

Evaluation of Interfacial Bonding Utilizing Ag₂O-Derived Silver Nanoparticles Using TEM Observation and Molecular Dynamics Simulation

Tomo Ogura*, Masumi Nishimura, Hiroaki Tatsumi, Naoya Takeda, Wataru Takahara and Akio Hirose

Division of Materials and Manufacturing Science, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

Abstract: The interfacial bonding utilizing Ag₂O-derived silver nanoparticles was evaluated using TEM observation and molecular dynamics simulation. The TEM observation reveals that the crystal orientation of the sintered silver corresponded to that of the gold substrate. This is considered that the epitaxial layer of silver was formed through in-situ formation of silver nanoparticles from Ag₂O paste, and oriented in the direction of the gold crystal. MD simulation successfully recreated the sintering behavior of silver nanoparticles and the gold substrate. The simulation results clearly showed the epitaxial layers of silver atoms were formed on the substrate. The existence of the closed pore indicates the acceleration of the sintering between nanoparticles and the gold substrate to minimize the total sum of surface energy and grain boundary energy.

Keywords: Silver nanoparticle, molecular dynamics simulation, interfacial bonding, sintering, epitaxial layer.

1. INTRODUCTION

Electric devices are required to not only work successfully at elevated temperatures but also reduce power consumption when packaged. The bonding technology that can handle these requirements must be developed. In particular, workable alternatives to lead (Pb)-rich high melting point solders which contain chemical substances hazardous to the environment are indispensable. The difficulty in the development of alternative lead-free solders to be utilized at high temperatures arises from the requirement that the thermal characteristics ensure the long-term reliability of the metallic bonds between semiconductor-chip-mounted parts and various wiring connections. In particular, in addition to the fact that semiconductor-chip-mounted components (i.e., die-bonded parts) generate ever more heat and thus need ever better thermal resistance, the discharge characteristics of certain parts must be maintained to enable chips to operate stably [1, 2].

It is well known that when particles are reduced in size to less than 10 nm, their characteristics are different from those in the bulk state [3-5]: i.e. the melting point and the sintering temperature become detectably lower than that of the bulk state. Such a sintering phenomenon is based on the driving force originated from the large surface energy of the nanoparticles. If this activated nature of the nanoparticles efficiently affects the surface atoms of the bulk metal, a metal-to-metal bonding using the nanoparticles as a filler material can be achieved at a significantly lower bonding temperature than that in the conventional fusion welding or diffusion bonding. The unique properties of nanoparticles

could be used in bonding materials in electric devices in order to satisfy such a severe condition. The authors have proposed a novel bonding process using silver nanoparticles [6-9] that can be an alternative to the current micro soldering using a high-temperature solder, such as Pb-10Sn or Pb-5Sn. At the interface of the sintered silver and gold substrate, the crystal orientation of silver corresponds well to that of gold, indicating that the epitaxial layer of silver formed by the silver nanoparticles is oriented in the direction of the gold crystal. This technique has been widely accepted and Hu *et al.* has reported a silver paste directly condensed from the silver nanoparticle solution through centrifugation [10]. The authors recently developed the novel bonding process through in-situ formation of silver nanoparticles from Ag₂O instead of the filler material of the silver metallo-organic nanoparticles [11]. However, the precise study of the interfacial microstructure has not investigated yet. It is also important to clarify the initial stage of interfacial sintering of silver atoms on a substrate. Unfortunately the dynamics of the sintering process cannot be observed with conventional techniques, and therefore computational investigations are a useful tool to inquire into the atomic behavior of silver nanoparticle sintering [12].

In the present study, the interfacial microstructures utilizing Ag₂O-derived silver nanoparticles were evaluated using TEM, and the initial process of sintering silver nanoparticles on a gold substrate was investigated using molecular dynamics simulation. From the results obtained, the sintering mechanism for silver nanoparticles on a gold substrate will be discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Bonding Conditions Using Ag₂O Particles for TEM Observation

The size distribution of Ag₂O particles is 2~3 μ m. These particles were mixed with triethylene glycol (TEG) and

*Address correspondence to this author at the Division of Materials and Manufacturing Science, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan; Tel: +81-6-6879-7538; Fax: +81-8-6879-7570; E-mail: tomo.ogura@mapse.eng.osaka-u.ac.jp

processed to the paste for bonding. Bonded metal substrates were copper coated with gold. The schematic illustration of the bonded joint are shown in Fig. (1). The mixed paste was supplied on the surface of the lower substrate and the samples were preheated under particles-specific optimum temperatures in order to remove excess TEG. Subsequently, putting an upper substrate down on the lower one, then the specimens were heated up to 433 and 523K in a heating rate of 1K/s under 5MPa using an infrared heating furnace. Samples for SEM observation of the sintered silver layer were prepared using a microtome in order to avoid damaging the cross-sectional surface possibly. The thin sample of the silver/gold bonding interface was extracted using Focused Ion Beam (FIB) for TEM observation.

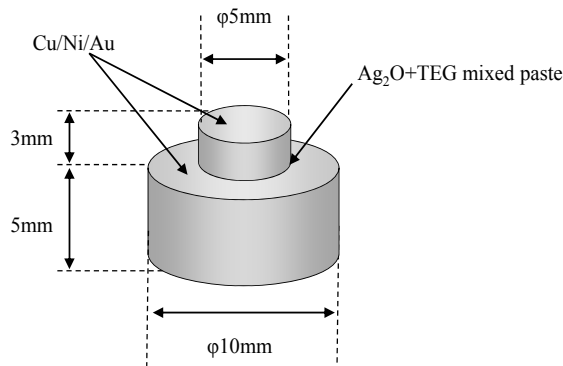


Fig. (1). Schematic illustration of the bonded joint.

2.2. Simulation Model

Molecular dynamics simulation was carried out using Materials Explorer 5.0 made by Fujitsu Ltd. For a potential function, GEAM04(Generalized Embedded Atom Method 04) was applied with cut off distance set to 1nm, whose actual potential data was referred to [13]. Two nanoparticles with (001) orientation (the sizes are 4nm) were set on the (011) gold substrate as shown in Fig. (2a). As close as the experimentally phenomena, the nanoparticle at right side is tilted with 45 degree from the one at left side. The simulated temperature was 523K. Periodic boundary condition was set over 1nm distance from the nanoparticle in order to remove the interaction between nanoparticles. The velocity of atoms below 1nm of the surface in a substrate was set as 0. For the recurrence model, periodic boundary condition was also set. In order to estimate the wettability of the nanoparticle, the neck size ratio, r_s , was referred to as follows,

$$r_s = \frac{x_1 + x_2}{2d} \quad (1) \text{ (The pore exists)}$$

$$r_s = \frac{x}{2d} \quad (2) \text{ (After the pore is disappeared)}$$

where x is the diameter at the interface during calculation and d is the initial diameter as shown in Fig. (2b, c).

3. RESULTS AND DISCUSSION

3.1. Interfacial Microstructures of the Silver/Gold Joint Using Ag₂O-TEG Paste

Fig. (3) shows typical SEM image of the silver/gold interface using Ag₂O paste. It was confirmed that the

uniformly sintered silver layer was formed in the joint using Ag₂O-TEG paste. This image clearly shows that silver nanoparticles from Ag₂O were in-situ formed and were successfully sintered on gold substrate. The detailed interfacial microstructure of the joint was observed using TEM. Fig. (4) shows TEM image and corresponding diffraction patterns of the silver/gold interface bonded at 433K. At 433K, although there are some voids in submicron size, the densely sintered silver layer formed. The diffraction pattern of silver near the interface well corresponded to that of gold. To observe more detailed interface structure, HR-TEM observation of the interface was performed. Lattice images of the silver/gold interface are shown in Fig. (5). The image reveals that the crystal orientation of silver corresponded to that of gold. From these results, it is revealed that the epitaxial layer of silver was formed through in-situ formation of silver nanoparticles from Ag₂O paste, and oriented in the direction of the gold crystal during the adhering process of the silver nanoparticles to the gold substrate, that behavior is same as those using metallo-organic silver nanoparticles [9].

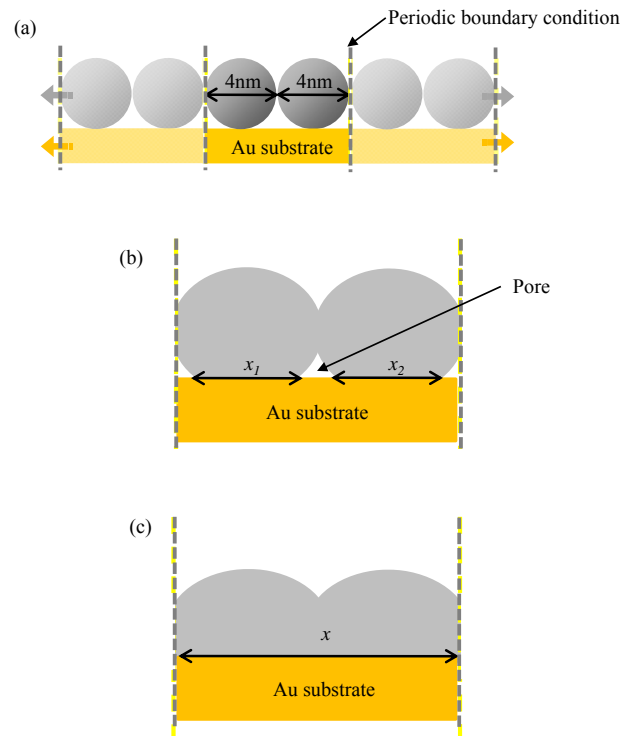


Fig. (2). Schematic illustration of (a) simulation model and measurement of the neck size ratio (b) The pore exist and (c) after the pore is disappeared.

3.2. MD Simulation of the Interface Between Silver Nanoparticles and a Gold Substrate

To evaluate the initial process of sintering of silver nanoparticles dynamically, molecular dynamics simulation was applied to sintering of two silver nanoparticles on the gold substrate. Fig. (6) shows the results of atom arrangements of 4nm-sized silver particles and the gold substrate with (011) orientation at 523K. Silver atoms in nanoparticles migrated at the beginning of the run, and

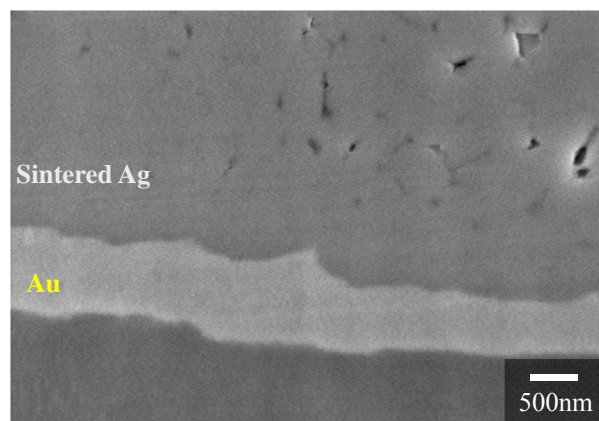


Fig. (3). The SEM image of the sintered Ag layer bonded at 523K with a pressure of 5MPa for 300s.

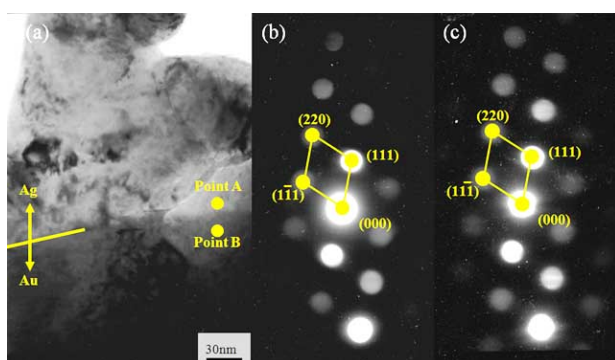


Fig. (4). TEM image (a) and corresponding diffraction patterns ((b) point A and (c) point B) of the sintered silver/gold interface using Ag_2O -TEG paste heat up to 433K with a pressure of 5MPa and quenched.

sintered wetly on the gold substrate. It can be clearly seen that epitaxial layers were formed on the substrate. Moreover, it should be noted that the epitaxial arrangement was promoted at the pore between nanoparticles and the gold substrate, which was clearly seen at 30 and 40ps in Fig. (6). It was also found that there was no mutual diffusion of silver and gold atoms at the interface in all conditions during this simulation time.

To evaluate such a wettability precisely, the neck size ratio was estimated to all silver nanoparticles. Fig. (7) shows the results of the neck size ratio as a function of sintering time in 4nm-sized particles. To clarify the effects of the pore between two nanoparticles and gold substrate, the result of a 4nm-sized nanoparticle is also shown [14]. In both results of one and two nanoparticles, it can be seen that the neck size ratio increases at the beginning of sintering (3ps), and reaches an almost constant value with holding time longer than 20ps. In the initial stage of sintering (<6ps), the rate of neck size ratio in two nanoparticles is lower than that in one nanoparticle, however, it should be noted that, the neck size ratio in two nanoparticles showed higher than that in one nanoparticle at 10ps. In this time, it was recognized that the pore between nanoparticles and the gold substrate was disappeared as shown in Fig. (6).

The result of the rapid increase of the neck size ratio in two nanoparticles suggests that the closed pore between nanoparticles and the gold substrate influences the sinterability of nanoparticle on the substrate. To understand precisely the neck growth in two nanoparticles, the tracks of silver atoms during sintering were investigated. The tracks of silver atoms are shown in Fig. (8). The green lines show the track of the surface atom at the cross section of the silver nanoparticle. It was found that surface atoms of nanoparticles near the pore were rapidly oriented to the substrate, and the pore was gradually shrunk. This is considered to minimize the total sum of surface energy and grain boundary energy. In this time, moreover, atoms were epitaxially oriented to the substrate, which is considered to reduce the misfit energy between silver atoms and the gold substrate. Once the atoms were oriented on the substrate, they were never migrated on the substrate. The surface atoms far from the substrate, on the other hand, were migrated not to the substrate, but to the atoms that were oriented on the substrate, and did not affect to neck formation and growth.

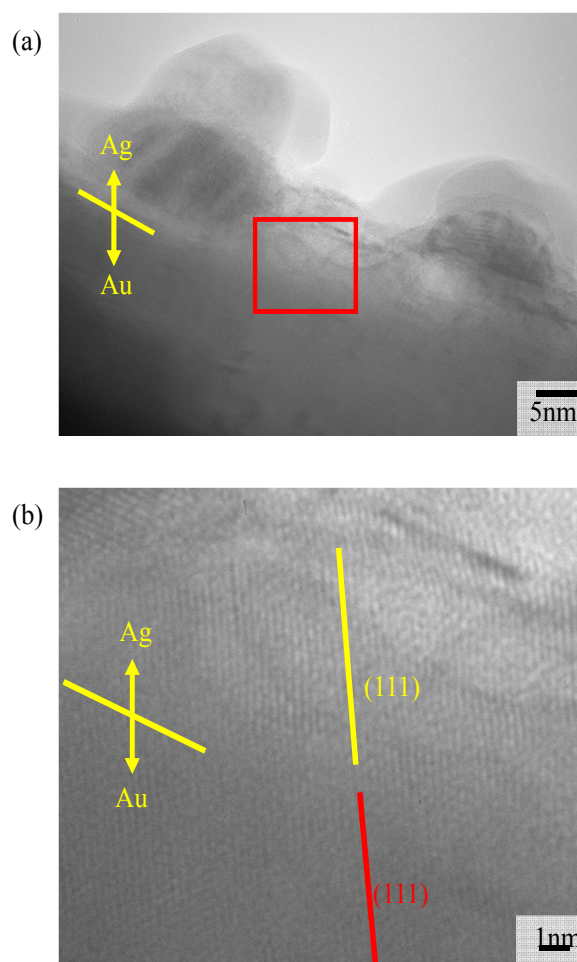


Fig. (5). TEM (a) and lattice (b) images of the sintered silver/gold interface using Ag_2O -TEG paste heat up to 433K with a pressure of 5MPa and quenched.

From the obtained results, the process of atom migration of several silver nanoparticles is considered as follows. Silver nanoparticles derived from Ag_2O are closely gathered on gold substrate. At this time, there are many nano-scale pores between two nanoparticles and substrate. When

nanoparticles begin to sinter, neck growth of nanoparticles

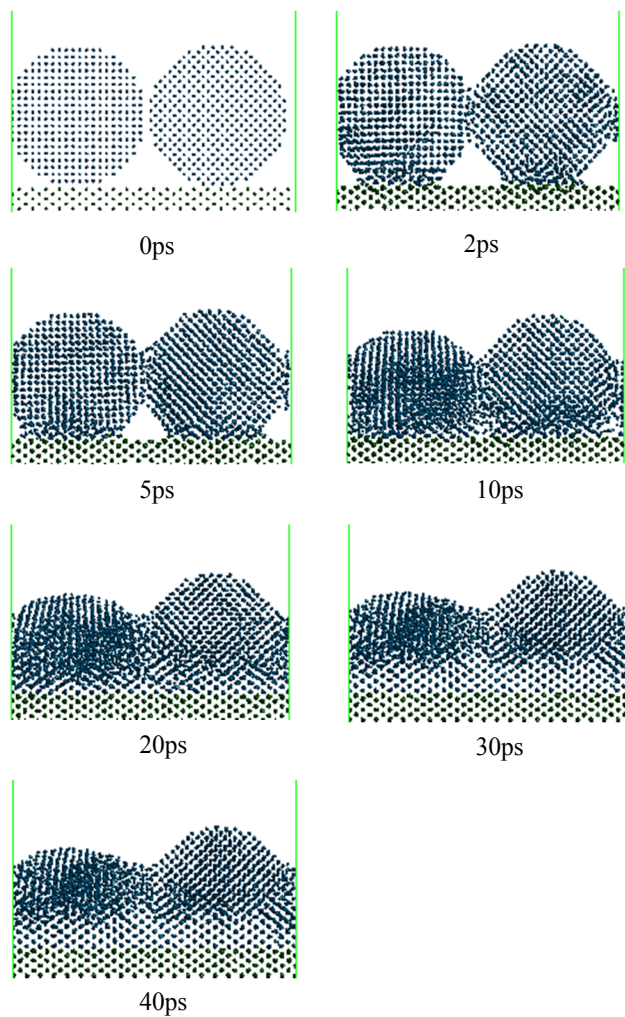


Fig. (6). Atom arrangement of 4nm-sized silver nanoparticles and the gold substrate with (011) orientation at 523K. Corresponding simulation times are also shown.

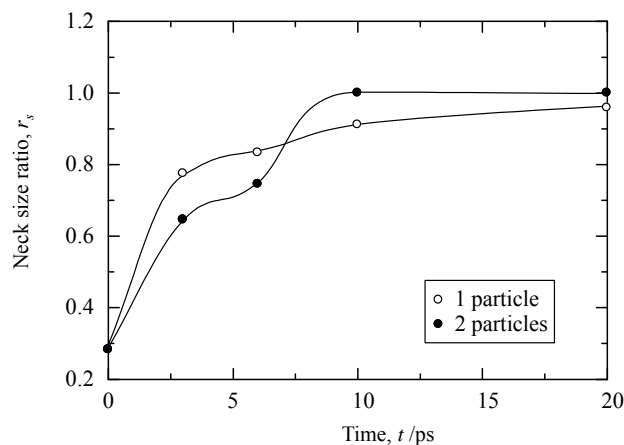


Fig. (7). Relationship between the neck size ratio and calculated time from MD simulation for one and two silver nanoparticle and the gold substrate at 523K.

occurs, therefore, the pore gradually shrinks. The shrinkage of the pore accelerates atom migration to minimize the total sum of surface energy and grain boundary energy. After the pore is disappeared, atoms are epitaxially arrangement on substrate. Finally adherent bonding are achieved at the interface. In the experimental process of metal-to-metal bonding using the nanoparticles, pressure and much longer holding time than the present calculation time must accelerate the neck growth and epitaxially arrangement of nanoparticles, which gives broadly silver layers epitaxially oriented on the gold substrate and uniformly sintered silver layer was formed in the joint as shown in Figs. (3, 5).

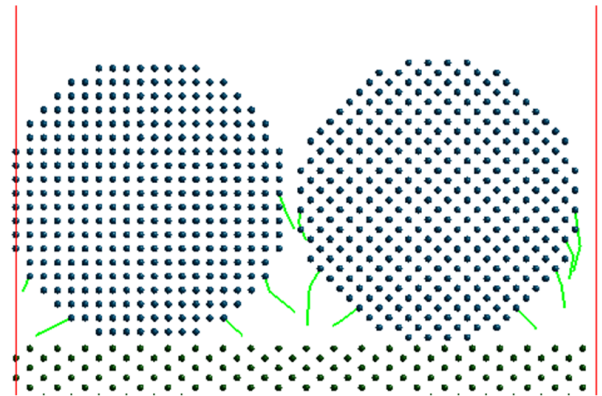


Fig. (8). Tracks of atoms during MD simulation of sintering between 4nm-sized silver nanoparticles and the gold substrate at 523K.

4. CONCLUSIONS

The interfacial microstructure utilizing Ag_2O -derived silver nanoparticles was evaluated using TEM observation and molecular dynamics simulation. The TEM observation reveals that the crystal orientation of the sintered silver corresponded to that of gold substrate. This is considered that the epitaxial layer of silver was formed through in-situ formation of silver nanoparticles from Ag_2O paste, and oriented in the direction of the gold crystal, which is same as those using metallo-organic silver nanoparticles. MD simulation successfully recreated the sintering behavior of silver nanoparticles and a gold substrate, and clearly showed the epitaxial layers were formed on the substrate. The existence of the pore between nanoparticles and the substrate indicates the acceleration of the sintering between them to minimize the total sum of surface energy and grain boundary energy.

ACKNOWLEDGEMENT

The computation was mainly carried out using the computer facilities at Research Institute for Information Technology, Kyushu University. This work was supported by Grant-in-Aid for Scientific Research (B) No. 19360332, Japan, and by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES

- [1] Morita T, Yasuda Y, Ide E, Akada Y, Hirose A. Bonding technique using micro-scaled silver-oxide particles for in-situ formation of silver nanoparticles. *Mater Trans* 2008; 49: 2875-80.
- [2] Morita T, Ide E, Yasuda Y, Hirose A, Kobayashi KF. Study of bonding technology using silver nanoparticles. *Jpn J Appl Phys* 2008; 47: 6615-22.
- [3] Goldstem AN, Esher CM, Alivisatos AP. Melting in semiconductor nanocrystals. *Science* 1992; 256: 1425-7.
- [4] Takagi M. Electron-diffraction study of liquid-solid transition of thin metal films. *J Phys Soc Japan* 1954; 9: 359-63.
- [5] Gladkikh NT, Niedermayer R, Spiegel K. Surface and volume decay of the concentration of photoexcited holes in silver bromide. *Phys Status Solidi* 1966; 15: 181-92.
- [6] Ide E, Angata S, Hirose A, Kobayashi KF. Metal-metal bonding process using Ag metallo-organic nanoparticles. *Acta Mater* 2005; 53: 2385-93.
- [7] Ide E, Hirose A, Kobayashi KF. Influence of bonding condition on bonding process using Ag metallo-organic nanoparticles for high temperature lead-free packaging. *Mater Trans* 2006; 47: 211-7.
- [8] Zhou Y, Ed. *Microjoining and nanojoining*. Cambridge: Woodhead Publishing Limited 2008.
- [9] Akada Y, Tatsumi H, Yamaguchi T, Hirose A, Morita T, Ide E. Interfacial bonding mechanism using silver metallo-organic nanoparticles to bulk metals and observation of sintering behavior. *Mater Trans* 2008; 49: 1537-45.
- [10] Hu A, Guo J Y, Alarifi H, *et al.* Low temperature sintering of Ag nanoparticles for flexible electronics packaging. *Appl Phys Lett* 2010; 97: 153117.
- [11] Hirose A, Tatsumi H, Takeda N, *et al.* A novel metal-to-metal bonding process through in-situ formation of Ag nanoparticles using Ag₂O microparticles. *J Phys Conf Series* 2009; 165: 012074.
- [12] Nguyen N H, Henning R, Wen JZ. Molecular dynamics simulation of iron nanoparticle sintering during flame synthesis. *J Nanopart Res* 2011; 13: 803-15.
- [13] Zhou X W, Johnson RA, Wadley HNG. Misfit-energy-increasing dislocations in vapor-deposited CoFe/NiFe multilayers. *Phys Rev B* 2004; 69: 144113.
- [14] Ogura T, Nishimura M, Tatsumi H, Takahara W, Hirose A. Evaluation of interfacial bonding behavior between silver nanoparticle and gold substrate using molecular dynamics simulation. *J Electron Mater* 2011; (submitted).

Received: October 26, 2010

Revised: December 10, 2010

Accepted: January 8, 2011

© Ogura *et al.*; Licensee *Bentham Open*.This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.