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4C10Sn clusters in Ge-rich $C_xSn_yGe_{1-x-y}$ dilute alloys

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ABSTRACT

The self-assembling conditions of 4C10Sn clusters in Ge-rich $C_xSn_yGe_{1-x-y}$ ($0.01 < x < 0.03$, $0.005 < y < 0.081$) dilute alloys are represented. 4C10Sn clusters are carbon tetrahedrons surrounded by Sn atoms. The considerable decrease of the internal strains is a cause of self-assembling. High density of 4C10Sn clusters may be obtained up to 800 °C. The majority of carbon atoms are in 4C10Sn clusters at 800 °C if the carbon content is less than, equal to or several times more than that of Sn. 1C4Sn tetrahedral clusters with insignificant density should also form. These theoretical results open up the possibility to produce $C_xSn_yGe_{1-x-y}$ dilute alloys with a desired density of 4C10Sn clusters.

1. Introduction

In the last few years, the interest in semiconductors doped with the isoelectronic impurities renewed in the search of materials for fabrication of single-photon emitters [1–3]. Pairs of such impurities form the localized exciton traps ensuring sharp emission lines with well-defined wavelengths. The exciton traps formed by pairs of the nearest neighbour impurities are deep and, therefore, they are mainly studied. The theoretical estimates demonstrated that quadruplets of the nearest isoelectronic impurities should produce the exciton traps deeper than in the case of impurity pairs and, accordingly, should be more promising [4,5]. However, an occurrence of such quadruplets of highly mismatched atoms is hardly probable from the strain energy standpoint [6]. Although isolated carbon atoms should form the isoelectronic exciton traps in Ge:C [7], the carbon quadruplet formation should cause considerable strains and is unlikely. This situation can be changed if Ge-rich $C_xSn_yGe_{1-x-y}$ dilute alloys are considered instead of C_xGe_{1-x} dilute alloys. As it was shown [8], the strain energy decreases greatly after self-assembling (SA) of 4C10Sn clusters in Ge:(C, Sn) with carbon in the ultra dilute limit. They occur due to the compensation of the lattice expansion and contraction produced by isolated carbon and Sn atoms, respectively. These clusters are shown in Fig. 1. 1C4Sn clusters shown in Fig. 2 also should form in such alloys. SA of 4C10Sn clusters in $C_xSn_yGe_{1-x-y}$ may be preferable in comparison with SA of 1C4Sn clusters from the thermodynamics standpoint if the carbon content is close to that of Sn or greater [8]. However, an occurrence of polyatomic 4C10Sn clusters under the conditions described in [8] can be difficult because of the very small carbon contents. 4C10Sn cluster is arranged in several atomic planes of the crystal lattice. So, to form 4C10Sn clusters, high temperature annealing most likely will be necessary. Larger carbon contents in $C_xSn_yGe_{1-x-y}$ will reduce the annealing temperature up to a level where SA of 4C10Sn clusters with the desired density is very possible. The $C_xSn_yGe_{1-x-y}$ crystalline films with carbon and Sn contents up to $x = 0.021$ and $y = 0.081$ and polycrystalline films with $x = 0.058$ and $y = 0.113$ were grown via molecular beam epitaxy [9]. These experimental results demonstrate that the consideration of SA conditions with the preferential formation of 4C10Sn clusters in Ge-rich $C_xSn_yGe_{1-x-y}$ dilute alloys is reasonable. Here, the SA conditions with the preferential formation of 4C10Sn clusters in $C_xSn_yGe_{1-x-y}$ dilute alloys with the carbon content up to 3% are represented.

2. Model

SA of 4C10Sn and 1C4Sn clusters changes only the free energy of mixing since the chemical bonds between atoms in $C_xSn_yGe_{1-x-y}$ do not form. The free energy of mixing expressed as a sum of the strain energy and configurational entropy term $f^M = u - Ts$ is considered. The portions of carbon atoms in 4C10Sn and 1C4Sn clusters are 4C10Sn and 1C4Sn cluster order parameters denoted by α and β, respectively. The conditions for the cluster order parameters $\alpha + \beta \le 1$ and $2.5\alpha + 4\beta \le y/x$ should be fulfilled. The strain energy is given by

$$u = u_C(1-\alpha-\beta)x + 0.25u_{4C10Sn}\alpha x + u_{1C4Sn}\beta x + u_{Sn}(y-2.5\alpha x-4\beta x)$$

where u_C, u_{Sn}, u_{4C10Sn} and u_{1C4Sn} are the strain energy due to isolated carbon and Sn atoms and 4C10Sn and 1C4Sn clusters, respectively. The strain energies are equal, respectively, to $u_C = 1.72 \times 10^5$ Jmol^{-1}, $u_{Sn} = 1.36 \times 10^4$ Jmol^{-1}, $u_{4C10Sn} = 3.18 \times 10^5$ Jmol^{-1} and $u_{1C4Sn} = 7.03 \times 10^4$ Jmol^{-1} [10,11]. They demonstrate a tendency to SA of 4C10Sn and 1C4Sn clusters.

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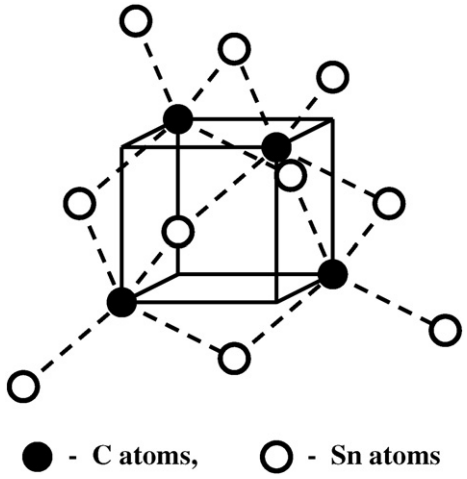

Fig. 1. 4C10Sn cluster.

The configurational entropy term is

$$-Ts = RT(1-\alpha-\beta)x\ln\frac{(1-\alpha-\beta)x}{1-\frac{7}{2}\alpha x-5\beta x}+RT\left(y-\frac{5}{2}\alpha x-4\beta x\right)\ln\frac{y-\frac{5}{2}\alpha x-4\beta x}{1-\frac{7}{2}\alpha x-5\beta x}$$
$$+RT(1-x-y)\ln\frac{1-x-y}{1-\frac{7}{2}\alpha x-5\beta x}+RT(1-\alpha-\beta)x\ln\frac{1-\alpha-\beta}{1-\alpha}$$
$$+RT\beta x\ln\frac{\beta}{1-\alpha}+\frac{1}{4}RT\alpha x\ln\frac{27}{4}\alpha x+RT\left(\frac{1}{27}-\frac{1}{4}\alpha x\right)\ln\left(1-\frac{27}{4}\alpha x\right).$$

The configurational entropy was obtained by using the number of the permutations of atoms. This number is represented as a product of three factors. The first one is the number of permutations of isolated carbon and Sn atoms at the fixed arrangement of 4C10Sn and 1C4Sn clusters. The second factor is the number of arrangements of 1C4Sn clusters at the fixed allocation of 4C10Sn clusters and carbon and Sn isolated atoms. The third factor is the number of permutations of 4C10Sn clusters.

The cluster order parameters are obtained by minimizing the free energy of mixing. An occurrence of 4C10Sn and 1C4Sn clusters from the isolated carbon and Sn atoms decreases the strain energy and configurational entropy. The transformation of clusters and isolated atoms (4C10Sn) → 2(1C4Sn) + 2(C) + 2(Sn) increases the strain energy and configurational entropy. The transformation (4C10Sn) + 6(Sn) → 4(1C4Sn) increases the strain energy. The configurational entropy decreases or increases after this transformation depending on the carbon and Sn concentrations. The entropy decreases if the carbon and Sn concentrations are equal or the concentration of Sn is less than that of carbon. The entropy rises during this transformation if the carbon concentration is significantly less than that of Sn. Thus, SA of both types of clusters and transformations between clusters and isolated carbon and Sn atoms change the value of the free energy of mixing. The difference of the values of the free energies of mixing depends on the carbon and Sn contents, temperature and cluster order parameters. Therefore, SA of both types of clusters as well as transformations between clusters and isolated atoms are competing processes.

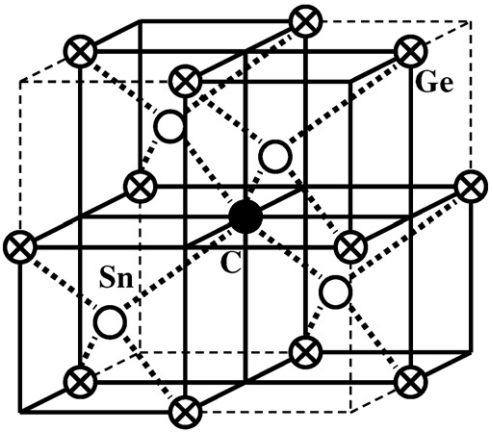

Fig. 2. 1C4Sn cluster.

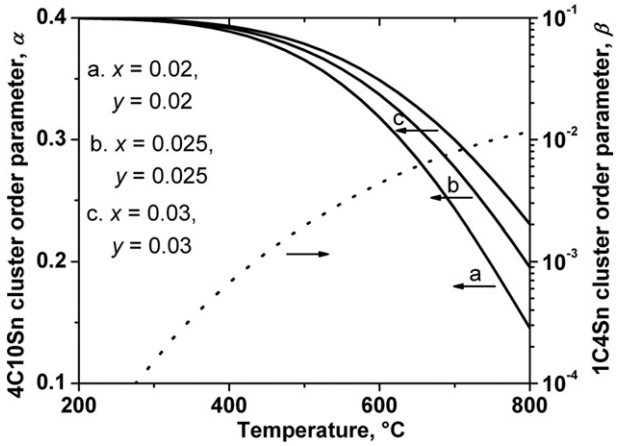

Fig. 3. The temperature dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curve) cluster order parameters with carbon and Sn concentrations $y = 2\times, x = 0.01$ (a), $x = 0.02$ (b) and $x = 0.03$ (c).

3. Results and discussion

The carbon and Sn contents in $C_xSn_yGe_{1-x-y}$ alloys from $x = 0.01$ to $x = 0.03$ and from $y = 0.005$ to $y = 0.081$, respectively, were chosen to assess the SA conditions at temperatures up to 800 °C. The high-temperature SA conditions could be used for a thermal treatment to transform a random alloy into an alloy with clusters if a random alloy was grown under non-equilibrium growth conditions. The high-temperature treatment of Ge-rich $C_xSn_yGe_{1-x-y}$ can be a long time due to the negligibly small equilibrium pressure of carbon, Ge and Sn over such alloys. It is the important advantage of $C_xSn_yGe_{1-x-y}$ over GaAs:(B, Sb) in which SA of multiatomic clusters is also preferable from the thermodynamics standpoint [12]. The temperature

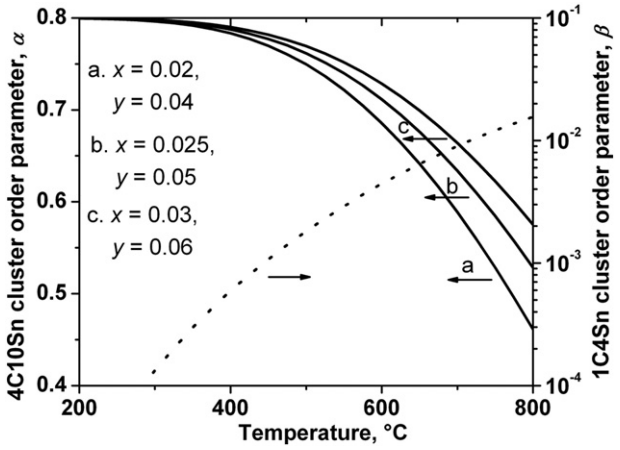

Fig. 4. The temperature dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curve) cluster order parameters with carbon and Sn concentrations $y = 0.5\times, x = 0.01$ (a), $x = 0.02$ (b) and $x = 0.03$ (c).

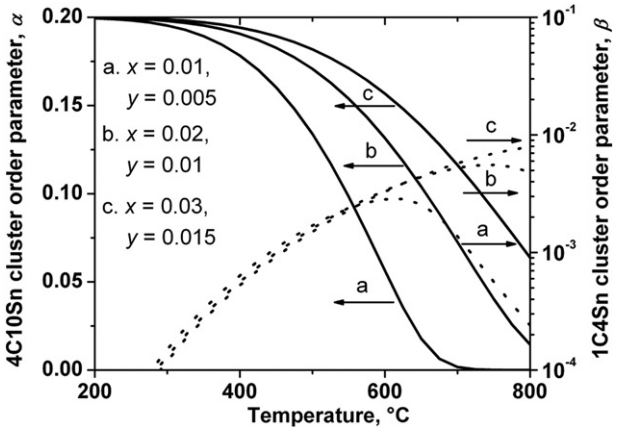

Fig. 5. The temperature dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curves) cluster order parameters with carbon and Sn concentrations $x = y = 0.02$ (a), $x = y = 0.025$ (b) and $x = y = 0.03$ (c).

dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curve) cluster order parameters in alloys with $y = x$, $x = 0.02$ (a), $x = 0.025$ (b) and $x = 0.03$ (c) are shown in Fig. 3. The maximal value of 4C10Sn cluster order parameter at this content ratio is equal to 0.4. In this case, all Sn atoms are in 4C10Sn clusters. The significant portion of Sn atoms (more than 50%) is in 4C10Sn clusters at 800 °C (Fig. 3). This indicates that thermal annealing should be effective treatment for the redistribution of carbon and Sn atoms to form 4C10Sn clusters. The dependencies of 1C4Sn cluster order parameters differ insignificantly. The densities of 1C4Sn clusters are considerably smaller than those of 4C10Sn clusters. Thus, these SA conditions should allow obtaining $C_xSn_xGe_{1-2x}$ with a large density of 4C10Sn clusters. The temperature dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curve) cluster order parameters in alloys with carbon and Sn concentrations $y = 2\times$, $x = 0.02$ (a), $x = 0.025$ (b) and $x = 0.03$ (c) are shown in Fig. 4. These contents should provide the maximal density of 4C10Sn clusters. The high density of the 4C10Sn clusters may be also formed up to 800 °C. Thus, also in this case, the high-temperature annealing can be effective to transform $C_xSn_{2x}Ge_{1-3x}$ random alloy into an alloy with clusters. The values of 1C4Sn cluster order parameters are as well as at the other carbon and Sn contents considerably smaller than the values of 4C10Sn cluster order parameters. The dependencies of 1C4Sn cluster order parameters are shown only by one curve since they differ insignificantly. The temperature dependencies of 4C10Sn (solid curves) and 1C4Sn (dotted curves) cluster order parameters in alloys with $y = 0.5\times$, $x = 0.01$ (a), $x = 0.02$ (b) and $x = 0.03$ (c) are shown in Fig. 5. The maximal value of 4C10Sn cluster order parameter at this ratio between the carbon and Sn contents is equal to 0.2. The values of 1C4Sn cluster order parameters are also much less than those of 4C10Sn cluster parameters. However, the density of 4C10Sn clusters in $C_xSn_{0.5x}Ge_{1-1.5x}$ with $x = 0.02$ and $x = 0.03$ is approximately two times less than in the case of $x = y$. Thus, these contents may be chosen if a significant density of 4C10Sn clusters is undesirable. The estimated 4C10Sn and 1C4Sn cluster parameters in $C_xSn_yGe_{1-x-y}$ with carbon and Sn contents $x = 0.021$ and $y = 0.081$ [9] at 800 °C are $\alpha = 0.860$ and $\beta = 0.022$, respectively. Such significant 4C10Sn clustering is due to the considerable configurational entropy caused by isolated Sn atoms. The obtained results demonstrate that Ge-rich $C_xSn_yGe_{1-x-y}$ dilute alloys are more promising semiconductors than Ge:(C, Sn) with carbon in the ultra dilute limit considered in [8].

The theoretical estimates show that nitrogen quadruplets should form the deep exciton traps in GaN_xAs_{1-x} and GaN_xP_{1-x} dilute alloys [4,5]. These traps capture an electron since the electronegativity of nitrogen is larger than those of As and phosphorus and after that a hole will bind to the Coulomb potential. The electronegativity of carbon is also much larger than those of Ge and Sn. Accordingly, it is expected that 4C10Sn clusters should form the deep exciton traps in $C_xSn_yGe_{1-x-y}$ dilute alloys as well as nitrogen quadruplets in GaN_xAs_{1-x} and GaN_xP_{1-x} [4,5]. Moreover, SA of 4C10Sn clusters decreases significantly the strain energy of $C_xSn_yGe_{1-x-y}$. It is an additional point in support of the formation of exciton traps by 4C10Sn clusters.

4. Conclusions

In summary, the self-assembling conditions of 4C10Sn clusters with the high density in Ge-rich $C_xSn_yGe_{1-x-y}$ dilute alloys are obtained by using the thermodynamic considerations. Self-assembling reducing the internal strains is preferential up to 800 °C from the thermodynamics standpoint. The high temperature conditions allow using a thermal treatment to form 4C10Sn clusters arranged in several atomic planes of the crystal lattice. The insignificant density of 1C4Sn clusters along with 4C10Sn clusters should also form under the described conditions. Self-assembling in $C_xSn_yGe_{1-x-y}$ alloys forming 4C10Sn and 1C4Sn clusters differs from the well known short-range order in substitutional alloys. 4C10Sn and 1C4Sn clusters are identical in size, shape and composition unlike various clusters in alloys with the conventional short-range order. The demonstrated theoretical results provide the valuable guidance for synthesizing the Ge-rich semiconductor material with a desirable density of 4C10Sn identical clusters.

Acknowledgements

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References

[1] T. Fukushima, Y. Hijikata, H. Yaguchi, S. Yoshida, M. Okano, M. Yoshita, H. Akiyama, S. Kuboya, R. Katayama, K. Onabe, Photoluminescence from single isoelectronic traps in nitrogen delta-doped GaAs grown on GaAs(111)A, Phys. E. 42 (2010) 2529–2531.
[2] S. Marcet, R. Andre, S. Francoeur, Excitons bound to Te isoelectronic dyads in ZnSe, Phys. Rev. B 82 (2010) 235309.
[3] Y. Harada, T. Kubo, T. Inoue, O. Kojima, T. Kita, Extremely uniform exciton states in nitrogen delta-doped GaAs studied by photoluminescence spectroscopy in external magnetic fields, J. Appl. Phys. 110 (2011) 083522.
[4] P.R.C. Kent, A. Zunger, Evolution of III-V nitride alloy electronic structure: the localized to delocalized transition, Phys. Rev. Lett. 86 (2001) 2613–2616.
[5] P.R.C. Kent, A. Zunger, Theory of electronic structure evolution in GaAsN and GaPN alloys, Phys. Rev. B 64 (2001) 115208.
[6] V.A. Elyukhin, V.M. Sánchez-R., O.V. Elyukhina, Self-assembling in $Al_xGa_{1-x}N_yAs_{1-y}$ alloys, Appl. Phys. Lett. 85 (2004) 1704–1706.
[7] H.P. Hjalmarson, P. Vogl, D.J. Wolford, J.D. Dow, Theory of substitutional deep traps in covalent semiconductors, Phys. Rev. Lett. 44 (1980) 810–813.
[8] V.A. Elyukhin, Self-assembling of 1C4Sn and 4C10Sn clusters in Ge:(C, Sn), J. Appl. Phys. 109 (2011) 086105.
[9] T. Yamaha, K. Terasawa, H. Oda, M. Kurosawa, W. Takeuchi, N. Taoka, O. Nakasuka, S. Zaima, Formation, crystalline structure, and optical properties of $Ge_{1-x-y}Sn_xC_y$ ternary alloy layers, Jpn. J. Appl. Phys. 54 (2015), 04DH08.
[10] V.A. Elyukhin, S.F. Díaz Albarrán, Self-assembling of C and Sn in Ge, Phys. E. 28 (2005) 552–555.
[11] V.A. Elyukhin, L.P. Sorokina, V.A. Mishurnyi, F. de Anda, Self-assembling of 4C10Sn clusters in Ge co-doped with C and Sn, Phys. E. 40 (2008) 883–885.
[12] V.A. Elyukhin, Nanoscale order in GaAs:(B, Sb), Phys. E. 43 (2011) 1874–1877.