Stability and Melting of FCC Truncated Octahedral Ag Nanoparticles by Molecular Dynamics Simulation

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1. Introduction

Ag nanoparticles (NPs) have been successfully used in bonding of flexible electronics [1] and as a replacement of lead based solders [2]. Fundamental understanding of the thermal properties of the Ag NPs could improve the bonding process. Metallic NPs have lower melting points (T_m) than bulk materials and could exist in different solid configurations [3]. The stable solid phase is known to be formed based on the minimization of the surface energy and the internal strain of the NP. High curvature of very small NPs increases the surface energy of the particle. In general, icosahedral configuration is characterized by high internal strain and low surface energy, makes it a favorable structure for the smallest NPs. Decahedral configuration is stable for intermediate sizes of NPs due to its higher surface energy and lower internal strain. Large NPs mostly exist in FCC truncated octahedral configuration, which is characterized by low internal strain and high surface energy. However, metallic NPs may not follow these rules due to possible kinetic effects playing a role in formation of the stable solid configuration. Solid to solid phase transitions has been observed during heating of NPs and may have been driven by thermal and kinetic effects [3]. In this work, molecular dynamics (MD) simulation based on embedded atom method (EAM) [4] has been applied to determine melting points (T_m) of FCC truncated octahedral Ag NPs in size range of 1.2 to 20 nm and to determine their solid phase stability. The melted NPs were cooled down to room temperature to find the freezing points and the frozen solid structure toward drawing a phase map of stable solid phases at each size and temperature.

2. Computational Methods

The performed simulation was based on voter-chen version [5] of embedded atom method (EAM). The atoms in each NP were initially constructed based on FCC truncated octahedral configuration shown in Fig. 1. Each NP was relaxed at 300 K, heated periodically up to 1675 K, and then cooled down with the same rate to 300 K (room temperature). The holding time at each temperature was 20 picoseconds with a step size of 2 femtoseconds. The temperature of the NP was calculated based on equation (1)

$$T = \frac{2\langle E_k \rangle}{k(3N-6)} \qquad [1]$$

where E_k is the total kinetic energy of all atoms in the NP, k is Boltzmann constant, and N is the total number of atoms.

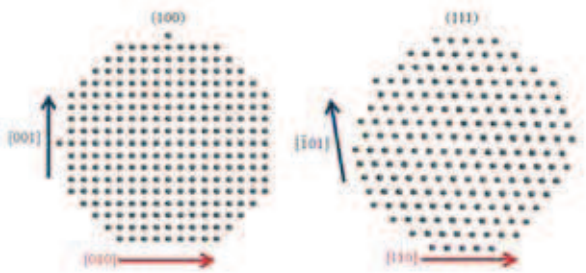

Fig. 1. Initial atomic arrangement of the 4 nm Ag particles showing (100) and (111) facets of the truncated octahedral configuration [3].

3. Results and Discussion

Fig. 2 shows the atomic arrangement and average PE values during heating and cooling of 1 nm Ag particle. Point A is the initial constructed FCC octahedral configuration. The NP passed through dynamic coexistence melting (DCM) during heating to point I, which means that the NP transits between the solid icosahedral structure at points C,E,F,H, and I and the quasi-liquid phase at points B, D, and J. The amorphous configuration is identified as quasi-liquid since the NP diameter is less than the minimum thickness of liquid Ag (1.8 nm) [6]. The quasi-liquid state shows higher average PE values than the icosahedral structure. At temperatures higher that Point I, The NP remained in the quasi-liquid-state. Thus, Point I can be considered as the T_m of the NP. During the cooling cycle, the NP froze into an icosahedral configuration at point M, which is lower than T_m showing the thermal hysteresis between melting and freezing. The NP remained into the icosahedral structure as NP cooled down to room temperature at point N.

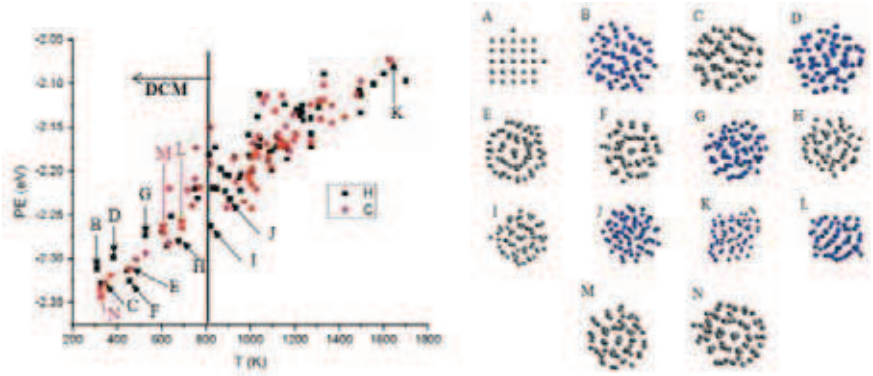

Fig. 2. (a) Potential energy (PE) values during heating and cooling cycles of 1 nm (65 Atoms) Ag particle. The vertical line shows the border between DCM and the quasi-liquid phase (b) Atomic arrangement of the particle at different temperatures shown by letters on the PE curve. Atoms are represented by dots [3].

Simulation of 1.2 nm and larger NPs has not shown DCM. The 1.2 nm particle remained stable below 385 K and then transformed to the icosahedral configuration. larger NPs remained stable in the FCC truncated octahedral during heating below the melting point of the NP. The melting points increased as the NP size of the particle increased and reached the bulk T_m at 20 nm particle. Thermal hysteresis between melting and freezing occurred for all sizes of NPs. The 2.8 nm particle froze into decahedral configuration showing the stable configuration while smaller NP froze into the icosahedral structure.. Larger NPs froze into different solid configurations that are still under investigation.

4. Conclusions

Based on freezing of liquid droplets, the most favorable structure for 2.8 nm Ag NP is decahedra. Smaller NPs froze into icosahedral structure while larger NPs showed different morphologies that are still under investigation. FCC truncated octahedral NPs of 1 nm is not stable at room temperature while the 1.2 nm is only stable below 385 K. Larger FCC truncated octahedral NPs are stable below T_m of the particle. Thermal hysteresis between melting and freezing were observed for all simulated sizes. This work aims toward constructing a phase map of Ag NPs at different sizes and temperatures.

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