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PHOTOELECTRON SPECTROSCOPY OF II-VI SEMICONDUCTOR HETEROSTRUCTURES*

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We are growing ZnSe, ZnS and CdSe layers epitaxially on GaAs(001) substrates by atomic layer epitaxy and molecular beam epitaxy. The substrates are prepared by a H-plasma method in order to obtain a sharp interface between substrate and layer. The quality of our samples is controlled by reflection high energy diffraction and X-ray diffraction. Furthermore, the samples are characterized *in situ* by photoelectron spectroscopy. We observe resonant Zn $3d^8$ and Cd $4d^8$ satellites, which are used to check the layer quality. As a result, the valence band offsets of CdSe/ZnSe and ZnSe/CdSe were obtained. The values are $\Delta E_v(\text{ZnSe/CdSe}) = -(0.13 \pm 0.07)$ eV and $\Delta E_v(\text{CdSe/ZnSe}) = -(0.13 \pm 0.07)$ eV, which confirm the commutativity rule.

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1. Experiment

ZnSe, ZnS and CdSe layers are epitaxially grown on GaAs(001) substrates by molecular beam epitaxy (MBE), which is mostly used in the atomic layer epitaxy (ALE) mode. The quality of the surfaces is *in situ* controlled by reflection high energy diffraction (RHEED). In order to control structural properties of the samples high resolution X-ray diffraction is used. The valence band offset between these materials is determined by photoelectron spectroscopy (PES) with synchrotron radiation. A MBE-chamber was built, which has been attached to an analyzer chamber positioned at BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH). With this equipment heterostructures are grown in steps of monolayers and the surface is investigated during the growth interruptions *in situ* by UPS. In the ALE mode the different effusion cells are alternately opened. The successive openings of the cells containing the respective elemental II- and VI-materials is defined as one shuttercycle (SC). For the growth parameters see Ref. [1].

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2. Results

2.1. Hydrogen plasma preparation

The GaAs(001) substrates are cleaned by a chemical wet etching process [2]. A hydrogen plasma is used to remove the oxide overlayer. The substrate temperature is 200°C. Figure 1 shows the spectra of a chemical etched GaAs(001) substrate without and with H-plasma treatment for various periods. Whereas in the first spectrum the oxide components of the core levels [3] and a strong oxide signal in the valence band dominate, these signals are obviously reduced after a 2 minutes' H-plasma treatment. A 4 minutes' treatment finally leads to a GaAs surface, where only the bulk components of the GaAs-core levels are seen but the oxide signal in the valence band is totally removed.

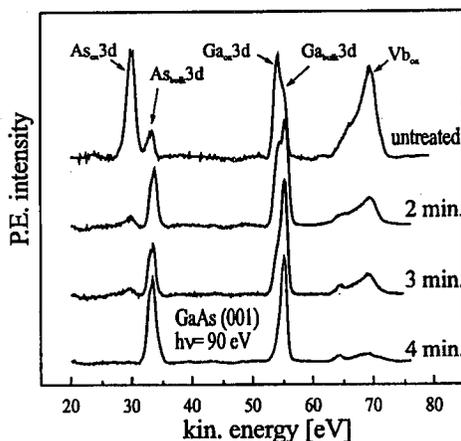


Fig. 1. UPS spectra of GaAs(001) before and after H-plasma treatment.

The preparation of ZnSe- and CdSe-surfaces leads to analogous results. The oxide components of the core levels are removed and the bulk components increase. A Se deficiency at the surface is observed, which completely vanishes after growth of a few SC ZnSe or CdSe, respectively.

2.2. d^8 -satellites

GaAs(001) substrates and ZnSe- or CdSe-epilayers are treated with hydrogen plasma. On these surfaces thin ZnSe- and CdSe-layers are grown and investigated with PES. Figure 2a shows different photoionization processes, which are especially relevant for the cases of Zn 3d- and Cd 4d-levels. The transition *A* describes the direct excitation of a *d*-shell electron into the continuum leading to a single hole nd^9 final state. *B* is the MVV Auger process, *C* is a non-resonant shake up and *D* the resonant shake up. They all lead to two hole nd^8 final states. Furthermore, the photoexcitation *C* and *D* have the same final states and therefore give rise to resonant emission if the photon energy is near the np threshold.

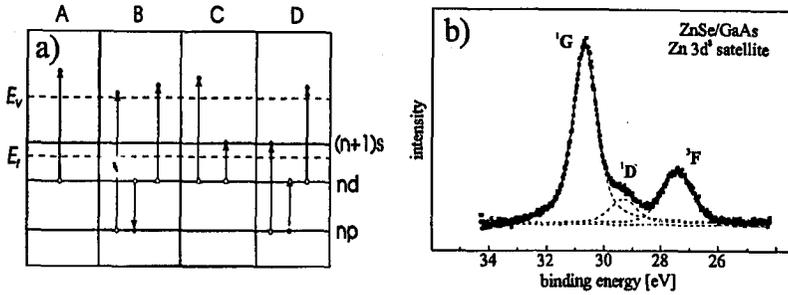


Fig. 2. (a) Excitation channels of a nd^{10} -core level, (b) Zn $3d^8$ -satellite in ZnSe.

We write for the non-resonant shake up (C)

$$\hbar\omega + np^6nd^{10}(n+1)s^0 \longrightarrow np^6nd^8(n+1)s^1 + e^-,$$

and for the resonant Auger (D)

$$\hbar\omega + np^6nd^{10}(n+1)s^0 \longrightarrow np^5nd^{10}(n+1)s^1 \longrightarrow np^6nd^8(n+1)s^1 + e^-.$$

When the direct photoexcitation can be described by $E_{\text{kin}} = \hbar\omega - E_B - \phi$ (ϕ — work function) and Koopman's theorem $E_B = -\varepsilon_j$ (ε_j — one-electron energy) is valid for the two hole final states (B, C, D) the following relation holds:

$$E_B = -(\varepsilon_j + U_{\text{eff}}), \quad U_{\text{eff}} \text{ — effective Coulomb interaction.}$$

Here the effective Coulomb interaction is the total additional energy, which is necessary to excite a second hole at the same atom and which deviates from two "one hole" energies. For a more detailed study of that process see Ref. [4].

Figure 2b shows the Zn $3d^8$ -satellite observed at a photon energy of about $\hbar\omega \approx 90$ eV. The multiplet splitting of the two-hole state should be the same for all Zn compounds, whereas the intensity ratio $I(d^8)/I(d^9)$ and the effective Coulomb interaction depend on the material (see Table).

TABLE

Characteristic results for the Zn $3d^8$ -satellite normalized to the Zn $3d^9$ -signal.

Compound	$I(d^8)/I(d^9)$	1G [eV]	1D [eV]	3F [eV]	U_{eff}
ZnSe (this work)	16%	21.5	20.2	18.2	-12.3
ZnS (this work)	21%	21.5	20.0	18.3	-12.9
Zn (metal) [5]	6%	22.3	—	16.8	-10.3
ZnO [6]	12%	21.3	20.4	18.1	-10.5

These two values should change if there are ternary regions in the grown heterostructure or if islands of the elemental materials are formed. We indeed observed a decrease in the intensity ratio $I(d^8)/I(d^9)$ at rough surfaces. Furthermore, while investigating this ratio for different photon energies it is possible to "scan" the $3p$ -level of Zn and to obtain the $3p^{1/2}$ - $3p^{3/2}$ splitting. We find $\Delta E_{\text{so}}(\text{Zn}3p) = (3.03 \pm 0.05)$ eV.

Analogous measurements have been performed at a photon energy of $\hbar\omega \approx 70$ eV for Cd 4d in CdSe. We observed an intensity ratio $I(d^8)/I(d^9) = 5\%$, an effective Coulomb interaction $U_{\text{eff}} = -8.8$ eV and a Cd 4p-splitting $\Delta E_{\text{so}}(\text{Zn}3p) = (7.54 \pm 0.05)$ eV.

2.3. The valence band offset ZnSe-CdSe

We have grown ZnSe on CdSe and CdSe on ZnSe in steps of a few monolayers and measured UPS spectra during growth interruptions to investigate the valence band offsets. The valence band edge is extrapolated by a straight line. Then the difference between the edge of the pure ZnSe and that obtained after growth of 70SC CdSe is determined. In the same way we treated the heterostructure ZnSe/CdSe. These differences have to be corrected for the band bending [7], which normally can be evaluated from the shift of the core levels. In the case of ZnSe-CdSe heterostructures, however, the only evaluable Se 3d signal has to be fitted by a large number of different components (overlayer, CdSe, ZnSe, mixing components), which leads to a large uncertainty. For the Se 3d core level of the pure materials we find $E_{\text{B}}(\text{Se}3d/\text{ZnSe}) = 54.09$ eV and $E_{\text{B}}(\text{Se}3d/\text{CdSe}) = 53.83$ eV. These binding energies are determined as well for the heterostructure. By subtracting both core level differences we obtain the band bending.

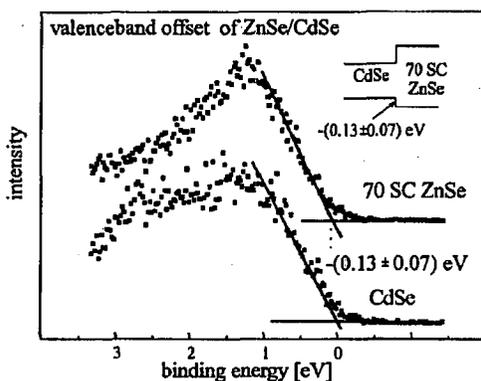


Fig. 3. The valence band offset at the interface of ZnSe/CdSe.

Figure 3 shows the valence band offset of ZnSe/CdSe corrected by the band bending. The results for both directions ZnSe/CdSe and CdSe/ZnSe are

$$\Delta E_{\text{v}}(\text{ZnSe}/\text{CdSe}) = -(0.13 \pm 0.07) \text{ eV} \text{ and}$$

$$\Delta E_{\text{v}}(\text{CdSe}/\text{ZnSe}) = +(0.12 \pm 0.07) \text{ eV}.$$

It is obvious that in the case of ZnSe-CdSe heterostructures the commutativity rule is confirmed, which was found as well in ZnSe-ZnTe [8]. These results agree well with results, which are derived from optical measurements of quantum wells by Lankes [9], who found $\Delta E_{\text{v}}(\text{ZnSe}-\text{CdSe}) = \pm(0.17 \pm 0.01)$ eV.

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