Journal of Alloys and Compounds 692 (2017) 49–58

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ab initio study of stability and migration of point defects in copper-graphene layered composite

T.L. Yang [a], L. Yang [a, *], H. Liu [a], H.L. Zhou [a], S.M. Peng [b], X.S. Zhou [b], F. Gao [c], X.T. Zu [a]

[a] School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu, 610054, China
[b] Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, 621900, China
[c] Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI, USA

ARTICLE INFO

Article history:
Received 18 April 2016
Received in revised form
28 August 2016
Accepted 29 August 2016
Available online 30 August 2016

Keywords:
Copper-graphene composite
Defects
Ab initio calculation
Defect recombination

ABSTRACT

Ab initio calculations based on density functional theory have been performed to determine the relative stabilities and migration of point defects in a copper-graphene layered composite (a single graphene layer is inserted between multi Cu(111) layers, Cu/gr/Cu for short). The results indicate that the total trapping region around the graphene layer for point defects is about 15 Å, i.e. the interface in the composite consists of the graphene layer and three Cu layers on each side of the graphene. The interface reduces the formation of C vacancies with a lower formation energy than that in pristine graphene, but slightly affects the formation of C interstitials. However, the formation energies of Cu point defects near the graphene significantly decrease, compared to these in bulk Cu. The migration energy barrier of a C vacancy in the graphene layer of the composite is lower than that in the pristine graphene without full relaxation, while the migration energy barriers of Cu vacancies near the graphene are much smaller than that in the bulk. The Cu vacancies prefer to jump toward the interface center through the nearest neighbor Cu layers rather than jumping within the same Cu layer. The C and Cu interstitials favorably jump between the two nearest fcc sites by passing through a hollow site, and the migration of Cu interstitials in the interface is also easier than in bulk Cu. These results suggest that the interface in the Cu/gr/Cu composite provides a strong sink for trapping defects and preferring sites for their recombination.

1. Introduction

With the development of advanced nuclear energy systems, their internal materials require higher radiation tolerance, which is a challenge to currently available materials. In irradiation environment, displacement cascades under high-energy radiation lead to the generation of vacancies and interstitials, which will evolve into defect clusters, dislocations and grain boundaries within irradiated materials [1–7]. The synergistic interaction of those defects with the radiation-induced impurities would result in swelling, high temperature intergranular embrittlement, surface roughening and blistering. These phenomena would significantly degrade the mechanical properties of materials. Hence, the behaviors of the primary defects are important in microstructural evolution and changes in material properties subjected to irradiation environments, which have been investigated for many years [1–14].

Graphene, a single-atom-thick layer of sp^2-hybridized carbon atoms packed into a two-dimensional hexagonal crystalline, has exceptional physical mechanical, thermal and electronic properties which make graphene-based materials exceedingly promising [15]. Kim et al. [16] designed a nanolayered composite consisting of alternating layers of metal (copper or nickel) and monolayer graphene. They found that the two-dimensional geometry, high intrinsic strength, and modulus can effectively constrain dislocation motion, resulting in the significant strengthening of the metals. The effectiveness of graphene in blocking dislocation propagation cross the metal-graphene interface suggests that the synthesis of metal-graphene nanolayered composites may enhance the radiation damage resistance. Huang et al. [17] have investigated the radiation damage resistance and interface stability of copper-graphene nanolayer composite by molecular dynamics method. Their results show that the number of surviving point defects in the bulk region after displacement cascade is less than that of pure copper. Based on these results, they concluded that the copper-graphene composite exhibits excellent ability to resist radiation damage. However, it is known that the radiation tolerance of

* Corresponding author.
E-mail address: yanglildk@uestc.edu.cn (L. Yang).

http://dx.doi.org/10.1016/j.jallcom.2016.08.311
0925-8388/

materials depends on many factors, such as the number of surviving point defects produced in displacement cascades, the diffusion of point defects and the further evolution fate within the irradiated materials [1,4,5].

The interface of the copper-graphene nanolayered composite (Cu/gr/Cu) may act as sinks for defects, similar to grain boundaries [11,12], which is somewhat proved by the studies of Huang et al. [17]. However, further understanding of intrinsic point defects in the interface of the Cu/gr/Cu is important for exploring this composite as a radiation tolerance material. In this work, the effects of the interface of the Cu/gr/Cu on the formation and migration behavior of point defects were investigated using *ab initio* calculations based on density functional theory (DFT).

2. Methodology

The DFT calculations were performed using Vienna *ab initio* simulation package (VASP) code. Standard pseudopotential was obtained from the VASP library. The projector-augmented wave method was used to determine the interaction between ions and electrons [18,19], while exchange and correlation interactions were described by different functionals. Plane-wave basis sets with an energy cutoff of 400 eV were used to investigate the structural properties. Van der Waals (vdW) interaction corrections were introduced in the DFT calculations. The lattice constant of copper was calculated with Perdew-Burke-Ernzerhof (PBE) with and without vdW correction, see Table 1. It is found that the PBE without vdW correction predicts a higher lattice constant. Moreover, the previous studies indicate that the vdW correction plays a key role in describing the interaction of graphene/metal interfaces [20]. Available vdW correction methods of vdW-DF [21–23], DFT-D3 [24], DFT-TS [25], and TS+SCS [26] have been tried, as shown in Table 1. Here, different exchange correlations were considered for every vdW correction method. The vdW-DF includes the original vdW-DF, the "opt" functionals and the vdW-DF2. In Table 1, revPBE is original vdW-DF, but optB86b, optB88, and optPBE are "opt" functionals where the exchange functionals are optimized for the correction part. The rPW86 is the vdW-DF2 of Langreth and Lundqvist groups [23]. The dispersion coefficients in the DFT-D3 method of Grimme et al. [24] are geometry dependent and one more correction term is adopted. The exchange correlations of DFT-D3 include PBE, PBEsol, revPBE and RPBE, which GGA parameters are PE, PS, RP and RE, respectively. The dispersion coefficients and damping function of the DFT-TS method are charge-density dependent. However, in the TS+SCS method, Tkatchenko et al. [26] proposed a computationally efficient way to account for electrodynamic response effects and the interaction of atoms with the dynamic electric field due to the surrounding polarizable atoms.

It is found that the lattice constants obtained by vdW-DF method with optB86b and optB88 are close to the experimental value, while the other exchange corrections evidently overestimate the lattice constant. The DFT-D3 and DFT-TS methods underestimate the lattice constant, although the TS scheme was used in Ref. [20]. The vdW correction of TS+SCS predicts well the lattice constant of copper. The lattice constant of a pristine graphene (pri-graphene) calculated by the vdW-DF with optB86b and TS+SCS vdW correction to PBE GGA functional are 2.466 Å and 2.465 Å, which are close to the experiment value of 2.46 Å [28]. Based on these results, the vdW-DF with optB86b and TS+SCS vdW correction to PBE GGA functional were used in the following Cu/graphene (Cu/gr) interface calculations.

The geometry of the Cu/gr/Cu composite used in the present work was decided based on the stable structure of the Cu/gr interface that was modeled by a slab of seven (5×4) Cu atomic layers of (111) planes and a vacuum gap of 20 Å with a graphene on the top layer of Cu. The top five atomic layers were allowed to relax freely, while the bottom two layers were fixed. Brillouin zone (BZ) sampling was performed using the Monkhorst-Pack scheme with $4 \times 4 \times 1$ k-point meshes. The Cu/gr interlayer distance and binding energies for three interface geometries (top-hcp, top-fcc and fcc-hcp) [20,29] are displayed in Table 2, along with the results in Ref. [20] for comparison, where top, hcp and fcc are defined according to the adsorption sites on the (111) surface of face-centered cubic (fcc) lattice [30], for example, the top-hcp geometry means the C atoms are located on the top and hcp adsorption sites on the Cu(111) surface. It is clear that the binding energy and the interface distance obtained by optB86b are closer to those of TS (DMOL) vdW correction in Ref. [20]. In addition, as described above, the optB86 is also proper to reproduce the structures of fcc Cu and pri-graphene. Thus, the vdW-DF with optB86b correction is chosen in the following calculations. Both TS+SCS and optB86b predict that the interfaces of top-fcc and top-hcp are slightly more stable than fcc-hcp due to the higher binding energy, although their interface distances and binding energies are different for the two vdW corrections. Therefore, based on the most stable Cu/gr interfaces, top-fcc and top-hcp, the sandwich structure of Cu/gr/Cu composites was built by adding four copper atom layers above the graphene along [111] direction of fcc Cu in three ways [20]. We calculated the total energies of six geometries of Cu/gr/Cu interfaces (fcc-top-fcc, hcp-top-fcc, top-top-fcc, fcc-top-hcp, hcp-top-hcp, and top-top-hcp), and found that the fcc-top-fcc interface (see Fig. 1) is the lowest-energy structure and the vertical distances between the graphene and the two nearest Cu layer are similar, about 3.38 Å.

The calculations of point defect properties in the interface of a Cu/gr/Cu composite were mainly carried out in a 132 atom supercell (named box1) with a fcc-top-fcc interface, as shown in Fig. 1, which is a composite containing a graphene at the center of an fcc Cu structure. The box1 contains 108 Cu atoms and 24 C atoms. Two more supercells (box2 and box3) with different sizes were used to

Table 1
Lattice constant (Å) of copper for different vdW corrections in GGA, along with the result of PBE without vdW correction and experimental data.

vdW correction method	Exchange correlation	Lattice constant
vdW-DF	optB86b	3.601
	optB88	3.628
	optPBE	3.651
	revPBE	3.705
	rPW86	3.750
DFT-D3	PBE	3.567
	PBEsol	3.515
	revPBE	3.575
	RPBE	3.535
DFT-TS	PBE	3.546
TS+SCS	PBE	3.607
No vdW	PBE	3.635
Expt.		3.615 [27]

Table 2
Properties of Cu/graphene interfaces: binding energy E_b (eV) and interface distance $d_{Cu\text{-}gr}$ (Å) calculated by different vdW corrections.

Stacking	GGA + vdW						LDA (DMOL) [26]	
	TS+SCS		optB86b		TS (DMOL) [20]			
	E_b	$d_{Cu\text{-}gr}$	E_b	$d_{Cu\text{-}gr}$	E_b	$d_{Cu\text{-}gr}$	E_b	$d_{Cu\text{-}gr}$
top-fcc	0.17	3.50	0.07	3.38	0.03	3.46	0.15	2.31
top-hcp	0.17	3.55	0.07	3.38	0.03	3.46	0.13	2.82
fcc-hcp	0.16	3.50	0.06	3.39	0.02	3.70	0.10	3.20