese, and D. E. Aspnes, Appl. Surf. Sci. **123/124**, 237 (1998).

[23] A. I. Shkrebtii, N. Esser, W. Richter, W. G. Schmidt, F. Bechstedt, B. O. Fimland, A. Kley, and R. Del Sole, Phys. Rev. Lett. **81**, 721 (1998).

[24] U. Rossow, L. Mantese, and D. E. Aspnes, J. Vac. Sci. Technol. B **14**, 3070 (1996).

[25] J. Woll, G. Meister, U. Barjenbruch, and A. Goldmann, Appl. Phys. A: Mater. Sci. Process. **60**, 173 (1995).

[26] K. Hingerl, D. E. Aspnes, I. Kamiya, and L. T. Florez, Appl. Phys. Lett. **63**, 885 (1993).

[27] P. B. Johnson, and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[28] G. Chiarotti (Ed.), Landolt-Börnstein New Series III-24b (Springer, Berlin, 1995).

[29] B. Cord, R. Courths, and H. Wern, Phys. Rev. B **31**, 1164 (1985).

[30] W. Jacob, V. Dose, and A. Goldmann, Appl. Phys. A: Mater. Sci. Process. **41**, 145 (1986).

[31] W. L. Mochán and R. G. Barrera, Phys. Rev. Lett. **55**, 1192 (1985).

[32] R. A. Bartynski and T. Gustafsson, Phys. Rev. B **33**, 6588 (1986).