Thin Solid Films 613 (2016) 11–18

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Nonstoichiometry problems of ZnSe: From single crystals to nanofilms

Igor Avetissov [a],*, Tran Khanh [a], Rasim Saifutyarov [a], Elena Mozhevitina [a], Andrew Khomyakov [a], Roman Avetisov [a], Albert Davydov [b], Sergei Neustroev [b], Nikolai Zhavoronkov [b]

[a] D. Mendeleyev University of Chemical Technology of Russia, Russia
[b] Research Institute of Material Science and Technology, Russia

ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form 24 October 2015
Accepted 28 October 2015
Available online 30 October 2015

Keywords:
Zinc selenide crystal
Thin film, stoichiometry
Nonstoichiometry

ABSTRACT

Selenium nonstoichiometry in ZnSe under bivariant and monovariant equilibriums was studied by a direct physical–chemical method. ZnSe single crystals grown from the melt and the vapor phase were used as starting materials. It was found out that at $T > 720$ K, overstoichiometric Se generates mainly electrically neutral defects. ZnSe thin films (50–300 nm) were prepared by vacuum thermal sputtering on “cold” glass substrates. To control the nonstoichiometry of the films, a specially designed two-chamber evaporator was used. The nonstoichiometry, electrical properties and morphology of the ZnSe films were investigated under various preparation conditions. It was demonstrated that it is possible to form *p*–*n* junction by varying the nonstoichiometry of ZnSe nanofilms.

1. Introduction

ZnSe is an important II–VI semiconductor due to the promising optoelectrical and electrical properties of its wide direct band gap (2.68 eV at 300 K). It is applied as a semiconductor in lasers [1], blue diodes [2], X-ray detectors [3] and VIS-IR transmitting windows for lasers [4].

The structure-sensitive properties of ZnSe-based materials are determined by both doping and native point defects. The existence of native point defects in the binary chemical compound ZnSe is thermodynamically inevitable at $T > 0$ K [5]. The overstoichiometric zinc results in *n*-type conductivity [6,7] and an extra pure oxygen free ZnSe has been proposed to obtain *p*-type conductivity by Se doping (private communication). In Ref. [8] we analyzed the ZnSe homogeneity limits at $S_{ZnSe}L_{(Se)}V$ monovariant equilibrium conditions (Se-rich side) with a direct physical–chemical technique [9]. However, above 1100 K, the solidus line for the Se-rich side was nearly independent of temperature. To prove this temperature independence, we conducted further experiments in which we assumed that more accurate results could be obtained by establishing the $S_{ZnSe}L_{(Se)}V$ monovariant equilibrium as the final point of the $S_{ZnSe}V$ bivariant equilibrium.

The need to develop any ways to produce high-efficiency, high-power, low-cost thin film transistors for organic light-emitting devices (OLED) [10] is urgent due to the extreme increase in the OLED market. In this context, the use of cheap inorganic materials such as ZnSe is preferable because these materials are superior to organic materials in both carrier mobility and durability. One of the problems for inorganic materials is the ability to fabricate a thin film transistor on a “cold” (*i.e.*, non-heated) organic substrate, which is the basis for future organic electronics.

In this study, in addition to preparing ZnSe thin films (100–230 nm) and analyzing their electrical, optical and structural properties, we also studied the nonstoichiometry of ZnSe (zinc blend modification) at $S_{ZnSe}V$ bivariant equilibrium in the 963–1173 K temperature range, and we analyzed the nonstoichiometry of ZnSe crystals grown from both melt and vapor.

2. Experimental details

2.1. Synthesis and analysis of ZnSe nonstoichiometric preparations

Recent nonstoichiometry investigations revise the data obtained 20–40 years ago because of new achievements in purity analysis, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Glow Discharge Mass Spectrometry (GDMS) and Secondary Ion Mass Spectrometry (SIMS). Therefore, special attention to purity is required in the nonstoichiometry investigation.

The initial polycrystalline ZnSe (zinc blend) preparations were produced using three methods: a direct vapor synthesis (ELMA, Zelenograd, Russia) (ELMA-ZnSe), a multi-step sublimation process (MSS-ZnSe) [11] and a Chemical Vapor Deposition (CVD) process (CVD-ZnSe) [12]. To prevent surface oxidation, we ground the ZnSe samples to powder (50 ± 20 μm) under an argon atmosphere. The highest purity was detected for the MSS-ZnSe preparation using an

---

* Corresponding author at: D. Mendeleyev University of Chemical Technology of Russia, Miusskaya pl.9, 125047, Moscow, Russia. Tel.: +007 495 4966177.
E-mail address: igor_avetisov@mail.ru (I. Avetissov).

http://dx.doi.org/10.1016/j.tsf.2015.10.067
0040-6090/

ICP-MS (NexION 300D, Perkin Elmer Inc.) in kinetic energy discrimination and dynamic reaction cell modes, and SIMS (MiniSIMS, MillBROOK Ltd.) was determined as 99.9998 wt.%. We also analyzed the preparations after all steps of the nonstoichiometry investigation. The worst preparation's purity was 99.9993 wt.%.

We then annealed the nonstoichiometric ZnSe in a quartz glass ampoule at controlled selenium partial pressure [5]. To prevent oxygen diffusion through the ampoule wall, we treated the inner surface of the wall by extra pure acetone pyrolysis. The annealing was conducted in a single-zone tube furnace at $S_{ZnSe}L_{(Se)}V$ monovariant equilibrium and in a dual-zone tube furnace at $S_{ZnSe}V$ bivariant equilibrium with further quenching of high temperature equilibriums.

In the context of the $S_{ZnSe}V$ bivariate equilibrium, the vapor pressure over solid ZnSe was calculated from the mechanical stability of the closed system, the reference data on the composition and vapor pressure of various selenium molecules [13] and the dissociation constant of ZnSe, solving Eq. (1) with respect to p_{Se_2}.

$$\left(k_{diss}/p_{Se_2}^{1/2}+p_{Se_2}+\sum_{i=1,i\neq 2}^{8}\left(k_i\cdot p_{Se_2}\right)^{2/i}\right)_{T_1}=\left(\sum_{i=1}^{8}p_{Se_i}^{0l}\right)_{T_2}, \qquad (1)$$

here k_{diss} is the ZnSe dissociation constant according to the reaction $ZnSe^{s}\rightarrow Zn^{v}+1/2\cdot Se_2^{v}$ [14]; $p_{Se_i}^{0l}$ is the partial pressure of the i-molecule over pure liquid selenium at T_2; k_i. is the equilibrium constant between the *i*-molecule and the Se_2 molecule in the vapor phase at T_1.

The nonstoichiometry determination was measured in quenched samples by the “extraction” technique [9]. In short, this technique consists of collecting the vapor from over the solid phase of the stoichiometric component, transporting the vapor to the “cold” part of the ampoule, condensing it on the ampoule walls and performing further quantitative determination by the ICP-MS technique. The detection limit of ZnSe nonstoichiometry is 1×10^{-8} excess moles of Se and 2×10^{-8} of excess moles of Zn per mole of ZnSe.

2.2. ZnSe nanofilms fabrication

The ZnSe thin films were deposited on a glass/quartz glass substrate using a thermal vacuum sputtering technique at $P<10^{-3}$ Pa. To control the nonstoichiometry of the films we designed a special evaporator (Fig. 1), which allowed independent heating of the ZnSe source (the “hot” upper zone) and the Zn source (the “cold” bottom zone) with temperature accuracy higher than 1 K. The double diaphragm cover of the crucible was filled with carbon fiber to prevent the solid and liquid phases from scattering. The film thickness was monitored in real-time by a quartz microbalance. We made films with a different topology for various investigations (Table 1), including nonstoichiometry determination (NS) (Fig. 2a) and optical and electrical measurements (EC) (Fig. 2b-e). The films with NS and EC structures were prepared at the same process (N1,…,N5) simultaneously. They were marked as $N1_{NS}$,…,$N5_{NS}$ and $N1_{EC}$,…,$N5_{EC}$, correspondingly.

Surface morphology of the films was observed using a Scanning Electron Microscopy (SEM) Tescan VEGA3 LMU SEM system (Tescan Orsay Holding) with an acceleration voltage of 10 kV to prevent damage to the films. Compositional analysis of the films was performed using energy dispersive X-ray (EDX) analysis (INCA Energy 3-D MAX, Oxford Instruments) attached to the SEM.

The optical measurements were carried out in the 190–1100 nm wavelength range using the UNICO 2800 spectrophotometer system.

A custom UT-7712 setup with resistivity up to 10^{14} Ω × cm, equipped with an electrometer UT-701 with input resistance $>10^{15}$ Ω, was used for the Hall measurements and the current–voltage characteristics of the samples. A detailed description of this setup is given in Ref. [24]

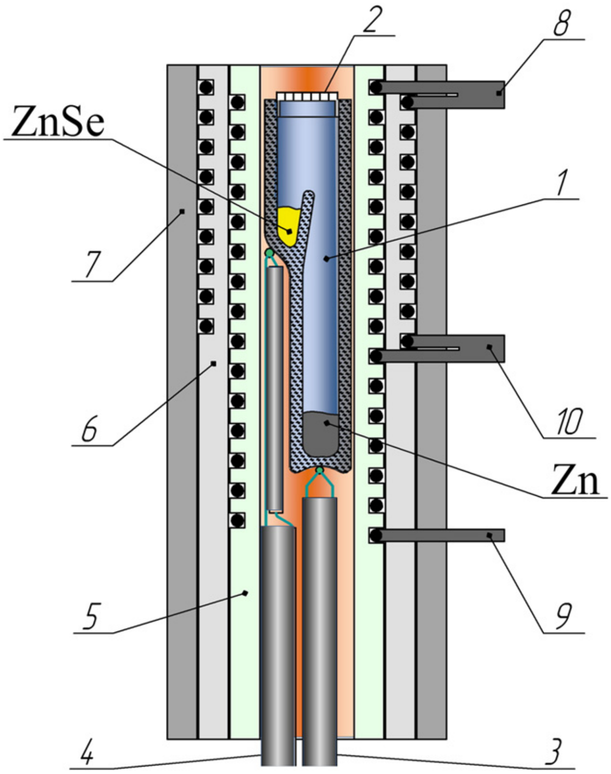

Fig. 1. Scheme of the two-zone high-temperature coaxial evaporator: 1 — two-zone quartz glass crucible, 2 — double diaphragm crucible cover, 3 — thermocouple of the bottom “cold” zone, 4 — thermocouple of the upper “hot” zone, 5 — internal coating on the heating element for the bottom zone and the internal heating element of the upper zone, 6 — middle coating on the external heating element for the “hot” zone, 7 — external coating, 8 — current lead of the upper zone heating element, 9 — current lead of the bottom zone heating element, and 10 — ground wire.

3. Results and discussion

3.1. Nonstoichiometry of crystalline ZnSe

The ZnSe homogeneity limits were investigated in the 850–1173 K temperature range. We confirmed the previous data on Se solubility [8] at 850–1100 K (Fig. 3). However, at T > 1100 K, we obtained higher Se solubility in ZnSe. The solidus line demonstrated retrograde behavior similar to the Zn-rich side and the behavior of other $A^{II}B^{VI}$ compounds [16]. The homogeneity region of undoped ZnSe (zinc blend) included the stoichiometric composition, which agrees with the data [15] investigating the 3C–2H polymorphous transition in ZnSe with the DTA technique close to the melting temperature of ZnSe.

Table 1
ZnSe thin film fabrication conditions by vacuum thermal sputtering.

Process no.	T_{ZnSe} °C	T_{Se} °C	Growth rate, nm/s	Thickness, nm	
				EC	NS
N1	860	–	0.104	95	217
N2	870	408	0.124	104	230
N3	860	416	0.115	93	200
N4	870	423	0.142	115	229
N5	870	440	0.148	116	233

EC — samples for electrophysical and optical measurements, NS — samples for nonstoichiometry composition determination.