Molecular Dynamics Simulation of Large Cluster Growth

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Abstract

Classical Molecular dynamics simulation of silicon cluster growth (up to 1000 atoms) have been conducted using the Stillinger-Weber 3-body interaction potential. The cluster binding energy has been fit to an expression that separates the surface and bulk contribution to the energy over a wide temperature and size range. Cluster growth simulations show that large heat release results from new bond formation at gas kinetic rates (i.e. sticking coefficient = unity). Temperature was found to be the primary controlling process parameter in the evolution of cluster morphology from an aggregate to a coalesced cluster below 1000 K, with the impact parameter playing a secondary role.

Introduction

Nanometer processing is receiving considerable interest from a variety of communities, including those from microelectronics and advanced materials. One of the challenges in this area is the processing of very fine particles. This would include their controlled growth, chemical reactivity and transport properties. Considerable attention has been paid to the growth of particles in the range of 100nm and up, however process modelers have implicitly assumed that small particle growth is unimportant. These issues however have reemerged due to the interest in nanometer particle processing[1]. Several outstanding issues are of primary concern in phenomenological models and pedagogical approaches to controlling particle formation[2]. This is true from both the perspective of much of the microelectronics community which hopes to minimize particle growth in the vapor during chemical vapor deposition and the ceramics community which hopes to develop the ability to grow from the vapor, spherical, unagglomerated nanometer scale particles[3,4]. This implies that attention should be addressed toward understanding the nature of the cluster growth kinetics and their morphology.

In this paper we address the dynamics in the formation of silicon particles up to 3 nm from an atomistic view.

Computation Method

The approach used in this work is to apply an atomistic simulation using classical molecular dynamics (MD) methods [5,6]. Computations were conducted using the three body formulation of the silicon potential proposed by Stillinger and Weber (SW) [7]. 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.

Equilibrium Cluster Energetics

Because of the large surface to volume ratio, cluster properties vary with size. The approach to bulk properties as cluster size is increased is in general specific to the property of interest. Fig. 1 shows the effect of cluster size on binding energy per atom at various temperatures. As the cluster size increases the cluster binding energy increases as one would expect for the case where

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the ratio of bulk to surface atoms increases. Freund and Bauer [8] have discussed the effect of cluster binding energy with cluster size for metal clusters. Their work has the same qualitative dependence on cluster size, however the effects they observe are approximately twice as great as those we have seen . One possible explanation is that unlike metals which like to form close packed structures, silicon has a lower coordination number (< 4) with highly directional covalent bonding. This would imply that metallic like clusters would have a larger fraction of dangling bonds and are therefore more sensitive to cluster size.

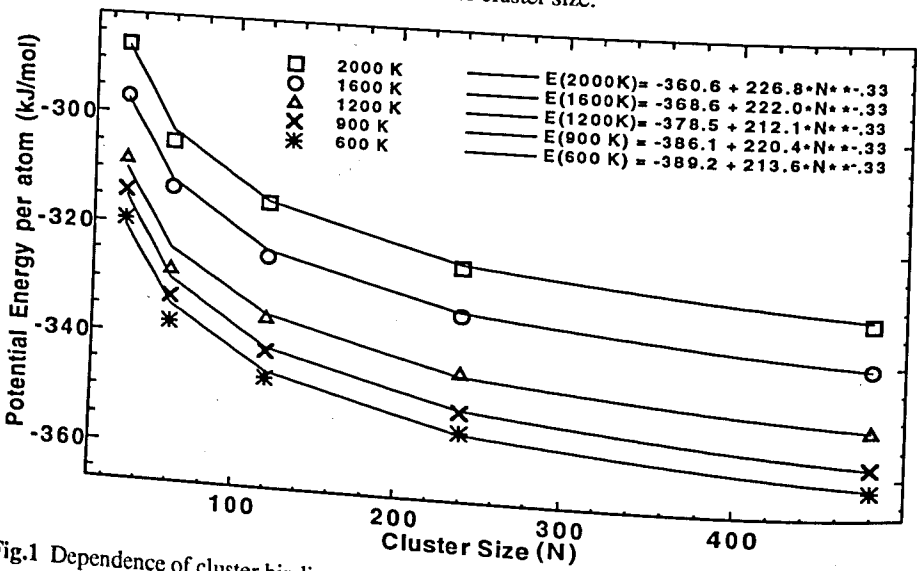


Fig.1 Dependence of cluster binding energy per atom on cluster size (N atoms)

By taking the cluster potential per atom as a function of cluster size we can fit to an expression for the relative importance of bulk (volume) and surface energy (surface area) contribution.

$$\text{Binding Energy} = -E_b N + E_s N^{2/3} \quad (1a)$$

$$\text{Binding Energy/per atom} = -E_b + E_s N^{-1/3} \quad (1b)$$

The fits shown in Fig. 1 are fit to Eq. 1b. By fitting to the temperature dependence one can obtain an expression that encompasses all the data.

$$E_b = 420.0 - T^{0.54}$$

$$E_s = 196.7 - T^{0.44}$$

Vibrational energy transfer processes are very important to the mechanism of cluster stabilization during cluster growth as well as its radiative properties. Fig 2. shows the density of vibrational states as a function of cluster temperature. A comparison with another calculated phonon spectra is also included for comparison purposes [9]. It is clear that the phonon spectra are not significantly altered as a result of the large number of surface atoms. The spectra show the two dominant modes found in bulk silicon (acoustic - 150cm^{-1}; optical- 400 cm^{-1}). As the cluster temperature is increased the phonon density increases, shows broadening and a softening of the modes to lower frequencies.

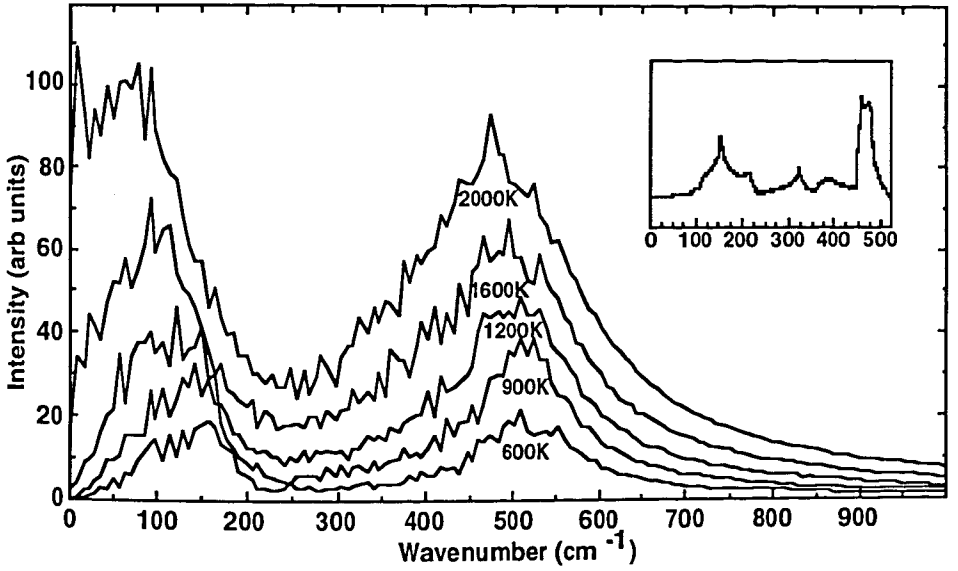


Fig. 2 Phonon density of states for 480 atom cluster as a function of temperature; comparison with spectra for bulk Si calculated with the Bond Charge Model [9].

Cluster Kinetics

Cluster-cluster collision simulations have been conducted on clusters varying in size from 15 atoms up 480 atoms, as a function of temperature and impact parameter. Fig. 3 shows the result of the collision of two 60 atom clusters.

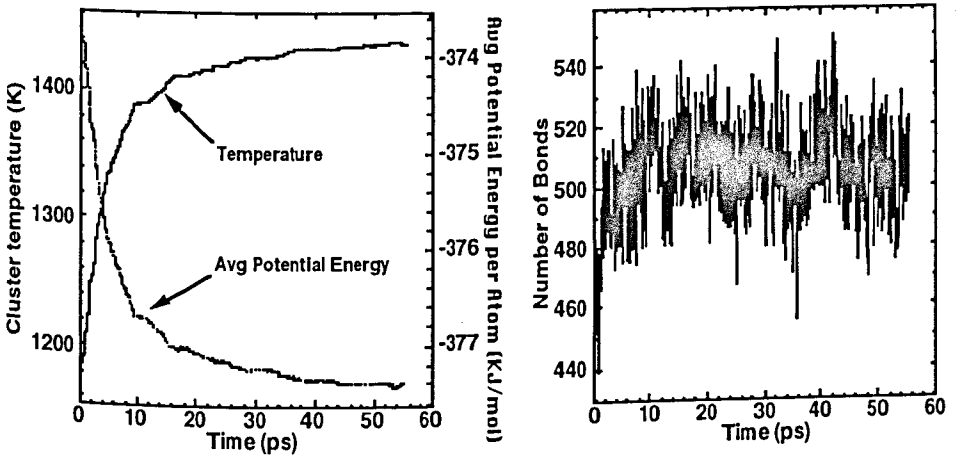


Fig. 3 Dynamics of cluster growth from the collision of two 60 atom clusters at 1200 K

The formation of new chemical bonds during the collision results in a decrease in the internal energy of the resulting cluster with increasing time, as the newly formed cluster finds an increasing stable configuration, by decreasing its surface area and thus the number of dangling bonds. Since this is an adiabatic problem the energy release goes into the thermal motion of each

atom within the cluster and is seen as a rise of the cluster temperature. Note that the cluster temperature increases by several hundred degrees, such that following growth, new clusters will be significantly hotter than the surrounding gas. Radiative and conductive cooling will eventually lead to a return of the cluster temperature back to the ambient environment, on a time scale, however, significantly slower than the period of the cluster heating.

For all simulations conducted under thermal energy collision energies, cluster-cluster aggregation kinetics occurred with a sticking coefficient of one. This is an important result in that it provides evidence for the commonly used assumption in phenominological modeling of particle growth, of a gas kinetic growth rate[2,3]. This is in contrast to small cluster nucleation which can show nucleation kinetics that are well below gas kinetic rates, with negative temperature dependence to the rate constants resulting from energy transfer effects [10,11]. Unlike small cluster growth which requires an external collider to dissipate energy, large clusters have sufficient number of internal oscillators to redistribute the excess energy. As a result the smaller clusters experienced the largest temperature rise.

One of the issues of great importance in the formation of nanophase processing of fine particles is the morphology of the resulting clusters during growth. Many, if not most gas phase processes result in chained agglomerates of small particles. Minimization of such structures is a goal to those interested in utilizing the properties of nanoscale particles. The change in morphology is however a very difficult process to study experimentally, although one that we can track through MD in a relatively straight forward manner. Fig. 4 shows the temporal approach to spherical morphology for two colliding (impact parameter =0) 240 atom clusters as a function of cluster temperature.

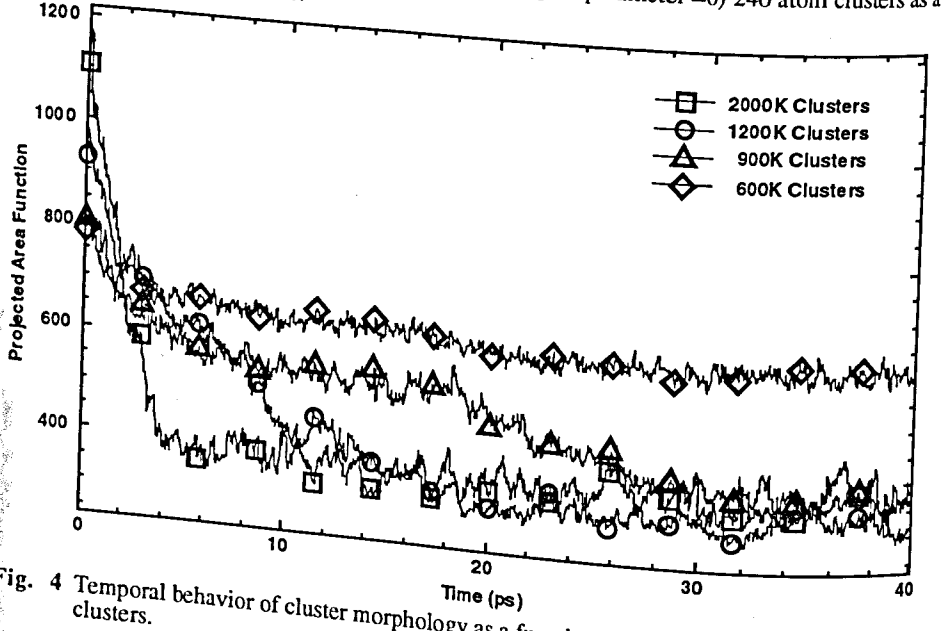
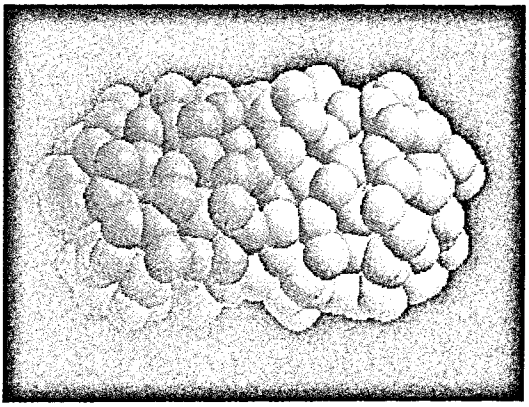


Fig. 4 Temporal behavior of cluster morphology as a function of temperature for two 120 atom clusters.

The projected area coefficient is defined as the area of a circle, obtained from the diameter of the smallest sphere that can be drawn around the two coalescing clusters. The results show that cluster coalescence is very temperature sensitive. Clusters at temperatures above 1000 K show coalescence times that are complete within the simulation period, while showing a substantial decrease in the coalescence rate below 1000 K. Clusters at 600 K shows initial neck growth to be

rapid but no evidence for coalescence. 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. Data of this nature could eventually be used to develop scaling relationships for the calculation of sintering rates. An example of the kind of morphology observed, is shown in Fig. 5 for the collision of two 120 atom clusters at temperatures of 600 and 2000 K at 45 ps after the collision.

600 K Cluster



2000 K Cluster

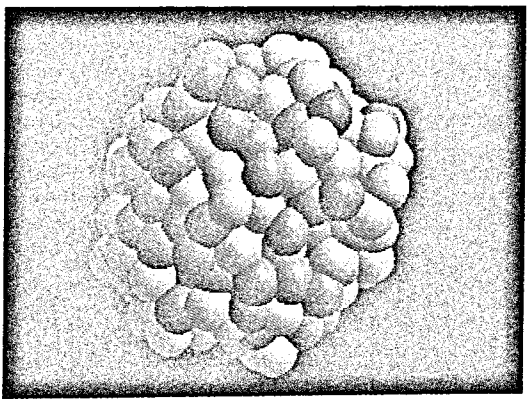


Fig. 5 Cluster morphology during growth at 600 and 2000 K at 45 ps.

Cluster morphology changes require the movement of atoms via internal cluster diffusion. Shown below in Fig. 6 is a measure of the extent of atomic mixing defined as the ratio of the number of nearest neighbors an atom has originating from the other cluster to that of its own cluster. It is clear that the extent of mixing is very temperature sensitive with the coldest clusters showing no evidence for atomic mixing. Even at the highest temperatures studied clusters are still not statistically mixed (a value of 1 would be perfectly mixed). It is clear that particle coalescence is a much faster process than atomic mixing.

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. 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. Atomic mixing is shown to be a slower process than the overall process of cluster coalescence. Future work will be aimed at correlating these observations to scaling laws that can be applied to phenomonological models of particle growth.

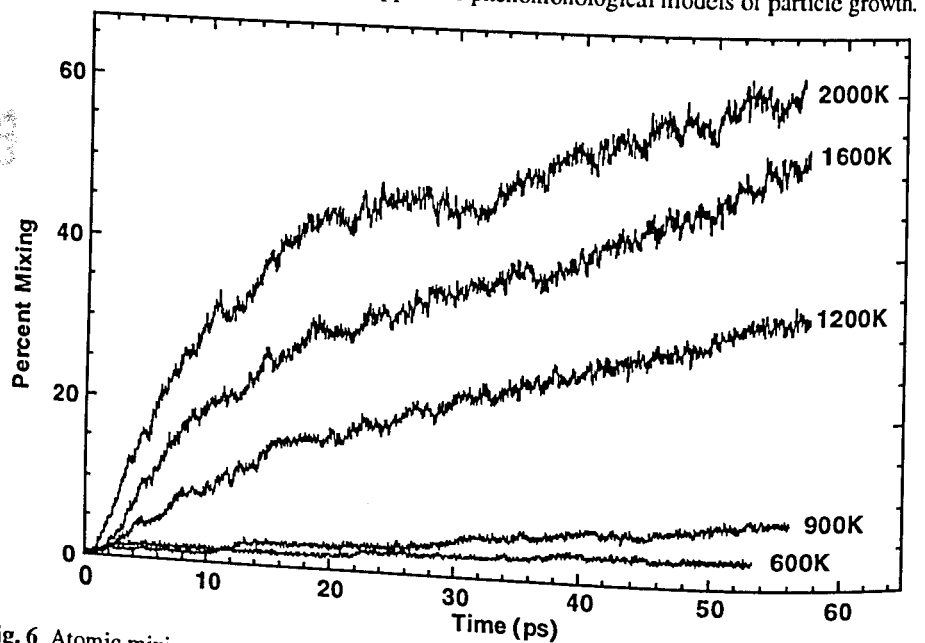


Fig. 6 Atomic mixing as a function of time for various cluster temperatures.

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