Computational Materials Science 156 (2019) 104–110

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Coalescence and epitaxial self-assembly of Cu nanoparticles on graphene surface: A molecular dynamics study

Ping-Chi Tsai[a,*], Yeau-Ren Jeng[a,b,*]

[a] *Department of Mechanical Engineering, National Chung Cheng University, Chia-Yi 621, Taiwan*
[b] *Advanced Institute of Manufacturing with High-Tech Innovations, National Chung Cheng University, Chia-Yi 621, Taiwan*

ARTICLE INFO

Keywords:
Nanoparticles
Graphene
Molecular dynamics
Coalescence
Melting
Nucleation

ABSTRACT

A detailed understanding of surface decoration and interconnecting technologies is essential in realizing high-performance functional devices incorporating metal nanoparticle/graphene nanohybrids. This study employs classical molecular dynamics (MD) simulations to investigate the formation of amorphous copper (Cu) layers on a graphene surface via the collision, coalescence and nucleation of individual Cu nanoparticles (NPs) at temperatures in the range of 300–1300 K. The results indicate that the coalescence and melting temperatures are both sensitive to the particle size and the presence of the substrate. Moreover, an epitaxial interaction is found between the Cu NPs and the graphene substrate, in which mobile Cu atoms are captured and dragged to the graphene surface to produce self-assembled NP layers via a nucleation process. A series of structural evolutions and phase transitions are revealed during the thermalization process of the NPs. Finally, the results show that the presence of the substrate and associated contact epitaxy phenomenon play a key role in governing the structural morphology and thermal behavior of the Cu NP-based thin film.

1. Introduction

Graphene-based nanomaterials, e.g., carbon nanotubes (CNTs), carbon nanohorns (CNHs), and carbon nanofibers (CNFs), have attracted significant attention for their potential application in surface decoration and coating technologies [1–5]. The controlled deposition of metal, alloy, metal oxide and semiconductive nanoparticles (NPs) on graphene surfaces has drawn particular interest. The resulting NP-graphene hybrids have emerged as an important class of compounds, with electronic, magnetic, optical, chemical and mechanical properties which differ greatly from those of the bulk material and are governed mainly by the effects of the NP-graphene interactions [6–10]. For such materials, the material parameters, e.g., the particle size, morphology and structure, play a vital role in determining the surface energy and binding activity at the NP-graphene interface and facilitate the nucleation and immobilization of supported NPs along *in-plane* graphene domains [11–14].

Many studies have shown that post-synthesis thermal treatment provides an effective strategy for optimizing the NP-graphene interactions by tailoring the material parameters, e.g., the particle size, surface faceting, and near-surface elemental distributions. Habenicht et al. [15] demonstrated that the shape and size of the NPs formed through the annealing of Au film on a graphene surface are dependent on the temperature and film thickness. Xi et al. [16] employed a thermal annealing process to realize the controlled growth of Au NP-embedded porous graphene thin films for electrochemical sensing applications. Similarly, Iyer et al. [17] used a thermal annealing process to control the freestanding geometries of Au nanostructures on graphene in order to improve the surface-enhanced Raman spectroscopy (SERS) effect. Félix et al. [18] showed that graphene surfaces decorated with bimetal PtNi NPs and processed by controlled thermal annealing have both excellent magnetic properties and pronounced hysteresis loops. Grillo et al. [19] showed that the nobilities and aggregations of Pt NPs on graphene exhibit a size- and temperature-dependent scaling effect.

In general, the studies above show that thermally-controlled nanostructure decoration of graphene plays a key role in determining the properties of the resulting NP-graphene hybrids. Furthermore, the graphene surface not only serves as a nano-support with a relatively huge surface area, but also as a stabilizer which anchors the catalytically active metallic NPs. Therefore, to optimize the performance of NP-graphene hybrids, it is essential that the growth of metal nanostructures on graphene substrates be properly understood. However, relatively few investigations have been performed on the processes and mechanisms involved in the thermally-induced diffusion and epitaxial nucleation of Cu nanostructures on graphene surfaces. In particular, no previous studies have performed a comparative investigation into the

---

[*] Address: Department of Mechanical Engineering, National Chung Cheng University, Chia-Yi 621, Taiwan.
E-mail addresses: pctjbenchen@gmail.com.tw (P.-C. Tsai), imeyrj@ccu.edu.tw (Y.-R. Jeng).

https://doi.org/10.1016/j.commatsci.2018.09.039
Received 23 April 2018; Received in revised form 7 September 2018; Accepted 17 September 2018
0927-0256/

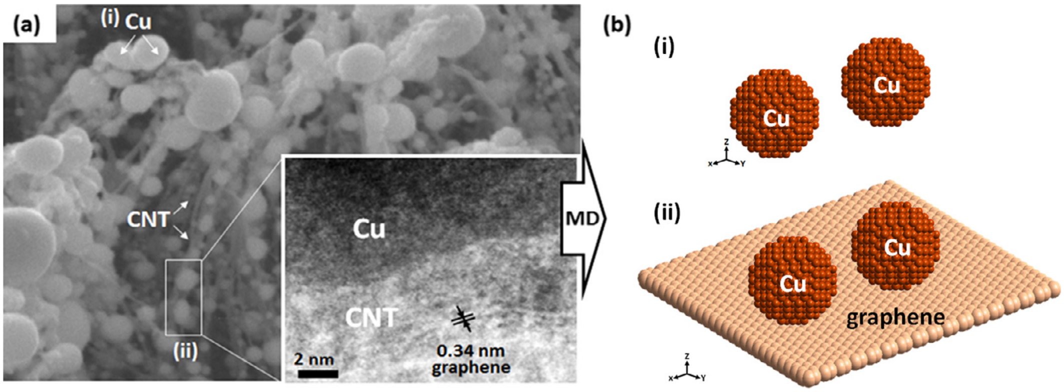

Fig. 1. (a) SEM and HRTEM images of Cu nanoparticle-decorated graphene surface [3], and (b) schematic representations of MD simulation models for Cu NPs (i) without and (ii) with a single-layer graphene sheet, respectively.

structural evolution and thermal stability of heat-treated Cu NPs with and without the presence of a graphene substrate, respectively.

Accordingly, this study employs classical molecular dynamics (MD) simulations to explore the coalescence, nucleation and melting behaviors of Cu nanostructures with various particle sizes at temperatures in the range of 300–1300 K. To clarify the effect of graphene as a support on the thermodynamic performance and thermal stability of the Cu NPs, the simulations are performed both with and without the presence of a graphene substrate, respectively.

2. Simulation methodology

Fig. 1(a) presents a scanning electron microscope (SEM) image and high-resolution transmission electron microscope (HRTEM) image of a Cu NP-decorated graphene surface [3]. Fig. 1(b) shows the two simulation scenarios considered in the present study, namely the coalescence and melting behavior of two Cu NPs in the absence of single-layer graphene sheet (Fig. 1(b)(i)) and in the presence of single-layer graphene sheet (Fig. 1(b)(ii)), respectively.

Due to the large time scales (of the order of 10^6 ps) involved in simulating the Cu NP coalescence and melting processes, the CsbndC interactions are modeled using the Tersoff-Brenner many-body potential [20–25]. This potential has many advantages for numerical modeling, including its simplicity and generality, a good agreement between the simulation results and the experimental observations or empirical interatomic calculations, and a much lower computational cost than quantum mechanics-based methods. As a result, it is ideally suited to the present problem involving carbon-based nanostructures and a relatively large graphene surface area. In implementing the simulation model, a periodic boundary condition is imposed on the graphene substrate to ensure homogeneous thermal conditions and maintain lattice symmetry. The graphene substrate consisted of a square single-layer graphene with a network of sp^2-hybridized carbon atoms, which were organized into a hexagon. Moreover, the Morse potential is adopted to model the Cu-Cu atomic interactions in the Cu NPs. Although the accuracy of the Morse potential does not match that of the tight-binding (TB) [26] and embedded-atom-method (EAM) [27] potentials, it is nevertheless adopted in the present study due to its simplicity, computational efficiency and proven ability to provide qualitative estimates [28–31]. Finally, the interatomic potentials between the Cu and C atoms are described using the Lennard-Jones (*L-J*) potential, where the *L-J* parameters (e.g., the collision diameter ($\sigma_{Cu\text{-}C}$) and energy depth ($\varepsilon_{Cu\text{-}C}$)) are calculated using the Lorentz-Berthelot mixing rule (see Table 1).

In this MD study, for the case of the isolated NPs upon graphene sheet, the workpiece is divided into three different zones, namely, the fixed-atom zone, the thermostat-atom zone, and the Newton-atom zone, as shown in Fig. 2. The fixed atoms are arranged at the ends of the graphene sheet (i.e. atomic motion is completely suppressed at the end of graphene sheet). A total of 3564 atoms are then arranged adjacent to the fixed atoms at either end of graphene sheet. These atoms are used to simulate thermostatic effects in the graphene sheet and to guarantee that the equilibrium temperature efficiently approaches the desired value. The graphene sheet contains 9046 free atoms in the Newton-atom regions. These atoms are arranged between the two thermostat atom regions in the graphene sheet and their displacements are governed by Newton's equations of motion. To identify the thermal processes which take place as the NPs coalesce and melt, the present simulations trace the structural changes of the NPs under constant volume and temperature conditions (i.e., an NVT ensemble) using the Nose-Hoover thermostat [32] and the Verlet algorithm [33], in which a time step (Δt) of 1 fs is applied to ensure the optimal integration of the motion and energy conservation equations. As in the simulation study of Kayhani et al. [34] on the coalescence of Pt clusters, the present simulations apply an initial time step of 2×10^4 ps to bring the MD model into equilibration at a temperature of 300 K before heating. The temperature is then gradually increased toward a maximum value of 1300 K at a rate of 10 K per time step. For each specified temperature, energy minimization is performed with 10^4 MD steps (Note that a similar technique was used to avoid variations in the initial structure energy by Ding et al. [35] and Tsai et al. [36]). To clarify the size effect on the coalescence and melting characteristics of the Cu NPs, the simulations consider Cu NPs comprising various numbers of atoms (Cu_N), namely N = 462, 982, 1788, 3185, 4512, and 7098. After the end of the equilibration process, the different nanoparticle sizes with diameters of D = 19.2, 27.8, 35.6, 42.2, 48.4, and 57.8 Å are corresponding to Cu_{462}, Cu_{982}, Cu_{1788}, Cu_{3185}, Cu_{4512}, and Cu_{7098} NPs, respectively.

Table 1
Pair potential parameters between nanoparticle atoms and substrate.

Atomic pair	ε (eV)	σ (Å)
CsbndC	0.004555	3.851
CusbndCu	0.167	2.314
CsbndCu	0.02578 (=$(\varepsilon_C \varepsilon_{Cu})^{1/2}$)	3.0825 (=$(\sigma_C + \sigma_{Cu})/2$)

3. Results and discussions

Fig. 3 shows the relationship between the potential energy (PE) per atom in the two representative Cu_{982} NPs with a diameter of 27.8 Å and the temperature for the two different scenarios considered in the present study, namely with (lower black line) and without (upper red line) the presence of a graphene substrate, respectively. For both scenarios, the PE of the Cu NPs increases with an increasing temperature. Interestingly, the PE of the NPs supported by the graphene substrate is less than that of the unsupported NPs for all values of the temperature. This