Full Length Article

Behavior and impact of sulfur incorporation in Zinc Oxysulfide alloy grown by metal organic chemical vapor deposition

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ABSTRACT

Highly mismatched $ZnO_{1-x}S_x$:N alloy films with various x were deposited on c-plane sapphire substrates by a near-equilibrium method, metal-organic chemical vapor deposition. The sulfur concentration in the films could be tuned by changing the flow rate of H_2S during the growth process. The films that could maintain single phase have an upper limit for $x \sim 0.15$, which is smaller than the x values obtained from other non-equilibrium-grown samples ($x \sim 0.23$). When $x > 0.15$, phases other than the wurtzite ZnO (W-ZnO) one appeared. Those phases were ascribed to the sulfur-diluted W-ZnO like phase, low x W-ZnO like phase, and high x W-ZnS like phase. The S contents in different phase has been determined by using Vegard's law and the X-ray photoelectron spectroscopy. Meanwhile, the compositional dependence of the bandgap energy in the $ZnO_{1-x}S_x$ alloyed material has been investigated and studied comparing with other reported results. The dispersed bowing parameter b and the mechanism of the phase separation in samples grown by both the near-equilibrium method and the non-equilibrium one have also been discussed based on the difference of the atomic radius and electronegativity of the oxygen and sulfur atoms. Furthermore, the Raman and photoluminescence spectra have shown that the sulfur incorporation may suppress zinc interstitials related defects, while the oxygen vacancies related defects may be easily formed at the same time. These results indicate that $ZnO_{1-x}S_x$ films could be beneficial to the realization of p-type doping in ZnO, although no obvious p-type characteristic has been attained in the work yet.

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1. Introduction

Zinc oxide (ZnO) is a potentially efficient ultraviolet optical material for numerous optoelectronic device applications [1]. Unique properties like wide direct bandgap (3.4 eV) and large exciton binding energy (60 meV) at room temperature make it a prime candidate for high efficient ultraviolet light-emitting diodes and lasers up to high temperatures [2]. Meanwhile, a relatively broad range of tuned bandgap through cationic (Be, Mg, Cd) [3–5] or anionic (S, Se, Te) [6–8] alloying also expands the spectral region from deep ultraviolet to green [9]. Unfortunately, the difficulties in fabrication of high-quality homo p–n junction mightily impede the development of ZnO-based devices depending on bipolar conduction including light emitting devices [10,11]. As with other wide bandgap semiconductors, ZnO experiences a serious doping asymmetry problem due to the lower valence band maximum with

respect to the vacuum, which means the relatively deep acceptor states. [12] On the other hand, serious compensation from intrinsic donor defects with low formation energy such as vacancies or interstitials also hinders the stable p-type doping [13,14]. Based on these consideration, fabricating high-quality ZnO and shallowing the acceptor state are the keys to overcome the doping asymmetry problem [15].

Typically, alloying ZnO with isovalent anion (S, Se, Te) can conspicuously tune the bandgap structures [16]. The strong non-linear repercussions on optical and electrical properties of those ZnO-based semiconductor alloys ($ZnO_{1-x}S_x$, $ZnSe_xO_{1-x}$, $ZnTe_xO_{1-x}$) have been observed and explained in the framework of the Band Anticrossing (BAC) model [17]. The O atoms have a large electronegativity and size mismatch with respect to other chalcogens, which could be utilized to shallow the ionization energy of deep acceptor and to modulate the crystallographic structure [18]. Compared with Se and Te, S has the minimal size difference with O ($r_S/r_O = 1.3$) [19] that means S has relatively large solubility in ZnO [16]. However, according to Hume-Rothery rules [20], the substitutional solid solutions occur only if the atomic radius of the solute and solvent

atoms differ by less than 15%. The difference of r_O and r_S is about 36%, which implies that alloying of ZnO and ZnS is impossible at thermodynamic equilibrium state and so the $ZnO_{1-x}S_x$ alloys are still difficult to be formed [21]. Actually, via chemical transport reactions, Locmelis et al. [22] grew bulk $ZnO_{1-x}S_x$ mixed crystals at 900 °C, and found an almost symmetric solubility of about 5 mol% for the $ZnO_{1-x}S_x$ crystals, i.e. $0 \leq x \leq 0.05$ in the O-rich and $0.96 \leq x \leq 1$ in the S-rich regions, respectively. Furthermore, from the viewpoint of equilibrium thermodynamics, it is easy to form sulfates or sulfur dioxide on the anionic site rather than substitution [23].

However, at the non-equilibrium growth conditions, the alloying of ZnS and ZnO may be relatively easier to be realized. In fact, various non-equilibrium approaches such as pulsed layer deposition (PLD) [19,24–30] and radio-frequency magnetron sputtering [31–35], have been reported to study the crystallographic and optical properties of the alloys. He et al. reported that the single phase wurtzite alloy films can only be realized in the limited S range ($0 \leq x \leq 0.23$, $0.94 \leq x \leq 1$) by PLD [21]. Zhu et al. reported the phase separation in films with $11.9\% < x < 70.4\%$ by reactive sputtering [33]. Jaquez et al. reported a wurtzite structure for alloys throughout the composition range by radio-frequency magnetron sputtering [35]. In fact, the composition range in which homogenous alloys are formed differs from techniques and conditions for the film deposition.

As to the case for p-type realization in the $ZnO_{1-x}S_x$ alloys, Park et al. fabricated phosphorous-doped $ZnO_{1-x}S_x$ films with weak p-type conductivity [34], while Datta et al. indicated that the incorporation of S may not give desired p-type due to the inactivation of acceptor atoms as well as self-compensation effects caused by native defects [24]. Kobayashi et al. proposed that the interstitial SO_3 or SO_4 clusters and V_{Zn}-H complexes are the appropriate acceptors [36], while no more authentic evidences have been reported.

Metal-organic chemical vapor deposition (MOCVD) is considered to be a powerful tool to grow high quality III–V and II–VI semiconductor films and related alloys, which is normally operated under thermodynamic equilibrium [37]. In the case, MOCVD is considered to be difficult to be employed for highly mismatched $ZnO_{1-x}S_x$ alloys growth [38]. Actually, there is no reports found to focus on the growth of $ZnO_{1-x}S_x$ alloys via such thermodynamic equilibrium growth method.

In this work, we attempt to employ MOCVD method to synthesis a series of $ZnO_{1-x}S_x$ alloy films with different composition of sulfur. The effect of substitution of S for O on films was studied systematically. By Varying S concentration, the dynamic relations among crystallographic, optical, electrical properties of $ZnO_{1-x}S_x$ films are discussed in details. The basic structural and optical properties of these films were investigated using X-ray diffraction (XRD), Raman spectrometry, optical absorption spectra and photoluminescence. Furthermore, Hall test measurement was carried out on the films for obtaining the electrical properties.

2. Experimental details

$ZnO_{1-x}S_x$ alloy films were deposited on c-plane sapphire substrates by a home-built MOCVD with diethylzinc and O_2 used as Zn and oxygen source, respectively, which are introduced into the reactor separately. The detail of the reactor can be found elsewhere. Before being transferred into the chamber, the sapphire substrates were subsequently cleaned ultrasonically in acetone, ethanol, deionized water and dried under a high-purity N_2 flow. After loaded into the reactor, the sapphire substrates were heated up to 1373 K for 5 min in N_2 and H_2 ambience at the pressure of 15 kPa for surface cleaning and pretreatment. After that, the substrate temperature and reactor pressure were lowered and kept at 700 K and

200 Pa, respectively, for $ZnO_{1-x}S_x$ alloy growth. Diethylzinc carried by high-purity N_2 was used as zinc precursor at the mole fraction of 10.7 μmol/min, O_2 was used as oxygen precursor at the flow rate of 200 sccm, leading to a O/Zn ratio of 833 during growth process. Radio frequency plasma ionized N_2O is used as nitrogen doping precursor at the flow rate of 24 sccm. The flow rate of H_2S varied in the range of 0.04–0.5 sccm, leading to a S/O (S/Zn) ratio changed from 2×10^{-4} (0.17) *to* 2×10^{-3} (2.08) in the gas phase. During growth process, the reactor pressure was fixed at 220 Pa to obtain high efficiency of RF ionization of N_2O, which provides possible atomic nitrogen doping in the growing film.

After growth, the films structure and crystallinity were analyzed by a high-resolution x-ray diffractometer equipped with Cu Kα radiation source at the wavelength of 0.15405 nm in θ-2θ configuration (Philips'X pert Pro diffractometer, Netherlands). The Raman modes were excited with a Ar laser (λ = 514.5 nm) and recorded using a JOBIN YVON HR800 UV Raman system at room temperature. The measurements were carried out in backscattering configuration and the scattered light was analyzed with a multichannel detector worked at 202 K with accuracy better than 0.65 cm^{-1}. Photoluminescence measurements were performed at both room temperature and low temperature by using a He-Cd laser (325 nm) as the excitation source with a wavelength resolution of 0.2 nm. The absorption spectra of the films were also measured at room temperature on an ultraviolet-visible spectrometer. Apart from this, the electrical properties of the films were characterized by Hall effect measurements using indium as the ohmic contact metal at room temperature in Van der Pauw's configuration.

3. Results and discussion

Fig. 1(a) presents the θ-2θ scan XRD spectra of $ZnO_{1-x}S_x$ films, in which the intensities of (002) peaks have been normalized to unity for comparison. Diffraction peaks around 28.4° and 34.4° are attributed to wurtzite ZnS (W-ZnS) (002) like and wurtzite ZnO (W-ZnO) (002) like patterns respectively as the diffraction angles of W-ZnS (002) and W-ZnO (002) are previously reported at 28.4° (JCPDS 36–1450) and 34.4° (JCPDS 36–1451), respectively. With the increase of the H_2S flow rate, a distinct shift and broadening have been observed. The broadening of ZnO-like peaks is due to the influence of S incorporation on crystal lattice. It indicates the crystal quality decreases rapidly with the S incorporation. For the samples grown at the flow rate of 0.1 sccm or below, a small shift to lower angle of the (002) ZnO-like diffraction peaks can be observed by sulfur incorporation, with diluted sulfur doped ZnO single phase (for several percent of x) formed. As for the sample grown at the flow rate of 0.2 sccm, besides the further shift of the diffraction peak, a small shoulder located at $2\theta = 33.7°$ can be resolved. This peak shows a much larger shift, indicative of more sulfur incorporation and can then be assigned as low x ZnO-like phase (for about ten percent of x). Meanwhile, a small weak peak located at 28.4° can also be detected and attributed to high x ZnS-like phase (for seventy to eighty percent of x). A further increase of the sulfur incorporation has verified the above assignment, with much enhanced low x ZnO-like phase and high x ZnS-like phase related peaks. Of course, a small shoulder can also be decomposed, indicative of the existence of diluted sulfur doped ZnO phase even with high sulfur incorporation.

Theoretically, the radius of S^{2-} (1.84 Å) is larger than that of O^{2-} (1.32 Å). If S substitutes for O, the diffraction angle of W-ZnO like (002) should move toward lower angle due to the compression of lattice caused by substitution. Meanwhile, with the increasing of S/ZnS in gas phase, W-ZnS like (002) peak shifts towards lower also shows the substitution of S for O in ZnS-like phase. Additionally, The Vegard's law [39] has been verified in $ZnO_{1-x}S_x$ alloys previ-