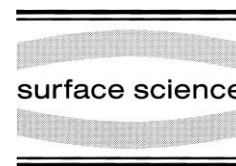




ELSEVIER

Surface Science 402–404 (1998) 556–560



Direct transition in the system Ag(111) studied by one- and two-photon photoemission

S. Pawlik *, R. Burgermeister, M. Bauer, M. Aeschlimann

Laboratory for Technical Chemistry, ETH Zurich, CH-8092 Zurich, Switzerland

Abstract

Structures in two-photon photoemission (2PPE) spectra are usually related to initial and intermediate states by the peak shifts with an incident photon energy. Based on the direct sp-transitions in thin silver films evaporated on Cu(100), we demonstrate that the linear shift in the 2PPE spectra is a strict requirement but not a sufficient criterion for assigning the feature to an intermediate state. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ag(111); Direct transition; Photon photoemission

1. Introduction

Electronic states of metals have been studied extensively by photoemission measurements. However, the accessible energy range is obviously restricted to initial states below E_F and to final states above E_{vac} . In order to investigate the unoccupied states between E_F and E_{vac} , other techniques have to be used, e.g. inverse photoemission and two-photon photoemission (2PPE). Compared with the well-established inverse photoemission method, the relatively new technique of 2PPE can simultaneously probe both the occupied and the unoccupied states with the same high-energy resolutions and allows polarization selective excitation to determine symmetry properties [1].

The 2PPE method is based on a two-step excitation. The first photon excites an electron from the

initial state E_i to an intermediate state E_{int} . A second photon brings the electron to the final state E_f above the vacuum energy so it can leave the surface and be detected. A stringent condition for this method is that the photon energy is smaller than the work function in order to avoid one photon photoemission, which would completely obscure the 2PPE spectrum. The 2PPE data are generally given as a plot of the number of detected electrons versus electron energy and reflect the joint density of states of the initial, intermediate and final state distributions. It has been demonstrated that a peak in a 2PPE spectrum can be easily related to an initial or intermediate state by the peak shifts with a change of the incident photon energy. When varying the photon energy by $\Delta h\nu$, the peak positions of occupied states shift by $\Delta E_{kin} = 2\Delta h\nu$, whereas the peak positions of unoccupied states shift linearly by $\Delta E_{kin} = \Delta h\nu$ [1,2].

In this context, it is of interest to examine

* Corresponding author. Fax: (+41) 1 632 11 62;
e-mail: pawlik@tech.chem.ethz.ch

whether a shift by $\Delta E_{\text{kin}} = \Delta h\nu$ is in general sufficient to assign a structure in the spectrum clearly as an unoccupied state. This paper demonstrates that this criterion, together with a stronger one, the lack of a corresponding feature in the relevant energy region of the UPS spectra, is insufficient proof that a feature in a 2PPE spectrum originates from an unoccupied state. Based on the prototype system Ag(111), we will show that a structure in the 2PPE spectrum, observed previously by Giesen et al. [3], who considered it to be an unoccupied surface state, is in fact a direct band-to-band transition in the bulk.

2. Experimental details

The two central elements of the experimental apparatus, the laser system and the electron energy analyzer, are described separately elsewhere [4]. In brief, the experiments were performed at room temperature in an UHV chamber equipped with a cylindrical sector energy analyzer. We used generally a pass energy of 4 eV, leading to a resolution of roughly 80 meV.

A -4.0 V bias was applied to the sample to eliminate the effects of any stray electric fields. The photoelectrons are detected along the surface normal. We used a femtosecond mode-locked Ti:sapphire laser system as a light source, which delivered 40 fs pulses of up to 18 nJ pulse^{-1} at a repetition rate of 82 MHz. For the 2PPE spectra, the linearly polarized output was first frequency-doubled in a 0.75 mm thick LBO crystal to produce UV pulses at $h\nu = 3\text{--}3.3$ eV. For the one-photon photoemission (1PPE) spectra, the laser fundamental at $h\nu = 1.5$ eV was quadrupled using the same LBO crystal in a first stage and a 1 mm thick BBO crystal in a second stage, generating photon energies of 6.0 eV. Furthermore, a low-pressure gas discharge lamp (He I, photon energy $h\nu = 21.2$ eV) was used for additional UPS studies. The angle of incidence of the polarized laser beam was 45° with respect to the surface normal of the sample. For p-polarization (s-polarization), the electric field vector is parallel (perpendicular) to the plane of incidence.

The samples used were 10–200 Å thick Ag films

on a Cu(100) substrate. The growth mode of Ag on Cu(100) is well known from earlier investigations [5]. Despite the lattice mismatch of 13.2%, a silver monolayer deposited on Cu(100) adopts a $c(10 \times 2)$ structure. This structure is a slightly strained Ag(111) layer compressed and expanded by about 2% in two orthogonal directions; the areal density of Ag atoms is essentially unchanged by the strain. Kürpick et al. showed that the UPS spectrum observed at 7 ML is practically identical to that from a bulk Ag(111) crystal surface [6].

The Cu (100) crystal was prepared carefully by several sputtering and annealing cycles. Auger spectroscopy (AES) and low-energy electron diffraction (LEED) were used to examine the cleanliness and the crystal structure. The Ag films were evaporated from a Knudsen cell type evaporation source at a rate of 2 ML min^{-1} on to the Cu(100) substrate at room temperature. The coverage was controlled by a calibrated quartz thickness monitor. During the Ag evaporation process, the pressure was kept in the 10^{-10} mbar region.

3. Results

Fig. 1 shows a series of 2PPE spectra for increasing thickness of the silver film. The data are plotted as a function of the final state energy. After the depositions of 10 ML Ag, a small structure was visible at 5.3 eV, becoming stronger and dispersing to lower energies with increasing coverage. This pronounced peak was only observed for p-polarized light; no structure was seen when s-polarized light was used.

Furthermore, by changing the photon energy by $\Delta h\nu$, this structure shifts with approximately $1 * \Delta h\nu$ (Fig. 2a), typical of an intermediate state. Hence, these two observations lead to the assumption that the structure originates from an unoccupied surface state at an energy of ~ 2.1 eV above E_F . For additional proof that the structure results from an intermediate state, UPS spectra of the same silver film were measured (Fig. 2b). The Ag 4d band emissions begin at initial state energies of -4 eV, in agreement with previous measurements [7]. If the structure observed in the 2PPE spectra originated from an occupied state, a peak would be

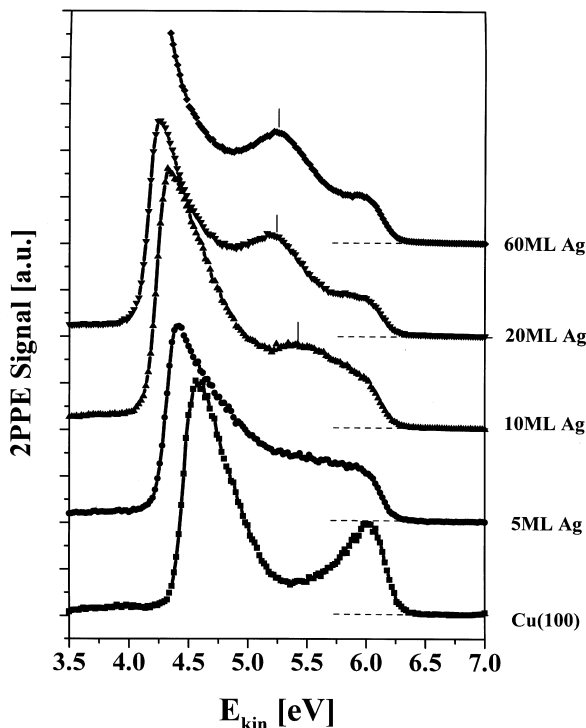


Fig. 1. Two-photon photoemission (2PPE) signal taken at $h\nu = 3.22$ eV as a function of the kinetic energy from clean Cu(100) and Cu(100) covered with Ag overlayers of different thickness.

expected in the UPS spectrum at around 1 eV below the Fermi level. As can be seen in the inset, no such structure can be observed in the relevant energy range, strongly supporting the previous interpretation.

4. Discussions

Ag (111) has a sp-bandgap from -0.31 eV below to 3.85 eV above E_F in the normal direction ($k_{\parallel}=0$) [8]. No theoretical work has predicted an unoccupied surface state in the region of 2.1 eV above E_F for an Ag(111) surface, nor has this state ever been seen in inverse photoemission studies. This leads to the assumption that the strain in the Ag layers has shifted up the occupied surface state to 2.1 eV above E_F . A similar shift was observed by Neuhold et al. on Ag(111) on Si(111) [9]. The pronounced structure was also

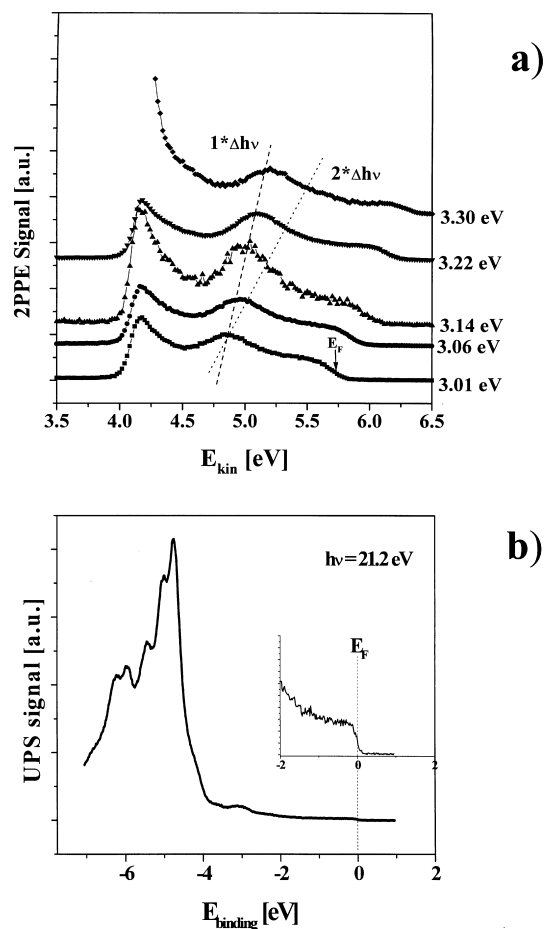


Fig. 2. 2 PPE signal versus kinetic energy from Cu(100) covered with 60 ML Ag for different photon energies. In general, the 2PPE peak position of an unoccupied (occupied) state shifts with one time (twice) the photon energy as indicated by the dashed (dotted) line. UPS spectra (He I, photon energy $h\nu = 21.2$ eV) taken in normal emission from the same sample.

reported, however, on an Ag(111) single crystal surface in pioneering 2PPE-investigations by Giesen et al. [3]. By increasing the photon energy, they also found a shift with $1*\Delta h\nu$, pointing to an unoccupied state located at 1.92 above E_F . In addition, they observed that the intensity of the structure decreases with increasing photon energy and vanishes at an excitation energy of 3.84 eV. In a later study, they reported a similar structure in Ag(100) at 1.7 eV above E_F [10]. They assigned this peak to the well-known unoccupied surface resonance on Ag(110) facets located according to

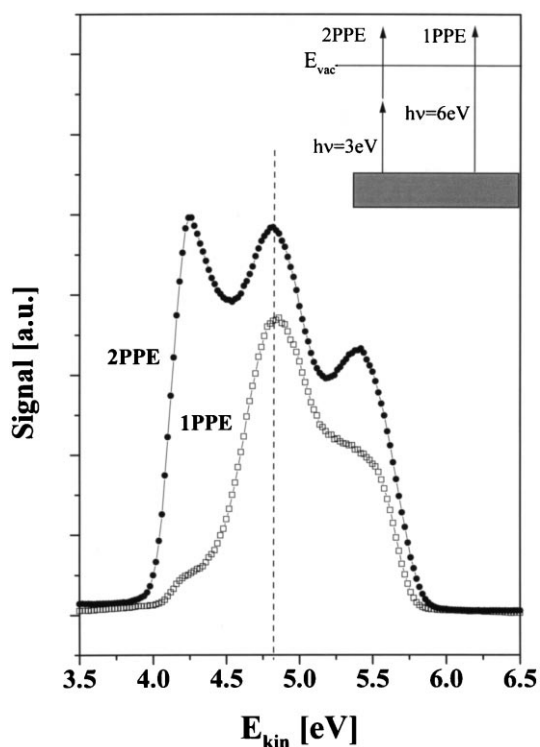


Fig. 3. Reduced zone scheme of Ag along the [111] direction. Direct two-photon transitions for photon energies of 3.0, 3.15 and 3.3 eV are indicated by vertical arrows.

previous inverse photoemission measurements at 1.6 eV to 2.5 eV above E_F . They argued that silver is known for its tendency to form rough surfaces, e.g. for the existence of facets of different crystal structures at the (111) and (001) surfaces.

Our interpretation is quite different and is based on recent photoemission results reported by Miller et al. [11]. Near the Fermi level, the sp-band of Ag(111) is known to be nearly free electron like. In the surface normal direction, this band gives rise to a direct band-to-band transition (see Fig. 3) [12]. Due to the bending of the bands, this peak disperses with varying photon energy with approximately $1 \cdot \Delta h\nu$. At photon energies above 12 eV, the band-to-band transition disappears and, hence, cannot be resolved in our UPS measurements.

As final proof of our interpretation, we performed a one-photon photoemission (1PPE) spectrum with the quadruplet output of our Ti:sapphire laser. If Giesen et al.'s interpretation is

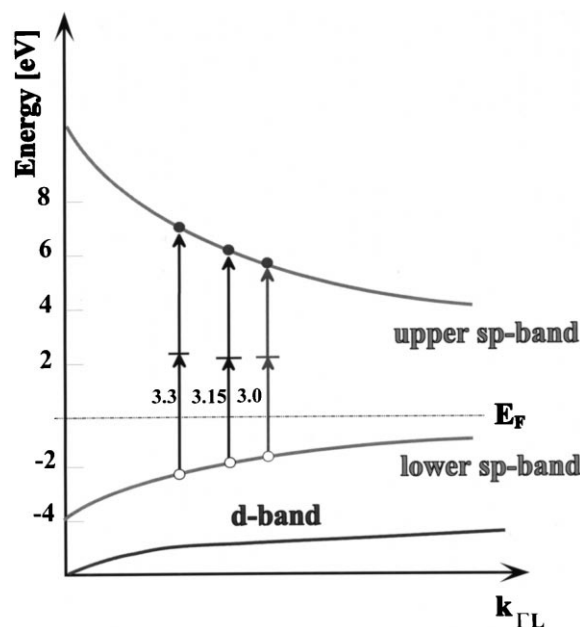


Fig. 4. 2PPE spectra at $h\nu=3.0$ eV (\bullet) and 1PPE spectra at $h\nu=6.0$ eV (\square) of Cu(100) covered with 200 ML Ag.

correct, the peak at $E_{kin}=4.7$ eV should not show up in the 1PPE spectra. A comparison of the 2PPE intensity with this 1PPE spectra intensity as a function of kinetic energy of the electrons is shown in Fig. 4. Both spectra exhibit the structure at $E_{kin}=4.7$ eV. This is clear evidence that the structure in the 2PPE spectrum cannot be caused by an unoccupied intermediate state.

5. Conclusions

This study demonstrates that the shift of nearly $1 \cdot \Delta h\nu$ of a feature in a 2PPE spectrum and the lack of an equal feature in the relevant energy region of the UPS spectra are not sufficient criteria for assigning a structure to an unoccupied state. Comparison of the 2PPE spectra with additional 1PPE measurements, taken at the same initial and final states, is an effective method to rule out misinterpretation.

Acknowledgements

The work was supported by the Swiss National Science Foundation by Grant No. 2024-046349.96.

References

- [1] T. Fauster, W. Steinmann, in: P. Halevi (Ed.), *Photonic Probes of Surfaces*, Elsevier, Amsterdam.
- [2] H. Ueba, *Surf. Sci.* 334 (1995) L719–L729.
- [3] K. Giesen, F. Hage, F.J. Himpsel, H.J. Rieß, W. Steinmann, *Phys. Rev. Lett.* 55 (1985) 300.
- [4] M. Aeschlimann, M. Bauer, S. Pawlik, *Chem. Phys.* 25 (1996) 127–141.
- [5] P.T. Sprunger, E. Lægsgård, F. Besenbacher, *Phys. Rev. B* 54 (1996) 8163.
- [6] U. Kürpick, G. Meister, A. Goldmann, *Surf. Sci.* 328 (1994) 58.
- [7] G.V. Hanson, S.A. Flodström, *Phys. Rev. B* 17 (1978) 473.
- [8] R. Rosei, C.H. Culp, J.W. Weaver, *Phys. Rev. B* 10 (1974) 484.
- [9] G. Neuhold, K. Horn, *Phys. Rev. Lett.* 78 (1997) 1327.
- [10] K. Giesen, F. Hage, F.J. Himpsel, H.J. Riess, W. Steinmann, *Phys. Rev. B* 35 (1987) 971.
- [11] T. Miller, W.E. McMahon, T-C. Chiang, *Phys. Rev. Lett.* 77 (1996) 1167.
- [12] P.S. Wehner, R.S. Williams, S.D. Kevan, D. Denley, D.A. Shirley, *Phys. Rev. B* 19 (1979) 6164.