

On the composition dependence of $\text{ZnO}_{1-x}\text{S}_x$

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We report on the optical and structural properties of a series of $\text{ZnO}_{1-x}\text{S}_x$ films deposited by radio-frequency sputtering on float glass and sapphire substrates. In the range $0 < x < 0.4$ we find that the films have wurtzite symmetry and the lattice constant varies linearly on the composition as confirmed by photoelectron spectroscopy and Rutherford backscattering. Raman measurements show that the spectral position of the $A_1(\text{LO})$ mode is sensitive to the sulfur content in the films. The composition dependence of the band gap was evaluated by analyzing the absorption coefficient as a function of the square root of the photon energy (direct transition). The energy gap shifted by more than 500 meV to lower energies indicating a bowing of appr. 2.5 eV in contrast to previous predictions.

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1 Introduction Modification of the band structure by alloying is an important aspect for the fabrication of wide band gap heterostructures in ZnO. Whereas Mg-alloying may shift the band gap considerably into the UV, Cd-alloying is employed for tuning to the blue spectral range. However, the thermodynamic solubility limit is rather low ($x = 0.02$ for $\text{Cd}_x\text{Zn}_{1-x}\text{O}$), experimentally a maximum Cd-concentration of $x = 0.07$ was found [1]. Anion substitution i.e. replacing oxygen by sulfur has been reported recently [2] but only in a very narrow range ($0 < x < 0.14$). It was speculated that the ZnOS compound materials system might have bowing parameters as large as GaNP and GaNAs due to the large electronegativity differences between O and S [3]. This would allow to tune the band gap energy over a wide range with only small amounts of sulfur in ZnO and avoid large lattice mismatch beneficial for the growth of quantum structures. However, it is not reported whether $\text{ZnO}_{1-x}\text{S}_x$ can be synthesized as a random alloy or if phase separation occurs. It was, therefore, our interest to synthesize $\text{ZnO}_{1-x}\text{S}_x$ over a wide composition range and to determine the respective changes in the lattice parameters and band gap energies as a function of the $\text{ZnO}_{1-x}\text{S}_x$ composition.

2 Experimental We report on a series of samples deposited by radio-frequency (RF) sputtering on glass and c-plane sapphire substrates. We used a ceramic ZnS target, Ar and O_2 as working and reactive gases, respectively. Substrate temperature was 340 °C and typical film thickness was 300 nm for 30 minutes of sputtering at a sputter power of 300 W. The films were characterized by θ - 2θ X-ray-diffraction (XRD), optical transmission and Raman measurements at room temperature, X-ray photoelectron spectroscopy (XPS, UPS) and Rutherford backscattering (RBS) of the compositional dependence.

3 Results and Discussion In this report we focus on the oxygen rich side of $\text{ZnO}_{1-x}\text{S}_x$ thin films. By increasing the Ar/ O_2 ratio from 1.1 to 4.6 the (0002) reflection of ZnO shifted continuously from 33.6° to

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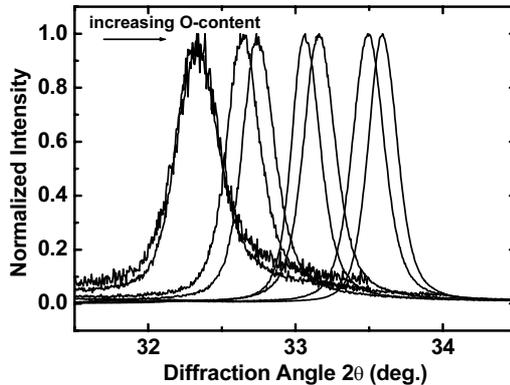


Fig. 1 The dependence of the (0002) reflection on the O-content of $\text{ZnO}_{1-x}\text{S}_x$ films detected by XRD.

31.7° (see Fig. 1). The grains are c-axis oriented and have an average diameter around 60–70 nm. These findings are independent whether float glass or sapphire were used as substrates.

In order to determine the composition of the films we employed XPS and RBS which within experimental error and accuracy delivered the same results. As an example we show the XPS spectra of two $\text{ZnO}_{1-x}\text{S}_x$ films (see Fig. 2) with zero S-content and for a composition $x = 0.4$. Apart from the core states of Zn (3d-, 3p- and 3s-states) and the LMM Auger excitations we see the respective O 1s and S 2p in the alloyed films. The C 1s signal originates from a carbon contamination either on the surface or within the film. The area under the respective O 1s, S 2p, and Zn 3p signals can be used to determine the composition of the $\text{ZnO}_{1-x}\text{S}_x$ films.

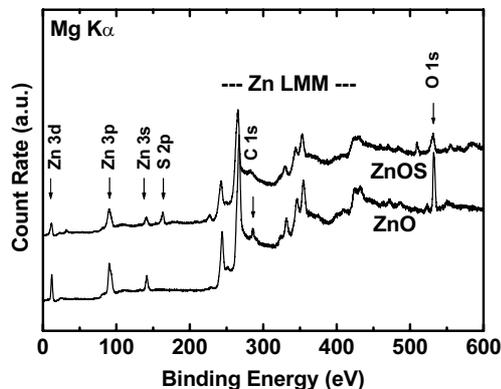


Fig. 2 A comparison of XPS spectra of ZnO and $\text{ZnO}_{0.6}\text{S}_{0.4}$. The O 1s, S 2p, and Zn 3p signals were used to identify the composition of the $\text{ZnO}_{1-x}\text{S}_x$ layers.

The results from the θ - 2θ X-ray and XPS measurements are summarized in Fig. 3. The composition varies linearly with the diffraction angle within this composition range if one assumes that the lattice constant can be linearly interpolated between the two binary end points ZnO and ZnS, respectively. The nice agreement between XRD and XPS confirms that this assumption is correct and Vegard's rule [4] is valid at least for this range of compositions. We used the lattice constants for the wurtzite crystal structures of ZnO and ZnS. Four circle XRD-measurements indeed showed sixfold symmetry within the composition range synthesized [5]. Since ZnS is known to be polymorph, it can exist in cubic and wurtzite structure, the sputter conditions as well as the substrate orientation in the case of sapphire favor the (0002) c-axis oriented growth of the films.

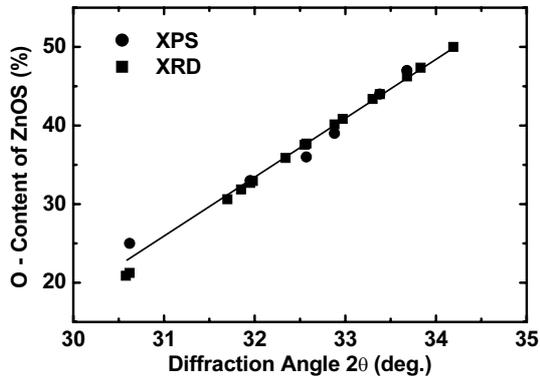


Fig. 3 The correlation between the XRD and XPS results and the O-content of $\text{ZnO}_{1-x}\text{S}_x$.

In Fig. 4 we compare the Raman spectra of the sapphire substrate (a), a ZnO film (b) and a $\text{ZnO}_{1-x}\text{S}_x$ film (c) with $x = 0.04$. The eigenfrequencies of the phonons of an alloy depend in a characteristic way on the stoichiometry. One can distinguish three different types: one mode, two mode and three mode behaviour. In the simplest case of the one mode behaviour the number of modes does not change with stoichiometry and the frequency of the modes depends nearly linearly on the composition of the material [6]. In the ZnO film (Fig. 4.b) we see two characteristic lines corresponding to the host phonons of ZnO, the one at 438 cm^{-1} the $E_2(\text{high})$ mode and the one at 578 cm^{-1} which we attribute to the $A_1(\text{LO})$ mode. Already with a small amount of S in the films the $E_2(\text{high})$ mode rapidly broadens and is hardly detectable. The $A_1(\text{LO})$ shifts in the alloyed film towards lower frequencies, however, a splitting typical for a two-mode behaviour does not appear. Due to the large line width it might not be possible to resolve it. In the AlGaN alloy system a two-mode behaviour was found for the TO-modes but not for the LO-mode and the $\text{ZnO}_{1-x}\text{S}_x$ alloy might behave in the same way.

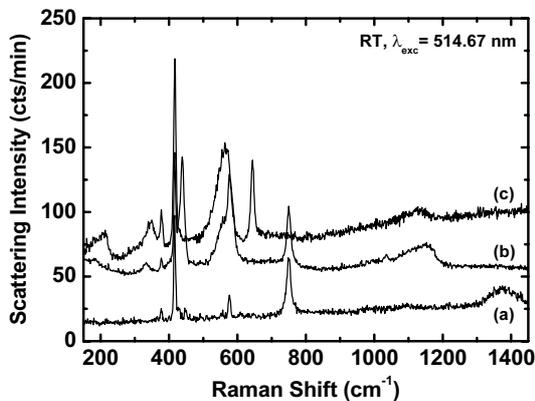


Fig. 4 The Raman spectra of a sapphire substrate (a), a ZnO layer (b), and a $\text{ZnO}_{1-x}\text{S}_x$ film (c).

The transmission measurements at room temperature of a series of $\text{ZnO}_{1-x}\text{S}_x$ films are shown in Fig. 5. With increasing sulfur content the onset of the transmission shifts continuously red. From the transmission spectra the absorption coefficient was calculated according to Beers law. The composition dependence of the band gap was evaluated by analyzing the absorption coefficient as a function of the square root of the photon energy (direct transition) [7]. The energy gap shifted by more than 500 meV (see inset in Fig. 5). The energy gap of a ternary alloy compound semiconductor $\text{ZnO}_{1-x}\text{S}_x$ is described by

$$E_{\text{ZnOS}}(x) = x E_{\text{ZnS}} + (1-x) E_{\text{ZnO}} - b (1-x) x,$$

where E_{ZnS} and E_{ZnO} are the band gap energies at 300K of the binary compounds 3.6 and 3.2 eV, respectively and b is the optical bowing parameter. The analysis of our data results in a bowing of appr. 2.5 eV.

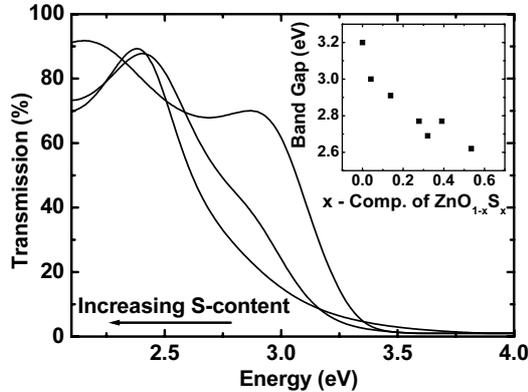


Fig. 5 The optical transmission spectra of $\text{ZnO}_{1-x}\text{S}_x$ films with different compositions and the energy gaps resulting from these measurements.

$\text{ZnO}_{1-x}\text{S}_x$ follows the trends known also for the other II–VI chalcogenides $\text{ZnSe}_x\text{Te}_{1-x}$, $\text{ZnS}_x\text{Te}_{1-x}$ and $\text{ZnS}_x\text{Se}_{1-x}$. Within their range of solid solubility Vegard's rule holds, ZnSSe has a bowing parameter between 0.4 and 0.65, for ZnSeTe it is around 1.3 and for ZnSTe between 2.4 and 3 eV [8].

4 Summary In conclusion, $\text{ZnO}_{1-x}\text{S}_x$ films have been synthesized over a large range of compositions by radio-frequency sputtering from a ceramic ZnS target and changing the Ar/O_2 pressure ratio. The films have wurtzite structure, show a linear variation of the lattice constant as follows from Vegard's rule. In contrast to recent predictions the optical bowing parameter is appr. 2.5 eV only and the band gap energy can only be tuned down to appr. 2.7–2.8 eV for $x = 0.5$.

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