In this paper, we have discussed in detail the electronic structure and optical characteristics of the silicon nanoclusters. One of the main conclusions is that the comparison between theoretical calculations and experimental results are correct. We shows the possibility of different radiative channels for the recombination in porous silicon. We now analyze the case of stronger disorder as obtained in amorphous silicon (a-Si), it is comparable to what is obtained for c-Si; (b) what is the behavior of disorder-induced localized states in this regard. It has been often assumed that quantum confinement effects are small in a-Si nanoclusters due to the short coherence length of free carriers in these materials. We will see that this is not true.

We calculate the electronic structure of a-Si and a-Si:H spherical clusters using the parametrized density functional theory (PDFT) model [1]. The starting structure for the a-Si or a-Si:H nanoclusters is obtained by selecting the atoms belonging to the respective atoms unit cell. Due to the new boundary conditions the structure is no more in equilibrium and we have thus relaxed the atomic positions using a Keating potential.

Keywords: metrology, nanoclusters, calculation, measurement.

1. INTRODUCTION

Today, favorable conditions have been formed for intensifying research in the direction of ensuring metrological reliability of the results of measurements of the optical, electronic, mechanical, and other characteristics of the nanoclusters [1]. The task of the article consisted in a systematic presentation of the basic principles of the metrological analysis of the physicochemical characteristics of such objects [2].
2. LITERATURE REVIEW

The efforts of many researchers are aimed at obtaining and processing information on nanostructures (NS), which today are obtained using nanotechnology (NT) — a new generation of technological processes [3—5]. NTs penetrate deeper and deeper into all spheres of human activity: from medicine to robotics [6]. The accelerated development of NTs is also associated with integrated semiconductor electronics — nanoelectronics (NE) and investigation of the nanoclusters [7, 8]. The main principle here is to increase the level of integration by reducing the size of the active elements placed on the chip [9,10].

Research into semiconductor clusters is focused on the properties of quantum dots (QD) — fragments of semiconductor (for example, Si) consisting of some to hundreds of atoms — with the bulk bonding geometry and with surface states eliminated by enclosure. QD exhibit strongly size-dependent optical and electrical properties [4, 11]. Two peculiar characteristics of semiconductors influence the ways in which we think of an ideal semiconductor cluster, which is often called a QD. First, it is important to realize that in any material, substantial variation of fundamental electrical and optical properties with reduced size will be observed when the electronic energy level spacing exceeds the temperature. In semiconductors, this transition occurs for a given temperature at a relatively large size compared to metals, insulators, or molecular crystals [11].

The luminescence observed for por-Si raises an interesting problem related to the possibility of using Si in optoelectronics [2]. One likely explanation is quantum confinement, induced by the formation of nanocrystallites, whose effect is to break partially the optical selection rules and allow the material to luminesce.

The most striking property of semiconductor nanocrystals is the massive change in optical properties as a function of size. As size is reduced, the electronic excitations shift to higher energy, and the oscillator strength is concentrated into just a few transitions. These basic physical phenomena of quantum confinement arise as a result of changes in the density of electronic states and can be understood by considering the relation between position and momentum in free and confined particles. For a free particle, or a particle in the periodic potential of an extended solid, the energy and the crystal momentum can both be precisely defined, whereas the position cannot. For a localized particle, the energy may still be well defined, but the uncertainty in position decreases, so that momentum is no longer well defined.

For example, the kinetic stability of tetrasilatetrahedrane (Si₄H₄), hexasilaprismane (Si₆H₆) and octasilacubane (Si₈H₈) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si₈Y₈ (Y = t – Bu) is stable in an inert atmosphere, but is oxidized in air to give colourless solids. The 1, 1, 2-trimethylpropyl-substituted SinYm (Y = C · Me₂ · CH · Me₂) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange. These prismanes have absorptions tailing into the visible region. S₈Si₈H₈ has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge₆Y₆ (Y = 2,6 – I – Pr₂C₆H₃) has a maximum at 261 nm, which is red-shifted compared to that of Ge₆Y₆ because of the higher-lying orbitals of the Ge-Ge bonds [1,2].

3. RESEARCH METHODOLOGY

3.1 Results of the Calculations

A number of calculations have been performed over the last few years, as for quantum dots as for silicon nanoclusters since both possibilities have been invoked for porous silicon. They essentially belong to four classes: effective mass approximation (EMA), empirical tight binding (ETB), empirical pseudopotential (EPS) and finally ab initio local density functional theory (LDFT) [1]. In Fig. 1 we give the predicted band gaps versus size as obtained from LDFT calculations compiled in Ref. [5] for hydrogen-terminated Si-clusters, wires and slabs.

For example, the kinetic stability of tetrasilatetrahedrane (Si₄H₄), hexasilaprismane (Si₆H₆) and octasilacubane (Si₈H₈) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si₈Y₈ (Y = t – Bu) is stable in an inert atmosphere, but is oxidized in air to give colourless solids. The 1, 1, 2-trimethylpropyl-substituted SinYm (Y = C · Me₂ · CH · Me₂) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange. These prismanes have absorptions tailing into the visible region. S₈Si₈H₈ has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge₆Y₆ (Y = 2,6 – I – Pr₂C₆H₃) has a maximum at 261 nm, which is red-shifted compared to that of Ge₆Y₆ because of the higher-lying orbitals of the Ge-Ge bonds [1,2].

For example, the kinetic stability of tetrasilatetrahedrane (Si₄H₄), hexasilaprismane (Si₆H₆) and octasilacubane (Si₈H₈) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si₈Y₈ (Y = t – Bu) is stable in an inert atmosphere, but is oxidized in air to give colourless solids. The 1, 1, 2-trimethylpropyl-substituted SinYm (Y = C · Me₂ · CH · Me₂) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange. These prismanes have absorptions tailing into the visible region. S₈Si₈H₈ has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge₆Y₆ (Y = 2,6 – I – Pr₂C₆H₃) has a maximum at 261 nm, which is red-shifted compared to that of Ge₆Y₆ because of the higher-lying orbitals of the Ge-Ge bonds [1,2].

For example, the kinetic stability of tetrasilatetrahedrane (Si₄H₄), hexasilaprismane (Si₆H₆) and octasilacubane (Si₈H₈) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si₈Y₈ (Y = t – Bu) is stable in an inert atmosphere, but is oxidized in air to give colourless solids. The 1, 1, 2-trimethylpropyl-substituted SinYm (Y = C · Me₂ · CH · Me₂) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange. These prismanes have absorptions tailing into the visible region. S₈Si₈H₈ has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge₆Y₆ (Y = 2,6 – I – Pr₂C₆H₃) has a maximum at 261 nm, which is red-shifted compared to that of Ge₆Y₆ because of the higher-lying orbitals of the Ge-Ge bonds [1,2].

For example, the kinetic stability of tetrasilatetrahedrane (Si₄H₄), hexasilaprismane (Si₆H₆) and octasilacubane (Si₈H₈) depends strongly on the steric bulkiness of the substituents (matrix). The silyl-substituted Si₈Y₈ (Y = t – Bu) is stable in an inert atmosphere, but is oxidized in air to give colourless solids. The 1, 1, 2-trimethylpropyl-substituted SinYm (Y = C · Me₂ · CH · Me₂) is very stable even in air and survives for two weeks in the solid state. The prismanes with Si and Ge skeletons are yellow to orange. These prismanes have absorptions tailing into the visible region. S₈Si₈H₈ has an absorption band with a maximum at 241 nm tailing to ca 500 nm. The absorption band of Ge₆Y₆ (Y = 2,6 – I – Pr₂C₆H₃) has a maximum at 261 nm, which is red-shifted compared to that of Ge₆Y₆ because of the higher-lying orbitals of the Ge-Ge bonds [1,2].
They are compared to the results obtained in our group using DFT approach with parameters (PDFT [3]) providing an extremely good fit to the bulk band structure. One can notice a good agreement between the LDFT and PDFT predictions which gives some confidence into the reliability of these theoretical values. At this stage it is important to notice that the LDFT gap values include a rigid shift of 0.6 eV since it is known that LDFT underestimates the bulk band gap by this amount. Note that the theoretical calculation grossly overestimate the blue shift.

They must then be discarded since EMA can be considered as an approximation to the best ETB or EPS descriptions which match the effective masses. One can, however, wonder why parameterized techniques should provide quantitative estimates of the one-electron gap. The basic point is that they are based on the postulate of transferability of the parameters from the known bulk band structure (to which they are fitted) to the unknown crystallite case. If this is accepted, then an essential criterion by which a particular semi-empirical model can be judged is how well it describes the bulk band structure. So from Fig. 1 we could conclude that PDFT as well as corrected LDA techniques are likely to give reliable predictions for crystallites.

3.2 Results of the Experiments

Fig. 2 presents a compilation of data showing that observed luminescence energies on porous silicon or silicon nanocrystals in an oxide matrix are consistently lower that the predicted optical gaps of Fig. 1. On the other hand, they qualitatively agree with optical absorption data.

Recent results [8, 10] also show that the luminescence of fresh porous silicon samples is subject to a large red shift when it is exposed to air and when the average size of the nanocrystals is smaller than 3 nm. On the other hand, recent luminescence measurements on silicon crystals obtained by silane decomposition are in good agreement with theory, but the luminescence is only observed for the largest crystallites. The situation is thus complex, even if it seems that the degree of oxidation of the samples plays an important role in the recombination mechanisms. All these results suggest that other channels for the radiative recombination are possible. Large Stokes shifts might be consistent with the eventual existence of deep luminescent centers. The problem is that nothing is presently known regarding the nature and origin of these states. Both from PDFT and LDA calculations that such states indeed exist under the form of self-trapped excitons, most probably at the surface. A possible situation is the trapping of an exciton on a Si-Si bond of a surface dimer whose dangling bonds are saturated by hydrogen atoms. We have found another interesting situation with very small crystals, containing less than about 50 silicon atoms, where we systematically obtain a large atomic relaxation in the excited state which induces an important reorganization of the bonds in the cluster. The consequence is a large Stokes shift between the absorption and the emission energies. Therefore, small nanocrystals could play a role in the luminescence of porous silicon.

We are presently investigating the possible existence of defect states in the band gap induced by the oxidation of the surface. Among different systems that we have studied, preliminary results show that an oxygen atom doubly bonded to a silicon atom (Si=O) at a nanocrystal surface is a good candidate to be involved in the luminescence of porous silicon.

Structural dependence of the band gap G. Allan with coworker’s shows that the radiative recombination rate in spherical silicon nanocrystals (calculated as in Ref. [4]). It is low and it decreases for smaller band gap because of the indirect bulk band gap. In this regard, it would be of interest to use a direct gap phase of silicon such as Si-III (BC8) or to use materials like SiGe alloys or amorphous silicon because the disorder breaks the selection rules. But an essential question arises about the existence of quantum confinement.
effects in disordered materials. Here we describe recent results that we have obtained on these problems. The Si-III (BC-8) crystal phase is obtained for bulk samples by releasing the pressure on the high-pressure beta-tin phase (Si-II).

Existing theoretical calculations show that the valence band maximum and the conduction band minimum occur at the same H point in the Brillouin zone. BC-8 silicon is thus a direct gap material but the calculations conclude that it is close to a zero gap semiconductor. To calculate the electronic structure of BC-8 crystallites with size in the 1 — 3 nm range, we have chosen the same non-orthogonal ETB technique as used for silicon crystallites with the diamond structure but we have developed a specific parameterization for that structure.

Our results show that the confinement effect is quite similar for BC-8 and diamond clusters. The only difference when one goes from the BC-8 cluster to the diamond one with the same size comes from the bulk gap value which simply shifts the cluster gap energy. We have also performed PDFT calculations. One can see that the values calculated with PDFT for two small clusters and shifted by 0.6 eV to take into account the underestimation of the bulk gap, are in very good agreement with our ETB calculation. This confirms the transfer-ability of the ETB parameters from the bulk material to clusters.

4. DISCUSSION OF THE RESULTS

Experimentally, it was shown [2, 6 — 10] than the BC-8 structure is obtained upon release of a high pressure on porous silicon. But the luminescence band remains practically unchanged except perhaps for a small shift (of order 0.1 — 0.2 eV) after release of the pressure. This finding completely disagrees with our predictions, where this redshift should amount to ~ 1 eV for crystallites of the same size. This would rule out quantum confinement as the origin of the observed luminescence band and favor other possibilities.

We compare the variation of the recombination rate as a function of the cluster gap for the BC-8 [5] and the diamond structures [8]. Because it has a direct bulk band gap, the recombination rate in the BC-8 phase remains constant and pretty high) when the cluster size increases and the blue shift decreases.

It is of the order of a few ms-1 (i.e. more than 103 times larger than in the diamond phase below 2 eV), but remains however lower than the result for GaAs (~ ns-1 ) which is also a direct gap semiconductor. However, the luminescence yield must be strongly improved for the BC-8 structure compared to the diamond structure.

With improved optical properties compared to silicon, SixGe1-x alloys are also interesting materials. We have studied the strong confinement effects in SiGe clusters performing ETB calculations with the parameters. We consider spherical clusters passivated by hydrogen atom where the atomic sites are occupied randomly by Si or Ge atoms following the composition x.

Our results shows that the band gaps of pyramidal Si nanoclusters are quite close, with comparable blue-shift [1]. This is due to the fact that the electronic states in bulk SiGe alloys are still delocalized, so they experience the full confinement effect as for crystalline Si (c-Si).

5. CONCLUSIONS

To characterize the luminescence of our a-Si clusters with 1.0 — 2.5 nm size we have first computed their fundamental gap, i.e. the distance in energy between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital). There is a substantial blue shift in both cases, more important for a-Si than for a-Si:H. Furthermore, our larger a-Si clusters give rise to a two-peak distribution. We have checked that the lower and upper peaks are, respectively, due to strongly and weakly localized or delocalized states. The relative intensity of the upper peak thus corresponds to the proportion of clusters which do not contain strongly localized states. The apparent blue shift in a-Si clusters has thus two origins: (a) the varying proportion of clusters with strongly localized states and (b) the normal confinement effect on the other states. This is confirmed on the sapie figure by the a-Si: H clusters which show only the second type of behavior.

Thus we have discussed in detail the theoretical calculations on the band gap of Si clusters. One of the main conclusions is that the comparison between theory and experiments shows the possibility of different radiative channels for the recombination in porous silicon which is a complex material.

REFERENCES / СПИСОК ИСПОЛЬЗОВАННЫХ ИСТОЧНИКОВ

1. Kovalchuk V., Kovalenko L., Smorzh M. (2019): Nanometrology: optical power of nanoclusters. Metrology & instruments (Ковальчук В., Коваленко Л., Сморж М. (2019): Нанометрологія: оптична сила нанокластерів.

2. Kovalchuk V. (2018) Optical Properties of clusters. J. Phys & Radioelectronics (Ковальчук В. (2018) Оптичні властивості кластерів. J. Phys & Radioelectronics)
3. Han, X., Li, S., Peng, Z., Al-Yuobi, A.O., Bashammakh, A.S.O., El-Shahawi, M.S., Leblanc, R.M. (2016): Interactions between carbon nanomaterials and biomolecules. J. Oleo Sci. 65, 1–7
4. Tian B. Xu, Zhao Z. (2012) Microscopic theory of hardness and design of novel su-perhard crystals, Int. J. Refract. Met. Hard Mater. 33, 93–106
5. Liu T.Y., X. Zhou, S.V. Khare, D. Gall (2014) : Structural, mechanical and electronic properties of 3d transition metal nitrides in cubic zincblende, rocksalt and cesiumchloride structures: a first-principles investigation, J. Phys. Cond. Matter 26, 25404-25410
6. Bukarev R. (2011) Introduction to the design of bionic nanosystems. Moscow, Publ. FIZMATLIT (Букарев Р. (2011) Вступ до проектування біонічних наносистем. Москва, Публ. ФІЗМАТЛИТ), 474 p/s.
7. Guo, D., Xie, G., Luo, J. (2014): Mechanical properties of nanoparticles: basics and applications. J. Phys. D, 47-51
8. Gentile, A., Ruffino, F., Grimaldi, M. G. (2016): Complex-morphology metal-based nanostructures: fabrication, characterization, and applications. Nanomaterials. 6-11
9. Pallavi, N., Shivaraju, H.P. (2017): A feasibility study on photocatalytic degradation of methyl benzene using N doped TiO2 nanoparticles. Int. J. Nanotechnol. 14, 762–774
10. Sim, L.C., Wong, J.L., Hak, C.H., Tai, J.Y., Leong, K.H., Saravanan, P. (2018): Sugarcane juice derived carbon dot–graphitic carbon nitride composites for bisphenol A degradation under sunlight irradiation. Beilstein J. Nanotechnol. 9, 353–363
11. Ankita R.,Rajesh Reddy, Uttkarshni Sharma, Priya Mukherjee, Priyanka Mishra, Aneek Kuila Lan Ching Sim Pichiah Saravanan (2018) : A review on the progress of nanostructure materials for energy harnessing and environmental remediation, Journal of Nanostructure in Chemistry, 8, 255–29

Отримано / received: 25.02.2020.
Стаття рекомендована до публікації д.ф-м.н., проф. О.В. Тюріним (Україна).
Prof. O.V. Tiurin, D. Sc. (Phys-Mat.), Ukraine, recommended this article to be published.