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著者別名	重川 秀実
journal or publication title	Physical review B
volume	62
number	24
page range	R16341-R16344
year	2000-12
権利	(C)2000 The American Physical Society
URL	http://hdl.handle.net/2241/100025

doi: 10.1103/PhysRevB.62.R16341

Modification of surface-state dispersion upon Xe adsorption: A scanning tunneling microscope study

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(Received 24 October 2000)

The modification of the surface electronic structure by an adsorbate is measured quantitatively with scanning tunneling microscopy and spectroscopy for the first time. The standing wave of the Cu surface-state electrons is utilized to probe the subtle change in the electronic structure on the Xe-covered Cu(111). The observed Fermi wavelength on the Xe-covered surface is longer by 15% than on the bare Cu surface. The change upon Xe adsorption is explained with the observed modified dispersion of the Cu surface state; upward shift by (130 ± 20) meV with almost same effective mass.

There has been interest recently in the surface state electrons, localized on the (111) surfaces of noble metals and the (0001), (10 $\bar{1}$ 0) surfaces of Be.¹⁻³ The electrons are known to play as important a role as the bulk electrons in surface-related phenomena, such as adsorption, surface magnetism, surface and step energetics, and catalysis.⁴ They reveal nearly two-dimensional (2D) characteristics with a nearly free-electron-like dispersion.⁵ The electrons in the surface states, therefore, form standing waves of quantum interference on the surfaces when there is a potential well or a barrier, created by a point defect or a line defect^{1,2} or even a quantum corral.⁶ This long range modulation of local density of states (LDOS) is explained with many electron effect like Friedel oscillation, change in the electronic state density near the Fermi level by electron screening of the defect potential. Direct imaging in real space of the modulation has been possible only with a scanning tunneling microscope (STM).^{1,2} Since the observation of the electron confinement in nanometer-scale structures,⁶⁻⁸ understandings in several surface-related phenomena, such as the shape of Fermi contour,^{3,9,10} surface state dispersions,^{1,2,11} surface state lifetime,^{12,13} and surface Kondo temperature,¹⁴ have been greatly advanced.

It is well known that adsorption of foreign atoms or molecules modifies the geometric structure, the work function, and the surface electronic state of a clean surface. In many cases, the adsorption removes the surface electronic state and leaves the bulk electronic state. In the case of alkali metals and rare gases, however, their adsorptions modify the surface electronic structure so slightly that the surface states are persistent.⁴ The changes of the surface states and their dispersions with adsorbates have been often studied with photoemission spectroscopy, including two photon photoemission spectroscopy (2PPES). Though the surface state dispersions on clean surfaces have been successfully measured with STM and scanning tunneling spectroscopy (STS),

influence of the adsorbates on the surface states has not been tried with STM. It has been believed that the surface state electrons may not tunnel through the adsorbate layer.

In this Rapid Communication, we report a way to quantitatively measure the change of the surface electronic state by an adsorbate on a metal surface with STM and STS for the first time. We measure the standing waves of the surface state electrons not only on the bare Cu(111) surface but also on the surface with one monolayer (ML) Xe. The small change in the Fermi wavelength (15%) and the modified dispersion relation of the surface state measured by STS are used to explain the proposed redistribution of the charge density with the adsorption of Xe.¹⁵

Our experiments are performed in a low temperature STM¹⁶ at the base pressure of $< 1 \times 10^{-10}$ torr. It works at the temperature down to ~ 5 K. A Cu(111) single crystal is cleaned by repeated cycles of Ar⁺ ion sputtering and annealing up to 900 K. High purity Xe gas is dynamically dosed through a precision leak valve and a stainless steel tube with the diameter of 1/16 inch to the cold sample surface. This dynamic supply ensures proper partial pressure of Xe gas around the sample surface, but not in the whole STM chamber. The sample can be annealed by controlling the liquid helium supply or using a heater attached on the back of the sample.

Xe atoms nucleate at step edges and defect sites on the Cu terrace at the coverage of ~ 0.7 ML dosed at 10 K. The Xe layer can be agglomerated by annealing at > 30 K (Ref. 17) and a flat Xe layer of 1 ML height can be obtained. The surface is, then, partially ($\sim 70\%$) covered with 1 ML high Xe patches as shown in Fig. 1(a). Bright small, hexagonal islands are Xe islands of 2 ML height, which are pinned around defects even after annealing. Using the Cu lattice image as in Fig. 1(b), the length scale can be self-calibrated exactly. Figure 1(c) is a high-resolution image of the Xe layer, showing the perfect crystallinity. The nearest neighbor distance of the Xe adlayer is determined to be (4.25

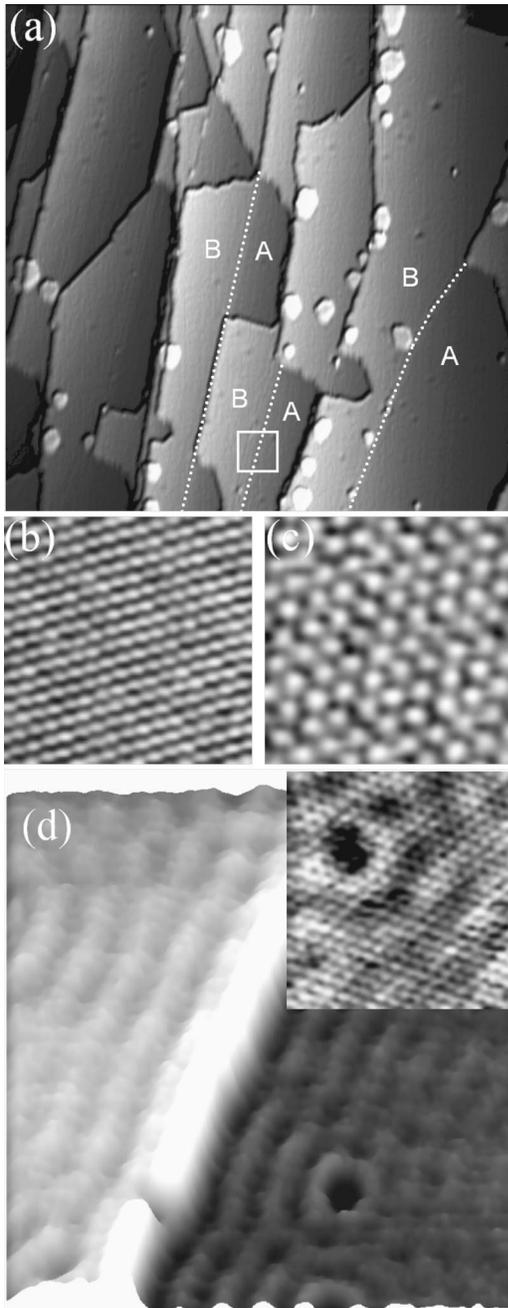


FIG. 1. Constant current STM image of (a) ~ 0.7 ML Xe-covered Cu(111) surface with $V_t=0.4$ V and $I_t=0.4$ nA at 5 K ($2000 \times 2000 \text{ \AA}^2$). The image is shown as if a light source is at right side. Some regions are marked for clarity (A: Cu terrace, B: Xe layer, dotted line: original Cu step). Atomically resolved image of (b) Cu terrace and (c) Xe layer in the region marked by A and B in (a), respectively [$I_t=1$ nA, $38 \times 38 \text{ \AA}^2$, $V_t=10$ mV (b) and 0.8 V (c)]. (d) A perspective view of the region marked by square in (a). Left side is Xe monolayer covering lower Cu terrace and right side is upper Cu terrace [$V_t=10$ mV and $I_t=0.4$ nA at 5 K ($150 \times 150 \text{ \AA}^2$)]. The inset shows an image obtained on Xe layer which shows both standing waves and Xe lattice [$V_t=10$ mV, $I_t=1.5$ nA ($75 \times 75 \text{ \AA}^2$)].

± 0.1) \AA , indicating that the Xe layer is incommensurate with the Cu substrate at <10 K. The standing waves of the surface state electrons are observed near defects or steps on clean Cu(111) surface at 5 K as reported earlier.¹ Surpris-

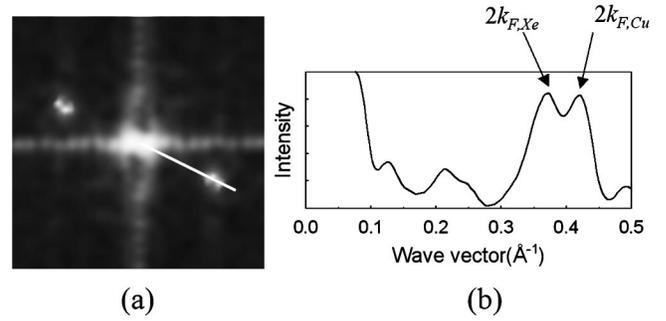


FIG. 2. (a) A Fourier-transformed (logarithm of the power spectrum) image of pair correlation of Fig. 1(d) ($1.2 \text{ \AA}^{-1} \times 1.2 \text{ \AA}^{-1}$). Two peaks at either side originate from different wavelengths of the standing waves on the Xe-covered and the bare Cu surface. (b) Cross section along white line in (a). A difference of $\sim 15\%$ is visible. $k_{F,Xe}$ and $k_{F,Cu}$ denote the Fermi wave vectors for the 1 ML Xe-covered and the bare Cu(111), respectively.

ingly, we observe the standing wave patterns even on the Xe-covered surface. With the step-flow growth of the Xe layer at the lower step edge at high temperature,¹⁷ standing waves are imaged both on the 1 ML Xe-covered surface on the lower terrace and on the bare Cu surface on the upper terrace simultaneously at the region, marked by a square in Fig. 1(a), as shown in Fig. 1(d). With this image, any possibility of artifacts due to the tip change can be excluded. The slight difference in height is due to the difference in LDOS on the Xe-covered and the bare Cu surface at the bias voltage. The white protrusions along the boundary are Xe atoms pinned at upper step edges of Cu during annealing process. The wavelength of the standing waves on Xe layer is longer by 15% than that on Cu surface.

The periodic structures can be revealed more clearly if the image is presented in the Fourier space. This technique was already applied to determine the Fermi contour with the electron standing waves.^{9,10} In order to visualize the two different periodicities, we take the Fourier transformation (FT) of a positional pair-correlation function, in which the positional pair-correlation function, $G(\mathbf{r})$, is defined as

$$G(\mathbf{r}) = \int h(\mathbf{r}') \cdot h(\mathbf{r}' + \mathbf{r}) d\mathbf{r}', \quad (1)$$

where $h(\mathbf{r})$ is the height in STM image at position \mathbf{r} . Figure 2(a) is an example of the FT of the pair-correlation. Two peaks are visible at both sides, confirming the existence of two standing waves with different wavelengths; those on the Xe-covered and the bare Cu surface. The features at the center and along the axis are artifacts that are originated from noise and insufficient sampling at small wave vectors. Figure 2(b) is the cross section along the line from center through these peaks, revealing two peaks with the instrumental and the thermal broadening. The wavelength on the Xe-covered surface is again found to be 15% longer than that on the bare Cu surface as deduced from this cross section.

At first sight, it is difficult to imagine how the standing waves can be observed on the Xe-covered surface, because (i) the Xe layer does not have a surface state near the Fermi level, (ii) the wavelength is too large to be the atomic corrugation of Xe (atomic radius = 4.3 \AA). In the case of Xe atoms, the highest occupied atomic orbital, $5p$, and the lowest un-

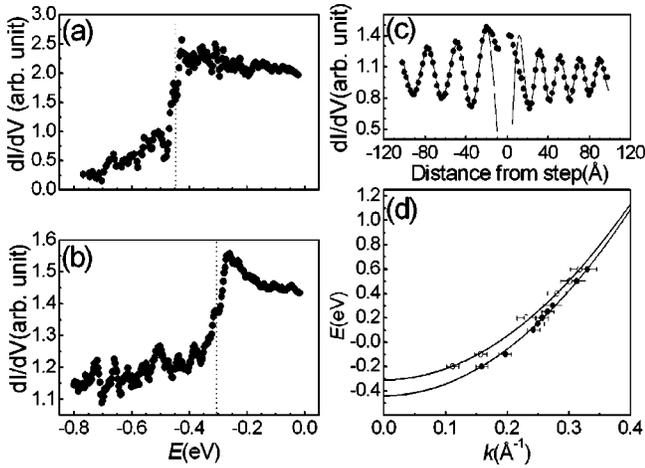


FIG. 3. Experimental dI/dV spectra taken from (a) Cu(111) and (b) 1 ML Xe-covered Cu(111) at 5 K. (c) dI/dV plot perpendicular to a step at $E = -200$ meV (solid circle). The line is a fit by Eq. (2). Left side (negative distance) is the Xe-covered surface and right side (positive distance) is the bare Cu surface. (d) Dispersion relation of the clean (solid circle) and Xe-covered (open circle) Cu(111) surface state at 5 K. The solid lines are quadratic fits to data.

occupied atomic orbital, $6s$, are far from the Fermi level.¹⁵ But according to a local density approximation calculation,¹⁵ the Fermi-level conduction electrons extend further out into the vacuum in the presence of Xe adsorbates than on clean metal surface. Previous experiments also suggested the pile-up of the conduction electron density at the Fermi level in the core of adsorbed rare gas atoms¹⁸ and reduced tunneling barrier of electrons through the adsorbed Xe layer.¹⁹ We conclude that the observed standing waves are caused by electrons in the Cu surface state of which the charge density extends through 1 ML Xe layer with a longer decay length than on the bare surface. No sign of standing waves can be found on 2 ML Xe patches such as bright islands in Fig. 1(a), indicating that the surface state electrons on Cu surface can contribute to the tunneling process only through the 1 ML Xe.

There can be several mechanisms, which can result in longer wavelengths on Xe-covered layer. (i) The confinement of the surface state electrons on a narrow terrace can result in different wavelength in the STM image.^{7,8} As our experimental results are obtained on wide terraces (>200 Å), the confinement effect can be neglected. (ii) It was shown that the bulk electrons also contribute to the formation of the standing waves with different wavelength.¹⁰ But this contribution near the step was found to be negligible¹⁰ and our results do not support this possibility since most of our images are obtained near steps. (iii) The longer wavelength may be explained with the modified dispersion of the surface state with 1 ML Xe. In order to verify this scenario, we perform STS on both the Xe-covered and the bare Cu surface. The measured dI/dV versus sample voltage dependence at one point is approximately proportional to the product of LDOS and the tunneling probability at the bias. It is obtained under open feedback condition with a lock-in amplifier. By measuring the local dI/dV spectra on both surfaces, the onsets of surface states can be determined as in Figs. 3(a) and 3(b). Well-known onset of the surface state at (440 ± 10) meV below Fermi level is visible on clean Cu surface in Fig. 3(a).

On the Cu surface with 1 ML Xe, the onset is shifted toward Fermi level by (130 ± 20) meV as shown in Fig. 3(b). A shift of ~ 100 meV was obtained in a 2PPES experiment.²⁰ In the case of alkali adsorbates, they change the surface electronic structure such that lowering of the work function and downward shift of the surface state are expected.²¹ Although the work function is lowered on 1 ML Xe on Cu(111),²⁰ the shift is upward, i.e., opposite direction. The dI/dV images were acquired simultaneously with constant current image. The dispersion of the surface states can also be determined by analyzing dI/dV images at varying bias voltages. We fit the dI/dV line scans perpendicular to a step by LDOS of the 2D nearly free electrons of effective mass m^* when they are scattered off the one-dimensional barrier (step). The LDOS, ρ_s , is given by

$$\rho_s = L_0 [1 - r J_0(2k_0 x)], \quad (2)$$

where J_0 is the zero-order Bessel function, $L_0 = m^*/(\pi \hbar^2)$, x is the distance from the step, $k^2 = 2m^*E/\hbar^2$, and r is the reflectance of the step. Figure 3(c) is one example of such a fit at $E = -200$ meV. The results are summarized in Fig. 3(d) on the Xe-covered and the bare Cu surfaces. Since the dI/dV image represents the convolution of the topography and the LDOS, the topographic contribution can be minimized by taking the image at a large tunneling gap.²² The measured dispersion on the bare Cu surface is similar to the one reported earlier.¹ Again it is confirmed that the dispersion of Cu surface with 1 ML Xe is shifted by (130 ± 20) meV and the effective electron mass is hardly changed within the parabolic band approximation [$(0.40 \pm 0.02)m_e$ and $(0.42 \pm 0.03)m_e$]. The change of other characteristics can be deduced from our data. For example, the onset of the surface state is broadened on the Xe-covered surface [compare Figs. 3(a) and 3(b)], suggesting the reduced lifetime of the surface state,¹² possibly due to the opening of a new decay channel resulting from phonons on Xe overlayer. We find that the shift of the surface state persists on 1 ML Xe islands as small as 20 nm^2 , discriminating the effect of impurity.

Our results clearly demonstrate that *significant parts of the signal from adsorbate-covered surface in STM can come from the substrate through the adsorbates*, especially which do not have much DOS near the Fermi level. We also believe that our findings can be extended to other adsorbate systems, such as alkali metals. Our result can be utilized such that the surface state may be intentionally modified with rare gas atoms to investigate whether the depopulation or population of the surface state influences growth behaviors and others,²³ which is in controversy recently.²⁴

In summary, we show that the effect of adsorbate on surface state can be successfully investigated with STM for the first time. The surface state electrons of Cu near Fermi level are still visible with the presence of 1 ML Xe layer due to the redistribution of charge density in such a way that it extends further at Xe adsorbates. It is believed that the longer wavelength of standing waves on the Xe-covered surface compared with the bare Cu surface is due to the shift of surface state dispersion of Cu with Xe adsorption.

After submission of this paper, we realize similar experiments are in progress on the alkali-covered noble metal surfaces.²⁵

The authors would like to thank N. D. Lang, J. Ihm, and J. Yu for carefully reading this manuscript. This work was partially supported by Korean Ministry of Science and Technology through Creative Research Initiative Program and Ko-

rean Ministry of Education, BSRI-98-2416. Support from Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sport and Culture of Japan is also acknowledged.

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