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Lateral confinement effects of $\overline{M}$-point Tamm state in vicinal Cu(100) surfaces

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ABSTRACT

Vicinal Cu(100) surfaces with different miscut angles and terrace widths are studied by angle resolved photoemission spectroscopy. The Tamm $\overline{M}$-point d-like surface state is strongly affected by the super periodic potential induced by the regular array of steps, as it shifts away from the Fermi level and its bandwidth is reduced. For smaller terraces, several replicas are observed, proving that the Tamm surface state is sensitive to the new superperiodic potential. For the largest terraces, the Tamm state starts splitting into incipient and non-dispersing quantum well states, indicating that a transition into a localized regime takes place as a function of terrace width. The results are rationalized using a Kronig–Penney model to simulate the step superperiodicity.

1. Introduction

Metallic vicinal surfaces have deserved ample attention due to their interest as templates for epitaxial growth and as model systems in the study of heterogeneous catalysis or thermodynamic properties of low dimensional solids [1–4]. Noble metal surfaces vicinal to a (111) plane have been also the subject of many studies [5–13]. The main reason is the presence in these surfaces of a Shockley free-electron-like surface state of sp orbital origin, which provides an excellent playground to test how the electron wave function is affected by the step superperiodic potential. A rich experimental phenomenology has permitted to probe the nanoscale physics of the electron wave function under reduced dimensionality conditions. Steps act as a potential barrier for the surface electrons and depending on the superperiodicity, the wave function of the surface state switches at a critical miscut angle from being localized at the terraces to being delocalized along the optical surface. This means that the 2D surface states displaying superlattice band folding split into 1D quantum well levels with increasing terrace size (d) [12,14–20]. The switching has been attributed to a decrease in the effective step barrier, due to the closing of the band gap after a critical miscut angle [12,14,21,22], or to localization induced by disorder [17].

It is an interesting question how other types of electron wave functions are affected by a regular array of steps. In particular, the Cu(100) surface supports a very well-known surface state localized at an absolute band gap centered at $\overline{M}$ points of the surface Brillouin zone (SBZ). The origin of the surface state is the electronic states near the top of the d bands, which are pushed out from the bulk continuum by an increased Coulomb repulsion, owing to the excess of s and p electrons at the surface. Thus, the electronic state is usually described as a Tamm surface state. Due to its d orbital origin, it is much more localized than sp surface states found in other noble metal faces. Furthermore, the particular orbital symmetry d_{xy} induces a strongly reduced interaction between adjacent planes along the surface normal, which leads to an extremely localized state, almost decoupled from the adjacent layers [23–27]. Due to these features, the surface state is very sensitive to changes produced in the surface. In fact, angle resolved photoemission spectroscopy (ARPES) measurements have revealed one of the narrowest peaks observed with photoemission in the solid state [28]. Previous ARPES results on vicinal Cu(610) have found superperiodicity related effects on the Tamm state, as a binding energy (BE) shift, reduced bandwidth and gap opening at new superperiodicity zone boundaries [29,30]. A theoretical tight-binding calculation has predicted that the surface state BE and bandwidth should be modified in Cu(N10) surfaces (N being an integer) by the step periodic potential [31].

We report here an investigation on the effect of a step periodic potential in the d-like Tamm state of vicinal Cu(100) surfaces using ARPES. We probe three different vicinal crystals, Cu(410), Cu(610) and Cu(12 1 0). In the small terrace regime, Cu(410) and Cu(610) stepped surfaces, the Tamm surface state is largely modified in BE and dispersion, so that the surface state is sensitive to the superperiodicity induced by the steps. For larger terraces, Cu(12 1 0) stepped surface, the Tamm state exhibits partial localization and incipient formation of quantum well states is identified. This behavior is an indication of a similar dimensional crossover for Tamm states, as described for Shockley states in (111) surfaces, supporting the idea of a general behavior independent from the surface state wave function character. A 1D Kronig–Penney model is used to analyze the degree

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of confinement across the steps. We obtain from this analysis a comprehensive understanding of the behavior of an extremely surface localized state with d-like orbital character, under the action of a periodic potential produced by a regular array of steps.

2. Experiment

Two different ultrahigh vacuum chambers (base pressure below 1×10^{-10} mbar) were used to performed ARPES and low-energy electron diffraction (LEED) experiments. The first apparatus receives He I and He II radiation from a plasma source (Gammadata) and uses an in-vacuum mobile electron analyzer ARUPS-10 (Vacuum Generators) mounted on a two-axis goniometer. The energy dispersion is measured with respect to polar emission angle in the horizontal plane. The energy resolution was set to 80 meV and the angle resolution for azimuthal and polar angles was 0.5°. This particular setup is suitable for measurements of Fermi surfaces (FSs) and constant binding energy surfaces. The second UHV chamber belongs to the APE beamline of the Elettra storage ring in Trieste (Italy) and it is equipped with a Scienta SES200 electron analyzer. The dispersion plane of the electron analyzer is horizontal in this setup. An energy resolution of 20 meV, and an angular resolution of less than 0.1° were selected. A complete electronic structure characterization was obtained using linearly polarized light (vertical and horizontal planes) with photon energies in the range from 21 to 50 eV. The Tamm surface state wave function has an odd symmetry with respect to the ΓXWK mirror plane, which is made to coincide with the analyzer (horizontal) dispersion plane. Thus, the Tamm surface state is seen with vertical polarized light.

Three vicinal Cu(100) crystals, corresponding to Cu(12 1 0), Cu(610), and Cu(410) orientations, were used in this work (see Fig. 1). The samples were oriented with 0.2° accuracy to their nominal directions (Surface Preparation Laboratory). All surfaces were prepared by Ar^+ sputtering (1 keV energy) and annealing to 775 K for some minutes. LEED was used to check the surface quality. After several cycles, LEED patterns with sharp spots and a well defined spot splitting were obtained, as it is typical of a homogeneous array of steps, characterized by a finite terrace size distribution. Typical LEED patterns from Cu(410) and Cu(12 1 0) surfaces are shown in Fig. 2. The splitting distance is consistent with the expected superperiodicity of the new regular step array. No signs of surface faceting have been detected in LEED.

Samples were oriented by LEED for ARPES measurements so that the $\overline{\Gamma M}$ surface high symmetry direction (perpendicular to the steps) coincides with the horizontal plane. The step orientation ("downhill" or "uphill") is determined from a measurement of the sp band dispersion and from a comparison with theoretical tight binding calculations (see below and Section 4.2). The direction normal to the average surface (optical surface) is used as a reference for the angular scale and is determined from this procedure and from the reflection of a laser shining through the electron analyzer. The combination of both procedures allows us to determine it with high accuracy. For all surfaces, parallel momentum is always calculated with respect to the optical surface normal.

Parallel and perpendicular components of the electron momentum inside the crystal are calculated assuming free-electron like final states from $k_{\parallel} = \sqrt{\frac{2m_e}{\hbar^2}E_{kin}sin^2\theta}, k_{\perp} = \sqrt{\frac{2m_e}{\hbar^2}(E_{kin}cos^2\theta + V_0)}$, where V_0 is the crystal inner potential, and E_{kin} and θ are the two relevant magnitudes measured by ARPES. A value of $V_0 = 7$ eV was used. Electronic band structure and constant energy surface contours were simulated using the ELAN code [32]. In this code the Slater–Koster (SK) tight binding approach [33] is used as an interpolation method to generate the band dispersion $E(k)$ at a large number of k-points for a given structure.

3. Surface structure

Copper surfaces vicinal to the [100] direction exhibit (100) terraces, but steps may be oriented along any direction in the (100) plane. In

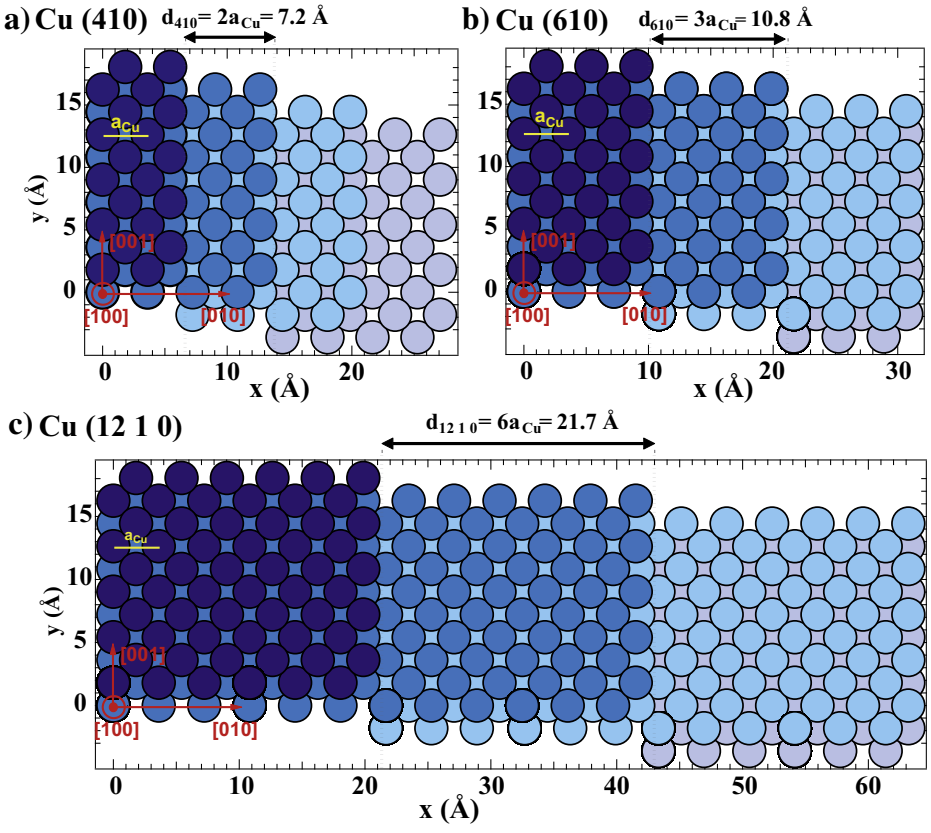

Fig. 1. Schematic ball models of the vicinal Cu(100) surfaces used in this work (top views): a) Cu(410), b) Cu(610), and c) Cu(12 1 0).