01 Jan 1992

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Recommended Citation

S. S. Salk et al., "Pressure and Temperature Effects on the Energy of Formation for Silicon Clusters," *Physical Review B (Condensed Matter)*, vol. 45, no. 3, pp. 1458-1461, American Institute of Physics (AIP), Jan 1992.
The definitive version is available at https://doi.org/10.1103/PhysRevB.45.1458

PHYSICAL REVIEW B VOLUME 45, NUMBER 3 15 JANUARY 1992-I

Pressure and temperature effects on the energy of formation for silicon clusters

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(Received 29 August 1990; revised manuscript received 8 August 1991)

At present most theoretical studies of atomic clusters are limited to their physical properties referred to 0 K. To the best of our knowledge, there exists no theoretical study of the simultaneous dependence of cluster formation and cluster-size distributions on both pressure and temperature. In the present work both pressure and temperature effects on the formation of silicon clusters are explored. A universal semiempirical formula is obtained to show a general trend in the variation of binding energy as a function of cluster size for both atomic and molecular clusters.

I. INTRODUCTION

Recently both experimental[1-7] and theoretical studies[8-10] of silicon clusters have been of great interest. Silicon clusters are produced in a laser vaporization expansion source and enter a vacuum-isolated ionization region.[6] Cluster-size spectra are then obtained by time-of-flight measurements, after ionization by a 193-nm ArF laser. The observed cluster-size distribution arises as a result of three distinct processes: (1) vaporization, (2) cluster formation or growth, and (3) photoionization and photofragmentation. The initial cluster-size distribution obtained by laser vaporization is expected to be dominated by silicon monomers, which are then subject to rapid associative reaction to form clusters. Cluster growth takes place well before the clusters reach the photoionization region. To closely simulate such an experimental environment of cluster formation, a theoretical formulation incorporating the simultaneous effects of both pressure and temperature is of great value.

The nonequilibrium process of cluster formation in the vaporization region may be subject to two stages, a rapid transient state period of far from equilibrium and a subsequent steady-state period of nonequilibrium. In the multistate kinetics approach of clusterization and nucleation processes, steady state is often assumed in estimating cluster formation rates or nucleation rates.[11] Further, in this method the formation energy and size distribution (concentration) including magic-number clusters are evaluated under the assumption of equilibrium. A preexponential correction factor known as the Zeldovitch factor[11] is then introduced to account properly for the nonequilibrium process of clusterization or nucleation. Indeed, using the formation energies and cluster concentrations evaluated at equilibrium, earlier we[12] found good agreement with observed nucleation rates associated with the molecular clusters of water. Despite the fact that quantal calculations for magic-number silicon clusters refer to a temperature of 0 K, they are often found to be in good agreement with experimental observation at finite temperatures.[8,10(a)] This suggests that the nonequilibrium process does not significantly alter the relative size distributions of clusters including the magic numbers, though it affects the rate of cluster formation.

The objective of the present study is twofold: (1) theoretical derivations of formation energy (energy of formation) and cluster-size distribution for both homogeneous and heterogeneous atomic clusters and (2) calculations of formation energies for silicon clusters at various temperatures and pressures. We know of no theoretical study that attempts to derive both the pressure- and temperature-dependent cluster-size distributions. The present formulation is expected to be of practical importance particularly for studying the cluster-formation processes which simultaneously depend on both temperature and pressure. Our theory differs from others in including the effect of multistate kinetics for the formation of atomic clusters from vapor phase.

II. THE FORMATION ENERGY AND SIZE DISTRIBUTION OF HETEROGENEOUS AND HOMOGENEOUS CLUSTERS

The present formulation of formation energy and size distribution for atomic clusters closely parallels our earlier theory[12] which was developed for the study of molecular clusters. Thus we introduce only rudimentary steps to avoid repetition. To treat the formation process of heterogeneous atomic clusters[6] (such as the metallic silicon cluster made of silicon atoms and a metallic atom, e.g., W, Cs, and Co; see Ref. 6), we introduce a two-component gas system made of rarely populated foreign particles of species A (e.g., metallic atom) and dominantly populated monomers of an atomic species B (e.g., silicon atom). Thus we first pay attention to the formation of heterogeneous atomic clusters[6] containing a foreign atom A, by the following clusterization process,

$$\begin{aligned} &A+B\rightleftarrows AB \ , \\ &AB+B\rightleftarrows AB_2 \ , \\ &\vdots \\ &AB_{i-1}+B\rightleftarrows AB_i \ . \end{aligned} \tag{1}$$

We now denote E_0, E_1, and E_i as the total electronic ground-state energies of the foreign atom A, monomer B, and heterogeneous cluster AB_i, respectively. The total binding energy ΔE_i of the heterogeneous cluster i at $T=0$ K is then given by

$$\Delta E_i = E_i - (E_0 + iE_1) \tag{2}$$

or

$$\Delta E_i = \sum_{j=1}^{i} \Delta E_{j-1,j} \ , \tag{3}$$

where

$$\Delta E_{j-1,j} = E_j - E_{j-1} - E_1 \tag{4}$$

with $i \geq 2$.

The number concentration n_i of cluster size i, that is, the cluster-size distribution is written,[12]

$$\begin{aligned} n_i = n_0 n_1 \exp(-\{\Delta E_i - kT[\ln(\xi_i/V) - i\ln(\xi_1^t/V)] \\ + kT\ln(\xi_0^t/V) \\ -(i-1)kT\ln(N_1/V)\}) \ . \end{aligned} \tag{5}$$

Here n_0 and n_1 are the number concentrations of the foreign atom A and the monomer B, respectively. ξ_i is the partition function of cluster i, describing translational, rotational and vibrational motions. ξ_0^t and ξ_1^t are the translational partition functions of the heteroatom A and the monomer B, respectively. N_1 is the total number of monomers B and V, the volume. k is the Boltzmann constant and T the absolute temperature.

Considering the dominance of monomer population over the foreign atoms and using the ideal gas law, (5) leads to[12]

$$\begin{aligned} n_i = n_0 n_1 \exp(-\{\Delta E_i - kT[\ln\xi_i/V - i\ln(\xi_1^t/V)] \\ + kT\ln(\xi_0^t/V) - (i-1)kT\ln S \\ -(i-1)kT\ln n_1^0\}) \ , \end{aligned} \tag{6}$$

with n_1^0, the equilibrium number concentration of the monomer B and S the saturation ratio.

We now cast (6) into the following form:

$$n_i = n_0 n_1 \exp(-\Delta\phi_i/kT) \ , \tag{7}$$

in order to write the formation energy of the heterogeneous cluster,

$$\begin{aligned} \Delta\phi_i = \Delta E_i - kT(\ln\xi_i' - i\ln\xi_1'^t - \ln\xi_0'^t) \\ -(i-1)kT\ln S - (i-1)kT\ln n_1^0 \ , \end{aligned} \tag{8}$$

or

$$\begin{aligned} \Delta\phi_i = \Delta E_i - kT(\ln\xi_i' - i\ln\xi_1'^t - \ln\xi_0'^t) \\ -(i-1)kT\ln(P/kT) \ , \end{aligned} \tag{9}$$

where

$$\xi_i' = \xi_i/V \ , \tag{10}$$

$$\xi_1'^t = \xi_1^t/V \ , \tag{11}$$

and

$$\xi_0'^t = \xi_0^t/V \ . \tag{12}$$

P in (9) is the partial pressure of the monomer gas B, e.g., silicon vapor pressure.

Now for the case of homogeneous atomic clusters (i.e., cluster made of a single species such as the silicon clusters of present interest), we can readily obtain the formation energy of cluster size i by replacing A with B in expression (1)

$$\begin{aligned} \Delta\phi_i = \Delta E_i - kT(\ln\xi_i' - i\ln\xi_1'^t) \\ -(i-1)kT\ln S - (i-1)kT\ln n_1^0 \ , \end{aligned} \tag{13}$$

or

$$\begin{aligned} \Delta\phi_i = \Delta E_i - kT(\ln\xi_i' - i\ln\xi_1'^t) \\ -(i-1)kT\ln(P/kT) \ . \end{aligned} \tag{14}$$

with

$$\Delta E_i = E_i - iE_1 \ . \tag{15}$$

It is obvious from (8) and (13) that at $T=0$ K, the energy of formation $\Delta\phi_i$ reduces correctly to the usual binding energy ΔE_i. This is the binding energy obtainable from quantal calculations[8-10] and is often used for the interpretation of observed magic-number clusters. Thus both pressure and finite-temperature effects are not taken into account in such studies. For this reason these effects are worthy of exploration for the actual clusterization process that depends on both temperature and pressure.

III. COMPUTED RESULTS FOR PRESSURE AND FINITE-TEMPERATURE EFFECTS ON THE FORMATION OF SILICON CLUSTERS

In view of current theoretical interpretations of the cluster-size distributions and the magic numbers of silicon clusters based on binding energy calculations referred to as $T=0$ K, it is of great interest to examine simultaneous effects of both silicon vapor pressure and temperature on the formation energies of clusters, including magic numbers. Using (14), computed results for the formation energies of Si clusters are shown in Figs. 1–3. The formation energy at $T=0$ K, i.e., the cluster binding energy ΔE_i in (14) was obtained by a recently reparametrized semiempirical effective Hamiltonian method[13] known as modified neglect of diatomic-differential overlap[14] (MNDO). Various optimized geometric structures did not significantly alter the relative magnitudes of formation energies for silicon clusters at widely different temperatures and pressures that we tried. Computed formation energies shown in the figures are for the temperatures of $T=0$, 150, 300, and 1000 K and for the silicon vapor pressures of $P=10^{-6}$ and 1 atm, respectively. The stability of atomic clusters of silicon is found to be far less sensitive than that of the molecular clusters to the variation of temperature and pressure. This is because the atomic clusters have much larger binding energies than the molecular clusters.

Figures 1–3 show that magic numbers (peak positions) predicted at $T=0$ K remain unchanged with the variation of pressure and temperature. Both pressure and thermal effects on the relative formation energies of silicon clusters were found to be rather small up to the temperature of 1000 K (Fig. 3) that we tested, although noticeable variation in their absolute magnitudes was seen. However this may no longer hold true at exceedingly high temperatures which allow for the coexistence of solid and liquidlike regimes.[15] For quantitative accuracy, anharmonicity effects should be taken into account in the calculations, particularly at such high temperatures. In particular, pressure effects are shown to play a surprisingly small role on the alteration of magic numbers, as shown in Figs. 1–3. The pressure dependence for the atomic clusters of silicon greatly differs from the case of molecular clusters; the atomic clusters are less sensitive to the variation of pressure. This is because the binding energies of the molecular clusters are much smaller than those of the atomic clusters.

Finally in order to find a general trend in the change of cluster binding energy for the atomic clusters of silicon and to see convergence to the bulk limit of cohesive energy, we computed the average binding energies ($\Delta\phi_i$ at 0 K) of larger clusters as a function of cluster size n. We found that the analytical expression of

$$B_n = B_\infty(1-n^{-\alpha}) , \tag{16}$$

with $\alpha=0.623$, tends to fit reasonably well the binding energies of the clusters of size up to $n=62$ that we tested. The bulk limit value from the use of (16) is found to be $B_\infty=4.875$ eV, in close agreement with the observed bulk value[16] of 4.63 eV. We may have found a universal trend in terms of this functional relation for the estimation of binding energy as a function of cluster size, which fits both the atomic and molecular clusters. It is of note that earlier we[12,17] showed the exactly identical formula for the molecular clusters of water with a somewhat different value of α.

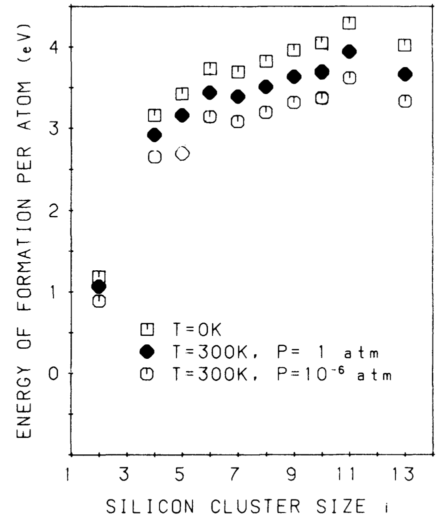

FIG. 2. Formation energies of silicon clusters as a function of cluster size at temperatures $T=0$ and 300 K and at pressures $P=10^{-6}$ and 1 atm.

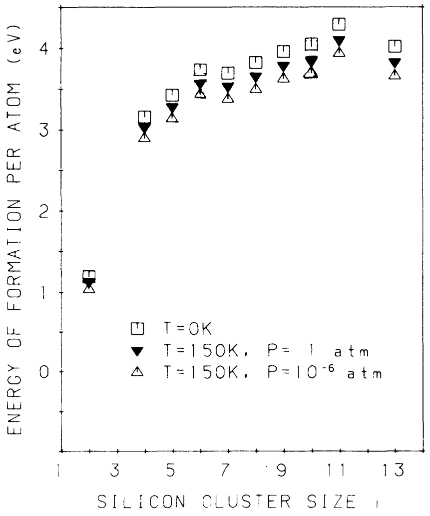

FIG. 1. Formation energies of silicon clusters as a function of cluster size at temperatures $T=0$ and 150 K and at pressures $P=10^{-6}$ and 1 atm.

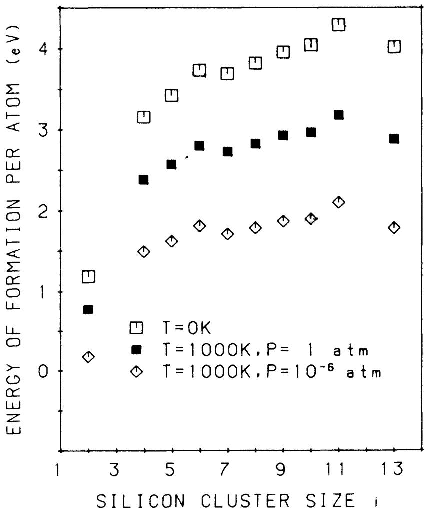

FIG. 3. Formation energies of silicon clusters as a function of cluster size at temperatures $T=0$ and 1000 K and at pressures $P=10^{-6}$ and 1 atm.

IV. CONCLUSION

Thus far most calculations of silicon clusters have been limited to the energy of formation corresponding to $T=0$ K. In the present study we have found that temperature and pressure effects on the relative magnitudes of the formation energies of silicon clusters are small. Thus magic numbers found at $T=0$ K are expected to maintain their identities well below the melting point. Consequently, the often-found excellent correlation between quantal calculations and observed silicon cluster-size spectra is now well explained. The functional relation for the estimation of binding energies for the atomic clusters of silicon was found to be of the same form as that of molecular clusters.[12] In short, the key points in the present study are (1) the formal derivations of formation energy and equilibrium cluster-size distribution which depend on both temperature and pressure for both homogeneous and heterogeneous atomic clusters, (2) the prediction of both pressure- and temperature-insensitive relative size distributions, and (3) the finding of a universal functional relation for the trend of formation energy as a function of cluster size for both atomic and molecular clusters.

The estimated binding energies of the small clusters at 0 K are relatively unreliable compared to the larger ones due to inherent inaccuracy in the semiempirical method.[13,14] However, the qualitative conclusions made above are expected to be unchanged. It will be of great interest to examine in the future the crossover points of temperature and pressure for the alteration of relative cluster-size distributions and thus of magic numbers. More precise quantal calculations[9,10(a)] at 0 K have demonstrated that the computed magic numbers agreed well with experiments measured at finite temperatures. It can be concluded from our present study that the nonequilibrium process of clusterization may not significantly affect the relative cluster-size distributions, thus maintaining the magic numbers up to a certain high temperature. This may hold true particularly for atomic clusters compared to molecular clusters, as the former are more tightly bound systems.

ACKNOWLEDGMENTS

We acknowledge the financial support of the National Science Foundation through Grant No. NSF ATM-8716918. One of us (S.H.S.S.) also acknowledges the Korean Ministry of Education and the Center for Molecular Sciences at the Korea Advanced Institute of Science and Technology for partial financial support He especially thanks Professor Tim Poston at Pohang Institute of Science and Technology for a critical reading of the manuscript.

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