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## TRANSIENT PHASES AND THEIR TRANSITION TEMPERATURES OF a-Si IN NON-ISOTHERMAL PROCESSES

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### ABSTRACT

The heating rate dependence of the phase transition temperature was formulated based on the temperature dependence of nucleation of a new phase. The glass transition temperature of a-Si was explained in terms of van der Waals fluid of a-Si pseudo-molecules which are produced by the fragmentation of continuous random networks of Si atoms. Transient phases and their transition temperatures as a function of the heating rate are summarized in the phase diagram.

### 1. INTRODUCTION

Tetrahedrally bonded amorphous solids such as amorphous silicon (a-Si) exhibit peculiar behavior in rapid thermal processes. Of particular interest are the reduced melting temperature,<sup>1-3</sup> direct amorphization from the supercooled melt,<sup>4-9</sup> and unique recrystallization behavior.<sup>3,10-13</sup> Those phenomena are observed almost exclusively in rapid thermal processes such as laser or electron beam irradiation, where the heating and cooling rates reach  $10^6$  to  $10^{12}$  K/s. On the other hand, a-Si usually exhibits no other phenomenon than crystallization in non-isothermal differential scanning calorimetric (DSC) measurements, where the heating rates are lower than  $\sim 1$  K/s. A variety of a-Si observed in heating and cooling processes must be controlled by the heating or cooling rate. We have, therefore, developed a procedure to estimate the heating rate dependent transition temperature from the transient time of the phase transition measured in a series of isothermal anneals.

In this paper, various features of a-Si observed in non-isothermal ramp annealings are arranged from the view point of the heating rate, and a model for the glass transition in a-Si is presented based on van der Waals fluid of a-Si pseudo-molecules. Results are summarized in a phase diagram of a-Si giving transient phases and their transition temperatures as a function of the heating rate.

### 2. Reduced melting temperature and the glass transition of a-Si

The melting temperature of a-Si has been estimated to be  $\sim 1400$  K based on DSC measurements of the heat of crystallization.<sup>14</sup> The transition from the solid Si to the liquid Si involves a fundamental change in bonding from the covalent 4-fold coordination to the metallic  $\sim 6$ -fold coordination,<sup>15,16</sup> so the transition is discontinuous and first order.<sup>1</sup> The supercooled metallic (mt) liquid Si has been experimentally detected above 1400 K by transient reflectance and transient conductance measurements.<sup>3,15-18</sup> It should be pointed out that the supercooled mt-liquid Si appears in very rapid heating. The lowest heating rate to produce supercooled mt-liquid Si is inferred to be  $\sim 10^8$  K/s from the data obtained by Olson et al. using pulsed dye laser irradiation.<sup>18</sup>

## The glass transition in a-Si

When the heating rate is not high enough to produce the supercooled melt-liquid state, a-Si crystallizes at some temperature below 1400 K.<sup>18,19</sup> There are, however, some indications that the softening of a-Si occurs at  $\sim 1200$  K when the heating rate is higher than  $\sim 10^2$  K/s. In fact, further low temperature melting of a-Si down to  $\sim 1170$  K is reported to occur under pulsed electron beam irradiation of  $\sim 10^6$  K/s.<sup>2</sup> Lower temperature melting of a-Si is further supported by the fact that enhanced diffusion of impurity atoms occurs at  $\sim 1200$  K in ramp anneals of  $\sim 10^2$  K/s. Such a deep supercooled liquid state is not metallic, since its conductance and reflectance are almost the same as those of the solid state a-Si. The deep supercooled liquid is strongly suggested to be  $\sim 4$ -fold coordination from the fact that unique microstructures such as disk-shaped Si flakes having amorphous cores were observed in fine-grained poly-Si produced by explosive crystallization.<sup>13</sup> Thus, the behavior of a-Si in the heating rate between  $\sim 10^2$  to  $\sim 10^8$  K/s is summarized as follows: a-Si turns to supercooled non-metallic liquid at around 1200 K and then crystallizes at a certain temperature below 1400 K. This behavior of a-Si is quite similar to the glass transition followed by crystallization observed for glasses in the heating processes, thus the temperature at which the deep supercooled liquid state appears could be the glass transition temperature.

The glass transition temperature  $T_g$  of a-Si has been calculated by Turnbull<sup>23</sup> and Stiffler et al.<sup>24</sup> The former can not be applied to high heating rate processes as  $10^2$  K/s, since continuous random networks formed by tetrahedrally bonded atoms are too rigid to exhibit fluidity in high heating rate processes.<sup>23</sup> The latter is also not to be applied to the glass transition of a-Si, since metallic glass has not yet been observed for Si under any quenching conditions.<sup>25</sup> There is no satisfactory model for the glass transition in a-Si so far.

The a-Si involves a high density of dangling bonds<sup>26</sup> and weak bonds,<sup>27</sup> thus a-Si is expected to fragment with increasing temperature if crystallization does not intervene. The fragmentation would at last produce relatively stable clusters, which may be called pseudo-molecules. Polk's continuous random network (CRN) model for a-Si and a-Ge,<sup>28</sup> having no dangling bond inside, could be applied to pseudo-molecules of interest. Then, such pseudo-molecules are presumed to consist of, at most, a few hundred Si atoms. The solid consisting of pseudo-molecules is a van der Waals (VDW) solid, which would turn to VDW fluid by further heating. VDW fluid of pseudo-molecules must be semiconductive (sc) liquid, since constituents of the fluid are  $\sim 4$ -fold coordination. These processes are capable of providing the transition from solid a-Si to supercooled sc-liquid Si.

### 3. THE PHASE TRANSITION TEMPERATURE AS A FUNCTION OF THE HEATING RATE

The transient behavior of phase transitions in condensed systems have been treated by many authors.<sup>29-32</sup> Phase transitions under the isothermal condition take place by nucleation of the new phase followed by successive growth of nuclei. In the classical theory, nucleation is assumed to occur by the formation of clusters of the new phase. The free energy of formation of a cluster goes through a maximum and then decreases with the cluster size because of their large surface-to-volume ratio. As a result, an incubation period or induction time for nucleation  $t_{in}$  is required for the cluster to surpass a critical size.<sup>29-36</sup> The phase transition begins when a nucleus is produced in the initial phase where there are no preexisting clusters. Then, the system passes over the point of no-return in the course of the phase transition. Although it is not easy to detect experimentally such a strict

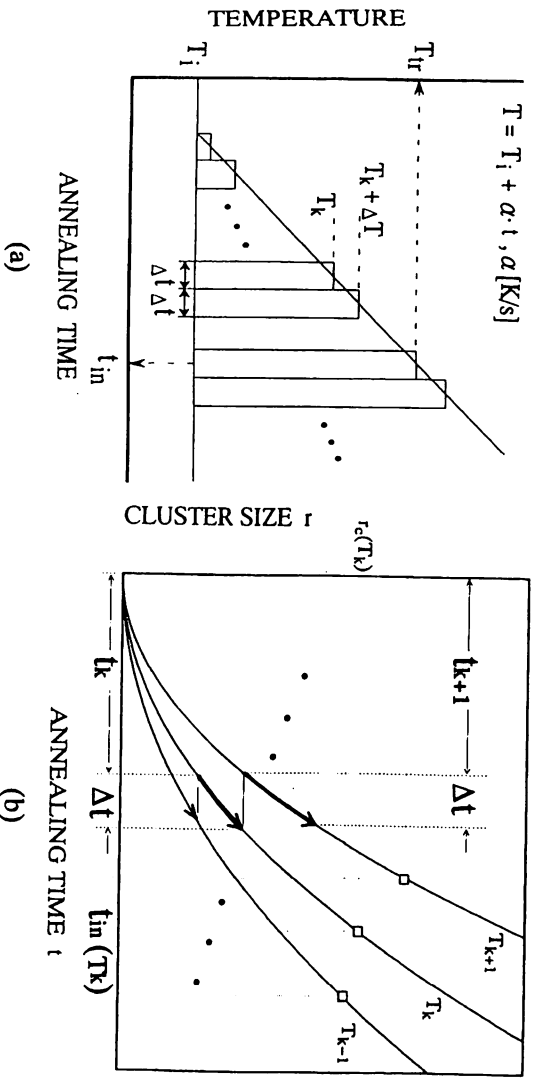


Fig.1 Non-isothermal rate-scan annealing and nucleation processes. (a) A medley of ascending isothermal annealings. (b) Cluster size in successive isothermal annealings is inherited from previous annealings.

onset of the transition,  $t_{in}$  could be approximated by extrapolating, for example, the plot of the crystalline fraction vs annealing time to a zero level fraction.<sup>2,36</sup>

If  $t_{in}$  is known as a function of temperature, the heating rate dependent transition temperature  $T_{tr}$  in the rate scan annealing can be estimated phenomenologically as follows: A rate scan annealing is regarded as a medley of ascending isothermal anneals as shown in Fig.1 (a). The nucleation processes at each new temperature are assumed to be inherited from the previous anneals as shown in Fig.1 (b). Thus, the inherited time  $t_{k}^{(e)}$  from the previous annealings plus the annealing time  $\Delta t$  at temperature  $T_k$  is reduced to  $t_{k+1}^{(e)}$  which is succeeded to the next annealing at  $T_{k+1}$  ( $= T_k + \Delta T$ ) as given below:

$$t_{k+1}^{(e)} = \gamma(T_{k+1}) (t_k^{(e)} + \Delta t) \frac{t_{in}(T_k + \Delta T)}{t_{in}(T_k)} \quad (1)$$

where  $\gamma(T_{k+1})$  is a parameter involving nonlinear characters of the nucleation process.  $\gamma(T_k)$  approaches unity when  $\Delta t$  approaches zero.

The system reaches the transition temperature  $T_{tr}$  in the non-isothermal rate scan anneal when the sum of the reduced annealing time reaches  $t_{in}(T_{tr})$ . This situation is expressed by the following equation :

$$\int_{T_i}^{T_{tr}} \frac{1}{t_{in}(T)} \frac{dT}{\alpha} = 1 \quad (2)$$

where  $T_i$  is the initial temperature at which the rate scan anneal starts and  $\alpha$  is the heating rate. This equation provides the relation between the transition temperature  $T_{tr}$  and the heating rate  $\alpha$ .

## Solid Phase Crystallization of a-Si

At heating rates lower than  $\sim 10$  K/s, only solid phase crystallization is observed for a-Si. The crystallization temperature  $T_c$  of amorphous solids can not be determined uniquely, since it depends on the heating rate.  $T_c$  of a-Si is, in fact, a function of the heating rate.

In the case of the phase transition from a-Si to crystalline Si, the transient time  $t_{tr}$  has been measured using X-ray diffraction, Raman scattering, transmission electron microscopes, conductance changes etc.,<sup>32-36</sup> and the experimental data of  $t_{tr}$  obtained from those measurements in a series of isothermal anneals fit well the following Arrhenius form with the activation energy  $E_{in}$ .<sup>32-26</sup>

$$t_{tr}(T) = \tau_0 \exp\left(\frac{E_{in}}{kT}\right) \quad (3)$$

where  $T$  is the isothermal annealing temperature, and  $\tau_0$  is the pre-exponential factor. Experimental results of  $t_{tr}$  involve, more or less, growth processes of crystallites after nucleation. Data of  $t_{tr}(T)$  in ref.35 contain minimal traces of the growth process of crystallites after nucleation, since the detection level of crystallites is reduced as low as possible. Those data could be approximated to be  $t_{in}(T)$ , so eq.(2) can be calculated in the case of solid phase crystallization.

### Transient phase diagram

Various features of a-Si observed in ramp annealings are arranged in a phase diagram, in which the phase transitions are shown as a function of the heating rate.

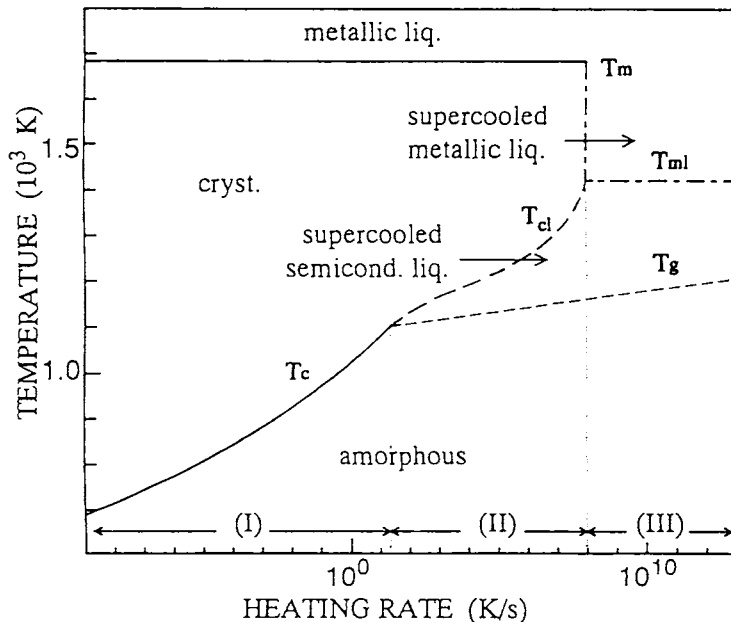


Fig.2 Transient phase diagram for a-Si.  $T_c$ ,  $T_{cl}$ : crystallization temperatures in the liquid state and in supercooled liquid state respectively.  $T_g$ : the glass transition temperature.  $T_m$ : the melting temperature (metallic liquid).

The solid curve  $T_c$  in Fig.2 is the calculated crystallization temperature from eq.(2) using data of  $t_{in}(T)$  in ref.35. A measured  $T_c$  at 40 K/min obtained from DSC<sup>37</sup> coincides well with the calculated  $T_c$  shown in Fig.2. The calculated  $T_c$  is invalid above  $T_g$ . The supercooled liquid phase may appear in advance of crystallization in some heating conditions, as mentioned in the previous section. At present we do not have any data about  $t_{in}(T)$  for nucleation of the supercooled sc-liquid phase, so numerical calculation of eq.(2) for  $T_g$  can

not be performed.  $T_g$ , however, could be inferred from experimental data reported so far.  $T_g$  at  $\sim 10^6$  K/s is taken to  $\sim 1170$  K from the experimental results reported by Baeri et al.<sup>2</sup>  $T_g$  at 40 K/min is higher than at least  $\sim 1020$  K, since  $T_c$  at 40 min is reported to be 1014 K.<sup>37</sup> Taking into account the weak heating rate dependence of  $T_g$ , it could be taken to around 1100 K at  $\sim 10^2$  K/s. Then a dotted curve for  $T_g$  is drawn as shown in Fig.2, where  $T_g$  intersects  $T_c$  at the point ( $\sim 2 \times 10^1$  K/s,  $\sim 1100$  K). In this scheme, the supercooled sc-liquid state appears in the ramp anneals with  $\alpha$  higher than  $2 \sim 3 \times 10^1$  K/s.

Numerical calculation of the heating rate dependent crystallization temperature,  $T_{cl}$ , above  $T_g$  is once again not possible because of the lack of data about  $t_{in}(T)$  for crystallization in the sc-liquid phase.  $T_{cl}$ , however, can be directly inferred from experimental results under some heating rates. For example, the transient reflectance measurements using cw Ar<sup>+</sup> ion laser irradiation showed that heating around  $10^6$  K/s produces not supercooled mt-liquid Si but poly-Si,<sup>19</sup> so that  $T_{cl}$  at  $\sim 10^6$  K/s is estimated to be lower than 1300 K.

Pseudo-molecules are expected to dissociate into atoms at  $\sim 1400$  K, since the heat of crystallization calculated for CRN model of a-Si<sup>38</sup> agrees roughly with that of a-Si which gives  $\sim 1420$  K as  $T_m$ .<sup>14</sup> Thus,  $T_{cl}$  must terminate at  $\sim 1400$  K on the line of  $\alpha$  at  $10^8$  K/s, so a broken curve for  $T_{cl}$  could be drawn from ( $\sim 2 \times 10$  K/s,  $\sim 1100$  K) to ( $\sim 10^8$  K/s,  $\sim 1400$  K) as shown in Fig.2. An almost vertical line on  $10^8$  K/s in Fig.2, which separates the supercooled mt-phase from the crystalline phase, should be drawn from  $\sim 1400$  K to the melting temperature  $T_m$  (1685 K) of crystalline Si.  $T_m$  of a-Si is defined only for  $\alpha$  larger than  $\sim 10^8$  K/s.

The behavior of a-Si in the rate scan anneal is, thus, categorized in three characteristic regions as shown in Fig.2. In the region (I) of low heating rates, solid-phase crystallization exclusively takes place at  $T_c$ . In the region (II), a-Si turns to the supercooled sc-liquid state at  $T_g$  and then crystallizes at  $T_{cl}$ . On the other hand, in the region (III) of high heating rates, crystallization does not occur. The a-Si goes into the supercooled mt-liquid phase through the supercooled sc-liquid phase. Similar phase diagrams for other amorphous materials will be obtained applying similar procedures. Most glasses do not have the supercooled mt-liquid phase, so rather simple diagrams will be obtained if they do not exhibit phase separation. Phase diagrams for the cooling processes could also be developed.

#### 4. CONCLUSION

Transient phases and their transition temperatures as a function of the heating rate are summarized in the phase diagram. The heating rate dependence of the transition in the rate scan annealing is controlled by a competition between clusters of different new phases in which one exceeds first the critical size for stable growth. The phase transition temperature in a rate scan annealing was, thus, formulated as a function of the heating rate based on the temperature dependence of a new phase. The glass transition in a-Si was explained in terms of van der Waals fluid of a-Si pseudo-molecules which are produced by the fragmentation of continuous random networks of Si atoms.

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