The wide band-gap II-IV semiconductor ZnSe is an important material for fabricating light-emitting devices in blue-green spectral region. Detailed knowledge of its bulk and surface electronic structure is crucial for improving the quality and lifetime of these devices. Angle-resolved ultraviolet photoemission (ARUPS) is the most powerful technique for providing k-resolved information about the occupied electronic states. By exploiting the MBE growth technique ZnSe surfaces with different crystallographic directions can be prepared for photoemission measurement. By appropriate choice of photon energy and detection angle one is able to probe the same directions in the Brillouin zones (BZ) of differently oriented samples. This gives a unique opportunity to distinguish between surface and bulk features and to verify the sample preparation procedures.

Figure 1: EDC’s for single crystal and thin film ZnSe samples. After background substraction the energy distribution curves were normalized and plotted on a grayscale. Binding energies are referred to the Fermi level.
We have investigated two different types of ZnSe samples. The first were single crystals grown by Bridgman method in Torun, Poland [1]. Such samples usually suffer from low conductivity so special treatment and contacts were necessary to make the photoemission experiments. The sample was cleaved under UHV to provide clean (110) surface. Similar ARUPS measurements on cleaved ZnSe(110) have been reported previously [2].

The second sample was a thin layer of ZnSe(100) grown by MBE on a GaAs(100) substrate at Würzburg University. The sample was capped with Se and transported to Hamburg under UHV conditions (pressure always lower than 3·10^-9 mbar). On the ZnSe(100) surface a variety of different reconstructions can be prepared depending on the decapping temperature: the lower the temperature the more Se-rich is the surface [3]. The results shown here were recorded on a just decapped (100°C) Se-rich surface which showed a sharp 1x1 LEED pattern. Experimental and theoretical investigations of the ZnSe(100) electronic structure were carried out recently [4][5].

Figure 1 shows sets of spectra along the $\Gamma$-K-X direction in BZ for both samples plotted on a grayscale together with the theoretical bulk bands (solid lines). The spectra are plotted assuming direct transitions model with free electron final states. It should be noted that the free electron final state model is not always adequate - especially for photon energies lower than 20 eV.

Another problem arises from difficulties in evaluating the inner potential $V_0$. This parameter is crucial when performing off-normal measurements when one assumes free electron final state since it defines the role of refraction in the ARUPS experiment. We found that $V_0 = 13.5$ eV for the single crystal and 10.5 eV for the thin film sample provides the best fit to the theoretical calculations. These values are close to the value 12 eV cited in most articles [2][4].

EDC’s for the single crystal were recorded in normal emission for photon energies 15-35 eV. For the thin film measurements were made at different emission angles and photon energies to follow the $\Gamma$-K-X line in the Brillouin zone. Preliminary normal emission spectra (not shown here) were taken to evaluate the inner potential $V_0$. The orientation of the sample was established using the LEED pattern. The base pressure in the experimental chamber was lower than 1·10^-10 mbar during measurements.

We find relatively good agreement with the theoretical calculation. The width of the valence band is around 0.5 eV larger than the theoretical value. It is apparent that more knowledge concerning the final states is crucial for obtaining a better understanding of the band structure.

In the future we plan to perform measurements on the other chalcogenides (also ternary and quaternary compounds). We would also like to perform systematic investigations on the other reconstructions of ZnSe(100) surfaces and combine the results with our structural investigations using surface x-ray diffraction and scanning tunneling microscopy.

References