

UDC 621.315.592:535
PACS numbers: 05.05.70.Ce
doi: 10.15330/jpnu.3.1.65-70

THERMODYNAMICS OF THE POINT DEFECTS IN THE METALLIC PHASE OF THE SAMARIUM MONOSULPHIDE

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Abstract. The equilibrium values of the vacancy concentration of chalcogen and antistructural samarium atoms in metallic phase of SmS were calculated by minimization of the crystal thermodynamic potential. It was determined that the dominant defects are Sm_s^+ at the concentration of samarium 50,5-54 at. % and at the temperature of $T=300-400$ K. Also the concentration of negatively charged sulfur vacancies V_s^- is less on 1-2 points. The concentration dependence of samarium monosulphide density was explained using this offered model.

Keywords: samarium monosulphide, point defects.

1. INTRODUCTION

Samarium monosulphide is a promising material for using it in many branches of electronics that is conditioned by the complex of unique qualities [1-3]. In particular it concerns the huge tensor resistive effect, isomorphic phase transition of the I kind semiconductor-metal at the low pressure and also the appearance of electric power at steady warming of this sample under the condition of absent external temperature gradients [1-3].

The wide spectrum of properties is caused by the peculiarities of the material energetic structure and first of all by the presence of crystal of low energetic band formed by the metal atoms 4f-electrons at band gap [1, 2]. Point defects have a great influence on electrical properties of SmS whose concentration can reach to $\sim 10^{21} \text{ cm}^{-3}$ due to wide zone of compound homogeneity displaced to direction of the samarium surplus. Accordingly to the researches [3, 5, 8] in crystals with samarium surplus the dominant defects are antisite samarium SmS atoms that form shallow donor levels with ionization energy 0,045eV in crystal band gap. Also sulphur vacancies can be formed in samarium monosulphide [6], that are considered to be shallow acceptors accordingly to [7]. But their predominant zone or their quantitative correlation between the V_s and S_m s concentrations are not expressly established.

The main aim of this work is determination of dependence species, charge state and concentration of dominant point defects on the degree of nonstoichiometry in the samarium monosulfide crystals.

2. METHOD OF CALCULATION

Concentrations of point defects in crystal at the temperature T can be determined by minimization of free energy F [8]. Taking into account the fact that all defects and samarium f-electrons are ionized in metallic phase and that the holes concentration is lesser than the concentration of electrons and point defects we can present the crystal thermodynamic potential as:

$$F = F_0 + (E_{V_s^-} + F_{vib,V_s^-})[V_s^-] + (E_{Sm_s^+} + F_{vib,Sm_s^+})[Sm_s^+] + (n_s + n_d)\mu - TS_{k,a} \quad (1)$$

where F_0 – free energy that is independent on defects, E – energy of point defects forming (vacancy or antisite atom); F_{vib} – free vibrational energy of defect; $[D]$ – defect concentration; n_s, n_d – electron' concentration in s- and d-zone of conduction [9], $S_{k,a}$ – configuration entropy of anion sublattice.

Energies of single ionized donor and acceptor defects are determined according to the formula:

$$E_1 = E_0 - \varepsilon_1, \quad E_1 = E_0 + \varepsilon_1, \quad (2)$$

E_0 – energy of neutral defect forming, E_1 – energy of formed defect ionization.

Change of the free vibrational energy of crystal at vacancy forming [10]:

$$F_{vib} = -\left\{3kT \ln\left(\frac{T\theta}{T}\right) - kT\right\} + x \cdot 3kT \ln\left(\frac{\omega}{\omega_0}\right) \quad (3)$$

and at the forming of antisite defect:

$$F_{vib} = x \cdot 3kT \ln\left(\frac{\omega}{\omega_0}\right) \quad (4)$$

x – the amount of atoms that changed frequency of their vibrations from ω_0 to ω Entropy was determined using the Boltzmann law

$$S_{k,a} = k \ln(W_{k,a}) \quad (5)$$

where $W_{k,a}$ – thermodynamic probability:

$$W_{k,a} = \frac{N!}{(N-\sum[D])! \cdot \prod[D]!} \quad (6)$$

where N – concentration of sites in anionic sublattice.

Concentrations of electrons in s- and d- zone of conduction can be determined using the formula:

$$n_s = \left(\frac{2\pi m_s^* kT}{h^2}\right)^{\frac{3}{2}} a e^{b \frac{\mu}{kT}}, \quad n_d = \left(\frac{2\pi m_d^* kT}{h^2}\right)^{\frac{3}{2}} a e^{b \frac{\mu - \Delta E_c}{kT}} \quad (7)$$

where the coefficients a and b – amendments that include degree of carrier degenerations and they are calculated by approximation of Fermi integral; μ – chemical potential of electrons, m_s^*, m_d^* – effective electron mass in s and d zones respectively; ΔE_c – distance between bottoms of s and d zones.

Chemical potential of electrons is determined from the equation of electroneutrality. Taking into account that density of the states in d-zone depends on the carrier concentration we can get:

$$Z_{V_s^-}[V_s^-] + Z_{Sm_s^+}[Sm_s^+] + N = N_{C,s} \cdot a \exp\left(b \frac{\mu}{kT}\right) + (N_{C,0})^2 \left(\frac{6}{10^5}\right)^6 \exp\left(-2b \frac{dE_c}{kT}\right) \cdot a^2 \exp\left(2b \frac{\mu}{kT}\right) \quad (8)$$

Therefore

$$\mu = \frac{1}{b} kT \ln\left(\frac{-B + \sqrt{B^2 + 4A \cdot ZZ}}{2A}\right) \quad (9)$$

where:

$$A = (N_{C,0})^2 \left(\frac{6}{10^5}\right)^6 \exp\left(-2b \frac{dE_c}{kT}\right) \cdot a^2$$

$$B = N_{C,s} \cdot a$$

$$ZZ = Z_{V_s^-}[V_s^-] + Z_{Sm_s^+}[Sm_s^+] + N$$

Electrons concentration in s-zone is lesser than in d-zone and that's why we get:

$$\mu \approx \frac{1}{b} kT \ln \left(\frac{\sqrt{A \cdot ZZ}}{A} \right) = \frac{1}{b} kT \ln \left(\sqrt{\frac{ZZ}{A}} \right) = \frac{1}{2} \frac{1}{b} kT \ln \left(\frac{ZZ}{A} \right) \quad (10)$$

Free energy of crystal is:

$$F = F_0 + (E_{V_s^-} + F_{vib, V_s^-})[V_s^-] + (E_{Sm_s^+} + F_{vib, Sm_s^+})[Sm_s^+] + ZZ \frac{1}{2b} kT \ln \left(\frac{ZZ}{A} \right) - kT(N \ln N - [V_s^-] \ln [V_s^-] - [Sm_s^+] \ln [Sm_s^+] - (N - [V_s^-] - [Sm_s^+]) \ln (N - [V_s^-] - [Sm_s^+])) \quad (11)$$

By minimizing (11) we get the equilibrium values of defects concentrations.

Thus it is important to include the condition:

$$[Sm_s^+] + [V_s^-] = X_{Sm} \quad (12)$$

When $Na \gg Sm_s^+ + V_s^-$ we get analytical expression for the determining of defects' concentrations. It's necessary for this to calculate the sulphur vacancy concentration from the condition (12) as a function of antisite defects concentration and to substitute it into (11). Differentiating (11) on the concentration of antisite defects and equating this expression to zero we can get:

$$[Sm_s^+] = \frac{X_{Sm}}{1 + \exp\left(\frac{(E_{Sm_s^+} + F_{vib, Sm_s^+}) - (E_{V_s^-} + F_{vib, V_s^-})}{kT} + \frac{Z_{Sm_s^+} - Z_{V_s^-}}{2b}\right) \left(1 + \ln\left(\frac{N}{A}\right)\right)} \quad (13)$$

This formula is correct for rather narrow interval of defects concentration that's why we get the results in this investigation by the minimizing of the thermodynamical potential (11). The method of random disturbance was used for the searching function minimum (11) and the penalty function method was used to take into account the condition (12).

Energies of neutral defects forming according to (8) were accepted equal $E_0(V_s) = 10.69$ eV, $E_0(Sm_s) = 6.24$ eV. Antisite defect was considered to be shallow donor with energy of ionizing 0,045 eV [3], and sulphur vacancy as shallow acceptor with energy of ionizing $E_V + (\approx 0.1)$ eV [7]. The density was determined by the formula:

$$\rho = \frac{4}{a^2} M_{Sm} + [Sm_s^+](M_{Sm} - M_S) + \frac{4}{a^2} M_S - [V_s^-] M_S \quad (14)$$

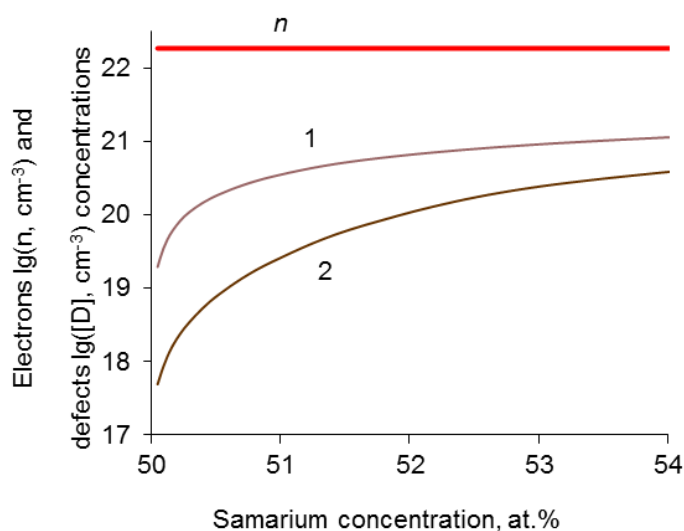
3. RESULTS AND DISCUSSION

As you can see on the picture (Fig. 1, a) with the growth of super stoichiometric samarium content concentration of sulphur vacancies and antisite samarium atoms is increasing. But concentration growth of the antisite samarium atoms is slower. Such character of correlation change between point defects determines non-linearity concentration dependence of samarium monosulphide density (Fig. 1, b): at the low content of surplus samarium the increase of density is caused by the increase of antisite defects concentration; and vacancy concentration does not significantly influence on this change; at the subsequent increase of Sm content concentration of sulphur vacancies becomes the same as concentration of antisite defects and the density increase of SmS is slowing.

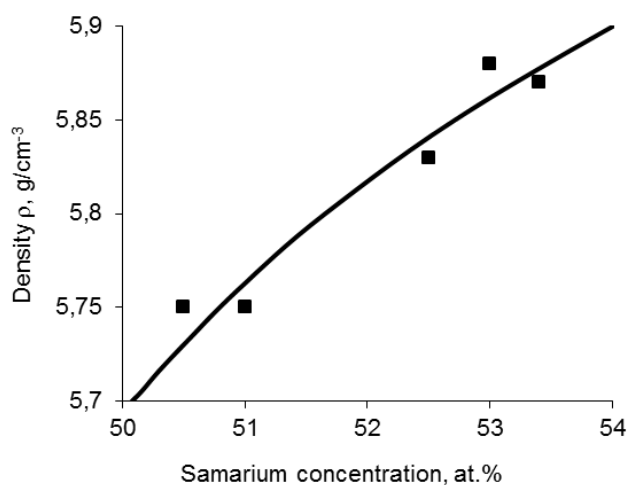
In comparison with semiconducting phase of SmS, which defective subsystem is reported in [8], the concentration of sulphur vacancies V_s^- is rather higher in metal phase. Such effect can be explained that the chalcogen vacancies, forming vacant levels near the valence band top, are traps for the free electrons that go down from the bottom of the conductivity zone on the localized levels V_s , and predetermine increase according to the module of crystal free energy on the one level of the band gap width (area $\sim 2,3$ eV). Substantial increase of electrons concentration that takes place at isomorphic phase transition semiconductor-metal promotes the sulphur vacancies appearance because it causes to the considerable winning in complete crystal's energy.

It should be mentioned that the change of vibrations frequency of atoms near defects was accepted

as one in calculation. For the antisite defects Sm_s^+ as it is showed in [8], such supposition is correct but for sulphur vacancies – the situation is more complicated: exactness of the theoretical methods of calculating ω/ω_0 is insufficient for using calculated numerical values at the modeling, and experimental determination of this value has different difficulties. But as far as calculation curve q (X_{Sm}) (Fig.1 b) satisfactorily describes experimental data it should be supposed that real value ω/ω_0 for sulphur vacancy is indeed close to one.



a)



b)

Fig. 1. Dependences of the electron concentrations n , point defects (1– Sm_s^+ , 2 – V_s^-) (a) and density ρ (b) on content of Sm in metal phase of samarium monosulphide.

4. CONCLUSIONS

1. Using the method based on the minimization of thermodynamical potential of crystal as function of defects concentration, dependences of the sulphur vacancies and antisite samarium atoms concentration in the area of homogeneity were calculated.

2. It was investigated that at the concentration of the superstoichiometrical samarium 0,5–4,0 at% the predominant type of defects is antisite samarium atoms and the concentration of sulphur vacancy is on 1-2 points lower.

3. Non-linear growth of the SmS density with the increase of samarium atoms amount in the range ~ 0,5 to 4,0 at% Sm was explained on the base of the obtained dependences of the point defect concentration on chemical composition of crystals.

ACKNOWLEDGMENT

This work according to scientific projects of the MES of Ukraine (registration number 0115U002303), and NATO diplomacy department publicly pursuant program we "Science for Peace" (NUKR, SEPP 984536).

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Received: 01.03.2016; **revised:** 05.05.2016.

Горічок І.В., Шевчук М.О., Бойчук В.М. Термодинаміка точкових дефектів у металічній фазі моноссульфіду самарію. *Журнал Прикарпатського університету імені Василя Стефаника*, 3 (1) (2016), 65–70.

Мінімізацією термодинамічного потенціалу кристала визначено рівноважні значення концентрацій вакансій сульфуру та антиструктурних атомів самарію у металічній фазі моноссульфіду самарію SmS. Встановлено, що при вмісті атомів металу у сполуці 50,5-54 at. % за температур 300-400 К домінуючими дефектами є однократно позитивно іонізовані антиструктурні дефекти Sm_s^+ , а концентрація негативно заряджених вакансій сульфуру V_s^- є на 1-2 порядки нижчою. На основі запропонованої моделі дефектної підсистеми пояснено монотонну залежність густини самарій моноссульфіду від вмісту самарію.

Ключові слова: моноссульфід самарію, точкові дефекти.