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ARPES study of the oxygen-induced reconstructed Cu(332): Surface state confinement

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ABSTRACT

We report the study of the Cu(111) surface state in the vicinal surface Cu(332) after the surface reconstruction induced by oxygen exposure. The reconstructed Cu(332) presents a striped surface consisting of Cu(111) and Cu(110)–O(2×1) facets. The angle resolved photoemission spectroscopy reveals a confinement of the original Cu(111) L-Gap surface state in the region of (111) facets due to the potential at (110)O(2×1) facets, forming a quasi-one dimensional state.

1. Introduction

The study of quantum-confined systems is of great importance in the understanding of fundamental concepts in condensed matter physics and for technological applications. The experimental study of such systems has developed in the last years thanks to improved control of surfaces and nanostructures. The Shockley surface state is a natural confined state found in metallic surface; the confinement between the crystal band gap and the vacuum barrier leads the surface state (SS) to behave like a two-dimensional electron gas with a parabolic dispersion [1–5]. Introducing boundaries at the surface determines further confinement of the SSs. This can be obtained by (self-) assembly or self-organization of nanodimensional structures on the surface [6–14]. For instance, vicinal surfaces with regular arrays of steps can impose a lateral confinement to the SS electrons [6–8,12,15–17]. Additionally, it has been proposed that the interplay between structural periodicity and SS energetics has an active rule in the long-range ordering in step bunched vicinal surfaces [18]. Concerning the scattering at step-edges, SS electrons can be confined to a quasi-one-dimensional (1D) electronic structures, depending on the barrier height imposed by the step-edge potential [15]. Such barriers can be modified by the incorporation of an adsorbate at step-edge [9,11]. The confinement of the electronic states can be studied in detail using angle-resolved photoemission spectroscopy (ARPES) [6–9,11,12,15–19] and also by scanning tunnelling spectroscopy (STS) as recently shown [10,13,14,19–22]. The combination of both probes ideally adds extended and local information and it has been applied to the study of surface SS in nm sized Au clusters on graphite [19] as well as in Cu(111) [5].

In the present work, we study the confinement of the Cu(111) L-Gap SS determined by the oxygen-induced reconstruction of the vicinal Cu(332); O/Cu(332). The Cu(332) surface corresponds to a miscut angle of 10° relative to the (111) surface towards the [1 1 −2] direction yielding a well-ordered step superlattice aligned along the [−110] direction and exhibiting (111) terraces with 5–6 atomic rows ($d = 12$ Å). In the Cu(111), the L-Gap SS presents an in-plane isotropic dispersion that is well approximated by a parabolic dispersion for states below Fermi energy. Small deviations from parabolic curve for energies near to the Fermi edge have been attributed to the significant hybridization of the Shockley SS and bulk states at higher wave vectors and energy [5]. In the clean Cu(332), the occupied SS band has an anisotropic quasi-parabolic dispersion, which can be modelled by two effective electron mass: $m^*_{[2]} > m^*_{[-110]}$, resulting in an ellipsoidal Fermi-surface for the SS [23]. The Cu(332) surface can be modified by oxygen exposure. Dosing O_2 on atomically clean Cu(332) induces the formation of periodic stripes, developing at the step edges and parallel to them, consisting of Cu(110)O(2×1) facets [24] that therefore isolate other parallel stripes of atomically clean Cu(111) as depicted in Fig. 1a. The surface synthesis conditions, i.e. oxygen dose and substrate temperature, can be controlled to tailor the periodicity of the stripes on the same primitive vicinal surface [25]. The ARPES data show important

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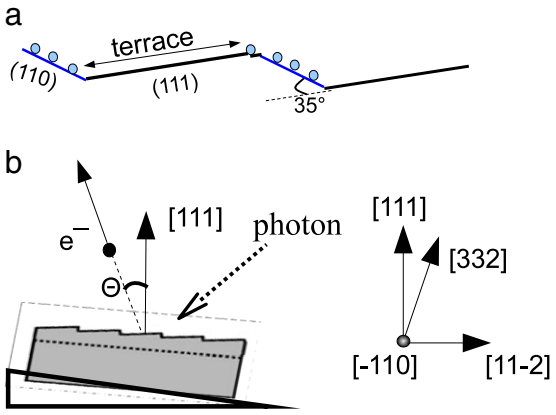

Fig. 1. (a) Detail of the surface of the oxidized Cu(332), the circles represent the oxygen atoms. (b) Geometry for the ARPES measurement.

changes in the Cu(332) SS after the oxygen exposure, indicating the full confinement of the SS in the (111) terraces. The SS in O/Cu(332), in contrast with the bare Cu(332), displays characteristics of a *quasi 1D terraces system*. We observed an almost flat dispersion perpendicular to the stripes, which is typical of quantum confined electron states, giving the evidence of the strong confinement of the SS in this direction perpendicular to the quasi 1D terraces.

2. Experiment

The Cu(332) surface was first prepared by several cycles of sputtering (Ar+, 600 eV) and annealing at 740 K followed by slow cooling to room temperature. The long range order was probed by low-energy electron diffraction (LEED), while the morphology and local order were probed by scanning tunnelling microscopy (STM) which works at room temperature. The preparation and STM chambers are UHV interconnected to the photoemission spectrometer chamber receiving the polarized synchrotron radiation from the APE beamlines of IOM-TASC CNR at the Elettra synchrotron radiation laboratory in Trieste [26]. This allows the in-situ synthesis, characterization and spectroscopy. The Cu(332) was held at T = 100 °C during the oxidation process. Five minutes exposure to 99.998% oxygen gas at a partial pressure of 5e − 8 mbar (1e − 7 mbar), followed by a 10 min annealing at 100 °C (150 °C), repeatedly produced a 4 nm (6 nm) periodic striped structure, in which the average (111) terrace width was 3.3 nm (4.5 nm), as measured by STM. The synthesis protocol and characterization of this system are described in detail in Ref. [25].

The APE low-energy beamline provides variably polarized synchrotron radiation with high spectral purity in the energy range 10–100 eV from an Apple II-type quasi-periodic undulator. The light is monochromatized by variable-spacing gratings and then focused on the sample into a spot size 200 × 50 (H × V) μm². Incoming photons impinge on the sample at 45° from its normal. The emitted photoelectrons are detected by a SES-2002 hemispherical analyser with an acceptance angle of ±7° operated with an angular resolution of 0.2°. The experiment was carried out at room temperature with a total energy resolution of 26 meV. Linearly polarized radiation was chosen, and oriented in the horizontal scattering plane (p-polarization). The sample was mounted in an inclined sample holder in such a way that the azimuthal axis is parallel to the [111] direction. The normal emission (θ = 0°) is then defined relative to the [111] direction as shown in Fig. 1b.

3. Results and discussion

ARPES measurement was first performed on the clean Cu(332). The SS in the clean Cu(332) propagates parallel to the macroscopic surface, having an *average-surface modulation* character [7,15,23]. In this regime, the perpendicular component of the crystal momentum of the SS is spanned along the [332] direction and therefore it resides outside from the L-Gap of bulk states [15]. The main consequence is that the SS is resonant with the bulk states and has higher penetration in the bulk crystal. For that reason, the SS in the Cu(332) is less sensitive to the scattering potential of step edges, allowing the electronic coupling from terrace to terrace. The result of such coupling is evident in terms of *weak-potential* approach [15] where a gap and the zone-folding of the quasi-free-electron band are expected. Our data are fully consistent to those reported in literature for Cu(332) or similar system [7,15,23,27]; namely: (i) the photoemitted bulk electrons are diffracted by the optical plane (332) and do not present any evidence of perturbation from the periodic surface potential. (ii) The SS band presents a quasi-parabolic dispersion, and the band bottom appears always shifted in k-space in the [11-3] direction by half surface Brillouin zone from the Γ point; that is $dk = \pi/d = 0.26$ Å^{-1}. The SS band bottom is therefore measured in our setup at the emission angle $\theta_b = 10° - arcsin\{0.26/[(2\ m/\hbar^2)\ E_{kin}]^{1/2}\}$, where E_{kin} is the kinetic energy of the photoemitted electron. θ_b clearly depends on the photon energy. (iii) We measured a value of 0.30 eV for the bottom energy of the SS band (maximum binding energy); consistent values in literature are reported ranging from 0.29 to 0.30 eV [7,23,27]. (iv) Using a photon energy of 36 eV, we were able to measure a zone-folding of the SS band dispersion. Such a feature was already reported for Au(223) [15].

After the oxygen exposure, the photoemission intensity from SS decays in few hours, even if the sample is kept in UHV conditions; which points to a higher surface reactivity in comparison with the clean copper surface. In Fig. 2 we see the electronic dispersion of the SS for the O/Cu(332) with 4 nm periodicity measured with 36 eV photon energy. The SS band appear centred at $\theta_b = 0$, which corresponds to an electron emission along the [111] direction. It

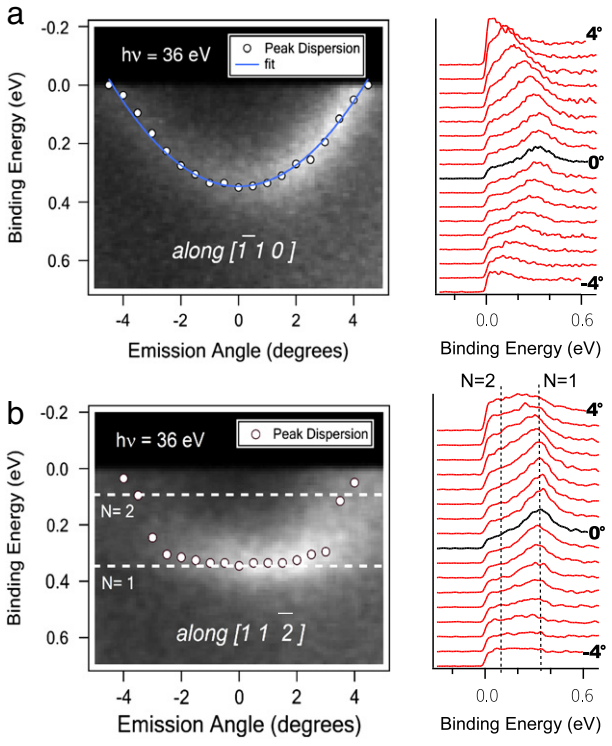

Fig. 2. EDC curves scanned along the directions parallel (a) and perpendicular (b) to the stripes from the O/Cu(332) with 4 nm periodicity. The open circles indicate the centre of the Lorentzian curve used to fit the dispersion of an integrated slice of 0.2°. The dispersion in direction perpendicular to the stripes (b) is compared with the two lowest levels (N = 1,2) of a one-dimensional infinite quantum well; they are represented by the horizontal (vertical) dashed lines in the left (right) panel. The maximum binding energy is 0.33 eV. The data was acquired at 80 K with photon energy of 36 eV.