Charge Accumulation at InAs Surfaces

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Angle-resolved photoelectron spectroscopy has been used to directly prove the existence of a charge accumulation layer at clean InAs surfaces. The formation of an accumulation layer is shown to be a common property of polar InAs surfaces, with the precise surface Fermi level position above the conduction band minimum determined by the surface geometry. The emission from states in the accumulation layer is studied with respect to its photon energy and angular dependence. [S0031-9007(96)00127-5]

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Interfaces involving InAs have long been known to exhibit unusual properties [1–3], e.g., negative resistivity at Schottky contacts, type III alignment at heterojunctions, and charge carrier sign-inversion in *p*-doped samples. These effects have been explained as due to formation of an electron accumulation layer in the near-interface region, i.e., a peculiar tendency of InAs to adjust its energy bands in such a way that the Fermi level (E_F) becomes located above the conduction band minimum (CBM). More recently, charge accumulation on an adsorbate covered InAs surface has been studied by electron spectroscopical methods [4]. While these observations were early established, their physical origin was not clarified. The natural question was therefore raised whether such electron accumulation also occurs on atomically clean InAs surfaces. Indeed, from observations of plasmon excitations in HREELS experiments on As- and In-terminated InAs(100) surfaces it was concluded that this is the case [5]. In accord with the earlier experiments it was found that the accumulated charge is in the range of 10^{12} cm^{-2}. Furthermore, the data inferred that although the charge is located in the surface region, its density at the outermost surface layer is vanishingly small, as expected for a quantum well confined electron gas.

Angle-resolved photoelectron spectroscopy (ARPES) is the most direct method for detailed characterization of occupied electron states. In this work we have used ARPES to study several clean InAs surfaces, and show that charge accumulation is a common phenomenon for InAs. It is also shown that the excitations reflected by photoelectrons from the electron gas occur within a vary narrow phase range, at the center of the three-dimensional Brillouin zone. In agreement with the mentioned HREELS results, we find that the presence of the electron gas is doping independent. This observation, together with the fact that the effect is found on very different surfaces, leads us to the conclusion that the accumulated charge most likely stems from native surface defects.

The experiments were carried out at beam line 41 at the Swedish national synchrotron radiation facility MAX-lab [6,7]. All spectra reported were excited with *p*-polarized light, and recorded in the plane of incidence. The overall experimental energy resolution was approximately 0.1 eV, and the angular resolution 2°. The samples were 1×1 cm^2 pieces of double-sided polished *n*-type (8.7×10^{16} cm^{-3}) InAs(111) and both *n*- and *p*-type (3.0×10^{16} and 2.1×10^{17} cm^{-3}, respectively) InAs(100) wafers. Two preparation methods were used for each surface: repeated cycles of 500 eV Ar$^+$ sputtering and annealing (IBA) and molecular beam epitaxy (MBE) in a dedicated MBE system connected to the photoelectron spectrometer.

The following surfaces were studied: InAs(111)-(2×2) (IBA and MBE), InAs($\bar{1}\bar{1}\bar{1}$)-(2×2) (MBE), InAs(100)-(4×2) (IBA and MBE), and InAs(100)-(2×4) (IBA and MBE). In all cases the surfaces were well ordered, as judged by the quality of the electron diffraction (LEED and RHEED) patterns and the valence band photoelectron spectra.

Figure 1 shows a photoelectron spectrum from the IBA-prepared InAs(111)-(2×2) surface, covering the energy region of the upper valence bands and the lowest conduction band. The indicated location of the valence band maximum (VBM) is based on analysis of In 4*d* emission [6] and the In 4*d*–VBM separation [8]. Focusing on the energy region of the conduction band, a small peak "*P*" is seen. The high-energy cutoff of *P* is at the same energy as E_F; i.e., the surface is metallic. We also note that the separation between the low-energy edge of this peak and VBM corresponds well to the band gap of InAs. The angular dependence of peak *P* around the surface normal is shown in Fig. 2. As the emission is observed only over a very limited angular range (0° ± 2.5°), it must reflect electron states strongly confined in reciprocal space.

Another characteristic feature of peak *P* is its intensity dependence upon photon energy. Figure 3 displays a set of normal emission spectra obtained for the (111)-(2×2) surface. From this sequence of spectra it is clear that the intensity exhibits pronounced variations, with local maxima at approximately 20 and 44 eV photon energies. Combined with the strongly dispersive behavior

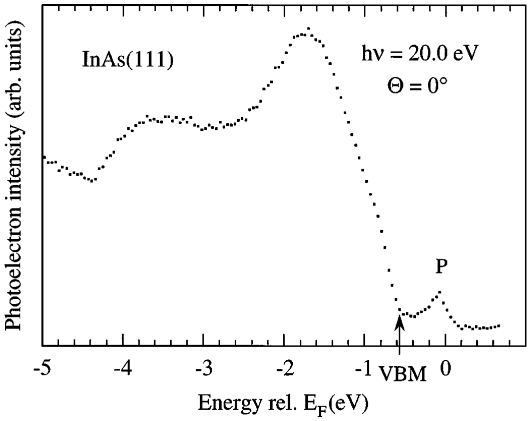

FIG. 1. Photoelectron spectrum from an IBA-prepared InAs(111)-(2 × 2) surface showing the presence of a narrow peak “*P*” just below E_F. The E_F energy was determined by photoemission from a Mo foil.

(revealed by the narrow angular range of observation), these intensity variations show that the excitation is of the direct interband type. The photon energies at which intensity maxima should be expected can be estimated from simple model calculations. Assuming free-electron-like final bands and an inner potential of 8 eV (found appropriate in analysis of valence band spectra from InAs [6]), we find that interband excitations of states at CBM should occur around 41 eV photon energy, in fair agreement with the observed intensity maximum at 44 eV. A similar intensity maximum is found at 26 eV photon energy in off-normal spectra probing the $\overline{\Gamma}_{1\times1}$ point in the $\overline{\Gamma}\overline{M}'$ azimuth, which is close to a value of 24 eV predicted by the simple model. These findings suggest that peak *P* represents excitations from the center (Γ) of the bulk Brillouin zone (BZ), i.e., states at CBM. We note that our observations strongly resemble those reported for CBM photoemission from heavily Sb-doped Si(100) [9]. It is, however, also true that quite similar spectral properties can be displayed for emission from a surface state [7]. Therefore, before definitely deciding on the assignment, we must consider the possibility that peak *P* may be due to a surface state.

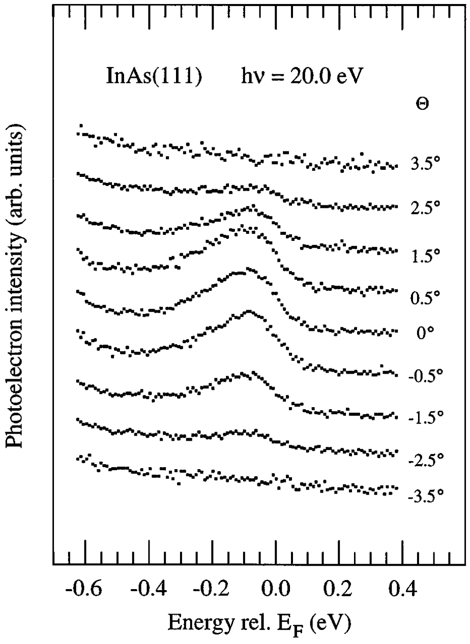

FIG. 2. The angular dependence near normal emission of the peak *P* seen in Fig. 1.

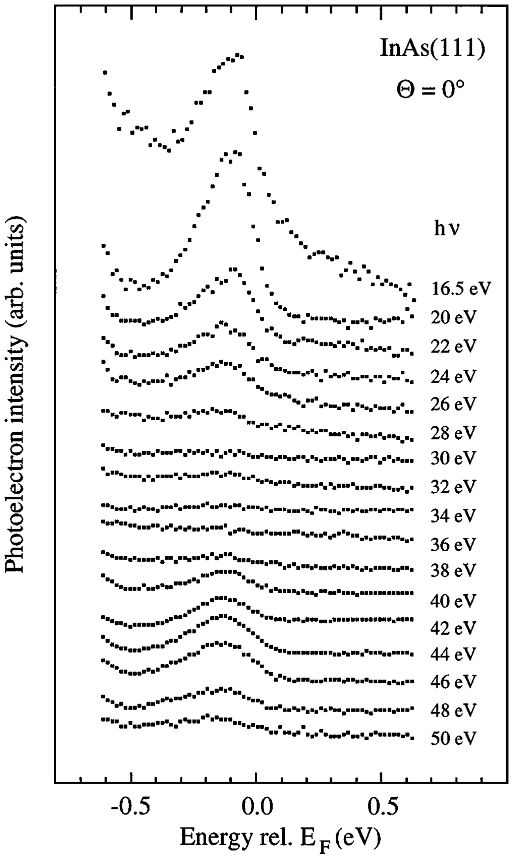

FIG. 3. Normal emission spectra from InAs(111)-(2 × 2).

To distinguish between these two interpretations, we make use of the fact that in the case of a reconstructed surface, the central peak of different surface BZs ($\overline{\Gamma}$) do not always coincide with the projected bulk BZ central peak (Γ). More specifically, for the (111)-(2 × 2) surface the center of the second surface BZ does not coincide with a bulk BZ center, a situation which is described at the top part of Fig. 4. Thus, any spectral features related to the bulk center should be observed at the first and third $\overline{\Gamma}$, but not at the second one. On the other hand, structures representing excitations at $\overline{\Gamma}$ (i.e., surface states) should be present at all $\overline{\Gamma}$ points. Spectra representing $\overline{\Gamma}$ points of the first, second, and third zones of the (111)-(2 × 2) surface are displayed in Fig. 4. We see directly that the peak is missing at the center of the second surface BZ. This allows us to conclude that peak *P*

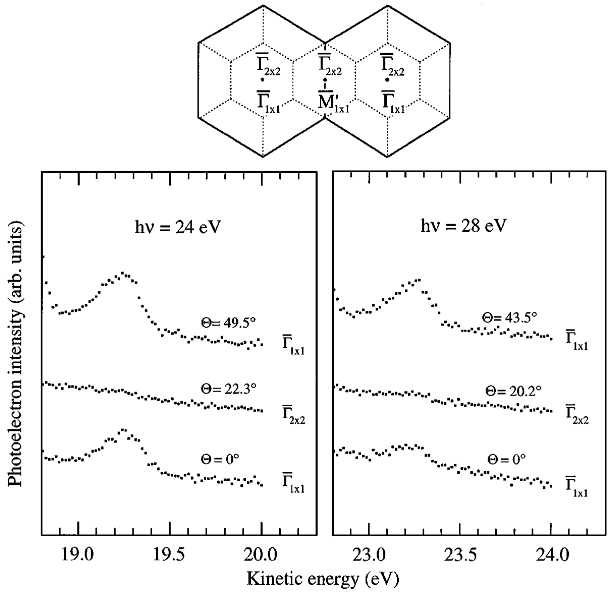

FIG. 4. Spectra from InAs(111)-(2×2) covering the CBM energy range at emission angles corresponding to the surface BZ center of an ideal and a reconstructed (111) surface.

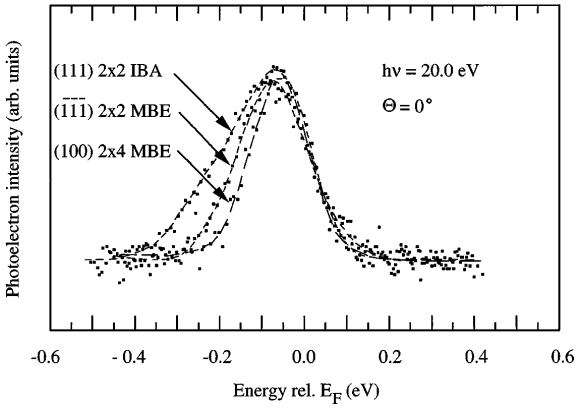

FIG. 5. Spectra of the peak below E_F for different InAs surfaces. The spectra are normalized at their maximum intensity.

indeed reflects an excitation at the center of the *bulk* BZ. Consequently, the charge accumulation layer must extend into the crystal significantly deeper than the range of the surface reconstruction. Having definitely associated peak P with conduction band states within the potential well formed by the downwards band bending, the charge density can be estimated. Under the assumption of a two-dimensional free-electron gas with an effective electron mass of $0.023m_0$ and the Fermi energy at 0.2 eV above CBM, we arrive at an electron density of $\sim 10^{12}$ cm^{-2}. These results are consistent with the mentioned HREELS-based conclusions [4,5]. The derived electron density is indeed a very small number on the sensitivity scale of photoelectron spectroscopy. The momentum selectivity in angle resolving photoelectron spectroscopy, however, makes the states clearly observable due to their localization in **k** space.

In the mentioned HREELS study of InAs(100) it was found that the charge density is an order of magnitude higher on the As-terminated surface than on the In-terminated one [5]. Our studies of these two surfaces (the MBE-prepared 2×4 and 4×2 reconstructions, respectively) fully confirm these observations: For the 2×4 surface E_F was found to be pinned well above CBM, and a clear emission from the CBM states was observed. For the 4×2 surface, on the other hand, the E_F position was very close to CBM, and no emission above VBM could be detected. Reversible switching between the two situations was also confirmed.

Examination of a variety of surfaces showed that emission from CBM is a common feature of InAs, though the precise E_F position can vary somewhat between different reconstructions. Figure 5 exemplifies this observation for the A and B sides of a (111) wafer and for a (100) surface. While somewhat different E_F pinnings were observed on different surfaces, the substrate doping has no decisive influence in this context, at least at the present doping levels. This conclusion is based on the observation of different pinnings on the two sides of the same (111) crystal, and on the fact that similar pinnings were observed on n- and p-doped (100) crystals with the same surface structure.

The combined observations clearly point towards a general tendency of InAs surfaces to have E_F pinned above CBM. To identify the nature of the electronic states responsible for this pinning, we first consider the surface band structure of the studied surfaces. From previous studies of surface electronic structure of different III-V surfaces, it can be concluded that surface states at InAs surfaces are very similar to those at the corresponding surfaces of, e.g., GaAs. This means that in none of the cases has it been possible to detect an occupied surface state above VBM. The surfaces are therefore intrinsically semiconducting rather than metallic. The same conclusion is reached from electron counting arguments. We can thus rule out the possibility that "regular" surface states are acting in the pinning process. The obvious alternative in the present context is native point defects which, in fact, are known to pin III-V semiconductor surfaces (with the exception of those prepared by cleavage). In a study of native defects in III-V compound semiconductors it was actually proposed that cation antisites could provide the pinning levels needed to locate E_F far up in the conduction band in InAs [10]. Their charge is then transferred into the lower lying states at CBM.

Predicting the abundance of such defects is by no means an easy task [11]. However, we note that to obtain charge neutrality the charge at CBM must be the same as the ionized donors. It can thus be concluded that the surface defect density is at least $\sim 10^{12}$ cm^{-2}, which corresponds roughly to 0.1% of a monolayer. From previous discussions of E_F pinning at semiconductor surfaces [12] (mainly in the context of the Schottky barrier problem) we also know that for typical dopings in the range $10^{16}-10^{17}$ cm^{-3} the surface E_F becomes pinned by defect densities above $\sim 10^{12}$ cm^{-2}.

Returning to E_F pinning at Schottky contacts, it is likely that in this case the native defects are screened by metal induced gap states [13]. Following previous discussions of the Schottky barrier problem, the pinning should then be expected to occur at the "effective midgap energy" E_B [14]. This is a property of the three-dimensional band structure of the semiconductor and is defined as the energy at which the character of electron states turns from valence to conduction bandlike. In InAs this point is located well above CBM, a peculiar feature resulting from the excursion of the lowest conduction band well below the "average" conduction band minimum [15]. Considering the unusual location of E_B in InAs, it is interesting to note that similar pinning situations are encountered on clean surfaces and at InAs-metal interfaces. In this respect InAs does not differ from other compound semiconductors, and it is tempting to suggest that the two pinning mechanisms are connected. In the case of one-dimensional systems it has in fact been pointed out that "surface states" which pin E_F (i.e., neutral when half filled) tend to fall near E_B [16]. In this sense, it appears that defect states behave similarly.

Finally, we make a few comments on the reduced dimensionality of states in the accumulation layer. In the two-dimensional potential well formed by the downwards band bending at the surface, the electron states should be quantized along the surface normal. On oxidized InAs, quantization was early inferred from magnetoresistance experiments [3], and was clearly demonstrated by means of electron tunneling [17]. This picture is also supported by the more recent HREELS studied of clean InAs(100) and hydrogenated InAs(110) [4,5]. According to results from Shubnikov–de Haas studies of a metal-oxide-InAs interface [18] two subbands are expected to be occupied in the case of a charge density of $\sim 10^{12}$ electrons cm^{-2} and from the mentioned electron tunneling experiment the energy splitting of the two lowest subbands is ~ 0.1 eV. One characteristic property of the quantum states is a vanishing amplitude at the barrier. In photoemission, which is a very surface sensitive probe to begin with, one should then expect to find an increasing intensity from these states with increasing probing depth. From the spectra in Fig. 3 it may indeed look like this is the case: The maximum intensity observed at 20 eV photon energy (probing depth of ~ 10 Å) is about 4 times larger than at the second maximum around 44 eV photon energy (probing depth ~ 5 Å). However, it should then be stressed that similar intensity differences are found in the emission around VBM, so we must conclude that observed intensity variations do not reflect the expected properties of the lowest confined states. On the other hand, detailed examination of the spectral shapes (Fig. 5) shows that the peak observed on surfaces with the highest pinning is asymmetric. Assuming that the more symmetric spectral shape, found for the more shallow pinning positions, arises from a single populated quantum state, this asymmetry could be explained as due to population of a second state, in accord with previous literature.

In conclusion, we have used ARPES to obtain direct evidence for the existence of charge accumulation on free and clean InAs surfaces. From the angular dependence we have been able to conclude that the emission derives from conduction band states. By examining spectra from different surfaces on differently doped crystals, we have found that the phenomenon is a general property of InAs.

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