Observation of Quantum Size Effects in Photoemission from Ag Islands on GaAs(110)

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A set of extra peaks, which dominate the region of the silver *s-p* band, are observed in angle-resolved photoemission from Ag islands formed on GaAs(110) by low temperature deposition and annealing to room temperature. The thickness dependence of peak spacing demonstrates that the new peaks originate from wave vector quantization due to electron confinement. The overall features of the spectra are reproduced within a model based on a superposition of emission from a distribution of island sizes, and are interpreted as quantum size effects in these small metal "quantum dots."

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Atomic scale spatial confinement of valence electrons in low-dimensional structures can give rise to electron wave vector quantization. While the study of such phenomena in semiconductor quantum wells and other low-dimensional structures has attracted extensive interest [1], quantum size effects (QSE) in metal structures have only been observed in a few studies, such as resistivity oscillations in tunneling experiments [2], work function changes versus thickness [3], and direct observations in valence level photoelectron spectroscopy and inverse photoemission from two-dimensional metal overlayers [4–10]. Metal structures of lower dimensions, such as small clusters (quantum dots) have been prepared by depositing mass-selected clusters on a solid substrate [11], but quantum size effects have not yet been found in such structures. For evaporated metals on solid substrates, the distribution of island sizes may preclude an observation of quantum size effects by laterally averaging techniques. However, changes in deposition temperature and/or annealing can modify the overlayer morphology, which may lead to a more uniform island size distribution [12,13]. Here we demonstrate how special deposition conditions can cause an island size distribution which leads to the manifestation of quantum size effects in photoemission from small silver islands on a GaAs(110) substrate.

The experiments were performed in several ultrahigh vacuum photoemission chambers, equipped with Knudsen cells for metal overlayer deposition, low energy electron diffraction (LEED) optics, cleaving tools for substrate surface preparation, and a crystal holder which allowed sample cooling to 100 K. Photoelectron spectra were recorded using light from the BESSY (Berliner-Elektronen-Speicherrings-Gesellschaft für Synchrotronstrahlung) storage ring in Berlin, using toroidal grating monochromators with a photon energy range from about 10 to 120 eV. Photoelectrons were energy analyzed and detected using a hemispherical electron energy analyzer (HA 50 from VSW Ltd, Great Britain), with an overall resolution of about 50 meV. The substrates were prenotched bars of *n*- and *p*-type GaAs (Wacker Chemitronic, Germany) which were cleaved *in vacuo* and showed mirror-like surfaces with only a few large-scale steps. Temperatures were measured with a thermocouple attached to the samples.

The growth mode of silver overlayers on GaAs(110) was derived from the intensity of the substrate Ga 3*d* core level line as a function of Ag deposition (Fig. 1). Previous photoemission work has shown that clusters form upon room temperature (RT) deposition [14–16]. An exponential attenuation of the substrate Ga 3*d* line for deposition at 100 K is taken as evidence for a quasi-layer-by-layer growth, due to random deposition of adparticles which are immobile since diffusion is inhibited by the low substrate temperature [13,14,17]. The data in Fig. 1 yield an electron mean free path $\lambda = 5$ Å, in agreement with the literature [18]. Once the substrate is warmed up after deposition of the first 20 Å (Fig. 1), the substrate emission I_{Ga} increases again since the disordered layer develops into crystalline islands which leave large areas of the substrate uncovered, enhancing substrate emission. This cycle may be repeated several times as shown in Fig. 1, with a slightly changing slope of I_{Ga},

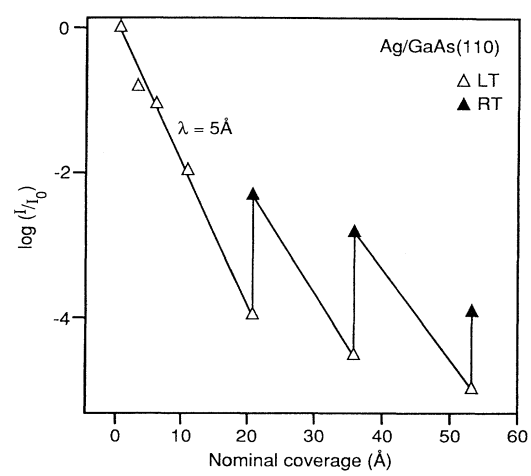

FIG. 1. Intensity of the bulk component of the Ga 3*d* core level line as a function of Ag metal deposition at 100 K (open symbols) and various annealing steps (solid symbols) as indicated. An electron mean free path $\lambda = 5$ Å results from the observed decay behavior.

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probably due to a growth morphology affected by the shape of the clusters (see below).

Detailed information on the shape of the crystallites generated by the deposition-annealing cycles is obtained from LEED studies by Bolmont *et al.* [19], scanning tunneling microscopy (STM) experiments by Trafas *et al.* [20], as well as our own LEED observations. Both LEED and STM data show that the Ag islands are crystallites which expose (111) and $(11\bar{1})$ surfaces at 25 and 45 deg with respect to the substrate surface, in a rooflike fashion. In plan view, they appear as rectangles in the STM images, with a length-to-width ratio from roughly 1:1 to 1:2, and their long axis parallel to the GaAs [110] direction. The growth of well ordered crystallites with this particular orientation has been related by Bolmont *et al.* [19] to the lattice match of the Ag (441) plane along the $[\bar{1}\bar{1}8]$ azimuth, being within 2% of 3 times the GaAs periodicity along the [001] azimuth on the (110) surface. Trafas *et al.*, on the other hand, relate it to the reconstruction of GaAs(110) which induces an asymmetry in the surface [20]. The hexagonal LEED pattern of the Ag crystallites formed by deposition and annealing, with its center displaced from the (0,0) beam of the GaAs(110) pattern, is much sharper than that from RT deposited films, indicating better ordering achieved through this process.

Direct evidence for the influence of the clustering process upon annealing is obtained from the valence level spectra in Fig. 2. The bottom spectrum, recorded from a 53 Å thick layer of Ag deposited at 100 K, and annealed at 203 K, shows the familiar region of the silver s-p band which is flat and featureless (except for direct transitions not observed here) from the Fermi energy E_F down to the region of the onset of the d bands (about 4 eV below E_F). Upon warming to 249 K, some structure develops in the s-p region, which becomes clearer as higher temperatures are reached. Eventually, at 300 K, five peaks may be discerned, with a smaller structure close to E_F. The new peaks have no counterpart in the s-p part of the band structure of silver [21]; also, they do not exhibit shifts in binding energy with photon energy as expected from bulk band direct transitions. Neither do they correspond to the known surface states on any of the low-index silver surfaces [21]. The possibility that the bare GaAs(110) surface could contribute to the spectrum was excluded in careful comparisons of clean and metal-covered surface spectra; GaAs(110) has only weak features, and none close to E_F in any case.

The number of peaks observed with the range of the Ag s-p band shown in Fig. 2, and their binding energies, depend on the amount of Ag deposited. This is shown in Fig. 3, where spectra for different nominal coverages were recorded after cycles similar to those in Fig. 1. Such behavior strongly suggests [5–7] an interpretation of the Ag-induced peaks in Figs. 2 and 3 as due to electron confinement in the Ag islands. Spectra were recorded in a geometry normal to the (111) silver facet planes, at about 25° polar angle along the [001] azimuth. With increasing Ag deposition, the number of peaks increases and consequently the peak separation decreases. The intensity modulation, i.e., peak to valley height ratio, decreases for nominal coverages higher than 100 Å. However, even at a thickness of 158 Å the peaks can be readily discerned; a close inspection reveals twelve separate

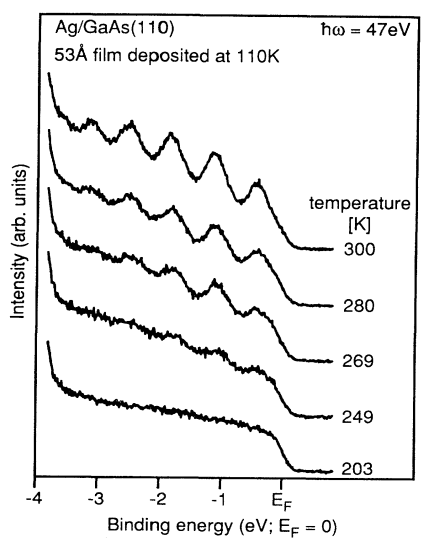

FIG. 2. Valence photoelectron spectra of a 53 Å silver layer on GaAs(110), deposited at 100 K, for several annealing temperatures. Photon energy was 47 eV. Slight difference in background as compared with spectra of Fig. 3 are caused by lower instrumental resolution in this set of spectra.

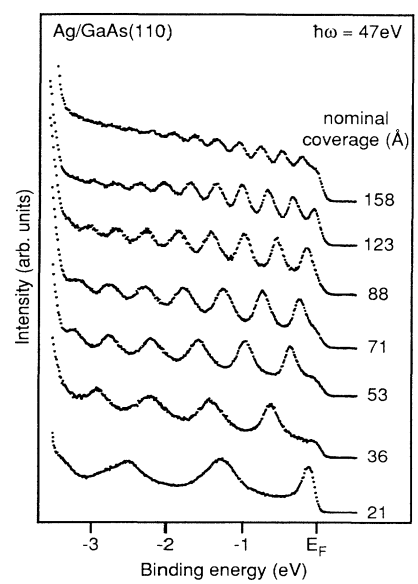

FIG. 3. Valence photoelectron spectra of seven Ag layers of different thickness as indicated, prepared by deposition at 100 K and subsequent annealing to room temperature. Spectra were recorded at 25° polar angle with respect to the surface normal along the [011] azimuth of the GaAs(110) surface.

peaks at this stage. An overall intensity modulation is superimposed on the peaks, particularly obvious in the spectrum for 123 Å, which causes the peaks about 1.5 eV below E_F to have the highest intensity. This large modulation (about 50% of peak intensity near E_F in the fourth spectrum from the bottom) suggests that a large proportion of deposited Ag is present in a configuration which gives rise to the observation of the QSE peaks; if the islands were a minority species, the usual structureless Ag s-p emission would dominate the spectrum. In this context it is important to note that none of the features in Figs. 2 and 3 was ever observed in silver layers grown at room temperature, suggesting that low-temperature deposition and annealing to room temperature gives rise to a much narrower island size distribution than RT deposition.

In order to interpret the data, the case of the familiar quantum-mechanical potential well problem with hard walls may serve as a starting point, as in the interpretation of previous electron tunneling data [2]. In this model, the energy of the nth quantized state depends on well width w according to

$$E_n = (\hbar^2/2m)(n\pi/w)^2 . \quad (1)$$

A wide distribution of island sizes in the sampled area would cause a superposition of states from wells of different width w. In order to observe quantum size effects in photoemission from an ensemble of crystallites, it might be argued that their size distribution is required to have a spread which is less than that of the electron wavelength, i.e., on the order of a few Å, for the QSE to be observed. This is a stringent requirement not easily met by a real layer. However, a certain spread in island size can be reconciled with the observation of QSE as pointed out by Jaklevic and Lambe [2], who noted that variations in thickness in the ensemble are not continuous, but must correspond to an integral number of lattice spacings, such that the well width $w = Nd$ (N is the number of layers and d the lattice spacing). The wave vector is then given by $k = n(\pi/Nd)$. The phase shifts at the vacuum-metal and metal-semiconductor boundaries are neglected. Since the total phase shift is 2π at most, this introduces a maximum error of $\Delta n = 1$ in the determination, which may be neglected for large N as in the present case. An actual experiment deals with an ensemble of crystallites with differing N. It is therefore necessary to average over this ensemble, employing a distribution function $P(N)$ which models the actual size distribution. Here a Gaussian with a distribution parameter α is used. Adding lifetime broadening on each state E_n gives a broadened distribution $\rho(E)$ of quantum states. The photoemission spectrum samples contributions from crystallites of different N which are superimposed according to their population $P(N)$, and can be written as [2]

$$R(E) = \sum_N \left(\sum_n [\rho(E - E_n(N))] P(N) \right) . \quad (2)$$

Since the width of the quantum well can only be varied by fixed amounts, i.e., the width of one atomic layer, there exist certain states which have equal energy and wave vector *irrespective of thickness*. Consider a wave function which has nodes at each atomic layer. The addition of one (or more) layers will not change the wave function and the energy of the state, since the boundary conditions are also met and the wavelength does not change. In general, for each of the states where the wave vector has a rational value $k = (S/Q)(\pi/d)$, where S/Q represents an irreducible rational number, such so-called commensurate states [2] exist. In the framework of the electronic band structure, commensurate states will exist halfway towards the Brillouin zone (BZ) boundary ($S/Q = \frac{1}{2}$), at the zone boundary ($S/Q = 1$), and at other points inside the BZ. Based on the above model, we have calculated quantum well states for a mean layer thickness of $N = 37$, and a Gaussian parameter $\alpha = 0.3$; results are shown in Fig. 4. The Lorentzian-broadened energy levels for each separate crystallite are given in the bottom traces, weighed by the population function $P(N)$. The sum of these contributions, multiplied by the Fermi distribution, is given in the center trace.

With E_F at 7.21 eV above the bottom of the well from band structure calculations [21] the commensurate state at which $S/Q = 1$ (marked in Fig. 4) is located about 0.4 eV below E_F. Since data were recorded from the (111) surface, this point corresponds to the L point in the BZ. This agrees with the fact that the silver s-p band disperses in a range close to the L point along Γ-L, and

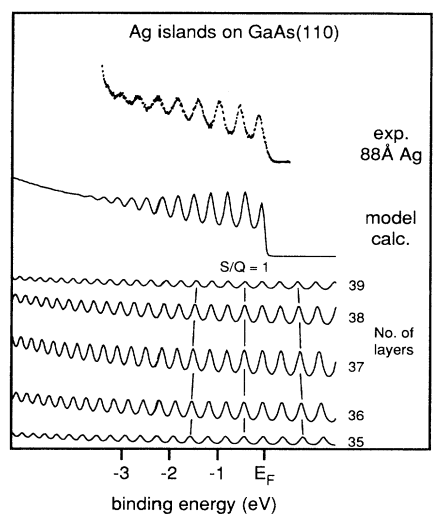

FIG. 4. Model calculations of Lorentzian-broadened one-dimensional well quantum levels for different layer thicknesses (bottom). The energy levels have been weighed by the population function $P(N)$ centered at $N = 37$ layers. Thicknesses are given in units of one layer along the Ag(111) axis, equivalent to 2.35 Å. The label "$S/Q = 1$" indicates the state at the Brillouin zone boundary (i.e., the L point). The sum of these level schemes (center trace) is folded with a Fermi distribution (see text). The top trace shows the photoemission spectrum for a nominal 88 Å Ag layer.

reaches it at about 0.1 eV below E_F. Spectra recorded over a range of photon energies also demonstrate that transitions near the L point are responsible for the new peaks. These were found to be strongest at $h\nu = 52$ eV, with appreciable intensity over the range 37 eV $< h\nu <$ 57 eV [22]. Hsieh *et al.* [23] have shown that in transitions from surface states on Ag(111) to a free-electron final state, the L point is reached at $h\nu = 54$ eV, with a broad range in their surface state resonance curve from 45 to 58 eV. Thus the Ag band structure, the quantum well model calculation, and the photon energy dependence all give support to our interpretation that the new peaks arise from wave vector quantization of the Ag s-p band, observed through direct transitions near the L point. As calculated by Jalochowski *et al.*, for a 25 layer Pb film on Si(111) a mismatch between the initial and final state wave vector reduces the transition matrix element by only about 20%, explaining the wide range of photon energies at which the QSE peaks are observed. Despite the simplicity of the model, the overall similarity between the calculated distribution (center trace) and a spectrum for a nominal thickness of 88 Å (top trace in Fig. 4) is evident. In the model, the states $E(n)$ at E_F correspond to $n \sim 70$ for the highest coverage in Fig. 3. This explains why the levels are equidistant within the range accessible to experiment: Only a small segment of the entire energy level diagram ($58 > n > 70$ for the top spectrum) is detected, and a linear relation is a fair approximation to the dependence of $E(n)$ in Eq. (1) at these n values.

The observation of quantum size effects in thin metal layers has so far only been reported for films which are two dimensional (2D), grown epitaxially on well lattice matched substrates [3–8]. In such systems, each quantum well state is a 2D subband because of the in-plane motion of the electrons. The wave vector component $k_\parallel$ parallel to the surface is a good quantum number, with a free-electron-like dispersion, $k_\parallel = (2m/\hbar)E_{\rm kin}\sin\theta$, where θ is the electron polar take-off angle. For the crystallites studied here, the lateral dimensions are small, length and width are fairly similar, such that free-electron-like dispersion might not be expected. In search of this effect, spectra were recorded over a range of $k_\parallel$ along the $[21\bar{1}]$ azimuth of the Ag(111) plane ([001] substrate azimuth) and its normal, i.e., the $[1\bar{1}0]$ substrate azimuth. For a layer with seven separate QSE peaks, a peak shift of less than 0.1 eV over a $k_\parallel$ range of 0.34 Å^{-1} was observed along the [001] azimuth, where free electron dispersion would predict a shift of 1.3 eV. A similar result was obtained for the [110] azimuth. Both lateral dimensions of the Ag islands are apparently small enough such that $k_\parallel$ is not a good quantum number, a result that may be compared with a study of 2D *epitaxial* Ag layers on Cu(111), where Mueller *et al.* [7] found excellent agreement with free electron behavior, with a reduced mass serving as fitting parameter. We believe that this is the first observation of zero-dimensional quantum size effects in photoemission from small metal islands.

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