PHYSICAL REVIEW B VOLUME 33, NUMBER 8 15 APRIL 1986

Electronic properties and chemistry of Ti/GaAs and Pd/GaAs interfaces

R. Ludeke and G. Landgren*
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 15 July 1985)

Photoemission experiments have shown that strong chemical reactions occur at clean Pd/GaAs(110) and Ti/GaAs(110) interfaces formed at room temperature in ultrahigh vacuum. In both cases elemental Ga was found dispersed in the metal film, which also had a metal-As compound segregated to its surface. In addition, what appears to be elemental As was observed on the Pd-covered surfaces. Subsurface reactions were identified well below monolayer (ML) coverages. The evolution of band bending with increasing metal coverage starting near 0.001 ML is strongly dependent on the metal and results in Schottky-barrier heights of 0.73 (0.70)±0.05 eV for Ti and 1.01 (0.42)±0.05 eV for Pd on *n*-type (*p*-type) GaAs(110). Strong emission from the transition-metal *d* orbitals in the band-gap region of the GaAs was observed for coverages $\gtrsim 0.01$ ML and represents the first direct spectroscopic identification of occupied interface states responsible for Fermi-level pinning. The latter observation together with differing coverage dependences for the final pinning positions for Pd and Ti indicate a new mechanism for the formation of a Schottky barrier. It is suggested that rebonding between the transition metal and the GaAs at the interface produces partially occupied *d* orbitals which lie in the semiconductor band gap. In addition, several refinements of the photoemission technique and data analysis are discussed and shown to be relevant to both the accurate determination of band bending and the chemical characterization of the interface.

I. INTRODUCTION

A number of studies on metal overlayers on GaAs(110) surfaces have recently been reported.[1-5] Much of the work that has been carried out thus far in clean, ultrahigh-vacuum environments has largely addressed interface reactions between the GaAs and noble metals or simple group-III metals. From both scientific and technological standpoints it is therefore of great interest to extend such studies to include transition metals.[5,6] Energetic considerations and preliminary results indicate that such interfaces should be very reactive.[6,7] It has been argued that the formation of a stable interface compound should prevent interdiffusion and thus result in abrupt interfaces.[3] However, the details of such reactions have never been clarified.

Another point of considerable interest is the origin of the Schottky barrier present at the metal-semiconductor interface. The recently popular "unified defect model" of Spicer *et al.*[8] has so far been supported only by data from simple metals; the noble metals in general exhibit barrier heights outside the estimated range of the defect model. Its validity in the presence of adatoms with partially filled *d* shells which could act as localized donors or acceptors has not been tested. Furthermore, the commonly used method of core-level shifts to determine the position of the Fermi level in the band gap[1] may be complicated by the occurrence of chemically shifted components in the photoemission spectra. Particularly with a reactive interface, this may lead to erroneous conclusions unless appropriate precautions are taken.

In the work reported here we have undertaken a detailed photoemission study of two important transition-metal—GaAs(110) interfaces, namely, those with Pd and Ti. Pd/GaAs was selected to facilitate comparison with the previously studied Ag/GaAs system. Since Pd and Ag are neighbors in the same row of the periodic system with nearly the same lattice constant, this comparison should emphasize the differences introduced by an exposed *d* shell. As the second example, we have chosen the Ti/GaAs interface. Ti is commonly used as a gate metal in the fabrication of GaAs field-effect transistors. Hence, the technological importance of this interface is obvious. In addition, Ti is near the beginning of the transition-metal series whereas Pd is at the very end, a fact which could elucidate expected chemical trends. The experimental approach included high-resolution photoelectron core-level spectroscopy to follow chemical and electronic changes, excitation by tunable synchrotron radiation for control of probing depth, and computerized modeling of the spectra to aid in the interpretation. The results indicate strong "exchange-type" reactions for both Pd and Ti but showed remarkable differences in their effects on the Fermi-level position.

II. EXPERIMENTAL DETAILS

The experiments were performed using the IBM 2D electron spectrometer[9] and synchrotron light from the National Synchrotron Light Source at Brookhaven National Laboratory. A 3-m toroidal grating monochromator was used to disperse the incident radiation and focus it onto the sample. The photon energy was varied between 30 and 90 eV. Photoelectrons were collected over a large solid angle of about one steradian and the combined electron and photon energy resolution was better than 0.2 eV for all cases reported here. Photon energies were chosen to enhance either bulk or surface features in the Ga and As 3*d* core-level spectra. Electron-escape depths of 5 and 20 Å, for kinetic energies of 45 and 6 eV, respectively, were calculated from the bulk and surface contributions to the clean-surface spectrum. These values are in excellent agreement with previous determinations for comparable kinetic energies in GaAs.[10,11]

Samples were prepared by cleaving GaAs in a vacuum of less than 2×10^{-10} torr. The GaAs was *n* or *p* doped (Si or Zn) to $(5-10)\times10^{17}$ cm^{-3}. Only good quality cleaves exhibiting band bending $\lesssim 100$ meV were used. After recording a spectrum for the clean surface, successive layers of metal were sublimated directly from a filament heated by a constant-current power supply. The sample was at room temperature throughout the experiment. Control experiments showed that contamination introduced by the repetitive deposition-analysis procedure was negligible. The average metal deposition rate was determined by a quartz-crystal thickness monitor. Stable deposition rates as low as 0.001 monolayers (ML) per sec could be attained [1 ML is equivalent to a GaAs(110) surface atom density of 8.86×10^{14} cm^{-2}]. In general, the metal thicknesses will be expressed in Å; only for coverages near or below a monolayer [referred to the GaAs(110) surface] is it meaningful to express thicknesses in ML. The latter is obtained by multiplying the mean thickness of the metal in Å by 0.7.

The photoelectron spectrometer was completely computer controlled and the data was analyzed using a least-squares curve-fitting routine.[12] After a smooth, essentially linear background subtraction the experimental spectrum was compared to a synthesized spectrum consisting of a number of Lorentzians broadened by Gaussians, each exhibiting the same spin-orbit-splitting and branching ratio. An iterative procedure optimized the values for energy, Gaussian and Lorentzian widths, and relative intensity. The values for the spin-orbit-splitting and the branching ratio were determined from the clean-surface spectrum and assumed not to change with metal deposition. The Gaussian broadening function contains contributions due to instrumental resolution as well as contributions from inhomogeneous band bending and nonuniform bonding configurations in the interface region. The bulk GaAs-derived component was generally narrower than the chemically shifted components. In order to minimize the number of parameters to be optimized, a common Lorentzian width was assumed for all components; the Gaussian width was allowed to be varied for all components. This restriction did not introduce any ambiguities in the interpretation of the spectra, since the existence of all features could be independently ascertained by following changes in the spectra as a function of metal coverage. The fits always used the smallest possible number of components and an acceptable fit was always found with only two or three components, most of which were already apparent by inspection of the raw data.

For the reacted Ga and As component dispersed in the metal film it was necessary to include many-body contributions to the line-shape analysis. The origin of this effect, which has not been previously considered for reacted and interdiffused metal-semiconductor interfaces, is due to the strong screening and creation of electron-hole pairs at the metallic Fermi edge.[13] A useful and closed-form expression for the expected line shape has been formulated by Doniach and Sunjic[14] and consists of convoluting a power-law term $\propto 1/E^{1-\alpha}$ with a Lorentzian. The resulting expression is

$$f(E)=\frac{\Gamma(1-\alpha)\cos[\pi\alpha/2+(1-\alpha)\arctan(2E/\gamma)]}{[E^2+(\gamma/2)^2]^{(1-\alpha)/2}}\ ,$$

where α is an asymmetry factor, which can be expressed in terms of the square of the screening charges,[13] γ is the Lorentzian full width at half-maximum (FWHM), and Γ is the Γ function. The Doniach-Sunjic line shape reverts back to a Lorentzian for $\alpha=0$. In the present application this line shape was further convoluted with a Gaussian.

III. CHEMISTRY: Ti ON GaAs(110)

The evolution of the Ga 3*d* core-level spectrum with increasing coverage of Ti is depicted in Fig. 1. The top spectrum represents that of the clean, cleaved surface

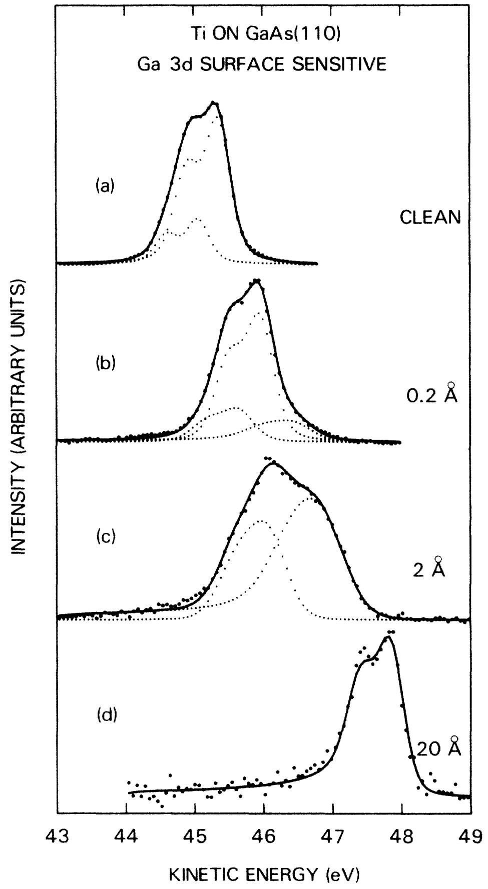

FIG. 1. Decompositions of Ga 3*d* surface-sensitive spectra for indicated coverages of Ti on *n*-type GaAs(110). The solid line is the sum of the components (dotted spectra); the larger dots represent the experimental data. Note that the high kinetic energy (KE) components for spectra (b)—(d) are fitted with a Doniach-Sunjic (DS) line shape, with curve (d) requiring but one component. Photon energy is equal to 70 eV.

(solid line), which has been decomposed into a bulk (major component) and surface contribution (minor component). The points overlying the solid curve represent the experimental data after a suitable background subtraction. The decomposition is in agreement with previously reported results.[10,12] Evidence for a chemical interaction between the Ti and the substrate is already apparent in the Ga 3*d* spectrum for coverages as low as 0.07 Å (0.05 ML). The spectrum for a 0.2 Å (0.14 ML) deposit of Ti is shown in (b) of Fig. 1. The spectral decomposition reveals a new peak shifted by 0.5 eV to higher kinetic energy (KE) relative to the GaAs bulk peak. In addition, a still prominent clean-surface component is present with an intensity, relative to the bulk component, nearly equal to that for the clean surface; this indicates a disturbance by the Ti which is localized at the chemisorption site and leaves the remainder of the surface unperturbed. The 0.5-eV chemical shift of the new structure seems too small compared to the shift expected for metallic Ga [$\sim$0.9 eV (Ref. 2)], and rather suggests the presence of atomic size clusters of Ga or a mixed phase of Ga with Ti or As. At higher coverages this peak increasingly dominates the spectra and shifts yet to higher kinetic energies. The resolved spin-orbit splitting of this peak for the highest Ti coverages (20 Å) indicates a well-defined Ga environment, which suggests either small metallic Ga clusters or more likely a Ga-Ti alloy. The shift to higher kinetic energies of the bulk GaAs component is largely due to increased band bending with coverage. This band bending is not homogeneous across the surface, which results in spectral smearing and an apparent loss in resolution. This broadening is manifested by an increase in the Gaussian FWHM from $\sim$0.3 eV for the clean surface to $>$0.6 eV for coverages beyond a monolayer (the calculated Lorentzian widths remain near a value of 0.1 eV).

The fit to the data for the 20-Å coverage is accomplished by a single-component (albeit spin-orbit-split) Doniach-Sunjic (DS) line shape with $\alpha = 0.12$ convoluted with a Gaussian. Failure to consider such a lineshape forced a two-component fit to account for the low KE tail, with the results being physically unrealistic.[15] The chemically shifted components in all of the spectra were fitted with the DS line shape, with computed values of α consistently determined to be 0.11 ± 0.01.

The corresponding analysis has also been carried out for the As 3*d* spectra, as shown in Fig. 2. Changes in the spectra with Ti coverage are not as clearly defined as for Ga because the dominant shifted peak overlaps the surface core level of the clean surface. This is an important point which could be construed erroneously as an indication of a lack of initial chemical interaction of the Ti and the As, when in reality the intensity of the shifted structure is made up of a coverage-dependent decreasing surface component and an increasing chemically shifted peak, which nearly cancel at low coverages. For coverages exceeding $\sim$1 Å the new peak becomes discernible and dominates the spectra beyond 2 Å. Its kinetic energy relative to the bulk component is increased by $\sim$0.8 eV (equivalently its binding energy is decreased by this value) and suggests strong Ti-As interactions. The peak cannot be attributed to metallic As, for which a shifted structure should appear on the low kinetic energy side of the bulk peak. This is indeed observed for Pd, and will be disussed in the next section.

The low KE structure can only be identified with bulk GaAs for coverages less than a few Å, beyond which it corresponds to a new phase, as electron-escape-depth considerations limit the GaAs bulk contribution for larger coverages. This notion is supported by the observation that under bulk-sensitive conditions an As 3*d* signal was not seen for Ti coverages exceeding 5 Å. We conclude from this that the As exists in two different surface phases, one of which has a binding energy $\sim$0.3 eV less than in GaAs and constitutes a minor component on the surface. Although the data for the 20-Å coverage in (d) of Fig. 2 can be fitted with a single DS component (this curve is represented by crosses in the figure) the large value of $\alpha = 0.132$ which is necessary suggests that a two-component fit is more reasonable. For intermediate coverages (not shown) a two-component fit is clearly demanded.

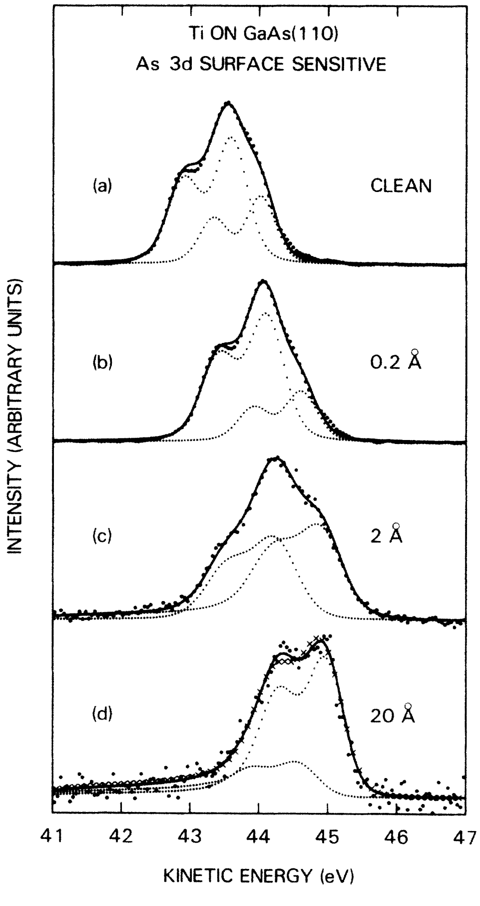

FIG. 2. Decompositions of As 3*d* surface-sensitive spectra for indicated coverages of Ti on *n*-type GaAs(110). The solid line is the sum of the components (dotted spectra); the larger dots represent the experimental data. Note that the high KE components for spectrum (c) and both of (d) are fitted with a DS line shape. The crosses in spectrum (d) represent a single-component DS fit (see the text). Photon energy is equal to 90 eV.

Figure 3 shows the intensity variations with Ti coverage of the Ga and As $3d$ core levels. The intensities are normalized to those of the clean surface. Representative curves are shown for the total core-level signal, that is, the sum of the "substrate" (i.e., GaAs) and the shifted component, as well as that of the "substrate" alone (the reason for the quote is that the GaAs substrate signal is trackable only up to a few monolayers of coverage, beyond which the extracted component, as will be discussed later, is no longer representative of the GaAs substrate). The most apparent observation in the data of Fig. 3 is the extremely fast attenuation of the Ga $3d$ "substrate" signal for both surface- and bulk-sensitive conditions, with effective electron-escape depths of ~ 1 and 1.5 Å. (The As $3d$ "substrate" component under surface-sensitive conditions tracks that of Ga and is not shown for reasons of clarity.) These surprisingly short effective electron-escape depths are the consequence of the disrupted layer of Ga and As, in addition to Ti, which lies on top of the GaAs. In addition, the electron mean free path in the Ti overlayer is short as well, with estimates of 2 and 2.5 Å (± 0.5 Å) for KE's of 45 and 6 eV, respectively, obtained for low coverage from the intensity curves of Fig. 3 of the total signal. These values are consistent with theoretical estimates of 2.3 and 3 Å for Ti based on Penn's free-electron model.[16]

An indication of the depth distribution of reacted constituents of the GaAs can be ascertained by comparing core-level spectra obtained for different electron-escape depths. Such a comparison is shown in Fig. 4 for a Ti coverage of 0.7 Å. The spectral decomposition indicates that the ratio of the unshifted and shifted components is roughly the same in the two spectra. This observation is independent of Ti coverage. An adequate explanation of this observation depends on the growth morphology of the Ti. Clustered growth, for instance, would demand either a strong concentration gradient of Ga and As under the Ti and/or a substantial difference in the electron-escape depths in the Ti for surface- and bulk-sensitive conditions. The latter is not observed and the rapid decay of the "bulk" GaAs signal in Fig. 3 strongly argues against clustered growth.[17] Instead, a fairly uniformly spread Ti deposit, which initially interacts strongly with the substrate, is consistent with the data. Even initially, the Ti remains predominantly on the surface, with reaction products (Ga and As) located at the GaAs/Ti interface, as well as dispersed in the GaAs. Because of the comparable mean free paths in the metal film for the two KE ranges used, the data of Fig. 4 can only be explained if reaction products have diffused into the GaAs. The extent of the penetration cannot be determined, particularly since one cannot assume the same escape depths observed for the clean, unperturbed GaAs.[12]

The short electron mean free paths through the Ti present difficulties in the detection of the true bulk signal needed for an accurate determination of the band bending. The shifts in KE of the various spectral components of the Ga and As $3d$ core levels as a function of Ti thickness are shown in Fig. 5 for n-type substrates; the shifts are relative to the KE of the core levels for the clean surface.

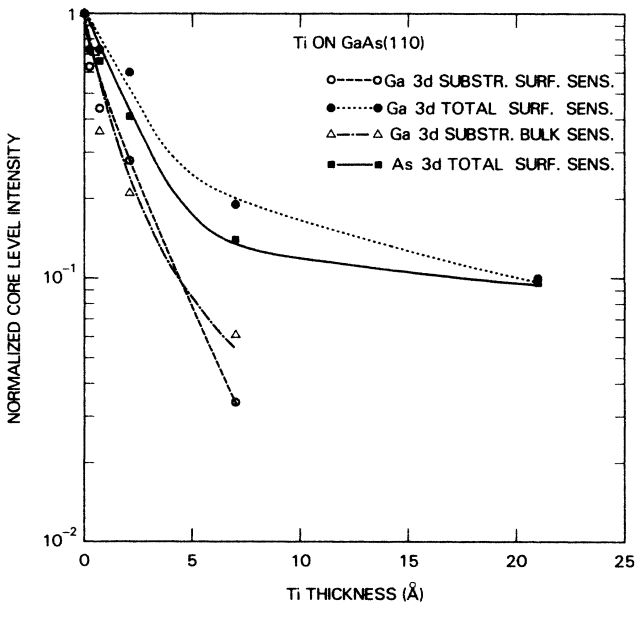

FIG. 3. Attenuation of total and component intensities of Ga and As $3d$ core levels with Ti coverage.

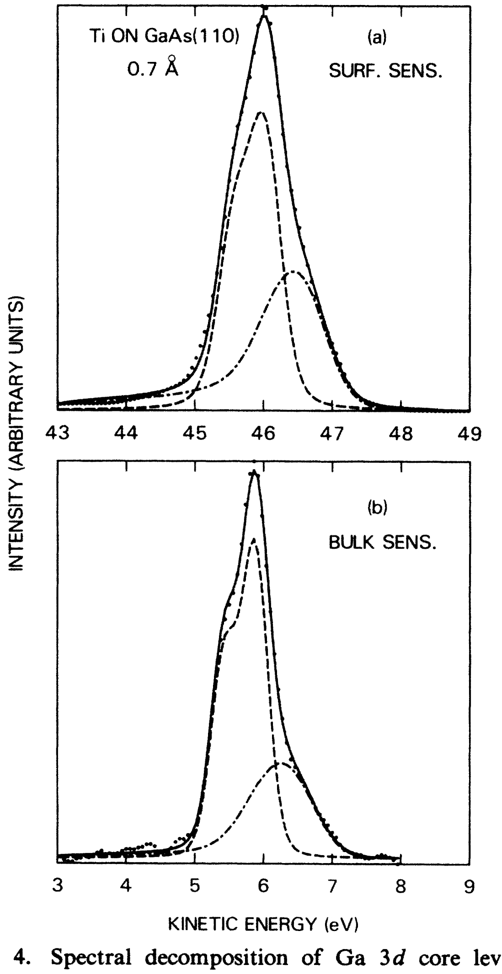

FIG. 4. Spectral decomposition of Ga $3d$ core levels for 0.7-Å coverage of Ti obtained under (a) surface-sensitive ($h\nu = 70$ eV) and (b) bulk-sensitive ($h\nu = 30$ eV) conditions.

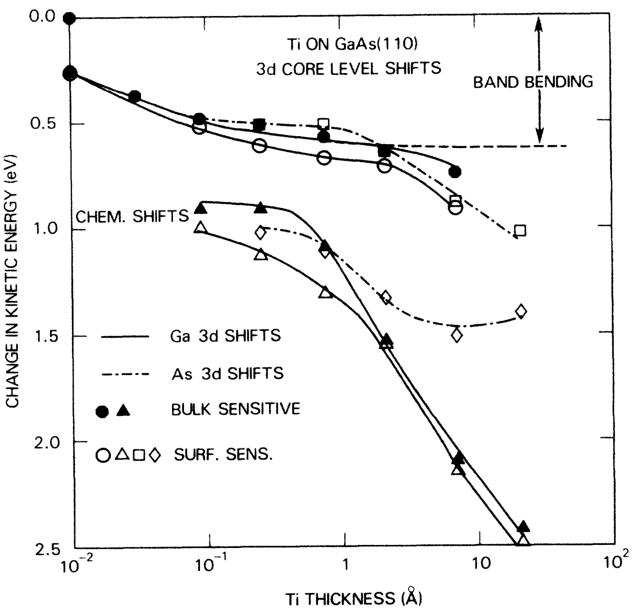

FIG. 5. Shifts of spectral components of Ga and As 3*d* core levels as a function of Ti coverage.

For coverages to ~0.1 Å only spectral components corresponding to the GaAs substrate are observed, the bulk component of which is shown in the figure. Its change in KE is due to band bending. For larger coverages the chemically shifted components become extractable from the spectra and their shifts for further coverages are shown as well. The shift in the bulk components, particularly the Ga 3*d* component taken under bulk-sensitive (low KE) conditions, levels off before additional shifts occur beyond 2 Å of coverage. These additional shifts, which are further accentuated for surface-sensitive conditions are not representative of band bending, but are due to the emergence of the new chemically shifted component which dominates the spectra as already discussed in relation to Fig. 1. The strong low KE tails of this component makes the extraction of the weakening bulk component inaccurate for the thicker coverages. The problem is less severe but nevertheless exists under bulk-sensitive conditions. Failure to use the DS line shape further diminishes the accuracy in extracting the bulk components. The large (1—1.5 eV) changes in KE of the Ga 3*d* components are not chemical shifts, i.e, initial-state effects, but can be attributed to extranuclear relaxation effects due to the polarizability of the Ti host. This effect increases as the Ga becomes more dispersed in the Ti at larger coverages. Similar effects have been observed for noble-gas atoms imbedded in noble metals.[18]

The chemistry of the Ti with the GaAs can be summarized as follows: Interactions occur for coverages beginning far below a monolayer. The resulting Ga by-product is not laminarly distributed at the interface, but appears to be diffused over several GaAs lattice planes beneath the interface. The corresponding distribution of the Ti or As is not known. Considerable out-diffusion of Ga and As into the growing Ti film is observed throughout the coverage range. The constantly decreasing binding energy for the Ga 3*d* core level strongly suggests a dilution effect in the Ti host, rather than the presence of a stoichiometric compound. Furthermore, the bulk-sensitive data suggest that the Ga is distributed throughout the Ti film. On the other hand, As appears to be segregated more on the surface, little is detected under bulk-sensitive conditions. A single reacted component is observed for Ga and two for As, although only the one with the lowest binding energy (large KE) dominates at the larger Ti coverages. As Fig. 3 indicates, the total Ga and As signals appear to level off for larger film thickness. The estimated coverage in this limit is 0.17 ML, assuming strict surface segregation. Smaller values are expected for other distributions, e.g., 0.1 ML for a homogeneous distribution within several electron-escape depths of the surface.[19]

IV. CHEMISTRY: Pd ON GaAs(110)

The chemical reactions proceed somewhat differently at the Pd/GaAs(110) interface as compared to the Ti/GaAs case. The Ga 3*d* core spectra for increasing Pd coverages are shown in Fig. 6. For coverages $\gtrsim 0.07$ ML of Pd, a

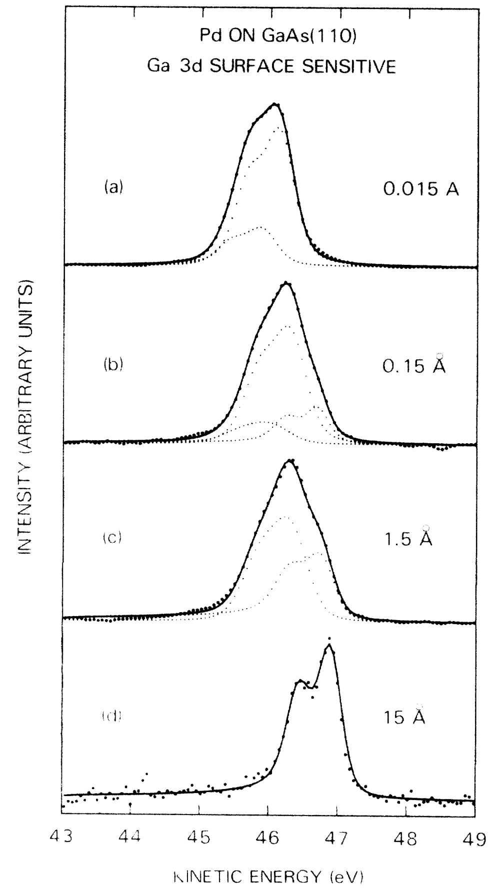

FIG. 6. Decompositions of Ga 3*d* surface-sensitive spectra for indicated coverages of Pd on *n*-type GaAs(110). The solid line is the sum of the components (dotted spectra); the larger dots represent the experimental data. The low KE component in (a) and (b) is the remnant of the surface core level of the clean surface. The high KE components for spectra (b)—(d) are fitted with a DS line shape, with curve (d) requiring but one component. Photon energy is equal to 70 eV.

new component is observed, shifted 0.4 eV to higher kinetic energy. This shift again is too small for metallic Ga, although such an interpretation was suggested by Kendelewicz *et al.*[5] As the Pd thickness increases the shift also increases to 0.6 eV, which is still insufficient to be attributed to metallic Ga. Although evidence for metallic Ga has been reported for room-temperature depositions of Pd on ion-bombarded and annealed (110) surfaces,[20] for which stoichiometric deviations toward Ga-rich conditions may be expected, in the present case a mixed Pd-Ga-As compound is a more likely possibility. Evidence for a ternary phase was recently obtained from transmission electron microscopy studies of Pd deposited on (100) surfaces at room temperature.[21] Again, as for Ti, it was necessary to fit the chemically shifted peaks for both Ga and As with a DS line shape with values of $\alpha \sim 0.10 \pm 0.01$. Such a single-component fit is shown in (d) of Fig. 6. We do not believe that a bulk component can be reasonably extracted from $\gtrsim 10$ Å Pd coverages, as previously reported;[5] instead, the extracted peak appears to be an artifact of the deconvolution with a KE near that expected for the bulk.

Arsenic, on the other hand, clearly exhibits two chemically shifted components, as shown in Fig. 7. The one on the low KE side of the bulk GaAs peak is probably due to elemental As, a conclusion also reached by Kendelewicz *et al.*[5] This peak remains a minor component of the total As signal for all coverages studied, and shifts to higher KE for Pd thicknesses exceeding 1 Å, as shown in Fig. 8. This shift, as well as that for the Ga component in the figure, may again, be due, as for Ti, to final-state effects resulting from the dilution of the constituents in the Pd host. The second As component is initially difficult to extract from the spectra because its energetic position is close to that of the surface component for the clean surface. For coverages $\gtrsim 1$ Å it can be readily extracted from the spectra (Fig. 7); its change in KE is represented in Fig. 8. As will be noticed, the binding energy of this component increases with coverage and crosses the value for bulk GaAs. This crossing is potentially problematic in the interpretation of the spectra, which could easily be interpreted as resulting from the bulk; only the details of careful data analysis and the knowledge of short escape depths can avoid an erroneous interpretation. The origin of this component is not known, but could be related to a Pd-As-Ga ternary *phase*.[21,22]

As with Ti, the bulk-sensitive spectra are essential in revealing the depth distribution of the reacted Ga and As. In Fig. 9 it can be seen that the Ga 3*d* intensity ratios of the reacted component in the surface- and bulk-sensitive spectra are quite similar, being 30% and 20% of the total signal, respectively. Since the decrease of the clean-surface component is nearly proportional to the Pd coverage, it can be concluded that the Pd is distributed rather than clustered at submonolayer coverages. The rapid decrease in intensity beyond a monolayer suggests that the growth continues to be distributed. The morphology is thus similar to that of Ti, with strong intermixing between the Pd and the GaAs. In addition, subsurface penetration of Pd is a strong possibility, as indicated by the data of Fig. 9. The bulk-sensitive results for Pd films thicker than 5 Å strongly suggest that the reacted As and Ga species are distributed throughout the Pd.

V. FERMI-LEVEL CHANGES

The position of the Fermi level at the interface as a function of metal coverage is shown in Fig. 10, where the Ti and Pd curves are also compared to Ag data previously measured in the same way.[4] The latter has been corrected for both surface potential variations due to distributed Ag clusters and bulk band-bending variations in the electron-escape-depth region.[22] The most striking features of this figure are the large band bending for Ti on *p*-type material and for Pd on *n*-type material at <0.1 ML. This observation is a clear indication that metal-derived states, in particular, the *d* states, play an important role in determining the Schottky-barrier height. The discussion of the valence-band spectra, to be presented in the next section will further support this notion. From simple band-filling arguments, as well as from electronegativity considera-

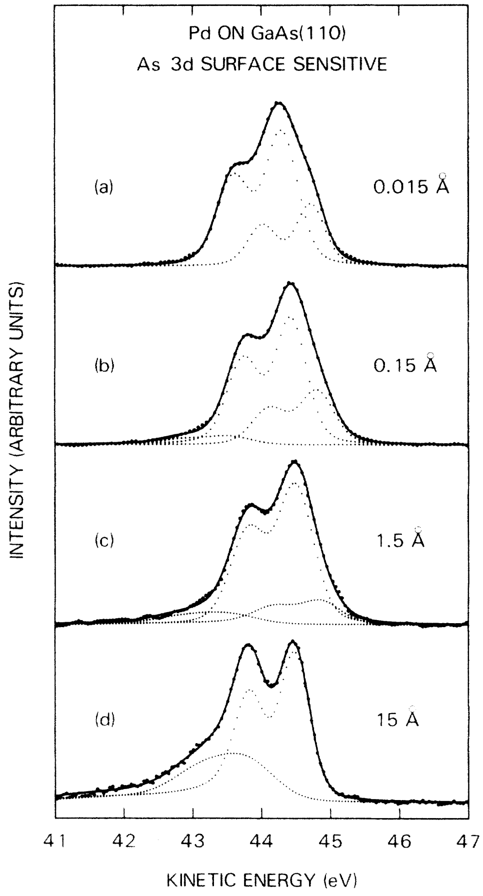

FIG. 7. Decompositions of As 3*d* surface-sensitive spectra for indicated coverages of Pd on *n*-type GaAs(110). The solid line is the sum of the components (dotted spectra); the larger dots represent the experimental data. The high KE component in (a) and to a lesser extent in (b) contains major contributions from the surface core level, and with increasing coverage, as in (c), only the chemically shifted contribution. The high KE components for spectrum (c), and both of (d) are fitted with a DS line shape. Photon energy is equal to 90 eV.

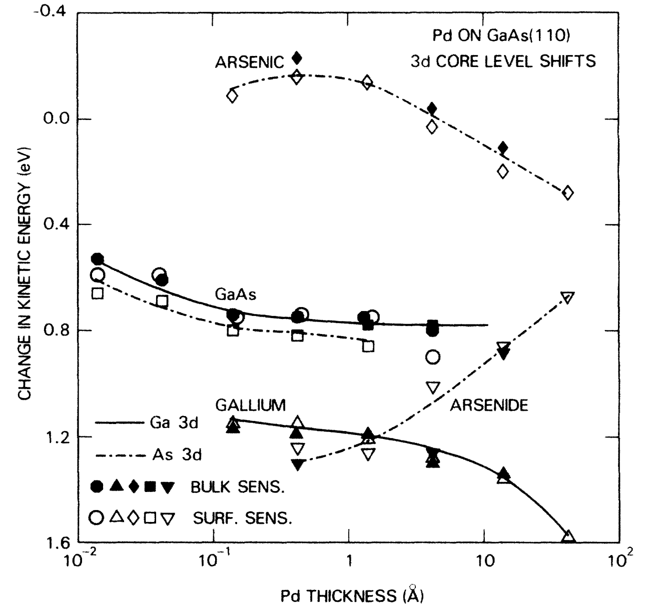

FIG. 8. Shifts of spectral components of Ga and As $3d$ core levels as a function of Pd coverage.

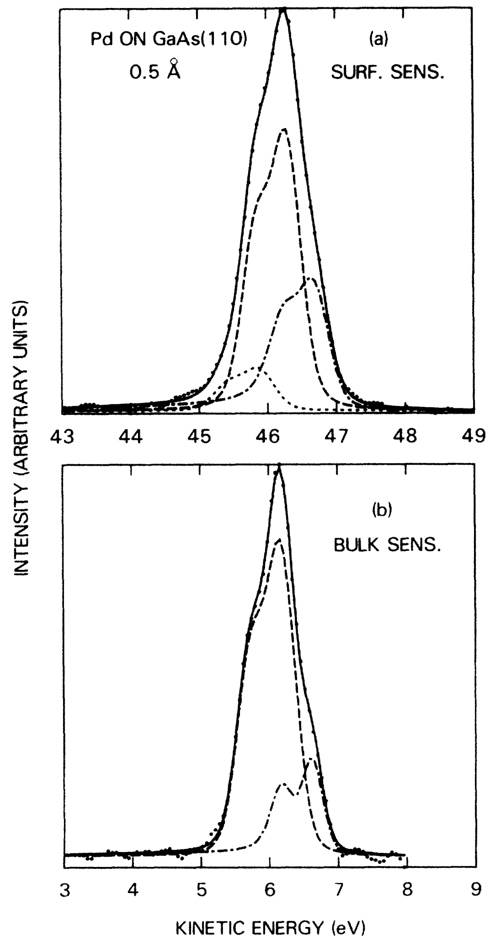

FIG. 9. Spectral decomposition of Ga $3d$ core levels for 0.5-Å coverage of Pd obtained under (a) surface-sensitive ($h\nu=70$ eV) and (b) bulk-sensitive ($h\nu=30$ eV) conditions. Note that contrary to Ti (Fig. 4) a remnant of the surface core-level contribution (dotted curve) is still discernible in (a).

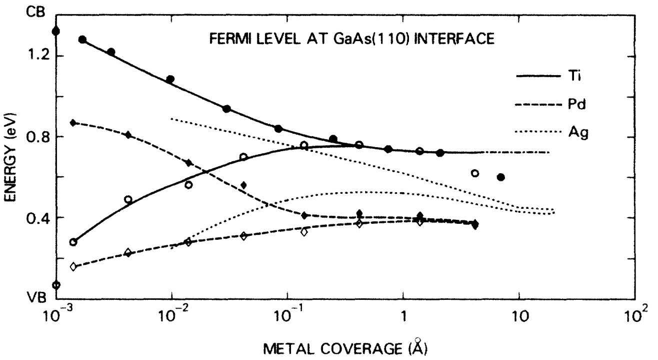

FIG. 10. Position of the Fermi level in the band gap as a function of metal coverage of Ti (solid line), Pd (dashed line), and Ag (dotted line) on n- and p-type GaAs(110). The clean-surface values are indicated on the left ordinate. VB indicates the valence band and CB the conduction band.

tions, one would expect that metals with few d electrons should be efficient donors and hence cause large band bending on p-type material compared to the band bending caused by a noble metal. Conversely, a metal with a nearly full d band should be an effective acceptor and cause band bending on a n-type sample. These trends are observed for Ti (d^2) and Pd (d^{10}). The formal number of d electrons should actually be somewhat smaller due to the reactions with GaAs as is evident from the chemical shift data. Furthermore, it should be noted that the chemical reactions proceed identically for both doping types. The results for Ag, a noninteracting metal, give additional support for this interpretation, although the contribution of the $5s$ electrons have been implicated as well in the pinning process.[4]

These results are clearly not compatible with the concepts of the unified defect model.[8] This model assumes that the Fermi-level position is determined by an intrinsic GaAs defect and is independent of adsorbate. For p-type semiconductors this level is thought to be at 0.5 eV and for n-type semiconductors the level is thought to be at 0.7 eV above the valence-band maximum. This position should be well established at 0.1-ML coverage and an abrupt change in the shape of the curve should occur between 0.001 and 0.01 ML, depending on the doping *concentration.*[22,23] Such a behavior can in no way be reconciled with our data. Furthermore, the intrinsic defect is thought to be generated by the metallization process. In the present case both Pd and Ti severely disturb the GaAs, thus potentially generating the required defects; yet the final pinning positions for the two metals are outside the range expected for a single intrinsic defect. Furthermore, the pinning position for both n- and p-type material is the same for all three metals. We believe this to be a general case, although previous results typically indicated a difference of about 0.2 eV.[8] The reason for the discrepancy can be attributed to the use of heavily doped substrates[22] and difficulties in extracting the true bulk signal under the surface-sensitive conditions commonly used. Furthermore, the assumption that the Fermi level for a well-cleaved p-type crystal is near the valence-band edge can lead to further errors, as even for doping levels in the low 10^{18} cm^{-3} the Fermi level lies about 0.07 eV in the band gap. In this work we have attempted to minimize such difficulties by use of both bulk- and surface-sensitive conditions and a combination of high-resolution spectroscopy and computer-aided spectral analysis in order to resolve and track the bulk spectral features.

VI. VALENCE-BAND SPECTRA

Some evidence to the origin of the interface states that pin the Fermi level for both Ti and Pd can be obtained from the valence-band spectra and, in particular, the valence-band difference spectra for various coverages. These are shown for Ti on n-type GaAs in Fig. 11; corresponding results were obtained on p-type material. The difference spectra were obtained by shifting the clean-surface spectrum by the amount of band bending obtained from the core spectra and adjusting the intensity of the As $4s$ level to coincide with that of the metallized spectrum. For coverages as low as 0.08 Å the valence spectra indicated extra emission at the position of the Fermi level, which is clearly evident in the difference spectra shown in (a) of Fig. 11. This rather sharp spectral peak grows rapidly in intensity with further Ti coverage. Its origin is unquestionably due to Ti d electron states. The onset of emission of the states begins at the Fermi level for all coverages, as indicated in Fig. 11. This correspondence between the emission and the position of the Fermi level, particularly at low coverages, establishes a new, previously not considered source of interface states that can determine the position of the the Fermi level at the interface, namely, the d orbitals of the transition-metal atoms. This notion is supported by other considerations as well. First, rebonding at the interface is expected to create bonding or nonbonding (donor) and antibonding (acceptor) levels, in agreement with the low-coverage data. That these states should lie in the band gap is suggested from theoretical calculations for substitutional transition-metal impurities, including Ti in GaAs and other binary *semiconductors*.[24,25] We do not try to suggest here that a simple substitutional defect is responsible for the pinning, but merely use the concept as a plausibility argument. The observed chemistry is too complicated to warrant such a simple view and not sufficiently known to suggest alternative complexes. Further evidence of the chemistry involving the Ti $3d$ electrons is indicated by the appearance of extra emission peaks in the valence spectra near 2 and 5 eV below the Fermi level, which suggest predominant hybridization with the Ga and As $4p$ electrons. Recent inverse photoemission experiments demonstrated the presence of empty d-orbital states in the band gap, which correlated well with the position of the Fermi level.[26] This observation lends strong support to a Ti substitutional impurity which exhibits both the acceptor and donor states needed to pin n- and p-type GaAs. Our results thus represent the first unequivocal spectroscopic identification of filled and empty band-gap states, although earlier work reported the presence of metal-induced states in the band gap for coverages at which metallic behavior is generally dominant.[27]

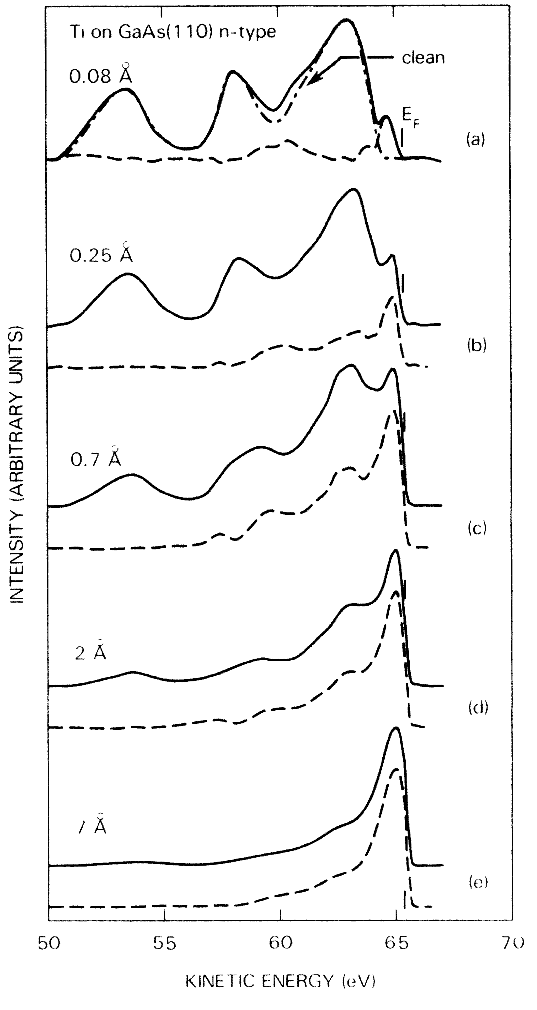

FIG. 11. Valence-band (solid line) and valence-band difference spectra (dashed line) for Ti on n-type GaAs(110). The dashed-dotted curve in (a) is the spectrum of the clean surface. In (b)—(e) the spectra have been separated vertically to clarify details. The vertical lines near the onset of emission marks the position of the Fermi level.

A second supportive argument for the proposed pinning states is based on their large density. A conceptual difficulty with the unified or intrinsic defect model concerns the generation of sufficient defects ($>10^{14}$ cm^{-2}) to pin the Fermi level in the metallic regime, usually for coverages $\gtrsim 0.5$ ML.[23,28] The chemical changes in the surface necessary to accommodate this defect density (several tenths of a monolayer) should have been detected by current high-resolution photoemission techniques, particularly for weakly interacting systems (e.g., noble metals, In, Ga, etc., on III-V semiconductors). This issue is not a problem with Ti. The observations throughout the studied thickness range indicate that the first few monolayers of Ti strongly interact with the GaAs. This provides a sufficiently large density of available states, as demonstrated by the top of the valence-band emission, to compensate for any metallic screening in the limit of thick coverage.

Similar conclusions can be reached for Pd. The valence-band emission curves, as well as the difference spectra are shown in Fig. 12. The noticeable difference from Ti is that the Pd $4d$ emission spectra is substantially broader and for similar coverages substantially more intense, both consequences of the filled d shell. Again, a direct correspondence is found at all coverages for both n- and p-type GaAs between the position of the Fermi level and the onset of d-band emission. As with Ti, at low coverage most of the hybridization of the Pd d electrons occurs with states near the top of the GaAs valence band, that is predominantly with the As and Ga $4p$ orbitals. The degree of interaction between the Pd and the GaAs appears to be more extensive than for Ti, as the metallic Fermi edge does not become Pd-metal-like until an ~20-Å coverage.

The results reported here are also inconsistent with the concept of metal-induced gap states, first proposed by Heine[29] and subsequently defined by Tejedor *et al.*[30] and Tersoff.[31] These models are based on the existence of continuum states in the metal that decay in the semiconductor (evanescent states), and therefore require metallic character of the overlayer at the interface. As Fig. 10 shows, the pinning of the Fermi level is essentially completed at coverages for which metallic behavior is observed (usually 0.5—1 Å of average metal thickness). Consequently, a different pinning mechanism is at least responsible in the low-coverage (<1 ML) range. If the onset of metallic character were to generate a second pinning level, one would expect to observe this experimentally by a change of slope in some of the curves of Fig. 10, unless the energetic position of both pinning levels is accidentally the same for each metal. Hence, there is no compelling reason to invoke a dual pinning mechanism for the three metals discussed here.

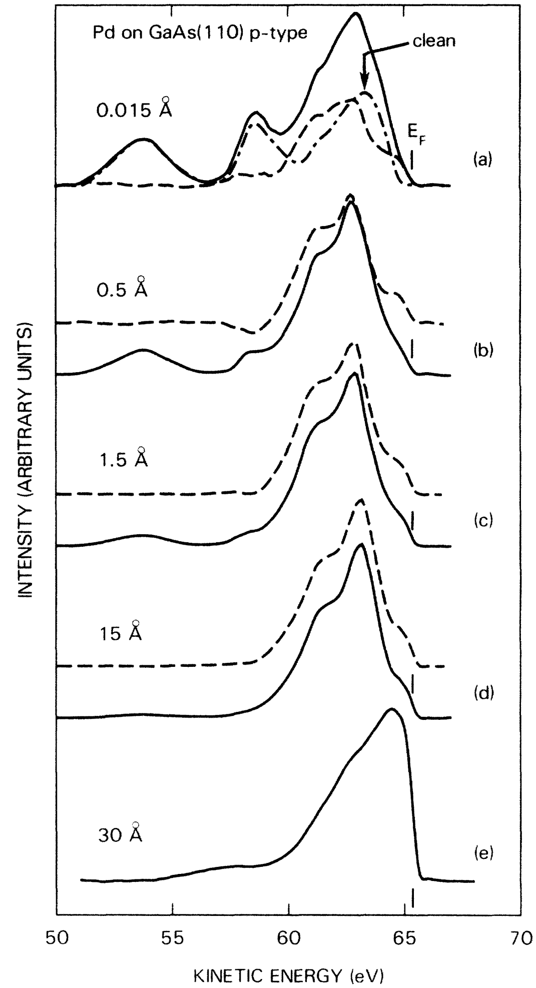

FIG. 12. Valence-band (solid line) and valence-band difference spectra (dashed line) for Pd on p-type GaAs(110). The dashed-dotted curve in (a) is the spectrum of the clean surface. In (b)—(d) the spectra have been separated vertically to clarify details. The vertical lines near the onset of emission marks the position of the Fermi level.

VII. CONCLUSIONS

In summary, we have studied trends in the chemical reaction of two d-electron metals deposited on cleaved GaAs surfaces. For both metals strong interactions with resulting out-diffusion of Ga and As are observed. Only a single Ga phase is observed for both metals. Considerable dilution is observed for Ga in Ti, with the resulting anomalously large binding-energy shifts due to Ti-host screening effects suggesting an alloy phase. For Pd, it is suggested that the Ga exists in a chemical phase which may also involve As. For both Ti and Pd the As exist in two separate phases in the surface region. One of the As phases on Pd has been assigned to elemental As. Subsurface reactions have been observed at very early stages of the interface formation. The results are similar to recently reported observations for oxygen on GaAs.[12] Thus concepts, such as microscopically abrupt interfaces, can no longer be tacitly assumed without careful experimental verification.

Finally, we have also seen that band bending caused by Ti or Pd on GaAs(110) cannot be explained by a native GaAs defect model. The large difference between the behavior of the two metals emphasizes the role of the metal-derived electronic states. We have observed the onset of strong metal d-electron emission at the Fermi level over a broad coverage range beginning near 0.01 Å and propose that the hybridized d-electron states are responsible for the pinning of the Fermi level at the interface. Because of the reactivity of the transition metals in general, it is suggested that the proposed mechanism is not restricted to the two metals studied here.

ACKNOWLEDGMENTS

We would like to thank the staff of the National Synchrotron Light Source, Brookhaven National Laboratory, for their assistance and hospitality. We gratefully acknowledge fruitful discussions with John Morar and Franz Himpsel, and the technical assistance of M. Prikas and A. Marx. This research was partially supported by the U.S. Army Research Office under Contract No. DAAG-29-83-C-0026.

*Present address: Institute of Microwave Technology, Box 70033, S-100 44 Stockholm, Sweden.

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