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Elastic vibrations of silicon and germanium nanoparticles and the influence on their optical properties

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The paper deals with the problem on the connection of mechanical and optical properties of silicon and germanium nanoparticles. Experimental evidence of insignificant influence of nanoparticle sizes on oscillatory motions of lattice ions of medium is considered. In particular, the experimental results obtained by thermoluminescent methods and the excitation of acoustic vibrations by light in nanoparticles and macroenvironment are examined. It is shown that the theory of elasticity can be applied to describe the vibrations of nanoparticles. Using the equations of elasticity theory, the values of radial eigen frequencies of vibrations for the spherical silicon and germanium nanoparticles are calculated. The optical properties of such nanoparticles and the possibility of their modulation by elastic oscillations are considered. The applications of obtained results to the design of sensor systems (for the detecting of medium oscillations in the kilohertz frequency range) as well as for the use in information technologies are examined.

Keywords: silicon and germanium nanoparticles, elastic oscillations, optical absorption and light emission, sensors.

Пружні коливання наночастинок кремнію та германію та їхній вплив на оптичні властивості. *В.М.Ящук, І.В.Лебедєва, О.В.Борисейко*

Розглянуто проблему зв'язку механічних та оптичних властивостей кремнієвих та германієвих наночастинок. Розглянуто експериментальні докази неістотного впливу розмірів наночастинок на коливальні рухи іонів гратки середовища. Зокрема, проаналізовано експериментальні результати, що отримані термолюмінесцентними методами та при збудженні світлом акустичних коливань у наночастинках та макросередовищах. Показано, що для опису коливань наночастинок може бути використана теорія пружності. Застосовуючи рівняння теорії пружності, розраховано значення власних частот радіальних коливань для сферичних наночастинок кремнію та германію. Розглянуто оптичні властивості таких наночастинок та можливість їх модуляції пружними коливаннями. Запропоновано застосування отриманих результатів для створення сенсорних систем (для детекції коливань середовища у кілогерцовому діапазоні частот) в інформаційних технологіях.

Рассмотрена проблема связи механических и оптических свойств кремниевых и германиевых наночастиц. Рассмотрены экспериментальные доказательства несущественного влияния размеров наночастиц на колебательные движения ионов решетки среды. В частности, проанализированы экспериментальные результаты, полученные термолюминесцентными методами, а также при возбуждении светом акустических колебаний в наночастицах и макросредах. Показано, что для описания колебаний наночастиц может быть использована теория упругости. Применяя уравнения теории упругости, рассчитано значения собственных частот радиальных колебаний для сферических наночастиц кремния и германия. Рассмотрены оптические свойства таких наночастиц и возможность их модуляции упругими колебаниями. Предложено применение полученных результатов для создания сенсорных систем (детекции колебаний среды в килогерцовом диапазоне частот) в информационных технологиях.

1. Introduction

Metal and semiconductor particles having characteristic dimensions of the order of tens of nm exhibit special electron-optical properties different from those for continuous media (bulk materials).

Particles of this size are called nanoparticles or quantum dots. It is known [1] that the limitation in particle sizes of 2–100 nm is significant for electrons and holes and effects on spectral properties of nanoparticles. At the same time, the local vibrations of molecules or atoms at the lattice nodes do not "feel" the significant effect of such a spatial confinement (including particles of the order of several nm in size). The movements of ions of the spatial lattice of semiconductor materials and metals are much less dependent on the size of the nanoparticles than the motion of electrons.

Therefore, such mechanical properties as elasticity have to be preserved for bodies of very small size, since even for two neutral molecules interacting due to dispersion forces (the Lennard-Jones potential), in the case of small deviations from their equilibrium position, the Hooke law is fulfilled. One of the experimental evidence of the small effect of nanoparticle sizes on the vibrational motions of the lattice ions is the proximity of the trap energies for the charge carriers obtained by thermoluminescent methods for semiconductors and their nanoparticles [2]. The thermal ejection of curriers from traps in crystals, is connected namely with the vibrations of the lattice ions of materials as was shown by A.Gumeniuk and co-authors [3]. Another proof is the closeness of the mechanical constants of the nanoparticles and the macroscopic samples obtained by the excitation of acoustic vibrations by light in the nanoparticles [4, 5]. The comparatively small differences (up to 18 %) in the values of these constants are explained by the effect of the difference in the processes of dislocation formation in nanoparticles and macromaterials [4].

The above gives the reason to apply the theory of elasticity to the study of mechanical vibrations of nanoparticles of this type in the specified size range. On the other hand, the dependence of optical characteristics on the size of the nanoparticles makes it possible to modulate them, exciting mechanical vibrations of the nanoparticles. In this paper, the elastic mechanical vibrations of semiconductor spherical (ball) nanoparticles of silicon and germanium are studied. In particular, it is shown that the natural radial oscillation frequencies of this type of nanoparticles are in the kilohertz range. The effects of modulation of the optical properties of the nanoparticles by mechanical vibrations are considered.

2. Analytical analysis of elastic vibrations of silicon and germanium nanoparticles

The spatial bodies of canonical form (both isotropic and different anisotropic), such as a sphere, a cube, an ellipsoid, are known to be most often chosen to model the behavior of nanoparticles [1, 5, 9]. For anisotropic elastic bodies, the three-dimensional problem on analytical and even analytical-numerical determination of the spectrum of ушпут frequencies oscillations is rather complicated and requires a large amount of calculations.

The statement of the problem is simplified, when one of the characteristic sizes is much smaller than the other (plates, shells, shell elements), or the geometric axis of symmetry and the axis of anisotropy of the transversely isotropic body are coincided. Then the dimension of the problem decreases, the equations of the state are simplified and it is possible to use the applied theory of plates and shells (the Kirchhoff flat cross section hypothesis, the theory of Tymoshenko type shells), or to obtain an accurate analytical solution [6].

The problems on oscillation of isotropic spatial elastic bodies are much simpler. In the cases of reducing of these problems to the flat ones (homogeneous cylinder, rectangular plate, etc.), a biharmonic boundary value problem is usually obtained [7]. The solution to such a problem is also quite complicated.

For isotropic spherical bodies it is also possible to simplify the general statement of the problem on elastic vibrations. The main forms of oscillation under consideration are radial (spherical mode), circumferential (elliptical mode) and torsional oscillation (torsion mode). Such forms of oscillation are caused by different types of external loading of an elastic macroscopic body. In most cases, such loads cannot be applied to the nanoparticle. However, these cases are also quite interesting and noteworthy. G.Lamb's fundamental work [8] deals with the problem on oscillations of an incompressible elastic ball in a three-dimensional formulation, and, as a partial case, the problems on free elliptic and torsional oscillations. Radial modes for incompress-

ible material are impossible and are not considered in [8].

In the case of a load uniformly distributed over the surface by time-harmonic external pressure, the problem is axisymmetrical. In this case, the solution to the radial oscillation problem can be obtained explicitly by solving of the two-dimensional boundary-value problem of mathematical physics by the method of eigenfunctions [9], or by going directly to the equation in amplitudes [1]. In [9], the chosen system of functions is not complete, so the results obtained are contrary to the physical statement of the problem, namely, the condition of zero displacement of the center of the sphere. In our work (see also [1]) the complete analytical solution of the problem was obtained. It allows to get a spectrum of dimensionless frequencies. Assuming the similar elastic behavior of nanoparticles and macroscopic bodies of the same shape, we can determine the real resonant frequencies by a simple recalculation.

Let us consider the problem on radial oscillations of a homogeneous isotropic elastic sphere under the action of an external time-harmonic pressure distributed uniformly over the surface of the spherical body [1].

We are looking for an expression for the variable radius of the nanosphere in the form

$$R(t) = R_0 + u_r(R_0,t).$$

The problem will be solved in a spherical coordinate system. Since the movement of the particles of the sphere is radial, the displacement vector will have only one non-zero component:

$$\boldsymbol{u} = \boldsymbol{e}_r u_r(r,t).$$

Because of the central symmetry of the problem, the complete system of equations of elasticity theory will be simplified in a spherical coordinate system.

The Cauchy ratios could be formulated as follows:

$$\varepsilon_r = \frac{\partial u_r}{\partial r}, \quad \varepsilon_\varphi = \varepsilon_\theta = \frac{u}{r}.$$

The expressions for the non-zero components of the stress tensor through the radial displacements of the particles can be given in the form:

$$\sigma_r = \frac{E}{(1-\nu)(1-2\nu)}\left((1-\nu)\frac{\partial u_r}{\partial r} + 2\nu\frac{u_r}{r}\right),$$

$$\sigma_\varphi = \sigma_\theta = \frac{E}{(1-\nu)(1-2\nu)}\left(\frac{\nu\partial u_r}{\partial r} + \frac{u_r}{r}\right).$$

Here E is the Young's modulus, ν is the Poisson ratio of the sphere material.

We obtain the differential equation of motion from the equations of equilibrium by adding inertial terms:

$$\frac{\partial\sigma_r}{\partial r} + 2\frac{\sigma_r - \sigma_\varphi}{r} = \rho\frac{\partial^2 u_r}{\partial t^2}.$$

The boundary conditions can be set as follows:

$$\sigma_r\big|_{r=R_0} = \sigma_0 e^{i\omega t}.$$

Here σ_0 is the amplitude of the external harmonic load.

Let us express the stresses through the radial displacements in the equation of motion, and thus we get a simplified differential equation of motion in displacements (the Lame equation)

$$\frac{\partial^2 u_r}{\partial r^2} + \frac{2}{r}\frac{\partial u_r}{\partial r} - \frac{2}{r^2}u_r = \frac{\rho}{(\lambda+2\mu)}\frac{\partial^2 u_r}{\partial t^2},$$

where λ, μ are the Lame coefficients.

Taking into account the nature of the load, we will search for an unknown radial displacement function in the form of a harmonic function of time:

$$u_r(r,t) = u(r)e^{i\omega t}.$$

Then, the ordinary homogeneous second order differential equation is obtained to determine the amplitude of displacements:

$$r^2\frac{d^2u}{dt^2} + 2r\frac{du}{dr} + ((\kappa r)^2 - 2)u = 0,$$

where

$\kappa = \sqrt{\frac{\rho\omega^2}{(\lambda+2\mu)}} = \frac{\omega}{c}$ is the wave number, ω is the angular frequency of vibrations,

$c = \frac{1}{\sqrt{\frac{\lambda+2\mu}{\rho}}} = \frac{1}{\sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}}}$ is the speed of propagation of radial spatial waves.

The general solution to this equation is as follows:

$$u(r) = C_1 j_1(\kappa r) + C_2 y_1(\kappa r).$$

Here $j_1(\kappa r)$, $y_1(\kappa r)$ are the spherical Bessel functions of the first and second kinds. Since the displacement of the sphere center

is equal to zero and $\lim_{r->0} y_1(r) = -\infty$, we set $C_2 = 0$. Then

$u(r) = C_1 j_1(\kappa r)$. Finally, the expression for the variable radius of the nanosphere can be written in the form:

$$R(t) = R_0 + u_r = R_0 + C_1 j_1(\kappa R_0) e^{i\omega t}.$$

From the boundary conditions we find the amplitude of the radial component of the stress tensor

$$\hat{\sigma}_r = \frac{EC_1}{(1-\nu)(1-2\nu)}((1-\nu)kj_0(\kappa r) + \frac{2}{r}j_1(\kappa r))$$

and the unknown constant of integration C_1:

$$C_1 = \frac{(1+\nu)(1-2\nu)}{E} \cdot \frac{\sigma_0 R_0}{(1-\nu)(\kappa R_0)j_0(\kappa R_0) + 2j_1(\kappa R_0)}.$$

The condition of infinite increase of the forced oscillations amplitude yields the equation for the determination of dimensionless resonant frequencies ($\vec{f} = \kappa R_0$):

$$(1-\nu)(\kappa R_0)j_0(\kappa R_0) + 2j_1(\kappa R_0) = 0.$$

Further, the dimensional frequencies can be obtained by the formula: $f = k/R$, where $k = \vec{f}c/2\pi$.

For germanium nanoparticles ($\nu = 0.278$; $E = 1.38 \cdot 10^{11}$ Pa; $\rho = 5323$ kg/m^3) with a radius of $R_0 = 100$ nm, the values of the first resonant frequencies are 770 Hz; 1385 Hz, 2019 Hz; 3285 Hz.

For silicon nanoparticles ($\nu = 0.266$;E = $1.89 \cdot 10^{10}$ Pa; $\rho = 2329$ kg/m^3) with a radius of $R_0 = 100$ nm, the values of the first resonant frequencies are 1411 Hz; 2542 Hz, 3704 Hz; 4882 Hz.

It should be noted that the attempt to describe the mechanical oscillations of the nanoparticles was made in [10] in the case when oscillations were excited by heating the nanoparticles using laser radiation. The nanoparticle temperature reached the melting point. That is why the authors used the Navier equation (as for liquids, not for a rigid deformable body) to describe the resulting oscillations. The authors showed that the values of the frequencies of mechanical vibrations of the nanoparticles in this state are in the gigahertz range. The method of excitation of oscillations of a particle due to its laser heating was also applied in [11]. In this case, a resonant frequency of radial oscillations was obtained of 40 megahertz for a gold nanoparticle with diameter of 136 nm.

3. Modulation of the optical response of Si and Ge-nanoparticles by acoustic vibrations

The effects of the acoustic modulation of the optical properties of metallic nanoparticles have been considered in a number of papers, see f.e. [1, 10, 11]. In particular [1], it was demonstrated that the optical properties (absorption spectra) of nanoparticles of this type are influenced not only by the electron motion limitation, but also by the dependence of plasmon processes on the size nanoparticles. For semiconductor nanoparticles (starting, from a certain size) the finite motion of electrons and holes plays a major role in their optical properties. Therefore, the spectra of absorption and fluorescence, as well as quantum yield, are to great extent dependent on the size of the nanoparticles.

The wavelength of the maximum absorption of semiconductor nanoparticle under conditions of finite motion of the carriers increases with the nanoparticle size. In general, for semiconductor nanoparticles, the finiteness of carrier motion leads to the following dependence of the energy of the longwave electron transition (and hence of the absorption spectrum) on the size of the nanoparticle [12, 13] (the formula written for a cubic nanocrystal)

$$\Delta E = E_g + \sum_{i=x,y,z} \frac{h^2\pi^2 n_i^2}{2d_i^2}\left(\frac{1}{m_e + m_h}\right),$$

where d_i is the size of the nanoparticles, m_e is the effective mass of the electron, m_h is the effective mass of the hole, E_g is the energy of the band gap of the macromaterial. It should be noted that semiconductor nanoparticles exhibit intense fluorescence as opposed to metallic ones. It turns out, as shown in [14], the quantum yield of the fluorescence of a semiconductor nanoparticle also depends significantly on its size R. So

$$\eta = \frac{1}{1 + \beta R^2},$$

where β is the constant that depends on the nanoparticle features.

Thus, changing over time the size of the nanoparticles should lead to changes in the

absorption spectra, fluorescence spectra, and quantum fluorescence yield. Therefore, mechanical oscillations of the nanoparticles can modulate their optical absorption, spectra, and fluorescence intensity. The elastic oscillation frequencies obtained for the silicon and germanium nanoparticles obtained in this work are in the kilohertz frequency range. At such frequencies, the above-mentioned optical characteristics can be modulated. In our opinion, these results can be used to design the sensor systems for recording kilohertz oscillations that propagate in the environment. To the other hand, the possibility of modulation of light beam characteristics can be used in information technologies. Particularly sensitive sensor systems can be created on the basis of nanoparticles formed in porous silicon, which exhibit intense fluorescence in the visible range. The modulation of the optical characteristics of germanium nanoparticles (in the ultraviolet range) can also be used in sensing systems of the specified type or information processing.

4. Conclusions

The arguments in favor of using the theory of elasticity to describe oscillation processes in nanoparticles are examined.

Using the equations of elasticity theory, the values of radial own oscillations for the spherical silicon and germanium nanoparticles were obtained.

The optical properties of silicon and germanium nanoparticles and the possibility of their modulation by elastic eigen oscillations are considered.

The application of these modulation techniques in sensor systems for the detecting of medium oscillations in the kilohertz frequency range as well as in information technologies is proposed.

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