Study on coalescent properties of ZnO nanoclusters using molecular dynamics simulation and experiment

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Abstract

The coalescent properties of ZnO clusters were studied through experiment and molecular dynamics simulation in combination with the tight-binding potential and ZnO potential. The results from the simulation show that the linearly relationship between the melting temperature and the function of atom numbers of \( N/K^{1/3} \) was obtainable. Extrapolating the result yield at a melting point of 2130 K for \( N/\infty \) (i.e., \( N^{−1/3}→0 \)) was slightly lower than the bulk value of 2248 K. In addition, the neck diameter of two ZnO clusters was a function of temperature during coalescence. The contact length was influenced by the coalescence temperature and time, when a cluster was simulated being deposited onto a substrate. The experimental results showed that the grain size increased when the coalescence temperature and sintering time were increased.

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1. Introduction

Nanoclusters and its coalescence properties are currently attracting lots of attention due to their unique characteristics [1–5]. In the past years, many researchers studied the coalescence properties of metal clusters using molecular dynamic simulation. Lewis et al. [6] developed a molecular-dynamics simulation using the embedded-atom method to study the melting, freezing, and coalescence of gold nanoclusters. Qi et al. [7] investigated the melting and freezing of Ni nanoclusters using molecular dynamics with the many-body force field. Zhao et al. [8] studied the coalescence of three identical size nanoclusters through molecular dynamics simulation with an analytic embedded-atom potential. Shim et al. [9] studied the thermal stability of gold nanoparticles, using molecular dynamics simulation in combination with the modified embedded-atom-method potential.

Recently, Bilalbegovic [10] studied aggregates of gold clusters by molecular dynamics simulation. Ding et al. [11] utilized molecular dynamics simulation to show that the coalescence of iron nanoclusters occurs at temperatures lower than the cluster melting point, and that the difference between coalescence and melting temperatures increased as the cluster size decreased. Arcidiacono et al. [12] investigated the coalescence process of two gold nanoparticles using a host of initial temperatures and measuring the starting radii in a vacuum with the help of molecular dynamics simulation.

Zinc oxide (ZnO) has a wide band gap and good piezoelectric properties. It will have an important application in the field of nanodevices [13–16]. However, very little literature studies coalescent properties of ZnO clusters. In this paper, the effect of the temperature and the structure on the coalescent properties of ZnO nanoclusters was studied using molecular dynamics simulation with the tight-binding potential, ZnO potential and an experimental method.

2. Simulation procedure

The interaction forces between ZnO nanocluster zinc atoms, oxygen atoms and zinc atom to oxygen atom were complicated. The many-body tight-binding potential [17] is adopted to simulate the interatomic energy between zinc atoms and expressed as:

\[
E_c = - \sum_i (E^b_i + E^l_i) 
\]
where $E_i^b$ represents the band-structure energy of the $i$th atom and $E_i^r$ denotes the repulsive energy of the $i$th atom and they are expressed as:

$$E_i^b = \frac{1}{2} \sum_{j \neq i} \langle \epsilon_{ij} \rangle e^{-2q \left( \frac{r_{ij}}{r_0} \right)}$$

$$E_i^r = \sum_j A e^{-\frac{q^2}{p^2 \left( \frac{r_{ij}}{r_0} \right)}}$$

where $r_{ij}$ is the distance between zinc atoms $i$ and $j$; $r_0$ is the first-neighbors distance in the lattice and $p$, $q$, $\xi$ and $A$ are constants which they are listed in Table 1.

An ionic potential is used to perform the pair interaction sums among oxygen and zinc atoms and it is expressed as [18]

$$\Phi = A_{ij} \exp(-B_{ij} r) - \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^8} + \text{sgn} \frac{e^2}{r}$$

where $A_{ij}$, $B_{ij}$, $C_{ij}$ and $D_{ij}$ are the potential parameters and listed in Tables 2 and 3 for various atoms and sgn = ± 1 depending on whether the ions are of similar or opposite charge.

### 3. Experimental details

The ZnO nanoparticles were about 50 nm in diameter and were coalesced in a vacuum chamber. The chamber temperature could be controlled at better than 0.5 K and was adjusted from 700 to 1300 K. The surface morphology of the coalescent clusters after the thermal sintering process was observed with atomic force microscopy (AFM) operated in a noncontact mode and scanning electron microscope (SEM).

Coalescent ZnO clusters are insulators and must become conductive to yield scanning electron microscope images through coating a layer of Au. Since the electron beam also generates X-rays emission characteristics of the elements present, energy dispersive spectroscopy (EDS) of the X-rays provides a means of elemental identification. EDS can provide rapid qualitative or with adequate standards, quantitative analysis of the elemental composition with a sampling depth of 1–2 μm.

### 4. Results and discussion

Fig. 1 depicts the dependence of the melting temperature on the ZnO atoms cluster size. The dashed line reflects the linearly relationship between the melting temperature and a function of $N^{-1/3}$. The melting point decreased linearly due to curvature effects [11] as the number of atoms decreased. The result was in agreement with previous studies [11,19]. The melting point of 400, 800, 1200, 2800 and 6400 atoms were 1345, 1460, 1590, 1720 and 1815 K, respectively. Extrapolating the result for $N/N_0$ (i.e. $N^{-1/3} \to 0$) yields a predicted value for a cluster consisting of very large $N$ and a melting point of 2130 K, which was slightly lower than the bulk value of 2248 K. The discrepancy might be explained because the cluster calculations have a free surface.

Fig. 2 illustrates the relationship between the radial distribution function and the radial separation for a ZnO cluster of 1200 atoms at various temperatures. According to the statements of Fig. 1, it is a solid state for a cluster with 1200 atoms at 700 and 1100 K while a liquid cluster exists at 1700 K. For the cluster in the solid state, it can be seen in the figure that the radial distribution function has higher peaks and deeper valleys than those in the liquid state due to the density effect.
Fig. 3 shows the snapshots of ZnO clusters consisting of 1200 and 400 atoms at a temperature of 1500 K during coalescence. As expected, the two clusters coalesced and gradually became similar to a sphere as the time was increased.

Fig. 4 depicts the neck diameter of two ZnO clusters consisting of the same 1200 atoms and a function of temperature during coalescence. The neck diameter increased as the time was increased and finally it reached the diameter of the coalescence sphere. The increasing rate of the neck diameter increased while increasing the temperature of coalescence due to the higher energy.

Fig. 5 illustrates the initial configurations of different ZnO clusters consisting of 400 atoms. In Fig. 6, the variation of the average center distance of ZnO clusters consisting of 400 atoms at different time steps and a temperature of 1000 K. The average center distance decreased as the time was increased during coalescence because they gradually formed a sphere.

To study the behavior of the coalescence of a spherical cluster deposited on a substrate, the snapshots of a ZnO cluster consisting of 1200 atoms deposited on a ZnO substrate consisting of 3200 atoms at a temperature of 2000 K during coalescence is shown in Fig. 7.
The spherical cluster was gradually deposited onto the substrate as the time was increased. The contact length between the cluster and the substrate at various coalescence temperatures is illustrated in Fig. 8. In the case of 2000 and 3000 K, the atoms are in a liquid state and the contact length quickly reached a constant value, although, a very long time was required at 1000 K since they were in a solid state.

The behaviors of coalescence for ZnO nanoparticles were also studied by using an experimental method. Fig. 9 illustrates EDS of ZnO nanoparticles sintered at a temperature of 1100 °C at different coalescence times. Au is shown in the figure since ZnO was an insulator and must become a conductor for yielding SEM images through coating a layer of Au.

The grain size obtained from the experiment increased while increasing the coalescence time and is shown in Fig. 10. Fig. 11(a) and (b) are the AFM image and SEM image, respectively, of the coalescence of ZnO clusters at 1100 °C after 8 and 10 h. It can be observed that a larger grain size was yielded after 10 h than at 8 h. In addition, the grain size also rapidly increased while increasing the coalescence temperature and is shown in Fig. 12. The color of ZnO samples from the experimental observation, not shown here, changed from white...
to green to brown when the coalescence temperature was increased from 700 to 1300 °C.

5. Conclusions

In this paper, the effect of the temperature and the structure on the coalescent properties of ZnO clusters was studied using molecular dynamics simulation and experimental method. The following results were obtained:

1. The melting point of the ZnO clusters decreased linearly as the simulated atom increased due to a function of $N^{-1/3}$ of the curvature effect.
2. The neck diameter rate of increase of two simulated ZnO clusters increased as the temperature during coalescence was increased.
3. The contact length between a simulated ZnO cluster and ZnO substrate increased as the coalescence temperature and time were increased.
4. The grain size obtained from the experiment increased when increasing the coalescence time.
5. The grain size rapidly increased while increasing the coalescence temperature.

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References
