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| 学位の種類 | 博士（学術） |
| 学位記番号 | 博甲第271号 |
| 学位授与の日付 | 平成10年9月30日 |
| 学位授与の要件 | 課程博士（学位規則第4条第1項） |
| 学位授与の題目 | A Study of Phase Transitions in Amorphous Semiconductors during Non-isothermal Processes（昇温過程における非晶質半導体の相転移に関する研究） |
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# 学位論文要旨

An amorphous semiconductor is a glass which exhibits a glass transition usually followed by a crystallization in a heating process. The glass transition is a complex dynamical phenomenon. Although a number of models, such as relaxation, mode-coupling and fragmentation, have been proposed to explain various aspects of the glass transition phenomena, there still remain a number of problems to be solved. Further investigations on the glass transition are necessary for better understanding of phase transitions between amorphous and crystalline states in amorphous semiconductors for real device applications.

Recently, in fragmentation model, it has been suggested that an amorphous solid decomposes into fragments due to thermally-assisted bond breaking processes on heating. Thus, the number of fragments increases, their average dimension decreases with increasing temperature, and the glass begins to behave like a liquid when the fragment size reaches a critical value. Above the glass transition, the system is a supercooled liquid until crystallization intervenes.

Electron spin resonance (ESR) spectroscopy is a well-established technique in which paramagnetic spin probes have been employed to obtain structural and dynamical information in a wide variety of solid

and liquid materials. ESR technique can be used to explore the structural properties of supercooled liquids during non-isothermal, rate-scan, heating. This liquid is actually in a thermodynamic non-equilibrium state, so its structures and properties change in a relatively short time. Therefore, the ESR measurement in a supercooled liquid should be performed in a short period of time during the rate-scan heating. Most of the multicomponent chalcogenide glasses, however, do not manifest any ESR signals due to having a low unpaired spin density, so transition metal ions are sometimes added as a spin probe to the materials from which the glass is originally prepared.

Although many investigations have been devoted to the study of ESR of paramagnetic ions in chalcogenide glasses, most of the papers concern structural studies of the glasses using ESR measurements at elevated temperatures during isothermal conditions, or at room temperature after isothermal annealing. For the first time, it has been attempted to make ESR measurements in the 0.1 at.% Mn-doped $Se_{70}Te_{30}$, $Ge_{15}Te_{85}$ and $As_{23}Te_{70}Ge_{7}$ chalcogenide glasses during non-isothermal heating processes in order to explore the microscopic structural changes occurring at the glass transition.

The glasses used in the present study were prepared by the conventional melt- quenching technique. The ESR spectra were recorded on a JEOL model ESR spectrometer equipped with a digital temperature control unit, an air compressor and a heat blowing tube. A heating rate of about 2 °C/min was maintained by means of the digital temperature controller throughout the ESR mreasurements. The spectrometer was operated at X band with a 100 KHz field modulation frequency. The amplitudes of field modulation and of microwave field were low enough to preclude distortion and saturation of the spectra at various measuring temperatures. The temperature of the sample was estimated by calibrating copper-constantan thermocouple at 3.5 cm below the position of the sample inside the

ESR cavity, and also by considering the temperature gradient. The peak-to-peak linewidth was estimated from the first derivative ESR signal. In the undoped glass, no ESR absorption was observed.

It was observed that the Mn-doped $Se_{70}Te_{30}$ glass exhibits single-line ESR signal of $g$ = 2.00 at various measuring temperatures through the glass transition and crystallization temperature during the rate-scan heating. No remarkable change in the peak-to-peak linewidth occurs from room temperature up to the glass transition temperature , but the linewidth begins to decrease around the glass transition temperature and to increase above the crystallization temperature.

In the Mn-doped $Ge_{15}Te_{85}$ and $As_{23}Te_{70}Ge_7$ glasses, two characteristic signals with $g$ values centered at 2.00 and 4.3 are observed at various temperatures during heating from room temperature up to a temperature which is above the glass transition but below the crystallization temperature. It is found that the linewidth of either of the resonance lines does not change remarkably from room temperature up to near the glass transition. However, the linewidth of the $g$= 2.00 line begins to decrease and that of the $g$= 4.3 line starts to increase around the glass transition temperature.

The narrowing of the $g$= 2.00 signal around the glass transition may be interpreted as resulting from the fluidity enhancement of the supercooled liquid induced through free-volume increase and fragment-size decrease with increasing temperature. On the other hand, the broadening of the $g$= 4.3 line above the glass transition is caused by the reduction of the degree of covalency between Mn and its coordinated atoms which may be induced by the fragmentation processes of the random network during heating.

In addition, from the present study, the drastic change in viscosity at the glass transition is clearly understood by the fragmentation processes in the amorphous solids on heating.

# 学位論文審査結果の要旨

T.KChakraborty 氏は，カルコゲナイド系非晶質物質のガラス転移の研究を行った。対象物質としては，１次元鎖状構造の物質，２次元層構造物質，さらに２次元と３次元構造がミックスした３種類の材料を選び，それらに Mn をプローブとして添加した材料の ESR 測定を行った。非晶質物質はガラス転移温度以上では緩和時間の短い非平衡状態にあるので，２℃／min の一定の昇温速度で加熱中に次々と測定を行い，過冷却液体の状態変化を捉えることを試みた。Mn からの ESR 信号は非晶質構造を反映した g＝2.00 と g＝4.3 の信号が観測されるが，前者は Tg を越すと顕著な narrowing を起こすことを見出した。一方，後者のシグナルは Tg 以上では broadening を示した。これらの結果から，過冷却液体出現のメカニズムについて考察を行った。即ち，非晶質物質は Tg を越えると fragment 化し，そのサイズが減少するので粘性の大きい過冷却液体となるというモデルに基づき，narrowing と broadening が起こる様子をミクロスコピックな観点から明らかにした。g 値が 2.00 の信号の narrowing は fragment 化した系では激しい運動が生じるためであり，g 値が 4.3 の信号の broadening は fragment のサイズが減少することにより Mn とその配位原子との結合状態が影響を受けることによると結論している。Chakraborty 氏のこのような研究により，ガラス転移に関する理解は大幅に進展したと言え，博士後期課程における学習結果と合わせて学位の授与に値すると判断される。