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Molecular Dynamics Study on External Field Induced Crystallization of Amorphous Argon Structure

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A molecular dynamics study has been conducted on an external-force-field-induced isothermal crystallization process of amorphous structures as a new low-temperature athermal crystallization process. An external cyclic-force field with a dc bias is imposed on molecules selected randomly in an amorphous-phase of argon. Multiple peaks smoothed out in the radial distribution functions for amorphous states appear very clearly during the crystallization process that cannot be achieved otherwise. When the amorphous material is locally exposed to an external force field, crystallization starts and propagates from the interfacial region and crystallization growth rates can be estimated.

Key Words : Molecular Dynamics Simulation, Crystallization, Amorphous Structure

Nomenclature

A : Amplitude of external force
B : DC bias for external fields
F : External force
g : Radial distribution function
L : Simulation domain size
m : Molecular mass
N : Total number of molecules
r_{ij} : Inter-distance between molecules i and j
T : Temperature
x,y,z : Cartesian coordinates

Greek Symbols

ε : Energy parameter
ρ : Number density
σ : Length parameter
Φ : Potential function
τ : Time

Superscript

$*$: Dimensionless

1. Introduction

The objective of present study is to investigate the constant-temperature external force field-induced crystallization of an amorphous material without crystalline seeds, using the molecular dynamics (MD) simulation technique. Since the crystallization from amorphous structure can be achieved more quickly as the coordination numbers of the constituent atoms increase (Tanaka et al., 1999), the crystallization of Lennard-Jones molecules are investigated as a first step towards the external force field-induced crystallization of an amorphous material, rather than silicon. The coordination numbers for Lennard-Jones and silicon atoms are 12 and 4, respectively.

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Although current study is mainly focused on the external force field-induced crystallization of amorphous Lennard-Jones molecules, this research will make a contribution to the advances in the fabrication of polycrystalline silicon (poly-Si) from a-Si at low temperatures in order to avoid the problems involved in high-temperature processes (Sameshima, 1998 ; Yoon et al., 2001 ; Ahn et al., 2002 ; Zhao et al., 2000). Especially, it is shown that the external force field can reduce the silicon-crystallization process temperatures significantly, using MD simulation (Park et al., 2004), although the crystallization requires crystalline seeds.

Without problems involved in conventional fabrication methods such as metal contamination, long process times, small process windows, or non-uniformities, low-temperature crystallization processes using an alternating magnetic induction or microwave heating have been investigated to bring about a more effective crystallization of a-Si on a glass substrate at temperatures around 500℃. However, mechanisms for the alternating magnetic field crystallization (AMFC) or microwave assisted crystallization (MAC) as well as those for metal induced crystallization processes (MIC) are not clearly understood yet (Yoon et al., 2001 ; Ahn et al., 2002). It can be conjectured that AMFC or MAC is due to heating of a-Si by eddy current losses in an alternating magnetic field or microwave heating and due to field-enhanced oscillation or movement of defects or ions. Heating due to eddy current loss in AMFC is considered not to be relevant, since it is almost impossible to heat up the a-Si film alone without heating the glass substrate except using the excimer laser crystallization (ELC) technique and the process temperature around 500℃ is too low to increase easily the temperature of a-Si film up to effective annealing temperatures for solid-phase crystallization. Contribution of heating by microwave in MAC is also negligible, since the specimen temperatures have been carefully controlled by the adjustment of the microwave power (Ahn et al., 2002). The second hypothesis that field-enhanced molecular movements may result in global crystallization will be tested in this study to optimize the control parameters for the process. In addition, it is shown that metal concentration in the material and external electric field strength are the most important factors for MIC (Yoon et al., 2001). There are, however, not many theoretical and microscopic tools available to examine the effect of field-enhanced molecular movements on the crystallization. Therefore, it is decided to apply the MD technique to determine whether externally forced molecules will cause crystallization or not, although the forced molecules are selected randomly and the external forces are artificially imposed in this study.

The MD technique is known to have a capability of providing very detail information on various unexplained phenomena ranging from micro- to nano-scales by virtual experimentation of those phenomena (Allen and Tildesley, 1987 ; Mandell et al., 1976 ; Mandell et al., 1977 ; Pickering and Snook, 1997 ; Swope and Anderson, 1990 ; Tanemura et al., 1977 ; Yang et al., 1998 ; Cho and Park, 2002 ; Lee et al., 2002). Recently, Caturla et al.(1995), Weber et al.(1997), and Motooka (1997) showed that MD simulation is a useful tool to study the microscopic process of Si crystallization and amorphization induced by ions and defects. There are, however, few reports available to investigate the possibility of crystallization induced by externally imposed force fields using MD technique. The progress of crystallization at constant temperature is observed through the radial distribution functions (RDF) instead of observing the structure factor and conducting voronoi analysis (Swope et al., 1982 ; Swope and Anderson, 1990).

2. Simulation Model

In order to monitor the external field induced crystallization process of amorphous structure as it evolves from its initial to final states, the well-known Lennard-Jones (LJ) 12-6 pair potential has been applied in this MD simulation, given as

$$\Phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad (1)$$

The LJ potential is truncated to zero for distance larger than 2.5σ for expedition of the calculation. The simulation domain is basically a cubic or a rectangle $(L_x^* \times L_y^* \times L_z^* = 9.5 \times 9.5 \times L^*)$ for an initial crystalline fcc structure as a reference, a slightly expanded domain for amorphous supercritical fluid, and a long rectangle $(L_x^* \times L_y^* \times L_z^* = 9.5 \times 9.5 \times 3L^*)$ during the recrystallization process. Here, L^* denotes the size of the domain in x, y, and z directions. The equation of motions are solved by the "velocity Verlet" algorithm (Swope et al., 1982) with a time step of 5 fs, or $\Delta\tau^* = 2.335 \times 10^{-3}$. In this work all quantities with an asterisk are nondimensionalized with respect to σ, ε, and m, which use the values of argon such that $\sigma = 0.34$ nm, $\varepsilon = 1.67 \times 10^{-21}$ J, and $m = 6.63 \times 10^{-26}$ kg.

Prior to conducting the simulation for an isothermal crystallization process, a crystalline fcc structure is designed and placed at the center of the computation domain in which molecular number density is 1.001 at $T^* = 0.496$ below the triple point of argon, $T^* = 0.693$. To effectively obtain the amorphous structure the volume of the calculation domain is expanded by 0.2% and its temperature is raised up to $T^* = 2.48$, which is much higher than the experimental value of critical temperature of argon, $T^* = 1.085$. After 100000 steps, the system is equilibrated in a supercritical state and thus in an amorphous structure. This amorphous fluid is located in the center of the computational domain that is expanded in z direction from L^* to $3L^*$ to avoid the artifacts due to periodic boundary condition in z direction and it is suddenly cooled down to temperature $T^* = 0.496$ by the velocity scaling. This supercooled liquid undergoes another equilibration process of 100000 steps. After this preprocessing, the equilibrated amorphous structure at temperatures below its triple point is obtained and used as an initial structure. In the simulation, a velocity scaling is performed at each step to make sure that the system is maintained at the designed temperature, $T^* = 0.496$, since without velocity scaling for an isothermal condition the crystallization process will accompany the temperature increase with the expense of potential energy. At each time step the structure change is monitored using 3D graphs and the radial distribution function (RDF) (Haile, 1992), given as

$$\rho^* g(r^*) = \frac{1}{N} \left\langle \sum_{i}^{N} \sum_{j \neq i}^{N} \delta[r^* - r_{ij}^*] \right\rangle \tag{2}$$

where ρ^* is the number density, N is the total number of atoms, and the angular brackets represents a time average.

3. Results and Discussion

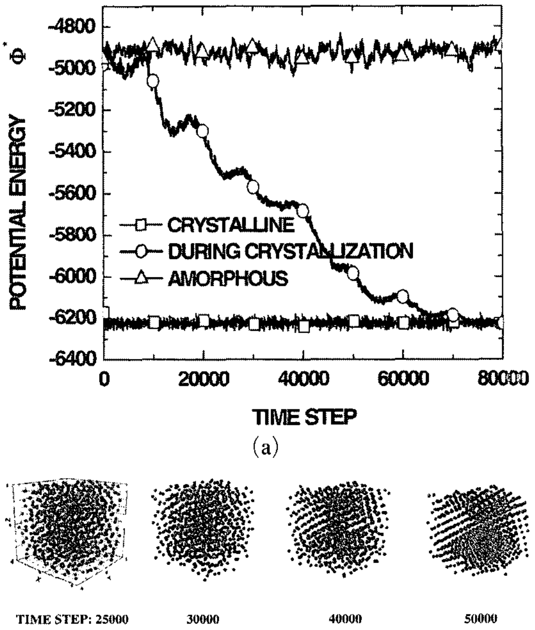
To investigate the crystallization phenomena induced by external field, a cyclic force with a dc bias is imposed on a small portion of molecules in the amorphous structure, in addition to the inherent intermolecular forces. Practically this force may be applied to susceptor molecules due to direct electric fields, electric fields induced by external magnetic field, or other excitation sources. Since the internal force in the LJ molecules is based on the van der Waals interactions and there does not exist any ion or susceptor in the system, electric fields are not supposed to influence the molecular motions directly. In this study, however, it is assumed that some molecules can act as susceptors of external forces, only to induce an artificial molecular movements selectively and to observe the subsequent crystallization behavior. As discussed previously, the result from this study might be a clue to mechanisms involved in the crystallization of a-Si to poly-Si, which is athermal and induced by molecular movements. The artificial force is estimated from the internal force field experienced by each molecule. Since the molecules are not in a perfect crystalline position, there always exists a force imbalance, which may be induced by thermal excitation, defects, non-crystalline structures, or other disturbing sources. At each time step, therefore, the forces acting on each molecule by neighboring molecules are averaged and the averaged force is used as the amplitude of the external force. The external force acting on suscepting molecules is modeled as

$$F_{ext}^* = A^*[\cos(\omega^* t^*) + B^*]/(1 + B^*) \tag{3}$$

where A^* is based on the averaged force and B^* is the dc bias for the oscillation.

Another parameter to be determined is the period of the externally induced vibration. Representative periods are estimated from the Debye frequency of argon (Kittel, 1996) and the natural frequency of the LJ potential linearized as a harmonic potential, which are 521.6×10^{-15} sec and 1781×10^{-15} sec, respectively. The characteristic periods are relatively close to each other and can be expressed in terms of simulation time steps of 104 and 356, respectively. Based on these periods, cyclic forces are imposed on some molecules selected randomly from the system.

Figure 1 shows the potential variations during external field induced crystallization with potentials of crystalline and amorphous states and molecular distributions during the crystallization process at $T^*=0.496$. In this simulation the force constant, A^* in Eq. (2) is 1.5 times the averaged force, B^* is 0.5, the period is 10400 time-steps, one hundred times of the natural frequency. For values of A^* close to the averaged forces and B^* smaller than 0.1, the crystallization cannot be achieved until 500000 time-steps, even though solid-phase argon is known to be crystallized quickly. The importance of B^* can be understood by the experimental results obtained by Jang et al. (1998). They showed that metal concentration in the material and external electric field strength are the most important factors for the MIC and that the rate at which the MIC took place was markedly enhanced, especially under an electric field of 0 to 100 V/cm. For example, the crystallization time at 500℃ decreased from 25 hours to 10 minutes on application of 80 V/cm electric field. However, the underlying physics has not been uncovered, yet.



(a)

(b)

Fig. 1 (a) Comparison of potential energies and (b) molecular distributions during the crystallization process induced by an external force-field at $T^*=0.496$

In this simulation, five of susceptors are selected randomly from 864 molecules in $L_x^*\times L_y^*\times L_z^*=9.5\times9.5\times28.5$. Preliminary simulation showed that the crystallization can be achieved, when the number of susceptors is less than 2% (16 out of 864), if exist. If the susceptors are too many, the crystallization cannot be achieved efficiently, while it can be achieved most effectively, when the number is five.

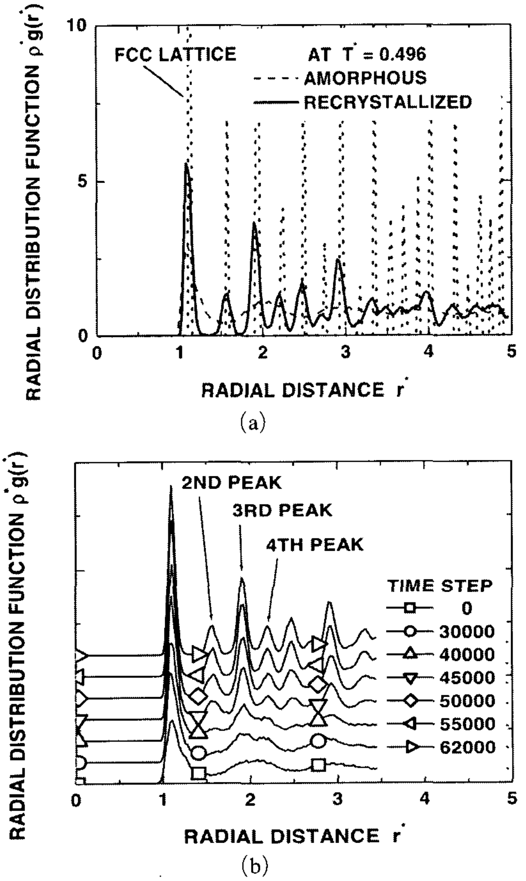
While the potential variation for amorphous and crystalline structures fluctuates about their mean values, the potential during crystallization decreases from the values of amorphous to those of crystalline states with a sinusoidal fluctuation synchronized to the external cyclic-force. It can be understood that the structure has been changed from amorphous to crystalline states, but the initiation of crystallization cannot be easily detected from this potential variation shown in Fig. 1(a) and molecular distributions in Fig. 1 (b).

Figure 2(a) compares the RDF's for fcc lattice, amorphous and recrystallized structures. The RDF for recrystallized structure (solid line) overlaps the RDF for crystalline structure at the same temperature ($T^*=0.496$) and has multiple peaks at the same locations that the fcc structure does, while some peaks are not shown in the RDF for amorphous structure. Figure 2(b) shows the variation of the RDF's from time step 0 to 62000 for the same case discussed in Fig. 1. The

RDF at time step 0 is for amorphous structure after 100000 steps equilibration period of the rapid quenched state, in which the second peak is smoothed out and the third and fourth peaks are merged into one peak. Around time step 30000 the second peak starts to reappear and the third peak does to disengage from the fourth peak. These behaviors become very clear at step 40000. After time step 55000 the shape of the RDF becomes very close to that for crystalline structure.

Especially, appearances of the second and third peaks are remarkable in the incipient stage of crystallization, as described in Fig. 3. The abrupt increases of those peaks are clearly and simultaneously detected near 40000 steps, which imply that the material is undergoing a global crystallization process, although the creation or destruction of crystalline nuclei cannot be detected. In order to observe the nucleation characteristics in detail an analysis should be conducted based on voronoi polyhedron (Swope and Anderson, 1990), which is not included in this study. Comparing to the variation of potentials shown in Fig. 1, the variations of the second and third peaks are prominently clear during crystallization process.

In addition to the global crystallization, local crystallization and its propagation are simulated for the calculation domain of $L_x^* \times L_y^* \times L_z^* = 9.5 \times 9.5 \times 114$. The total number of molecules in amorphous state is 3456 and the molecules are located initially within a rectangle $9.5 \times 9.5 \times 40$ in the center of the calculation domain as shown in Fig. 4. The number of susceptors is 5 and they are selected from the molecules located within $-19 < z^* < -15$ in order to simulate the local crystallization. Here, the force constant, A^* in Eq. (2) is the averaged force, B^* is zero, the period is 10400 time-steps. Of course, the crystallization can be achieved more effectively for B greater than zero. At time step zero the structure is in its amorphous state after undergoing the same procedure for global crystallization. After a long exposure period of external fields about



(a)

(b)

Fig. 2 (a) Comparison for fcc lattice, amorphous, and recrystallized structures and (b) variations of radial distribution functions during external field induced crystallization at $T^* = 0.496$

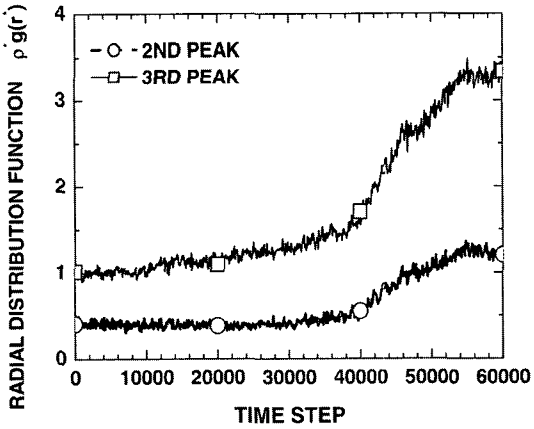


Fig. 3 The second and third peaks in radial distribution functions during external field induced crystallization at $T^* = 0.496$

200000 steps crystallized structure appears near the other end of the structure ($z^* \cong 20$), i.e. the interfacial region between the solid-phase and gas-phase and this crystallization propagates towards the source of excitation. After 410000 steps the crystallization front reaches the region of excitation and the crystallization does not propagate into the region, as discussed for global crystallization that is not achieved easily by pure sinusoidal oscillation ($B^*=0$). Based on sudden jumps of the second and third peaks in the RDF as a crystallization criterion, Fig. 5 shows the propagation of crystallization fronts with respect to time. The slope of the data may indicate the crystal growth rate, which is 24.26 m/s in this simulation condition. This growth rate is a little bit higher than those (5 — 10 m/s) for silicon from the MD simulation using Tersoff potential, while these values are much higher than the realistic crystal growth rates (~1 mm/min) (Motooka, 1998).

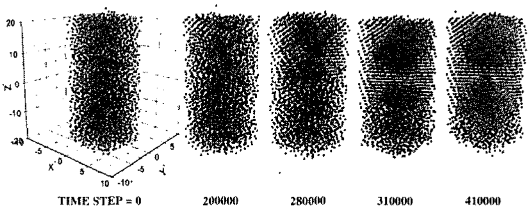


Fig. 4 Molecular distributions during crystallization process from amorphous to crystalline structures

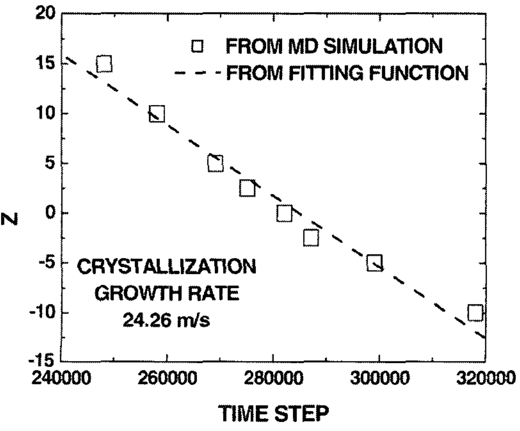


Fig. 5 Crystallization front and its growth rate

4. Conclusions

A molecular dynamics study has been carried out to understand crystallization mechanisms behind the alternating magnetic field crystallization and microwave-induced crystallization processes of amorphous silicon at low temperatures.

For the simplification of the simulation, current study is mainly focused on the external force field-induced crystallization of amorphous Lennard-Jones molecules. Although the external force acting on molecules are artificially designed, it is assumed that susceptor molecules are under the influence of external forces such as electric, magnetic fields, or other excitation sources.

Based on those assumptions, it is shown that a small number of molecules whose movements are under an external cyclic force field with a dc bias can induce a crystallization of amorphous structure and that this new mechanism might be able to control and accelerate the crystallization process at low-temperatures without thermal problems.

Through comparisons of the radial distribution functions (RDF) for crystalline and amorphous states, the degree of crystallization can be estimated. Abrupt increases of the second and third peaks in RDF are observed during the process, which occurs simultaneously with the steepest decent of potential energies. The growth rate of crystalline phase can be estimated from those abrupt changes of the peaks.

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References

Ahn, J. H., Lee, J. N., Kim, Y. C. and Ahn, B. T., 2002, "Microwave-Induced Low-Temperature Crystallization of Amorphous Si Thin Films," *Current Applied Physics*, Vol. 2, pp. 135~

139.

Allen, M. P. and Tildesley, D. J., 1987, *Computer Simulation of Liquids*, Oxford University Press, New York.

Caturla, M. J., Diaz de la Rubia, T. and Gilmor, G. H., 1995, "Recrystallization of a Planar Amorphous-Crystalline Interface in Silicon by Low Energy Recoils : A Molecular Dynamics Study," *J. Appl. Phys.*, Vol. 77, pp. 3121~3125.

Cho, S. S. and Park, S. H., 2002," Molecular Dynamics Simulation of Adhesion Processes," *KSME Int. J.*, Vol. 16, pp. 1440~1447.

Haile, J. M., 1992, *Molecular Dynamics Simulation*, John Wiley & Sons, pp. 260~267.

Jang, J., Oh, J. Y., Kim, S. K., Choi, Y. J., Yoon, S. Y. and Kim, C. O., 1998, "Electric-Field-Enhanced Crystallization of Amorphous Silicon," *Nature*, Vol. 395, pp. 481~483.

Kittel, C., 1996, *Introduction to Solid State Physics*, 7th Ed., John Wiley & Sons, p. 126.

Lee, J. I., Park, S. H., Kwon, O. M., Choi, Y. K. and Lee, J. S., 2002, "Characterization of Thin Liquid Films Using Molecular Dynamics Simulation," *KSME Int. J.*, Vol., pp. 1477~1484.

Mandell, M. J., McTague, J. P. and Rahman, A., 1976, "Crystal Nucleation in a Three-Dimensional Lennard-Jones System : A Molecular Dynamics Study," *J. Chem. Phys.*, Vol. 64, pp. 3699~3702.

Mandell, M. J. McTague, J. P. and Rahman, A., 1977, "Crystal Nucleation in a Three-Dimensional Lennard-Jones System. II. Nucleation Kinetics for 256 and 500 Particles," *J. Chem. Phys.*, Vol. 66, pp. 3070~3075.

Motooka, T., 1997, "Molecular Dynamics Simulations for Amorphous/Crystalline Si Interface : Amorphization and Crystallization Induced by Simple Defects," Nuclear Instruments and *Methods in Physics Research B*, Vol. 127/128, pp. 244~247.

Motooka, T., 1998, "The Role of Defects during Amorphization and Crysatllization Processes in Ion Implanted Si," *Materials Science and Engineering*, Vol. A253, pp. 42~49.

Park, S. H., Kim, H. J., Lee, D. B., Lee, J. S., Choi, Y. K. and Kwon, O. M., 2004, "Heterogeneous Crystallization of Amorphous Silicon Expedited by External Force Fields : A Molecular Dynamics Study," *Superlattices and Microstructures*, Vol. 35, pp. 205~215.

Pickering, S. and Snook, I., 1997, "Molecular Dynamics Study of the Crystallization of Metastable Fluids," *Physica A*, Vol. 240, pp. 297~304.

Sameshima, T., 1998, "Status of Si Thin Film Transistors," *J. Non-Crystalline Solids*, Vol. 227-230, pp. 1196~1201.

Swope, W. C. and Anderson, H. C., 1990, "10^6 — Particle Molecular-Dynamics Study of Homogeneous Nucleation of Crystals in a Supercooled Atomic Liquid," *Physical Review B*, Vol. 41, No. 10, pp. 7042~7054.

Swope, W. C., Anderson, H. C., Berens, P. H. and Wilson, K. R., 1982, "A Computer Simulation Method for the Calculation of Equilibrium Constants for the Formation of Physical Clusters of Molecules : Application to Small Water Clusters," *J. Chem. Phys.*, Vol. 76, pp. 637~649.

Tanaka, K., Maruyama, E., Shimada, T. and Okamoto, H., 1999, Amorphous Silicon, John Wiley & Sons, pp. 27~29.

Tanemura, M., Hiwatari, Y., Matsuda, H., Ogawa, T., Ogita, N. and Ueda, A., 1977, "Geometrical Analysis of Crystallization of the Soft-Core Model," *Prog. Theor. Phys.*, Vol. 58, pp. 1079~1095.

Weber, B., Gartner, K. and Stock, D. M., 1997, "MD-Simulation of Ion Induced Crystallization of Amorphization Process in Silicon," *Nuclear Instruments and Methods in Physics Research B*, Vol. 127/128, pp. 239~243.

Yang, J. X., Gould, H. and Klein, W., 1998, "Molecular Dynamics Investigation of Deeply Quenched Liquids," *Physical Review Letters*, Vol. 60, No. 25, pp. 2665~2668.

Yoon, S. Y., Park, S. J., Kim, K. H. and Jang, J., 2001, "Metal-Induced Crystallization of Amorphous Silicon," *Thin Solid Films*, Vol. 383, pp. 34~38.

Zhao, Y., Wang, W., Yun, F., Xu, Y., Liao, X., Ma, Z., Yue, G. and Kong, G., 2000, "Polycrystalline Silicon Films Prepared by Improved Pulsed Rapid Thermal Annealing," *Solar Energy Materials & Solar Cells*, Vol. 62, pp. 143~148.