Measuring Surface Stress Discontinuities in Self-Organized Systems with X Rays

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(Received 6 April 2001; published 18 January 2002)

We have performed a grazing incidence x-ray diffraction study of the self-organized N/Cu(001) system. Diffraction satellites associated with self-organization are particularly intense around Bragg conditions of the bulk crystal. Bulk elastic relaxations due to surface stress discontinuities at domain boundaries are responsible for this feature. A quantitative analysis shows that these relaxations, computed by molecular dynamics or continuum elasticity, explain very well the whole diffraction study. A difference in surface stress of 7 $\mathrm{N\,m^{-1}}$ between uncovered and N-covered regions of the Cu surface is shown to be the driving force for self-organization.

DOI: 10.1103/PhysRevLett.88.056103 PACS numbers: 68.65.–k, 61.10.Eq, 68.43.Hn

Self-organized surfaces are intensively studied nowadays since they are seen as promising templates for further growths [1–7]. Two alternative long-range interactions are generally admitted as driving forces for the mesoscopic organization of two phases on a surface: electrostatic interactions due to the difference in work function between the two phases [8] or substrate-mediated elastic interactions due to the difference in surface stress [9,10]. On one hand, as pointed out by Vanderbilt [8], these two interactions lead to similar dependence of the system energy on the geometrical configuration of the two phases. When one of the two phases is a chemisorbed phase, quantitative estimates do not allow one to choose between these two driving forces [8]. On the other hand, in spite of the universality of the arguments given by Marchenko [9], the chemisorbed systems leading to observation of self-organization are very rare [2,5,11]. The predicted exponential dependence of the characteristic length of self-organization with the surface stress is a possible explanation for such a rarity. Moreover, the surface stress associated with a chemisorbed phase is very difficult to predict even by *ab initio* calculations.

Direct measurements of the stress difference at a microscopic scale for self-organized chemisorbed surfaces seem therefore really important. Since elastic interactions are mediated by the bulk, a determination of the bulk elastic relaxations should lead to the stress difference. Previous studies [12] indicated that grazing incidence x-ray diffraction (GIXD) should be a valuable way to reach such a measure of the bulk relaxations. Our GIXD measurements on the self-organized N/Cu(001) system do indeed show that the periodic bulk relaxations are responsible for the intensity of the diffraction satellites associated with the self-organized arrangement. Thus, they clearly establish that this technique is a route for the measurements of surface stress difference in self-organized systems. Our quantitative analysis allows us to conclude that elasticity is the driving force of N/Cu(001) self-organization.

Nitrogen adsorbed on Cu(001) is one of the few chemisorbed systems leading to self-organization [2,5,11]. After activation, nitrogen chemisorbs on Cu(001). Bare Cu regions coexist with N-covered regions, characterized by a $c(2 \times 2)$ structure and saturated at a coverage, τ, of 7.65×10^{14} nitrogen atoms $\cdot\ \mathrm{cm}^{-2}$ [13] (we will define this coverage as 1 in the following). Using scanning tunneling microscopy (STM), Leibsle *et al.* [5] have shown that the $c(2 \times 2)$ phase of nitrogen self-organizes in square shaped domains of almost constant size. The authors estimate their size to be 5.2 nm. A regular array of such square shaped domains is obtained just before domain coalescence. Using LEED with spot profile analysis, Sotto and Croset [14] have shown that, after direct adsorption, the chemisorbed layer exhibits regular arrangements for $0.2 \leq \tau \leq 0.8$, with a constant period of 5.6 nm. The careful and extensive STM study of Ellmer *et al.* [15] solves this apparent contradiction: the square shaped domains are organized in rows, the intrarow period being constant and equal to 5.4 nm while the inter-row period decreases with coverage to reach 5.4 nm around $\tau = 0.8$ which corresponds to a square array of domains.

Experiments were performed on the 6-axes diffractometer DW12 at LURE with 15 keV photons. The sample is a disk 9 mm in diameter and 4 mm in thickness from Surface Preparation Laboratory. Before each N adsorption, the sample was cleaned by Ar ion sputtering followed by annealing at 770 K. N adsorption was obtained using a procedure quite similar to previous studies [14,15]: use of the ion-gun filament to activate nitrogen, adsorption performed at 550 K for 30 min and at various pressures around 10^{-4} Torr. Coverages were measured using the ratio N_{381} peak/Cu_{61} peak obtained with a cylindric mirror analyzer Auger spectrometer as compared to the same ratio at layer completion.

We concentrate our GIXD study on a 0.8 coverage which corresponds to a 2D square array of N domains. Since we use the standard fcc mesh of the Cu substrate, the bulk Bragg positions are defined by integer h, k, l values of the same parity. An intensity map in the (h, k) plane around the crystal truncation rods $(11l)$ is shown in Fig. 1. Diffraction satellites are clearly visible and exhibit the same elongated shape as the bulk truncation rods (CTR). This elongated shape and its orientation are controlled by the resolution function of the diffractometer. The sharpness of the satellites demonstrates the good quality of the long-range order of the self-organized 2D array, the Lorentzian profile in the thinner direction leads to a coherence length of 10 nm. The satellite positions correspond to a period of 5.1 nm for the square array of domains, in reasonable agreement with previous measurements [14,15], and, for further calculations, we use this period which corresponds to 14 $\langle 100 \rangle$ interatomic distances. The satellite sharpness allows us to treat the satellite rods as ordinary rods. By doing scans in the h direction and using the ANA program [16], we measured structure factors associated both with the satellites and the CTRs, and we applied corrections adapted to the h-scan geometry taking into account the partial integration of the rods due to the resolution function orientation [17]. The coincidence between the CTR profiles obtained by the h-scan procedure and by the standard θ-scan procedure attests to the validity of our corrections.

The structure factors are reported in Fig. 2. An important point must be noted: around each CTR, the intensity of the satellites sharply increases for values of l approaching the Bragg condition of the bulk Cu. This point is of major importance. Such a feature cannot be explained if the diffracted intensity is solely due to the periodic chemical contrast on the surface. On the contrary, *it indicates that the diffracting periodic object has, as the main spatial period in the direction perpendicular to the surface, the interplanar distance of the bulk Cu crystal.* The analysis can be driven forward. In Fig. 2, it is worth noting that the maxima of the satellite structure factors reach values 10 times greater than the CTR minima [see, for instance, the maximum of satellite $(2 - \delta q, 0, l)$]. These values are

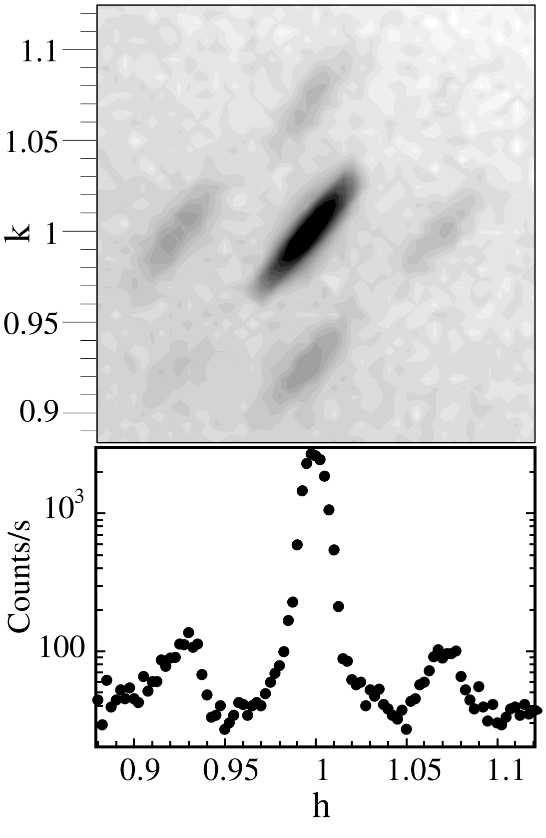

FIG. 1. Intensity map around (1, 1, 1.3) at $\tau = 0.8$. The 20 grey level scale is logarithmic, each level corresponding to a factor of 1.26. The curve displays the intensity profile along the $k = 1$ line.

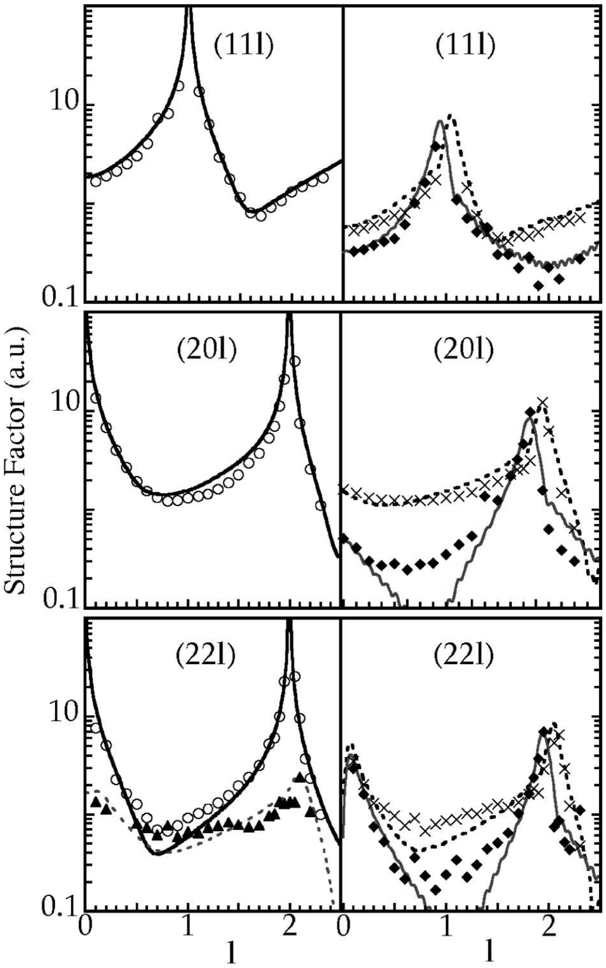

FIG. 2. Experimental and calculated structure factors. The symbols correspond to experimental results and lines to best fit with displacements generated by surface forces of 2.4×10^{-9} N · atom^{-1}. Bulk (h, k, l) CTR: ○ and black solid line; $(h + \delta q, k, l)$ satellite: ◆ and grey solid line; $(h - \delta q, k, l)$ satellite: × and dotted lines; $(h - \delta q, k - \delta q, l)$ satellite: ▲ and grey dotted line. $\delta q = 0.071$.

equivalent to approximately five Cu planes with all atoms diffracting in-phase, indicating that the periodic source of diffraction is not confined to the very first planes. Elastic relaxations of the substrate, which should penetrate deeply into the crystal, seem therefore excellent candidates to explain the variation of the satellite structure factors.

To go further and in order to determine atomic displacements of the bulk, two contributions to the strain must be distinguished. To each surface phase, bare Cu and N-covered surface, a surface strain and a surface stress can be associated. In the absence of any reconstruction of the inner planes of the substrate, the only nonzero component of the intrinsic surface strain is ϵ_{zz}. Because of electronic screening effects, this surface strain is confined to the very first planes and corresponds to variations of the first interplanar distances. At mechanical equilibrium, the only nonzero components of the surface stress tensor are the in-plane components, $\sigma_{xx}, \sigma_{yy}, \sigma_{xy}$. Both for the bare substrate and the $c(2 \times 2)$ adsorbed phase, symmetry arguments lead to $\sigma_{xx} = \sigma_{yy}$ and $\sigma_{xy} = 0$. The coexistence of the two surface phases implies the existence of phase boundaries. The surface stress discontinuity at these boundaries is equivalent to in-plane forces normal to the boundaries and equal to the stress difference $\delta\sigma$. This distribution of forces, $\mathbf{F}(x, y)$, leads to elastic displacements in the bulk, $\mathbf{u}(\mathbf{r})$. The elastic energy gain due to these displacements is the driving force of the self-organization in the elastic approach of Marchenko [9]. We have employed two methods to compute these displacements: quenched molecular dynamics (QMD) and continuum elasticity.

The QMD calculations are performed on slabs of 21 952 Cu atoms. A force is applied on each Cu atom belonging to the boundary of a $c(2 \times 2)$ domain, and relaxations are computed using a semiempirical many-body potential [18] derived from the second moment approximation and adjusted to the elastic properties of Cu [19]. In the in-plane directions we used periodic boundary conditions corresponding to the self-organized domain array; in the out-of-plane direction we used two surfaces separated by 56 planes. We verified that thicker slabs did not lead to appreciable variations of the displacements. This QMD approach has two advantages: it accounts for the elastic anisotropy of the substrate and for the variation of the elastic coefficients when approaching the surface.

For the elastic calculations, we used the displacement response to an in-plane point force at the surface of a semi-infinite isotropic elastic medium [20]. We used as elastic coefficients the values corresponding to polycrystalline Cu. The displacement response can be analytically integrated on the straight portion of each boundary. We then performed numerically the summation on the different domains of the array.

For the two calculations, we used square shaped domains. While the STM images obtained by Ellmer *et al.* [15] show size fluctuations and nonsystematic corner truncations, we neglect, in a first approach, any disorder. The detailed influence of such disorders should require further studies; they probably slightly affect the precise value of the force that we have obtained.

Figure 3 displays a transverse cross section of the 3D-displacement field obtained by the two methods for 12×12 Cu atom domain with a domain distance of 14 Cu atoms [this corresponds to a coverage $\tau = (13 \times 13)/(14 \times 14) = 0.86$]. The two patterns are quite similar, exhibiting a vertex about the fifth Cu plane, i.e., 0.7 nm under the surface. As expected, the displacements penetrate deeply into the substrate: they decay at 1 order of magnitude every 15 planes. The main difference between the two methods is the displacement magnitude, i.e., for the same displacements, the elastic approach needs forces 20% greater. We think that this discrepancy is mainly due to the elastic anisotropy of the substrate which is not considered in our elastic calculations and we choose molecular dynamics results for further use.

To determine the intrinsic strain associated with each phase, we performed diffraction measurements along five CTR $(11l)$, $(1\bar{1}l)$, $(20l)$, $(0\bar{2}l)$, and $(22l)$ for the bare substrate and along the same CTR, plus the $(10l)$ superstructure rod for the complete N monolayer. We fitted the measured structure factors by a least squares fit procedure using, as parameters, a scale factor, the first and second interplanar Cu distance, d_{12} and d_{23}, and in the case of the N monolayer, the distance of the N plane to the first Cu plane, d_N (which is an almost irrelevant parameter). For the sake of simplicity, we use a fixed and isotropic Debye-Waller factor (DWF) corresponding to $\sqrt{\langle u_x^2 \rangle} =$ 0.0087 nm [21] for the bulk Cu atoms. For the first three Cu planes, different but isotropic DWF were used: for the bare substrate, values issued from molecular dynamics

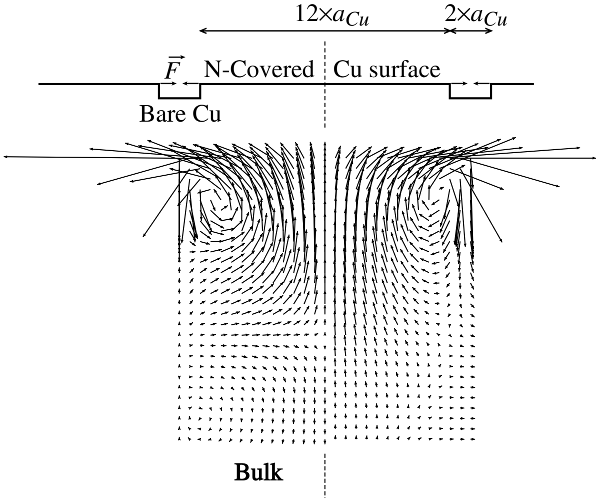

FIG. 3. Transverse section of the atomic relaxations of two consecutive (100) planes. The relaxations are magnified by a factor 50. The dashed line indicates the center of a domain and the section is perpendicular to a line of domains. Left: relaxations computed by molecular dynamics with surface forces $F = 2.4 \times 10^{-9}$ N · atom^{-1}. Right: relaxations calculated in the frame of the linear elasticity with surface forces $F = 2.9 \times 10^{-9}$ N · atom^{-1}.

were kept fixed, and for N-covered regions, DWF were used as fit parameters. We assumed that the $c(2 \times 2)$ superstructure is due to N atoms sitting in every other fourfold site. The ability of our calculated values to reproduce the low intensities of the observed superstructure rod $(10l)$ corroborates this assumption. For the bare substrate, we found $\delta d_{12}(0) = [d_{12}(0) - d_\infty]/d_\infty = -2.1\%$ and $\delta d_{23}(0) = 0.3\%$. For the complete monolayer, we found $\delta d_{12}(1) = 14\%$, $\delta d_{23}(1) = 1.5\%$, and $d_N = 0.087 * d_\infty = 0.016$ nm, $d_\infty = 0.181$ nm being the distance between two Cu planes in the bulk. These results are in good agreement with previous determinations by ion channeling [$\delta d_{12}(0) = -2.4\%$, $\delta d_{23}(0) = 1\%$ [22], $\delta d_{12}(0) = -4\%$, $\delta d_{23}(0) = 1\%$ [23], $\delta d_{12}(1) = 15\%$, $\delta d_{23}(1) = 3\%$ [13]].

At 0.8 coverage, we added to the CTR the structure factors of the more intense satellites, to reach a total of 262 structure factors. In the fitting procedure, to the parameters previously used which were kept fixed at the values determined at null coverage and saturation, we added the atomic displacements computed by the QMD approach. These displacements are multiplied by a parameter which allows us to determine the force at boundaries. The best fit of the experimental structure factors *with this single free parameter* is shown in Fig. 2. A reliability factor, $R = \sum(|F_{\mathrm{obs}}| - |F_{\mathrm{cal}}|)^2/\sum|F_{\mathrm{obs}}|^2 = 0.06$, is obtained for the optimized force of value $2.4 \pm 0.5 \times 10^{-9}\ \mathrm{N} \cdot \mathrm{atom}^{-1}$. The agreement between the calculated and the observed structure factors is excellent; the three main experimental features are quite well reproduced: a sharp increase of the satellite intensities around Bragg conditions of the bulk, an inversion between the $+\delta q$ satellite and $-\delta q$ satellite when crossing the Bragg conditions, and an observation of an intense diagonal satellite around the $(2, 2, l)$ CTR.

The measured stress difference between the two phases, $\delta\sigma = 2.4 \times 10^{-9}\ \mathrm{N} \cdot \mathrm{atom}^{-1} = 7\ \mathrm{N} \cdot \mathrm{m}^{-1}$ agrees perfectly with the ion channeling experiments; these measurements indicate strong atomic disorder in the near surface region corresponding, in the elastic model, to $\delta\sigma = 2.2 \times 10^{-9}\ \mathrm{N} \cdot \mathrm{atom}^{-1}$ [13]. Our result is also in good agreement with values measured by macroscopic direct methods on similar chemisorbed systems [24], for example, $\delta\sigma = 5.4\ \mathrm{N} \cdot \mathrm{m}^{-1}$ for O/Ni(001) [25]. The determination by Tibbets *et al.* of the work function difference, 0.18 eV [26], allows us to show that the contribution of the elastic terms to the system energy is 3000 times greater than the electrostatic contribution. Finally, to obtain a rough estimate for the microscopic boundary energy cost, we used the expression of the size, D, of an isolated domain determined by Marchenko [9] for a 1D self-organized system:

$$D = 2a \exp\left(1 + \frac{2E_{\mathrm{micro}}}{E_{\mathrm{elas}}}\right), \quad \text{with } E_{\mathrm{elas}} = \frac{1-\nu}{\pi\mu}(\delta\sigma)^2,$$

μ and ν being the shear modulus and the Poisson ratio of the substrate and a, a cutoff length. If we choose for a the distance between Cu atoms in a domain boundary, we have $D/a = 12$ and we obtain $E_{\mathrm{micro}} = 0.18\ \mathrm{eV} \cdot \mathrm{atom}^{-1}$.

To summarize, grazing incidence x-ray diffraction experiments allows one to study bulk elastic relaxations in the self-organized N/Cu(001) system. The quantitative analysis of the structure factors leads to the measure of forces at a microscopic scale and to the first direct evidence that surface stress is the driving force for self-organization of a chemisorbed system. These observations of diffraction satellites due to bulk relaxations convince us that GIXD will be a very useful tool in future studies of the physics of self-organized systems.

We thank E. Le Goff for his help.

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