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Quantum-well states in Cu/Fe/Cu(111) coupled to the bulk band through the barrier

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Abstract

The quantum-well state (QWS) has been observed on the surface of Cu/Fe/Cu(111). The confinement of the states on the top Cu layers is due to the minority spin barrier of the Fe underlayer. This QWS coexists with the Shockley surface state, which is observed on a clean Cu(111) surface. The resonant behavior of this QWS versus photon energy results from the vertical transition to the unoccupied bulk band, which is possibly due to the coupling between the overlayer Cu and the substrate Cu(111).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The quantum-well state (QWS) in metal surfaces has been studied for more than a decade [1] and shows very intriguing phenomena involving magnetic layered systems [2]. Understanding electronic properties resulting from quantization of electron motion by limiting the thickness of the layers is one of the interesting areas in nanoscience [3]. However, there are still a number of fundamental questions concerning this QWS. The intensity of photoelectrons from this QWS is shown to change as a function of photon energy. One explanation for this change in photoelectron intensity is the interference between the photoelectrons reflected from the surface and interface with a sharp change in potential. Ag/V(001) is an example of this interference effect [4]. In this case, the resonant behavior of this QWS depends on the kinetic energy of the photoelectrons and the thickness of the layers on top of the substrate that act as a barrier. The well width is determined by the thickness of the overlayer, while the substrate and the vacuum act as a potential barrier. This then becomes a simple quantum-well problem as encountered in quantum mechanics. Another explanation for the change in photoelectron intensity is the vertical transitions from the QWS to the continuum state of the of the bulk crystal comprising the overlayer. This process involves the conservation of the perpendicular wavevector during the transition. So the resonant behavior of the photoelectrons is predicted by assuming a continuous unoccupied state. Several systems show this resonant behavior near the vertical transition region [5]. The multipole plasmon effect is also producing enhancement of the photoyield [6]: however, this effect is considered when the photon energy is less than the bulk plasmon energy.

Here we report a very interesting case of a QWS for the limiting case of a thin Cu overlayer on top of a thin Fe barrier. When the overlayer thickness is small and does not develop the bulk band, there can be a quantized state. This state depends only on the thickness of the overlayer and the kinetic energy of the states since the barrier has been fixed by the substrate and vacuum. Even though the quantized unoccupied state due to the overlayer exists, if the photon energy of the probe is greater than 10 eV, it is not possible to fit the excitation between the quantized occupied and unoccupied states. Therefore, this type of resonant behavior is not observed at higher photon energies. When it comes to the bulk bands, we can see the resonance due to the direct interband transition observed in photoemission. This direct interband transition can be easily distinguished from the quantum-well state due to the change in its resonant behavior. The position of this direct transition state in the energy distribution curve is dependent on the photon energy since the resonant condition is different for different initial states. If the thickness of the Fe barrier is not large, then the Cu overlayer on top of the barrier Fe can be coupled to the bulk Cu(111) substrate. In this case, the direct transition from the QWS to the continuous bulk band could be possible.

2. Experimental details

The experiments were conducted in a ultrahigh vacuum (UHV) chamber, where photoemission spectroscopy(PES), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) can be performed. All the measurements were performed at room temperature and at a base pressure of less than 1.0×10^{-10} Torr. The photoemission spectroscopy has been done at Pohang Accelerator Laboratory (PAL) on the 2B1 bending magnet beam line. The sample was a single crystal of Cu(111), with two degrees off along the $(1\bar{1}0)$ axis. The substrate Cu(111) was prepared by repeated Ar sputtering followed by annealing at 800 °C. The crystalline order and the contaminants on the substrate were checked by low energy electron diffraction and Auger electron spectroscopy. The Fe metal was deposited by e-beam bombardment of 2.0 mm high purity Fe wire (99.99%). The Fe deposition was carried out at room temperature, and the pressure during deposition was below 2.5×10^{-10} Torr. The Fe thickness was monitored with a quartz-crystal-based film-thickness monitor, which was calibrated with the aid of AES and core-level PES. One way to form a uniform capping layer of Cu or Ag on a magnetic overlayer of Cu and Ag is simply to anneal it. It has already been proven that surface segregation of low surface-energy materials such as Cu [7] and Ag is quite severe, especially at an elevated temperature. For Fe/Ag and Fe/Cu systems, annealing results in the formation of a uniform overlayer. Since the intensity of the QWS is also related to the uniformity of the overlayer, it is quite convenient to form a uniform layer by annealing instead of further deposition of substrate materials. We annealed this system at 300 °C to form a uniform Cu capping layer on it. The thickness of the Cu capping layer is also dependent on the temperature and annealing time. The way we control the thickness of the segregated Cu layer is as follows. First we monitor the ratio between the 2p core-level intensities of Cu and Fe upon deposition of Fe on Cu(111). Second, starting with thick layers of Fe (say, 8 ML), when we anneal this sample at 350 °C, the ratio saturates at 1.3 which is comparable to 3.3 ML. It takes about 30 min and the amount of segregation is proportional to the annealing time before it reaches equilibrium. If we deposit more Cu on this saturated surface, this ratio increases again to the value before the anneal but this ratio reduces to the previous value when we anneal it at the same temperature. Below this equilibrium thickness limit, the thickness can be controlled by the annealing time, maintaining the temperature, which will be reported separately [8]. It has also been suggested that Fe/Cu(111) is thermally stable up to a certain critical temperature [9] so that we have to anneal at a higher temperature than this critical temperature. In Fe/Cu(110), this critical temperature is known to be around 220 °C [10].

3. Results and discussion

We have checked the possibility of the QWS itself of the Cu/Fe/Cu(111) system. In the case of Co, contrary to the (100) and (110) surfaces of Cu, the Cu overlayers on Co/Cu(111) do not show a QWS [11]. The growth of Fe on top of Cu(111) has been studied previously [12]. It has been probed by STM and several other techniques and it was found that for thicknesses up to two and a half monolayers, an fcc structure with twinning [13] is maintained. The bcc phase with ridge structure is seen for thicknesses greater than three monolayers, which manifests the (110) surface of bcc Fe. Magnetism for three or more layers of Fe on Cu(111) exhibits a ferromagnetic order with the magnetization in the plane [14]. If we consider the Fe(110) overlayer on top of Cu(111) then, due to exchange splitting of the Σ band, there is a hybridization gap in the Fe band. Thus, electrons from the minority spin state in the Cu overlayer cannot move into this Fe layer within a particular binding energy range. Figure 1 shows the bulk band structure of Fe [15] along the Γ to N symmetry line, and also that of Cu [16] along the Γ to L. Although there might be a slight distortion of the overlayer structure of Cu on top of Fe/Cu(111), we could expect that, for binding energies from 0.6 to 2.3 eV, electrons in the minority spin state cannot move into the Fe barrier. It is also quite interesting that for binding energies between 3.5 and 4.8 eV the majority spin state electrons can be bound in the top Cu layers where, except quite near a binding energy of 3.5 eV, no appreciable sp-state electrons of Cu exist. This raises the possibility and energy range of the QWS in this system.

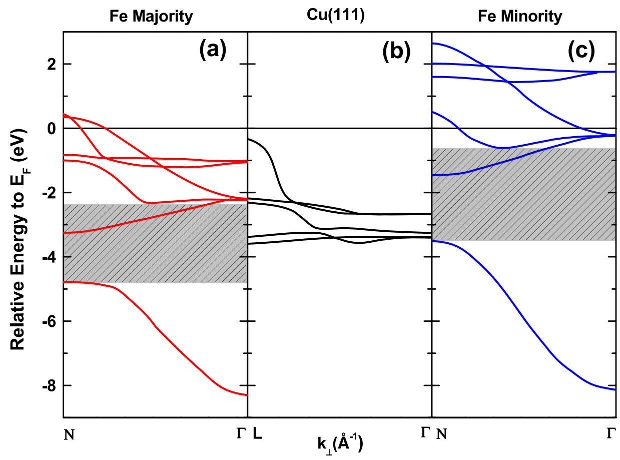

Figure 1. Calculated band structure for majority (a) and minority (c) spin states of the Fe(110) bulk band along the Σ symmetry line. At the center the calculated band structure for Cu(111) along the Λ symmetry (b) is represented. The shaded regions in (a) and (c) are the s–d hybridization gap for the electrons in Fe layers.

If a QWS exists in this system, the intensity of this QWS is also expected to change. The origin of this oscillation could be either interference between the surface and interface coherent photoelectrons as found in Ag/V(001) [4] and Pd(110) [17] or the vertical transition from QWS to the unoccupied bulk band, as in Cu/Co(100) [18]. If the overlayer Cu is too thin to generate the bulk band, then this second scenario will not be possible. However, if the ferromagnetic barrier (Fe in our study) in this system is thin enough to allow the coupling between the capping Cu layer and the substrate Cu, the characteristics of the QWS of capping layers will be dependent

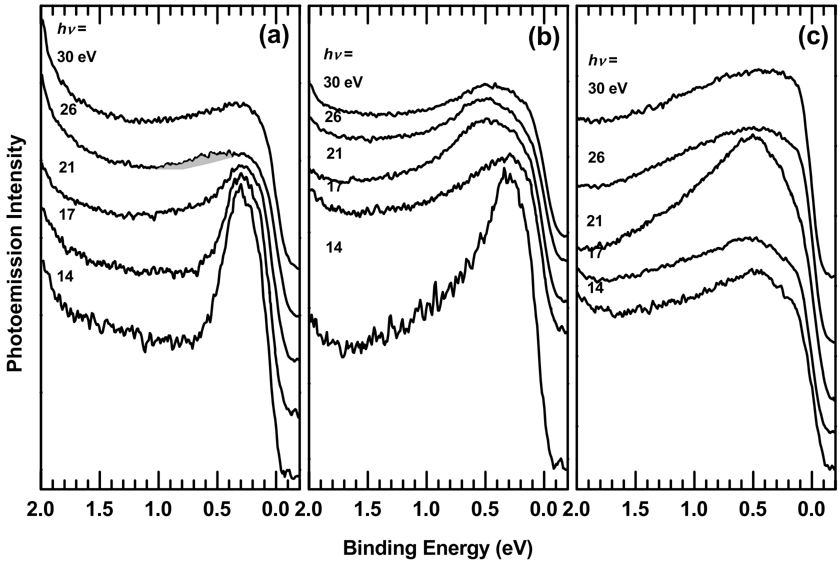

Figure 2. Normal-emission photoelectron spectra of (a) 0.5 ML of Fe on Cu(111), (b) 1.0 ML, (c) 3.0 ML at five different photon energies (14, 17, 21, 26 and 30 eV).

on the substrate bulk band. Our concern in this report is the limiting case of the Cu capping layer, where the bulk band is not quite developed since the thickness of this capping layer is too thin.

We have shown the normal-emission photoelectron spectra at coverages of 0.5 ML, 1.0 ML and 3.0 ML Fe on top of Cu(111) in figure 2. As we deposited more Fe, the surface state evident at low photon energies (14–21 eV) disappeared and the 3d state of Fe at 0.5 eV appeared. This state is clearly shown in the coverage of 3 ML at a photon energy of 21 eV. At low coverage (0.5 ML), it is interesting to note that the states in the region of 0.5–0.9 eV (shaded areas) are quite clearly seen at a photon energy of 26 eV (not at 21 eV). Hybridization of the impurity with the Shockley surface band and the bulk band has been studied previously [19]. The d-band impurity electrons are hybridized mainly with the conduction bulk bands. Thus the Shockley surface state of Cu(111) is not much affected by the overlayer d-band of Fe. This shaded area can be the result of a step decoration where the polarization vector of the synchrotron light can be important in excitation of plasmons at the surface, with the existence of steps [20].

Figure 3(a) shows the normal-emission photoelectron spectra for 3 ML of Fe on top of a Cu(111) substrate as a function of photon energy. There is no remarkable structure near the Fermi level except, as has been mentioned, the Fe 3d peak approximately 0.5 eV below the Fermi energy. The L-gap surface state of the Cu(111) surface is not shown at this Fe coverage. Although the growth of Fe on top of the Cu(111) surface gets rougher due to the twinning effect and low interlayer mass transport, we do not see the bare substrate at this coverage at room temperature. Figure 3(b) shows the experimentally determined band of this 3 ML of Fe on Cu(111) along the Λ symmetry lines. As a guide, we have shown the previously reported Cu-band calculation (solid line). The state that deviates significantly from Cu near the center of this Λ corresponds to the Fe bulk band (dotted line) along the

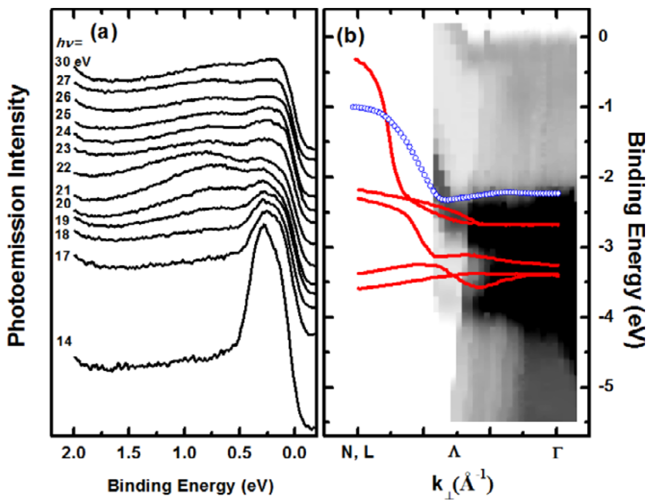

Figure 3. (a) Normal-emission photoelectron spectra for 3 ML of Fe on Cu(111) at different photon energies marked on the left of each spectra. (b) The bold line (red) represents the band structure of Cu(111), while the dotted line (blue) represents that of Fe(110) (references in text). The experimentally determined band structure along the Λ symmetry lines is shown in the 2D plot including higher binding energy states not shown in (a).

Σ symmetry line in the Fe(110) surface. The general trends exactly match those of the previous report on Fe(110) [21]. For photon energies between 13 and 14 eV (near the center of Σ) a clear binding energy shift of the majority spin state towards lower binding energy is observed.

The annealing condition to form a monolayer Cu on 3 ML Fe/Cu(111) is to anneal it at 300 °C for 5 min. We cannot rule out the possibility of the formation of the bare Cu(111) surface and clustering Fe islands after the anneal. However, this picture cannot account for the equilibrium thickness of segregation as we have mentioned in the experimental section. Instead of simple surface diffusion, there should be a bulk diffusion

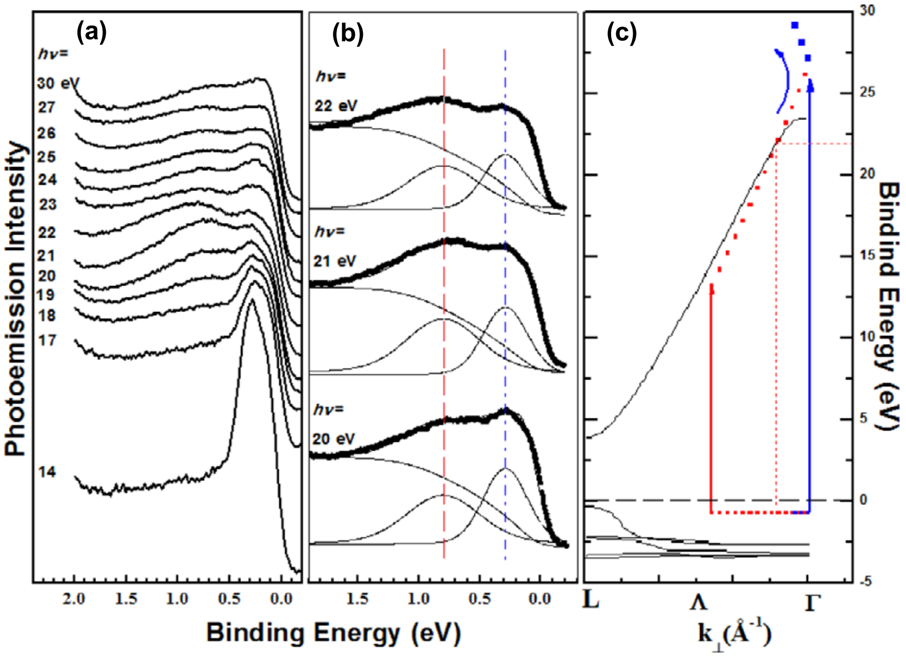

Figure 4. (a) Normal-emission photoelectron spectra for 3 ML of Fe on Cu(111) near the Fermi level, followed by annealing at 300 °C. (b) Detailed fitting of the spectra in (a) for three different photon energies. (c) Cu bulk band structure showing the direct bulk band transition starting at 0.78 eV from the Fermi level.

of Fe and Cu for the segregation of Cu. The change in the valence band as a result of annealing is shown in figure 4(a). Two major features can be seen. One is the recovery of the surface state observed at 0.3 eV below the Fermi energy. This is clearly shown at a photon energy of 14 eV. The cross section of this Shockley surface state is known to be large near the L gap [22] and smallest near the Γ gap. This is quite true even though we are away from the L gap. As the photon energy approaches 14 eV, its intensity is greatest since it is nearest to the L gap. The second feature is a state approximately 0.8 eV below the Fermi energy. This state has been greatly enhanced at a photon energy of 22 eV. The dispersion-like shift is mainly due to the variation of the intensity of this surface state. We have decomposed the peak into two regions so that their binding energy remains the same versus photon energy. The result of band mapping along the Λ symmetry line is shown in figure 4(c). This clearly shows the 0.78 eV state at certain k-perpendicular values corresponding to the different photon energies. The s–p free-electron-like state, 3 eV above the Fermi level at the L gap, is responsible for the transition of this state shown at a binding energy of 0.78 eV. We have shown with an arrow the direct interband transition from this 0.78 eV state to the unoccupied state, together with the photon energy involved. The line represents the bulk band while the dot is the position of the direct band transition at the relevant photon energies. The crossover of this direct band transition with the bulk band occurs at a photon energy of 22.4 eV, which exactly matches our experimental data shown in figure 4(a). This confirms that the intensity oscillation in our Cu/Fe/Cu(111) is quite the same as in the case of Cu/Co/Cu(100). This is also an indication of the formation of Cu capping layers upon annealing.

It is interesting to note that the Cu overlayer, which is aimed to be a monolayer in our study, shows a resonance at a photon energy corresponding to the bulk band crossing position. This top Cu layer is separated by 3 ML of Fe from the substrate Cu(111). This separation is sufficiently large that minority electrons at the Cu overlayer are confined at the top and form a quantized state. However, it is sufficiently small that the separated overlayer of Cu is influenced by the substrate Cu and maintains the surface state, which is clearly shown at the L gap. The surface state and the QWS have been observed to be similar to the Ag/Au(111) system [1]. However, in our case, one atomic layer cannot develop a band similar to bulk bands. Although the top Cu layer is coupled to the substrate via the Fe interlayer with a different lattice parameter and electrons, the position of the surface state does not change. This can be a characteristic of the Shockley surface state since, with a substantial potential across the barrier, the local bond can be maintained if the barrier is thin. This is an example of the Fano anomaly. When a discrete state is coupled to the continuum bulk substrate, it shows the resonant behavior. We have resolved the surface state and the QWS. Following the previously reported intensity plot of this Shockley surface state [22], we have checked the intensity variation of this QWS. A small bump was observed near 17 eV, which clearly shows the Fano characteristics.

4. Conclusion

In conclusion, we have shown the existence of the QWS in Cu/Fe/Cu(111). Surface electrons at the overlayer Cu can be coupled to the bulk substrate Cu when the Fe barrier is thin. As a result of this coupling, even though the overlayer is not thick enough to form a bulk band, it can be excited to the unoccupied bulk band to show a resonant behavior.

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