Breakup of Quasiparticles in Thin-Film Quantum Wells

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Quantum well states in thin films are commonly described in terms of a quasiparticle confined in a quantum box, but this single-particle picture can fail dramatically near a substrate band edge, as shown by this angle-resolved photoemission study. Atomically uniform Ag films are prepared on Ge(111) to facilitate accurate line shape and dispersion relation measurements. A quantum well peak is observed to split into two peaks near the Ge valence band edge. The unusual line shapes are shown to be due to many-body interactions and are quantitatively explained by a Green's function calculation.

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Electronic structure of metal films with thicknesses in the nanometer range is an area of intense scientific interest and technical importance [1,2]. Quantum confinement of electrons at such length scales can lead to a host of interesting and useful properties. A standard and highly successful model for thin-film quantum wells is to treat the electrons in the film as quasiparticles with their dynamic behavior governed by wave mechanics, or the Bohr-Sommerfeld quantization rule, and to decouple the substrate from the problem by embedding its detailed electronic structure in an effective reflectivity and phase shift for the quasiparticle at the interface. This decoupling and resulting simplification is crucial to the utility and success of the usual quantum well model [2]. Yet this approach fails dramatically in the present study of atomically uniform films of Ag on Ge(111), in which the measured dispersion relations of quantum well states show anomalies near substrate band edges that must be addressed explicitly in terms of many-body interactions.

For the system under investigation, valence electrons in the Ag with energies within the fundamental gap of Ge are fully confined. The resulting quantum well states disperse with in-plane momentum k_{\parallel} to form subbands [2-6]. The dispersion can bring a state out of the Ge gap, resulting in a partially confined resonance state with a larger linewidth. In our experiment, angle-resolved photoemission is employed to map the subband dispersion of a quantum well state as it crosses the edge of the Ge confinement gap. The results show that, in addition to the expected linewidth change, the peak splits into two with an appearance resembling a two-level anticrossing. This unusual line shape evolution precludes a single-particle explanation. Many-body interactions are important, as demonstrated by a Green's function calculation similar to the impurity and adsorbate models of Anderson and Newns [7,8]. The results establish that the coupling effect near a band edge must be treated at the wave-function level involving both the film and the substrate. Another useful outcome is a method to accurately extract the substrate band structure. The choice of Ag and Ge for the present study is motivated by several scientific and technical considerations: Ag is a simple metal; it has the lowest room-temperature resistivity of all metals; Ge is a well studied electronic substrate material; and Ag and Ge do not intermix. Despite a large lattice mismatch, Ag films of atomic uniformity can be prepared on Ge(111). This level of film perfection is critical for the present experiment, as a single-monolayer change in film thickness can lead to substantial changes in electronic structure.

The experiment was performed at the Synchrotron Radiation Center, University of Wisconsin-Madison on the PGM beam line using a Scienta SES-100 analyzer. The data presented below were all taken with a photon energy of 50 eV, and the in-plane dispersion was measured along the $\overline{\Gamma} \overline{K}$ direction of the Ag(111) films. The photoelectron spectra were recorded as two-dimensional images with the energy and the polar emission angle θ as two independent variables. Each image spans a range of $\Delta \theta = \sim 10^{\circ}$. The sample was rotated relative to the analyzer in steps of 5° to create a set of overlapping images, which were combined to create a wider angular span. A clean Ge(111)- $c(2 \times 8)$ surface was prepared by sputtering at a substrate temperature of 500 °C followed by annealing at 600 °C. Ag was evaporated from a tungsten crucible, heated by a feedback-controlled electron beam, onto the Ge substrate maintained at 100 K. The sample was annealed at 300 K after deposition and then cooled back to 100 K for the photoemission measurement. Additional Ag, if needed, was added by deposition at 100 K followed by annealing at 300 K. The resulting Ag films were oriented along (111) with the $\overline{\Gamma} \overline{K}$ direction parallel to the same in the substrate [9,10]. The absolute film thickness was determined by atomic-layer counting as for the Ag/Fe system [11].

Figure 1 shows gray-scale representations of the photoemission results for film thicknesses of 8, 8.6, and 9 monolayers (ML) of Ag. In each case, the intense peak located just below the Fermi level at E = 0 and covering a limited angular range centered about $\theta = 0$ corresponds to the Shockley surface state of bulk Ag(111) (labeled SS in the figure). It is fairly insensitive to the film thickness due to its short decay length away from the surface. The rest of the emission features are rather complex in detail, but exhibit, very roughly, overall parabolic dispersions. These are the quantum well peaks of interest, and are labeled by a quantum number n [2,9]. The films are sufficiently thick that direct emission from the Ge substrate is negligible. Looking closer, the circle in Fig. 1(b) indicates a band splitting in comparison with the corresponding regions in Figs. 1(a) and 1(c). In fact, the two bands within the circle represent a linear combination of the band in Fig. 1(a) and the band in Fig. 1(c). Here, a thickness change by 1 ML causes a noticeable shift of the band. The band splitting in Fig. 1(b) simply reflects the fact that the film consists of two thicknesses, 8 and 9 ML, and the same n = 2 band is present for the two different thicknesses simultaneously.

This atomic-layer resolution and, more importantly, atomic-layer uniformity at integer monolayer thicknesses, is better illustrated by the energy distribution curves shown in Fig. 2. In Fig. 2(a), the n = 2 quantum well peak is seen to move discretely from its 8 ML position to the 9 ML position. In Fig. 2(b), the n = 3quantum well peak behaves similarly. In each case, the 8 ML peak is absent in the 9 ML spectrum, and vice versa, thus establishing the atomic uniformity of the films at integer monolayer thicknesses. Figures 2(c) and 2(d) contain additional examples. However, the data in Fig. 1 show no evidence for such splitting at normal emission $\theta = 0$. The reason is that the states are quantum well resonances with broad linewidths that obscure the peak splitting. In this system, atomic-layer resolution is evident only within the Ge gap, and the gap region is accessible only for off-normal emission.

The three concave curves in each part of Fig. 1 represent the topmost projected bulk band edges of Ge based on a band structure calculation [12]. The highest point of all three curves is the valence band maximum of Ge. Above the top curve is the absolute gap of Ge, where





FIG. 1 (color). Angle-resolved photoemission data presented as gray-scale images as a function of energy and emission angle for (a) 8, (b) 8.6, and (c) 9 ML of Ag on Ge(111). The three concave curves represent projected bulk band edges in Ge. The label SS stands for the surface state of Ag(111), and the quantum numbers for the two top subbands are indicated.

FIG. 2 (color online). Energy distribution curves for various emission angles and film thicknesses as labeled. In each panel, the film thickness is incremented by 1 ML from the bottom curve to the top curve, and the vertical dotted lines indicate discrete peak evolution.

the quantum well peaks are sharp; below it the resonance peaks are much broader due to degenerate coupling to the substrate states. The roughly parabolic dispersions of the quantum well peaks show a break (or kink) as they cross the top band edge, in addition to a change in linewidth. A good example is the portion of the dispersion curve within the rectangular box in Fig. 1(a). Similar breaks are also present for the other two lower band edges, but, because the peaks are much broader, such breaks are not necessarily apparent.

To illustrate the crossover behavior near the band edge in detail, the data contained within the rectangular box in Fig. 1(a) are shown in a larger format in Fig. 3(a), and the corresponding energy distribution curves are shown in Fig. 3(c). The quantum well peak is seen to split into two peaks near the crossover point, and the appearance is very similar to the usual anticrossing in which two noninteracting energy levels crossing each other are allowed to interact or hybridize. However, in the present case it is a single state crossing over into a continuum, and therefore the anticrossinglike behavior may appear puzzling at first glance.

The results are explained as follows. Consider that a quantum well state ϕ moves, as a function of k_{\parallel} , through the edge of a continuum of substrate states φ . While the

physical situation is different, the mathematical problem is similar to the impurity and adsorbate models of Anderson [7] and Newns [8]. A straightforward derivation for the present case yields the retarded Green's function G:

$$G(E)^{-1} = E - E_q + i\delta_q - \int_{-\infty}^{E_0} \frac{|V|^2}{E - \varepsilon + i\delta_s} g(\varepsilon) d\varepsilon,$$
(1)

where E_q is the energy of the quantum well state without coupling, δ_s and δ_q are the lifetime broadenings of the substrate and the quantum well states, respectively, V is the coupling matrix element between ϕ and φ , and E_0 is the band edge. The density of substrate state $g(\varepsilon)$ near the band edge has the following one-dimensional form:

$$g(\varepsilon) = \frac{A}{\sqrt{E_0 - \varepsilon}} \Theta(E_0 - \varepsilon), \qquad (2)$$

where A is a constant and Θ is the unit step function. Assuming that the lifetime widths and the matrix element are constant within the limited range of interest, the integration can be carried out analytically to yield the spectral weight function

$$\rho(E) = -\frac{1}{\pi} \operatorname{Im}(G) = -\frac{1}{\pi} \operatorname{Im}\left(\frac{1}{E - E_q + i\delta_q - \pi A|V|^2 (E - E_0 + i\delta_s)^{-1/2}}\right).$$
(3)

Figure 3(b) is a fit to the data shown in Fig. 3(a), and the same fitting results are also indicated in Fig. 3(c). In the fit, we assume that the line shape function given by Eq. (3) rides on a linear background function. A surface state peak is added, and the total spectral function is multiplied by the Fermi-Dirac function. The quantities E_0 and E_q as a function of θ are assumed to be evenorder polynomials up to the fourth order. These dispersion functions deduced from the fit are shown as solid and dashed curves in Fig. 3(b), respectively. The fit to the photoemission data is very good over the whole range. Specifically, the peak splitting, the apparent anticrossing behavior, and the variation in peak width are all well reproduced by the calculation, and this is achieved with δ_s , δ_q , and V all treated as constants. The dispersion of E_0^{-1} as a function of k_{\parallel} derived from the fit is in close agreement with a band structure calculation [12], suggesting that the present analysis can be useful for an accurate determination of the band edge dispersion.

The apparent anticrossing behavior is a result of the functional form of the one-dimensional density of states. Equation (2) has a divergent, but integrable, singularity at the band edge. With lifetime broadening, the singularity resembles a skewed peak at E_0 . The net effect is very

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much like a discrete state at the band edge superimposed on a smooth varying continuum below the edge. This density-of-states peak at E_0 is directly responsible for the apparent two-level anticrossing behavior. If the calculation is redone with the density of states substituted by a form for two or three dimensions, for which there is no divergent singularity at the band edge, the results show no peak splitting. Thus, the apparent anticrossing behavior is specific to the one-dimensional case associated with the angle-resolved geometry of the experiment. This type of behavior is not normally expected in the treatment of bulk impurities or adsorbates as in previous many-body calculations.

The coupling between quantum well states and substrate continuum has been described in the past in terms of lifetime broadening and phase shift. These singleparticle or effective-medium descriptions, however, are not sufficient for a line shape analysis, and cannot explain the peak splitting even on a qualitative basis. Indeed, some previous experiments in related systems have reported subtle variations in quantum well peaks near substrate band edges [3,4], and the observed results are fairly similar to what we report here. The present work shows conclusively that this phenomenon is caused by a manybody effect, and the quantum well system represented by



FIG. 3 (color). (a) Same data from the rectangular box in Fig. 1(a) to show the line shape evolution in detail. (b) Calculated photoemission results from a fit to the data. The solid and dashed curves show the dispersion relations of the Ge band edge and the uncoupled quantum well state from the fit. (c) Energy distribution curves based on the data and the fit.

atomically uniform films provides an excellent platform for verifying the basic physics of many-body interactions.

In summary, the electronic structure of Ag films on Ge(111) is investigated with a focus on the coupling between the Ag valence electrons and the Ge substrate states. Ag states within the Ge fundamental gap form fully confined quantum well states, while Ag states outside the Ge gap form partially confined quantum well resonances. The crossover from full to partial confinement is marked by a change in linewidth and a peak splitting. The complicated dispersion curves and line shape evolution as measured by angle-resolved photoemission are well described by a Green's function calcu-

lation, thus establishing the many-body origin of the observed effects. The results clarify the basic physics of quantum wells represented by films supported on substrates. This work is made possible by the successful preparation of atomically uniform films of Ag on Ge, despite a large lattice mismatch, which by itself has significant implications in regard to thin-film growth. Another useful outcome of this work is a means for accurate determination of the substrate band edge dispersion.

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