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D.A. Volkov, Y.V. Terenteva, S.A. Beznosyuk

Altai State University, Barnaul, Russia
(E-mail: bsa1953@mail.ru)

Attosecond nanotechnology: quantum dots of nanoelectromechanical systems of $CuIn_xGa_{1-x}S_2$ compounds

In the paper the thermodynamic stability and variability of the internal energy of continuous substitution solid solutions based on the $CuIn_xGa_{1-x}S_2$ chalcopyrite lattice (CIGS) in a state of the nanoelectromechanical system (NEMS) are studied. These substances are the most effective materials for phototransformation processes. It is known that maximum efficiency reached using a photoconverter based on $CuIn_xGa_{1-x}S_2$ composition amounted up to 21 %, while the same value for photoconverter based on silicon could reach only 15 %, which underlines the relevance of studies of the subject compositions. The equilibrium bond lengths and binding energy values are presented. The change to the internal energy at different temperatures and the change to distribution functions of atoms over radial pairs in a stable system of nanolayers are shown. It was revealed that changing of indium atoms concentration in the system causes non-linear relative changes to the parameters of stable CIGS NEMS nanolayers. It was shown that given behavior is the consequence of a significant difference in both In–S and Ga–S bond lengths and binding energy values in the first coordination area of sulphur.

Keywords: radial pair distribution function, semiconductor, solar cells, nanoelectromechanical system, graphs, Vegard's law.

Introduction

The production and use of semiconductor compounds with specific properties has become associated with the further development of solid-state optoelectronics. In connection with this, at the end of the twentieth century, interest in studying semiconductor materials with a chalcopyrite structure of type $A^1B^3C^6_2$ began to gain interest. Beginning in the second half of the twentieth century, after the publication of many publications about the prospects for the development of thin-film photocells based on $A^1B^3C^6_2$ structures, the reality of the practical use of these compounds became clear as an effective optical material. They became the subject of close attention of scientists and technologists.

Cu (In, Ga), S_2 (CIGS) and related materials were investigated for thin-film solar cells, since their high absorption coefficient and adjustable band gap can achieve high conversion efficiency. Recently, several groups have reported cell efficacy of over 20 % with alkaline treatment on the surface of CIGS [1–6].

This article describes the study of the stability of nanoelectromechanical systems (NEMS) of CIGS structures conducted using the approximating quasiparticle density functional (calculating the NEMS energy of atomic dimers (Table 1) and the method of steepest descent along the surface of a particle.

The study of the quantum relaxation kinetics of NEMS CIGS was carried out at the temperature of liquid nitrogen (T_1 = 77 K) and normal conditions (T_2 = 293 K). These temperatures are realized by the special method of NEMS kinetics [7].

Table 1

Parameters of dimer bonds

Dimer	Equilibrium bond energy U_0, kJ/mol	Equilibrium bond length R_0, nm	The frequency of zero oscillations ω_0, cm^{-1}
In–S	–293	0.23	359
Cu–S	–193	0.24	268
Ga–S	–243	0.25	349

From the data obtained, it is clear that during the transition, from gallium to indium, the energy and bond length increase, and the frequency of zero-point oscillations decreases.

Computer modelling

For further experiment, we needed to build models of nanolayers CIGS. The parameters of the crystal lattices, $CuInS_2$ and $CuGaS_2$ with the chalcopyrite structure (a = 5.5170, c = 11.0600) were used for the construction.

Thus, the models of semiconductor nanolayers $CuInS_2$ and $CuGaS_2$, consisting of 6400 atoms of size 20×20×1 e. (221.2 nm × 110.34 nm × 5.170 nm). The image of the structures obtained (with enlarged fragments) is shown in Figure 1. Figure 2 shows the link graph of these structures.

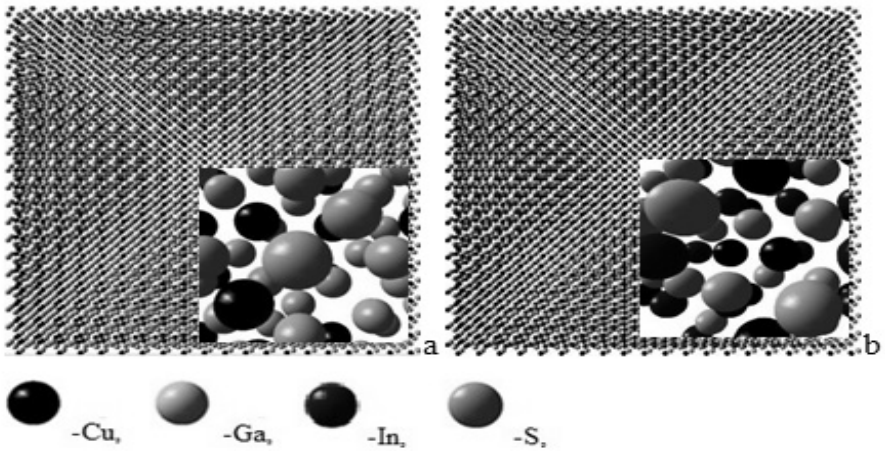


Figure 1. Models of nanolayers with a larger fragment $CuInS_2$ (*a*), $CuGaS_2$ (*b*)

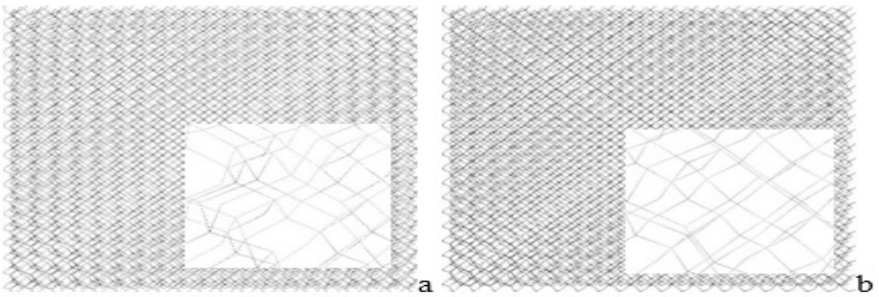


Figure 2. Coupled graphs of nanolayers with an enlarged fragment $CuInS_2$ (*a*), $CuGaS_2$ (*b*)

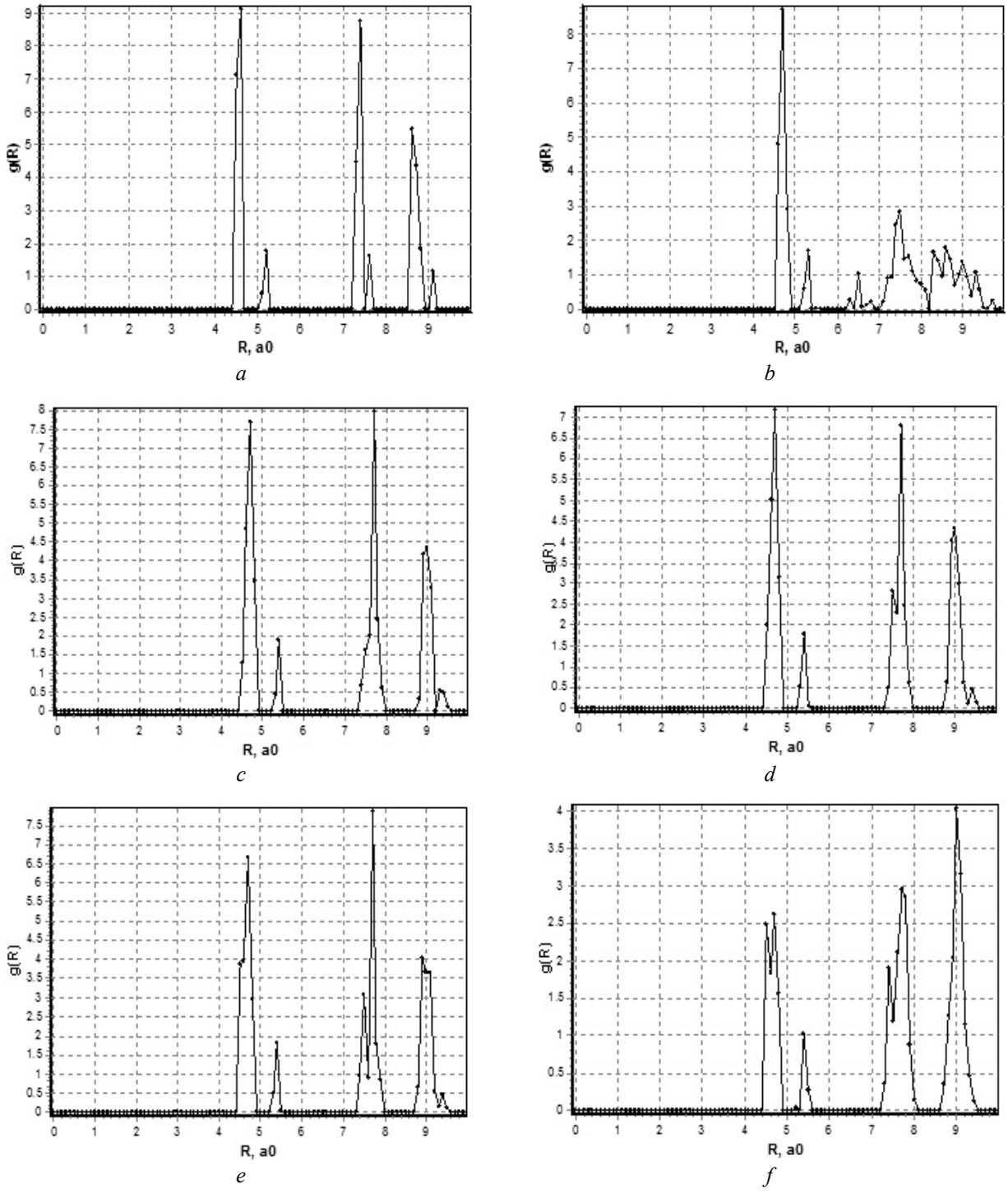
To obtain a complete picture of the correlation of internal energy and changes in the crystal lattice of nanoelectromechanical structures, the use of the «CompNanoTech» [6] software package is required, which uses the parameters of atomic couple bonds obtained by the nonlocal density functional method. This package is used to optimize the geometry of the nanofilm during the pulse action at different temperatures [7].

As a result of a computer experiment at T_0 = 0 K, optimized CIGS nanolayer structures ($CuIn_xGa_{1-x}S_2$) were obtained. The values of the energies of nanolayers obtained in the experiment are presented in Table 2 and in Figure 3.

Table 2

The total NEMS bond energies of variable composition $CuIn_xGa_{1-x}S_2$

Nanolayer composition	Nanolayer energy, kJ/mol
$CuGaS_2$	–238
$CuIn_{0,25}Ga_{0,75}S_2$	–246
$CuIn_{0,5}Ga_{0,5}S_2$	–250
$CuIn_{0,75}Ga_{0,25}S_2$	–258
$CuInS_2$	–266



a — $CuGaS_2$ in the initial state; *b* — $CuGaS_2$; *c* — $CuIn_{0.25}Ga_{0.75}S_2$;
d — $CuIn_{0.5}Ga_{0.5}S_2$; *e* — $CuIn_{0.75}Ga_{0.25}S_2$; *f* — $CuInS_2$

Figure 3. Radial pair distribution functions of atoms

Figures show 3 *b–f*, a peak that corresponds to the distribution of copper atoms at distances of 5.2–5.3 *a*0 with an intensity of 2.4, as can be seen from the figures, there is a consistent change in peaks, namely: a decrease in the peak of Ga at distances of 3.7–3.8 *a*0, the peak decreases in values from 2.6 to 0 with increasing In concentration from 0 to 100 %, and, accordingly, the growth of In peak in the range 5.8–6.0 *a*0 from 0 to 2.2 when the concentration of Ga drops to 0 %.

It follows from the analysis that when the In concentration in the system changes over the B^3 sublattice from 0 to 1, a monotonous, quasilinear change in the first coordination sphere occurs, and a decrease in the peaks in the second and third coordination spheres is observed.

Since the NEMS energy of a nanolayer is determined by the radial distribution function of atoms in the system, and the first coordination sphere has the largest contribution to the energy of the nanolayer, a quasilinear dependence of the nanolayer energy on the concentration x occurs (Fig. 4), which shows the Vegard law when the NEMS composition changes.

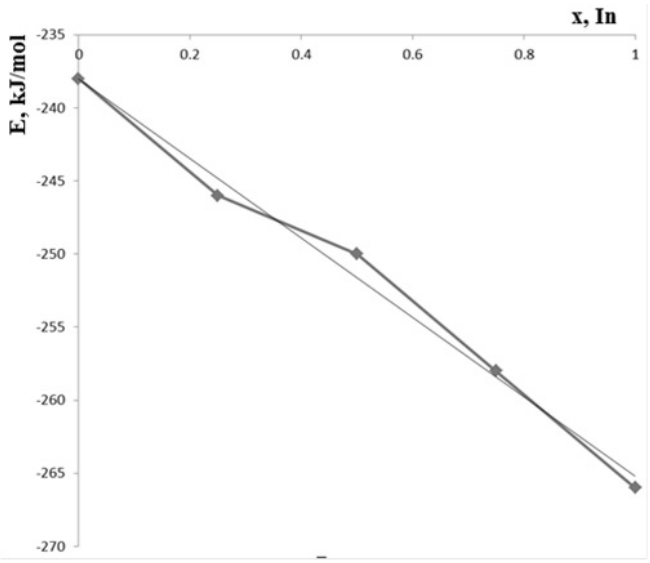


Figure 4. Concentration dependence of the energy of $CuIn_xGa_{1-x}S_2$ semiconductor nanolayers at $T_0 = 0$ K

According to the results of computer simulation using quantum nanokinetics at two temperatures: $T_1 = 77$ K and $T_2 = 298$ K, optimized structures of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$ were obtained, and kinetic curves (Fig. 5) of the system energy change during relaxation were constructed highly nonequilibrium semiconductor NEMSs of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$.

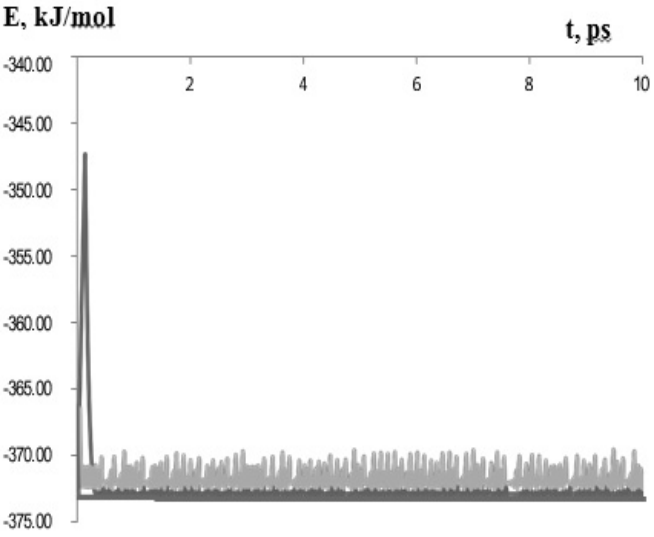


Figure 5. An example of a kinetic curve for the relaxation of $CuGaS_2$ systems

The results of a computer experiment to study the kinetics of relaxation and finite stability of the studied nanolayers, obtained from the kinetic curves constructed for all the $CuIn_xGa_{1-x}S_2$ systems under study in the framework of the electromechanical model, are presented in Table 3.

Table 3

Indicators of femtosecond processing of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$ and at different temperatures

Nanolayer composition	Femtosecond Processing Indicators						
	E_0, kJ/mol	E_{77}, kJ/mol	t_{77}, ps	A_{77}, kJ/mol	E_{298}, kJ/mol	t_{298}, ps	A_{298}, kJ/mol
$CuInS_2$	–416	–415	0.12	0.91	–414	0.09	3.60
$CuIn_{0.75}Ga_{0.25}S_2$	–404	–403	0.77	0.85	–402	0.11	3.333
$CuIn_{0.5}Ga_{0.5}S_2$	–392	–391	0.55	0.84	–390	0.28	3.37
$CuIn_{0.25}Ga_{0.75}S_2$	–386	–385	0.70	0.79	–383	0.20	3.31
$CuGaS_2$	–373	–372	0.44	0.79	–371	0.12	3.22

According to the Table 3 we can draw the following conclusions: for semiconductor nanostructures, femtosecond relaxation from the activated state at $T_0 = 0$ K leads to the state with the greatest stability, with an exact lower energy limit, with low amplitude atomic.

The time interval of the output of an activated nano-layer on a «plateau» depends on temperature, and the evolution of nanolayers in a non-equilibrium state achieves relaxation over different times.

According to the results of computer simulation using the quantum NEMS kinetics at two temperatures $T_1 = 77$ K and $T_2 = 298$ K, radial distribution functions of atoms in the NEMS were constructed for nanolayers of continuous solid solutions of variable composition $CuIn_xGa_{1-x}S_2$.

Conclusions

1. The formation of continuous substitution solid solutions on the B^3 sublattice of compounds of the composition $CuIn_xGa_{1-x}S_2$, as a whole, obeys the Vegard law. Deviations from Vegard's law are due to transformations of the second and third coordination sphere of nanolayers with changes in indium concentration.

2. In $CuIn_xGa_{1-x}S_2$ systems, at indium concentrations $x \leq 0.38$, a stabilizing nonlinear contribution is observed, and for $x > 0.38$, a non-linear, destabilizing positive energy contribution is observed.

3. Under cryogenic (T = 77 K) and standard (T = 298 K) conditions, the order of the coordination spheres above the first one collapses more with increasing temperature. As the relaxation temperature rises from cryogenic (T = 77 K) to standard (T = 298 K) conditions, the average energy of NEMS at all concentrations decreases by 1 kJ/mol, and quantum fluctuations increase from 0.64 kJ/mol to 3.06 kJ/mol.

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Д.А. Волков, Ю.В. Терентьева, С.А. Безносюк

Аттосекундты нанотехнологиялар: $CuIn_xGa_{1-x}S_2$ қосылысының наноэлектрмеханикалық жүйелерінің кванттық нүктелері

Мақалада халькопирит $CuIn_xGa_{1-x}S_2$ (CIGS) торы негізіндегі қатты ерітінділердің наноэлектрмеханикалық жүйе (НЭМЖ) күйіндегі термодинамикалық тұрақтылығы мен ішкі энергия өзгерісі зерттелді. Берілген заттар қуаттылығы жоғары фототүрлендіргіш жасауда тиімді болып есептелді. $CuIn_xGa_{1-x}S_2$ құрамды фототүрлендіргіштің максималды тиімділігі 21 % көрсетті, ал кремний негізіндегі ең жақсы фототүрлендіргіштің көрсеткіші 15 % ғана құрайды, бұл берілген құрамдағы зерттеудің өзектілігін көрсетеді. Зерттеу жұмысында ішкі энергия көрсеткіштері, нөлдік тербеліс, жиілік, тепе-теңдік байланыс ұзындықтарының шамалары берілген. Әртүрлі температура кезіндегі ішкі энергия көрсеткіштерінің өзгерісі және наноқабаттардың тұрақты жүйесіндегі радиалды бу бойынша атомтардың таралу функциясының өзгерісі көрсетілген. CIGS НЭМЖ тұрақты наноқабаттары параметрлерінің қатысты өзгерісі жүйедегі индий атомдарының концентрациясына сызықты емес тәуелді екендігі анықталды. Бұндай жағдай In–S және Ga–S НЭМЖ энергиясы мен байланыс ұзындықтары шамаларының айырмашылығынан болатындығы көрсетілді.

Кілт сөздер: таралудың радиалды бу функциясы, жартылайөткізгіш, күн батареялары, наноэлектромеханикалық жүйелер, графалар, Вегард ережесі.

Д.А. Волков, Ю.В. Терентьева, С.А. Безносюк

Аттосекундные нанотехнологии: квантовые точки наноэлектромеханических систем соединений $CuIn_xGa_{1-x}S_2$

В статье изучены термодинамическая стабильность и изменчивость внутренней энергии твердых растворов непрерывного замещения на основе решетки халькопирита $CuIn_xGa_{1-x}S_2$ (CIGS) в состоянии наноэлектромеханической системы (НЭМС). Данные вещества наиболее эффективны для создания фотопреобразователей максимальной мощности. Максимальная эффективность фотопреобразователя на основе состава $CuIn_xGa_{1-x}S_2$ была достигнута до 21 %, в то время как лучший фотопреобразователь на основе кремния мог достигать только 15 %, что подчеркивает актуальность исследования данного состава. В ходе работы представлены значения внутренней энергии, частоты нулевых колебаний и длины равновесной связи. Показаны изменения внутренней энергии при разных температурах и функций распределения атомов по радиальным парам в устойчивой системе нанослоев. Выявлено, что относительное изменение параметров стабильных нанослоев НЭМС CIGS нелинейно зависит от концентрации атомов индия в системе. Показано, что такое поведение является следствием существенного различия в энергии и длине связей НЭМС In–S и Ga–S в первой координационной сфере атомов серы.

Ключевые слова: радиальная парная функция распределения, полупроводник, солнечные батареи, наноэлектромеханическая система, графы, правило Вегарда.