ly longer times. This may have been the case for the precession measurement of the 1.1-$\mu$s fission isomer[11] of $^{237}$Pu ($g = 0.17$) implanted into lead for which $g$ could be determined.

We have shown in the present work that $\alpha$-$\gamma$ recoil-implantation TDPAC experiments can be used to study the electronic properties of actinide ions, as well as to imitate in a simple way the recoil implantation of nuclei following nuclear reactions. For the case of Np in Pb we were able to determine that the Np is in the +6 ionization state, that its $5f$ electron is in a localized state, and that the atomic relaxation rate is $4.3 \times 10^{12}$ $\mathrm{s}^{-1}$. Lead was shown to offer a good perturbation-free environment for the Np implants. Some of the conclusions of the present work, even though deduced for the specific case of $^{237}$Np in Pb, are likely to be valid for other actinides as well.

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# Chemisorption-Induced Defects on GaAs(110) Surfaces

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Chemisorption of Ge on GaAs(110) at 320 °C simultaneously introduces acceptor- and donor-type surface states with the same density. The acceptor levels were found to be linked to $E_{cs}$. Under the assumption of the same behavior for the donor levels, the band bending versus coverage curve was calculated for samples at 20 °C, and very good agreement was found with the experimental data of Spicer *et al.* for metal overlayers on GaAs(110). It is concluded that chemisorption on GaAs(110) surfaces introduces a single type of defect.

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In recent years progress has been achieved towards an understanding of metal-semiconductor contacts and semiconductor heterostructures. For example, energy levels of defects formed already in the early stages of metal coverage were proposed to account for the barrier heights in metal-III-V-semiconductor contacts.

The formation of such defects was first considered by Spicer *et al.*[1] They found the band bending at GaAs (110) substrates to saturate at the same value with overlayers of different metals and of oxygen. This "pinning of the Fermi level" occurs at 0.65 and 0.9 eV below the bottom of the conduction band with $n$- and $p$-type substrates, respectively, and is completed for coverages larger than 0.1 of a monolayer.[2] These space-charge layers are caused by chemisorption-induced states since clean and well-cleaved GaAs (110) surfaces exhibit no intrinsic surface states[3-5] and therefore have flat bands. Spicer *et al.* concluded that chemisorption-induced donor- and acceptor-type states, respectively, are responsible for the pinning of the Fermi level at the interface, and they correlated these states with *two* different defects.

The formation of Ge:GaAs(110) heterostructures grown by the molecular-beam-epitaxy technique was studied by Mönch and Gant.[6,7] Up to a coverage of half a monolayer the changes in band bending $e_0V_s = E_{vs} - E_{vb}$ and in work function $\Phi = E_{\text{vac}} - E_{\text{F}}$ were found to agree within the limits of experimental error for both $p$- as well as $n$-type substrates. Since the work function of a semiconductor can be written as

$$\Phi = I - e_0 V_s - E_g + W_n = I - e_0 V_s - W_p, \tag{1}$$

the ionization energy $I = E_{\text{vac}} - E_{vs}$ remains unchanged by the chemisorption of Ge on GaAs (110). $W_n = E_{cb} - E_{\text{F}}$ and $W_p = E_{\text{F}} - E_{vb}$ are the bulk potentials. Thus, the more precisely determined $\Delta\Phi$-vs-$\theta$ curves could be read as band bending as a function of coverage. Least-squares fits to the experimental data yielded chemisorption-induced states of acceptor type at $E_{cs} - 0.55$ eV and of donor type at $E_{cs} - 0.88$ eV which are simultaneously present at a density of $0.06 \pm 0.04$ of the Ge atoms chemisorbed. These results strongly support the concept of defect formation during chemisorption. Gant and Mönch concluded that only *one* type of defect is produced.

It is of interest now to compare the experimental data obtained by Spicer *et al.* with the surface-state data evaluated by Gant and Mönch. However, both groups held their samples at different temperatures during the measurements, room temperature and 320 °C, respectively. In this temperature interval the band gap of GaAs varies by 0.13 eV.[8] The position of the defect levels with respect to the band edges as function of temperature is unknown and has to be determined experimentally. This can be done from measurements of the temperature dependence of the work function, as explained below.

The space charge of a depletion layer on an $n$-type semiconductor with donor concentration $N_D$ is given by

$$Q_{\text{sc}} = +[2\epsilon\epsilon_0 N_D(e_0|V_s| - k_B T)]^{1/2}. \tag{2}$$

Discrete, acceptor-type surface states of density $N_{\text{ss}}$ at $E_{\text{ss}}^A = E_{cs} - E_{\text{ss}}^a$ carry a surface charge

$$Q_{\text{ss}} = -e_0 N_{\text{ss}}\left[1 + 2\exp\left(\frac{E_{\text{ss}}^A - E_{\text{F}}}{k_{\text{B}}T}\right)\right]^{-1} \tag{3a}$$

which can be approximated to within 10% for band bendings $e_0|V_s| \geq E_{\text{ss}}^a - W_n$ by

$$Q_{\text{ss}} \approx -\tfrac{1}{2}e_0 N_{\text{ss}}\left(1 - \frac{-E_{\text{ss}}^a + e_0|V_s| + W_n}{k_{\text{B}}T}\right). \tag{3b}$$

Charge neutrality at the surface, i.e., $Q_{\text{ss}} + Q_{\text{sc}} = 0$, yields, together with Eqs. (2) and (3b), the band bending as

$$e_0|V_s| \approx \tfrac{1}{2}k_{\text{B}}T + E_{\text{ss}}^a - W_n, \tag{4}$$

for a doping of $N_D \approx 10^{18}$ cm$^{-3}$ and a density of surface states $N_{\text{ss}} \approx 5 \times 10^{12}$ cm$^{-2}$ corresponding to a coverage of 0.1 of a monolayer, the parameters of the experiment to be discussed. The work function is then given by

$$\Phi \approx I + \tfrac{1}{2}k_{\text{B}}T + E_{\text{ss}}^a - E_g. \tag{5}$$

Since the ionization energy is independent of temperature,[9] it follows that

$$\frac{d\Phi}{dT} \approx \tfrac{1}{2}k_{\text{B}} + \frac{dE_{\text{ss}}^a}{dT} - \frac{dE_g}{dT}. \tag{6}$$

Above room temperature the band gap of GaAs nearly linearly decreases with $dE_g/dT \approx -5.0 \times 10^{-4}$ eV K$^{-1}$,[8] and the temperature variation of the energetic position of the acceptor-type surface states results as

$$\frac{d(E_{cs} - E_{\text{ss}}^A)}{dT} \approx \frac{d\Phi}{dT} - 5.4\times 10^{-4}\ (\text{eV K}^{-1}). \tag{7}$$

The experimental setup has already been described.[6,7] Clean (110) surfaces were prepared by cleaving a Si-doped GaAs bar with $n(300\text{ K}) = 2.6 \times 10^{17}$ cm$^{-3}$ using the double notch and double wedge technique. Ge was evaporated from a molecular-beam effusion cell. The coverage $\theta$ is given in monolayers, which is defined as the total density of atoms in a (110) plane. During growth the sample was held at 400 °C. The changes in work function were measured by the Kelvin method.

A typical experimental result is shown in Fig. 1. Up to approximately 260 °C the work function of the sample increases in proportion to the temperature with a slope $d\Phi/dT = 4.6(\pm 0.9) \times 10^{-4}$ eV K$^{-1}$. At this temperature the curve exhibits a break, and the slope decreases to $d\Phi/dT = 2.8 \times 10^{-4}$ eV K$^{-1}$. The error bar of ±10 meV accounts for the reproducibility after repositioning of the Kelvin probe.

At low temperatures the acceptor-type behavior of the defects dominates on $n$-type GaAs since the Fermi distribution is sharp and is unity at the energy of the donor-type level. Thus, the above simple analysis can be applied. From Eq. (7) and the slope of the contact potential difference versus temperature (CPD-vs-$T$) curve below 260 °C the change in the acceptor-type defect level with temperature results as $d(E_{cs} - E_{\text{ss}}^A)/dT = -0.8(\pm 0.9) \times 10^{-4}$ eV K$^{-1}$, i.e., this level is linked to the lower edge of the conduction band.

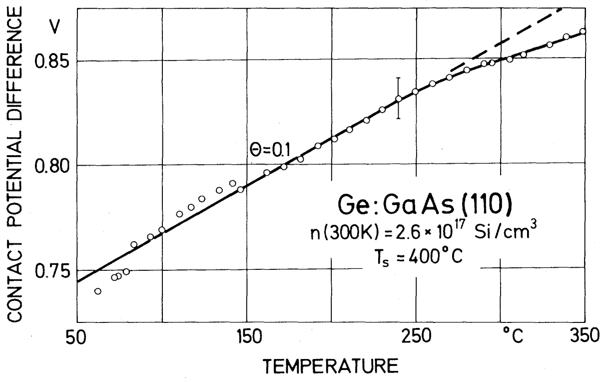

FIG. 1. Contact potential difference as a function of sample temperature for a (110) surface cleaved from $n$-type GaAs and covered with 0.1 of a monolayer of Ge at 400 °C.

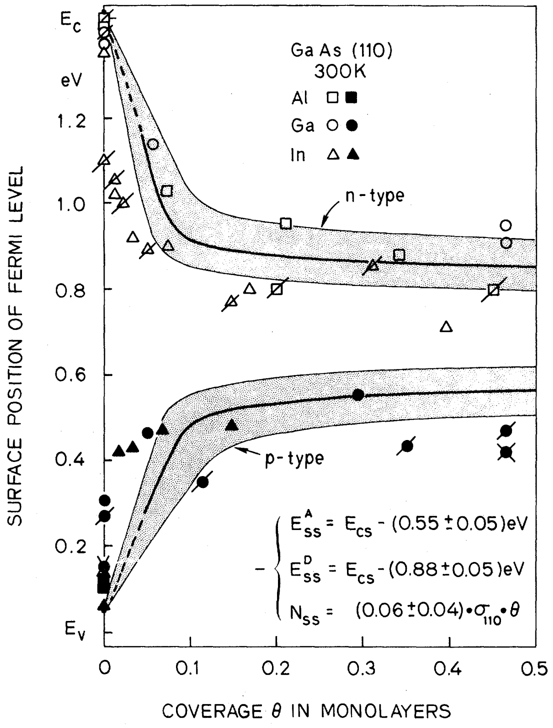

FIG. 2. Position of Fermi level with respect to band edges on (110) GaAs surfaces versus coverage as determined for various metals (Refs. 11 and 12) and calculated from data measured with Ge coverage (Ref. 7).

At higher temperatures the Fermi level moves towards midgap in the bulk, and the Fermi distribution broadens. This causes some of the defects to become positively charged, and the slope $d\Phi/dT$ will decrease, as observed experimentally. This result gives additional evidence for the acceptor- and the donor-type defect states being simultaneously present and supports the conclusion that only a single type of defect is formed during chemisorption of Ge on GaAs (110).

The analysis of the CPD-vs-$T$ curve cannot be carried out in detail for $T > 260\,^\circ$C, since other experiments[10] have revealed chromium to be present in the ingot. The temperature behavior of the donor-type defect level can be directly studied with $p$-type samples. Such experiments are in progress.

Since both levels, acceptor and donor, are thought to originate from one kind of defect it is *assumed* that the donor level is also linked to the conduction band. With this *sole* assumption the $e_0 V_s$-vs-$\theta$ curve can be evaluated not only for $n$-type but for $p$-type samples at RT as well.

The positions of the Fermi level with respect to the band edges at room temperature, as calculated by using the parameters of the surface levels induced by chemisorption of Ge on GaAs (110) and as measured by Skeath *et al.*[11,12] with metals evaporated onto GaAs (110), are compared in Fig. 2. Because of the high doping level in their samples, the depletion layers are only ≈150 Å in width. Since the average escape depth measures ≈12 Å the band bendings given by them have to be increased by 60 to 70 meV for $\theta > 0.1$. Within the limits of experimental error both sets of data agree. This supports the above assumption that the donor level is also linked to the conduction-band edge.

With In on $p$-type substrates the data seem to indicate a steeper increase for very low coverages. However, for the In source Skeath[13] quotes a large error in the evaporation rate.

One set of the data points for In on $n$-type GaAs shows an initial band bending of approximately 0.3 eV. At a coverage of $\theta \approx 0.1$ these data points merge with those obtained with substrates exhibiting (nearly) no band bending in the beginning. The same behavior was found with Ge on $n$-type GaAs (110) surfaces while for $p$-type substrates the same $e V_s$-vs-$\theta$ dependence was always measured (see Fig. 1 in Ref. 7). Initial band bendings on the $n$-type substrates are caused by acceptor-type surface states introduced by cleavage steps.[4,5,14,15] Their energetic position, $E_{cs} - E_{st}{}^a = 0.8$ eV,[15] is different from the chemisorption-induced levels. The temperature dependence of the work function clearly showed that no donor-type surface states are correlated with cleavage steps on GaAs.[15] This means that the chemisorption-induced defect states can in no way be related to those correlated with cleavage steps, as was tried recently.[16]

The step-related states are destroyed by coverages up to 0.1 to 0.2 of a monolayer (see Fig. 2, and Fig. 1 in Ref. 7). Above this coverage the band bending is homogeneous over the whole surface of *n*-type samples regardless of differing distributions of steps. This explains the observations that photoemissive electron energy-distribution curves (EDC's) measured with *p*-type samples always exhibit sharp valence-band features while they are much less pronounced in EDC's of most *n*-type samples; covering those *n*-type substrates with approximately 0.1 of a monolayer of metal or oxygen gives sharp EDC's, too (e.g., see Refs. 11 and 17). Local variations in the density of cleavage steps, and thus in band bending, spatially result in rigid shifts of the valence band with respect to the Fermi level, and, when photoemission samples a nonuniformly stepped area, the EDC measured exhibits no sharp features. However, these are restored after adsorption has eliminated the step states.

Since, as Fig. 2 shows, the $e_0 V_s$-vs-$\theta$ data of metal-covered GaAs (110) surfaces are very well described by the surface-state parameters determined from Ge chemisorption on such surfaces, it is to be concluded that chemisorption on GaAs (110) surfaces generally creates only one type of defect. These defects are stable between room temperature and 400 °C. The observed donor- and acceptor-type levels are the occupancy levels for the differently charged defects $D^+$, $D^0$, and $D^-$. The energetic distance $E_{ss}{}^A - E_{ss}{}^D = 0.33$ eV is then the Coulomb repulsion energy which was calculated as 0.25 eV for the silicon bulk vacancy[18] and as 0.3 eV for the $P_{Ga}$ antisite defect in GaP.[19]

The nature of the defects is open to discussion. The linking of the defect levels to the conduction-band edge indicates that they are conduction-band–derived states. Daw and Smith[20] calculated two energy levels for arsenic surface vacancies at 0.54 and 0.86 eV below the conduction-band edge. On the other hand, Allen and Dow[21] considered surface antisite defects and found, for As on Ga sites, two levels at 0.45 and 0.85 eV below the conduction-band edge. Both groups claim that the defects considered can explain the trends in the barrier heights of Au Schottky contacts and metal-insulator-semiconductor structures in the $Ga_{1-x}Al_xAs$ and $In_{1-x}Ga_xAs$ alloy series (see references in Refs. 21 and 22). This means that further experiments are necessary to clarify the type of defect produced by chemisorption on GaAs (110) surfaces.

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