Quantum Size Effects in Epitaxial ErAs on GaAs(001)

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The electronic structure of very thin epitaxial ErAs layers on GaAs(100) is studied with angle resolved photoelectron spectroscopy. Clear evidence is found for confinement induced quantization of states around the Fermi level. From the dispersive properties of the quantum well states effective masses are obtained, representing electron motion parallel to the surface layers and orthogonal to the layers. We find, for the first time, that effective masses along equivalent bulk directions (XW) are significantly different in the thin layers. Furthermore, the bottom of the highest occupied band shifts towards the Fermi level when going from very thin to thick ErAs layers. [S0031-9007(96)01835-2]

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The electronic properties of ultrathin layers are expected to deviate from those of the corresponding bulk materials as a result of the quasi-two-dimensional confinement. In the case of semiconductors this is well manifested via optical and transport properties of quantum well structures. Although applications involving structures based on thin metal layers are just as interesting, experimental information on such layers is scarce. One reason for this imbalance is the difficulty in making sufficiently perfect and stable metal layers. In recent years attention has been focused on heteroepitaxy between ErAs and GaAs. Because of the relatively small lattice mismatch (1.58%) two-dimensional ErAs layers can be grown on GaAs(100) up to a layer thickness of about 70 Å [1]. Furthermore, according to recent reports, it is also possible to grow good quality GaAs on ErAs after the insertion of one monolayer Mn [2]. This compound system is thus a good candidate for devices based on buried metal layers.

For any advanced applications detailed understanding of the electronic structure of the thin metal layer is crucial. The properties of such layers cannot in general be predicted from the properties of the bulk material. One example of this is the observation of a thickness dependent band gap in α-Sn layers on CdTe(110) [3]. In the case of ultrathin ErAs layers a semimetal to semiconductor transition is predicted [4].

To investigate the quantum size effects we have studied angle resolved photoelectron spectra from thin molecular-beam epitaxy-(MBE)-grown ErAs layers on GaAs(100). In this Letter we focus our attention on spectra probing the phase space around the X point in the Brillouin zone, where an electron pocket is predicted in the bulk band structure [5]. We find that the states forming this pocket do indeed exhibit clear quantization characteristics. While quantum size effects in photoelectron spectra have been reported previously for free-electron-like metal layers on metals and semiconductors [6–8], the present observations are, to our knowledge, the first ones on a heteroepitaxial compound system.

The experiments were carried out at the Swedish National Synchrotron Radiation Centre MAX-lab, where a dedicated MBE system is attached to a photoelectron spectrometer at the TGM beam line. One of the MBE effusion cells was filled with Er (99.95% purity). The substrates were 1×1 cm^2 GaAs wafers, In-glued to Mo holders. Prior to ErAs evaporation a buffer GaAs layer was grown until a good quality 2×4 reflection high-energy electron diffraction (RHEED) pattern was observed. The ErAs was grown with the substrate at 450 °C at a rate of $\sim$0.30 Å/s. The growth rate was determined by means of RHEED oscillations, which become visible after deposition of an amount of ErAs exceeding 3 ML (monolayers) [2], and decay very slowly with increasing layer thickness. The low decay rate is indicative of a very regular layer-by-layer growth, which is important for generating an overlayer with uniform thickness. As a rule the growth was terminated at peak RHEED intensity. All surfaces showed very sharp, low background 1×1 LEED patterns.

Photoelectrons were excited with synchrotron light incident at 45° in p polarization. The spectra were recorded using an angle resolving hemispherical analyzer with angular acceptance of $\pm 1°$. The combined monochromator-analyzer energy resolution was about 0.15 eV. Sets of spectra obtained from ErAs layers with different thicknesses are shown in Fig. 1. The spectra were recorded in the plane of light incidence, at polar angles in the [010] azimuth. They all focus on a feature just below the Fermi level, appearing in a range of emission angles where excitations along the W-X-W line [see inset in Fig. 1(a)] in the three-dimensional Brillouin zone are probed. The angular dependence shows directly that the structures represent crystal-momentum conserving interband excitations. The similarity in the angular dependence for the different overlayer thicknesses indicates that the underlying momentum selectivity derives from periodicity in the surface plane. A simple calculation within an empty lattice model indicates that excitations of states near the X point in this

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photon energy range involve [311]-type reciprocal lattice vectors. Thus, as the polar angle is varied in the plane of incidence, we essentially probe the dispersions along a WXW line parallel with the surface plane.

The data for the thinnest layer in Fig. 1 (20 Å) show a weakly dispersing peak, with a minimum at 0.25 eV below E_F. (E_F as indicated by the vertical dashed line in each spectrum was determined by photoemission from a Ta foil in contact with the sample.) As this energy minimum is reached around the 23° emission angle, the peak has its maximum amplitude. The same qualitative behavior is observed for the 10 Å layer (not shown), though the minimum energy is somewhat shallower, around 0.15 eV below E_F. With the thickness increased to 30 Å we find a peak that disperses to a deeper minimum energy, 0.35 eV below E_F. After adding another 10 Å we find a qualitatively different set of spectra. With a 40 Å thick overlayer two clear peaks are observed around the 23° emission angle. The lower of the two peaks disperses to about the same minimum energy as that seen in the 30 Å spectrum, while the upper one is located 0.20 eV closer to E_F. The spectra from a 50 Å thick layer (not shown) are qualitatively similar to those with 40 Å, but the different components are not so well resolved. For "thick" overlayers (up to 1000 Å), the spectrum consists of one structureless, weakly dispersing peak. In Fig. 1 this is exemplified by the data from a 135 Å thick layer. One noteworthy observation is that the width of the 30 and 40 Å spectra is more than 0.1 eV larger than that of the thick layers; i.e., the bottom of the occupied band is deeper.

The thickness dependence observed in Fig. 1 is caused by electron confinement along the surface normal. Assuming a "normal" pinning situation in GaAs at the interface, the electrons at E_F experience a potential step of around 0.7 eV in the direction towards the substrate, and an image potential barrier towards vacuum. The data show that for overlayer thicknesses below 30 Å only one quantum well state is supported by this potential. Just as expected, the energy of this state is gradually lowered with increasing width of the potential well. At a thickness of about 40 Å a second occupied state is observed.

The properties of quantum well states depend on the shape of the potential well and effective mass parameters. From the dispersions in Fig. 1 we can in principle directly estimate the effective electron mass along the XW line parallel to the surface plane. Unfortunately, detailed determination of the peak positions in Fig. 1 is somewhat uncertain due to interfering "density-of-states" structures. These structures are quite pronounced in the present case due to the very rapid dispersions and the relatively wide angular acceptance in the analyzer. They are stationary in energy, and appear at turning points of the dispersive peaks [9]. In Fig. 1 we find clear examples of this effect in the 30 and 40 Å spectra, where shoulderlike structures are observed at the turning point energy of the lower dispersing peak even for emission angles well off the turning point angle. Another, equally disturbing feature is the "residual" peak present just below E_F in spectra recorded in the angular ranges 17°–19° and 25°–27°. We associate this peak with an interband excitation involving a low energy band that is actually located above E_F. Because of lifetime broadening this state has a spectral weight extending below E_F, and gives rise to the observed peak. An analogous situation has been discussed in connection with inverse photoemission [10]. These effects appear to be least serious in the data set for the 30 Å layer. As indicated in Fig. 1(b), the angular range of the main peak is around ±3°, over

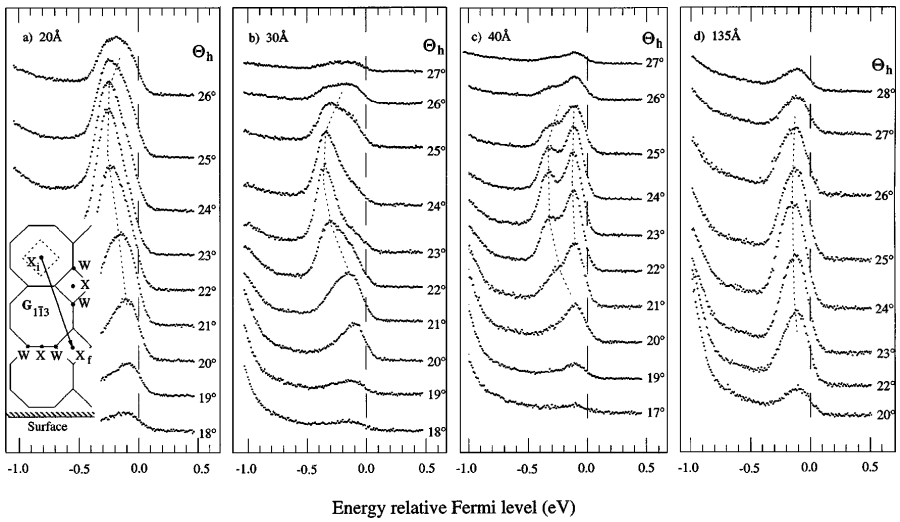

FIG. 1. Photoelectron spectra from (a) 20, (b) 30, (c) 40, and (d) 135 Å thick ErAs layers on GaAs(001). All spectra were recorded in the plane of incidence at different polar angles of emission (Θ_h). The inset in (a) shows the section through the bulk Brillouin zone defined by the plane of detection. The arrow joining the initial and final state k points (X_i and X_f, respectively) represents the acting reciprocal lattice vector $\mathbf{G}_{1\bar{1}3}$. The estimated peak positions are marked with thin dashed lines.

which the peak disperses 0.35 eV. From these numbers we obtain an average effective electron mass along the XW azimuth in the plane of the layer $m^*_{XW\|} = 0.2m_0$ (m_0 = free electron mass). This result is in fairly good agreement with the value of $0.17m_0$ obtained from low-density approximation (LDA) band structure calculations on ErAs [11] and also with that from measurements of Shubnikov–de Haas (SdH) oscillations in the XWU plane [i.e., orthogonal to the (001) direction] in bulk $Er_xSc_{1-x}As$ [12].

Our interpretation of the photoexcitation process indicated above implies that we can probe the dispersion from X towards Γ by an angular scan in the direction perpendicular to the ΓXW plane while keeping the in-plane angle at a fixed value of 23°. (To maintain a constant momentum component equal to ΓX it is in principle necessary to change the photon energy as well. However, for the small angles off the ΓXW plane studied here these corrections are negligible.) A set of spectra showing this angular dependence for the 30 Å layer is shown in Fig. 2. Compared with the spectra in Fig. 1(b) we see that the dispersion is significantly slower (the angular range is around 6°). As a consequence of this, the density-of-states features are much less pronounced. From the dispersion we obtain for the effective mass in this direction a value of $1.1m_0$. According to the cyclotron mass experiments and band calculations mentioned above the effective electron mass corresponding to motion in the ΓKX plane is about an order of magnitude larger than the XWU plane. The high anisotropy observed in the present work is thus in qualitative agreement with the Fermi surface data.

The energy quantization perpendicular to the layers should of course be reflected in photoemission via a nondispersive behavior along this direction. To test this we have recorded spectra at different photon energies while keeping a constant in-plane momentum component. A set of spectra obtained in this way for the 30 Å sample is displayed in Fig. 3. We observe that the peak position is very constant over an 8 eV photon energy range. With an effective mass of $0.5m_0$ in this direction (see below), the k vector range probed in this way is 0.2 $Å^{-1}$, i.e., about the same as that spanned by the angular variations in Fig. 1. This result is thus fully consistent with the expected behavior of a quantum well state.

Because of a lack of detailed knowledge about the shape of the potential well, a full analysis of the quantum well states cannot be done. From the observed dispersions it is possible, however, to extract some approximate results. The simplest way to model the quantum well is in terms of a one-dimensional box with high barriers on each side and a constant potential in between. Under this assumption

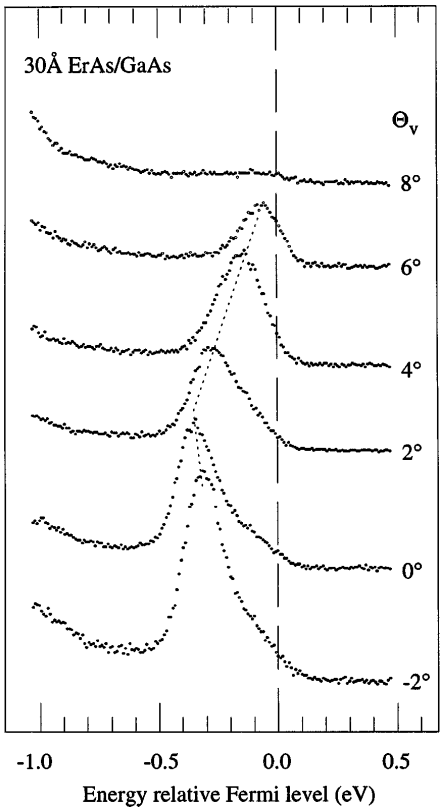

FIG. 2. Spectra from the 30 Å ErAs layer for different polar angles orthogonal to the plane of incidence.

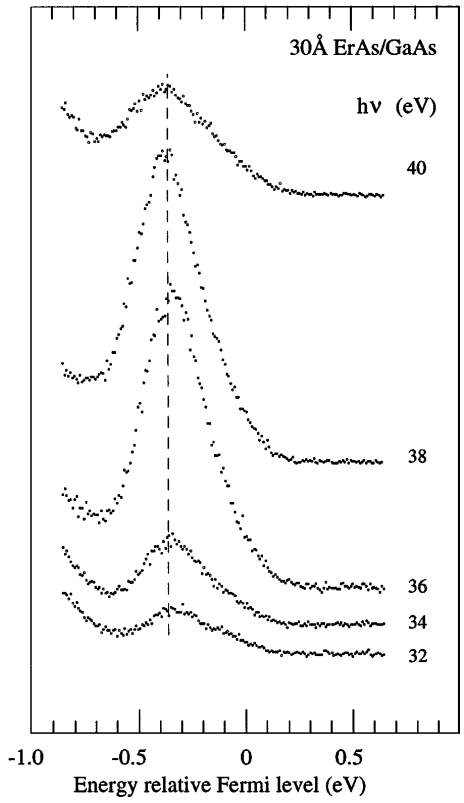

FIG. 3. Spectra from the 30 Å ErAs layer excited with different photon energies, and detected at polar angles adjusted to probe states with the same momentum component in the surface plane.

we can directly relate the electron energies at the minima in the dispersions seen in Fig. 1 (i.e., near the X point) to the width of the potential box. By keeping the momentum component in the surface plane fixed and changing the photon energy, we probe the band dispersion along XW (see inset Fig. 1). The observed energy shift between the 20 and 30 Å layers thus implies an effective mass $m^*_{XW\perp} = 0.5m_0$, while the energy separation between the two levels found for the 40 Å layer (0.20 eV) gives $m^*_{XW\perp} = 0.4m_0$. With an effective mass of this size, the expected shift between 30 and 40 Å widths is only 37 meV. This is consistent with our observation of nearly equal energies in the two cases. For the 10 Å layer the same reasoning does not hold. In this case the predicted shift is 0.56 eV, which is clearly above the observed shift of 0.8 eV. Alternatively, a 0.08 eV shift would imply that $m^*_\perp = 3.2m_0$. This deviation is not totally unexpected, as the simple model applied here must fail when the range of the barrier is not negligible in comparison with the layer thickness. We note that the value for $m^*_{XW\perp}$ is about half of that for $m^*_{XW\parallel}$, which is remarkable as the two directions are equivalent in the bulk.

In summary, we have shown that the electronic structure of thin epitaxial ErAs layers on GaAs is quantized due to the confinement imposed by the layer thickness. All layers investigated show (semi-) metallic properties, i.e., no signs are found for a predicted metal-semiconductor transition. On the other hand, it is found that the energy band structure of the thin layers deviates from that in bulk ErAs in two respects: (a) the bottom of the filled band at X is deeper in the thin layers and (b) the effective masses along XW directions are not identical as in the bulk. Thus, the electronic properties of the very thin layers cannot be predicted simply on the basis of the bulk electronic structure.

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