Electronic structure of HgSe(001) investigated by direct and inverse photoemission

D. Eich, D. Hübner, R. Fink, and E. Umbach
Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

K. Ortner, C. R. Becker, and G. Landwehr
Experimentelle Physik III, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

A. Fleszar
Theoretische Physik I, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
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Stimulated by recent photoemission results which suggest a positive fundamental energy gap in HgSe, we have investigated the electronic structure of molecular beam epitaxially grown HgSe(001) $c(2\times2)$ layers by a combination of direct ultraviolet photoemission spectroscopy (UPS) and inverse (IPES) photoelectron spectroscopy. Our UPS results do not support the finding of additional peaks above the valence band maximum (VBM) of Gawlik *et al.* [Phys. Rev. Lett. **78**, 3165 (1997)]. A comparison of angle-integrated UPS and IPES spectra and *ab initio* calculated density of states of HgSe and HgTe demonstrates dissimilar behavior of the two compounds in the dispersion of the conduction bands between 0 and 2 eV above the VBM. Our results are compatible with the common view that HgSe is a semimetal.

I. INTRODUCTION

In II-VI compound semiconductors the mercury based compounds HgSe and HgTe represent an exceptional class because of their inverted band structure. This commonly accepted picture of a semimetal is based on magnetoabsorption measurements[1,2] and optical experiments.[3,4] The semimetallic behavior of HgSe is also corroborated by recent quasiparticle band structure calculations.[5] In contrast to this well established knowledge, a positive fundamental gap has been suggested for HgSe(001) $c(2\times2)$ based on photoelectron spectroscopy results. Gawlik *et al.*[6] investigated cleaved HgSe(001) samples by a combination of angle-resolved photoemission and inverse photoemission. The authors found a positive energy band gap of about 0.42 eV at room temperature and furthermore a surface related state close to the Fermi level. According to their experiments, the Fermi level is located about 0.65 eV above the valence band maximum for their *n*-type HgSe. From these findings, the authors conclude that HgSe is a semiconductor and not a semimetal.

Because of these published photoemission results, the material HgSe and the photoelectron spectroscopy technique itself, are the subject of a controversial discussion.[7] However, the combination of direct and inverse photoemission has been demonstrated to be a powerful tool for the determination of bulk energy gaps of semiconductors with a direct band gap.[8–10] In the case of semimetals with an inverted band structure the valence and the conduction bands should cross, and hence UPS and IPES should detect a zero gap.[11]

Here we report on *k*-resolved photemission investigations of HgSe(001) $c(2\times2)$-reconstructed films grown by molecular beam epitaxy (MBE) under different growth conditions. Angle-resolved UPS measurements at two different photon energies ($\hbar\omega=21.22$ eV and 11.70 eV) show no evidence for additional states above the VBM which were previously reported for cleaved crystals.[6] Moreover, we have investigated the unoccupied conduction band states by IPES. The combined integrated UPS (occupied) and IPES (unoccupied) spectra of HgSe are compared with an *ab initio* calculated density of states (DOS). Furthermore, these HgSe data are compared with measured and calculated DOS of HgTe. Finally the special properties of the Se-based compound concerning their band gap determination by photoelectron spectroscopy are discussed.

II. EXPERIMENTAL DETAILS

The samples were grown in two Riber 2300 MBE chambers, one of which was used for the growth of a GaAs buffer and the other for Hg-based II-VI materials and heterostructures, both being connected via a UHV transfer module. Prior to growth the GaAs substrates were heated up to 625 °C under an As flux in UHV in order to remove oxygen from the surface. Then, a GaAs buffer layer was grown at 590 °C with an excess of As flux. After cooling down, the samples were transferred to the II-VI MBE chamber where a 2 mm thick ZnTe buffer layer was grown in order to minimize the lattice mismatch between the substrate and the subsequent HgSe layer.

The HgSe layers were then deposited using Hg and Se fluxes (beam equivalent pressures) of 1.6×10^{-4} and 1.2×10^{-6} Torr, respectively. All HgSe samples investigated here were approximately 100 nm thick. It is worth noting that two-dimensional growth can be obtained over a relatively wide range of temperatures from 65 to 170 °C. A $c(2\times2)$ reconstruction was observed during growth in reflection high-energy electron diffraction (RHEED). The growth was terminated by either closing the Se shutter while maintaining a constant Hg flux until a substrate temperature of 90 °C was reached, or simply by closing all shutters for temperatures below 90 °C.

After film growth, the samples were transferred under

UHV conditions ($p \leqslant 2\times10^{-9}$ mbar) from the MBE system to the photoemission spectrometer (VG ESCALAB Mk II). No surface contaminations were observed within the detection limit of XPS. In addition, the $c(2\times2)$ surface reconstruction was unchanged according to the LEED pattern observed after the transfer.

We have investigated ten HgSe(001) samples grown at different temperatures (165, 110, and 65 °C). UV photoemission experiments were performed at room temperature with a gas discharge lamp using He I ($\hbar\omega=21.22$ eV) and Ar I ($\hbar\omega=11.70$ eV) irradiation, respectively. The energy resolution was better than 0.1 eV for the UPS measurements, determined at the Fermi edge of a sputter-cleaned gold foil. The angle of acceptance of the electron analyzer was limited to $\Delta\theta\approx2°$ by an aperture for the k-resolved measurements.

The inverse photoemission (IPES) system installed in the same photoemission chamber consists of a Ciccacci-type low-energy electron gun with a BaO cathode.[12] IPES spectra were measured at an isochromat energy of 9.5 eV using a Dose-type detector equipped with a SrF_2 window and filled with Ar and I_2 gas.[13] The overall energy resolution of the IPES spectrometer is about 0.5 eV. The position of the Fermi level was established using a clean gold foil, and the energy position of the elastically scattered electrons was determined by the electron analyzer.

III. RESULTS AND DISCUSSION

For the zinc blende II^B-VI compounds (Zn, Cd, Hg as cations) it is known from calculations and experiments that the VBM and CBM (conduction band minimum) are located at the center of the Brillouin zone (BZ), i.e., at the Γ point. The $k_\perp$ value of electrons excited with a photon energy of about 12 eV falls near the Γ point of the BZ, according to results from photon energy dependent measurements using synchrotron radiation.[6] In Fig. 1, two normal emission spectra of the valence band region of HgSe(001) grown at 65 °C are shown for two different photon energies. In addition, for each photon energy a set of PE spectra was recorded by systematically varying the emission angle over an interval of about 50° (not shown). Spectrum (a) in Fig. 1 was obtained using He I excitation ($\hbar\omega=21.22$ eV); the corresponding $k_\perp$ value is located at about 60 per cent of the distance between the Γ and the X point. Curve (b) in Fig. 1 was measured with a photon energy of 11.70 eV (Ar I excitation), i.e., with a $k_\perp$ value very close to the center of the BZ. The spectra demonstrate the influence of the band dispersion as a shift in the energy position of the low-energy edge of the valence band.

The VBM in spectrum (b) was determined by a linear extrapolation of the valence band edge, as indicated by the two lines. The Fermi energy is located about 0.3 eV above the VBM. The fact that the Fermi level is shifted into the conduction band arises from the relatively high carrier density of the samples. The samples are n-doped with a carrier concentration of about 5×10^{18} cm^{-3} (at room temperature) as derived from Hall effect measurements in the van der Pauw configuration. A simple estimate of the Fermi energy position for a free-electron band with an effective mass of $m_{eff}=0.03$ and for the given carrier density yields a value of about 0.35 eV for the position of the Fermi level with respect
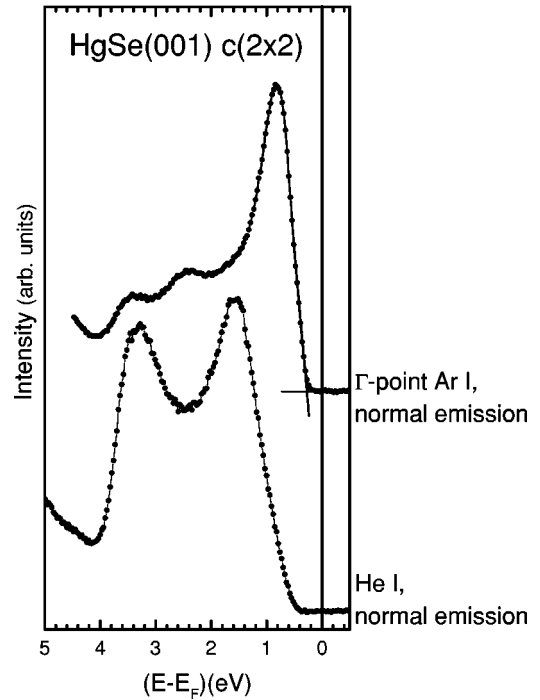

FIG. 1. UV photoemission spectra (relative to E_{Fermi}) of a HgSe(001) $c(2\times2)$ surface for two different experimental conditions. Bottom: He I ($\hbar\omega=21.22$ eV), $k_\parallel=0$ and $k_\perp$ corresponds to about 60% of the distance between Γ and X; top: Ar I ($\hbar\omega=11.70$ eV), normal emission, $k_\parallel=0$, $k_\perp$ at the Γ point. A determination of the VBM by linear extrapolation (cut-off determination) is indicated.

to the VBM. This rough estimate is in good agreement with our experimental result.

Furthermore as can be seen in Fig. 1, there are no hints for any photoemission intensity above the VBM that could correspond to a Γ_6 conduction band or a surface-derived state, as found by Gawlik et al. for HgSe(001) $c(2\times2)$ cleaved surfaces.[6] Following their argument, the lowest conduction band states should be occupied as a result of band bending in the surface region and thus were detectable in normal photoemission. The corresponding peak showed a dependence on photon energy, whereas the additional surface peak exhibited none.[6] With the exception of one sample, none of our HgSe(001) $c(2\times2)$ reconstructed films grown at various temperatures showed additional photoemission peaks above VBM. Just the first of our samples displayed an additional structure above the VBM. However, the magnitude of this peak was only about a tenth of the magnitude of the peak observed by Gawlik et al.[6] Furthermore, this peak exhibited no dispersion as would be expected for a conduction band. For the other samples no peaks were observed above the VBM in the normal emission spectra at various photon energies (Fig. 1).

Figure 2 compares angle-integrated UPS and IPES spectra of HgSe and HgTe with calculated three-dimensional DOS of the occupied and unoccupied states. The calculations have been done within the local-density approximation (LDA).[14] The usual underestimation of the energy gaps between occupied and unoccupied states in LDA has been corrected by a (nonuniform) energy shift of the conduction bands derived within the GW approximation.[15,16] In the lower part of Fig. 2
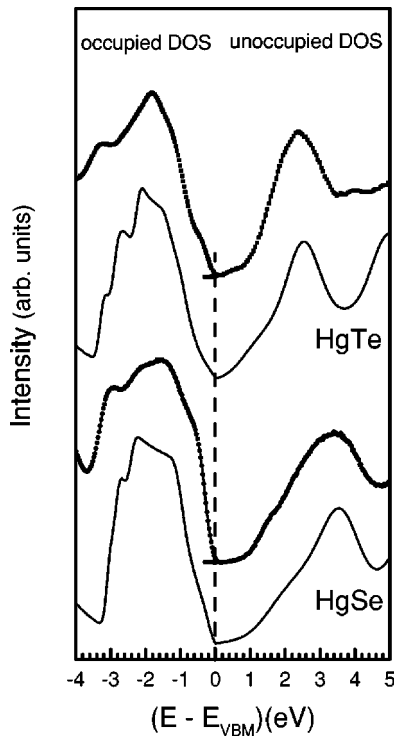
FIG. 2. Angle-integrated UPS and IPES spectra (relative to VBM; data points) for HgSe (bottom) and HgTe (top) are compared with the corresponding calculated DOS (solid lines) from semimetallic band structures. The main difference between the two compounds is the dissimilar DOS in the energy range between 0 and 1 eV above the VBM.

experimental spectra (open circles) and theoretical DOS (solid line) for HgSe are shown. In the upper part experimental (open squares) and calculated (solid line) data of HgTe are plotted for comparison. To compare theory with experiment we have integrated the angle-dependent UPS and IPES spectra to get an approximate experimental ''DOS.'' Furthermore, the calculated DOS of the unoccupied states was convoluted with a Gaussian curve with a FWHM of 0.5 eV in order to take the experimental resolution of the IPES setup into account. The left hand side of the calculated DOS for the occupied states is unchanged since in the UPS experiment the experimental resolution is significantly better.

As can be seen in Fig. 2, the overall agreement between theoretical and experimental line shapes and peak positions for occupied and unoccupied states is rather good for both, HgSe and HgTe. The most interesting point, however, is the difference in the DOS of the unoccupied states between HgTe and HgSe in the energy range between 0 and 1 eV above the VBM. For HgTe the calculated DOS exhibits a relatively steep increase in this energy range starting directly at the VBM. An increase in the unoccupied DOS is also found in the IPES measurements of HgTe. In contrast, the calculated DOS of HgSe shows only a weak increase of the DOS in this energy range in agreement with the small DOS observed by IPES. The reason for the difference between these two materials is the different band structure of the tellurides and the selenides. Both have comparable effective masses in the conduction band of about 0.03. However, HgSe exhibits a stronger dispersion of the Γ_8 band until it reaches the L and X point, respectively, leading to a much

smaller DOS. This is a characteristic material-dependent property which is also found in other II-Se and II-Te compounds.[17]

The comparison between HgSe and HgTe also supports the results and expectations by Rohlfing and Louie.[5] These authors conclude from their calculations that the DOS of bulk states above the VBM is rather low for HgSe, and hence no conduction band state should be observed in photoemission, as is the case in our experiment. Thus, the PES result is further corroborated by the (independent) IPES investigations.

The experimental HgTe data in Fig. 2 show the expected shape of the photoemission spectra of a semimetal, i.e., VBM and CBM coincide at the Fermi edge. Thus, a zero gap is obtained by applying the linear extrapolation scheme of the band edges (i.e., first steep slopes). However, doing the same for HgSe would result in an incorrect (much too large) value for the band gap because of the lack of IPES intensity just above the VBM. Together with the theoretical argument above our experimental results thus demonstrate that a straight forward gap determination using a combination of direct and inverse photoemission is not possible for HgSe. However, in connection with the calculated DOS, the combined UPS and IPES data of HgSe are in accordance with the inverted band structure (scheme) of a semimetal.

IV. CONCLUSION

We have investigated HgSe(001) $c(2 \times 2)$ layers grown at different temperatures by molecular beam epitaxy by direct and inverse photoelectron spectroscopy to study the electronic properties of HgSe. Our results give no hints for either a conduction band state or a surface state above the VBM in nine of ten samples, in contrast to previous findings.[6] The controversial results may be due to structural differences between our samples and those used in Ref. 6, as, e.g., much larger step or defect densities in the case of the cleaved surfaces. The structural differences might be related to the fact that the orientation of the cleavage plane strongly depends on the crystal temperature, and that the zinc blende (100) surface usually does not represent the favored cleavage plane. Furthermore, integrated UPS and IPES spectra of HgSe are compared with a calculated DOS. These are in turn compared with the experimental and theoretical results for the semimetallic HgTe. The latter comparison reveals differences in their material properties, as seen in UPS and IPES spectra. Our integrated UPS and IPES spectra are in good agreement with the calculated three-dimensional DOS of HgSe derived from a semimetallic band structure. Therefore we conclude that our photoemission results of HgSe are fully compatible with the general view, that HgSe is a semimetal, in agreement with recent results from magneto absorption experiments.[18]

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