Angle-resolved photoemission from atomic-layer-resolved quantum well states in Ag/Fe(100)

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Abstract

Angle-resolved photoemission from thin films of Ag on Fe(100) grown with a low temperature deposition and annealing technique shows clear quantum well peaks for coverages up to 12 monolayers. Pairs of peaks are sometimes observed in the spectra; atomic layer resolution is demonstrated and used to explain these pairs without invoking spin splitting. The peaks are observed only within an energy window defined by the minority spin hybridization gap within the Fe substrate. Large intensity variations of the quantum well states with photon energy are observed.

Keywords: Quantum wells; Photoelectron spectroscopy

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1. Introduction

Quantum well states have been observed in a number of systems including films of alkali metals [1], noble metals [2,3], etc., on a variety of substrates. Quantum well states involving magnetic materials have attracted considerable interest since the magnetic coupling between two magnetic layers separated by a non-magnetic interlayer can be related to quantum well states in the interlayer [4]. The basic physics of such spin-dependent coupling effects can be extracted from studies of nonmagnetic overlayers on magnetic substrates. The system of Ag on Fe is of special interest for a number of reasons, including the close lattice match in the (100) direction (mismatch is only 0.7%), the difference in lattice symmetry (fcc vs. bcc), and the simple electronic structure of Ag. Previous photoemission [5,6] and inverse photoemission [7] work confirmed quantum well states for ultra thin layers of Ag on Fe(100) but also raised a question. Namely, the quantum well states found so far are of minority spin character. No pronounced majority spin quantum well states are found in the system. In this work, we will focus on the atomic-layer-resolved evolution of quantum well states to larger film thicknesses. Employing a low temperature growth technique, we have been able to prepare very smooth films, which mostly exhibit just two distinct thicknesses differing by an atomic layer. Quantum well peaks derived from these discrete thicknesses are well resolved for a given film, and the peak evolutions have been followed for film...
thicknesses up to 12 monolayers (ML). The results reveal no spin-split peaks within this thickness range, and the quantum well peaks are observed only within an energy window defined by the minority spin hybridization gap within the Fe substrate. The quantum well peaks show substantial intensity variations as a function of photon energy and can become completely suppressed at certain energies. This observation reveals the importance of final state effects.

3. Results and discussion

Fig. 1 shows a small subset of our photoemission spectra for different Ag coverages ranging from 1.2 ML for the bottom spectrum to 11.5 ML for the top spectrum. The spectra reveal well-resolved quantum well peaks derived from different discrete layer thicknesses as indicated. The photon energy used is generally different for the different spectra in Fig. 1. As will be discussed below, the cross section of quantum well states depends strongly on the photon energy. The choices of photon energy shown in Fig. 1 are made to provide reasonable intensities of emission from the different contributions to the spectra. The relative intensities of the quantum well peaks are generally not a good indication of the relative coverages of the different discrete layer thicknesses.

2. Experimental

The photoemission experiments were carried out at the Synchrotron Radiation Center of the University of Wisconsin in Stoughton, Wisconsin, using the 4-m Normal Incidence Monochromator. Photoelectrons emitted in the surface normal direction were detected using an angle resolving hemispherical electron energy analyzer. The total instrumental resolution as determined from spectra of the Fermi level of the sample was between 30 and 50 meV. The substrate was a selected Fe(100) whisker. Sample preparation involved numerous Ar –ion sputtering cycles with beam energies between 1.5 and 0.5 kV and with the sample temperature starting at room temperature and reaching about 550°C at the end of the sputtering cycles. After each sputtering cycle the sample was annealed to about 550°C. An intense but very contamination sensitive surface state at the Fermi level was observed [8]. Ag was deposited onto the sample at 100 K from an effusion cell. A growth rate of about 0.5 ML/min was measured with a quartz microbalance, and was verified by an absolute thickness calibration obtained from counting the discrete quantum well peaks. After film deposition a featureless photoemission spectrum was obtained for the thicker layers, which evolved into pronounced and sharp quantum well peaks upon annealing for 90 s at about 300°C. All spectra shown in this work were taken at a sample temperature of 100 K. Adding Ag to pre-grown layers was done by depositing with the substrate at 100 K and annealing the layer as discussed above. This procedure can be repeated several times, but will lead ultimately to rough layers, which can only be recovered by starting over with a freshly prepared Fe surface.

![Fig. 1. Photoemission spectra from Ag films on Fe(100). The Ag coverage and photon energy used are shown to the right of each spectrum. The discrete layer thickness for each quantum well peak is labeled. Vertical lines indicate quantum well peaks derived from the same discrete layer thickness.](image-url)
A careful inspection of the original set of spectra involving a much finer coverage increment and a large number of photon energies allows us to follow the quantum well peaks for increasing discrete layer thicknesses. A quantum well peak with a given quantum number should disperse upward in energy for increasing layer thicknesses until it passes through the Fermi level and becomes invisible. As seen in Fig. 1, there is only one quantum well peak for a layer thickness of 1, 2, or 3 ML, and it shows the expected upward dispersion with film thickness. We never observed a peak that corresponds to a thickness of 4 ML, in agreement with the calculations by Crampin et al. [7] and Smith et al. [9]; this peak is actually located just above the Fermi level. At 5 ML, a new quantum well peak with a different quantum number moves into the well region from higher binding energies. This peak also shows an upward dispersion for increasing discrete layer thicknesses, and eventually moves beyond the Fermi level and becomes invisible at 10 ML. Similarly, an additional quantum well peak moves into the well region at 8 ML and 11 ML, respectively. In all, we have observed four quantum well peaks with different quantum numbers, and their energies as a function of discrete layer thickness are followed up to 12 ML. Most of the spectra in Fig. 1 show the presence of just two neighboring discrete layer thicknesses. An exception is the 9.2-ML film, which shows the simultaneous presence of 8, 9, and 10-ML discrete layer thicknesses in the system.

One interesting observation is that the top five spectra in Fig. 1 show apparent pairing of peaks. Without a detailed knowledge of the layer thickness dependence of the peak positions and the presence of more than one thickness in a film as discussed above, one might mistakenly assume this apparent pairing as an indication of spin splitting. Calculations have indicated that the majority and minority spin states are separated in energy by an amount similar to the discrete layer shift [7]. To prove that the observed pairing of peaks is not due to spin splitting, one can add a small amount of Ag onto a given film and watch the growth of one peak at the expense of the other within a pair. Fig. 2 illustrates this test. Here, all spectra are taken with the same photon energy of 13 eV. The bottom trace shows the spectrum from a film of 8.2 ML. The two quantum well peaks associated with the 8-ML thickness are very prominent at binding energies of 1.72 and 0.39 eV, while the 9-ML quantum well peaks at 1.38 and 0.15 eV are much weaker, but clearly visible. The next trace is obtained by adding 0.25 ML of Ag onto the sample for a total Ag coverage of 8.45 ML. The added Ag has caused the 8-ML peaks to diminish and the 9-ML peaks to grow. This same trend is continued after the addition of another 0.4 ML of Ag for a total Ag coverage of 8.85 ML, as seen in the third trace. Finally, the top trace shows the spectrum for a 9.2-ML total coverage. Here, one sees mainly peaks derived from 9- and 10-ML thicknesses, but a few percent of the surface is still covered with just 8 ML of Ag as indicated by a very small 8-ML peak. This result indicates that the residual roughness of our films is quite small. Utilizing the strong photon energy dependence of the cross section from different quantum well peaks (see below), one can detect the presence of ~1% of a given layer thickness.

Thus, no evidence is found for two sets of spin split peaks. This is in agreement with the observation by Carbone et al. [6] using spin polarized photoelectron spectroscopy that only minority spin peaks are
present in the spectra for films up to 3 ML thick. Our observed peak positions are also in good agreement with the calculation of Crampin et al. [7] assuming that the observed peaks are of minority spin character for the entire thickness range studied here. Returning to Fig. 1, it is clear that the quantum well peaks only appear in a region between about 2 eV binding energy and the Fermi level, even though the Ag sp band extends down to about 4 eV binding energy before it hybridizes with the Ag d bands. This gives an important hint on the coupling between the Ag and the Fe states. The threshold binding energy of 2 eV for the Ag quantum well states is very close to the maximum of the $\Delta_1$ minority band in Fe [10], which represents the lower edge of the minority hybridization gap in Fe. Thus, quantum well peaks are observed only within the minority hybridization gap of Fe. The absence of quantum well peaks beyond this gap (at binding energies larger than 2 eV) suggests that the coupling between the sp band states of Ag and Fe is quite strong, even though the two crystal structures are different (fcc vs bcc). This strong coupling leads to a non-confining interface potential. Additional information about the interface coupling can be deduced from the measured widths of the quantum well peaks [11].

Fig. 3 shows a set of spectra taken in the photon energy range of 12–20 eV from a sample with a Ag coverage of 6.6 ML. The results illustrate the strong dependence of the cross section of the quantum well states on photon energy and quantum number. For a bulk Ag(100) single crystal, one would expect to see a strong direct transition peak moving through as the photon energy is varied within this range. The 6.6-ML film does not show this direct transition peak, nor is it expected for this small layer thickness. Such a direct-transition peak is observed, however, at larger film thicknesses. Some very weak features can be seen in Fig. 3 at binding energies larger than 2 eV, which can be attributed to quantum well resonances. The main action in Fig. 3 is the strong modulation of the quantum well peak intensities. There are energies where the spectra are dominated by the 7-ML peak while for other photon energies this peak is completely suppressed, leaving the 6-ML peak as the only quantum well peak in the spectra. This behavior is summarized in the inset, where the intensities of the 6, 7, 8, and 9-ML peaks are plotted vs the final state energy of the peak. All four curves show a pronounced maximum followed by a zero-intensity minimum and a secondary maximum for increasing final state energy. These extrema are not found in identical positions, but move with layer thickness and quantum number. Also these peaks do not trivially coincide with the position of the direct transition peak of the bulk band structure, but deviate in energy by as much as about 1.5–2 eV. The observed intensity modulation is somewhat similar to that reported for Ag quantum wells prepared on Ni(111) [12], and a proper understanding of this observation must take into account of the transition matrix element involving both the initial and final states [13].
4. Conclusions

We have demonstrated atomic layer resolution of quantum well states in thin films of Ag on Fe(100) in the thickness range from 1 to 12 ML. By using submonolayer increments of deposition quantum well peaks from different discrete layer thicknesses can be identified. The apparent pairing of peaks in the spectra is caused by the fact that most of the films exhibit just two discrete layer thicknesses differing by an atomic layer. The roughness of the film is small due to the use of a low temperature growth technique. No evidence is found for two sets of spin–split peaks. The results are consistent with quantum confinement of the minority spin electrons in Ag within the minority hybridization gap in Fe. Outside this gap (at binding energies larger than 2 eV), quantum well peaks are not observed, suggesting a strong coupling between the Ag $\Delta_1$ band and the Fe $\Delta_1$ band in this energy region, even though Ag and Fe have different crystal structures. A strong photon energy dependence of the emission intensity of individual quantum well peaks is observed, with minimum intensities approaching zero. This is an indication of strong energy dependence of the transition matrix element. The intensity modulation can be exploited for emphasizing or deemphasizing contributions from different discrete layer thicknesses, thus permitting the detection of very small coverages of discrete thicknesses.

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References