

## Electronically Decoupled Films of InSe Prepared by van der Waals Epitaxy: Localized and Delocalized Valence States

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Submonolayer to several monolayer thick films of the layered semiconductor InSe were deposited on highly oriented pyrolytic graphite by van der Waals epitaxy and probed by energy dependent angle resolved photoelectron spectroscopy. The layers show a transition from two-dimensional bands with atomiclike states to molecularlike states localized along the  $c$  direction normal to the surface. The extended band structure showing band dispersion was observed for thicker films. [S0031-9007(97)04984-3]

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In contrast to the common elemental (Si, Ge) or compound semiconductors (e.g., GaAs) with diamond, zinc blende, or related structures the layered metal chalcogenides like MoS<sub>2</sub> or InSe exhibit strong anisotropic chemical bonding and can be considered as quasi-two-dimensional materials. They are characterized by covalently bound  $X-M-X$  or  $X-M-M-X$  ( $M$  = metal;  $X$  = chalcogen) sandwich layers with only weak van der Waals interactions along the crystal  $c$  axis, perpendicular to the layers [1]. The absence of directional chemical bonds at interfaces formed with the van der Waals planes allows heteroepitaxial growth despite lattice mismatches as high as 20% [2]. In addition, the absence of dangling bonds at the van der Waals planes results in a rather strong anisotropy of the surface tension of these materials which favors growth of two-dimensional layers rather than of three-dimensional islands.

We have investigated the thickness dependence of the electronic structure of thin films of the semiconductor InSe grown on semimetallic highly oriented pyrolytic graphite (HOPG). Both materials belong to the nonsymmorphic space group  $D_{6h}^4$  [3,4]. The crystallographic structure of InSe is shown in Fig. 1(a). Film growth proceeds along the  $c$  direction which corresponds to the  $\Delta$  symmetry line of the hexagonal Brillouin zone [Fig. 1(b)]. The electronic band structure along this direction as adopted from band structure calculations of Doni *et al.* [5] for InSe and of Tatar and Rabii [3] for graphite are shown in Fig. 1(d) together with their symmetry notations. Four well separated groups of valence bands [labeled A–D in Fig. 1(d)] are present for InSe. They are derived from Se  $4p_z$  (A), Se  $4p_{xy}$  (B), antibonding (C), and bonding (D) In  $5s$  orbitals, respectively [4,5]. For graphite the bands A and B belong to  $\sigma_{1,2}$  and to  $\pi$  states, respectively [3,6]. The uppermost valence bands of InSe (group A) are formed by  $\Delta_1$  and  $\Delta_2$  bands which have no correspondence in the graphite band structure at comparable binding energies. This implies that these states can form no strong chemical bonds with the substrates or, in other words, are electronically decoupled. Considering the films as a quantum well structure

embedded between graphite and vacuum we are dealing with large confinement potentials on either side in contrast to common semiconductor quantum well structures with confinement potentials of about 1 eV or less [7]. It should therefore, in principle, be possible to study the electronic properties of semiconductor quantum films and to follow the evolution of band structure by varying the film thickness from submonolayer to several monolayer coverage.

There exists a number of photoemission studies of quantum size effects of thin metallic films (see, e.g.,

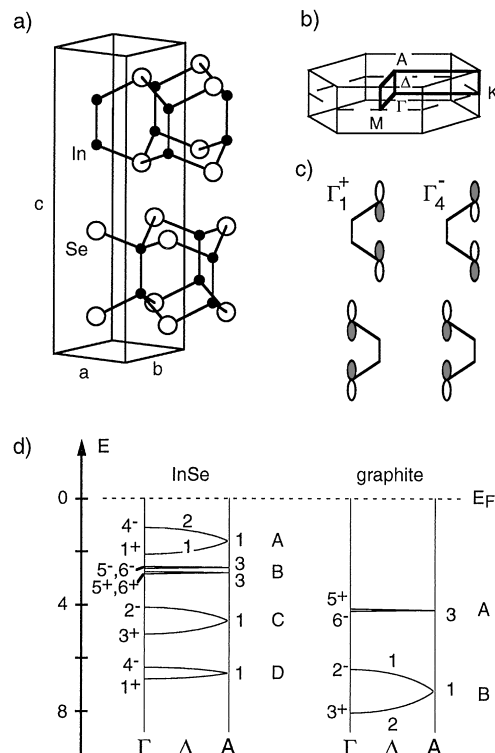


FIG. 1. (a) Crystallographic structure of InSe, (b) hexagonal Brillouin zone for InSe and graphite, (c) symmetrized combinations of Se  $4p_z$  orbitals according to states of  $\Gamma_1^+$  and  $\Gamma_4^-$  symmetry [5], and (d) electronic valence band structure along the  $\Delta$  symmetry line for InSe [5] and graphite [3].

Refs. [8–12] and references therein) as well as of metal and semiconductor nanoparticles [13,14]. We are not aware of any publications on quantum-size effects in two-dimensional semiconductor heterostructures with this technique. Observed quantum size effects are generally discussed in terms of discrete wave vectors selected from the bulk band structure [7–12,15]. This requires film thicknesses of several monolayers. With InSe it is not possible to separate the number of peaks occurring for several monolayer coverage due to the small band width of the upper valence band (group A) of about 1 eV. However, we have been able to study the electronic valence band structure of InSe quantum films which show atomlike states at (sub)monolayer coverages and molecularlike states for coverages of 1–2 monolayers whose observations are explained by group theoretical considerations. For thicker films we observed the valence band dispersion characteristic for single crystal InSe.

The experiments were performed with an angle resolving spectrometer (VG ADES 500) attached to the TGM7 beam line of the BESSY storage ring in Berlin. Two monochromator gratings were available supplying photons in the energy range between 12 and 25 eV and between 20 and 100 eV, respectively. InSe was deposited with a rate of 8 Å/min from a homemade Knudsen cell using crushed single crystals as source material [16]. The HOPG substrates are composed of microcrystals randomly oriented in the plane parallel to the surface but with their  $c$  axes aligned normal to the surface. This is evident from the ringlike low energy electron diffraction (LEED) pattern obtained from clean HOPG substrates. As a consequence also randomly oriented InSe overlayers showing ringlike LEED patterns are obtained. The ratio of the radii belonging to InSe and HOPG patterns is rather large and corresponds closely to the value expected from the equilibrium lattice constants of the respective materials (2.46 Å for HOPG and 4.05 Å for InSe). Because of the statistical orientation of the microcrystals in the surface plane the wave vectors of electrons emitted in off normal directions cannot be attributed to a specific symmetry direction of the graphite or InSe band structure. All spectra were thus measured only in normal emission probing the dispersion of valence band states along the  $\Delta$  symmetry line of the hexagonal Brillouin zone (for notation see Fig. 1). Binding energies are referenced to the Fermi level of the metallic sample holder and spectra are normalized with respect to the incoming photon flux. The nominal thicknesses were determined with a water cooled quartz microbalance and are attached to each spectra. To obtain real thicknesses the microbalance readings have to be multiplied by a factor of approximately 0.7 [16]. The substrates were cleaved in air and heated to 500 °C for 1 h prior to deposition. During deposition the sample was kept at  $T = 250$  °C.

In Fig. 2 photoelectron spectra recorded with  $h\nu = 21$  eV are presented in dependence of InSe film thickness. At the top of the figure we added, for comparison,

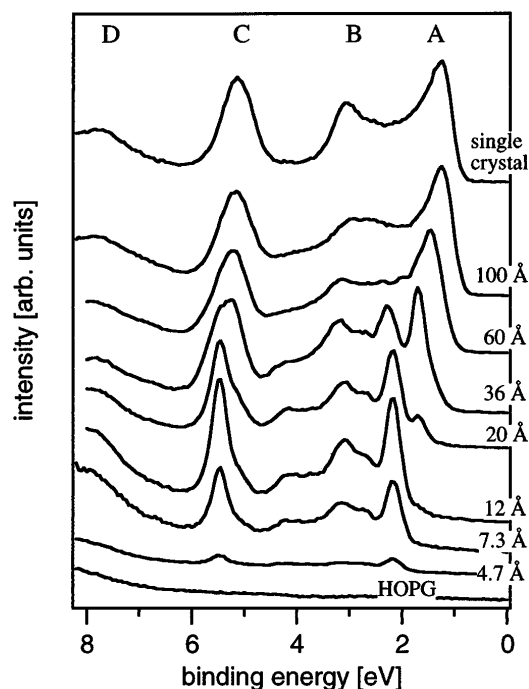


FIG. 2. Normal emission valence band photoelectron spectra recorded with  $h\nu = 21$  eV photon energy for InSe layers deposited on highly oriented pyrolytic graphite as a function of nominal layer thickness. The spectra of an UHV-cleaved InSe single crystal is added for comparison.

a typical spectrum from an UHV-cleaved InSe single crystal which clearly shows the emissions of the four groups of valence bands A–D [compare Fig. 1(d)]. The spectra for nominal coverages up to 12 Å are dominated by sharp peaks at binding energies  $E_B = 2.2$  eV and  $E_B = 5.6$  eV, respectively. Additional peaks grow in at  $E_B = 5$  eV and  $E_B = 1.7$  eV above 12 Å nominal coverage. At higher coverages the sharp emissions observed at lower coverages are replaced by broader bands which correspond well to the single crystal spectrum.

Figure 3 shows the photon energy dependence of the valence band spectra for layers of 12 Å (a), 36 Å (b), and 100 Å (c) nominal thickness. No shift in binding energy with photon energy  $h\nu$  is observed for the emissions at  $E_B = 2.2$  eV and  $E_B = 1.7$  eV for both 12 and 36 Å coverage. For 12 Å coverage the peak at  $E_B = 5.6$  eV also shows constant binding energy. This can be expected since no formation of electronic bands is possible along the  $c$  direction (normal to the van der Waals plane) for such small coverages. Small energy dispersion is obtained for the peak belonging to the group C bands at a coverage of 36 Å, while at 100 Å coverage considerable dispersion is observed for this peak and for the emissions at the valence band maximum (belonging to group A bands). The increase in binding energy of the Se  $4p_{xy}$ -derived states (group B bands) with increasing photon energy observed at all coverages, and also on InSe single crystals [17], should not be present since band structure calculations

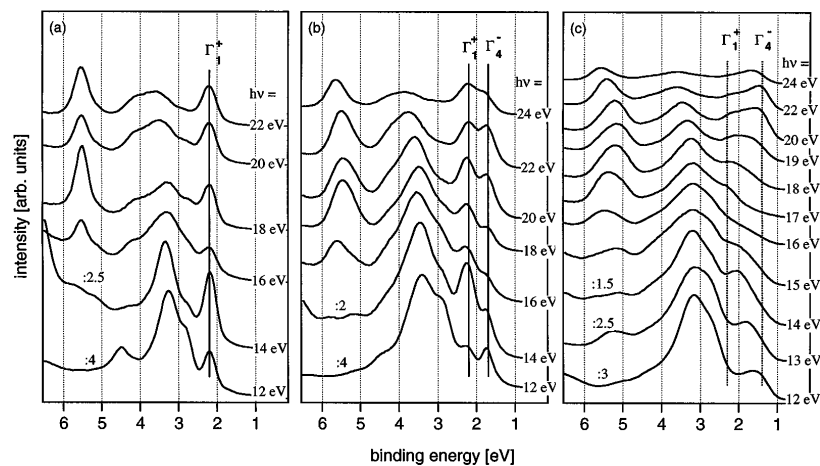


FIG. 3. Normal emission valence band spectra in dependence of photon energy for InSe layers of nominal thicknesses (a) 12 Å, (b) 36 Å, and (c) 100 Å. The emission from the upper valence states with  $\Gamma_1^+$  and  $\Gamma_4^-$  symmetry shows no dispersion at lower coverages.

show no dispersion of these bands along the  $\Gamma A$  direction [4,5]. However, band structure calculations lead to four nondegenerate group  $B$  bands having different binding energies along the  $\Gamma A$  direction. The observed shift in binding energy of these states can thus be reasonably assigned to a change of emission from the upper to the lower lying  $B$  bands with increasing photon energy induced by a change in final state symmetry. This interpretation is strongly supported by spin-resolved photoelectron spectra of GaSe and InSe single crystals [18].

In our discussion of the measured photoelectron spectra we will restrict on the valence bands with lowest binding energies ( $p_z$ -derived bands, group  $A$ ). First we want to compare the measured dispersion of the 100 Å film with band structure calculations. For simplicity we assumed a cosinelike dispersion of the  $\Delta_1$  and  $\Delta_2$  bands starting at  $\Gamma$  [compare Fig. 1(d)]. Only direct transitions to free electronlike final state bands folded with reciprocal lattice vectors  $(0, 0, n^*2\pi/c)$  were used. Since the lattice constant of  $\beta$ -InSe ( $c = 16.88$  Å) is rather high, comparatively large values of  $n$  (6, 7, and 8) have to be used for photon energies ranging from  $h\nu = 12$ –28 eV. The final state bands have  $\Delta_1$  symmetry for even  $n$ , while odd  $n$  gave final state bands with  $\Delta_2$  symmetry. Photoemission selection rules allow transitions to  $\Delta_1(\Delta_2)$  final state bands only from  $\Delta_1(\Delta_2)$  valence bands, respectively [4]. An identical procedure has been used for interpreting normal emission valence band spectra of graphite [6] and of WSe<sub>2</sub> [19]. The energy minimum of the final state parabola is set 5.5 eV below the Fermi energy. The result of the calculation is shown in Fig. 4 together with experimental peak positions. A good agreement between measured and calculated binding energy dispersion for the  $\Delta_1$  and  $\Delta_2$  bands as a function of photon energy is obtained assuming binding energies of  $E_B = 1.4$  eV for the  $\Gamma_4^-$  critical point and of  $E_B = 2.3$  eV for the  $\Gamma_1^+$  critical point, respectively. Included in Fig. 4 are, for comparison, experimental data of Larsen *et al.* [17]

obtained from an InSe single crystal which agree well with our results.

In Fig. 1(c) we show linear combinations of Se  $4p_z$  atomic orbitals according to  $\Gamma_1^+$  and  $\Gamma_4^-$  symmetry [5]. Hybridized with the corresponding higher lying In  $5p_z$ -orbital combinations these states form the upper valence states at  $\Gamma$  in bulk InSe. It is evident that for a single layer of InSe there is no possible state with  $\Gamma_4^-$  symmetry. Only  $\Gamma_1^+$  symmetry is allowed as can also be derived from group theory using the appropriate space group  $D_{3h}$  for an isolated single layer [4]. With these considerations we can assign the valence band peaks observed for different coverages and photon energies in Figs. 2 and 3 to their origin. For nominal coverages of up to 12 Å (actual thickness  $\approx 8$  Å corresponding to  $c/2$ ) the peak at  $E_B = 2.2$  eV corresponds to the valence band maximum of an InSe single layer formed by states with  $\Gamma_1^+$  symmetry. These states have an atomlike character

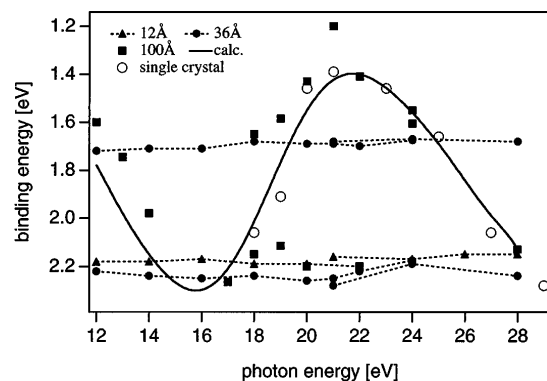


FIG. 4. Photon energy dependent binding energies of  $\Gamma_1^+$  and  $\Gamma_4^-$  states in the upper valence band region for nominal InSe film thicknesses of 12, 36, and 100 Å, respectively. Experimental data of Larsen *et al.* [17] obtained from an InSe single crystal and values calculated using theoretical band dispersion (see text) are added for comparison.

along  $\Delta$  as is evident from the sharp emission line and the lack of dispersion with excitation energy. When the coverage is increased beyond 12 Å the second layer starts growing, resulting in a splitting of the  $\Gamma_1^+$  state into  $\Gamma_1^+$  and  $\Gamma_4^-$  states which may be considered as bonding and antibonding orbital combinations of the single layer state. The valence band maximum is now formed by the  $\Gamma_4^-$  state. Both  $\Gamma_1^+$  and  $\Gamma_4^-$  states are observed with binding energies independent of photon energy because band formation has not yet occurred. For even higher coverages the upper valence bands show the dispersion of bulk InSe. The energy splitting between the  $\Gamma_1^+$  and  $\Gamma_4^-$  states has increased compared to the double layer film as expected for band formation. For bulk InSe either the  $\Gamma_1^+$  and  $\Gamma_4^-$  state can be observed at a particular photon energy as a consequence of photoionization selection rules (see above).

For film thicknesses above 2 monolayers but below the onset of band formation one would expect, in principle, additional localized states within the limits of the  $\Gamma_1^+$  and the  $\Gamma_4^-$  states [15]. But, because of the small binding energy difference between these states ( $\Delta_{BE} \leq 0.9$  eV) and the rather broad peaks, it was not possible to follow the transition between the double layer states and the extended states. For only a few excitation energies at intermediate coverages we were able to observe more than two clearly resolved states in the upper valence band.

From Figs. 2–4 it is evident that the  $\Gamma_1^+$  state has an almost constant binding energy in dependence of coverage while the binding energy of the  $\Gamma_4^-$  state decreases. The mean binding energy decreases by about 0.35 eV from the 12 Å to the 100 Å film. In contrast to this observation we would expect in the simplest approximation the  $\Gamma_1^+$ - $\Gamma_4^-$  splitting to be symmetric around the position of the monolayer  $\Gamma_1^+$  state giving a constant mean binding energy. We attribute this discrepancy to the InSe/HOPG boundary condition. A similar binding energy shift of about 300–400 meV with increasing coverage is observed for the In 4d core level and also for the work function of the sample; i.e., the InSe bands are shifted upwards in energy relative to the HOPG bands with increasing coverage. This is considered to be the consequence of a thickness dependent charge transfer between the layer and the substrate due to changes in the electronic structure of the InSe film and related shifts of the Fermi level position.

The observation of localized states of appropriate symmetry, especially for the single and double layer film, indicates that substrate-film interactions have only negligible influence on the observed valence band structures. This is only expected for such van der Waals epitaxy heterointerfaces with weak electronic coupling between the chemically saturated substrate and overlayer sandwich units as discussed (see Fig. 1). Such van der Waals epitaxy substrates should thus be ideally suited for investigating quantum effects in deposited nanosize particles.

In summary, we have presented valence band photoelectron spectra taken at different photon energies for

epitaxial thin films of InSe deposited on highly oriented pyrolytic graphite. In spite of the very weak interaction between the van der Waals planes of graphite and InSe almost ideal layer by layer growth is obtained which allows the preparation of two-dimensional layers of almost uniform coverage. Because of strong differences in the InSe and graphite band structures, which allow only very weak interactions between valence states of the film and the substrate, the growing films are electronically decoupled from the substrate. We were therefore able to measure the valence band structures of monolayer to multilayer films by angle resolved photoelectron spectroscopy. As expected the valence band features of thin layers showed no dispersion in  $z$  direction and very sharp atomiclike or molecularlike peaks while at 100 Å thickness bulklike structures and dispersion were found.

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