

ZnO based ternary transparent conductors

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Received 23 February 2006, accepted 26 June 2006

Published online 31 August 2006

PACS 78.30.Fs, 78.66.Hf, 81.05.Dz, 81.15.Cd

ZnO_{1-x}S_x films in the whole composition range were deposited by radio-frequency reactive sputtering on different substrates. Raman measurements verified that the LO phonon of ZnO shifts towards lower frequencies as a function of the S content in the alloyed films. The composition dependence of the band gap energy in the ternary system was determined by optical transmission and the optical bowing parameter was found to be about 3 eV. We compare this behavior to ZnOSe films which can, however, only be synthesized in a narrow composition range close to the binary constituents ZnO and ZnSe.

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1 Introduction

The replacement of the cation or anion by an isoelectronic element may have profound effects on the electrical and optical properties of a semiconductor especially if large differences exist in electronegativity and covalent radii between the host atoms and the replacing elements. One of the systems of current interest is GaAsN for lasers operating in the near infrared. For opto-electronic devices working in the blue-UV spectral range the band gap engineering of ZnO by alloying has become an issue. The substitution of Zn by Mg and Cd has been studied in detail and quantum confinement in two-dimensional heterostructures of ZnMg(Cd)O/ZnO/ZnMg(Cd)O has been achieved [1]. As a result the authors reported that the band gap in ZnMgO changed more or less linear with the Mg composition whereas the ZnCdO alloy exhibits a pronounced nonlinearity i.e. bowing. Due to the large electronegativity and size differences between O and S (Se) [2] one can expect that the bowing parameters of ZnOS and ZnOSe are large and thus comparable with those of GaPN and GaAsN [3]. Alloying of ZnO by replacing oxygen by sulfur or selenium has been reported recently [2, 4–6] only for a composition range $x < 0.2$. The intention of our work was to grow ZnO_{1-x}S_x layers over a wide composition range and to determine the dependence of the optical properties i.e. the band gap energies and Raman frequencies on the sulfur content. The first results on the behavior of ZnOSe thin films are also reported.

2 Experimental

The ZnO_{1-x}S_x and ZnO_{1-x}Se_x films were prepared on glass and *c*-plane sapphire (0001) substrates by radio-frequency (RF) sputtering. A ceramic ZnS or ZnSe target and Ar and O₂ as working and reactive gases, respectively, were used. The substrates were heated up to 340 °C. Typically the film thickness was about 300 nm for 30 minutes sputter process at a power of 300 W. The optical transmission was meas-

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ured by a PE Lambda 900 and the Raman spectra by a single grating DILOR LabRam spectrometer, both at room temperature. The crystal structure of the films was studied by θ - 2θ X-ray diffraction (XRD) using a Siemens D5000 diffractometer with Cu K_{α} ($\lambda = 0.15418$ nm) radiation. X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) were used to determine the composition and stoichiometry of the films. The XPS measurements were carried out with a VG ESCALAB system at a photon energy of 1253.6 eV (Mg K_{α} radiation). RBS experiments were performed using He^{+} or H^{+} ions with a typical energy of 800 keV and the ion beam perpendicular to the sample surface.

3 Results and discussion

The band gap dependence on the sulfur content was evaluated by analyzing transmission measurements. The optical transmission curves shift first red with increasing sulfur content and then they shift back for $x > 0.45$. Typical transmission measurements at room temperature of $ZnO_{1-x}S_x$ films are presented in Fig. 1. From these spectra the absorption coefficient was determined and further the band gap as a function of the square root of the photon energy (direct transition) [7]. The dependence of the band gap on the composition of the $ZnO_{1-x}S_x$ layers is shown in Fig. 2. The energy gap of a ternary compound semiconductor as $ZnO_{1-x}S_x$ is described by

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

whereas E_{ZnS} and E_{ZnO} are the band gap energies at 300 K of the binary compounds 3.6 [8] and 3.2 eV [9], respectively, and b is the optical bowing parameter. Our data interpretation results in a bowing parameter of appr. 3.0 eV.

In the sulfur dilute limit the slope is 22 meV/% whereas for the oxygen dilute limit it is 32 meV/%. Thus the bowing parameter in the ZnOS system might be expressed by a constant value of 3 eV i.e. it is independent of composition x . In Fig. 3 are the results obtained on ZnOSe thin films prepared and analyzed in the same manner. They could be synthesized only in a narrow composition range close to the binary constituents ZnO and ZnSe. It could indicate a limited solubility of O in ZnSe. A sizeable down shift in energy is, however, found and indicates a larger bowing. In contrast to the ZnOS system the slopes are markedly different, i.e. it is 78 meV/% in the Se dilute limit and appr. half of it 42 meV/% in the oxygen dilute limit. This is an indication that the bowing parameter b itself is a function of composition as found for $CdS_{1-x}Te_x$. However, due to the limited data only a composition independent value of b could be approximate and gives a bowing parameter around 7 eV. However, the trend known for other

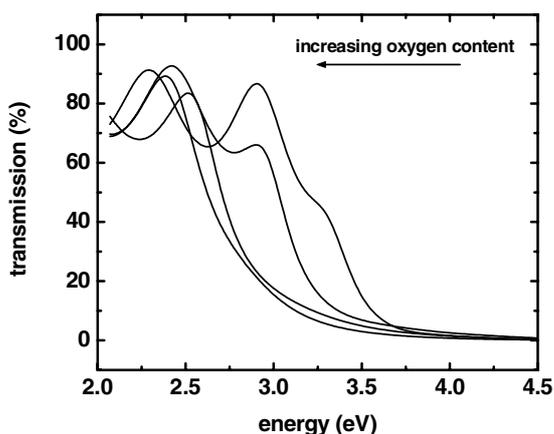


Fig. 1 Optical transmission spectra of sulfur-rich $ZnO_{1-x}S_x$ films with different compositions.

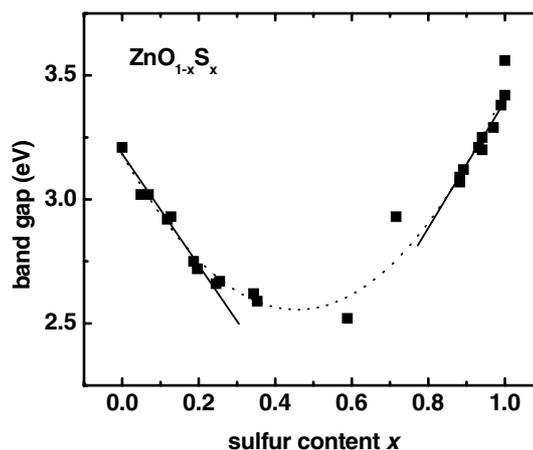


Fig. 2 Band gap energy of $ZnO_{1-x}S_x$ films as a function of the composition x .

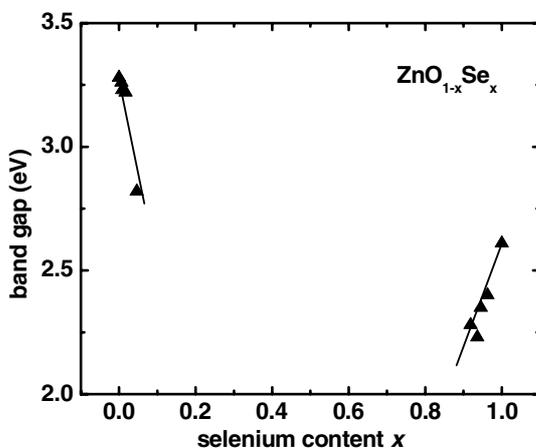


Fig. 3 Band gap energy of $\text{ZnO}_{1-x}\text{Se}_x$ films as a function of the composition x .

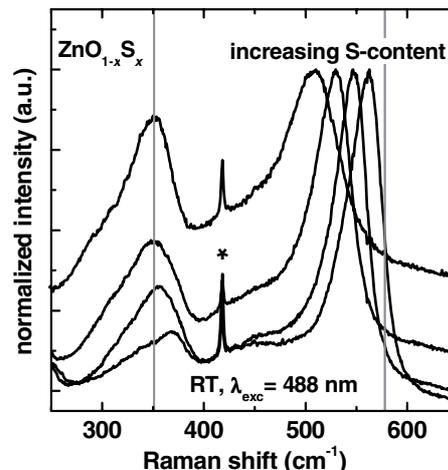


Fig. 4 Raman spectra of four $\text{ZnO}_{1-x}\text{S}_x$ films with $0.04 \leq x \leq 0.23$ recorded in backscattering geometry at room temperature. The grey lines indicate the frequencies of the LO phonon modes of the binary systems ZnS and ZnO. The sharp peaks labeled with an asterisk originate from the sapphire substrate.

II–VI compounds e.g. $\text{ZnSe}_x\text{Te}_{1-x}$, $\text{ZnS}_x\text{Te}_{1-x}$, and $\text{ZnS}_x\text{Se}_{1-x}$ is confirmed also for $\text{ZnO}_{1-x}\text{S}_x$ and $\text{ZnO}_{1-x}\text{Se}_x$. The bowing parameter for ZnSSe is between 0.4 and 0.65, for ZnSeTe it is about 1.3 eV and for ZnSTe between 2.4 and 3 eV [10].

In Fig. 4 we compare Raman spectra of $\text{ZnO}_{1-x}\text{S}_x$ samples with $0.04 \leq x \leq 0.23$. The spectra are taken in backscattering geometry with incident and scattered light in parallel polarization along the samples c -axis. They are normalized to the band around 500 cm^{-1} . Signals of the sapphire substrate are marked by an asterisk. The grey lines indicate the frequencies of the $A_1(\text{LO})$ mode of ZnO at 578 cm^{-1} and the $A_1(\text{LO}) = E_1(\text{LO})$ mode of ZnS at 351 cm^{-1} [11–13]. The Raman spectra of pure ZnO are typically dominated by the $E_2(\text{high})$ mode at 437 cm^{-1} . Introducing sulfur into ZnO the E_2 -line broadens immediately and is hardly detectable. Simultaneously the LO phonon shifts towards lower energies and the LO of ZnS appears as a broad structure around 350 cm^{-1} . Increasing the sulfur content up to $x = 0.23$ the ZnO LO mode reaches 507 cm^{-1} (see Fig. 5) and the ZnS LO band grows in intensity. The phonon frequencies of alloys depend on their stoichiometry in a characteristic way [e.g. 14–16]: phonons exhibit one- or multi-mode behavior. Contrary to our first assumption [17] the further investigations shown in this report revealed a two-mode behavior for the LO phonons of $\text{ZnO}_{1-x}\text{S}_x$, i.e. the existence of separate modes of both possible pairs of adjacent atoms.

The optical phonon frequency in a mixed II–VI crystal $\text{AB}_{1-x}\text{C}_x$ exhibits either an one-mode behaviour ($\text{Zn}_{1-x}\text{Cd}_x\text{S}$ [18]), a two-mode behaviour ($\text{ZnS}_x\text{Se}_{1-x}$, $\text{ZnS}_{1-x}\text{Te}_x$ [19, 20]) or intermediate-mode behaviour ($\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ [21]). Based on the work of Ref. [22] a two-mode behaviour is observed when the masses of the A, B and C atoms are such: $m_B < \mu_{AC}$ and $m_C > \mu_{AB}$, where μ_{AC} and μ_{AB} are the reduced masses of the two respective binary compounds. In the alloy system $\text{ZnO}_{1-x}\text{S}_x$ this criterion is fulfilled:

$$m_{\text{O}} (15.99) < \mu_{\text{ZnS}} (21.54) \quad \text{and} \quad m_{\text{S}} (32.064) > \mu_{\text{ZnO}} (12.74).$$

The results agree in principle with those we found for the $\text{ZnO}_{1-x}\text{Se}_x$ system. Figure 6 shows spectra of four samples turning from Se-rich (bottom, $x = 0.94$) to O-rich (top, $x = 0.06$). The values of the Se contents are estimated from X-ray diffraction measurements. The spectra are recorded in the same way as described above and shifted vertically for clarity. They are normalized to their maximum intensity. Grey

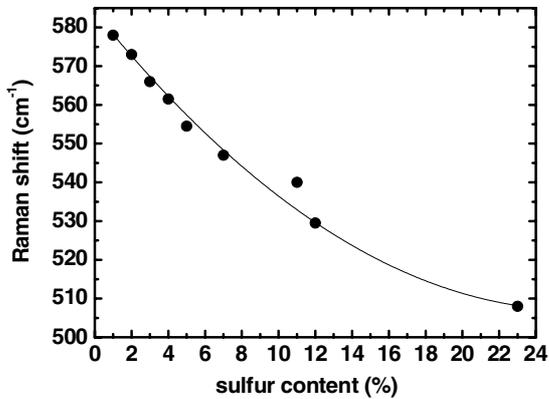


Fig. 5 Dependence of the LO ZnO-like phonon mode on sulfur content. The drawn line is a guide for the eye.

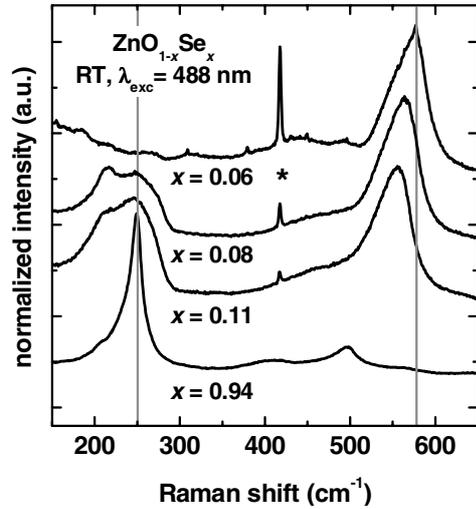


Fig. 6 Raman spectra of four $\text{ZnO}_{1-x}\text{Se}_x$ films with bottom-up decreasing Se content recorded in backscattering geometry at room temperature. The grey lines indicate the frequencies of the LO phonon modes of the binary systems ZnSe and ZnO. The sharp peaks labeled with an asterisk originate from the sapphire substrate.

lines mark the frequencies of the LO phonon modes of ZnO (578 cm^{-1}) and ZnSe at 250 cm^{-1} [23], the asterisk the signal from the sapphire substrate. The strongest feature in the spectrum of the O-rich sample is a ZnO-like LO phonon while that of the Se-rich sample is dominated by a ZnSe-like LO mode. Samples with $x = 0.11$ and 0.08 exhibit broad bands in the vicinity of the LO phonons of the binary alloys. As in the case of ZnOS the E_2 (high) line of ZnO broadens immediately and vanishes. The redshift of the ZnO-like LO phonon is less pronounced visible due to the fact that no ZnOSe samples are available so far with a comparable amount of Se and O. But the two-mode behavior of the LO phonons of the $\text{ZnO}_{1-x}\text{Se}_x$ system is also clearly observable.

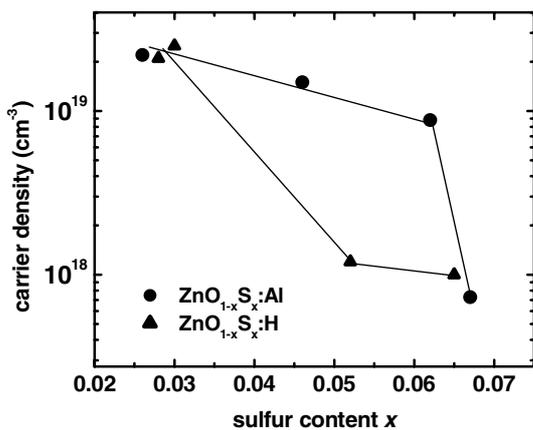


Fig. 7 Carrier density of ZnOS films as a function of sulfur content x doped by aluminum and hydrogen.

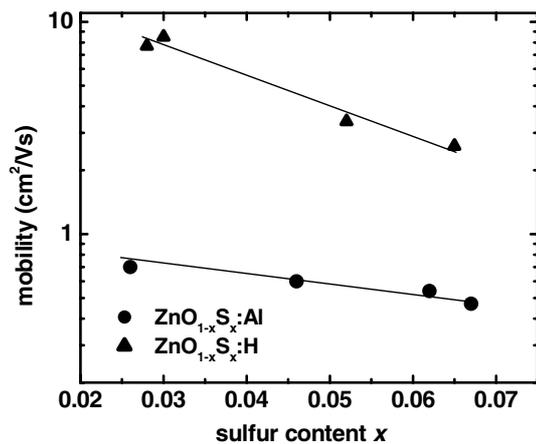


Fig. 8 Mobility of ZnOS films as a function of sulfur content x doped by aluminum and hydrogen.

The undoped ZnOS films were high resistive. For an application as a transparent conductor e.g. in protecting for UV radiation in electrochromic devices the layers were doped *in-situ* during sputtering. This could be achieved by using an Al doped target or adding hydrogen as a reactive gas to the working gas Ar. Hydrogen and Al are shallow donors in ZnO with binding energies of 46 and 52 meV, respectively. Samples were prepared for the sulfur dilute limit (see Figs. 7 and 8). For sulfur contents around 3% the carrier densities reached values around $2 \times 10^{19} \text{ cm}^{-3}$ for both dopands and for higher sulfur contents dropped to values in the high 10^{17} cm^{-3} and low 10^{18} cm^{-3} range (see Fig. 7). For sulfur contents <3% the resistivity of ZnOS:H is a factor of 16 lower ($0.03 \Omega \text{ cm}$) compared to ZnOS:Al ($0.5 \Omega \text{ cm}$). This result becomes understandable when comparing the respective mobilities (see Fig. 8). Although showing a similar trend as a function of the sulfur content the mobility in the ZnOS:H films is well above that for ZnOS:Al films.

In XRD the sputtered films showed a preferential (0002) orientation but are polycrystalline. Thus, the electrical transport is severely influenced by the grain boundaries which arise from dislocations and their arrangement. The electrical properties of dislocations may be associated with the presence of dangling or broken bonds. The dangling bond has an unpaired electron. If the broken bond defect is negatively charged it can be passivated by hydrogen which has a positive charge. This creates neutral defect pairs, reduces compensation, and thus enhances the mobility. Since Al is a substitutional donor no such effect occurs in ZnOS:Al.

4 Summary

In summary, $\text{ZnO}_{1-x}\text{S}_x$ films were grown by radio-frequency sputtering using a ceramic ZnS target and a variable Ar/O₂ pressure ratio. The absorption coefficients received from optical transmission measurements were used to determine the band gap energies and after all the optical bowing parameter of about 3.0 eV. The band gap energy can be adjust down to $(2.6 \pm 0.1) \text{ eV}$ for $x = (0.45 \pm 0.05)$. The first results on the ZnOSe alloy system suggest a bowing of about 7 eV. A two-mode behavior of the LO phonon modes has been observed in Raman measurements for both systems.

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