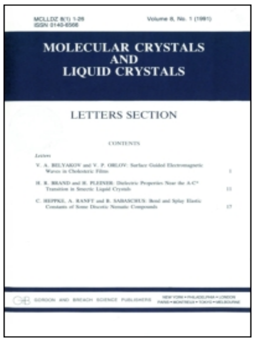
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Spectral and barrier properties of heterocomposites based on poly (para-phenylene) disposed between the silicon films

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ABSTRACT
Within the framework of the methods of the electron density functional and the *ab initio* pseudopotential, we have obtained the spatial distributions of the valence electrons density, the electron energy spectra and the Coulomb potential for heterocomposites based on poly (para-phenylene) and carbon nanotube disposed between the silicon films.

It was revealed that the maximal value of the potential barrier was noticed in a composite material from polyparaphenylene filaments placed between silicon films and completed with carbon nanotubes perpendicularly to the surface of the silicon films and along them.

KEYWORDS
Heterocomposite; polymer; carbon nanotubes; silicon films; *ab initio* calculation

Introduction

Modern electronic devices are increasingly being designed by combining materials with different electronic properties to be able to engineer the energy band gap or barriers, the electrical resistive or capacitive. For example, touch screens are becoming more and more popular as HMIs (human machine interfaces) not only for mobile phones and computers but every where mechanical switches are used today. To construct a touch screen a transparent electrode is necessary, the read-out electronics can be based on resistive or capacitive effects. Today the transparent electrode is mostly made of ITO (indium tin oxide) vacuum sputter coated glass or plastic film. However indium is a rare metal which is in short supply, its price has also been steadily rising. As ITO is a glasslike brittle material the most common failure mechanism of touch screens is the formation of micro cracks. The highly conductive material PH1000 (PEDOT:PSS Conductive Polymer) and its ready to use formulation Clevios$^{\mathrm{TM}}$ FE-T are used for touch screens as an alternative to ITO in technical films.

Changing the conductive properties of various polymers by methods of their physical and chemical modification (the introduction into their volume the various ingredients (fillers, plasticizers, stabilizers, etc.) has long been known [1,2]. On the other hand, changing in a wide range of electrically conductive properties of the polymer material may by using of a particular type of polymer. The highest conductive properties are polymers with polyene system of conjugated bonds in chain of the macromolecule itself (today, there are the most well known as polypyrrole, polyparaphenylene, polythiophene, polyacetylene, etc [3].

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Some disadvantages of these polymers (a high enough creep at low loads, low radiation resistance) can be optimized by creating composite materials, among which the system with a new type of fillers of polymer's matrix (carbon nanotubes) is drawn special attention. It should be noted that carbon nanotubes are characterized by an unsurpassed ratio between the length, the radius and unique mechanical, electrical and thermal properties. In the case of achieving a homogeneous distribution of nanotubes in the polymer matrix, the interaction between them and the macromolecules even at low content of carbon nanotubes ($\approx 1\%$) it is possible to obtain a significant improvement in elastic properties, mechanical firmest, electrical conductivity of nanocomposites [4].

In this study [5], poly(p-phenylene sulfide) based nanocomposites containing multi-walled carbon nanotubes (MWNTs) were produced by dilution of a 15 wt.% MWNT/PPS masterbatch via twin screw extrusion process. The electrical conductivities of the nanocomposites were measured and percolation threshold was observed below 0.77 vol.% MWNTs. The state of dispersion and distribution quality of MWNTs was analyzed on macro-and nanoscale through transmission light and scanning electron microscopy (SEM). A good deagglomeration of primary macroagglomerates and a homogenous MWNT distribution on nanoscale was found. The dependence of conductivity on MWNT concentration was estimated using statistical percolation theory which matches the experimental data quite well.

A new empirical equation was set up to fit the electrical conductivity using quantitative values of visible percolating MWNTs which were detected by charge contrast imaging in SEM.

Current research focuses on conjugated organic polymers, which fill in the space between the silicon films. We study the spectral and barriers properties of these heterocomposites, depending on the distance between the polymer's chains, the number of links in these chains, and the type of doping of Si film. Poly (para-phenylene) (PPP) was used as the polymer. PPP is recognized as an efficient high-performance material because of its thermal and chemical stability, its electrical and optoelectronic properties [1]. It is an aromatic polymer consisting of directly linked repeating phenyl units (benzene rings) as its backbone. PPP has a delocalized π-electron system along the carbon backbone, which leads to the cooperation between the polymer's chains. It is known that PPP becomes insoluble, infusible, and intractable at more than six repeating units due to its huge degree of crystallization [2].

We obtained the spatial distribution data of the valence electrons density and crossings of these spatial distributions, the Coulomb potential along the vector in heterocomposites, distribution of electron states density of the different models of the mentioned heterocomposite. We used the methods of the electron density functional and *ab initio* pseudopotentials. The calculation was performed using the proprietary source code [6].

Objects and methods of research

The basic states of the electron-nuclear systems were detected by means of the self-consistent solution of the Kohn-Sham equations, because electronic variables only were determined with the atomic cores fixed. Following Kohn-Sham, electronic density was written down in terms of occupied orthonormal one-particle wavefunctions:

$$n(\vec{r}) = \sum_i \left|\psi_i(\vec{r})\right|^2. \tag{1}$$

The point on the surface of potential energy in the Born-Oppenheimer approximation was determined as a minimum energy functional with regard to the wavefunctions:

$$E\left[\{\psi_i\},\{R_j\},\{\alpha_\nu\}\right]=\sum_i\int_\Omega d^3r\psi_i^*(\overleftarrow{r})\left[-\frac{\hbar^2}{2m}\nabla^2\right]\psi_i(\vec{r})+U\left[\{n(\vec{r})\},\{R_j\},\{\alpha_\nu\}\right], \tag{2}$$

where $\{R_j\}$ are coordinates of atomic cores;$\{\alpha_\nu\}$ are any external influences on the system.

In the generally accepted formulation, minimization of the energy functional (2) with respect to one-particle orbitals with additional orthonormal constraint on the one-particle orbitals $\psi_i(\vec{r})$ results in Kohn-Sham one-particle equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2+\frac{\partial U}{\partial n(\vec{r})}\right\}\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r}). \tag{3}$$

Distribution of electrons along the energy zones for Γ-state of catalyst structures was found by means of numerical calculation of derivative $\lim_{\Delta E\to 0}\Delta N/\Delta E$ (where ΔN is a number of the allowed states for the ΔE interval of energy). The one-particle energy spectrum was obtained from calculation of the eigenvalues of the Kohn-Sham matrix. In accordance with ideology of the electronic density functional, the occupied states at absolute zero temperature were defined. It allowed to define position of the last occupied state, their number being half the number of electrons (due to ignoring the spin of the electron), and position of the first free states. Attention should be paid to the fact that the Γ-point for superlattice calculations has the value of the Baldereschi mean-value point, which represents all vectors in the Brillouin zone.

The Coulomb potential have been carried according to the formula:

$$V_H(\vec{G})=\frac{4\pi e^2\rho(\vec{G})}{G^2}, \tag{4}$$

where $\rho(\vec{G})$ are Fourier components of electron density:

$$\rho(\vec{G})=\frac{2}{N_T}\sum_{\vec{k}}\sum_{\vec{j}}^{CC}\sum_{\alpha\in T}\sum_{\vec{G}'}b_j^*(\vec{k}+\vec{G}'+\alpha\vec{G})b_j(\vec{k}+\vec{G}')$$

As the calculation algorithm envisages translational symmetry in the explored atomic system, initially, the orthorhombic type artificial superlattice was created. The research object determined parameters of the superlattice and the atomic base. For simulation of the film composite, the lattice parameters along Z, X, Y axes had some correlation. In a plane perpendicular to the surface of Si films, such size of the elementary cell was chosen so that the translationally located films would not influence one another.

PPP is constructed by concatenating two or three benzene rings, the silicon films consist of from two to four atomic planes. The heterocomposites are modeled in a periodic cell with a determined size to compose the infinite couple of silicon films with PPP filler.

The polyparaphenylene filaments squeezed between silicon films complemented with carbon nanotubes. The calculation of atomic objects given below was conducted to distinguish electronic characteristics.

Object №1 (infinite PPP, small cell – infPPP SC) is a system of infinite filaments, chemical formula of which is $(C_6H_4)_n$. It was modelled placing it bias plane XY, artificial primitive cell with dimensions $a=b=5{,}43$ Å (the choice of characteristic c was defined with the condition of making infinite or finite objects). The basis set of artificial grid of primitive cell for the infinite filament PPP oriented across axis Z consisted of 12 atoms of C and 8 atoms of H,

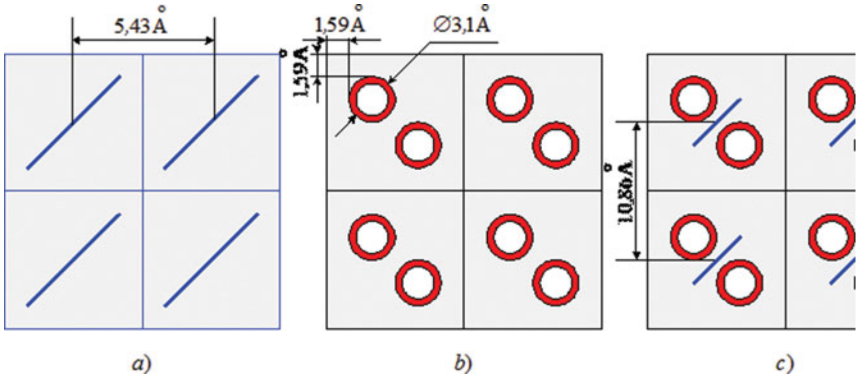

Figure 1. Schematic picture (view at plane XY of translation cell); placement of finite and infinite filament PPP (a); placement of finite and infinite CNT (b); simultaneous placement of CNT and PPP (c).

meaning 2 links of C_6H_4). Orientation of plane PPP filaments bias plane XУ of primitive cell was chosen as one of possible (see Fig. 1a).

Object №2 (finite PPP, small cell – fPPP SC) is a system of finite filament of polyparaphenylene (PPP) as long as 8,67 Å, placed bias artificial primitive cell with characteristics of $a = b = 5{,}43$ Å. The basis set of primitive cell of super grid for PPP filament restricted in length orientated parallel to axis Z consisted of 12 atoms of C and 8 atoms of H.

Object №3 (finite CNT, large cell – fCNT LC) is a system of restricted in length nanotubes (CNT) (4,0) with diameter 3,1 Å and length 8,46 Å was modeled placing them in primitive cell with their axis orientation parallel to Z, as it is shown in Fig. 1b. The basis set for finite tubes consisted of 64 atoms of C.

Object №4 (finite CNT+finite PPP, large cell – fCNT+fPPP LC), the system tubes CNT(4,0) restricted in length (8,46 Å) and restricted filament of polyparaphenylene PPP with length of 8,67 Å was modeled placing them in the cell in such a way that it is depicted in Fig. 1b.

Object №5 (Si(100), large cell – Si(100) LC) is a system of two infinite in directions X and Y. Si films (100) distributed with vacuum intervals with the depth of 8.46 Å was modeled with two atomic planes for each film. The basis set consisted of 32 atoms. The sides of artificial primitive cell were $a = b = 10{,}86$ Å.

Object №6 (Si(100) + finite PPP, large cell – Si(100)+fPPP LC) is a composite from filaments of polyparaphenylene with the length of 8,67 Å squeezed between silicon films. The basis set of primitive cell of artificial grid for structure consisted of 32 atoms of Si, 12 atoms of C, and 8 atoms of H. Orientation of plane filaments of PPP was bias plane XY of the primitive cell and perpendicularly to the surfaces of Si films (100). The sides of artificial primitive cell were $a = b = 10{,}86$ Å.

Object №7 (Si(100) + finite CNT, large cell – Si(100)+fCNT LC) is a composite from carbon nanotubes with length 8,46 Å, squeezed between silicon films. The basis set of primitive cell of artificial grid for the structure of composite consisted of 32 atoms of Si and 64 atoms of C. The sides of artificial primitive cell were $a = b = 10{,}86$ Å.

Object №8 (Si(100) + finite CNT+ finite PPP, large cell – Si(100)+fCNT+ fPPP LC) is a composite of polyparaphenylene filaments squeezed between silicon films and completed with carbon nanotubes.

For the estimation of the Coulomb potential in the studied systems, two directions were chosen: across axis Z and athwart it (Fig. 2).

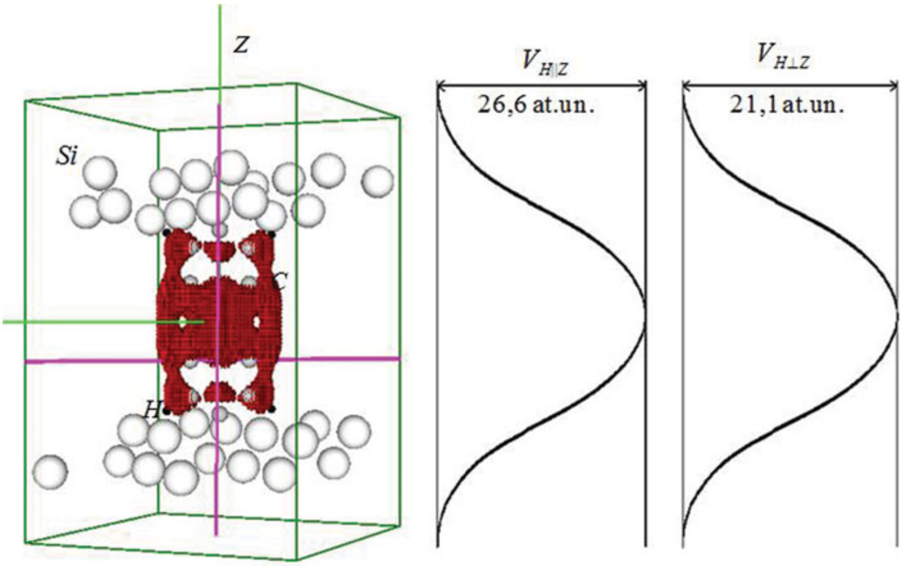

Figure 2. The spatial distributions of the valence electrons density within the interval of 1.0–0.9 of the maximum value for the object №6 and the lines that indicate the directions to calculate of the Coulomb (Hartree) potential (left); the Coulomb potential along the Z axis and perpendicular to it (right).

Results of calculation and their discussion

Table 1 represents information about the length of valence band ΔE_v, the length of band gap E_g, the Coulomb potential, which was calculated in the directions of axis Z of primitive cell $V_{H||Z}$ and perpendicularly to it $V_{H\perp Z}$ for objects described above.

While analyzing the data it was found out that the maximal values of the Coulomb potential, that is potential barrier, were observed in the composite from polyparaphenylene filaments, squeezed between silicon films and completed with carbon nanotubes in direction perpendicularly towards surface of silicon films (62,2 at.un.), as well as across them (46,1 at.un.).

The simplification of filling in interval between silicon films, notably polyparaphenylene filaments or CNT tubes, led to the decrease of potential barriers. Similar correlation between values of the barrier was observed only for filling (without restriction of silicon film fillers), notably the biggest barrier was observed in the structure of polymers and nanotubes, and the least barrier was observed in the system of polymers. Besides, the longer polymer was, the less potential barrier it produced (the Coulomb potential value along the infinite polymer was 0,21 at.un, as for the finite it was 10,5 at.un.).

Table 1. The valence band ΔEv, the band gap Eg, the Coulomb potential, which was calculated in the directions of axis Z of primitive cell $V_{H||Z}$ and perpendicularly to it $V_{H\perp Z}$.

Object number	Atomic structure of object	ΔE_v, eV	E_g, eV	$V_{H\|\|Z}$, at.un.	$V_{H\perp Z}$, at.un.
1	infPPP SC	51,68	0,054	0,21	3,4
2	fPPP SC	67,93	0,163	10,5	4,2
3	fCNT LC	30,11	0,213	27,30	17,98
4	fCNT+fPPP LC	33,14	0,068	44,2	32,3
5	Si(100) LC	1,98	0,008	5,3	0,3
6	Si(100)+fPPP LC	83,22	0,000	26,6	21,1
7	Si(100)+fCNT LC	11,87	0,082	36,4	24,3
8	Si(100)+fCNT+ fPPP LC	17,09	0,012	62,2	46,1

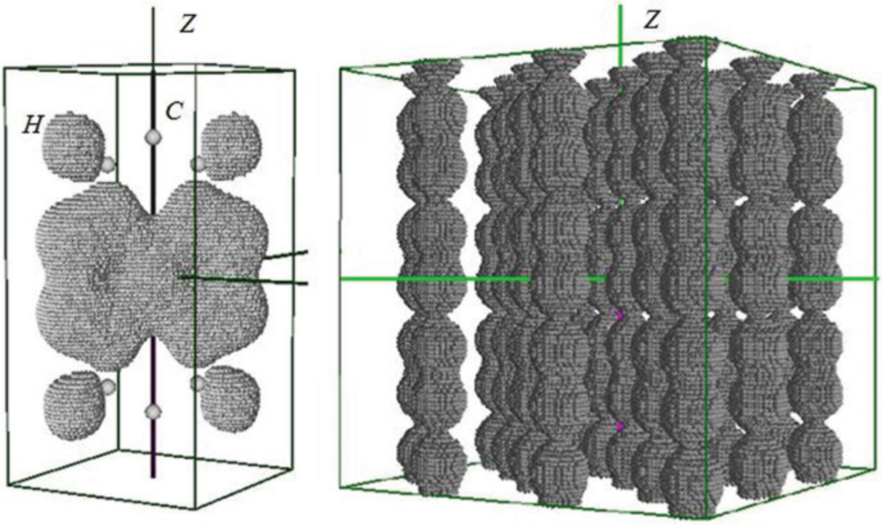

Figure 3. The spatial distributions of the valence electrons density within the interval of 0.2–0.1 of the maximum value for the object №2, №1.

The reduction of band gap was registered for the composite from polyparaphenylene filaments squeezed between silicon films. Besides, the biggest length of valence band was registered in comparison to the other objects of the research. The composite from carbon nanotubes squeezed between silicon films has quite big band gap (0,082 eV), which decrease with complementation of the composite with PPP filaments to the value of 0,012 eV.

As for spatial distribution of electron density between parts of composites the following peculiarities (see Fig 3.) were registered. Thus, in Figure 3 the spatial distribution of density of the valence electrons is shown for finite and infinite PPP. According to correlation of the Coulomb potentials, which forms across their length (see tab. 1, potential for the infinite PPP is smaller than that restricted between two links), in Fig. 3 significant concentration of spatial density of valence electrons is observed in the area between links of the restricted polymers.

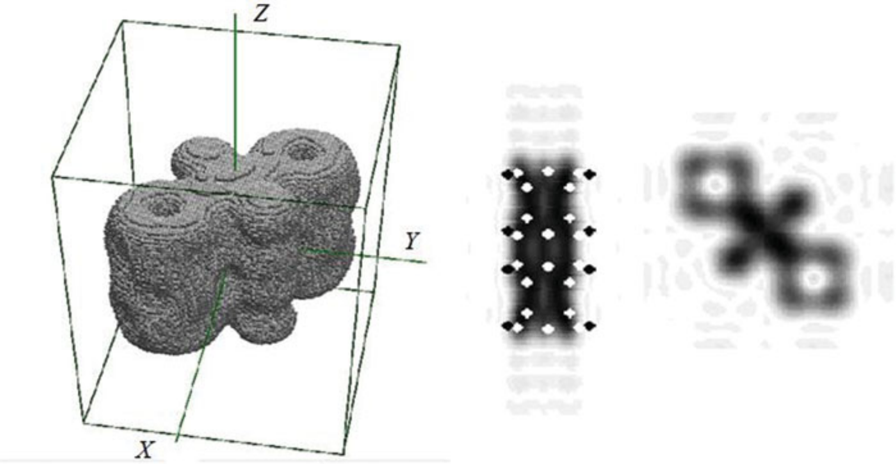

Figure 4. The spatial distributions of the valence electrons density within the interval of 0.2–0.1 of the maximum value for the object №4 (left); cross-sections of the spatial distribution of valence electron density in the object №4 (right).

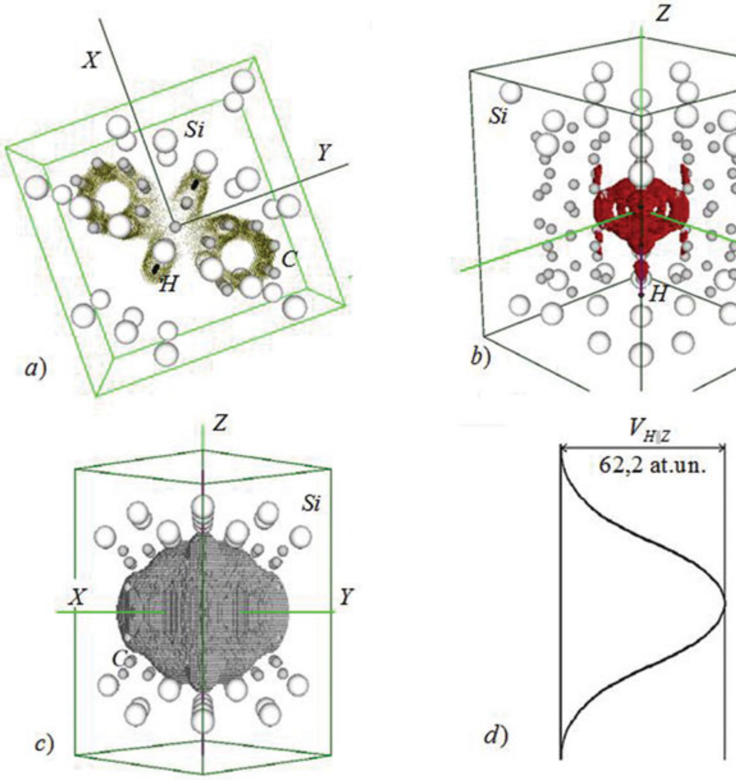

Figure 5. The spatial distributions of the valence electrons density within the interval of 0.6–0.5 of the maximum value for the object №8 (a); within the interval of 1–0.9 of the maximum value for the object №8 (b); within the interval of 0.2–0.1 of the maximum value for the object №8 (c); the Coulomb potential across the composites (d). In Fig. 6 it is seen that the degree of the filling of composite influences upon form and value of the barrier.

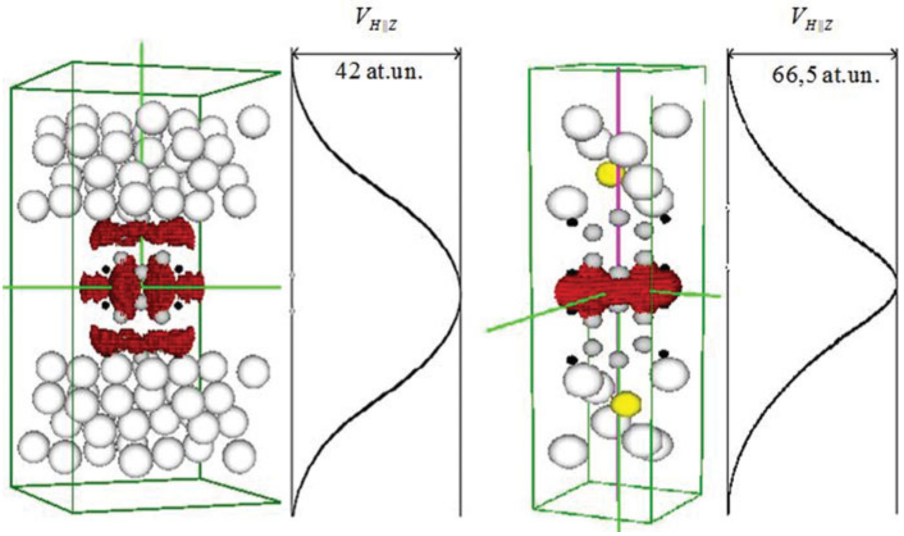

Figure 6. The spatial distributions of the valence electrons density within the interval of 1.0–0.9 of the maximum value and the Coulomb potential across the heterocomposites: (left) large cell with the couple of silicon (100) films filled PPP, the distance between the polymer's chains was 10.86 Å; (right) small cell, the distance between the chains was 5.43 Å.

Such concentration of valence electron density in the area between links of the polymer in comparison to the area in a link is observed for infinite polymer as well but with less intensity.

Figure 4 shows the spatial distribution of the valence electrons density and their intersections in their inter-perpendicular directions for atomic composition, which consists of nanotubes and polymers. The exchange in electrical densities between the polymer and nanotubes is observed for the mutual distance between these parts of composition, which have been chosen for calculation.

Figure 5 illustrates the special distribution densities of valence electrons for the composite from polyparaphenylene filaments put between silicon films and complemented with carbon nanotubes perpendicularly to the surface of silicon films (62,2 at.un.). As it is depicted in Fig. 5 the biggest electron density is localized in the polymer.

Conclusion

Within the framework of the methods of the electron density functional and the *ab initio* pseudopotential, we have obtained the spatial distributions of the valence electrons density, the electron energy spectra and the Coulomb potential for heterocomposites based on poly (para-phenylene) and carbon nanotube disposed between the silicon films.

It is revealed that the maximal values of potential barrier was observed in composite from polyparaphenylene filaments squeezed between silicon films and complemented with carbon nanotubes in the direction perpendicularly towards the surface of silicon films as well as along them.

It was registered that the disappearance of band gap for the composite from polyparaphenylene filaments squeezed between silicon films. The biggest width of the valence band was registered for this composite in comparison to other objects of the research. The composite from carbon nanotubes squeezed between silicon films has the biggest band gap, which diminishes by addition of PPP filaments.

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