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Research Article

Theoretical study of metal composite based on pyrolyzed polyacrylonitrile monolayer containing Fe-Co, Ni-Co and Fe-Ni metal atom pairs and silicon amorphizing admixture

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Abstract

An urgent problem of radio engineering and radioelectronics nowadays is the synthesis of composite materials with preset parameters that can be used as electronics engineering materials. Of special interest are MW range wide-band electromagnetic radiation absorbers. Special attention is paid to materials on the basis of ferromagnetic metals that are capable of effectively absorbing and reflecting incident waves and having a clear nanostructure. Development of nanocapsulated metals will allow controlling the parameters of newly designed materials. This is achieved with the use of polymer matrices, e.g. pyrolyzed polyacrylonitrile (PPAN). This work is a theoretical study of a PPAN monolayer model containing pairs of transition metal atoms iron, nickel and cobalt which possess ferromagnetic properties, in Fe-Co, Ni-Co and Fe-Ni combinations, with silicon amorphizing admixture. We studied the geometrical structure of the metal composite systems which are modeled as PPAN molecular clusters the centers of which are voided of six matrix material atoms, the resultant defects (the so-called pores) being filled with pairs of the metal atoms being studied. The metal containing monolayer proved to be distorted in comparison with the initially planar PPAN monolayer. We plotted single-electron spectra of the composite nanosystems and characterized their band gaps. The presence of metal atoms reduces the band gap of a metal composite as compared with pure PPAN. We determined the charges of the metals and found electron density transfer from metal atoms to their adjacent PPAN monolayer atoms. We calculated the average bond energy of the test metal composite systems and proved them to be stable. The studies involved the use of the density functional theory (DFT) method with the B3LYP functional and the 6-31G(d) basis.

Keywords

pyrolyzed polyacrylonitrile, transition metals, metal-carbon nanocomposites, DFT.

1. Introduction

An urgent problem of radio engineering and radioelectronics nowadays is the synthesis of composite materials with preset parameters that can be used as electronics engineering materials. Of special interest are composite materials consisting of a polymer matrix and filler. Introduction of metallic nanoparticles into the matrix produces materials having improved physicochemical properties. Introduction of ferromagnetic metals into nanocomposites opens the possibility of their application in various engineering fields: magnetic data recording systems [1], high frequency devices [2, 3], biomedicine [4], radiation protection systems [5], electronics etc.. Theoretical study of metal composites is an important task solving which we will be able to control their structure and parameters [6–8].

Of special interest are MW range wide-band electromagnetic radiation absorbers. Special attention is paid to materials on the basis of ferromagnetic metals that are capable of effectively absorbing and reflecting incident waves. This requires materials having a clear nanostructure on the basis of ferromagnetic metals Fe, Co, Ni [13]. These systems are synthesized, and their properties are studied, in the form of alloys obtained using different methods: in the form of thin Fe-Co films electrodeposited from metal sulfate [14], bimetallic clusters [15] and various ferromagnetic nanopowders [16–20]. However the radiation absorbability of these materials depends on the thickness and dimensions of the coating. Development of nanocapsulated metals will allow controlling the parameters of the newly designed materials. This is achieved with the use of polymer matrices, e.g. pyrolyzed polyacrylonitrile **(PPAN)**.

PPAN is synthesized by IR heating of polyacrylonitrile [21]. The use of polyacrylonitrile as a PPAN precursor is the cheapest industrially tested method and provides for the highest yield of the required material [22–27]. PPAN is a graphite-like layered structure which can be considered to be a polymer matrix capable of incapsulating metallic nanoparticles.

Aiming at the development of the most suitable radiation absorbing material, earlier theoretical and practical studies dealt with PPAN based nanomaterials with additions of iron, cobalt and nickel metals as well as with silicon and copper acting as the so-called amorphizing admixtures [28]. The use of amorphizing admixtures improves the bending and compression plasticity of the composite. This also allows producing bulk nanomaterials with controlled parameters [29]. Different pair combinations of Fe, Co and Ni in PPAN were studied [30].

Below we present computer simulation data for a PPAN monolayer based composite with embedded Cu-Co, Ni-Co and Fe-N metal pairs and a silicon atom acting as the amorphizing admixture. The calculations obeyed the molecular cluster model with the use of the density functional theory method **(DFT)**. We used the B3LYP hybrid functional with the 6-31G(d) basis set [31–33]. This functional is preferable for calculation of transition metal containing systems.

2. Geometrical and electron energy structure of pyrolyzed polyacrylonitrile based metal composites

The model was a PPAN monolayer cluster the center of which was voided of 6 atoms. The resultant structure contained 70% carbon atoms, 19% nitrogen atoms and 11% hydrogen atoms (Fig. 1).

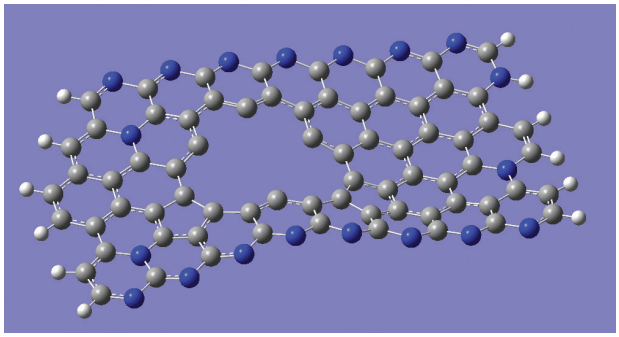

Figure 1. Optimized structure of PPAN nanocomposite.

The resultant vacancy defect (or pore) was filled with pairs of metal atoms Fe-Co, Ni-Co or Fe-Ni. A silicon atom was located above the monolayer in the vicinity of the metal atoms at a 2.5A distance. We denote the PPAN structures with embedded metal atom pairs and silicon as Ni-Co-Si/PPAN, Fe-Co-Si/PPAN and Ni-Fe-Si/PPAN. Analysis of the geometry of the systems obtained as a result of the fully optimized calculations indicated significant distortion of the monolayer upon embedding of each of the atom pairs considered (Fig. 2).

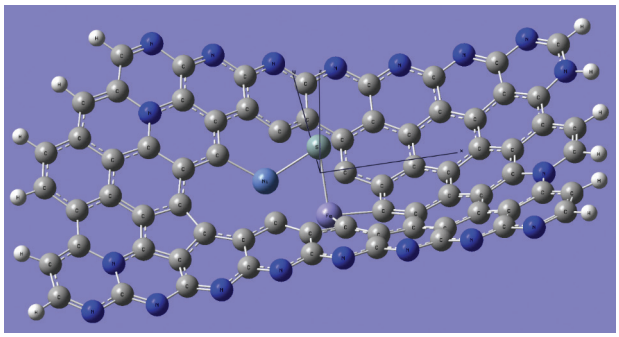

Figure 2. Optimized structure of Ni-Fe-Si/C nanocomposite.

Analysis of the structures showed that the silicon atom tends to chemically bind with the metal atoms. As a result the monolayer distortion decreased slightly as compared with similar models without silicon. It is safe to identify this process as the formation of PPAN encapsulated metal complexes in the structure.

Table 1. Distance between metal atoms in PPAN monolayer

Atom	Interatomic distance, nm					
	Fe-Co-Si/PPAN		Ni-Co-Si/PPAN		Ni-Fe-Si/PPAN	
	Fe	Co	Ni	Co	Ni	Fe
Fe	–	–	–	–	–	–
Ni	–	–	–	–	–	0.259
Co	0.243	–	0.275	–	–	–
Si	0.244	0.217	0.224	0.247	0.227	0.248

We plotted single-electron spectra of the metal composite systems. Their analysis yielded the value of the so-called band gap ΔE_g calculated as the difference between the energies of the high occupied and low unoccupied molecular orbitals (Table 2). The band gap is the narrowest for the structure containing Ni-Fe atoms with silicon atom admixture. This alloy exhibits low ferromagnetic properties. Iron atoms in this alloy may have magnetizations close to the ideal saturation for pure iron [34]. The metal atomic orbitals proved to give the greatest contribution to the so-called conductivity zone (Fig. 3). However in the PPAN structures with the Ni-Co and Fe-Co pairs and the Si atom the metals give a significant contribution to the last filled level. The Co atom proved to have but a little effect on the change of the band gap, unlike Ni the introduction of which noticeably reduced the band gap. Comparison between the metal composite systems containing a silicon atom acting as an amorphizing admixture (Ni-Co-Si/PPAN, Fe-Co-Si/PPAN and Ni-Fe-Si/PPAN) and the metal composite systems without a silicon atom (Ni-Co/PPAN, Fe-Co/PPAN and Ni-Fe/PPAN) showed that silicon atom addition reduces ΔE_g (Table 2). All the systems considered are semiconductors by conductivity type.

Table 2. Electron-energy characteristics of PPAN based metal-carbon nanocomposites with embedded pairs of metal atoms and an amorphous silicon atom

System	ΔE_g, эВ	E_b, эВ
PPAN	0.98	-9.93
Ni-Co-Si/PPAN	0.58	-8.69
Fe-Co-Si/PPAN	0.86	-8.73
Ni-Fe-Si/PPAN	0.63	-6.54
Ni-Co/PPAN	0.95	-8.73
Fe-Co/PPAN	0.99	-8.96
Ni-Fe/PPAN	0.55	-8.76

Notations: ΔE_g is the band gap; E_b is the bond energy.

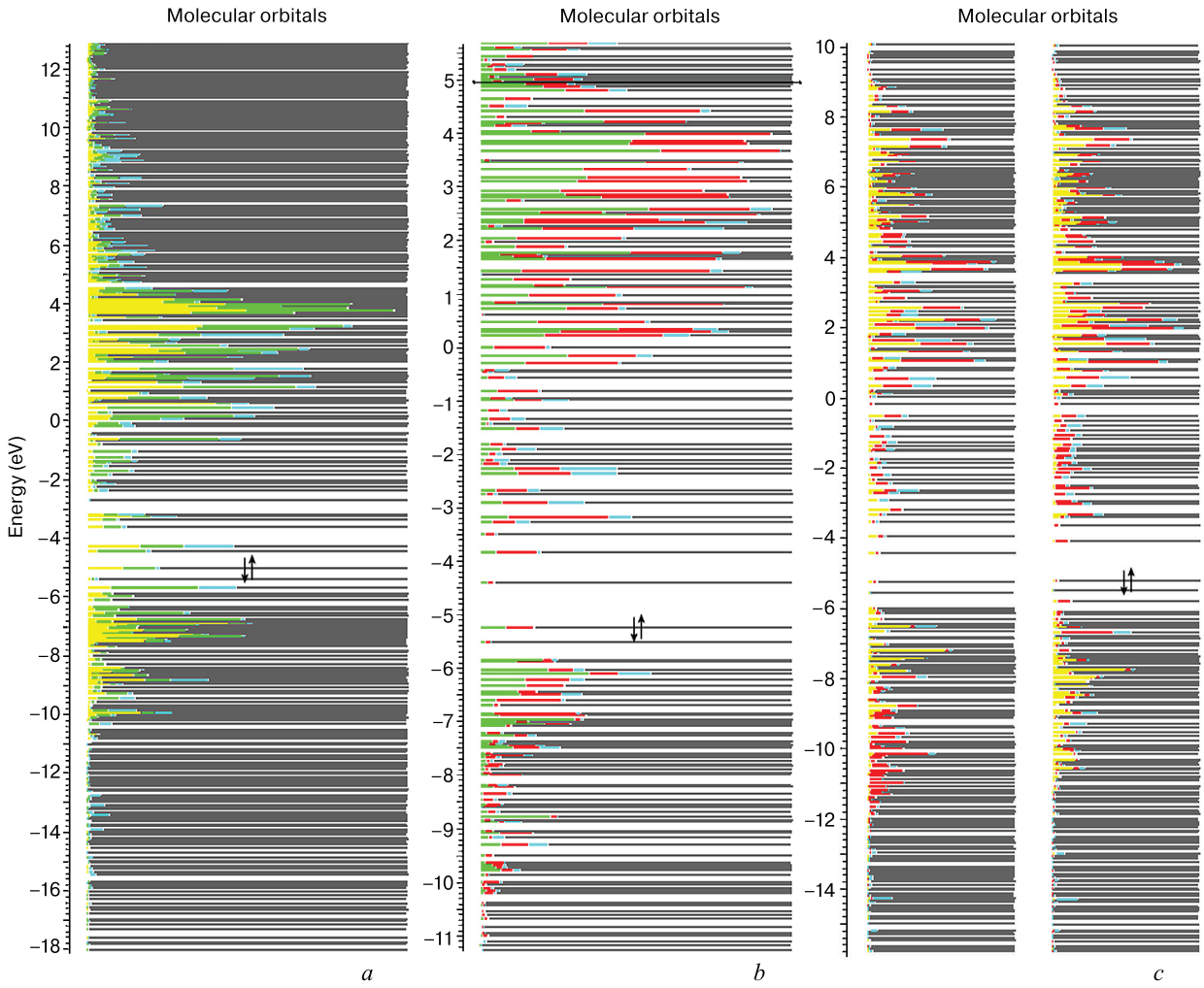

Figure 3. One-electron spectra of metal-carbon composites based on PPAN with introduced metal pairs: (*a*) Ni-Co-Sil; (*b*) Fe-Co-Si; (*c*) Ni-Fe-Si. The Fe orbitals are highlighted in red, Ni in yellow, Co in green, Si in blue, and the rest of the atoms in gray. The last occupied molecular orbital is marked with two arrows representing the electron spins.

Table 3. Charges on metal atoms in MC APT charges

Metal	Charges on metal atoms		
	Fe-Co-Si/PPAN	Ni-Co-Si/PPAN	Ni-Fe-Si/PPAN
Fe	–	-0.0051	–
Ni	–	–	0.0774
Co	0.1626	0.0055	–
Cu	0.0593	–	-0.0280
Si	0.8503	0.2032	-0.1201

Furthermore, we calculated bond energies for all the test structures (Table 2) which proved to be comparable with those of pure PPAN, confirming the stability of the metal-carbon complexes obtained.

Analysis of the charge distribution retrieved with atomic polar tensor charge (APT charge) method [35] showed that the metal atoms are positively charged for all the systems, the closest neighborhood atoms being negatively charged. Thus there is electron density transfer from the metal atoms to the PPAN monolayer atoms. The charges on metal atoms are shown in Table 3. These results agree well with the existing viewpoint on the interaction between metals and the conjugated bond system in PPAN. The electron clouds of the metal atoms shift towards the nearest atoms of the PPAN monolayer.

3. Conclusions

The theoretical studies carried out in this work showed that the PPAN monolayer based metal-carbon composites with embedded Ni-Co, Fe-Co and Ni-Fe metal atom pairs and silicon amorphizing admixture are stable systems. Metal introduction into PPAN reduces the band gap in comparison with that of pure PPAN due to the additional metal levels near the band gap edge. All the systems considered herein are semiconductors by conductivity type. These metal composites can be used as new magnetically soft materials capable of absorbing electromagnetic radiation due to possible electron transfers involving the new metal atom levels.

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