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Thin Solid Films

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

Nonstoichiometry problems of ZnSe: From single crystals to nanofilms

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ARTICLE INFO

Article history:

Received 21 May 2015

Received in revised form 24 October 2015

Accepted 28 October 2015

Available online xxxx

Keywords:

Zinc selenide crystal

Thin film, stoichiometry

Nonstoichiometry

ABSTRACT

Selenium nonstoichiometry in ZnSe under bivalent and monovariant equilibria 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.

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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 $S_{\text{ZnSe}}L_{(\text{Se})}\text{V}$ 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 $S_{\text{ZnSe}}L_{(\text{Se})}\text{V}$ monovariant equilibrium as the final point of the $S_{\text{ZnSe}}\text{V}$ bivalent 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 $S_{\text{ZnSe}}\text{V}$ bivalent 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 ($50 \pm 20 \mu\text{m}$) under an argon atmosphere. The highest purity was detected for the MSS-ZnSe preparation using an

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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 $S_{\text{ZnSe}}L_{(\text{Se})}V$ monovariant equilibrium and in a dual-zone tube furnace at $S_{\text{ZnSe}}V$ bivariant equilibrium with further quenching of high temperature equilibria.

In the context of the $S_{\text{ZnSe}}V$ 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} .

$$\left(k_{\text{diss}}/p_{\text{Se}_2}^{1/2} + p_{\text{Se}_2} + \sum_{i=1, i \neq 2}^8 (k_i \cdot p_{\text{Se}_2})^{2/i}\right)_{T_1} = \left(\sum_{i=1}^8 p_{\text{Se}_i}^{\text{ol}}\right)_{T_2}, \quad (1)$$

here k_{diss} is the ZnSe dissociation constant according to the reaction $\text{ZnSe}^s \rightarrow \text{Zn}^v + 1/2 \cdot \text{Se}_2^g$ [14]; $p_{\text{Se}_i}^{\text{ol}}$ 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 $10^{14} \Omega \times \text{cm}$, equipped with an electrometer UT-701 with input resistance $> 10^{15} \Omega$, 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]

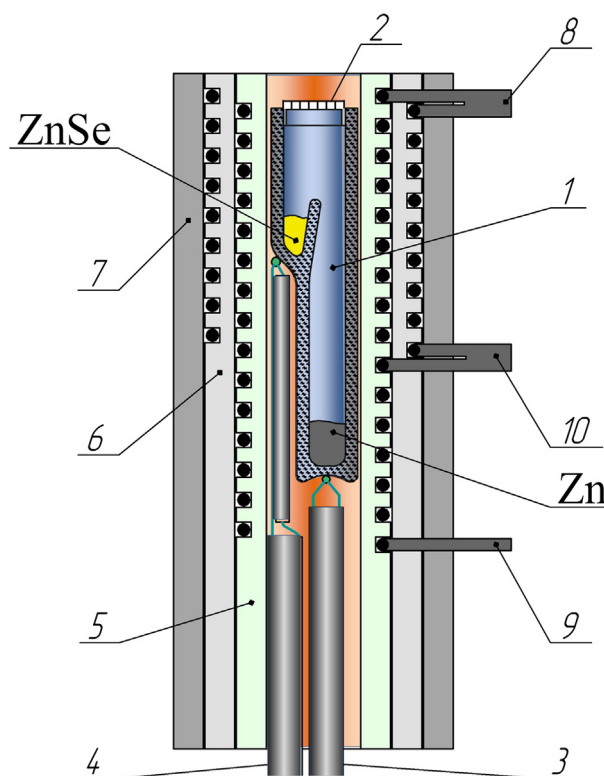


Fig. 1. Scheme of the two-zone high-temperature coaxial evaporator: 1 – two-zone quartz glass crucible, 2 – double diaphragm crucible cover, 3 – thermocouple of the bottom “cold” zone, 4 – thermocouple of the upper “hot” zone, 5 – internal coating on the heating element for the bottom zone and the internal 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 $A^{\text{II}}B^{\text{VI}}$ 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.

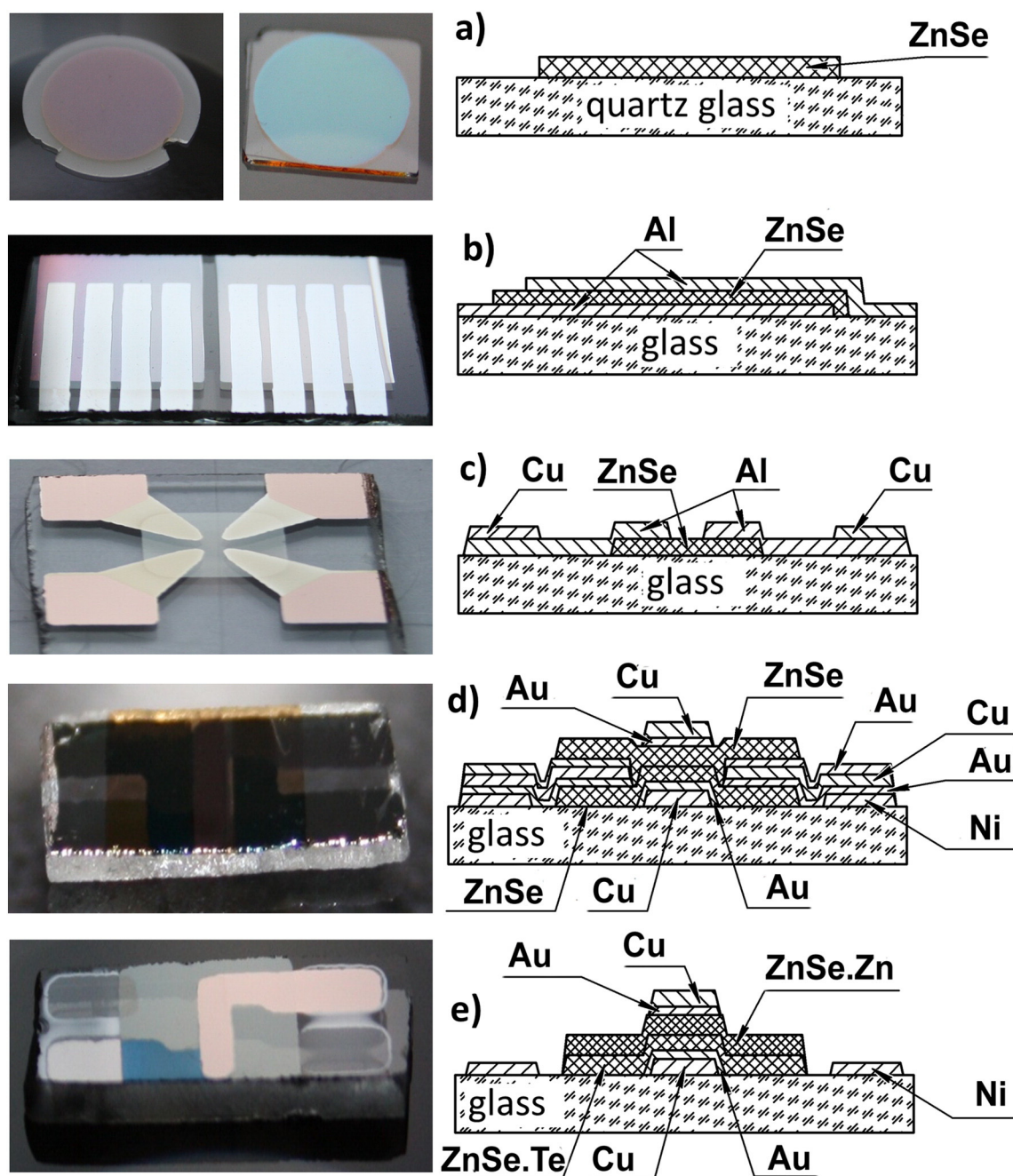


Fig. 2. Topology schemes (right) and photographs (left) of the ZnSe nanofilms for measurements of: nonstoichiometry (a), resistivity (b), the Hall effect (c, d) and the diode structure characteristics (e).

Selenium solubility in solid ZnSe was studied at the $S_{\text{ZnSe}}V$ bivariant equilibrium at 963, 1078 and 1173 K and P_{Se_2} varying from 10^4 to 5×10^5 Pa (Fig. 4). At the maximum point of selenium partial pressure $P_{\text{Se}_2}^{\text{max}}$ characterizing the Se solubility in ZnSe at $T = \text{const}$, we reached the $S_{\text{S-ZnSe}}L_{(\text{Se})}V$ monovariant equilibrium.

We found that a temperature increase from 850 to 1173 K caused the excess Se concentration ($x_{\text{Se}}^{\text{excess}}$) to increase more than 7 times from $(5.29 \pm 0.18) \times 10^{-5}$ to $(3.76 \pm 0.09) \times 10^{-4}$ mol excess Se/mol ZnSe. This increase corresponded to an increase in defect concentrations from $(1.19 \pm 0.04) \times 10^{18}$ to $(8.42 \pm 0.20) \times 10^{18} \text{ cm}^{-3}$. If just 1% of these defects were ionized, we would easily detect p -type conductivity in the samples. However, no such conductivity was detected. Therefore, comparing $x_{\text{Se}}^{\text{excess}}$ with the electrophysical characteristics of ZnSe crystals, we deduced that dissolving Se in a temperature range 963–1173 K and a range of Se_2 partial pressure 1.05×10^4 – 5.01×10^5 Pa resulted in the

generation of electrically neutral defects. Based on the quasi-chemical theory [5] the zinc blend structure, the obtained experimental results for Se dissolving in ZnSe at the $S_{\text{S-ZnSe}}V$ bivariant equilibrium and the similarity to other $\text{A}^{\text{II}}\text{B}^{\text{VI}}$ compounds [16], we propose that the vacancy disordering is the most probable native point defect generation mechanism, as described by reaction (2)



where n can take on a value 1/2, 1, 2,...8 according to the quasi-chemical theory of defect generation [5] and selenium vapor composition [13].

The concentration of excess selenium in ZnSe ($x_{\text{Se}}^{\text{excess}}$) is described by the expression:

$$X_{\text{Se}}^{\text{excess}} = \sum_{i=1}^k \left(P_{\text{Se}_2}^{n_i} \cdot \exp(\Delta H_i/RT + \Delta S_i/R) \right) \quad (3)$$

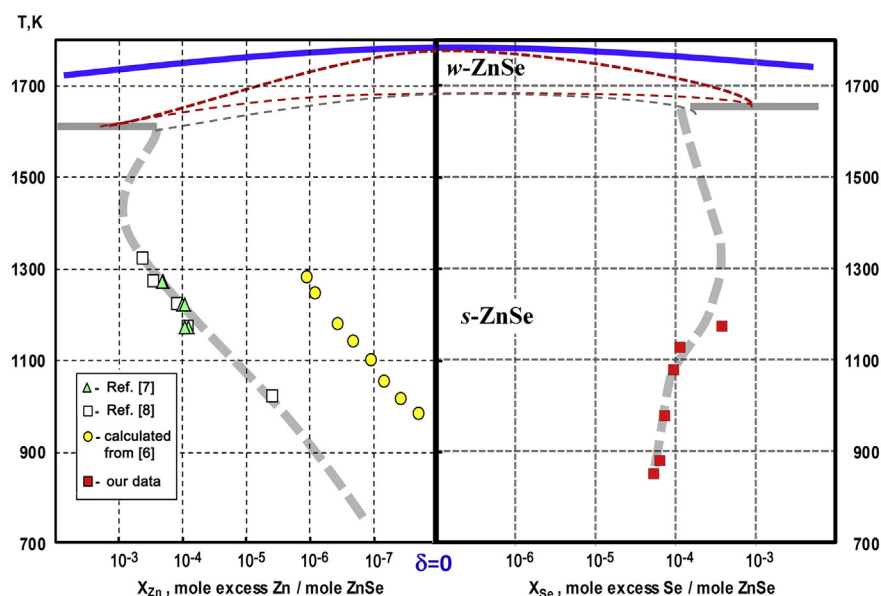


Fig. 3. ZnSe homogeneity region with the proposed 3C–2H polymorphous transformation scheme [15]; the blue line is liquidus; the dash lines are solidus' which limit the homogeneity range of s-ZnSe (gray line) and w-ZnSe (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

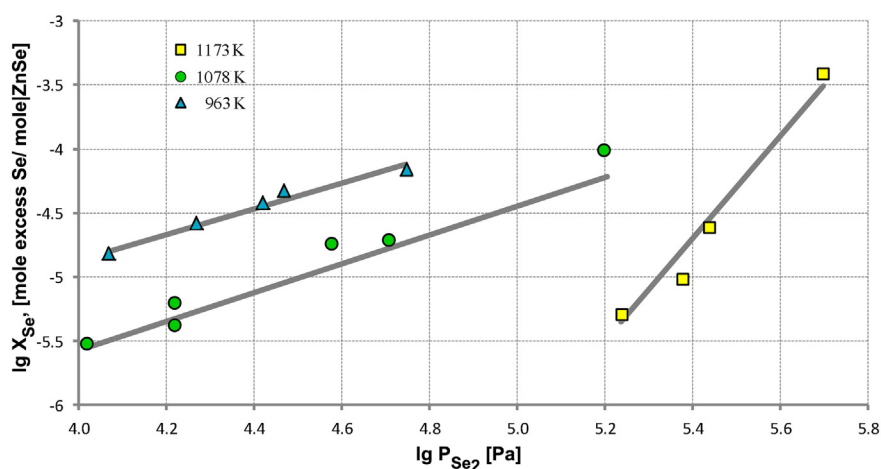


Fig. 4. Solubility of excess selenium in nonstoichiometric ZnSe vs. selenium vapor pressure: points – experimental data; solid lines – calculated from Eq. (3).

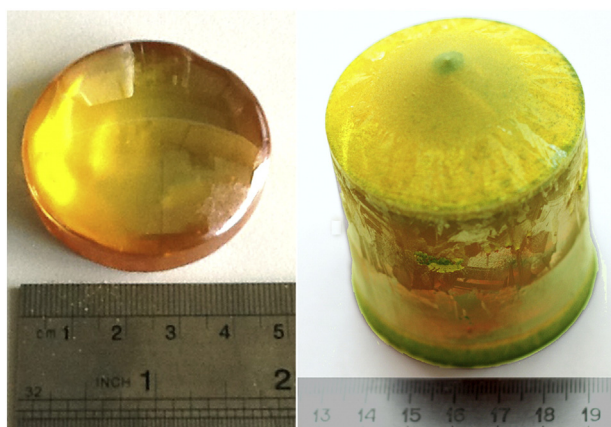


Fig. 5. ZnSe crystals grown from the vapor phase (left) and the melt (right) at high Ar pressure (100 atm).

where each addend in Eq. (3) contributes to determining the concentration of vacancy defects with an i^{th} -degree of association; otherwise, the excess Se forms clusters. Reaction (2) was found to be exothermic, and we were able to describe all of the experimental data taking into account the generation of 2-, 4- and 8-atom clusters. The degree of cluster association increased as both temperature and P_{Se_2} increased. The basic thermodynamic parameters for the formation of the smallest cluster $(V_{\text{Zn}})_2^{\times}$ were found to be $\Delta H_{(V_{\text{Zn}})_2^{\times}} = -116.4 \text{ kJ mole}^{-1}$ and $\Delta S_{(V_{\text{Zn}})_2^{\times}} = 290.6 \text{ J mole}^{-1} \text{ K}^{-1}$, and the increments determining the cluster growth were established ($\delta h = -116.4 \text{ kJ mole}^{-1}$, $\delta s = 515.5 \text{ J mole}^{-1} \text{ K}^{-1}$) for use in Eq. (4):

$$\Delta H_n = \Delta H_{(V_{\text{Zn}})_2^{\times}} + \delta h \cdot (n-1)/n; \quad \Delta S_n = \Delta S_{(V_{\text{Zn}})_2^{\times}} + \delta s \cdot (n-1)/n \quad (4)$$

The clusters grow as the temperature approaches the melting point, and they fully destroy the crystal while melting. In this situation “approaching the melting point” means not only the temperature is increasing but also that the system is changing from bivariant to

Table 2

Nonstoichiometry of ZnSe crystals. (A negative sign indicates Zn-excess concentration).

Crystal type	m_{ZnSe} , g	m_{Se} , $\text{g} \times 10^6$	m_{Zn} , $\text{g} \times 10^6$	$x_{\text{Se}}^{\text{excess}}$ mole frac.
HP melt-grown (graphite)	1.4561	3.25 ± 0.08	0.12 ± 0.01	$(3.90 \pm 0.12) \times 10^{-6}$
HP melt-grown (glassy carbon)	1.2356	28.8 ± 0.81	0.11 ± 0.01	$(4.24 \pm 0.12) \times 10^{-5}$
Vapor-grown	1.4482	0.26 ± 0.01	0.54 ± 0.01	$-(4.95 \pm 0.28) \times 10^{-7}$

monovariant equilibrium. High crystal lattice disorder at high cluster concentration, followed by an expanding of the homogeneity range, was observed for many nonstoichiometric phases close to the maximum melting points [17].

3.2. Nonstoichiometry of ZnSe single crystals

The nonstoichiometric results in ZnSe crystals grown with the Davydov–Markov technique from the vapor phase [18] (Fig. 5, left) and grown from the melt under high inert gas pressure (100 atm) (Fig. 5, right) are presented in Table 2. The details of this crystal growth technique were described in [8]. We confirmed the general trend found previously. The nonstoichiometry level in all crystals corresponds to the homogeneity limits of ZnSe (Fig. 3). The melt-grown crystals contained over-stoichiometric Se, while the vapor-grown crystal had a small concentration of excess Cd, which was close to the detection limit of the “extraction” technique [8]. See Table 2

Table 3

Nonstoichiometry and electrical properties of ZnSe thin films.

Process no.	T_{ZnSe} , °C	T_{Zn} , °C	NS film nonstoichiometry					EC film properties		
			Thickness, nm	m_{ZnSe} , $\text{g} \times 10^4$	m_{Zn} , $\text{g} \times 10^6$	m_{Se} , $\text{g} \times 10^6$	$x_{\text{Se}}^{\text{excess}}$ mole fraction	ρ , $\Omega \cdot \text{cm}$	Conductivity type	Free carrier concentration, cm^{-3}
N1	860	–	217	2.15	0.123	19.26	1.62×10^{-1}	2.4×10^7	<i>p</i>	5×10^{13}
N2	870	408	230	2.28	0.42	6.14	4.52×10^{-2}	6.1×10^{11}	–	$<1 \times 10^{12}$
N3	860	416	200	1.98	0.67	3.58	2.56×10^{-2}	1.8×10^{11}	–	$<1 \times 10^{12}$
N4	870	423	229	2.27	0.58	3.18	2.00×10^{-2}	7.2×10^{10}	–	$<1 \times 10^{12}$
N5	870	440	233	2.31	1.04	1.27	1.14×10^{-4}	5.9×10^9	<i>n</i>	2×10^{12}

$$x_{\text{Se}}^{\text{excess}} = (m_{\text{Se}}/M_{\text{Se}} - m_{\text{Zn}}/M_{\text{Zn}}) / (m_{\text{ZnSe}}/M_{\text{ZnSe}}).$$

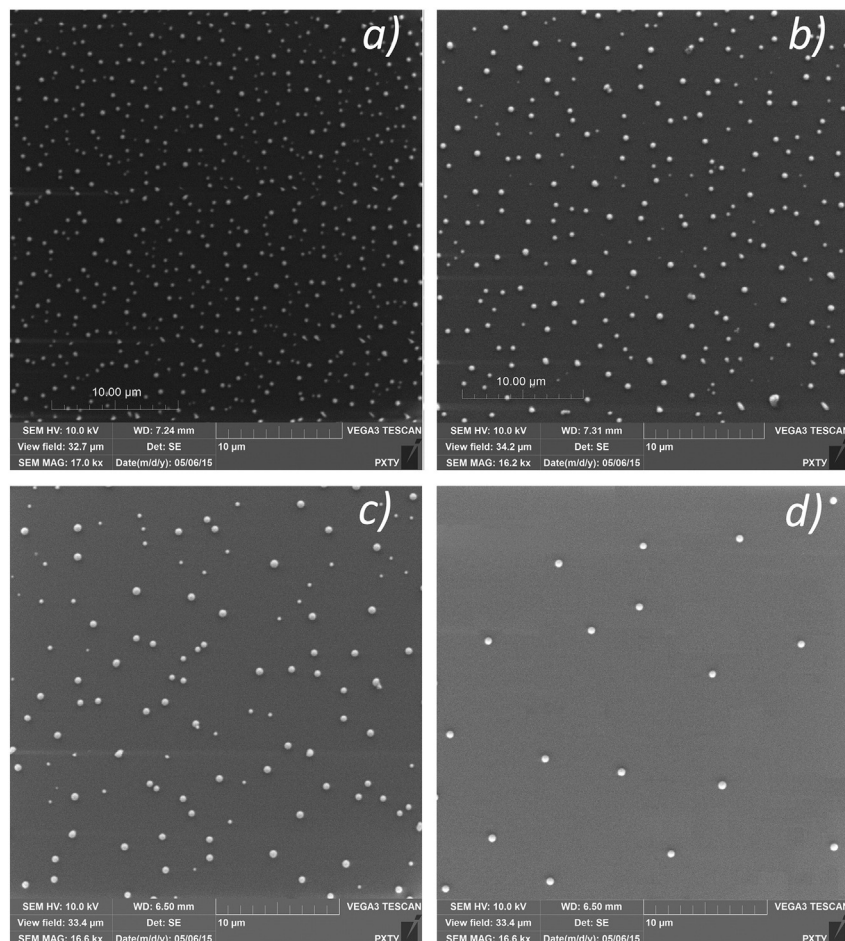


Fig. 6. SEM images of ZnSe films deposited at $T_{\text{ZnSe}} = 870^\circ\text{C}$ and $T_{\text{Zn}} = 0^\circ\text{C}$ (a), 408°C (b), 423°C (c) and 440°C (d) on “cold” glass substrates.

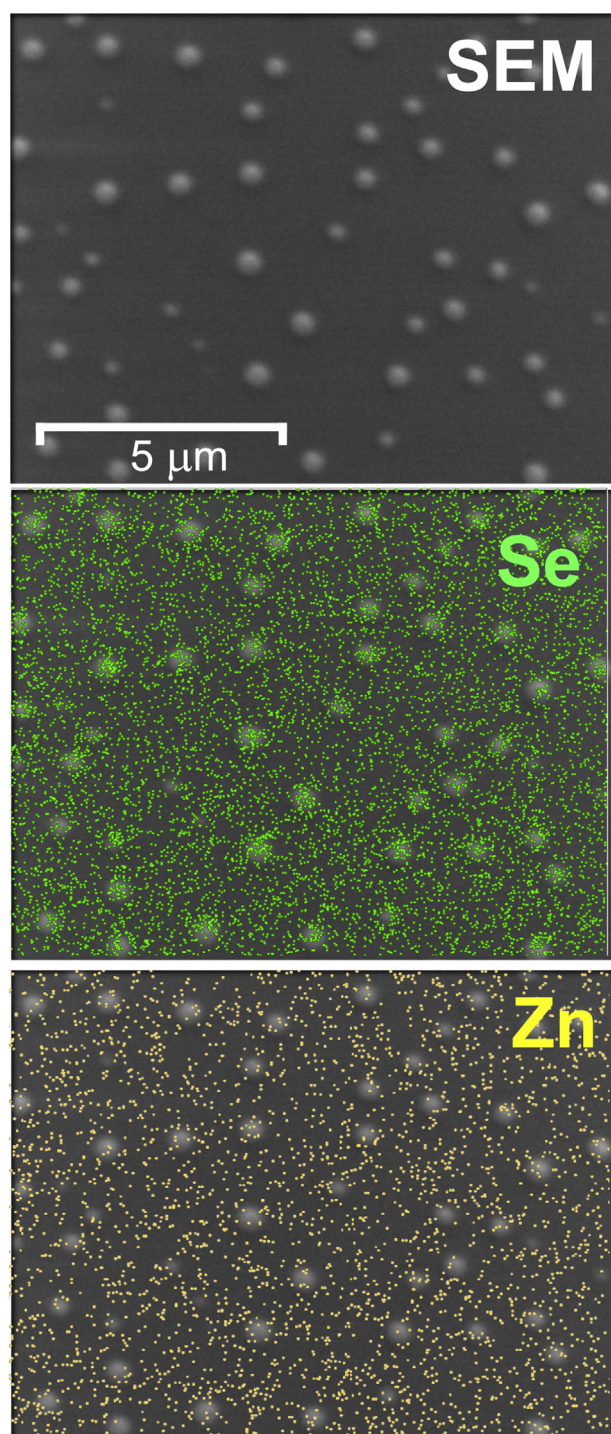


Fig. 7. SEM image of ZnSe films deposited at $T_{\text{ZnSe}} = 870\text{ °C}$ and $T_{\text{Zn}} = 0\text{ °C}$ (a) with EDX analysis of Se – green points (b) and Zn – yellow points (c) distribution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. ZnSe thin films properties

3.3.1. Nonstoichiometry of ZnSe nanofilms

The nonstoichiometry of ZnSe nanofilms on quartz glass substrates was determined by the “extraction” technique during the annealing step, as described in [9]. The results are listed in Table 3. We found the concentration of the excess Se concentration to be more than two orders

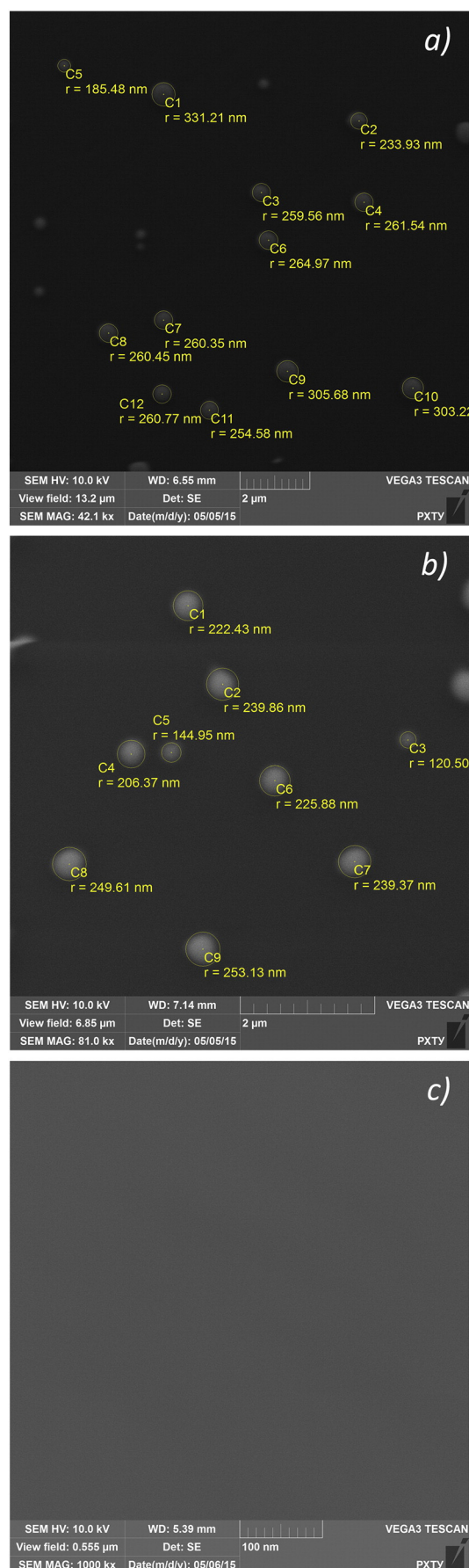


Fig. 8. SEM images with drop size analysis of ZnSe films deposited at $T_{\text{ZnSe}} = 870\text{ °C}$ and $T_{\text{Zn}} = 0\text{ °C}$ (a), 423 °C (b) and 440 °C (c) ($\times 10^6$) on “cold” glass substrates.

of magnitude higher than the equilibrium concentration, corresponding to the solidus line on the T–X diagram (Fig. 3).

In the case of deposition from the congruently sublimated ZnSe preparation, the nanosize films contained approximately 16 mol% of excess Se (see N1_{NS} in Table 3). To explain this result, we analyzed SEM images of the films, and we discovered many spherical droplets on the film surface (Fig. 6). The drop concentration decreased when we added Zn vapor from an additional source during the film deposition. The N5_{NS} sample deposited at $T_{\text{ZnSe}} = 870^\circ\text{C}$ and $T_{\text{Zn}} = 440^\circ\text{C}$ had only a few drops (Fig. 6d). The EDX mapping of the films indicated that the droplets were nearly pure Se (Fig. 7).

We propose the following explanation of Se droplet formation during vacuum thermal deposition of ZnSe. It is well known that ZnSe sublimates congruently [14,21] and dissociates nearly 99% according to the reaction $\text{ZnSe}^s = \text{Zn}^v + 1/2 \text{Se}_2^g$.

During the sublimation process, the vapor moves towards the “cold” substrate rather slowly. Under the experimental conditions (low density vapor flows and a 10^{-3} Pa vacuum) dissociated Se moved through the low temperature zone. According to the selenium vapor equilibrium conditions at low temperatures, Se-based vapor is saturated by Se_5 – Se_8 molecules [13]. These molecules do not react with monoatomic Zn vapor; instead they condense on the “cold” substrate and associate into droplets. Only a small part of the Se vapor close to the substrate exists as Se and Se_2 molecules, which react with Zn to form the ZnSe film. The rest of the Zn reacts with Se and Se_2 molecules at a higher temperature to form ZnSe, which condenses on the cylindrical tube walls of the protective shield placed between the evaporator and the substrate holder. When we heated the Zn evaporator, the Zn vapor flow increased, and the association of Se molecules was suppressed. As a result, the number of Se droplets on the film surface decreased drastically (Fig. 6d).

Analyzing the size of the Se droplets (Fig. 8) and their distribution showed a correlation between the calculated excess Se concentration (Table 3) and the concentration of droplets on the film surfaces. The N5_{NS} film had the lowest concentration of excess Se (1.14×10^{-4} mole fraction). This concentration is higher than the equilibrium value estimated from T–X data ($< 5 \times 10^{-5}$ mole fraction; see Fig. 3), but it also correlates with the small number of droplets on the film surface. Moreover, the transmission spectra of the ZnSe nanofilms (Fig. 9) showed that the N5_{EC} film had the highest transparency compared to other films with similar thickness. Only the N3_{EC} film with the minimum thickness, deposited at the lower ZnSe temperature (860°C) demonstrated the same transparency as the N5_{EC} sample.

The surface structure of the film N5_{EC(NS)} had a higher degree of perfection according to the SEM data (Fig. 7c). We did not observe any surface defects even at $\times 10^6$ magnification.

To compare the film's resistivity and nonstoichiometry, we assume that in the cases of the N1–N4 processes, we obtained two-phase films. Their electrical properties were determined by the Se phase and

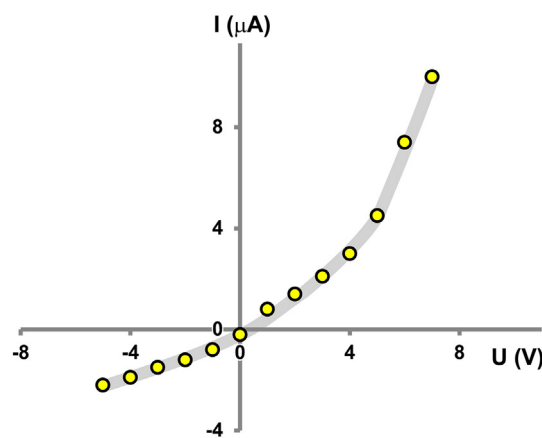


Fig. 10. Current–voltage curve for the structure with the topology in Fig. 2e.

the phase of Se-saturated ZnSe. When the Se phase had the highest concentration (N1 process), the N1_{EC} film resistivity was determined by the Se phase according to the percolation theory of conductivity [19]. Although the N1_{EC} film exhibited *p*-type conductivity, which was determined by the presence of the Se phase (N1_{NS}), it was not appropriate for a thin film transistor because of the large number of Se droplets (Fig. 6a). A small decrease in Se droplets in the N2_{EC} sample was associated with an increase in film resistivity (Fig. 6b), but the further decrease in the concentration of Se droplets resulted in a decrease in the films' resistivities (N3_{EC}–N5_{EC} samples). Although we detected Se excess in the N5_{NS} sample, the N5_{EC} film had *n*-type conductivity. Furthermore, we observed a normal trend in the change in resistivity between the N2_{EC} and the N5_{EC} samples, whereas the impurity concentration remained constant according to ICP–MS analysis. This means that the dominant electrically charged defects in the N5_{EC(NS)} ZnSe film, which are attributed to the dissolved Zn in ZnSe phase, were either V_{Te} or Zn_i native point defects [20,21], not impurity-based defects.

Usually, *p*-type ZnSe films are produced by N or Li doping [22,23]. However, these processes require high temperatures and cannot be used to fabricate ZnSe films on a “cold” substrate. We attempted to form *p*-type ZnSe films with Te as a dopant. We used an additional stand-alone evaporator to control the Te vapor pressure during film deposition. This film contained ~5 at.% of Te, and it was a solid solution film with *p*-type conductivity and a resistivity of $10^5 \Omega \times \text{cm}$. Using this *p*-type film, we made *n*–*p* junctions (Fig. 10) with a ZnSe (Zn saturated)/ZnSe_{0.9}Te_{0.1} structure deposited on a “cold” substrate with the topology shown in Fig. 2e. Until a breakdown occurred at 9 V, the resulting I–V curve was not very good for an OLED thin film transistor, but we believe that by further optimizing ZnSe films, it will be possible to make a transistor with the desired parameters.

4. Conclusion

We established that the homogeneity region of undoped ZnSe includes a stoichiometric composition in the 850–1173 K temperature range. The solidus line demonstrates retrograde behavior in both the Zn-rich and Se-rich sides. An analysis of the experimental data on Se solubility in nonstoichiometric *s*-ZnSe (zinc blend) showed that the data are adequately described by the quasi-chemical theory of defect generation, considering the generation of clusters (associations) based on electrically neutral vacancies in the Zn sublattice followed by exothermic reactions.

The enthalpy and entropy of the generation of associated vacancies are described by the simple expression ($E_n = E_{\text{min}} + \delta E \cdot \frac{n-1}{n}$), taking into account the formation enthalpy and entropy of the minimum cluster (E_{min}) and the increment ($\delta E \cdot \frac{n-1}{n}$) defined by the cluster size (n).

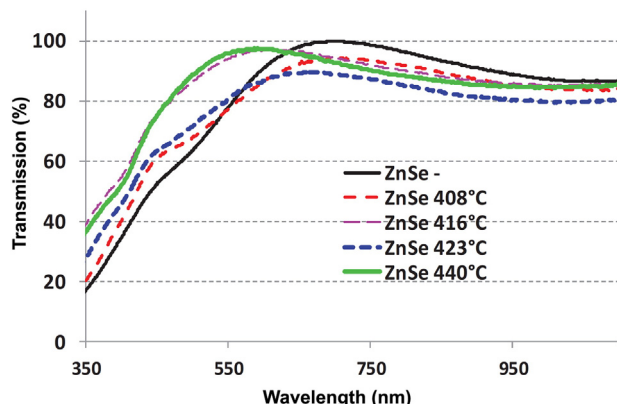


Fig. 9. Transmission spectra of the ZnSe thin films.

The degree of vacancy association increased with increasing temperature and the Se partial vapor pressure.

The nonstoichiometry of ZnSe crystals grown from the melt was less than 10^{-5} excess moles of the component per mole of ZnSe. The vapor-grown crystals had $\sim 10^{-7}$ moles of excess Zn per mole of ZnSe, which was close to the stoichiometric composition.

It is possible to fabricate 50–300 nm ZnSe films by vacuum thermal sputtering ZnSe on a “cold” substrate. The nonstoichiometry of the films could be controlled by controlling the Zn vapor partial pressure. Producing the ZnSe–ZnTe solid solution film, we were able to obtain a film with *p*-type conductivity, and we covered it with a ZnSe (saturated by Zn) layer to produce a *p*–*n* junction on a “cold” substrate.

Acknowledgments

The research was financially supported by the Russian Science Foundation (grant N 15-13-10028).

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