

Entropy of Cluster System in Silicon Melt

S.L. Khrypko, Oleksandr K. Golovko*

Zaporizhzhia State Engineering Academy, 226, Sobornyi Ave., 69006 Zaporizhzhia, Ukraine

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The full entropy's cluster component of the silicon melt is defined in the assumption of gamma-distribution of microcluster in the form of chains with covalent interatomic bonds. The entropy is calculated for temperatures characteristic of the practice of growing single crystals from the melt, as well for the precipitation of silicon from the vapor phase of individual silicon clusters. The estimation results are consistent with literary data for clusters' entropy in simple liquids. The entropy of two- and three-atom microcluster at temperatures close to the melting point of silicon changes not monotonously. This indicates that in the process of growing a single crystal in silicon melt there is a continuous structural alteration near to the crystallization front. This work's aim is to deepen the understanding of the crystallization's structural aspects of elementary semiconductors from melt, which may be useful for improving the processes of growing their single crystals and amorphous films.

Keywords: Micro- and nanoelectronics, Silicon, Melt, Microcluster, Nuclear chain, Density of probabilities, Entropy.

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1. INTRODUCTION

Silicon clusters of various structure are investigated for many years [1]. Silicon nanoparticles are characterized by valuable optical properties and therefore are a promising material for the manufacture of nanoscale optoelectronic devices. Individual (isolated) silicon clusters, for example, are created the condensation from the vapor phase at low temperatures [2]. Silicon microclusters are formed in a gas environment, as well as in a liquid environment (silicon tetrachloride).

The spontaneous formation of microcluster atoms or molecules is characteristic for disordered condensed medium, in particular, for simple and multi-atomic liquids: liquefied gases, water, melts of metals [3]. Using electron microscopy revealed the formation of silicon microclusters different sizes and shapes in layers of amorphous SiO₂, in the process of their annealing after ion implantation of Si⁺ [4]. Formation of clusters is observed in porous silicon [5].

The existence of covalent bonds between a portion of atoms in a silicon melt is confirmed on the basis of experimental studies in [6]. According to the work [7] authors' conclusions, the silicon clusters in the Al melt affect the particles morphology of primary silicon in the hypereutectic of the Al-Si alloy. Chain silicon clusters, which repeat the form of atomic chains of a crystalline silicon lattice, provide accelerated crystallization of this material [8].

The deepening of the notions about the structure of the silicon melt and the physical processes occurring in it at the atomic-molecular level are relevant for the development of the technologies of its nanostructures and for the further improvement of the processes of growing single crystals and epitaxial films for micro and optoelectronics.

2. STRUCTURE OF SILICON CLUSTERS. FORMULATION OF THE PROBLEM

The possible structure of individual (isolated) clusters of covalent materials was theoretically investigated by various simulation methods. The results of different researchers vary different. For example, according to the authors [2], the molecular-dynamic modeling with using of the Stillinger-Weber potential suggests that silicon clusters from 10 to 32 atoms are a noncrystalline phase of a substance in a condensed state. Their structure is characterized by the presence of the near order, but the symmetry elements in them are either absent or substantially different from the symmetry of the crystalline phase of silicon. The deposition of such clusters from the vapor phase, these researchers have received layers of amorphous silicon nanosized thickness [2]. However, in [9], by using a nonspherical symmetrized potential model was shown that clusters of chemical elements of group IV up to 20 atoms can be of two types - crystalline with 6-membered rings and amorphous with 4-membered or 5-membered rings. In [10], photoelectron spectra of silicon ion clusters up to 20 atoms were studied. The simulation results using the theory of density functionalities and pseudopotentials coincide well with the measurements data for clusters of all researched sizes apart from the 12 atomic ones. The researchers concluded that for individual silicon clusters of small sizes, the forms of trigonal prisms, that is, the trigonal crystal system, are characteristic. Note that silicon has a crystal lattice, which belongs to the structural type of diamond, the spatial group of symmetry Fd3m cubic crystal system [11]. Thus, the structure of individual silicon clusters according to [10] is significantly different in its symmetry from the crystalline phase of silicon. The research of the possible configuration of silicon clusters of 2 to 7 atoms by the pseudopotential method of MO-LCAO [12] showed that their linear and some planar configurations are sufficiently stable.

* akgolovko@gmail.com

In [13], according to the diffraction scattering of X-rays, it was found that atoms in the melt of germanium form chains with a covalent bond. Taking into account the crystallochemical and structural similarity of crystalline lattices of germanium and silicon [11], the conclusion [13] of the structure of clusters in the germanium melt can be transferred to the silicon melts. In favor of this assumption is evidenced by a very high similarity to the data [12] of individual clusters of germanium and silicon.

The significant factor of difference in the structure of clusters in the melt from the structure of individual clusters of the same substance can be explained, in our opinion, by the interaction of the cluster's atoms with the melt's atoms. In the case of a chain cluster, two electrons of a silicon atom inside a chain connect it with two neighbors by covalent bonds, and two other its valence electrons pass to the melt, forming metal bonds with the atoms of the melt. The atom at the edge of the chain is bound by a covalent bond with only one of its neighbors, and three of its other valence electrons form metal bonds with the atoms of the melt. Under the influence of thermal fluctuations, the chain can break or establish covalent bonds with other melt ions [14]. Unlike a cluster in the melt, the shape and structure of an individual cluster below its melting point is quite stable. The formation and decay of clusters in silicon melt under the action of thermal fluctuations is subject to statistical regularities. The informative characteristic of the statistical system is its entropy. To analyze the behavior of microforms in the atomic structure of the silicon melt, the study of the entropy of these formations is meaningful.

Silicon single crystals for microelectronics and solar energy are grown by the method of extracting from the melt (Czochralski process). In industrial plants which are used for crystal growth, the melt at the crystallization front is slightly overcooled, that is, its temperature T_F is about 10 K below the melting point T_m . At the same time, inside the quartz crucible and near its walls, the temperature of the silicon T_{ins} melt is maintained by 10...20 K higher than the melting point of silicon T_m in order to prevent uncontrolled crystallization. As shown in [8], microclusters in the melt substantially affects the mechanism and the rate of crystallization. Therefore, the study of their structure and entropy is of practical importance for optimizing the processes of growing silicon single crystals, as well as precipitation of individual clusters from the vapor phase.

The purpose of this work is to determine the distribution of the probability of microcluster by the number of atoms in the cluster, as well as the entropy component of the silicon melt, which is due to the self-organization of its atoms in the microcluster at temperatures characteristic of the practice of growing single crystals and individual silicon clusters.

3. CLUSTER COMPONENT OF SILICON MELT ENTROPY

To calculate the entropy of clusters, we use the general definition of the Boltzmann entropy [15]

$$S_{clust}(N) = -k \int_0^{\infty} f(N) \ln f(N) dN, \quad (1)$$

where k – the Boltzmann constant; N – the number of atoms in the cluster; $f(N)$ – the function of the distribution of clusters' probability density in the silicon melt by the number of atoms in the cluster.

Earlier [16], we proposed a gamma-distribution for statistical simulation of a micro cluster system in the form of chains in a silicon melt, the two parameters of which take into account the structurally dependent parameters of the melt – density and viscosity. The results of using this distribution agree well with the data [12] for micro clusters in the germanium melt.

The function of the distribution of clusters' probability density $f(N)$ is chosen in such form

$$f(N) = \frac{N^{\alpha-1}}{F(\alpha) \cdot \theta^{\alpha} \cdot \exp\left(\frac{N}{\theta}\right)}, \quad (3)$$

where $F(\alpha) = \int_0^{+\infty} N^{\alpha-1} \exp(-N) dN$ – gamma-function from argument α , $\alpha > 1$. The form parameter α and the scale parameter θ are chosen in the same way as in [16]:

$$\alpha = \frac{\eta(T)}{\eta(T_B)}, \quad (4)$$

$$\theta = \frac{d(T)}{d(T_B)} + \frac{d(T_m) - d(T_B)}{d(T_B)}, \quad (5)$$

where η – dynamic viscosity of the melt, $N \cdot s \cdot m^{-2}$; d – its density, $kg \cdot m^{-3}$; T – temperature, K; T_B – boiling point temperature of the melt, K; T_m – the temperature of its melting, K.

4. RESULTS AND THEIR DISCUSSION

Let's consider the distribution function of microcluster's probability density in a silicon melt by numbers of atoms in the cluster and their entropy at temperatures T_m , $T_F = T_m - 10$ K, $T_{ins} = T_m + 20$ K and T_B . To determine the numerical values of the quantities $\alpha(T)$ by expression (4) and $\theta(T)$ by (5) we use the data from [17] on the experimental dependences $\eta(T)$ and $d(T)$ for the silicon melt: $T_m = 1688$ K, $T_B = 2623$ K, $d(T_m) = 2530$ $kg \cdot m^{-3}$, $(T_B) = 2210$ $kg \cdot m^{-3}$, $\eta(T_m) = 8,8 \cdot 10^{-4}$ $N \cdot s \cdot m^{-2}$, $\eta(T_B) = 4,1 \cdot 10^{-4}$ $N \cdot s \cdot m^{-2}$.

Calculations by (3)-(5) showed (Fig. 1) that the distribution of microcluster by the number of atoms in them at the crystallization front (curve T_F) is more distinct from the distribution at the melting temperature (curve T_m), than at the temperature inside the crucible (curve T_{ins}).

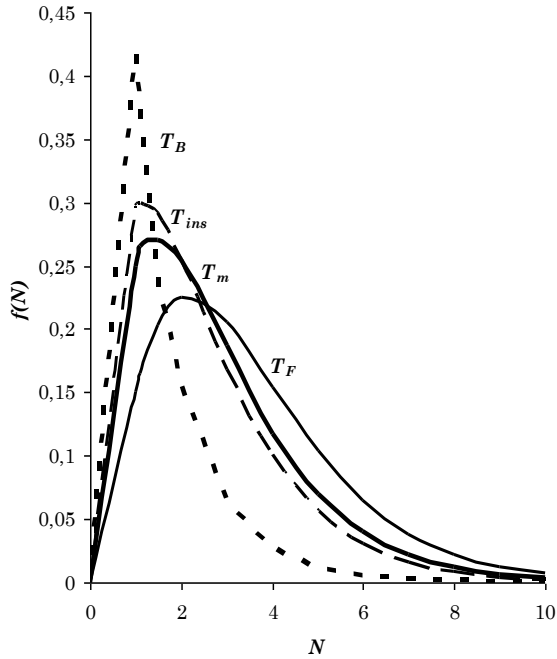


Fig. 1 – The probability density of the distribution of microclusters in the form of atomic chains by the number of atoms in them at different temperatures of the melt of silicon: melting (curve T_m), boiling (curve T_B), in crystallization front (curve T_F) and inside the crucible (curve T_{ins})

This feature of the temperature dependence $f(N)$ is connected with an abnormally strong increase in the density and viscosity of the silicon melt with a decrease in its temperature near the melting point, which affects the size of the parameters of the form α (4) and the scale θ (5). From the data of Figure 1 it is seen that in the melt at the crystallization front, the two-atomic ($N=2$) and three-atomic ($N=3$) clusters are the most probable, and in the crucible there are single atoms ($N=1$) and two-atomic clusters. At boiling temperature, the single atoms are maximally probable, but microclusters size up to 5 atoms have a statistically significant probability of more than 0,02.

According to figure 1, the function (1) was calculated and the entropy of clusters of different sizes was calculated by numerical integration (Fig. 2). Evidently that the entropy of two-atomic clusters at temperature inside the crucible (curve T_{ins}), is the same as at melting temperature (curve T_m) – 0,34 k , and at the crystallization front (curve T_F) is less than – 0,32 k .

With the temperature increase the entropy of clusters of different sizes changes not equally (Fig. 3): for two-atomic clusters – (curve 1) and three-atomic (curve 2) has a small maximum at melting point, and from five atoms (curve 3) – monotonically decreases with increasing temperature of the melt.

This indicates the progress of complex processes of restructuring the silicon melt structure near the crystallization front during the growth of single crystals by the Czochralski process.

During the single crystal's pulling out, the level of the melt in the crucible decreases. Accordingly, a next inner layer with a temperature $T_{ins} = 1708$ K becomes near-surface with a temperature $T_m = 1688$ K.

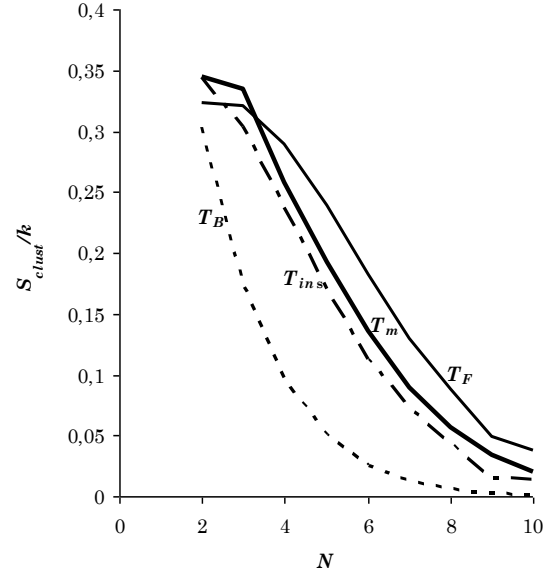


Fig. 2 – The entropy of microcluster with the number of atoms from 2 to 10 in the melt of silicon at different temperatures: melting (curve T_m), boiling (curve T_B), in the crystallization front (curve T_F) and inside crucible (curve T_{ins})

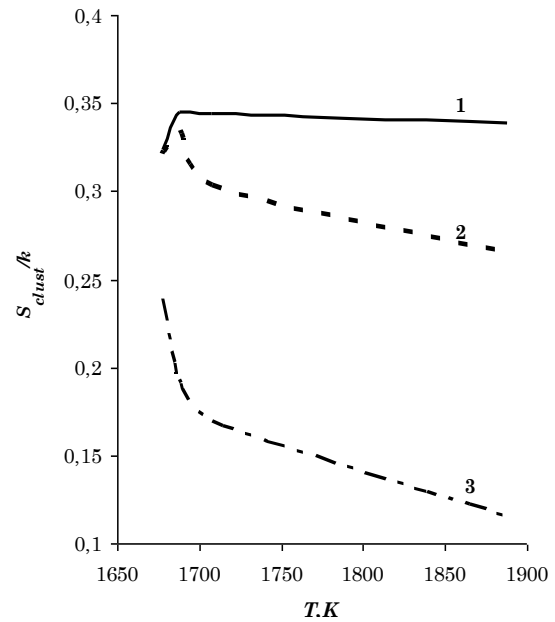


Fig. 3 – Temperature dependence of entropy of microclusters different sizes: two-atomic (curve 1), three-atomic (curve 2) and chains with 5-atoms (curve 3)

Next, the part of the melt that comes in contact with the crystallization front enters the meniscus and its temperature drops to $T_F = 1678$ K. During this process in the silicon melt, the number of two- and three-atomic microclusters initially increases, then decreases, and the number of chains with $N \geq 4$ monotonically increases. Such structural reorganization must affect the kinetics and the mechanism of the crystallization process.

The entropy of the aggregate system of clusters by expression (1), with increasing temperature, monotonically decreases (Fig. 4).

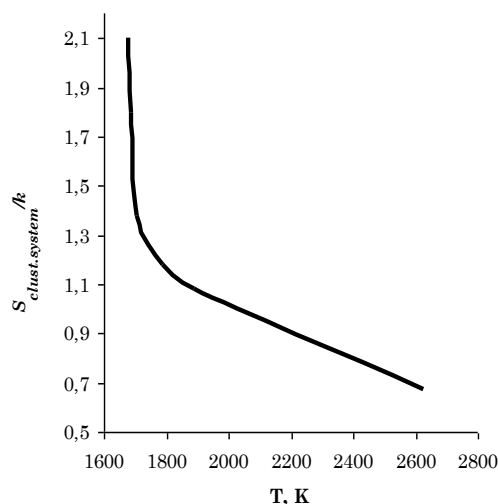


Fig. 4 – The temperature dependence of the full entropy's cluster component of the silicon melt

Let's compare the obtained results with literary data for simple liquids. In work [3], an approximated form of the functional (2) for simple liquids is given:

$$S_{clust.system} = k \left[\ln \theta + \frac{1}{2} \ln (17\alpha - 10,57) \right]. \quad (6)$$

For the melting point of silicon, by definition (4) $\alpha = 2,15; \theta = 1,29$ and, accordingly, the cluster component of the complete entropy of the silicon melt for (6)

$S_{clust.system} = 1,88 k$. According to our results of numerical integration of the function (1) for the melting point of silicon $S_{clust.system} = 1,81 k$. Taking into account that (6) is an approximated expression, the difference of these values by $\approx 4\%$ can be considered insignificant.

5. CONCLUSIONS

The results of statistical simulation showed that, near of the melting temperature in the silicon melt, the component of its entropy, which is due to two-atomic and three-atomic clusters, changes nonmonotonically. This result indicates a continuous process of complex reorganization of the silicon melt structure near the crystallization front during the growth of single crystals by the Czochralski process. However, the total cluster component of its entropy monotonously decreases. This is a consequence of the partial dissolution of clusters in the melt at the temperature increasing. As a result, the cluster system's contribution to the full entropy of the melt also decreases. Estimates of the contribution of the cluster system to the full entropy of the silicon melt are in good agreement with the literary data for simple liquids.

The established nature of the temperature dependence of the full entropy's cluster component of the silicon melt allows us to deepen the notion of the structural aspects of silicon crystallization.

The obtained results can be used in the development of new and improving existing methods for the production of semiconductor single crystals and nanostructures.

Ентропія кластерної системи в розплаві кремнію

С.Л. Хрипко, О.К. Головка

Запорізька державна інженерна академія, пр. Соборний, 226, 69006 Запоріжжя, Україна

Визначена кластерна складова повної ентропії розплаву кремнію в припущенні гамма-розподілу мікрокластерів у формі ланцюжків з ковалентними міжатомними зв'язками. Ентропія розрахована для температур, характерних для практики вирощування монокристалів з розплаву, а також осадження з парової фази індивідуальних кластерів кремнію. Результати оцінок узгоджуються з літературними даними для ентропії кластерів в простих рідинах. Ентропія двох- та трьохатомних мікрокластерів при температурах, близьких до температури плавлення кремнію, змінюється немонотонно. Це свідчить про те, що в процесі вирощування монокристала в розплаві кремнію поблизу фронту кристалізації відбувається безперервна структурна перебудова. Робота переслідує мету поглиблення уявлень про структурні аспекти кристалізації елементарних напівпровідників з розплаву, що може бути корисним для удосконалення процесів вирощування їхніх монокристалів і аморфних плівок.

Ключові слова: Мікро- та наноелектроніка, Кремній, Розплав, Мікрокластер, Атомний ланцюжок, Щільність ймовірностей, Ентропія.

Энтропия кластерной системы в расплаве кремния

С.Л. Хрипко, А.К. Головка

Запорожская государственная инженерная академия, пр. Соборный, 226, 69006 Запорожье, Украина

Определена кластерная составляющая полной энтропии расплава кремния в предположении гамма-распределения микрокластеров в форме цепочек с ковалентными межатомными связями. Энтропия рассчитана для температур, характерных для практики выращивания монокристаллов из расплава, а также осаднения из паровой фазы индивидуальных кластеров кремния. Результаты оценок согласуются с литературными данными для энтропии кластеров в простых жидкостях. Энтропия двух- и трёх-атомных микрокластеров при температурах, близких к температуре плавления кремния, изменяется немонотонно. Это свидетельствует о том, что в процессе выращивания монокристалла в

расплаве кремния вблизи фронта кристаллизации происходит непрерывная структурная перестройка. Работа преследует цель углубления представлений о структурных аспектах процесса кристаллизации из расплава элементарных полупроводников, что может быть полезным для усовершенствования процессов выращивания их монокристаллов и аморфных плёнок.

Ключевые слова: Микро- и наноэлектроника, Кремний, Расплав, Микрокластер, Атомная цепочка, Плотность вероятностей, Энтропия.

REFERENCES

1. J.M. Goicoechea, S.C. Sevov, *J. Am. Chem. Soc.* **126** No 22, 6860 (2004).
2. E. Blaisten-Barojas, D. Levesque, *Phys. Rev. B* **34** No 6, 3910 (1986).
3. G.A. Melnikov, V.N. Verveyko, V.G. Melnikov, D.V. Verveyko, A.Yu. Verisokin, *Vestnik Mosk. Univers., 3 Physika. Astronomiya* **5**, 23 (2011).
4. Roushdey Sath, L. Fitting, E.V. Sitnikova, M.V. Zamoreanskaya, B. Schmidt, Y.-J. Fitting, *Phys. Techn. Semicond.* **41** No 4, 397 (2007).
5. S.L. Khripko, *Programmynaya realizatsiya formirovaniya klasterного rosta poristykh struktur* (Algoritmy i programmy dlya issledovaniya fizicheskikh protsessov v tverdykh telakh: Zaporozhye, KPU: 2009).
6. K. Tsuji, T. Hattori, T. Mori, T. Kinoshita, T. Narushima, N. Funamori, *J. Phys. Condens. Matter.* **16**, 989 (2004).
7. C.L. Xu, Q.C. Jiang, *Mater. Sci. Eng.* **437** No 2, 451 (2006).
8. I.F. Chervonyy, Ye.Ya. Shvets, Yu.V. Golovko, S.G. Yegorov, *Est-Eur. J. Enterprise Technol.* No 6/5 (54), 79 (2011).
9. S. Saito, S. Ohnishi, S. Sugano, *Phys. Rev. B* **33** 7036 (1986).
10. J. Müller, Bei Liu, A.A. Shvartsburg, Serdar Ogut, J.R. Chelikowsky, K.W.M. Siu, Kai-Ming Ho, G. Gantefor, *Phys. Rev. Lett.* **85** 1666 (2000).
11. Ю.К. Егоров-Тисменко, *Кристаллография и кристаллохимия* (Москва: КДУ: 2005) (Y.K. Egorov-Tismenko, *Krystallografiya and krystallochimiya* (Moskva: KDU: 2005)).
12. G. Pacchioni, J. Kouřeký, *J. Chem. Phys.* **84** 3301 (1986).
13. V.P. Kazimirov, A.S. Roik, V.M. Perevertaylo, O.B. Loginova, S.A. Lisovenko, *Sverkhтвердые материалы* **4**, 35 (2008).
14. А.К. Головкин Рептация атомных цепочек в расплавах германия и кремния, *XI International scientific and practical conference – Modern european science, Vol.9, P.54-57 (Sheffield: Science and education LTD: 2015)*.
15. Большая энциклопедия нефти и газа (Bolshaya entsiklopedia nefi and gaza) ngpedia.ru/id620670p1.html.
16. E.J. Shvets, I.F. Chervony, O.K. Golovko, *J. Nano- Electron. Phys.* **7** No 4, 64 (2015).
17. *Properties of crystalline silicon* (Ed. by R. Hull) (London: 1 Inst. of Engin. & Technology: 2006).