A.7: Band offset at ZnO/GaP hetero-junction determined using synchrotron based photoemission spectroscopy

ZnO is a wide band gap (~3.37 eV at room temperature) semiconductor with a relatively large exciton binding energy (BE) of ~60 meV among other wide bad gap semiconductors like GaN (BE ~28 meV) and ZnSe (BE ~19 meV). ZnO has found numerous applications in various optoelectronic devices such as light emitting diodes (LEDs), ultraviolet (UV) photodetectors etc. ZnO layers have been grown on various p-type substrates like Si, GaAs, SiC etc. primarily due to the unavailability of reliable p-type ZnO layers to form hetero-junction based ZnO LEDs and photodetectors. In cubic symmetry based substrates, silicon substrate is most widely used for the growth of good quality ZnO layers. GaP is another cubic semiconductor that has very small lattice mismatch (~0.37%) with respect to Si. Thus, it is expected that ZnO layers of good crystalline and optical qualities can be grown on GaP substrate. The other inherent advantage of this material combination is that phosphorous can out diffuse into ZnO layer by post growth annealing process and can lead to p-type conductivity in the ZnO layer, because phosphorous doping has been shown to produce p-type ZnO layers. Hence, ZnO/GaP hetero-junction is important from the point of view of optoelectronic devices. Band alignment and band offset at the hetero-junction plays a key role in the carrier transport, recombination processes in the optoelectronic devices. The valence band offset (ΔE_v) at ZnO/GaP hetero-junction has not been determined using photoemission spectroscopy (PES), which has been commonly used to determine the band alignment and ΔE_v value at the hetero-junction.

In the present work PES measurements carried out at angle integrated PES (AIPES) beam line at Indus-I are used to determine the band alignment and the band offset value at ZnO/GaP hetero-junction. The experiments were performed using 70 eV of photon energy of synchrotron radiation source. The samples used in the study were grown by pulsed laser deposition (PLD) technique. The sample consists of a thin (~2.5 nm) ZnO layer grown on GaP(111) cubic substrate. The thin layer sample is chosen because photoelectrons from both the materials ZnO and GaP substrate can be detected in the PES measurements. The sample was sputtered by Ar^+ ions for 5 and 10 minutes to clean the surface as well as to reduce the top ZnO layer thickness, so that photoelectrons from GaP substrate could also be collected in the PES experiments.

PES data (not shown here) of 5 minutes sputtered ZnO/GaP hetero-junction sample shows Zn 3d core level peak at ~11 eV and there is no Ga 3d peak at ~19 eV. In addition to this, there is only one valence band onset corresponding to ZnO. This suggests that only photoelectrons from top ZnO layer could be collected in the PES measurements for 5 minutes sputtered ZnO/GaP hetero-junction sample. Thus, the thickness of top ZnO layer is still large compared to the escape depth of photoelectrons that prevents to observe the PES signal from GaP substrate. Figure A. 7.1 shows the PES spectrum after 10 more minutes of sputtering, where Ga 3d core level peak at ~19 eV is clearly observed in addition to the Zn 3d core level peak at ~11 eV. This observation shows that after sputtering of 5 minutes more, the thickness of top ZnO layer is reduced and the photoelectrons from the GaP substrate could also be detected in the PES measurements. The core levels have been fitted by using a Shirley background and Voigt (mixed Gaussian-Lorentzian) line shape functions. It is noted that the Ga 3d core level peak is a admixture of Ga $3d_{5/2}$, Ga $3d_{3/2}$

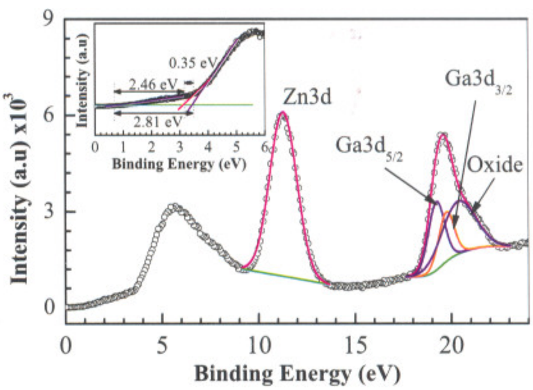

Fig.A.7.1: PES spectrum of sputtered ZnO/GaP hetero-junction sample taken by 70eV of photon energy. Inset shows the enlarged view of valence band region displaying three valence band onsets corresponding to GaP, GaO_x, and ZnO materials.

(spin orbit split components), and an oxide (GaO_x) peak at higher binding energy. Thus, the interface of ZnO and GaP consists of an additional layer of GaO_x, which is either formed during the deposition of ZnO and/or due to incomplete removal of native oxide present on GaP substrate before deposition. Inset to the Fig. shows an enlarged view of valence band region of the same sample depicting three valence band onsets corresponding to GaP, GaO_x, and ZnO materials. The ΔE_v value for the ZnO/GaP, GaP/GaO_x, and GaO_x/ZnO is determined to be 2.81, 2.46, and 0.35 eV respectively from the difference of the corresponding valence band onsets. A type-II band alignment at ZnO/GaP hetero-junction is also determined. The present PES study of band alignment and obtained values of valence band offsets at different hetero-junctions can be used to design optoelectronic devices. (For more details, please refer to S. D. Singh et al., Appl. Phys. Lett. 104, 012109, 2014).

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