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The Unoccupied Surface States of the Cu(110) Substrate

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ABSTRACT

Inverse photoemission spectroscopy is one of the advanced surface science technique for measuring unoccupied surface states with sufficient accuracy. The unoccupied surface states of the Cu(110) substrate has been investigated using an inverse photoemission spectroscopy with energy resolution of 0.5 eV. In this study, it has been introduced new unoccupied surface states. These unoccupied states are obtained from bulk bands and placed mainly in the outermost atomic layer. These states have been compared and contrasted with experimental and theoretical results. It has been also shown that at the $\overline{Y}$ point of the surface Brillouin zone, reflectance anisotropy spectra of the Cu(110) substrate possesses an unoccupied and occupied surface states.

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INTRODUCTION

Studying the surface electronic structure of the solid are received great attention experimentally and theoretically. An electronic state, which localized to a solid surface, is named a surface state. Surface states of metals are known as an important candidate for the investigation of electronics properties. In the surface states, the electron–electron interactions have been studied [1,2]. The bulk of the solid obtained from *s*- and *p*-states possess a almost parabolic form. These new states are called "bulk states" at the surface. The wave functions of these states are localized near the solid surfaces and which decrease exponentially on both into the bulk and the vacuum of the material. Surface state is an electronic state established at the surface of the crystal.

The low index faces of metal surfaces, i.e. Cu, Ag and Au, contain two surface states, i.e. occupied and unoccupied. Electrons of surface states can scatter from defects and step edges at the surfaces. For the transition metal of Cu(110), the *s,p*-state bands are well identified. The bulk band of Cu(110) substrate that is on the Fermi level (E_F), holds an unoccupied surface state, which is lying about 2 eV above the E_F [3–5], and the other surface state crosses the E_F [4]. The bulk states are all *s,p* derived.

As is well known since more than two decades, surface states have been investigated with a combination of ultraviolet photoelectron spectroscopy (UPS) [7-9], inverse photoemission spectroscopy (IPES) [3,10-14] and theoretical work [10,11,15-17]. UPS offers a great technique for the occupied electronic states at metal surfaces. IPES provides results concerning to empty surface state bands on solid surfaces. In case of UPS and IPES, these techniques have their weaknesses and strengths in presenting surface states at metal surfaces.

IPES promises to be an important surface science technique in this research area because of its ability to probe unoccupied electronic structures [18,19]. In IPES basically three types of unoccupied surface states are observed: Shockley surface states [20] which are *sp*-like, Tamm states [21] which are *d*-like surface states (often associated with surface reconstruction) and image potential states. Shockley and Tamm states are also seen in angle resolved photoemission spectrum (ARPES) but image states are not.

Reflection anisotropy spectroscopy (RAS), UPS, IPES and X-Ray Photoelectron Spectroscopy (XPS), have been used in this study. It is therefore very fascinating now to have an experimental technique at hand to compare available data. The aim of this study is to clarify the unoccupied surface states and to compare available data. It is therefore worthwhile to study electronic states at the Cu(110) clean metal surface. In this paper, it is reported new surface states in the unoccupied region.

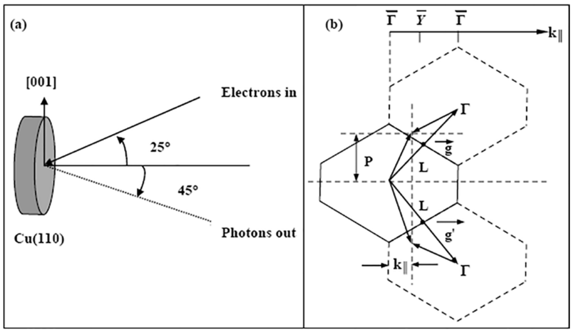

Figure 1. (a) For the IPES experimevvnts, the Cu(110) adjusted at the right angle. **(b)** SBZ diagram of the Cu(110) surface. The bulk reciprocal lattices are shown g and g′, p is the perpendicular wave vector.

EXPERIMENTAL

In this study, experiments were performed in an ultrahigh vacuum (UHV). This UHV contains Low Energy Electron Diffraction (LEED), Mass Spectrometer, UPS, IPES and XPS apparatus. The Cu(110) substrate was cleaned in UHV, the daily preparation involved Ar ion bombardment at 500 V for 30 minutes. After this procedure, the substrate annealed up to 600 K for 20 minutes. Cleanliness, surface order and surface orientation were verified by LEED and XPS. LEED presented a sharp (1x1) spots at room temperature (RT).

The IPES studies were completed in the base pressure of $1{\times}10^{-10}$ Torr. The IPES produces an emission current of 40 μA. The photons radiated from the sample are reflected on Micro-Channels Plates (MCP) detector by a holographic circular diffraction grating which has a diameter of 92 mm, 3600 lines per mm, a concave radius of curvature of 300 mm, and a focal ratio of 3.3. The electron gun was adjusted at 25° and along the [110] direction. The geometry shown in Fig. 1 corresponded to the $\overline{Y}$ point of the surface Brillouin zone (SBZ) in reciprocal space. In case of keeping the angle of 45° between emitted photons and the sample surface normal position constant. The experiments were carried out at the $\overline{Y}$ point i.e. the relevant angles in the experiment were adjusted so as to keep $k_{\parallel}$ constant.

The ion gauges had to be shut off during the IPES measurements because light from the ion gauge produced a background signal in the MCPs. All of the chamber windows were also covered during IPES scans to avoid any source of photons in the chamber. Finally, IPES spectra were recorded.

RESULTS AND DISCUSSION

The IPES experiments were determined at 9.1 eV electron energy and fixed photon energy [3,10,11]. There are two important points to note that the first is that IPES experiment has been employed the fixed electron energy and different photon energy ranges. In other words, the unoccupied surface states were monitored by IPES technique at the fluorescent mode. The second is that IPES has been carried out at the $\overline{Y}$ point in the SBZ of the clean Cu(110), with fixed kinetic energy of 19 eV. The geometric procedure is set up for electrons at 25° and for emitted photons is set up at 45° at RT can be seen in Fig. 1. Fig. 2 shows IPES experimental results for the Cu(110). For At the $\overline{Y}$ point, a surface transition was supposed to be 2.2 eV for the Cu(110), an occupied surface state was seen at 0.4 eV below the E_F [8], an unoccupied surface state was found 1.8 eV above E_F [5].

Table 1 shows the peak positions along with the experimental and theoretical references. The unoccupied bulk and surface states were resolved with an IPES energy resolution of 0.5 eV.

The experimental binding energies of the unoccupied states of Cu(110) are reported at 2.5 eV [3], 2.0 eV [10], and 1.8 eV [5]. The calculated values are reported at 2.5 eV, 4.85 eV, 6.4 eV, 6.9 eV and 7.3 eV [22] and 5.63 eV [23]. There are no reports on the unoccupied states at 2.3, 8.0 eV, 8.8 eV and 9.4 eV as observed in this study. All the thirteen peaks are real because they were reproducible and the uncertainty of each peak, $\pm\sqrt{N}$, is less than count N. It is important to note that without any contamination of the substrate should be taken into account to confirm these unoccupied states.

The peak 2.5 eV from a surface state [3] was associated with a number of principles: First of all, the surface states should exit bulk structure of the clean Cu(110). Then, it should separate electron's momentum. Lastly, a surface state should be sensitivity to surface contamination. For the unoccupied surface state band on Cu(110) substrate with 2.0 eV at the SBZ, it has been established. The calculated value was reported at 5.63 eV according to the density of states

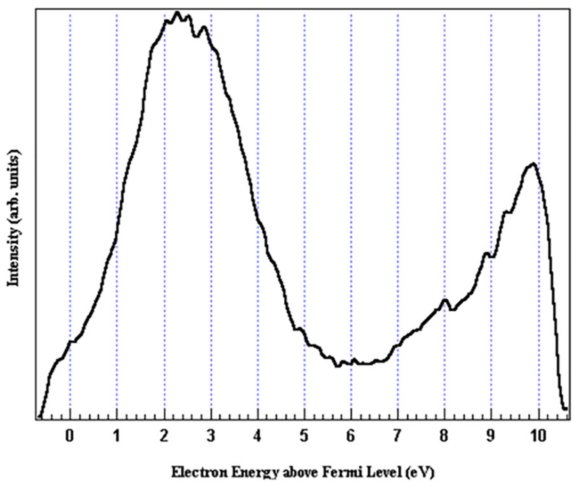

Figure 2. IPES spectrum of the Cu(110) obtained at the $\overline{Y}$ point in the SBZ, at RT and at off-normal electron incidence.

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Table 1. Peak energies in eV of the unoccupied surface states for the Cu(110).

Peak Energies in (eV)		Other Experimental Results	Reference	Other Theoretical Results	Reference
1.7		1.8	[5]	1.7	[29]
2.0		2.0	[10]	-	-
2.3	New Peak	-	-	-	-
2.45		2.5	[3]	2.5	[22]
2.8	New Peak	-	-	-	-
4.8		-	-	4.85	[22]
5.2		5.5	[22]	-	-
5.8		-	-	5.63	[23]
6.2		-	-	6.4	[22]
6.8		-	-	6.9	[22]
8.0		-	-	7.3	[22]
8.8	New Peak				
9.4	New Peak				

calculations [23]. Using an angle resolved photoemission spectroscopy, the energy of the lowest (n= -1) state at Cu(110) $\overline{Y}$ point is identified to be E_F-0.39eV [6]. The following lowest surface state is provided 2.0 eV [8], 2.5 eV [1] and 1.8 eV [5]. The surface state of the Cu(110) was found at 5.5 eV (22) above E_F. The unoccupied surface state for the substrate is presented in Fig. 3. At the $\overline{Y}$ point of the SBZ, an energy of 2.1 eV is obtained using RAS. In this study, this state has been probed using IPES. A number of different groups [3–5,13,24–31] have been analyzed this state by theoretically.

As seen in Fig. 3, the peak at 2.1 eV is associated with shifts between *p*-type occupied surface state and *s*-type unoccupied surface state at the $\overline{Y}$ point of the SBZ. The other peak at 4.2 eV in Fig. 3 is correlated with a shift at the $\overline{X}$ of the SBZ between the bulk *d*-bands of the occupied state and *p*-type surface state of the unoccupied state. At $\overline{Y}$ point, the occupied surface state possesses p_y character. The transition between states of the occupied and unoccupied is only permitted for light which polarized along [001] direction.

For the Cu(110), surface states are established in bulk band gaps. These bulk band gaps are positioned near the $\overline{Y}$

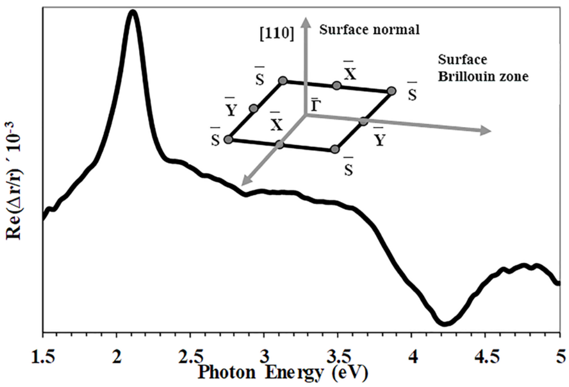

Figure 3. RAS spectra for the clean Cu(110) substrate.

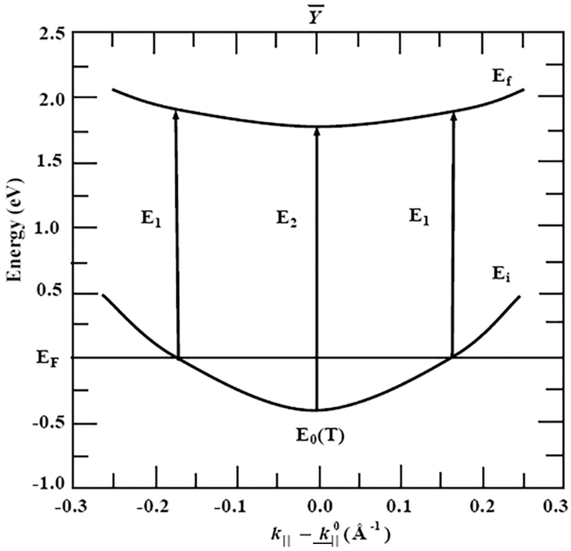

Figure 4. Energy illustrations nearby $\overline{Y}$ point.

point. The Cu(110) surface possesses one partly occupied and one unoccupied surface states as displayed in figure 4. For Cu(110) substrate, the Shockley state around $\overline{Y}$ point is shown anisotropic behavior. There is an evidence for this finding by using scanning tunneling microscopy [32].

At metal surfaces, such as Cu, electrons of the surface state spread from step edges and defects. These cause an increase quantum interference patterns.

CONCLUSION

In this study, the new unoccupied surface states of the Cu(110) at the $\overline{Y}$ point have been obtained using IPES surface science technique. The new unoccupied surface states are obtained from bulk bands and placed mainly in the outermost atomic layer. The findings have been compared and contrasted with available experimental and theoretical data. It has been also shown that reflection anisotropy spectra of the clean Cu(110) substrate possesses surface states at the $\overline{Y}$ point.

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