

Model for the glass transition in amorphous solids based on fragmentation

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A model for the glass transition in a heating process has been proposed. In the model, noncrystalline solids are assumed to be assemblies of pseudomolecules or structural units. When the noncrystalline solid is heated, a bond breaking process becomes dominant compared with a rebinding process of broken bonds. At high temperature, successive bond breaking causes the fragmentation of the solid and the fragment size becomes smaller as the temperature further increases. Consequently, the solid begins to show some viscous behavior when the fragment size reaches a critical value. To construct mathematical expressions for the fragmentation model, we employed a simple rate equation for the bond breaking process first and then obtained the temperature dependence of dangling bond density in a noncrystalline solid. Second, the expressions for the fragment density and size as a function of temperature were obtained based on the following assumptions: (1) bond breaking takes place mainly at the boundaries between pseudomolecules, (2) once buds of microcracks are generated, successive bond breaking occurs mostly at the tip of the microcracks, and (3) the fragments are Voronoy polyhedra. Finally, the diffusion coefficient in the system was obtained by assuming the vacancy mechanism in solids and then the temperature dependence of viscosity was derived through Stokes-Einstein relation. To examine the present model, applications of the model to the phase changes of *a*-Si in heating processes are carried out and the results were discussed.

I. INTRODUCTION

The term "glass" is often distinguished from the term "amorphous," since the glass transition is observed for the former in conventional thermodynamical measurements whereas the latter does not exhibit the glass transition and cannot be obtained by the conventional melt-quench method. Moreover, the preparation method for both is different, that is, glasses are usually prepared by quenching from a molten state, while amorphous solids are generally obtained in the film by the condensation from a vapor phase, e.g., by vacuum evaporation, sputtering, and chemical vapor deposition.¹

For the ability of glass forming, a number of models based on structural or kinetic aspects have been proposed since long ago. One can date back to 1926 when Goldschmidt presented the condition for binary ionic glass formers.²⁻⁴ In 1932, Zachariasen introduced the idea of a continuous random network to the modern glass science.² In his paper, Zachariasen made several structural requirements for oxide glass formation, e.g., cations are surrounded by oxygen tetrahedra or triangles, the oxygen tetrahedra or triangles share only corners, and some oxygen atoms are linked to only two cations and do not form further bonds with other cations. Recent remarkable structural consideration for glass forming ability for materials formed by covalent interatomic forces may be a model proposed by Phillips.⁵ He thought that materials had high ability of glass forming when mechanical constraints as a function of an average coordination number is equal to the degree of freedom associated with bond stretching and bond-bending interactions, and showed that an optimum coordination number for the randomly bonded covalent network would be 2.45. This model explains that many chalcogenide systems easily vitrify and tetrahedrally bonded solids are hard to vitrify.

Recently, however, hyperquenching has been attained using the melt-spin technique⁶ and pulsed laser irradiation,⁷ so that the glass forming ability has been expanded to those materials that cannot be vitrified by conventional melt-quench methods. For example, many metallic glasses are prepared by the melt-spin technique with the cooling rate more than 10^5 K/s,⁸ and tetrahedrally bonded amorphous Si (*a*-Si) can be directly produced from liquid Si in a cooling rate more than 10^9 K/s.⁹ The cooling rate is, thus, considered a predominant factor in vitrification, so kinetic approaches are important. The kinetic approaches to the glass forming ability are generally described by the conditions of avoiding crystal growth, since materials can vitrify in the conditions where both of the crystal nucleation and its stable growth are not attained.³ Although these models do not provide a simple index for the glass forming ability as Phillips' model does, the role of the cooling rate in the glass forming processes has been introduced phenomenologically in terms of the minimum (or critical) cooling rate for vitrification. Noncrystalline solids, which are in nonequilibrium states, exhibit phase transitions such as the glass transition and/or the crystallization in heating processes. These transitions are not uniquely determined by thermodynamic variables.¹⁰ They are dependent on the heating rate,¹¹ so in phase transitions involving nonequilibrium states the heating rate must be one of the important factors controlling the transition. A model for the heating rate dependence of crystallization temperature T_c has been developed based on the temperature dependence of the induction time for nucleation and of the critical size for stable growth of the nucleus.¹¹ On the other hand, the mechanism of the glass transition is still not clear, so various aspects around the glass transition remain to be solved.

The most distinctive feature in glass transition phenomena may be a large change in viscosity.¹² It is known that the viscosity in glass forming materials varies 15 orders of mag-

nitude between its molten and glassy states. To explain such a drastic change in viscosity, many theories have been developed based on distinct microscopic models, in which “free volume,”¹³ cooperative rearrangement of a group of molecules¹⁴ or other molecular-scale processes^{15–17} are considered. Phenomenological models based on the relaxation equation have also been developed.¹⁸ These theories describe fairly well nonlinear and nonexponential structural relaxation. More recently, computational experiments on glass transition using molecular dynamics¹⁶ and mode-coupling theory¹⁷ have been intensively studied. These theories are, explicitly or implicitly, based on the systems composed of definite units (molecules or atoms) as a hard sphere which interact each other through spherically symmetric potential. Computational experiments using these theories showed the drastic change in macroscopic dynamics of molecules (or atoms) around the glass transition temperature.¹⁹ The results, however, appear not to be applicable to many of inorganic glasses, since it is difficult to find such a suitable unit in those glasses at around the glass transition temperature although such a unit is defined at higher temperatures around the melting point. The nature of the glass transition is very complex. Another important aspect of the glass transition concerns the thermodynamical interpretation. No single theory that has been advanced so far is capable of accounting for all aspects of the glass transition. An insight is, thus, necessary to give a sudden decrease of viscosity above the glass transition temperature.

In this paper, a kinetic model for the structures of noncrystalline solids in the heating processes is proposed. This model is based on the fragmentation of the continuous random network. In fact, some experimental results suggest the fragmentation in a system above glass transition temperature²⁰ and therefore the concept of fragmentation in a system could be applied. Using this concept, the softening processes even for tetrahedrally bonded amorphous networks can be given. Further, some applications of this model to macroscopic phenomena in *a*-Si in the heating processes are also presented.

II. A MODEL FOR THE GLASS TRANSITION IN NONCRYSTALLINE SOLIDS

Noncrystalline solids formed with covalent bonds contain a number of weak bonds and dangling bonds.²¹ At high temperatures, bond breaking takes place briskly. Successive bond breaking is expected to reduce noncrystalline materials into fragments. As a result of the fragmentation, cohesive energy in the fragmented system more or less decreases, so viscous behavior of the system would change drastically.

To construct the fragmentation model, the following assumptions have been made. (1) Noncrystalline solids are basically assemblies of pseudomolecules. (2) “Pseudomolecule” is a cluster having a disordered lattice in which the valence requirement of constituent atoms is satisfied. That is, pseudomolecules have no definite defects such as under or overcoordinated atoms inside. (3) However, there exist defects in the boundary regions between pseudomolecules.

Although there is no direct evidence of a pseudomolecule, there is some relevant information suggesting the presence of the pseudomolecules. That is, infinite continuous random

networks with no defects such as under and/or overcoordinated atoms have not been found so far,²² and such an infinite continuous random network has not been generated even by computer experiments.²³ These results suggest that random networks having no definite defects cannot exceed a certain dimension. Conversely, a defect-free amorphous structural unit, of which dimension is smaller than a certain value, could be made up of continuous random networks. Such a unit may be called a pseudomolecule. The dimension and the shape of a pseudomolecule may be irregular and depend on constituent atoms. In *a*-Si, for example, Polk’s model consisting of ~500 atoms²⁴ could be applied to the pseudomolecule. It is, therefore, plausible that macroscopic noncrystalline solids are assemblies of pseudomolecules. In most cases, pseudomolecules would not exhibit clear features, since their boundary regions are also composed of random networks. There exists, however, much strain hence various defects in boundary regions. It is, thus, expected that amorphous solids involve networks of latent cracks. Bond breaking, therefore, produces cracks running along boundaries between pseudomolecules and at last causes the fragmentation of random networks, if the crystallization does not intervene.

A. Bond breaking processes

For simplicity, the bonding system is assumed to be represented by one sort of bonding mechanism. In noncrystalline solids, thermal excitation of electrons from the bonding state to the antibonding state would result in producing pairs of broken bonds, since there exists large strain in noncrystalline solids. The rate of bond breaking increases with temperature and is expected to be proportional to the density of bonds. Some pairs of broken bonds will rebind again, so the rate of rebinding of dangling bonds is expected to be proportional to the number of pairs of broken bonds. Therefore, rebinding processes proportional to the square of broken bonds, i.e., bimolecular processes, would be neglected.

Taking these reactions into account, the total number of bonds per unit volume as a function of t , $N(t)$, could be expressed by a following rate equation:

$$-\frac{dN(t)}{dt} = k_f N(t) - \frac{1}{2} k_r n_D(t), \quad (1)$$

where n_D is the number of dangling bonds per unit volume, and k_f and k_r are forward (bond breaking) and reverse (rebinding) rate constants. k_f and k_r are given by the Arrhenius forms, that is, $k_f = F \exp(-E_f/k_B T)$ and $k_r = R \exp(-E_r/k_B T)$. Here, F and R are frequency factors, E_f and E_r are the activation energy for bond breaking and rebinding, respectively, k_B is the Boltzmann constant, and T is the temperature. Since $N(t) = N_0 - (1/2)n_D(t)$, where N_0 is the total number of covalent bonds in amorphous materials, Eq. (1) yields

$$\frac{dn_D(t)}{dt} = -(k_f + k_r)n_D(t) + 2k_f N_0. \quad (1')$$

Let us suppose that the system is heated at a constant heating rate α . The temperature T at time t is, then, ex-

pressed by $T(t) = T_i + \alpha t$. Thus Eq. (1) with respect to time t is converted to a differential equation with temperature T :

$$\frac{dn_D(T)}{dT} = -\frac{1}{\alpha} [k_f(T) + k_r(T)]n_D(T) + \frac{2N_0}{\alpha} k_f(T). \quad (2)$$

The solution to Eq. (2) is given by

$$n_D(T) = [C(T) + N_D^0] \exp\left[-\frac{1}{\alpha} \int_{T_0}^T [k_f(x) + k_r(x)] dx\right], \quad (3)$$

$$C(T) = \frac{2N_0}{\alpha} \int_{T_0}^T k_f(x) \exp\left[\frac{1}{\alpha} \int_{T_0}^x [k_f(z) + k_r(z)] dz\right] dx, \quad (4)$$

where N_D^0 is a dangling bond density at $T = T_0$.

B. Fragmentation

As temperature increases, fragmentation processes due to bond breaking would proceed as follows. Bond breaking occurs mostly in the boundary regions between pseudomolecules, although it takes place even in pseudomolecules at high temperature. Once buds of microcracks are generated, successive bond breaks take place mostly at the tip of the microcrack. Microcracks spread branches out along the boundaries between pseudomolecules, so materials would break into fragments when the dangling bond density reached a certain level. The number of fragments, thus, increases and their average dimension decreases with temperature. It is, however, not necessary to break all bonds on the surface of the fragments to create fragments. The progress of the fragmentation would depend on amorphous structures and the bonding scheme. For example, if bond breaking occurs almost independently here and there, microcracks cannot be formed until the dangling bond density reaches a relatively high level. In the extreme case, the fragmentation would produce pseudomolecules at once. If pseudomolecules are stable enough, the fragmentation will stop when the system breaks into pseudomolecules. On the other hand, the fragmentation will proceed until the system breaks into atoms in the case of unstable pseudomolecules. The fragmentation processes in real systems may be somewhere between these cases depending on microscopic structures and bonding scheme of materials. In any case, the fragmentation would occur rather suddenly when the dangling bond density reaches a critical value.

The number and the average size of fragments can be approximately estimated from the density of dangling bonds as follows. For the present, let us suppose that the system is fragmented into n^3 irregular-surfaced polyhedra. Fragments could be regarded as Voronoy polyhedra which are produced from randomly distributed n^3 sites. The surface area of n^3 Voronoy polyhedra may be estimated by replacing them with Wigner-Seitz cells about close packed (twelvefold coordinated) lattices. This will hold well in those solids composed of isotropic random networks. The surface areas of Wigner-Seitz cells about close packed lattices are all $\sim 5.4/n^2$ cm² when the volume of Wigner-Seitz cell is $1/n^3$, so the cracked area to create n^3 fragments is approximated to be $[5.4/n^2][(n-1)^3/2]$. The fragments also contain internal

cracks of which area is assumed to be comparable to their surface area at the onset of fragmentation. Thus the number of dangling bonds required to produce n^3 polyhedra could be given by

$$n_D = 2(2.7n)N_a\sigma\xi(1+f), \quad (5)$$

where N_a is the atomic density on the cracked surfaces, ξ the average number of bonds per one atom on the cracked surfaces, σ the correction factor for surface irregularity of polyhedra, and f the numerical factor to count dangling bonds inside fragments. Internal cracks are expected to reduce to zero as the fragment becomes smaller, so we adopt $\exp[-(n-a)/b]$ as f , where a and b are constants. Thus $N_F (= n^3)$ can be determined as a function of n_D .

Once N_F is obtained, the most probable value for the fragment size $\langle d \rangle$, which could be taken as the average dimension of fragments, is given by

$$\langle d \rangle = \zeta \left(\frac{\pi}{6} N_F \right)^{-1/3}, \quad (6)$$

where ζ is a correction factor for the shape of the fragment and for simplicity ζ is taken to be unity.

As the fragmentation proceeds, N_F increases to the atomic density of the amorphous solid, n_0 , for the system of the weak pseudomolecule. On the other hand, in the case of the stable pseudomolecule, the maximum N_F is the density of pseudomolecules N_{PM} . There would be the minimum N_F , that is, there must be a critical value of n_D to cause the fragmentation.

These fragmentation processes should be modified for those noncrystalline solids with pseudomolecules having layered and/or chain structures.

C. Diffusion constant and viscosity of the fragmented system

One can expect that amorphous solids exhibit drastic changes of viscosity with the fragmentation. It is, however, difficult to estimate quantitatively viscosity of those systems in which the dimension of fragments is distributed and their shapes are irregular. Moreover, the character of cohesive energy of the fragmented system might change with progress of the fragmentation. At present, we do not have effective means to estimate the distribution and irregularity in those systems, so we try to estimate viscous behavior of the fragmented systems using a simplified model. We assume that in the fragment system viscosity is related to the diffusion coefficient through the Stokes-Einstein relation, in which the diffusion constant defined for the fragment with an average size is applied. The contribution of fast diffusion of small fragments to viscosity would be small, and viscosity is expected to be controlled mainly by the mobility of those fragments with the average dimension $\langle d \rangle$ given by Eq. (6). Hence this assumption may be a fairly good approximation to viscosity of the fragmented system. Then, we first calculate the diffusion constant of the fragment with the dimension of $\langle d \rangle$.

The systems composed of fragments are considered to involve holes which correspond to vacancies in crystalline solids, as pointed out by Hirai and Eyring.²⁵ If the dimension of the hole is assumed to be equal to the average size of

fragments, the equilibrium density of holes is determined by minimizing free energy associated with the introduction of holes. The change in entropy due to the mixing of holes and fragments must be much larger than the change of vibrational entropy caused by the formation of holes. Thus the equilibrium density of holes in the fragmented system, n_h , is given by²⁶

$$n_h = N_F \exp\left(-\frac{E_h + P v_h}{k_B T}\right), \quad (7)$$

where E_h is the average hole formation energy, P the pressure, and v_h the volume of the hole. In usual conditions, $P v_h$ is far smaller than E_h , so $P v_h$ can be neglected. On the analogy of the vacancy mechanism in diffusion phenomena,²⁷ the self-diffusion coefficient $\langle D \rangle$ in the fragmented system could be written as

$$\langle D \rangle = \frac{2N_F}{n_0} \theta \nu_0 (\kappa \langle d \rangle)^2 \exp\left(-\frac{E_h + E_j}{k_B T}\right), \quad (8)$$

where ν_0 is an average jump frequency of fragments, E_j the average fragment jump energy, θ a numerical factor associated with the number of available jump sites, and κ a numerical factor of the order of unity, since $\kappa \langle d \rangle$ represents a jump distance of fragments. θ is expected to be around 1/6 on the analogy of crystalline lattices. ν_0 of the fragmented system could be expressed by

$$\nu_0 = \omega_0 \left(\frac{2N_F}{n_0}\right)^{1/3}, \quad (9)$$

where ω_0 is the Debye frequency of the amorphous solid.

E_h and E_j are determined by the cohesive energy in the fragmented system. Even if the fragments have chemically stable surfaces because of surface reconstruction, there exists a weak attractive potential which originates from the induced dipole-dipole interaction. In this case, the potential energy is expected to be proportional to the molecular size.²⁸ If the density of residual bonds on the surface of fragments is not zero or the fragments have reactive surfaces because of incomplete surface reconstruction, the interactive force between fragments is proportional to the surface area of fragments. Therefore, E_h and E_j could be expressed by the power law of the fragment size $\langle d \rangle$:

$$E_h = \langle d \rangle^p \epsilon_0, \quad (10)$$

$$E_j = g E_h, \quad (11)$$

where ϵ_0 is the characteristic energy determined by the cohesive energy of the fragmented system, p a positive number depending on the character of the cohesive energy, and g a numerical factor. The exponent p ranges from 1 to 2 depending on the cohesive energy between fragments. E_j is usually a half of E_h ,²⁹ so g is taken to be 1/2. It should be noted that E_h and E_j decrease with the progress of the fragmentation.

Viscosity η is, now, obtained from the Stokes-Einstein relation using $\langle D \rangle$ and $\langle d \rangle$:

$$\eta = \frac{k_B T}{2\pi \langle d \rangle \langle D \rangle}. \quad (12)$$

η is a function of temperature T and the heating rate α , since $\langle D \rangle$ and $\langle d \rangle$ are functions of T and α . η begins to decrease drastically just after the onset of the fragmentation, and gives very similar temperature dependences of the empirical Fulcher-Vogel-Tammann equation. Peculiar viscous behaviors of noncrystalline materials are, thus, successfully given by the fragmentation model.

III. DISCUSSIONS

It was shown that the glass transition in noncrystalline solids can be understood in terms of the fragmentation model, in which noncrystalline solids are considered to be assemblies of pseudomolecules. The fragmentation model involves many parameters and assumptions, so the validity of the fragmentation model should be examined by applying it to viscous behaviors of noncrystalline solids. From this point of view, *a*-Si is quite an interesting material, which has been discriminated from glasses³⁰ since *a*-Si is normally prepared in a form of thin films from vapor phase on substrates and it does not exhibit the glass transition in thermodynamical measurements such as conventional differential scanning calorimetry. There are, however, some experimental results suggesting that *a*-Si is a glass.^{31,32}

The free energy of *a*-Si, which is larger than that of crystalline Si, exceeds that of liquid Si at around 1400 K,^{33,34} so that *a*-Si turns to liquid above ~ 1400 K. The supercooled liquid is metallic as well as molten Si.³⁵ On the contrary, transient enhanced diffusion in the ion-implanted *a*-Si suggests that there exists the supercooled liquid state below ~ 1400 K (Refs. 36–38) because of the fact that the activation energy for the diffusion is very small and that the diffusion coefficients of impurities are almost the same independent of the impurity species. The supercooled liquid state below ~ 1400 K does not exhibit metallic characters, so it is expected to be fourfold coordinated. The fact that *a*-Si can be obtained directly from a more than sixfold coordinated metallic liquid by ultrafast quenching⁹ also suggests that there exists a fourfold coordinated semiconductive supercooled liquid state between the metallic liquid and the semiconductive solid. However, three-dimensional amorphous networks formed by fourfold coordinated atoms are so rigid that they cannot exhibit fluidity in the high heating processes.³⁹

Both the supercooled metallic and semiconductive liquids are in nonequilibrium transient states which appear in certain temperature ranges during the fast heating or quenching processes. In fact, the supercooled metallic liquid is observed only when the heating rates are higher than $\sim 10^8$ K/s.⁴⁰ In the case of the supercooled semiconductive liquid, the lowest heating rate for appearance is inferred indirectly to be $10\text{--}10^2$ from transient enhanced diffusion in ion-implanted *a*-Si.^{37,38,41} Whether the supercooled semiconductive liquid states exist or not is an interesting subject in *a*-Si, so we apply the fragmentation model to *a*-Si in order to know the conditions of appearance of the supercooled semiconductive liquid.

A. Bond breaking and the fragmentation of *a*-Si

The fragmentation processes due to bond breaking described in the previous section can be directly applied to

TABLE I. Numerical values used for the calculation of dangling bond density in *a*-Si.

E_f (eV)	E_r (eV)	F (s^{-1})	R (s^{-1})	N_0 (cm^{-3})
2.50	1.32	2.0×10^{12}	9.0×10^7	1.0×10^{23}

a-Si, since there exists only Si-Si bonds and almost isotropic cracking is expected to occur. Numerical values used for calculation of the dangling bond density are listed in Table I. The activation energy for breaking the Si-Si bond in *a*-Si, E_f , is estimated 2.5 eV (Ref. 42) and the frequency factor F is taken to be the typical Debye frequency of solids. E_r and R are 1.32 eV and 9.0×10^7 s, which are chosen to increase the dangling bond density above ~ 700 K, since the spin density is reported to increase by annealing above 400 °C.⁴³ The dangling bond density n_D was, thus, calculated from Eqs. (3) and (4) using these values in Table I. Figure 1 shows n_D as a function of T when *a*-Si is heated with various heating rates α .

The fragment density, N_F , is calculated from Eq. (5) using numerical values listed in Table II. The atomic density on the cracked surface N_a , which is the average atomic density on the arbitrary plane in *a*-Si, is estimated to be $1.35 \times 10^{15} cm^{-2}$ from the atomic density in crystalline Si, $n_0 (=5 \times 10^{22} cm^{-3})$. The average number of bonds per one atom on the cracked surfaces, ξ , is taken to be 1, since cracked surfaces may be planes like a (111). For simplicity, a correction factor, σ , for irregularity in fragments is assumed 1. The constants a and b in $f = \exp[-(n-a)/b]$ are chosen to be $10^6 cm^{-1}$ and $1.15 \times 10^6 cm^{-1}$ to satisfy the assumption described in Sec. III B.

The temperature dependence of N_F is shown in Fig. 2. N_F increases with temperature and strongly depends on the heating rate. N_F and $\langle d \rangle$ at the onset of the fragmentation are calculated to be $1.7 \times 10^{18} cm^{-3}$ and 8.4 nm since we have assumed that the fragments contain internal cracks of which

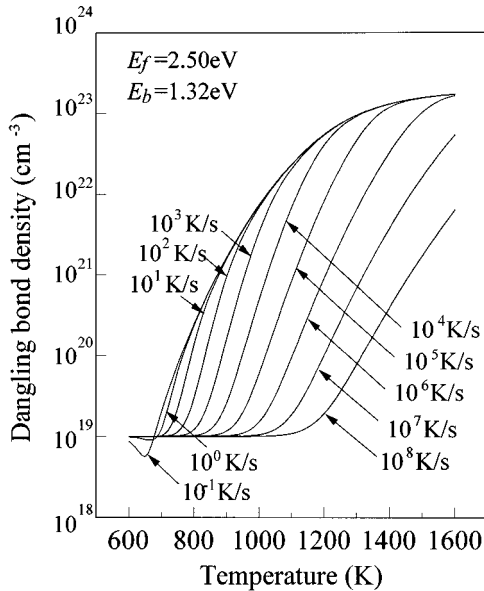


FIG. 1. Dangling bond densities in *a*-Si as a function of temperature when *a*-Si is heated at various heating rates α .

TABLE II. Numerical values used for the calculations of the fragment density and size.

N_a (cm^{-2})	ξ	σ	a (cm^{-1})	b (cm^{-1})	ζ
1.35×10^{15}	1.0	1.0	10^6	1.15×10^6	1.0

area is comparable to their surface area at the onset of fragmentation. The dashed line in Fig. 2 indicates N_F at the onset of the fragmentation. The dimension of fragment $\langle d \rangle$ at the onset of the fragmentation is reasonable, so the choice of the function f with the condition of the onset of the fragmentation are considered to be appropriate.

B. Viscosity and the glass transition of *a*-Si

Numerical values for calculation of the diffusion constant and viscosity are listed in Table III. The values for ξ , κ , θ , and ω_0 are those values given in the previous section. The characteristic energy ϵ_0 and the exponent p are chosen $3.0 \times 10^9 eV/cm^{1.5}$ and 1.5 to give reasonable diffusion coefficient $\langle D \rangle$, hence to give $10^{15} mPa s$ to η at around 1100 K in low heating rate. In fact, T_g of *a*-Si is expected to be ~ 1100 K at the heating rate around 10^2 K/s.¹¹ The exponent p must be larger than 1 because of remaining bonds on the surface of the fragment and/or of incomplete surface reconstruction. Therefore, in *a*-Si, 1.5 for p is plausible.

The temperature dependence of diffusion constant $\langle D \rangle$ and viscosity η calculated from Eqs. (8) and (12) are shown in Figs. 3 and 4, respectively. The dashed lines in Figs. 3 and 4 correspond to the point at which the fragmentation is expected to occur as shown in Fig. 2. Note that N_F , $\langle D \rangle$, and η in Figs. 3 and 4 are valid after the fragmentation occurs and before the crystallization takes place. $\langle D \rangle$ and η change drastically after the onset of the fragmentation and they shift to higher temperature as the heating rate increases. It should be pointed out that the fragmented system is a supercooled liquid until it is reduced into atoms or crystallization intervenes.

The glass transition temperature T_g of noncrystalline solids are estimated as the temperature at which viscosity reduces to $10^{15} mPa s$, so T_g of *a*-Si is obtained from Fig. 4. The heating rate dependence of T_g is drawn in Fig. 5, in

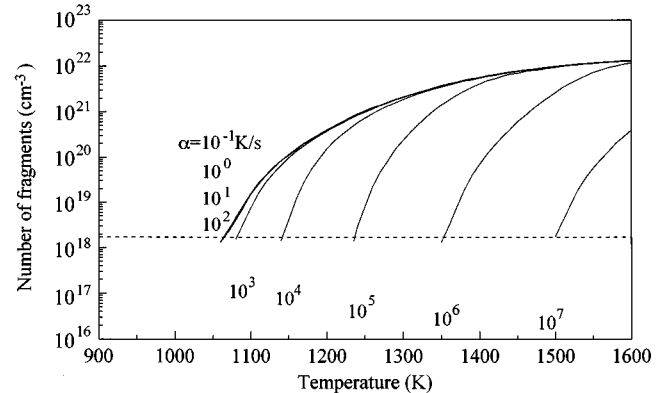


FIG. 2. Temperature dependence of the fragment density with various heating rates α . The dashed line indicates the onset of fragmentation.

TABLE III. Numerical values used for the calculations of diffusion coefficient and viscosity in *a*-Si.

n_0 (cm ⁻³)	κ	θ	ω_0 (s ⁻¹)	ϵ_0 (eV/cm ^{<i>p</i>})	p	g
5.0×10^{22}	1.0	0.16	3.0×10^{12}	3.0×10^9	1.5	0.5

which T_c , T'_c , T_{ma} , and T'_g are also shown. T_{ma} is the melting temperature of *a*-Si,³¹⁻³⁴ and T_c is the solid phase crystallization temperature which was calculated on phenomenological theory using the induction time for nucleation.¹¹ T'_c and T'_g are the inferred glass transition and crystallization temperatures above 10^2 K/s, which were estimated from experimental results.^{37,44} The calculated T'_g of *a*-Si coincides well with the inferred T'_g in the region of $\alpha < 10^3$ K/s. It should be emphasized that the fragmentation model gives the heating rate dependence of the glass transition, and that the glass transition in *a*-Si is, as seen in Fig. 5, observed only when the heating rate is higher than 5×10 K/s. This is because the crystallization precedes the fragmentation processes when $\alpha < 5 \times 10$ K/s.⁴⁵

The hole formation energy E_h given by $\epsilon_0 d^p$ is 2.1 eV at T_g where $\langle d \rangle$ is about 8.0 nm, and decreases to 0.3 eV when the fragment is reduced to the pseudomolecule of the size of about 2.0 nm. These values are reasonable ones as the activation energy for viscosity of the system composed of fragments. The fragment size $\langle d \rangle$ at T_g is very close to the value at the onset of the fragmentation obtained above, so it can be said that a set of parameters and assumptions made are on the whole reasonable.

However, the results obtained are not fully satisfactory, since T'_g increases rapidly so that it deviates from the inferred T'_g as the heating rate increases. If the heating rate is

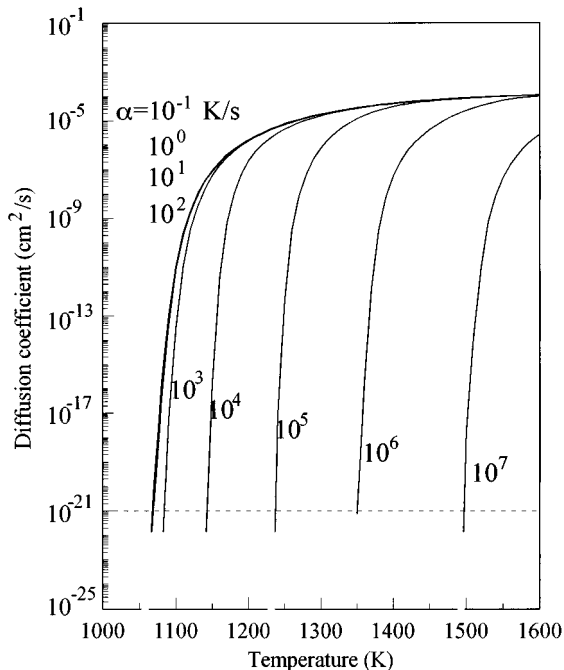


FIG. 3. Diffusion coefficient of *a*-Si as a function of temperature when *a*-Si is heated at various heating rates α . The dashed line corresponds to that shown in Fig. 2.

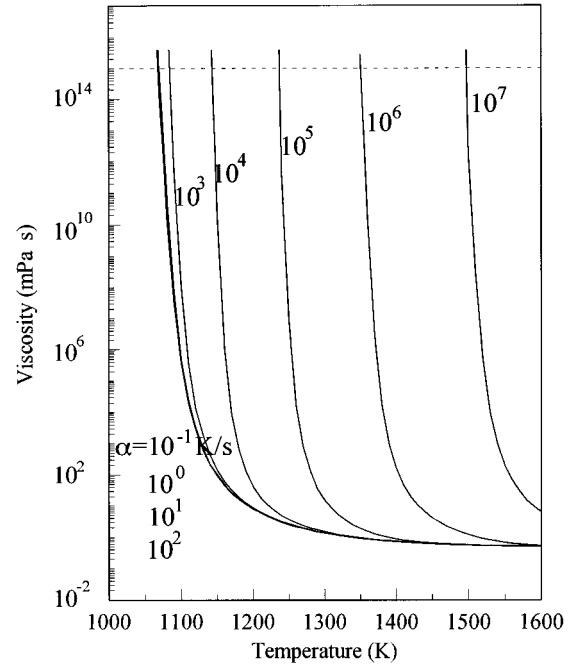


FIG. 4. Viscosity in *a*-Si calculated from Eqs. (10) and (14) as a function of temperature. The dashed line at which the viscosity is 10^{15} mPa s indicates the glass transition condition.

higher than 10^8 K/s, the supercooled semiconductive liquid turns to the supercooled metallic liquid at around 1400 K.⁴⁰ In other words, *a*-Si does not exhibit crystallization in the high heating rate, and the crystallization temperature, T'_c , between 10^2 and 10^8 K/s is expected to increase smoothly from ~ 1100 to ~ 1400 K as shown in Fig. 5, since the supercooled semiconductive liquid crystallizes below 1400 K when $\alpha < 10^8$ K/s.^{40,44} The glass transition temperature must lie below the crystallization temperature, but T_g rises above

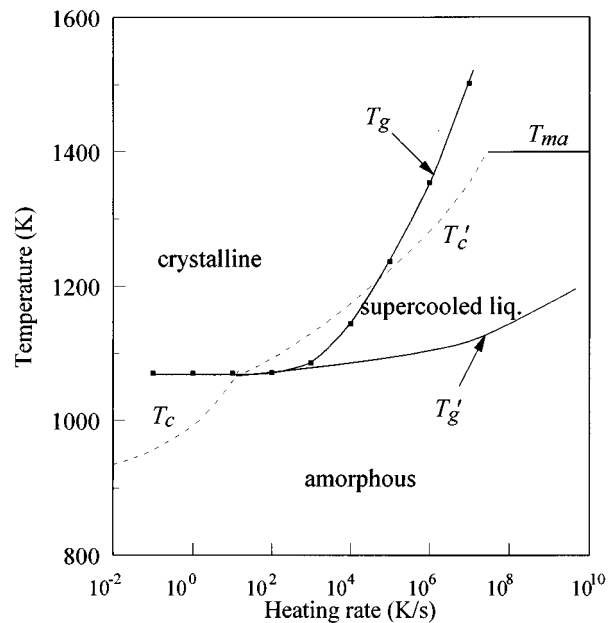


FIG. 5. The transient phase diagram of *a*-Si.

T'_c at around 10^4 K/s. The discrepancy between T_g and T'_g in the high heating rate region is considered to be due not to unsuitable choice of parameters. Here, we do not discuss the propriety of each parameter to avoid a long boring discussion. It should be, however, stated that one can bring T_g close to T'_g using other parameters than those listed in tables. Unfortunately a set of such parameters involves unreasonable ones or induces other difficulties. For example, smaller E_f and E_r greatly improve the behavior of T_g in the high heating rate region, but the spin density at low temperatures becomes unreasonable. Therefore, the discrepancy between T_g and T'_g should be ascribed to other causes.

Intense light beam from a flash lamp or a pulsed laser is used to attain the extremely steep heating rates. Thermallization processes of photoexcited carriers, of the order of 10^{-13} s,⁴⁶ are fast enough to raise lattice temperature even in extremely steep heating rates. However, photoinduced bond breaking would be dominant in higher heating rate processes, since probability of rebinding of broken bonds produced by photoirradiation would become smaller as the heating rate increases. Intense photoirradiation, therefore, enhances the fragmentation so that the glass transition temperature reduces.

In the present model, only thermal bond breaking is taken into consideration. Thus the discrepancy between T_g and T'_g in the high heating rate region is not due to the intrinsic defect of the present model. As far as the fragmentation is caused by heat, the present model is expected to hold well. If photoinduced effects are involved in the fragmentation processes, the situation will be improved. This subject remains to be studied.

Problems concerning irregularity in shape of the fragments and their size distribution are also very important. Actual fragments must be irregular-surfaced polyhedra and their sizes must be distributed in a wide range. Viscosity must be affected by both irregularity in shape of the fragments and their size distribution. At present we have no means to estimate the size distribution of fragments. It is desirable to develop the method of direct estimation of fluidity of the system composed of irregular fragments.

Finally, we will compare the fragmentation model with alternative models. Many models accounting for the glass transition phenomena are generally associated with a cooling process from liquid, which is of course useful for a glass forming technology. The mode coupling theory (MCT) based on fluctuating nonlinear hydrodynamics has been successful in explaining the sequence of time relaxation for dense fluids in a cooling process.¹⁷ MCT deals with the density correlation function involving the information about the time dependence of the local structure in a fluid. On the other hand, the present model is concerned with heating processes from solid, where the diffusive motion of particles changing their size with temperature is treated. Although the approach of the present model is quite different from MCT, some similarity can be seen. For example, the temperature dependence of viscosity η , which is directly related to the α -relaxation process, calculated by the present model also exhibits similar behavior to that predicted by the MCT, i.e., $\eta = \eta_0(T/T_x - 1)^{-\alpha}$.¹² Further, MCT describes some solidlike behavior or cooperative motion of molecules well above

$T_g (= 1.3T_g)$.¹² This can be easily understood in terms of clustering processes as a reverse process of the fragmentation. Thus the viscous behavior of glasses in the glass transition could be ascribed to the appearance of some molecular or atomic groups, or of fragments. The character of intermolecular or interatomic potential may be different from that of molecular groups or atomic groups appearing in glass transition, especially for network glasses, so that the change in the character of cohesive energy should be taken into account in the glass transition. Such a situation is involved in the fragmentation model, while it is not involved in MCT and molecular dynamic simulation.

It is worth noting that the entropy of the fragmented system increases as the fragmentation proceeds and at last reaches that of the liquid state. Partial release of fragment motions such as the rotative movements may occur in the early stage of the fragmentation. The partial release of fragment motions contributes to the specific heat. The glass transition appears to be a fuzzy first-order phase transition. Thermodynamical properties concerning the glass transition based on the fragmentation model will be found elsewhere.⁴⁷

IV. SUMMARY

We have constructed a model for the glass transition of a noncrystalline solid in a heating process, based on the idea that due to bond breaking the noncrystalline solids are fragmented into small clusters with increasing temperature. In this model, moreover, the fragments become smaller and smaller with further increase in temperature and the noncrystalline solid begins to behave like a liquid when the fragment size reaches some critical value. The mathematical expressions for the temperature dependences of dangling bond density and the fragment density were obtained by the present model. Diffusion coefficient and viscosity of the fragmented system were calculated, applying vacancy mechanism to the fragmented system in which the fragment becomes smaller and smaller with increasing temperature. It was, thus, shown that the noncrystalline solid begins to behave like a liquid when the fragment size reaches some critical value, and that the fragmented system exhibits viscous behavior similar to the empirical Vogel-Fulcher-Tammann equation. The heating rate dependences of the glass transition were also obtained.

Further, in order to examine the present model, we applied this model to the phase changes of α -Si in heating processes with various heating rates and the results of the calculation were compared with those of experiments previously reported. Consequently, some difference between the calculated and experimental results was found. This discrepancy was concluded that the experimental results were caused not only by thermal effects but also by photoinduced effects.

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- ¹J. Zarzycki, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, New York, 1991), Vol. 9, Chap. 2.
- ²W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932).
- ³J. Zarzycki, *Glasses and the Vitreous State* (Cambridge University Press, Cambridge, 1991), Chap. 3.
- ⁴I. Gutzow, I. Avramov, and K. Kästner, *J. Non-Cryst. Solids* **123**, 97 (1990).
- ⁵J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979).
- ⁶R. W. Cahn, in *Materials Science and Technology*, Ref. 1, Chap. 9.
- ⁷R. Tsu, R. T. Hodgson, T. Y. Tan, and J. E. Baglin, *Phys. Rev. Lett.* **42**, 1356 (1979); P. L. Liu, R. Yen, N. Bloembergen, and R. T. Hodgson, *Appl. Phys. Lett.* **34**, 864 (1979); A. G. Cullis, H. C. Webber, and N. G. Chew, *Phys. Rev. Lett.* **49**, 219 (1982).
- ⁸S. R. Elliott, *Physics of Amorphous Materials* (Longman, London, 1984).
- ⁹S. R. Stiffler, M. O. Thompson, and P. S. Peercy, *Phys. Rev. B* **43**, 9851 (1991); P. V. Evans and S. R. Stiffler, *Acta Metall. Mater.* **39**, 2227 (1991).
- ¹⁰G. W. Scherer, in *Materials Science and Technology*, Ref. 1, Chap. 3.
- ¹¹M. Suzuki and A. Kitagawa, in *Crystallization and Related Phenomena in Amorphous Materials—Ceramics, Metals, Polymers, and Semiconductors*, edited by M. Libera *et al.*, MRS Symposia Proceedings No. 321 (Materials Research Society, Pittsburgh, 1994), p. 743.
- ¹²C. A. Angell, *J. Phys. Chem. Solids* **49**, 863 (1988).
- ¹³M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959); D. Turnbull and M. H. Cohen, *ibid.* **34**, 120 (1960); **52**, 3038 (1970); M. H. Cohen and G. S. Grest, *Phys. Rev. B* **20**, 1077 (1979).
- ¹⁴G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965); C. A. Angell and W. Sichina, *Ann. N.Y. Acad. Sci.* **279**, 53 (1976).
- ¹⁵M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969); C. T. Moynihan and P. K. Gupta, *J. Non-Cryst. Solids* **29**, 143 (1978); S. A. Brawer, *J. Chem. Phys.* **81**, 954 (1984); K. L. Ngai, R. W. Rendell, A. K. Rajagopal, and S. Teitler, *Ann. N.Y. Acad. Sci.* **484**, 150 (1986); J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
- ¹⁶G. Frederickson, *Annu. Rev. Phys. Chem.* **39**, 149 (1988); A. E. Galashev, *High Purity Subst.* **6**, 594 (1993).
- ¹⁷W. Götze, in *Liquid, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991); W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992); *J. Non-Cryst. Solids* **172-174**, 16 (1994).
- ¹⁸A. Q. Tool, *J. Res.* **34**, 199 (1945); *J. Am. Ceram. Soc.* **29**, 240 (1946); O. S. Narayanaswamy, *ibid.* **54**, 492 (1971).
- ¹⁹H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, *J. Chem. Phys.* **88**, 3879 (1988).
- ²⁰J. M. Mikrut and L. E. McNeil, *J. Chem. Phys.* **109**, 237 (1989); G. Saffarini, *Solid State Commun.* **90**, 677 (1994); G. P. Johari, *J. Chem. Phys.* **98**, 7324 (1993).
- ²¹M. Kastner, O. Adler, and H. Fritzsche, *Phys. Rev. Lett.* **37**, 1504 (1976); N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979), Chap. 2.
- ²²P. H. Gaskell, in *Materials Science and Technology*, Ref. 1, Chap. 4.
- ²³J. L. Feldman, M. D. Kluge, P. B. Allen, and F. Wooten, *Phys. Rev. B* **48**, 12 589 (1993); E. Kim and Y. H. Lee, *ibid.* **49**, 1743 (1994); S. K. Mitra, *Philos. Mag.* **B 45**, 529 (1982).
- ²⁴D. E. Polk and D. S. Boudreaux, *Phys. Rev. Lett.* **31**, 92 (1973).
- ²⁵N. Hirai and H. Eyring, *J. Appl. Phys.* **29**, 810 (1958).
- ²⁶P. Ramachandrarao, B. Cantor, and R. W. Cahn, *J. Mater. Sci.* **12**, 2488 (1977).
- ²⁷B. Tuck, *Introduction to Diffusion in Semiconductors* (Peter Peregrinus Ltd., England, 1974), Chap. 5.
- ²⁸J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, London, 1991), Chap. 11.
- ²⁹R. A. Swalin, in *Atomic Diffusion in Semiconductors*, edited by D. Shaw (Plenum, London, 1973), Chap. 2.
- ³⁰F. Yonezawa and M. H. Cohen, in *Fundamental Physics of Amorphous Semiconductors*, edited by F. Yonezawa (Springer-Verlag, Berlin, 1981), p. 119.
- ³¹P. Baeri, G. Foti, J. M. Poate, and A. G. Cullis, *Phys. Rev. Lett.* **45**, 2036 (1980).
- ³²M. O. Thompson, G. J. Galvin, J. W. Mayer, P. S. Peercy, J. M. Poate, D. C. Jacobson, A. G. Cullis, and N. G. Chew, *Phys. Rev. Lett.* **52**, 2360 (1984).
- ³³F. Spaepen and D. Turnbull, in *Proceedings of the Symposium on Laser-Solid Interactions and Laser Processing*, edited by S. D. Ferris, H. J. Leamy, and J. M. Poate, AIP Conf. Proc. No. **50** (AIP, New York, 1979), p. 73.
- ³⁴E. P. Donovan, F. Spaepen, D. Turnbull, J. M. Poate, and D. C. Jacobson, *Appl. Phys. Lett.* **42**, 698 (1983); *J. Appl. Phys.* **57**, 1995 (1985).
- ³⁵D. H. Auston, C. M. Surko, T. N. C. Venkatesan, R. E. Slusher, and J. A. Golovchenko, *Appl. Phys. Lett.* **33**, 437 (1978); K. Murakami, H. C. Gerritsen, H. van Brug, F. Bijkerk, F. W. Saris, and M. J. van der Wiel, *Phys. Rev. Lett.* **56**, 655 (1986); H. C. Gerritsen, H. van Brug, F. Bijkerk, K. Murakami, and M. J. van der Wiel, *J. Appl. Phys.* **60**, 1774 (1986).
- ³⁶R. T. Young, C. W. White, G. J. Clark, J. Narayan, W. H. Christie, M. Murakami, P. W. King, and S. D. Kramer, *Appl. Phys. Lett.* **32**, 139 (1978); P. Baeri, G. Foti, J. M. Poate, and A. G. Cullis, *Phys. Rev. Lett.* **45**, 2036 (1980).
- ³⁷R. Kalish, T. O. Sedgwick, S. Mader, and S. Shatas, *Appl. Phys. Lett.* **44**, 107 (1984).
- ³⁸R. T. Hodgson, V. R. Diline, S. Mader, and J. C. Gelpey, *Appl. Phys. Lett.* **44**, 589 (1984).
- ³⁹D. Turnbull, in *Metastable Materials Formation by Ion Implantation*, edited by S.T. Picraux and W. J. Choyke, MRS Symposia Proceedings No. 7 (Materials Research Society, Pittsburgh, 1982), p. 103.
- ⁴⁰G. L. Olson, J. A. Roth, E. Nugren, A. P. Pogany, and J. S. Williams, in *Beam-Solid Interactions and Transient Processes*, edited by M. O. Thompson, S. T. Picraux and J. S. Williams, MRS Symposia Proceedings No. 74 (Materials Research Society, Pittsburgh, 1987), p. 109.
- ⁴¹J. Narayan, O. Holland, R. E. Eby, J. J. Wortman, V. Ozgud, and G. A. Rozgonyi, *Appl. Phys. Lett.* **43**, 957 (1983); G. S. Oehrlein, S. A. Cohen, and T. O. Sedgwick, *ibid.* **45**, 417 (1982).
- ⁴²R. Biswas and D. R. Hamann, *Phys. Rev. B* **36**, 6434 (1987).
- ⁴³I. Ohdomari, M. Kakumu, H. Sugahara, M. Hori, T. Saito, J. Yonehara, and Y. Hajimoto, *J. Appl. Phys.* **52**, 6617 (1981).
- ⁴⁴S. A. Kokorowski, G. L. Olson, J. A. Roth, and L. D. Hess, *Phys. Rev. Lett.* **48**, 498 (1982).
- ⁴⁵A. Kitagawa, S. Kanai, and M. Suzuki, *J. Non-Cryst. Solids* **164-166**, 239 (1993).
- ⁴⁶Z. Vardeny and J. Tauc, *Phys. Rev. Lett.* **46**, 1223 (1981).
- ⁴⁷Y. Masaki, M. Suzuki, and A. Kitagawa (unpublished).