



Morphology of the Si/ZnO Interface

Abstract

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The interface of Si-ZnO is studied with XPS and UPS with regards to the morphology of the interface. Magnetron sputtered ZnO films on Si(111) surfaces (H-termination and 7×7) were investigated step by step and the interface properties were studied in situ. All samples are handled in situ in UHV. Up to five different interface phases were detected depending on ZnO preparation. Beside a SiO_x film induced by the sputter process, a ZnO and Zn_2SiO_4 phase are resolved. In addition hydrogen as Zn-OH is found in considerable concentrations in the films.

Introduction

The interface of Si and TCO's like ZnO is of particular technological interest for thin film Si solar cells. The ZnO serves as a transparent and conducting overlayer. On the one hand the TCO should have a conductivity high enough not to limit the photocurrent of a cell. On the other hand the optical absorption should be as low as possible in the visible range for not limiting the photon flux to the Si absorber. Both parameters are determined by the doping and counteract one to each other. In addition interface states will give rise to an increased recombination rate. Here we will study another important property, the interface. In a heterojunction the electronic band offsets in a given device are determined by the contact materials and their electronic properties. However, even in the case of an atomically abrupt interface the prediction of the band offset from

fundamental material parameters is not straightforward. Here we will report on the properties of the Si-ZnO interface on an atomic scale as derived from XPS-data taken from Si-ZnO interfaces between the deposition steps ranging from 0.8 nm to 150 nm.

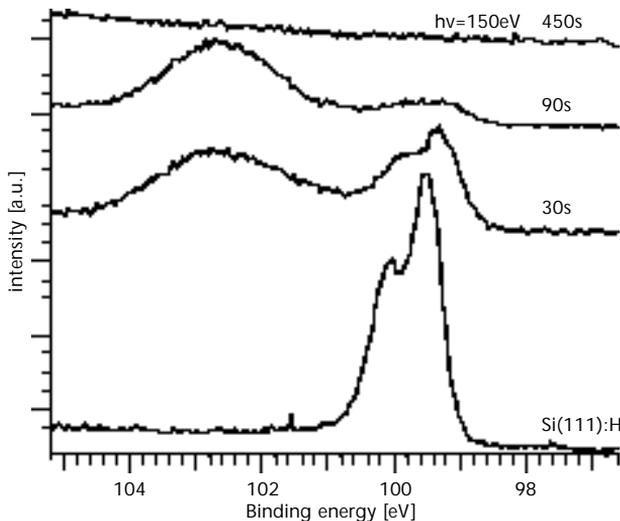
Experimental

Si samples were H-terminated *ex situ* and introduced into UHV with no considerable contamination (e.g. no oxide detected in *Fig. 1*). For controlling the role of H at the interface in addition Si(111)7x7 samples were prepared. Deposition took place in a UHV system equipped with a 2" Magnetron. The target was 5N pure ceramic ZnO with no admixture of dopant. Deposition parameters were in the range of 2×10^{-2} mBar Ar pressure, 30W RF power and the sample could be biased against the plasma potential. The sample could be heated to 600 °C. A second deposition facility was used to deposit ZnO by CVD from diethylzinc and water on the heated substrate. XPS and UPS spectra were taken in an UHV-transfer coupled spectrometer chamber equipped with an UV-He source, a monochromated Al-Ka source and a hemispherical analyzer (EA10MCD). Enhanced surface sensitivity was gained by using 150eV synchrotron radiation for examination of the Si 2p level at BESSY.

Results and Discussion

Si 2p spectra (*Fig. 1*) show clearly a deposition induced oxidation of the Si interface. This oxidation of the Si substrate is independent of substrate bias and additional oxygen dosage.

Figure 1
Si2p core level in the course of ZnO deposition. Si(111):H substrate, sample at ground potential, RF-power 30W. Spectra taken with $h\nu=150\text{eV}$ at BESSY. Surface sensitivity is increased by a factor of 4 in comparison to AlK α radiation.



In the corresponding Zn Auger line an admixture of ZnO shows up as a distinct shoulder at higher kinetic energies. This ZnO emission is sensitive to substrate bias and oxygen admixture (Fig. 2).

Examination of the Zn2p shows an asymmetric line for lower ZnO (<1nm) coverage. The corresponding 3d level taken with Hell excitation shows at least 3 different (spin orbit splitted) emissions belonging to chemically different Zn species at the interface indicating a complex interface chemistry. For the .8 nm thick film the XPS spectrum is shown in addition proving the same chemical states in the film as found for Hell excitation only a difference in intensity at higher binding energies hints to a surface species, as AlK α excited 3d electrons have by about a factor 3 larger escape depth as Hell excited electrons from the same core level.

In the O 1s level two chemical species are detected. As Si-oxides and OH groups tend to have a binding energy of about 532.8 eV and ZnO is found at 531 eV more detailed information was gained on heating a thicker sample in UHV: the shoulder at 532.8 eV is lost. In addition ex situ determination of the hydrogen content of the films by the ^{15}N -method gives a concentration of about $10^{21}/\text{cm}^3$ hydrogen in the film before heating and about two orders of

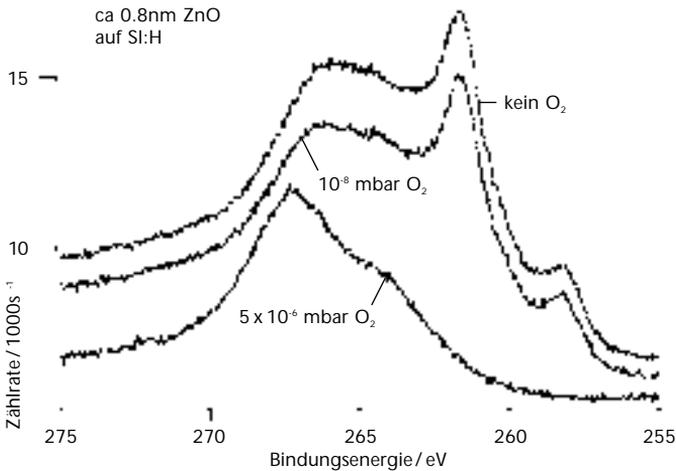
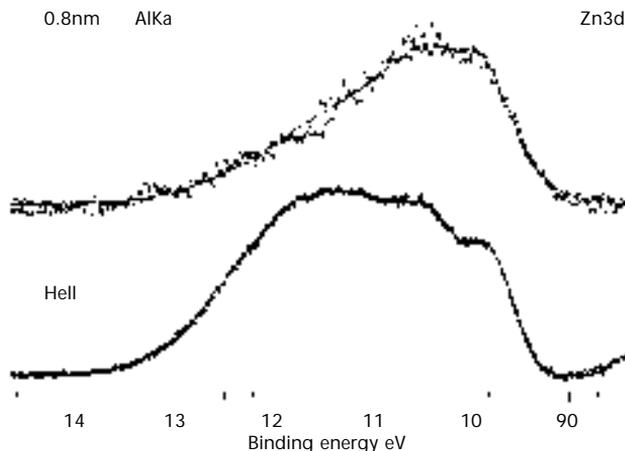


Figure 2

Zn-Auger emission of a sputtered film (sample at ground potential) with increasing oxygen admixture, showing a clear signature for reduced ZnO. ZnO is found only in close vicinity to the interface (not shown here)

magnitude less after heating the film to 400 °C for 40 min in 10^{-2} mBar O_2 . In the XPS spectra the shoulder at 532.8 eV is missing after heating. It is known that ZnO films contain considerable amounts of hydrogen, preferable as OH species we assign the O1s shoulder for thicker films to $\text{Zn}(\text{OH})_x$ species. For films below 5 nm for thicker films the oxidized part of the Si substrate contributes to the emission at 532.8 eV. A more detailed view on the Si 2p emission (Fig. 4) in the binding energy range where oxides are found reveals that beside the known SiO_x suboxide an

Figure 3
Hell and AlKa spectra
of the Zn3d emission for
a very thin ZnO film
(.8nm). The observed
structure is directly rela-
ted to the complex inter-
face morphology



emissions at 102.6 eV, which is situated between the SiO₂ and the suboxides, is found in the interfacial region. As this additional emission is restricted to the interface region and also in the Zn3d line an emission has to be assigned to an interface species beside the ZnO component, we conclude a Si-Zn-O mixed phase. In the literature a mineral termed willemite (Zn₂SiO₄) is known to have binding energies in this range. Taking these data into account we try to calculate the O1s intensity for the different species present at the Si-ZnO interface.

In *Fig. 5* the oxygen intensities were calculated from the spectra of the Zn and Si core level intensities and the respective components associated with a chemical phase. Signal intensities were corrected for escape depth. In the case of Zn₂SiO₄ the O1s intensities were derived from the Si2p level as well as from the fit result of the Zn2p line. In addition as a cross check the intensities were calculated on the base of the applied model for ZnO and the sum of all

intensities is summed up and compared to the total O1s intensity. As a model for the interface we assumed, that Si is covered by SiO_2 and the willemite phase is on top of the Si-oxide. The ZnO lies on top of the willemite. Zn-OH is diluted in the ZnO, which is assumed to grow with ZnO phase. The difference between measured total O1s intensity and the calculated sum of the assumed oxygen containing interface species is surprisingly small, indicating that a reasonable model is applied.

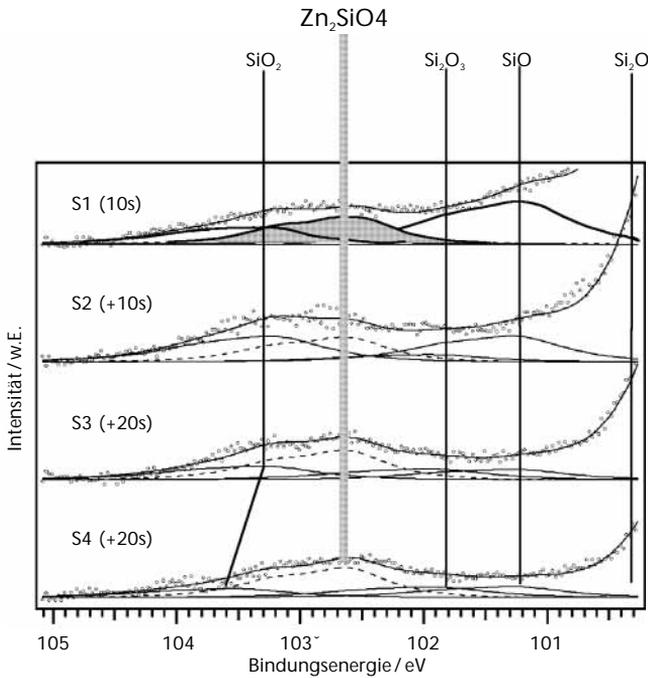


Figure 4
 Close look to the interface region in the Si2p emission. The shaded area is assigned to a Zn_2SiO_4 like phase (Willemite). All emissions are related to the line positions as obtained from a fit routine. Data points and sum of the fit result are given also.

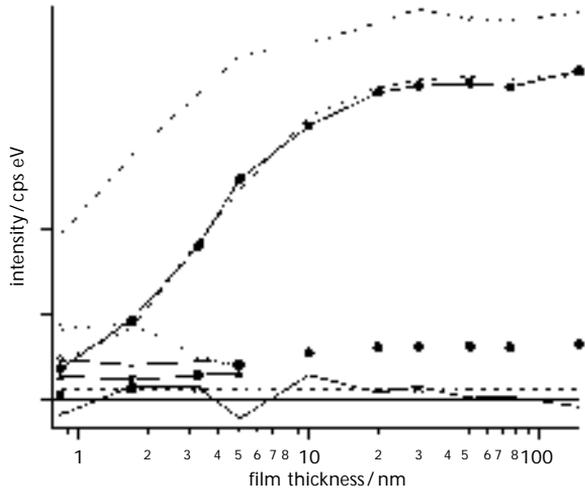


Figure 5
 Model calculation of the O1s intensities for the structure of the ZnO-Si interface in comparison to the measured values. Unprimed components are measured data, primed components are calculated and corrected for attenuation of the elastic escape depth.

- * * I' (O1s) measured
- - I' (O1s) component
- > I' (O1s(SiO2))
- I' (O1s(ZnO))
- I' (O1s(Zn(OH)₂))
- - I' (O1s(OH surface component))
- I' (O1s(Zn2SiO4))_Zn-derived
- I' (O1s(Zn2SiO4))_Si-derived
- sum {O1s(Zn, Si)}
- difference (- - - x)

In conclusion, a detailed analysis of the interface morphology by high resolution XPS gives valuable information on the structure and the chemical constituents contained in the Si-interface. The observed interface species are mainly generated by the deposition process, e.g. the presence of highly reactive species generated by the plasma of the magnetron. The renaissance of the discussion of the role of hydrogen in the doping mechanism in ZnO is also touched by our results. In all investigated films hydrogen is present. The content can be derived from the presence of Zn-OH by about 10-20 % of the ZnO.

Ongoing investigations will concentrate on the morphology of the OH species, as it seems that at the surface and within the film presumably at grain boundaries different kinds of Zn-OH species are present.