

## Contact relaxation phenomena in nano-structured composite materials

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There are discussed physical mechanisms of some effects related to both nano-material granularity and existence of the strongly branched contact area separating the nano-size grains. In the area the relaxation processes take place including electron level, i.e. substantial reconstruction of the electron subsystem and charge state in the grain boundary area. Estimations have been carried out for a concrete nano-composite material formed by metal and semiconductor substances with different charge volume density in the conductivity band. On the basis of the estimations and discussion, conclusion has been done on the possibility for controlled varying the phase and structure state as well as physical properties (magnetic, electrical, optical, etc.) of the nano-structured material by changing the granularity and composition.

**Keywords:** nano-structured composite materials, contact phenomena, granularity.

Рассматриваются физические механизмы появления некоторых эффектов, связанных с зернистостью наноматериалов и существованием сильно разветвленной контактной области, разделяющей наноразмерные зерна, в которой имеют место релаксационные процессы, в том числе и на электронном уровне, приводящие к существенным перестройкам электронной подсистемы в пограничной области зерен и их зарядового состояния. Выполнены конкретные оценки для нанокompозитного материала, образованного металлическими и полупроводниковыми веществами с различной объемной плотностью зарядов в зоне проводимости. На основании проведенного обсуждения и оценок сделан вывод о возможности контролируемого изменения как фазового и структурного состояний, так и физических свойств (магнитных, электрических, оптических и др.) наноструктурированного материала путем варьирования его зернистости и состава.

**Контактні релаксаційні явища в наноструктурованих композитних матеріалах.**  
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Розглядаються фізичні механізми появи деяких ефектів, пов'язаних із зернистістю наноматеріалів і існуванням сильно розгалуженої контактної області, що розділяє нанорозмірні зерна, в якій мають місце релаксаційні процеси, зокрема, і на електронному рівні, що приводять до істотних перебудов електронної підсистеми у прикордонній області зерен і їх зарядового стану. Виконано конкретні оцінки для нанокompозитного матеріалу, утвореного металевими і напівпровідниковими речовинами з різною об'ємною щільністю зарядів у зоні провідності. На підставі проведеного обговорення і оцінок зроблено висновок про можливість контрольованої зміни як фазового і структурного станів, так і фізичних властивостей (магнітних, електричних, оптичних і ін.) наноструктурованого матеріалу шляхом варіювання його зернистості і складу.

## 1. Introduction

Nano-crystalline (nano-structured) materials are polycrystals with grain size from about one to tens nanometers. These materials may consist of similar grains or different chemical composition ones. In the second case, the material is called composite. The main peculiarity of the material is that contact areas which are always have special properties occupy significant volume parts of each grain and the material as whole. That substantially effects on the material properties.

## 2. Theory and experimental

In the present work, physical mechanisms of some effects related to scale-structure peculiarity (granularity) of nano-materials are discussed. This peculiarity consists in existence of strongly branched contact area separating the nano-size grains including electron level. There takes place the substantial reconstruction of the electron subsystem in the grain boundary area that may substantially influence on the material structure and physical properties. The last investigations show that the mentioned influence is really observed, and its degree of manifestation increases with reducing the grain size in the material. For example, in [1] it was noticed that in the ferroelectric inclusion of ferroelectric-dielectric nano-composite, beginning from some grain size there takes place the transition into "domain-like" state with peculiarities of dielectric permittivity.

Peculiarities like these were observed in some other works [2–4]. In [5], polymorphism of Ga-In nano-material was observed, the kind of it was caused by both composition and granularity. Similar specific phenomena were observed also in [6–8] and other works [9–14].

Below we consider nano-composite material formed by metallic and semiconductor substances with different charge volume densities in the conduction band, and respectively, with the different Fermi energies. Such materials possess the known property, namely, occurrence of the electrical potential difference between isolated pair of adjoining diverse grains, the fact indicating electron migration from one to other grain through their interface. Obviously, that is followed as well by changing the charge state of the grains. All this may result in substantial changes in the nano-

material structure and properties which is the object of our further analysis.

### 2.1 Changing the charge state in nano-size grains in connection with redistribution of electrical charge at the interface

It is well known that if two samples of conductors, semiconductors, or their combination bring into contact, potential difference occurs between them called the Volta potential. If the contact between the samples is perfect, i.e. the surfaces are practically at atomic spacing, the value of the Volta potential (called in this case as internal) is determined by the following relation [15] (v.3,p.476), [16] (v.2, p.445):

$$U = (E_{F1} - E_{F2})/e, \quad (1)$$

where  $E_{F1}$  and  $E_{F2}$  are the Fermi energies for 1 and 2 grains, respectively,  $e$  is electron charge. Assuming for simplicity the grain temperature  $T = 0$  K, for  $E_F$  it can be written:

$$E_F = [h^2/2m](3n/8\pi)^{2/3}, \quad (2)$$

where  $h$  is the Planck's constant,  $m$  is electron mass,  $n$  [ $\text{cm}^{-3}$ ] is electron volume density.

From (1) and (2), taking into account that electron densities in the grains are  $n_1$  and  $n_2$ , it follows:

$$U = h^2/2me[(3/8\pi)^{2/3}(n_1^{2/3} - n_2^{2/3})]. \quad (3)$$

From (3) it is directly seen that the cause of occurring the Volta potential is the difference between electron densities ( $n$ ) in the contacting grains. If the pair of grains is isolated, then under establishing equilibrium, movement of electrons from the substance with larger  $n$  (larger Fermi level) into the substance with the smaller  $n$  is followed by lowering the energy of the system, on one hand, and on another hand, results in occurrence of the electrical potential difference  $U$  between the adjoining grains. In this case the quantitative evaluation by (3) for the most of metals and semiconductors gives about  $U = (0.1 \div 1.0)$  V. Such redistribution of the electrical charge between grains results in excess of electrons in the grain with the lower Fermi level and the deficiency in another one.

In our case of polycrystalline material, the grains form no isolated pairs, but are in short circuits. Occurring at interfaces the charge redistribution is localized near the grain boundaries. These processes are con-

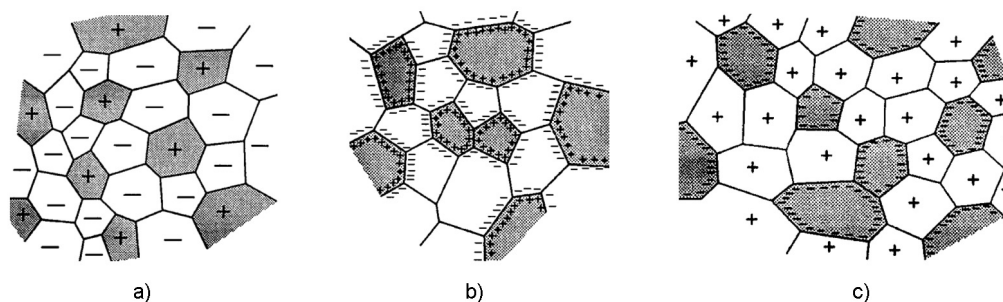


Fig. 1. Various kinds of nano-structured composite materials (schematic): a) nano-composite of  $p$  and  $n$  semiconductor crystallites; b) nano-composite from metallic crystallites with the different Fermi energies; c) nano-composite from metallic and semiconductor (unshaded) crystallites.

sidered from the point of view of solids plasma (SP) movement, i.e. degenerate plasma being gas of moving electrons and practically motionless but oscillating positively charged ions [16]. In [16] it was shown that solids plasma, as well as gas plasma, is practically neutral due to temporal fluctuations of the oscillating positive charges and shifts the movable charges so as to provide screening the occurring charges. If the SP electrical neutrality is disturbed by the extraneous induced charges, this mechanism also acts, field of the introduced charge being also screened by the opposite sign charges, and it decays exponentially quickly. The length of screening  $\delta$  is introduced which is defined for degenerate plasma (i.e. for SP) as follows [16]:

$$\delta^2 = \epsilon E_F / 3\pi e^2 n_0, \quad (4)$$

where  $\epsilon$  is dielectric constant determined by plasma properties, character of external influence, lattice crystallography, and in general, is a tensor;  $n_0$  is density of electrons in solids plasma determined by the number of valence electrons  $n_v$  in the atom and atomic volume  $\omega$ :

$$n_0 = n_v / \omega. \quad (5)$$

At distances from the charge larger than  $\delta$ , the exponential decay of the introduced particle potential is changed by its decaying oscillations [16]. Quantitative evaluations by (4) and (5) result in the following. In the case of metals,  $\delta$  is about several lattice parameters (a), i.e.  $\delta \approx 1$  nm. For semiconductors,  $\delta$  depends on the charge free carriers density which, in turn, is set by donor or acceptor dopant concentration. Quantitatively, the screening length  $\delta$  for semiconductors is in the range from 10 to 100 nm.

Thus, it can be thought, that electron crossing the grain geometric boundary, really is at  $\delta$  distance from it. On the other side of the boundary (i.e. in another grain) there is the opposite charge at the same distance  $\delta$ . So, frontier distribution of the charge, a kind of plane capacitor occurs. If the nano-grain size  $L$  is low ( $L \leq 2\delta$ ), such grains become charged oppositely. If grain size  $L \gg 2\delta$ , the boundaries would have properties of a plane capacitor (Fig. 1). In Fig. 1, different in composition nano-size crystalline composites with various distributions of the electrical charge in the bulk of contacting grains are shown schematically.

Let us evaluate the electrical charge density variation, i.e. densities of excess or deficiency of electrons in the contact area limited by thickness about  $2\delta$ . In the free (non-contacting) grain, the electrical charge density is determined by relation (5). For mono-valence metals, it can be assumed that each atom in the crystal give to SP one electron. At the contact of two grains, as a result of transferring the part of charges through the grain boundary, there occurs the charge distribution which to a first approximation can be considered similar to that in a plane capacitor ("minus" on the one side and "plus" on the other side of the boundary). So, charge surface density  $\sigma$  can be described by equation (as for the plane capacitor):

$$\sigma \approx \epsilon_0 \epsilon (U / 2\delta), \quad (6)$$

where  $\epsilon_0$  is dielectric constant,  $\epsilon$  is dielectric permittivity for SP, and  $2\delta$  is distance between the capacitor plates (boundary thickness between grains). If  $U$  is assumed as the value determined by (3), then taking (6) into account, we can evaluate variation

of the charge density  $\Delta\rho$  in the grain with linear size  $L$  as follows:

$$\Delta\rho \approx \varepsilon_0 \varepsilon U / (2\delta L). \quad (7)$$

For quantitative evaluations, it is conveniently to use relative variation of the electrical charge density in the grain bulk ( $\chi = \Delta\rho/\rho_0$ ) due to charge movement through the grain boundary. Taking (7) into account we obtain:

$$\chi = \Delta\rho/\rho_0 = \Delta\rho/n_0 e = \varepsilon_0 \varepsilon U \omega / (2\delta L e). \quad (8)$$

In the case of metals, at grain size of  $L \approx 10$  with  $\delta \approx 10$  nm,  $U \approx 1$  V, and  $\varepsilon \approx 10$ , the parameter  $\chi$  may achieve the value  $\approx 0.5$ . As the  $\chi$  parameter characterizes relative variation of the free electron density, it can be used to describe the variations of valence electron concentration per an atom, i.e.  $\chi = (n - n_0)/n_0$ . Here  $n_0$  and  $n$  are, respectively, the initial and changed (as a result of electron transfer through the grain boundary) numbers of valence electrons per atom. For monovalent metals, for example, noble metals as Au, Ag, Cu, and alkali metals Li, Na, K:  $n_0 = 1$ . Subsequently, the obtained numerical evaluation  $\chi \approx 0.5$  for such metals indicates the possibility of increasing the valence electron number per atom in the grain with size  $L \approx 10$  nm up to  $n \approx 1.5$  exceeding the limiting value ( $n = 1.48$ ), when the Fermi surface is wholly near the Brillouin zone and requires reconstruction of symmetry and lattice parameter.

For semiconductors, the screening length  $\delta$  achieves  $\approx 100$  nm, that is caused by small in comparison to the metals "free" electrons density  $c \cdot \rho_0 \approx 10^{23}$  e/m<sup>3</sup> ( $c$  is concentration of dopant which injects the charge carriers in the semiconductor). The noticed fact results in increasing  $\chi$  parameter (at  $U \approx 1$  V and  $L \approx \delta \approx 100$  nm) up to value of the order  $10^2$ . The transfer of electrons at the contact "metal-semiconductor" may result in increasing the electron density in the semiconductor by orders of value. Indeed, in this case charge carrier density achieves  $\rho \approx \chi \cdot \rho_0 \approx 10^{26}$  e/m<sup>3</sup>.

Thus, the evaluations above testify that in the nano-structured composite materials based on the metals and semiconductors, as a result of electrical charge carrier redistribution at grain boundaries, the state of electron subsystem is changed in whole bulk of the material. This condition may cause

appearance of the specific effects which are not observed in usual coarse-grain polycrystals but become possible in the nano-structured materials, the fact often observed recently. Below we discuss some of these effects.

### 3. Results and discussions

#### 3.1 Synthesis of the new phases

The assumption about possibility of the new phase appearance in the material under investigation is based on existence of the two Hume-Rothery rules which are valid for formation of binary metal alloys with "metallic" chemical bond, i.e. the bond caused by collective interaction of the free electrons with positively charged ion skeleton [17].

According to the first Hume-Rothery rules, there is a relation between the structure of realized phases and the average number of valence electrons per atom ( $n$ ) varying under the alloy formation. This relation is explained on the base of the band theory for solids [17]. In accordance with the theory, each value  $n$  for this or that phase corresponds the touching Fermi surface with the internal boundary of the Brillouin zone — that is the necessary condition for formation of the most energetically balanced crystalline structure. It should be underlined that this Hume-Rothery rule in its classic form is valid for formation of the binary solid substitutional solutions, for example, alloys: Cu–Zn, Ag–Al, Cu–Sn and many others. In the discussed case of the nano-structured composite materials, appearance one or another of the phases mentioned above can be predicted, however, not in the sequence characteristic to the usual coarse-grain polycrystals. This conclusion follows from that already in the initial state, due to electrons redistribution, the average number  $n_0$  of free electrons in the contacting grains does not equal to unity as in the case of the coarse grains and may achieve  $\approx 1.5$  (see Section 2). It is evidently that in such material during the alloy formation under increasing temperature, according to the Hume-Rothery rule, the new phase may be realized which would not correspond to the classic phase diagram characteristic to usual polycrystals with the same chemical composition.

In close connection with described above effect, there is the possibility of changing marginal concentrations limiting the existence of certain mono-phase composition for any binary substitutional solution. Accord-

ing to the abovementioned Hume-Rothery rule, during formation of the solid solutions, for each pair of chemical elements there is a maximum  $n$  value exceeding of which results in changing the concentration range for existence of the specific phase. Taking into consideration that in the nano-structured composite polycrystal, as a result of the valence electron redistribution in contacting grains, the  $n$  value varies up to  $\approx 1.5$  already in initial state, appearance of the solid solutions with marginal concentrations not corresponding to the values characteristic for the usual coarse-grain materials can be supposed. In particular, it can be expected that under conditions of increased temperature, in the nano-size grains, the alloy Ag-Fe may be realized in certain concentration which is never realized in the usual polycrystals.

Now let us discuss an effect which can appear during phase formation in the nano-structured composite materials in connection with changing conditions for validity of the second Hume-Rothery rule. According to this rule, formation of the binary solid solution of two substances is possible only under condition that atomic diameters of the solvent and the diluted substance differ not more than by 15 % (so called volume factor) [17]. Usually, the largest distance between atoms in the crystal of the substance under consideration is taken as atomic diameter. For example, it was established for the mentioned system Cu-Zn that zinc is diluted in copper without any phase transition up to concentration 38 at. % Zn, while in Cu-Cd system, Cd solubility in copper in the single-phase state is limited by 1.7 at. % Cd. The volume factors expressed in percents for mentioned systems are 4 % and 16.5 %, respectively. Thus, the examples given testify validity of the second Hume-Rothery rule for usual materials. However, it is easy to make sure, that in the case of nano-structured composite material, the volume factor for a pair of contacting substances may be changed, hence, changed may be values of marginal concentrations characterizing the mutual solubility of elements under consideration. Indeed, as it has been noticed, transfer of electrons from one to another grain changes electron density in the grain bulk; that is equivalent to action of additional "pressure"  $\Delta P$  from the side of electron gas onto ion crystalline lattice which is evidently proportional to the Fermi energy variation  $\Delta E_F$  of elec-

trons, and  $\Delta P$  can be estimated by the order of value using the relation  $\Delta P \approx \Delta E_F/\omega$ .

The pressure  $\Delta P$ , in turn, may result in changing the marginal concentrations characterizing the mutual solubility of contacting substances. Indeed, relative variation of lattice parameter caused by changing the pressure of electron gas can be evaluated by the relation:  $\Delta a/a \approx 1/3(\Delta P/K)$ , where  $K$  is compression modulus. As  $\Delta E_F \approx \chi^{3/2}E_F$  (see determination of  $\chi$  parameter and Eq. (2)), for evaluation of the lattice parameter variation we can use expression:

$$\Delta a/a \approx 1/3\chi^{3/2}E_F/\omega K. \quad (9)$$

At the reasonable values of constants:  $E_F \approx 5$  eV,  $\omega \approx 3 \cdot 10^{-29}$  m<sup>3</sup>,  $K \approx 10^{11}$  n/m<sup>2</sup> and  $\chi \approx 0.5$  we have:  $\Delta a/a \approx 0.1$ . This evaluation indicates that in the nano-structured composite materials, as a result of electron redistribution, the lattice parameter variation up to  $\approx 10$  % of initial value may take place in the contacting grains; that, in turn may change marginal concentrations characterizing the mutual solubility of substances during the solid solution formation.

Thus, phase diagrams describing formation of the binary solutions for the usual coarse-grain materials would be substantially changed for the nano-structured composite materials of the same composition. That is connected with variations of both the average number of electrons per atom and the lattice parameter in such material.

### 3.2 Changing the magnetic properties of transition metals in the nano-structured composite materials

It is known that a number of transition group materials are characterized by partially occupied 3d-band of electron energy spectrum. It is the fact that causes substantial magnetization of such metals due to possibility of occurring the electrons with parallel spin orientations under external magnetic field (ferromagnetism) [18]. Typical example of such metals is nickel (Ni). Calculations show that for complete occupation of 3d-band in nickel there is deficiency  $\approx 0.54$  of electron charge per atom. Consequently, it can be assumed that partial or complete occupation of 3d-band in nickel would be accompanied by decreasing the magnetic susceptibility of the metal up to disappearing the ferromagnetism. Such effect was observed indeed under studying the magnetization of (Ni-Cu) solid solution with

copper concentration  $\approx 60$  at. %. Copper, as it is known, is characterized by completely occupied  $3d$ -band and only partially occupied  $4s$ -band (one electron per atom). Hence, under formation of solid solution (Ni–Cu), there takes place nickel  $3d$ -band occupation at the expense of electrons from copper  $4s$ -band; that causes practically whole disappearance of ferromagnetic magnetization in the alloy.

In the case under consideration for the nano-structured material, occupation of nickel  $3d$ -band by deficiency electrons may be realized under formation of the Volta potential at the interface of different grains (see Section 2). Naturally, there is a good reason to believe that in materials containing ferromagnetic and usual mono-valence metals ( $n \approx 1$ ) as contacting components, even without mutual dissolution, the magnetic susceptibility may significantly decrease.

Besides the abovementioned ferromagnetic materials, also so-called low-magnetic substances belong to transition metals. These are characterized by magnetic susceptibility  $\psi \ll 1$ , in contrast to ferromagnetic with  $\psi \gg 1$ . Examples of such metals are palladium (Pd) and platinum (Pt). Palladium is paramagnetic with the positive magnetic susceptibility:  $\psi > 0$ . Such specific magnetization of palladium is related to the fact that it has incompletely occupied  $4d$ -band in contrast to  $3d$ -band for ferromagnetic metals. This is followed by significant decreasing "free" energy states density in comparison with ferromagnetic; the fact causes substantial lowering the magnetic susceptibility. Evidently, if palladium is one of the components in the nano-structured composite material, complete occupation of its  $4d$ -band by electrons from neighboring grain would be accompanied by even larger decrease of its magnetic susceptibility.

Another low-magnetic metal from the transition group is platinum (Pt). This metal is diamagnetic with negative magnetic susceptibility:  $\psi < 0$ . This is caused by the fact that even though platinum, as other transition metals, has partially occupied  $d$ -shell ( $5d$ -band), its paramagnetism is diamagnetism of "free" electrons (the Pauli diamagnetism [17, 19]). In this connection, it can be assumed that in Pt nano-size grain contacting with the metal with less Fermi energy, as a result of reducing the "free" electron density under formation of the Volta potential, the effect of lowering the

diamagnetic susceptibility down to paramagnetism, i.e. changing the sign of magnetic susceptibility may be realized.

Thus, the magnetic properties of the nano-structured composite materials may substantially differ from the properties of some usual coarse-grain material. Recently, the works are published where not only magnetic, electrical, but also elastic and plastic properties were observed to be changed.

### 3.3. Changing the electrical properties of the nano-structure composites

Let us discuss changing the electrical resistivity of such material in comparison with the usual coarse-grain polycrystals. It is known that electrical resistance of transition group metals (Ni, Pd, Pt, etc.) exceeds substantially the values for the noble ones (Cu, Au, Ag, etc.) [17, 19]. It is thought that the increased resistance of transition group metals is related with additional scattering  $s$ -electrons in incompletely occupied  $d$ -band. Hence, as occupation of  $d$ -states may take place in the nano-structured composite material, there can be expected decreasing the resistivity of such material in comparison with the coarse-grain material of the same chemical composition.

Besides the electrical resistance, an important parameter characterizing electrical properties is the value and sign of the Hall constant ( $R$ ). Considering this parameter is the most important under discussion of electrical properties for composites containing semiconductors. For electrons, the Hall constant is negative, therefore, for most of metals  $R < 0$ , and, as  $R \sim 1/\rho$ , by absolute value it is significantly less than  $R$  for semiconductors. It should be noticed, however, that for some metals due to specific structure of the electron subsystem, the Hall constant is positive ( $R > 0$ ). Examples of such metals are Sn, Be, W, etc. Moreover, under formation of the binary solid solution based on metals with different signs of the Hall constant, there takes place changing the both value and sign of  $R$  depending on the solution concentration. An example illustrating such situation is measurements of the Hall constant in Cu–Sn system in the concentration range from 0 to 30 at. % Sn [4]. In this specific case the  $R$  value is changed from "minus"  $\approx 5$  to "plus"  $\approx 8$ . Obviously, in the system under consideration there occurs gradual transition from the state with predominantly electron conductivity as for pure copper, to the state

with predominantly  $p$ -type conductivity ( $\beta$ -phase of Cu–Sn alloy).

In the nano-structured composite material discussed in our paper, as we already noticed, in the nano-size grains there may take place changing electron concentration up to the value characterized by the parameter  $\chi \approx 0.5$ , i.e. to  $\approx 50\%$  of initial concentration  $\rho_0$ . As  $R \sim 1/\rho$ , it is naturally to expect that in such material also the Hall constant may change like that occurs under formation of Cu–Sn solid solution.

In the case of the nano-structure composite materials with semiconductors, changing the concentration of charge carriers under occurring the Volta potential may result not only to changing the Hall constant absolute value but also its sign, because in this case the sign of the electrical charge main carriers may change.

Thus, electrical properties of the nano-structured composite materials as well may substantially differ from the electrical properties of the usual coarse-grain composites of the same chemical composition, that was observed, for example in [18] where modern nano-composites NiC, GaSe, and other were studied.

#### 3.4 Changing the optical properties

Possible changing the optical properties of the nano-structured composite materials consisting of metals and semiconductors is based on the following physical reasons. As it is known, optical properties of metals (ability to reflect and to absorb visible light) is determined by the character of electrons energy spectrum [17]. In the case under consideration, due to occurring the Volta potential at the interface of different grains, in whole bulk of the grain the average number of valence electrons per atom may change to the value  $n \geq 1.5$  (see Section 2). Naturally, so substantial changing the quantity of electrons is accompanied by changing the energy spectrum of the electron subsystem and, subsequently, the both light reflection and absorption spectra would change for such material.

Similar effect would appear also in the nano-structured composite materials based on semiconductors.

Indeed, as it was already noticed, as a result of the Volta potential occurrence, in the grain bulk the charge carrier density in semiconductor may be raised by a factor of several hundred or thousands. On the other hand, it is known that frequency of plas-

mons responsible for the absorption of light waves in semiconductors is proportional to square root of the charge carrier density ( $\nu \sim \rho^{1/2}$ ). Subsequently, it can be expected that in such material as a result of  $\rho$  changing, the optical properties may also substantially change.

#### 4. Conclusions

On the basis of quantitative evaluations and the discussion, general conclusion can be following. Varying the main parameters of the nano-structured material (grain size and composition) it is possible to change controllably phase and structure states as well as many physical properties of such material.

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