



Quantum well photoemission from atomically uniform Ag films: determination of electronic band structure and quasi-particle lifetime in Ag(100)

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Abstract

Photoemission from atomically uniform layers of Ag on a Fe(100) substrate is employed for the determination of the bulk electronic band structure of Ag. The high degree of control of the layer thickness allows the interferometric measurement of the electron momentum normal to the sample surface. This leads to an unprecedented precision in the electronic band structure determined from the experiment. The high quality of the layers also allows the discussion of the line shape of the quantum well peaks for the first time and gives access to the intrinsic and extrinsic broadening parameters of the line shape. © 2000 Published by Elsevier Science B.V.

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1. Introduction

Photoemission is the traditional experimental method for the determination of the electronic valence band structure of materials. Despite its indisputable success, the method has two intrinsic problems that limit the information gained in the experiment. First, the precision in peak position for three-dimensional samples, such as metal or semiconductor single crystals, is limited due to rather wide photoemission lines shapes. These wide line shapes are directly related to the three-dimensional nature of the electronic states involved. Second, the determina-

tion of the crystal momentum is hampered due to an unknown potential step at the sample surface that changes the electron momentum in the direction normal to the sample surface. Numerous approaches for the solution of the latter problem have been tried (compare Chap. 7 of Ref. [1]). In general, the first problem can only be circumvented by a detailed theoretical understanding of the photoemission process, meaning a calculation of the electronic wave function itself. However, a simple solution of both problems can be found by a controlled engineering of the sample, as will be demonstrated in this paper.

The reduction of the sample dimension in the photoelectron spectroscopy experiment has been proposed by Loly and Pendry [2] as a feasible method for band structure determination with ultimate accuracy. The authors argue that the reduced symmetry

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of the two-dimensional problem leads to a vanishing group velocity of the electron wave normal to the sample plane. Looking at the kinematics of the photoemission process, it is exactly this group velocity that connects the final state lifetime to the line width of the photoemission peak [3,4] and is responsible for the wide line shape in the spectra of a generic three-dimensional sample. (The initial state lifetime is, in general, at least one order of magnitude larger than the final state lifetime and thus, the line width is dominated by the final state lifetime.) This large line width of the peak hampers the exact determination of the position of the photoemission peak in the spectrum. In addition to the line width problem, the line shape is often asymmetric due to a contribution from surface photoemission to the spectrum. In case the initial state is dispersionless, such as a surface state (compare, e.g. Ref. [5]) or in special regions of the bulk electronic structure [6], the line width of the photoemission peak is only determined by the lifetime of the initial state involved in the photoemission process. This simplification has allowed detailed studies of surface states in many materials. The specific properties of the two-dimensional electron system allowed interesting experiments with relatively easy data acquisition methods. In case the thickness of a film is less than the coherence length of the electronic state involved in the photoemission process and the electrons of the film material are confined to the film, the symmetry argument for the group velocity of the electron initial state from the surface state also holds for the thin film state and one expects very narrow photoemission features that are only influenced by the initial state lifetime and possibly extrinsic contributions from the sample itself. In this way, one can study the bulk electronic structure without the influence of the final state lifetime.

The confinement of the electrons to the thin film is mandatory for the vanishing group velocity argument, but also adds one condition that is of equal importance to the experiment: the electron state can only be time-independent or stationary if the total phase accumulated on the round trip of the electron through the thin film is a multiple of 2π . This is the Bohr–Sommerfeld quantization rule or, in the language of the quantum wells and surface states, the “phase accumulation model” [7]. It means that nor-

mal to the surface, only specific electron wave vectors are “allowed” in the film:

$$2\mathbf{k}(E)Nt + \Phi(E) = m2\pi. \quad (1)$$

Here, $\mathbf{k}(E)$ is the electron wave vector as a function of energy, $\Phi(E)$ is the total phase shift experienced by the electron wave at both interfaces, and N is the number of monolayers (MLs) of thickness t in the film. In principle, $\Phi(E)$ is unknown, but it is not thickness-dependent, such that band structure and phase shift can be determined by analyzing data from films of different thickness using a parameterized band structure, as already demonstrated in the literature [8,9]. The precision of this process, however, critically depends on the accuracy of the film thickness determination. The relative error of the thickness calibration now determines the accuracy of the band dispersion determined from the experiment.

The expectation for photoemission spectra from electronic quantum wells is therefore the existence of narrow (in the absence of extrinsic broadening processes) quantum well peaks. The lifetime of the initial state, which is the lifetime of the valence band hole state, should be accessible from the peak width. In addition, the quantum well should show well-separated sets of peaks for each new ML grown in the film. A rough film should give rise to multiple sets of quantum well peaks in the valence band spectra. An example for these different sets of peaks can be found in Ref. [10], where quantum wells from thin Ag films on graphite have been studied. The nicely resolved peaks in the Ag films on graphite were also very narrow, but the film quality was not high enough yet to permit a detailed line shape analysis of individual peaks. The work to be discussed below employs atomically uniform films with precisely known thicknesses. The measured quantum well peak widths are dominated by intrinsic broadening mechanisms. An analysis of the peak positions and widths in terms of a Fabry–Perot model yields the band structure and quasiparticle lifetime.

2. Experimental details

All spectra were taken with a normal emission geometry using either the 4 m NIM monochromator

or the PGM undulator beam line at the Synchrotron Radiation Center of the University of Wisconsin in Stoughton, WI. Typical instrumental resolution was 30–50 meV, and the angular acceptance was about 1.5° . All spectra presented here were taken at a sample temperature of 100 K. The details of sample preparation are as follows: a selected Fe(100) whisker is cleaned with numerous sputtering and annealing cycles with Ar ion energies between 1.5 and 500 eV. The sputtering was done at sample temperatures between 100 and about 850 K. After each sputtering cycle, the sample was annealed at about 900 K. Sample quality was judged through the very contamination-sensitive Fe(100) surface state at the Fermi level [11]. Ag layers were then grown at 100 K from an effusion cell at a rate of about 0.5 ML/min. The as-grown sample did not show any quantum well

peaks in the valence band, but after annealing the sample to 300°C , sharp quantum well peaks appeared in the spectra. The preparation process is discussed in greater detail using Fig. 2 as an illustration in Section 3.

3. Results and discussion

It has been shown before [12,13] that the growth of Ag on Fe(100) whisker samples can be brought to exceptional perfection, such that the signal from consecutive MLs in the film is discernible directly from the raw data for a film thickness up to ~ 100 ML. These films are uniform on the scale of a single ML across the entire sample surface. Using films of

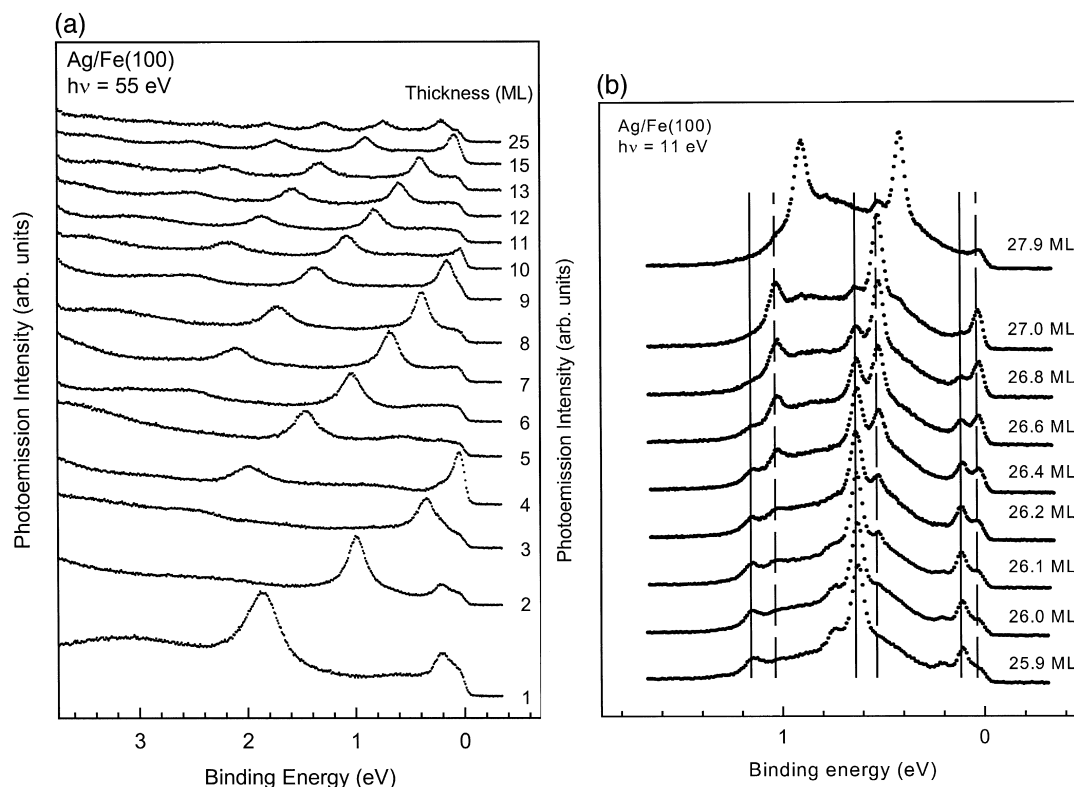


Fig. 1. (a) Photoemission spectra for Ag films on Fe(100) for layer thickness as indicated. All spectra are taken at a photon energy of 55 eV in normal emission geometry. Binding energies are referenced to the Fermi level. (b) Detailed investigation of the peak splitting and the film growth around a layer thickness of 27 ML. The deposition series shows the development of the peak intensities between a layer thickness of 25.9 ML and a thickness of 27.9 ML. The vertical lines mark the positions of quantum well peaks from areas of the film with 26 ML thickness (solid lines) and 27 ML thickness (dashed lines). Peaks characteristic of films 25 and 28 ML thick can also be seen in these spectra.

this quality, all the limitations of the analyses of metallic quantum well spectra should be removed. Fig. 1 shows an example for thinner layers where photoemission spectra from 1 to 25 ML taken at a photon energy of 55 eV are shown. The spectra clearly show a layer resolution in the quantum well peaks. The individual peaks seem to disperse with layer thickness towards the Fermi level. The peaks near the Fermi level seen in the two bottom traces are due to Fe bulk electronic states, which are present in spectra of the clean substrate as well. The layer-resolved growth is not only achieved for relatively thin layers, but can also be demonstrated for films as thick as ~ 100 ML.

The reason for this extraordinary growth perfection is presently unclear, but might be related to the good lattice match between Ag and Fe. Not only are differences in thickness of single atomic layers easily recognized from the raw data, the substrate quality can be increased to a level that allows the growth of films with exactly N MLs. Between 1 and 13 ML, every thickness could be prepared “exactly” as demonstrated in Fig. 1a. Any other film thickness tried could also be prepared with exact ML coverage, sometimes after some effort, but we found no hint for certain magic values for film thickness in this system as seemingly present in other systems [14]. A detailed illustration of our experimental sensitivity to different layer thicknesses that might be present in a film is shown in Fig. 1b. Valence band spectra taken at a photon energy of 11 eV are shown for film thicknesses ranging from 25.9 to 27.9 ML in sub-ML increments. In the beginning, 1/10 of a ML was used as the thickness increment to demonstrate the sensitivity of the spectral line shape. It is easily seen that the sample in Fig. 1b is not perfect, but has small areas of thickness variations of ± 1 ML. These are evidenced by small residual peaks around the main peaks at the film thickness of 26 and 27 ML. These peaks are just the next and the previous exact ML signatures. In general, our sensitivity for detecting the presence of a thickness can be better than 5%, and our best films are atomically uniform to within this detection limit.

Fig. 2 illustrates the sample preparation process. The center trace is from an as-grown film, which, as mentioned Section 2, does not show any sign of quantum well peaks in the valence band. Rather, the

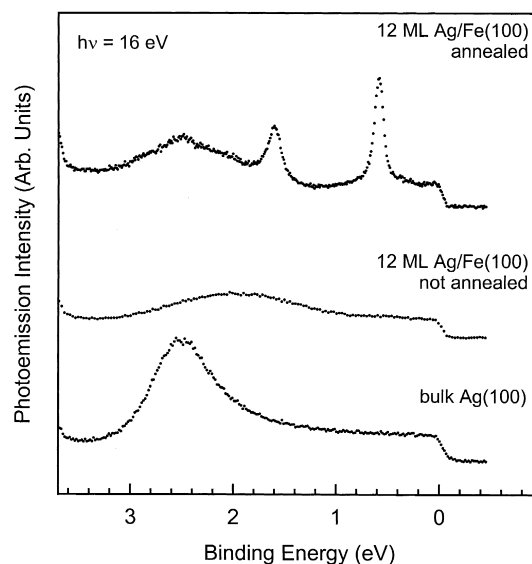


Fig. 2. Demonstration of the sample preparation process. All spectra are taken in normal emission geometry at a photon energy of 16 eV. The bottom trace shows the spectrum of a Ag(100) bulk single crystal. The broad feature at a binding energy of about 2.5 eV binding energy is the direct transition peak in the bulk band structure. The center trace is the spectrum from 12 ML of Ag grown on the Fe(100) substrate at a temperature of 100 K. The top trace shows the spectrum taken from the same sample after annealing to 300°C.

valence band spectra show a feature that looks like a direct transition in the Ag(100) band structure. This direct transition is wider than in the case of a bulk sample, which is shown in the bottom trace, and is also shifted in binding energy at identical experimental parameters. However, the as-grown film at the low temperatures is at least similar to bulk Ag with (100) orientation. The crystalline quality of the film seems very low as judged by the broad peak and its rather low intensity. The film does not show quantum well oscillations, but is not completely amorphous. Annealing the film for 90 s at 300°C changes the valence band spectrum drastically and the narrow and very pronounced quantum well peaks in the Ag *sp* band appear as shown in the top part of Fig. 2. This procedure of low-temperature deposition and subsequent annealing can be repeated and even sub-ML amounts of Ag can be added to previously grown films without deterioration of the film quality. Advantage has been taken of this fact to produce the data of most of the figures of this paper. This type of

growth process has been used before for the growth of metal films on semiconductors [15,16].

The ML resolution in the spectra demonstrated in Fig. 1 provides us with an intrinsic thickness calibration of the film. The film thickness determined directly from photoemission coincides with the reading from a quartz microbalance within 5%. The coincidence of the intrinsic thickness calibration with the calibration of the flux shows that the film is homogeneous and that in case there is a partial three-dimensional growth of the Ag film, this is negligible compared to the remainder of the film. By the subsequent deposition of sub-ML amounts of Ag on the Fe substrate and simple bookkeeping of the peak binding energies, a structure plot, i.e., a map of quantum well peak binding energies as a function of film thickness, was generated. This plot is shown in Fig. 3a. A band structure parameterized in the two-band model [17] in conjunction with the phase accumulation model is then used to fit the experimental data, and the phase shift and the band dispersion of

the initial state are obtained. The band structure parameter obtained from the fit are: $V = 3.033$, $E_{\text{VBM}} = -1.721$, $m_i = 0.759$, and $m_f = 0.890$. V is the band gap, E_{VBM} the energy of the valence band maximum, m_i the initial state effective mass and m_f the final state effective mass. The phase shift is approximated by a simple third-order polynomial [13]. The fitted model (for continuous variation of the layer thickness) is shown as solid curves, the experimental data are shown as dots. In order to show the deviation between model and experiment, the difference as a function of the film thickness is shown in Fig. 3b. In the beginning of the analysis, it was unclear at what minimum thickness the phase accumulation model would start to be valid, so the fit range had to be determined by recursion. Smith et al. [7] applied the phase accumulation model to relatively low coverages of Ag on Fe(100), but found that the model failed for the lowest coverages, including the clean surface of the substrate with its surface state. Likewise, in the current analysis, the peak positions of the 1, 2, and 3 ML quantum well peaks deviate considerably from the predictions of the model, which are made on the basis of the peaks associated with film thicknesses ranging from 5 to more than 50 ML. Furthermore, the inclusion of these data points changed the result of the fitted band structure and, to a larger extent, the fitted phase shift more than can be expected from their statistical weight, such that one has to conclude that the model is not valid at extremely low film thickness. The approximation of the edge effects of the well with a thickness-independent phase shift works already at a well thickness of 5 ML, i.e., the phase shift due to the reflection of the Ag electrons at the walls of the quantum well is not influenced by the well thickness from 5 ML onwards. This property of the phase shift is certainly related to the screening lengths in the metals involved in the structure.

The main purpose of this analysis is certainly not the reproduction of the quantum well peak positions, but the bulk electronic band structure of Ag in the (100) direction. This band dispersion is shown in Fig. 4, where the band dispersion of the initial state as determined from the experiment is shown together with computed band structures by Eckardt et al. [19] and Fuster et al. [20]. By checking the numerics of the fitting procedure and changing the amount of

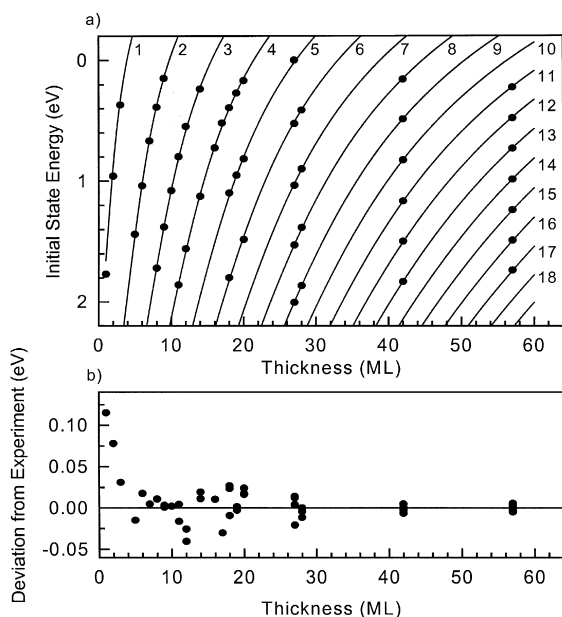


Fig. 3. (a) Structure plot of the Ag/Fe(100) quantum well. The experimental data are shown as dots while the simulation for a continuous film thickness variation is shown as solid curves. The curves are numbered by the convenient quantum numbers $N - m$. (b) Deviation of the model from the experimental data. The prediction varies only a few 10 meV from the actual quantum well peak positions for quantum wells thicker than 5 ML.

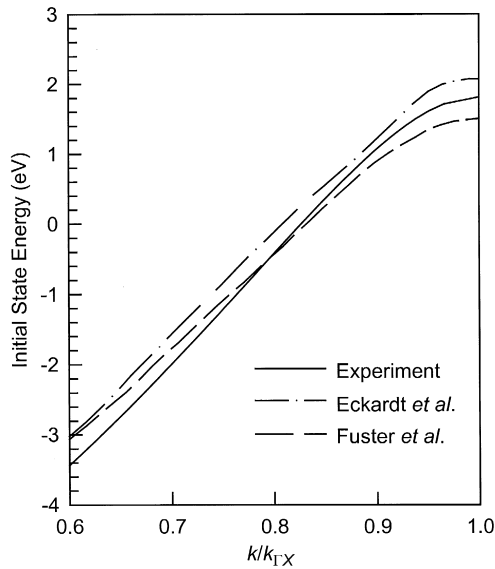


Fig. 4. Experimental results for the dispersion of the Ag *sp* band along the (100) direction. Quantum well data exist between a binding energy of 2 eV and the Fermi level; the curve beyond this range is determined by extrapolation in the framework of the two band model. Two theoretical results (Eckardt et al. [19] and Fuster et al. [20]) are shown for comparison.

data included in the fit of the structure plot, an absolute error of about 30 meV of the band position is expected. It is interesting to note that both band structure calculations for the *sp* band of this simple metal are at variance with our experimental band structure. It has to be remarked, however, that this method of band structure determination is only applicable in an energy range where the quantum well peaks exist, i.e., between a binding energy of 2 eV and the Fermi level only. In addition to the band dispersion, the limits of the energy range where the quantum well peaks are observed in the spectra give valuable information on the substrate electronic structure. The limits of the quantum well behavior in the film are determined by the band edges in the substrate electronic structure.

Reconsidering Fig. 1, it is obvious that the line shape, or rather the line width of a quantum well peak, depends on the film thickness as well as on the binding energy of the peak with respect to the Fermi level. The general trend is the thicker the layer and the closer the peak to the Fermi level, the narrower the peak. This observation has been investigated in

greater detail using Ag films between 12 and 119 ML thickness [13].

Previously, no line shape function for the quantum well peaks that included the electron lifetime as well as basic extrinsic broadening parameters was available. The problem, however, resembles the classical problem of a plane wave between two parallel mirrors. This is the Fabry–Pérot etalon and a basic example for multi-beam interference found in many introductory text books on optics. It can be shown that a modified Fabry–Pérot formula describes the spectral line shape:

$$I \propto \frac{1}{1 + \frac{4f^2}{\pi^2} \sin^2(kNt + \Phi/2)} A(E) + B(E), \quad (2)$$

with the finesse f given by:

$$f = \frac{\pi\sqrt{R} e^{-Nt/2\lambda}}{1 - R e^{-Nt/\lambda}}. \quad (3)$$

This is the Fabry–Pérot formula modified by an attenuation parameter $e^{-Nt/\lambda}$ to describe the finite lifetime of the electron wave in the quantum well, which is itself energy-dependent (λ is the mean free path). This is equivalent to a Fabry–Pérot etalon filled with an absorbing medium. $R = R(E)$ is an energy-dependent reflectivity of the interfaces forming the quantum well. $A(E)$ is the intensity of the quantum well peaks as a function of the energy (this depends on the optical matrix element). $B(E)$ is a smooth background function. The quantum well has a finite well depth and the reflectivity R is expected to change rapidly at the edge of the well. The band gap we are using for the generation of the quantum well states for Ag on Fe(100) is only the spin-dependent hybridization gap, the reflectivity of which is unknown in terms of magnitude and energy dependence.

The peaks in the line shape are observed for energies where the denominator in Eq. (2) reaches a minimum. This condition reproduces the phase accumulation model given by Eq. (1). Apart from this trivial requirement of consistency, the line shape formula also describes all of the spectra in the range from 12 to 119 ML with functions $\lambda = \lambda(E)$ and $R = R(E)$ that are independent of coverage. The spectra in Fig. 5 are fitted simultaneously with this

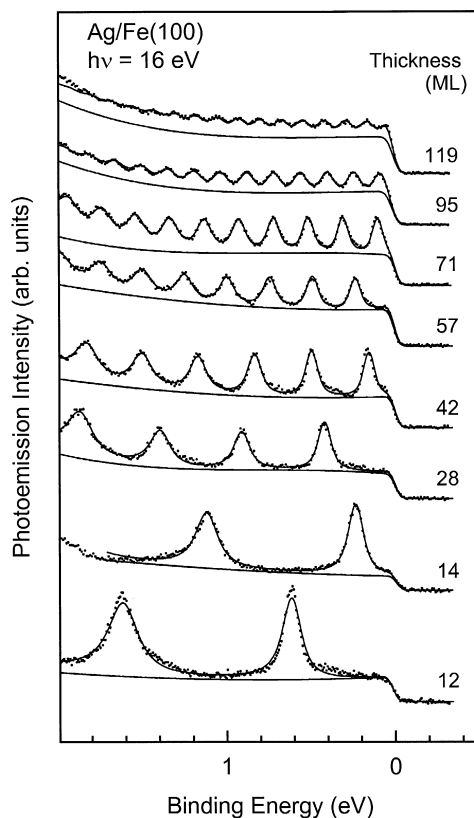


Fig. 5. Valence band spectra from Ag quantum wells of thickness as indicated. The spectra are fitted with the modified Fabry–Pérot formula. The fits are shown as solid curves.

formula, using identical band structure parameters (dispersion $k(E)$, attenuation length $\lambda(E)$, and reflectivity $R(E)$ of the well barriers). The function $\lambda(E)$ is related through the group velocity of the electrons to a carrier lifetime. The carrier lifetime can be regarded as the imaginary part of the electronic band structure. From a single spectrum, $\lambda(E)$ and $R(E)$ cannot be separated, but the simultaneous fit can solve the problem of parameter coupling through the difference in functional dependence. The reflectivity effect is independent from the sample thickness, while the finite carrier lifetime leads to an attenuation of the electron wave in the quantum well, which is thickness-dependent, and the two effects are separable. The result presented in greater detail elsewhere [13,18] leads to a lifetime width at the Fermi level of 25 meV, of which 14 meV can be attributed to phonon scattering. The remaining 11 meV are

assigned to residual defect scattering, since the Auger contribution to the hole lifetime in the metal should approach zero at the Fermi level in the Fermi liquid theory. The energy dependence of the temperature-independent term in the hole lifetime is parabolic and is in agreement with the expectation for the behavior of a Fermi liquid. The peaks in the spectra are broader than the lifetime widths as determined from the fits of the line shape to the spectra, since the lifetime only gives part of the intrinsic width of the peak. The width observed in the spectra includes additional contributions from the reflectivity and defect scattering. The reflectivity of the well barriers allows the calculation of a finesse of the Fabry–Pérot spectrometer “built” from the metallic quantum well. This figure of merit for the spectrometer is around 20, which is comparable to simple optical Fabry–Pérot spectrometers with metallic mirrors.

4. Summary

In conclusion, the growth of Ag on Fe(100) can be brought to such a precision and quality that, as proposed by Loly and Pendry [2] in 1983, the limits in accuracy of photoemission band structure determinations can really be removed by using thin film samples. The real, as well as the imaginary, part of the electronic band structure is easily accessible once the films are prepared with sufficient quality. In principle, the determination of the electronic structure of the well material is now reduced to an interferometric measurement of the electron wave vector, while the corresponding initial state energy (to the respective wave vector) is determined by the electron spectrometer. Momentum and energy measurement is thus split into two spectrometers. The film acts as a momentum spectrometer for the electron momentum normal to the film, while the electron energy analyzer is used to measure the electron momentum parallel to the surface as well as the kinetic energy of the electrons relative to the energy of the electrons emitted from the Fermi level of the sample. This realization of a precise band structure determination opens the grounds for more interesting experiments on the electronic structure of thin film samples and the bulk electronic structure of their constituents.

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