2D electron gas formation on InAs wurtzite nanosheet surfaces

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ABSTRACT

The two-dimensional electron gas (2DEG) that forms on a semiconductor surface can be used to explore a variety of phenomena in quantum physics and plays an important role in nanoscale electronics, such as transistors. Controlling its formation is, thus, relevant. Using angle-resolved photoemission spectroscopy (ARPES) and accumulating the signal over many nanocrystals, we find that on clean InAs nanosheets with non-polar surfaces and wurtzite (WZ) crystal structures, a 2DEG can be observed at the C-point. We suggest that the step morphology on the WZ InAs specimens facilitates the appearance of the electron gas, since previous studies on InAs nanowire surfaces with the same crystal facet and a similar defect density did not exhibit a 2DEG. Subsequently, bismuth deposition leads to the disappearance of the 2DEG as well as a shift of the valence band. This is in contrast to previous observations on InAs surfaces, in which metal deposition would lead to the formation of a 2DEG. The control of the 2DEG with the addition of Bi atoms is relevant for applications of InAs nanosheets in quantum technologies. This study also illustrates that ARPES accumulated over several 2D materials oriented randomly around their normal axis can provide valuable information on their band structure with a fast turnover and low irradiation.

InAs is a compound semiconductor that crystallizes in a zinc blende (ZB) structure when grown in bulk. However, it can be synthesized with a wurtzite (WZ) crystal phase in one-dimensional (1D) and two-dimensional (2D) materials by fine-tuning the growth parameters. Due to its high carrier mobility, direct bandgap in the IR range, and large spin–orbit coupling, InAs has potential applications in optoelectronics, high-speed/low-power transistors, and topological quantum computing technologies. It exhibits a narrow and direct bandgap at the C-point. Studies on the band structure of bulk InAs samples revealed that an electron accumulation layer often occurs on reconstructed, polar InAs surfaces. For non-polar surfaces, a 2D electron gas (2DEG) has been observed upon deposition of metallic atoms, surface reconstruction, and sulfur incorporation. 2DEGs have recently been the subject of considerable interest for studies on quantum physics and technologies (e.g., gatemon qubit), observations of Shubnikov–de Haas oscillations, hybrid topological superconductor devices, and wavelength conversion. Introducing Bi into the InAs lattice as a substitution of As is predicted to reduce the overall bandgap at the C-point until a Dirac–Weyl semimetal forms for pure InBi.

Previous studies on the incorporation mechanism of Bi into the surface of InAs WZ nanosheets have shown that the formation of InBi can be achieved in the top layer by increasing the substrate temperature. Angle-resolved photoemission spectroscopy (ARPES) is a powerful tool to determine the electronic nature of materials by directly measuring their band structures. Generally, a well-prepared surface of single crystals is needed to obtain good results. Since the angular
distribution of the observed band structure is related to the crystal orientation, polycrystalline samples will lead to a smearing out of the ARPES structure. As a result, micro- or nano-ARPES is often used to study, e.g., 2D nanoflakes, nanowires, or other confined structures.26–28 However, while summing the signal over nanostructures with completely randomly oriented crystal facets will not yield any meaningful ARPES data, an assembly of small 2D-like samples (e.g., InAs nanosheets) deposited on a flat wafer substrate still maintains a high degree of symmetry parallel to the surface plane. As their main crystal facet is facing toward the x-ray beam and the electron analyzer, interesting and meaningful information can still be acquired, despite the accumulation over the rotation around the normal axis of the nanosheets.

We present experimental ARPES data of WZ(11\(\bar{2}\)0) crystal facets on InAs nanosheets, including the band structure at the high symmetry points M and \(\Gamma\) displaying a 2DEG after the removal of the native oxide. Furthermore, we show the dispersion of the valence band (VB) along the \(\Gamma\)–K direction. Manipulation of the band structure at the \(\Gamma\)–point, induced by Bi deposition, is also observed. The study shows the relevance of ARPES even when summing over azimuthally disordered 2D materials.

InAs nanosheets were grown by molecular beam epitaxy1 and contact transferred on standard Si and GaN substrates with native oxides, as done for nanowires in previous studies.27 Briefly, the Si or GaN sample was placed in mechanical contact with the growth substrate exhibiting vertically grown nanosheets. By applying gentle, directional pressure, nanosheets were broken off and attached onto the Si or GaN surface. The width of individual nanosheets varied between 100 and 500 nm with an average length of 1.5 \(\mu\)m and a thickness of 20 nm. Due to the growth process, monolayers of ZB(110) can intercept the otherwise pristine WZ(11\(\bar{2}\)0) crystal facets. Figure 1(a) indicates the deposition density of nanosheets on a Si substrate and their lateral morphology via scanning electron microscopy (SEM). The native InAs oxide was removed in ultra-high vacuum (UHV) by heating the sample to 400°C and exposing it to atomic hydrogen, generated by a thermal cracker at an H\(_2\) pressure of 5 \(\times\) 10\(^{-6}\) mbar, which is a standard procedure.28 The unreconstructed, oxide-free surface was mapped via an Omicron scanning tunneling microscope (STM) at room temperature with a tungsten tip (see Fig. 1 and the supplementary material for larger overview areas). Later, Bi was evaporated from a low-temperature effusion cell for 1 h, while annealing the sample to 300°C. Subsequently, an additional annealing step was performed keeping the sample at 250°C for about 20 min. Data were recorded after each process step at around 35 K at the SGM3 beamline29 of the ASTRID 2 synchrotron in Aarhus with p-polarized x rays, a beam spot size of 90 \(\times\) 190 \(\mu\)m, and an energy resolution below 100 meV. By identifying the nanosheet region with the highest intensity of the In 4d core level signal on each sample, the optimal measurement positions were chosen. The data presented in each spectrum originates from a single measurement area, respectively. In each measurement area, several nanosheets were simultaneously exposed to the x-ray beam, resulting in an accumulative signal of these nanostructures.

After removing the native oxide, the quality of the nanosheet surfaces was confirmed with x-ray photoemission spectroscopy (XPS) for the As 3d and In 4d core levels for 70 and 130 eV photon energies at the corresponding ARPES measurement positions, as demonstrated in Fig. 1(c) (see the supplementary material for XPS spectra of all process steps). In both spectra, neither In nor As oxide species (should be at higher binding energies with respect to the InAs component30) nor metallic In (should be at lower binding energies31,32) or As (should be at higher binding energies between the oxide and InAs bulk component30) were observed. From these spectra, we conclude that the nanosheets are oxide free, and no metallic In clusters have formed on their surfaces during heating.

The corresponding ARPES spectrum is shown in a combined plot on the left side in Fig. 2(a). The data were recorded with 25 eV photon energy in normal emission at the \(\Gamma\)–point, and the entire spectrum can be seen in Fig. S3 in the supplementary material. After removing the native oxide, a parabolic band with a maximum at around 0.5 eV and an electron pocket ranging from the Fermi level to around 0.2 eV are detected. We interpret these as the onset of the VB

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**FIG. 1.** (a) SEM images showing the overall distribution and size variations of the InAs nanosheets on the measurement sample. (b) STM image of the WZ(11\(\bar{2}\)0) top facet of an InAs nanosheet. The arrow indicates four monolayers of ZB(110) present in the crystal (\(V = -3\) V and I = 100 pA). (c) XPS spectra of the As 3d (photon energy 130 eV) and In 4d core level (70 eV). No components related to oxides or metallic states are visible.
and a 2DEG, respectively. Cuts at distinct binding energies, as shown in Fig. 2(b), illustrate the pocket size of the 2DEG, the shape of the VB, and an overall radial symmetry in the in-plane momentum space. We observe a gap of \( \sim 350 \text{ meV} \) between the onset of the valence band and the 2DEG [see Fig. 2(c)] (information on the fitting procedure can be found in the supplementary material). This gap energy is slightly smaller compared to bandgap measurements done with other techniques on InAs WZ\((11\bar{2}20)\) nanostructures.\(^{36-39}\) Since the energy of the 2DEG does not necessarily coincide with the conduction band minimum,\(^40\) we expect the actual bandgap to be even smaller. A more detailed distinction between the 2DEG and the conduction band minimum is present in the supplementary material. Generally, a bandgap narrowing at the surface of InAs due to the presence of an electron gas has been observed before,\(^40\) and we attribute its presence to band bending at the InAs WZ surface induced by the steps along the crystal edges as will be explained later.

The VB appears to be smeared out, which can be attributed to \(k_z\) broadening of the band structure as a result of low-photon energies and a subsequent small escape depth of the photoelectrons.\(^{41}\) We also considered a potential broadening due to the presence of segments of ZB\((110)\) crystal phases inside the InAs nanosheets, which exhibit a signal for \(\Gamma\) at the exact same energy as WZ\((11\bar{2}0)\). However, based on surface analysis via STM, we believe that the \(k_z\) broadening is dominating since layers of ZB contribute less than 10% to the nanosheets compared to the WZ\((11\bar{2}0)\) facet.

By performing a photon energy scan, the dispersion of the VB along the \(\Gamma-K\) direction is detected [see Fig. 3(a)]. At a photon energy of around 72.5 eV, a valley with a minimum binding energy of \(\sim 3.7 \text{ eV}\) is found, as shown in Fig. 3(b). The M-point for the WZ reciprocal lattice is expected to become visible for photon energies around 66 eV based on free electron final state calculations and shown in Fig. 3(c) (more details can be found in the supplementary material). By comparing to previous \textit{ab initio} calculations,\(^39,42\) we find a good agreement between the experimental results and the theoretically calculated dispersion and multiple energy states at the M-point. Therefore, this band minimum is attributed to the M-point of the WZ\((11\bar{2}0)\) lattice.

Noteworthy, \(k_z\) broadening seems to be more pronounced at \(\Gamma\) in the center of the Brillouin zone as compared to the \(M\) symmetry point at the edge. This is a result of the stronger dispersion of the VB between \(\Gamma\) and \(K\), and therefore, an expansion of available energy states toward \(K\), in comparison to the dispersion between \(K\) and \(M\), as can be seen in Refs. \(39, 42, \) and \(43\).

\(\Gamma\)-points of adjacent Brillouin zones can be detected by increasing the photon energy further. We expect another \(\Gamma\)-point to appear at around 123 eV photon energy (see the supplementary material for more details on the free electron final state calculations), which is in good agreement with the signal detected at 121 eV. Even though the adjacent Brillouin zones are visible at higher photon energies, the overall signal decreases drastically, and an observation of the 2DEG is not possible.

By comparing the ARPES spectrum for oxide-free WZ\((11\bar{2}0)\) nanosheets with results for bulk InAs ZB\((110)\), it is interesting to note that 2DEGs on ZB\((110)\) substrates have only been observed after metal deposition.\(^7\) Therefore, we expect specific surface effects, i.e., the particular defect and step structure, on the InAs WZ\((11\bar{2}0)\) nanosheets to induce an electron gas.\(^6\) Our STM data (see Fig. S1) indicate that very few single-point defects are present in the nanosheet surfaces in
Contrast to line defects. This results in a large number of step edges on each nanostructure after removing the native oxide. Therefore, we believe that the single-point defects do not significantly contribute to the appearance of the 2DEG. This is in agreement with scanning tunneling spectroscopy (STS) experiments carried out on InAs nanowires with the same (1120) crystal facet and similar single-point defect density. Point defects induced only local band structure alterations. No long-range Fermi level pinning was detected, and thus, no electron accumulation. Hence, we conclude that the large number of line defects, i.e., the step morphology on the surface of the InAs nanosheets, leads to the presence of the 2DEG also observed via STS for InAs using the ARPES signal summed over many nanostructures.

Finally, by comparing measurements from regions with and without InAs nanosheets, we find that the detected signals are solely originating from the nanostructures. We do not observe any band structure for the Si substrate for photon energies between 18 and 120 eV due to the surface sensitivity of ARPES and the presence of the native Si-oxide. Additionally, measurements were carried out with GaN as carrier material. Both substrate types exhibit significantly larger bandgaps [Si: 1.12 and GaN: 3.4 eV (Ref. 47)] compared to InAs. Very similar ARPES data were collected (see Fig. S3 in the supplementary material), confirming the sole origin of the detected band structures from the InAs WZ nanosheets once more.

We now turn to the data obtained after depositing Bi onto the sample, while annealing to 300°C. Band structure changes at the Γ-point are observed in the ARPES spectrum when accumulating the signal over several 2D nanosheets, as shown in Fig. 2. The right side of Fig. 2(a) depicts the subsequent shift of the VB upwards by ~90 meV [also observable in Fig. 2(c)] with an upwards shift of the VB at the Γ-point. This indicates that the incorporated Bi atoms lead to a significant reduction in the number of free electrons on the surface. As discussed earlier, the 2DEG is expected to originate mainly from the step and edge morphology of the nanosheets. Earlier studies have shown a predominant InBi formation in the surface of InAs WZ nanosheets for Bi deposition at elevated temperatures, indicating the substitution of As atoms by Bi. It is reasonable to assume that this substitution process starts along step edges and was, indeed, observed for GaAs nanowires displaying a WZ(1120) crystal structure. Therefore, the incorporation of Bi atom starting along the edges of the surface terraces subsequently alters the electronic structure of the nanosheets, leading to the disappearance of the 2DEG and an upwards shift of the VB at Γ as observed in our experiments. As mentioned above, depositing other metals on InAs has led to the formation of an electron gas at the surface. However, as the Bi atoms can naturally bond with In, forming a semiconductor compound, the situation appears to have the opposite effect in the present case. A similar shift of the band structure is not observed for the spectrum taken at 72.5 eV photon energy. This indicates that the incorporated Bi atoms induce changes in the band structure in contrast to simply counteracting the observed band bending of the pristine WZ(1120) surface. For the later case, we would expect a similar upward shift of the VB at the M-point. After the Bi deposition, the sample was annealed to 250°C for 20 min without further Bi deposition to explore the stability of the induced changes. The corresponding ARPES spectra and energy distribution curves at Γ can be found in Fig. S5 in the supplementary material. The VB is shifted toward its original position after removing the native oxide but appears broader in k̂. However, the 2DEG does not reappear, indicating that Bi atoms are still influencing the band structure, consistent with the Bi 5d core level signal still observable in the XPS data (see the supplementary material). This can be understood from recent studies, which showed that Bi will both substitute into As positions in the InAs lattice and form metallic Bi on the surface during the deposition. It was found that subsequent annealing would lead to the evaporation of metallic Bi, while the newly formed compound InBi on the InAs surface is more stable. In general, this would further indicate that while metallic Bi influences the Fermi level position, it does not introduce a 2DEG observable in Fig. 2.

As using the ARPES signal summed over many nanosstructures with a random orientation parallel to the surface plane was not commonly used previously, it is worth considering its benefits and limitations. The optics of the employed ARPES setup allow for a wide variation in photon energies. Therefore, the energies yielding the best signal can be chosen avoiding extensive acquisition times. Furthermore, it is feasible to combine measurements with a rapid
turnover in annealing and deposition steps. Considering the specimen morphology with respect to the x-ray beam and analyzer, it becomes apparent that 2D nanocrystals are best suited for this type of measurement. They allow for only one specific crystal facet to face upwards when using the contact transfer technique. For nanostructures with a hexagonal or spherical cross section, a multitude of different crystal facets facing the x-ray beam and analyzer would be the result since their morphology does not induce a preferential facet to lie on. This reduces the band structure signal since the overall intensity does not originate from a single facet but is split over several. As a result, the respective Γ-point will be reached at different photon energies. That said, depositing two or more feasible nanostructures on a single sample allows for a direct and fast comparison of induced band structure changes after a single treatment step simply by moving the sample in the x-ray beam. This minimizes the risk of variations induced by the setup and manual handling during sample preparation.

In summary, we reported experimental ARPES data on InAs nanosheets with wurtzite crystal facet, including band structure measurements at the Γ- and M-point. A 2DEG is observed at the Γ-point, which contrasts with other non-polar InAs surfaces. As 2DEGs are used for high electron mobility transistors, and promising for spintronic and quantum devices, the potential control demonstrated via Bi deposition in this study paves the way toward implementing nanodevices based on InAs. Furthermore, the presence of Bi on the surface is shifting the VB upward. This effect is reversed upon subsequent annealing. Our experiments have demonstrated that accumulative ARPES setups can be employed to gain an understanding of the band structure of low-dimensional specimens with the advantage of tracking induced changes in a fast and easy way.

See the supplementary material for an overview of the clean WZ crystal structure measured via STM, entire XPS, and ARPES spectra taken after every process step and a more in-depth explanation of the fitting of the band onset, the presence of the 2DEG, as well as the free electron final state approximation.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

S. Benter: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). M. Bianchi: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). D. Pan: Resources (lead); Writing – review & editing (equal). J. Zhao: Funding acquisition (supporting); Supervision (supporting). H. Q. Xu: Resources (supporting); Writing – review & editing (equal). R. Timm: Funding acquisition (equal); Supervision (supporting); Writing – review & editing (equal). Ph. Hofmann: Formal analysis (equal); Writing – review & editing (equal). A. Mikkelsen: Conceptualization (equal); Funding acquisition (equal); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


