Journal of Materials Science & Technology 31 (2015) 979–985

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Spin States of 2D Nanocomposites of Ni and V Nanoclusters on Hexagonal *h*-BN, BC_3 and Graphene

P. Avramov [1,*], A.A. Kuzubov [2,3], S. Sakai [4], S. Entani [4], H. Naramoto [4], N. Eliseeva [2]

[1] *Kyungpook National University, 1370 Sankyuk-dong, Buk-gu, Daegu 702-701, Republic of Korea*
[2] *Siberian Federal University, 79 Svobodniy av., Krasnoyarsk 660041, Russia*
[3] *L.V. Kirensky Institute of Physics SB RAS, Krasnoyarsk, Academgorodok 660036, Russia*
[4] *Advanced Science Research Center, Japan Atomic Energy Agency, 2-4 Shirakata Shirane, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan*

ARTICLE INFO

Article history:
Available online 20 August 2015

Key words:
Electronic structure
Metal nanostructure
Nanocomposites
Graphene
h-BN
BC_3
Spin states

Atomic and electronic structures of adsorbed nickel and vanadium atoms and nanoclusters (Ni_n and V_n, $n = 1–10$) on hexagonal *h*-BN and BC_3 lattices were studied using DFT PBE/PBC/PW (Perdew–Burke–Ernzerhof potential of density functional theory/periodic boundary conditions/plane wave basis set) technique. For the sake of comparison the structure and properties of the same nanoclusters deposited on pristine graphene were calculated as well. It was found that for all types of supports an increase of *n* from 1 to 10 leaded to decrease of coordination types from η^6 to η^2 and η^1. The *h*-BN- and BC_3-based nanocomposites were characterized by high (up to 18 μ for Ni_{10}/BC_3) magnetic moments of the nanoclusters and featured by positive binding energies. The graphene-based nanocomposites revealed energetic stability and, in general, lower magnetic moments per unit cell. The direct potential energy barriers for migration of Ni η^2/η^2 and η^6/η^6 types of dimers on graphene were low (10.9–28.9 kJ/mol) with high reverse barriers for η^6/η^6 dimers, which favored dynamically equilibrated Ni clusterization on graphene.

1. Introduction

The 2D layered nanocomposites consisting of metal nanoclusters on free-standing or deposited graphene, *h*-BN or hexagonal BC_3 have attracted intensive interests because of their promising applications in nanoelectronics, nanospintronics, chemical catalysis and energy storage. Hexagonal 2D lattices of graphene[1], *h*-BN[2] and BC_3[3] are perfect 2D hexagonal substrates of one-atom thickness to create elements of nanoelectronics, nanospintronics and energy storage devices[4–6].

The structure and properties of deposited graphene on transition metal (TM) surface and TM adatoms on graphene were studied previously using theoretical and experimental methods, and well-arranged reviews can be found elsewhere (see, for example[7,8]). In comparison with graphene- and *h*-BN deposited on transition metal surfaces, the composites involving TM adatoms and their nanoclusters are much more attractive due to the perspectives of applications for nanospintronics and heterogeneous catalysis.

Several experimental studies of the formation of TM nanoclusters on graphene have been published up to date. The nucleated island density *n* was measured as a function of growth parameters for several kinds of transition metals[9] with specifically high *n* for Fe nanoclusters. It increases continuously with the deposited amount and shows no temperature-dependence. These unusual results indicate the presence of long-ranged repulsive interactions between the Fe adatoms. The adsorption of Au and Pt atoms and their dynamical behavior on graphene have been also investigated in Ref. Gan et al. [10]. *In situ* experiments at 600–700 °C discovered the two-dimensional diffusion within the plane as well as the one-dimensional diffusion along the open edges (activation energies of 2.3–2.5 eV). It was shown that Au and Pt atoms strongly interact with carbon atoms of graphene. In the study of Fe, Gd, Dy and Eu on graphene, the 3D island growth morphology was commonly confirmed[11]. In contrast to Eu, upon thermal annealing, the Fe, Gd, and Dy nano-islands display a small decrease of island density and an increase of the height/width aspect ratio. The annealing of Eu islands at 365 K results in the formation of a close flat film. The structure and formation mechanisms of defect graphene-based nanocomposites with Fe, Co and Mo adatoms were experimentally studied by scanning transmission electron microscopy[12]. The 0.1 nm defects were created by focused electron beams to trap migrating Fe, Co and Mo atoms. It was found that single metal atoms or clusters could be localized in or on graphene layers.

Based on the investigation of the adsorption energies and diffusion barriers of the relevant metal adatoms on graphene using *ab initio* calculations[11], it was predicted that most of the

* Corresponding author. Ph.D.; Tel.: +82 53 9506342; Fax: +82 53 9506330.
E-mail address: paul@iph.krasn.ru (P. Avramov).

http://dx.doi.org/10.1016/j.jmst.2015.08.008

transition, noble and rare earth metals on graphene should exhibit a 3D growth. Most of the metal nanostructures on graphene should be also stable against the further aggregation. The Fe, Co, Ni, Pt, and Gd islands on graphene can serve as good candidates for surface-supported catalytic applications due to their 3D morphology and high thermal stability. The Zr/graphene binding energies were obtained in zirconium-coated graphene sheets at several coverages by employing *ab initio* calculations[13]. It was found that the increase of the Zr/C coverage ratio leads to the clusterization of Zr atoms. The Zr–graphene binding involves the charge transfer to graphene, which comes from the 5*s* orbital of Zr and also depends on the coverage ratio.

Extensive *ab initio* density-functional calculations were performed to investigate the structural, magnetic, and electronic properties of Ni_n and Fe_n nanostructures ($n = 1$–4) adsorbed on hydrogen passivated zigzag graphene nano-ribbons (ZGNR)[14]. It was found that both Ni and Fe atoms are strongly bound at ZGNR. The Ni_n nanostructures are more strongly bound than Fe_n nanostructures, and their atoms had much smaller spin magnetic moments. In particular, Ni_n/ZGNRs always have the lowest energy with antiparallel edge spins, whereas among Fe_n/ZGNRs only one- or two-atom adsorbed clusters are antiferromagnetic. A combined experimental (Scanning Tunneling Microscopy (STM), X-ray Absorption Spectroscopy (XAS), X-ray Magnetic Circular Dichroism (XMCD)) and theoretical (*ab initio* generalized gradient approximation (GGA) plane wave (PW)) study[15] of atomic structure and magnetic properties of TM_n/graphene/SiC(0001) nanocomposites (TM = Fe, Co, Ni; $n \geq 1$) reveals nonmagnetic ground state of single Ni and Co adatoms. Increasing of n ($n \geq 1$) leads to magnetic states for Ni_n nanoclusters up to 0.85 μ per each Ni atom. Ni/graphene nanocomposites with perfect and defect graphene have also been studied using theoretical approaches[16,17]. It was found that the defects in graphene lattice strongly affect the electronic structure and magnetic properties of the metal complexes, increasing the binding strength of the TM cluster on to the graphene substrate. Size-dependent atomic and electronic structures of a set of vanadium clusters V_n ($n = 2$–5) on graphene were studied using *ab-initio* GGA DFT (density functional theory) calculations[18]. It was discovered that low-dimensional V_n clusters are easily formed on graphene with nonmagnetic state as the most stable magnetic configuration.

In the present study, the atomic and electronic structures and spin states of a set of 2D TM_n/*h*-BN and TM_n/BC_3 (TM = Ni, V) complex nanocomposites were studied using the PW PBE (Perdew–Burke–Ernzerhof) electronic structure calculations within the periodic boundary conditions (PW PBE PBC). For the sake of comparison the TM_n/graphene nanocomposites were calculated using the same method of electronic structure calculations. It was found that in contrast with graphene-based nanocomposites, the formation of TM_n/*h*-BN and TM_n/BC_3 ones is endothermic process. The increase of the number of atoms in Ni_n nanoclusters leads to the increase of the magnetic moments per unit cell and the decrease of the coordination degree of nickel atoms. The formation of Ni nanoclusters on graphene proceeds through the migration of nickel adatoms across hexagonal lattice with the direct/reverse potential energy barriers of migration, 10.9–28.9/15.1–80.3 kJ/mol, through η^2-type transition states. The analysis of the density of states clearly demonstrates the spin polarization of the supports induced by adsorbed TM adatoms and nanoclusters.

2. Method of Electronic Structure Calculations and Nanocomposite Structure Models

To study the atomic and electronic structures of 2D nanocomposites, Kohn–Sham DFT PW basis sets, Projector Augmented Wave (PAW) formalism[19], Grimme correction of weak dispersion interactions[20] and PBE DFT potential[21] in PBC were used. For all calculations the cutoff energy (E_{cutoff}) was equal to 400 eV. The VASP code[22] was employed to perform all electronic structure calculations. The geometry of the nanocomposites was optimized until residual forces became less than 0.1 eV/nm. The Γ-centered Monkhorst–Pack[23] ($3 \times 3 \times 1$) *k*-point Brillouin zone sampling scheme was used. The binding energies of the nanocomposites were estimated using the following equation:

$$E_b = E_{TM/sup} - E_{TM} - E_{sup}$$

where E_b is the binding energy of a nanocomposite, $E_{TM/sup}$ is the total energy of TM/support nanocomposite, E_{TM} is the total energy of free-standing TM_n nanocluster and E_{sup} is the total energy of *h*-BN, BC_3 or graphene support.

The atomic hexagonal lattices of *h*-BN and graphene are well known and the detailed illustrations will not be shown for simplicity. For *h*-BN the $8 \times 8 \times 1$ supercell with $a = b = 1.9909$ nm translation vectors was used. For graphene, the same $8 \times 8 \times 1$ supercell of elementary hexagonal unit was employed with $a = b = 1.9690$ nm translation vectors. The BC_3 hexagonal lattice is presented in Fig. 1. The BC_3 unit cell consists of two types of hexagons C_6 and C_4B_2 with two different types of chemical bonds (C–C and B–C)[4]. To calculate the TM/BC_3 composites (TM = Ni, Co, V), the $4 \times 4 \times 1$ supercell with $a = b = 2.0577$ nm translation vectors was employed. To avoid unphysical interactions between the PBC partners, the vacuum interval along *c* direction was equal to 2.00 nm in all cases.

The process of clusterization of TM atoms on the substrates starts from adsorption of single adatoms and consecutive formation of dimers, trimers, etc. and, finally TM_n nanoclusters. To study the initial stages of clusterization, knowledge about the structure and spin states of single adatoms, dimers and trimers is important. As an example of larger clusters, the Ni_{10} and V_{10} which can be formed as single- and double-layered structures were studied as well. All possible initial types of coordinations and atomic configurations of TM_n ($n = 1, 2, 3, 10$) on graphene, *h*-BN and BC_3 substrates were optimized using electronic structure calculations, but only a few structures were located. All optimized final structures of the nanocomposites are discussed in the text below.

Here and thereafter, we denote the coordination of a metal adatom at a middle of a chemical bond of hexagonal support lattice as η^2 type of coordination (see, for example, Fig. 2). The η^6 type of coordination means a complex bond between the metal and the center of hexagonal fragments (C_6 for graphene, B_3N_3 for *h*-BN and C_6 and B_2C_4 for BC_3, respectively). And finally the η^1 type denotes the coordination by one atom of the hexagonal lattices under consideration. For *h*-BN and BC_3-based composites, the actual sites of η^1 type of coordination are marked by chemical symbol of host lattice atom. For example, the B:η^1 denotes the coordination either by boron of BC_3 or *h*-BN, whereas N:η^1 denotes coordination of an adatom by nitrogen of *h*-BN support. For bilayer clusters η^1/η^1 and η^1/η^6 notations denote the coordination of atoms of the first metallic layer at η^1 or η^6 sites and η^1 type of coordination of the atoms of the second layer.

3. Results

3.1. Single Ni and V adatoms on h-BN, BC_3 and graphene

The details of atomic and electronic structures of Ni and V adatoms on *h*-BN, BC_3 and graphene are presented in Table 1 and Figs. 2 and 3. It is found that all three hexagonal lattices feature the η^6 coordination type of the adatoms. In addition, Ni adatoms at N:η^1, B:η^1 for Ni/*h*-BN; Ni at C:η^1 for Ni/BC_3; Ni at η^2 for Ni/graphene and