ATOMISTIC SIMULATION OF VAPOR-PHASE NANOPARTICLE FORMATION.

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Abstract

In order to understand from a fundamental view how nanoparticles form and grow, classical molecular dynamics simulations of cluster growth and energy accommodation processes have been conducted for clusters of silicon (< 1000 atoms), over a wide temperature range. Simulations involved solution of the classical equations of motion constrained with the three body Stillinger-Weber potential. The results show the large heat release and resulting cluster heating during a cluster-cluster collision event, and the corresponding time evolution of the internal energy to a more stable state. Dynamic effects associated with the temperature of the cluster and the impact parameter are also clearly evident. In particular, clusters show a large sensitivity to temperature in the rate of coalescence, particularly at low temperature. Calculated diffusion coefficients are significantly larger than surface diffusion constants stated in the literature. Phonon density of states spectra do not seem to show size effects.

Introduction

Nano-scale materials have the potential for accessing material properties that can be varied through control of particle size. One of the limitations in rapid use of such materials is an understanding of the size dependent properties such materials have . The other limitation is the relative difficulty in the characterization of very small clusters and the ability to control their growth. Vapor phase growth of small clusters is perhaps the most robust method of producing bulk quantities of such materials [1-4]. However, many questions and challenges remain, including control of growth, and a knowledge of chemical reactivity and transport properties.

Computation Method

The approach used in this work is to apply an atomistic simulation using classical molecular dynamics (MD) methods [5-7]. Computations were conducted using the three body formulation of the silicon potential proposed by Stillinger and Weber (SW) [8]. The three body formulation provides the mechanism by which the directional nature of the bonding can be realistically simulated. While many potentials are available to simulate silicon, the SW potential was chosen because it accurately predicts bulk melting characteristics. Because most cluster formation processes occur at high temperatures, liquid like characteristics should play an important role in any description of cluster growth. Classical MD was conducted by solving the Newtonian equations of motion with a time step of 5.7×10^{-4} ps. All simulations were started by first equilibrating the appropriate size cluster to a specified temperature prior to cluster collision. Each cluster was then given a bulk cluster velocity so that the collision kinetic energy along the line of centers of the clusters corresponds to twice the thermal energy. Both head-on and large impact parameter collisions were included.

Bulk vs Surface Properties

The size dependent properties of clusters can be thought to arise as a result of the rapid change in the surface to volume ratio. The cluster energy can be fit to an expression that involves a bulk and a surface contribution to the total energy, E_T.

$$E_T = \Sigma_i \text{ (Potential + Kinetic Energy)} \qquad i=1\text{-}N \qquad (1)$$

$$E_T = -E_b^{\text{Bulk}} N + E_s^{\text{Surf}} N^{2/3} \qquad (2)$$

Fig 1. shows the result of fitting the total energy to a bulk and surface energy contribution as expressed in equation 2. The results clearly show that the calculated results can be fit quite nicely to such an expression. The bulk energy term becomes more negative as the cluster size is increased (becoming more stable) while the surface term shows a shallow positive term. The ratio of bulk to surface energy for the two temperatures indicates the relative importance as a function of both temperature and cluster size. The results show that increasing temperature causes a decrease in the E(Bulk)/E(Surf) as average bond length increases and results in an increase in the bulk energy (potential energy). Increasing cluster size decreases the surface to volume ratio and results in a decrease in the relative importance of the surface energy. Under all conditions calculated here $E_T < 0$, which implies the cluster was always stable. Extrapolating the 2000 K results to $E_T = 0$ occurs at N < 1; i.e all cluster sizes below at least 2000 K are unconditionally stable.
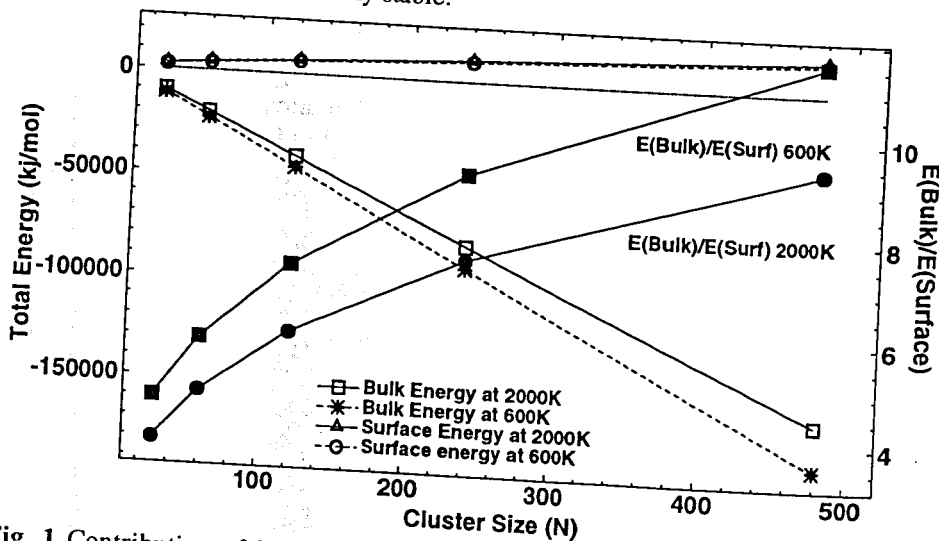

Fig. 1 Contribution of bulk and surface energy terms to the total cluster energy at 600 K and 2000 K

The approach to bulk behavior is one of the most interesting aspects to the understanding of nanostructured materials. These would include mechanical, optical, and chemical properties. One aspect of this approach to bulk behavior is the average binding energy of atoms as a function of particle size. Fig 2. shows the approach to bulk behavior as the derivative of the potential energy per atom with respect to cluster size. This effective gives a measure of the incremental increase in binding energy upon addition of an atom to the cluster. As seen in Fig. 2 the atomic binding energy in the cluster rapidly reaches an asymptotic behavior by 1000 atoms. This is one measure of the approach to bulk behavior.
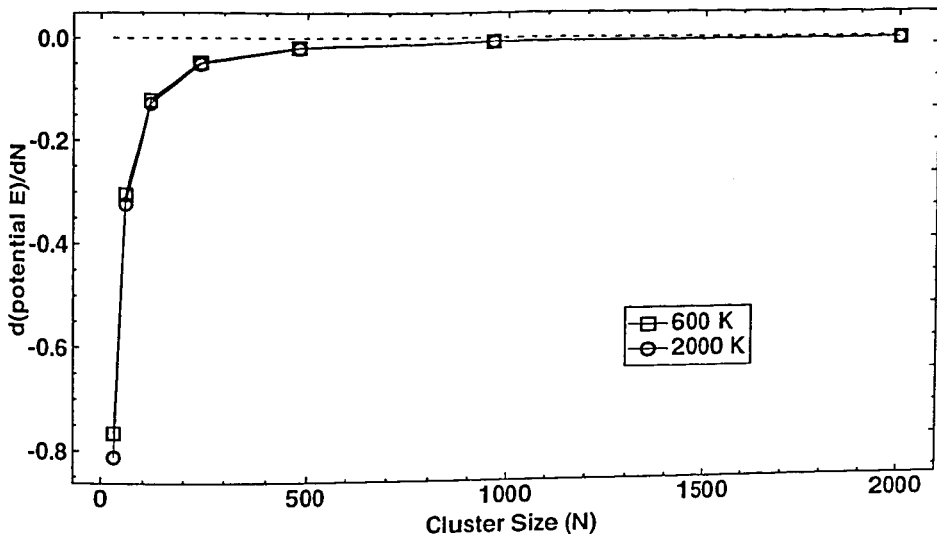
Fig 2. Approach to bulk binding energy

Fig 3. shows the phonon density of states as a function of cluster size at a temperature of 2000 K. The spectra show the two dominant modes found in bulk silicon (acoustic - 150cm^{-1}; optical- 400 cm^{-1}). However, we do not observe any size dependent structure and in fact the spectra basically track what is observed for bulk silicon. In contrast, some of our prior calculations on temperature dependance have shown a softening of the modes to lower frequencies as temperature increases [7].
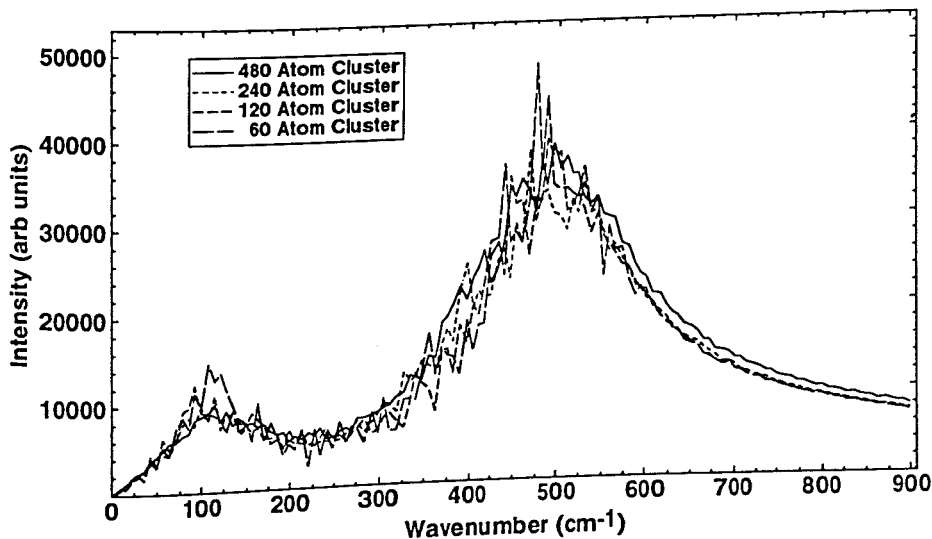

Fig 3. Phonon density of states for various cluster sizes at 2000 K

Cluster Growth

Cluster aggregation processes have been investigated by colliding equilibrated clusters at various temperatures and sizes ($15 < N < 480$; $600 < T < 2000$ K). Cluster collisions were conducted under thermal energy collision conditions, i.e. clusters were given relative collision energies commensurate with the temperature of the cluster. The result of a cluster-cluster collision is the formation of new bonds for surface atoms. The decrease in the number of surface dangling bonds lowers the potential energy and through conservation of energy, results in heating of the cluster (increase in thermal energy of the atoms). The extent of cluster heating is shown for different cluster sizes as a function of initial cluster temperature in Fig 4. The general trends observed are that smaller clusters have greater heat release resulting from a higher fraction of unsatisfied dangling bonds. Clusters with higher initial temperature have greater heat release. This is probably due to the higher energy state of the surface atoms in a hotter cluster. Grazing collisions result in smaller heat release as some of the energy goes into the angular momentum of the resulting cluster. In all cases, the collisions were reactive; i.e sticking coefficient = 1. This is in contrast to small cluster nucleation which can show nucleation kinetics that are well below gas kinetic collision rates [9].
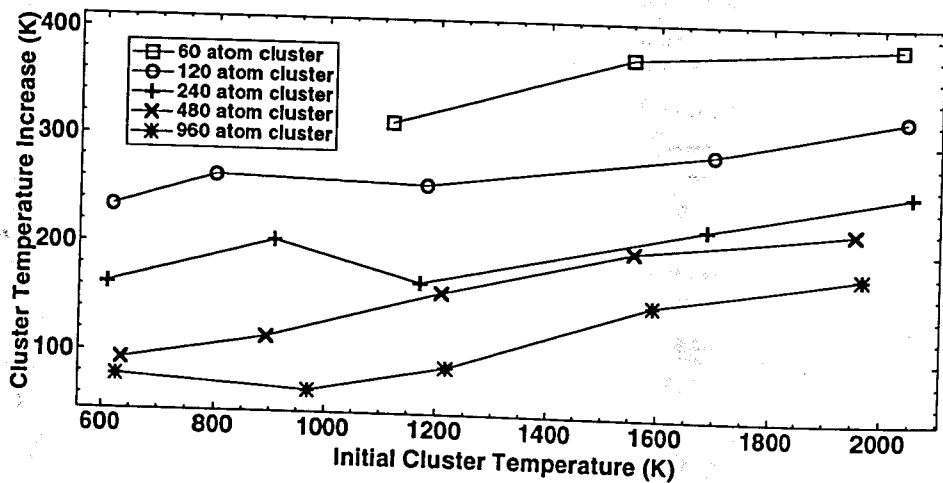

Fig. 4 Cluster temperature rise during cluster growth; head on encounter

One of the most important issues facing vapor phase growth of nano-particles is the problem of aggregate formation. The most desirable morphologies are spherical or soft agglomerates. Since coalescence (sintering) processes are ongoing during nucleation and growth, control requires an understanding of the time scales and basic physics behind sintering of nanoparticles. Our dynamic simulations can track the evolution of particle morphology during a cluster-cluster encounter. The results can be expressed in many forms. For the purposes here were show in Fig. 5 the time required for two cluster to coalesce, as a function of particle size and initial temperature. The results clearly indicate that cluster coalescence is very temperature sensitive. Coalescence times at the lower temperatures are very size sensitive, with the larger clusters showing the slowest coalescence rates. At higher temperatures (above 1200 K) cluster coalescence times are independent of size. In general, melted or near melted clusters coalesce spontaneously. While not shown here, calculations show that the melting temperature is well below the bulk value.
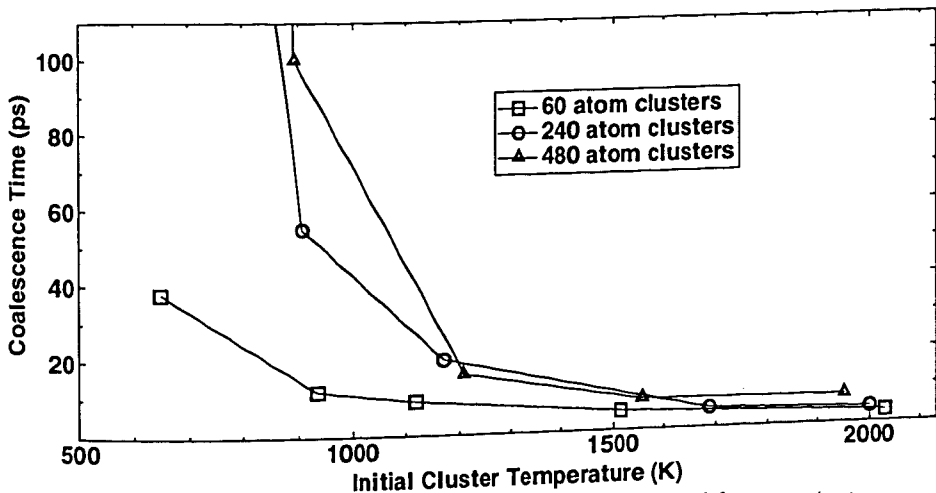
Fig. 5 Cluster coalescence times as various cluster sizes and initial temperature.

Cluster morphology changes resulting from sintering processes can be thought of as occurring through movement of atoms via atomic diffusion. Molecular dynamics computations lend themselves naturally to the calculation of diffusion constants. Figure 6 shows calculations of the mean square displacement (MSD) of atoms in a 480 atom cluster (at 600, 1200 and 2000 K) as a function of time. The diffusion coefficient can then be calculated from the initial slope of the MSD curves by the usual Einstein relation (eq. 4):

$$MSD = <| r_i (t) - r_i (0) |^2 > \tag{3}$$

$$D = 1/6 \text{ [initial slope of MSD]} \tag{4}$$

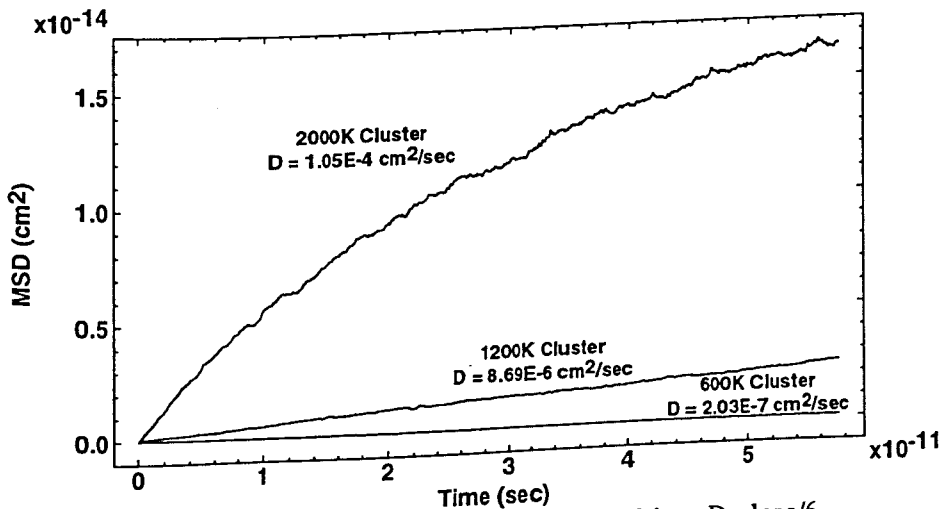**Fig. 6** Mean square displacement of atoms as a function of time; D=slope/6

Because clusters of this size are essentially composed of surface rather than volume type atoms, comparison with experiment is most appropriate with surface self-diffusion data. Unfortunately such data is scarce and of questionable accuracy. The most direct measurement has been made by Makowiecki and Holt [10] who reported a silicon surface diffusion constant of 4×10^{-8} cm^2/s at 1000 K. A curve fit of our data showed a diffusion constant at 1000 K of 5×10^{-6} cm^2/s which is significantly larger than the experimental results. At this time there is no obvious way to access this discrepancy. Certainly, it is well known that the Stillinger-Weber potential under predicts the binding energy in bulk silicon. This would tend to decrease the computed surface diffusion coefficient constant.

Conclusion

Atomistic simulations utilizing classical MD methods have been used to characterize the characteristics of equilibrium and kinetic properties of large silicon clusters undergoing growth via cluster-cluster collisions. The results show that the binding energy of clusters increases with cluster size and decreases with cluster temperature. Phonon density of states for liquid silicon clusters were found to be insensitive to size and similar to the bulk. Cluster kinetics indicate that significant heat release occurs as a result of new bond formation. Cluster morphology effects similar to those observed in nanophase particle processing are also evident. In particular, cluster coalescence is very sensitive to temperature below 1000 K. Mean square displacement calculations have been used to deduce diffusion constants, a comparison of which with experimental results for surface diffusion shows considerable discrepancy. Future work will be aimed at correlating these observations to scaling laws that can be applied to phenomenological models of particle growth.

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