Imperfections in amorphous chalcogenides. II. Detection and structure determination of neutral defects in As-S, Ge-S, and Ge-As-S glasses

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Structure and formation processes of neutral defects in Ge-S, As-S, and Ge-As-S glasses have been investigated by ESR spectroscopy. For the Ge-S system, a well-known paramagnetic defect species showing a single absorption at $g \cong 2.01$ was reexamined by detecting and analyzing ^{73}Ge ($I = 9/2$) hyperfine structure (hfs). The structure of the Ge-associated defect was estimated from the spin density measurement on a germanium atom (0.28) to be a germanium atom with three neighboring sulfur atoms in which the unpaired electron occupies a nonbonding sp^3-like orbital. The first observation of the formation of arsenic-associated paramagnetic defect in an as-prepared glass has been accomplished by selecting the Ge-As-S system. The spin density on the arsenic $4p$ orbital was calculated to be about 1.00 from the detection and analysis of hfs due to ^{75}As. The structure of the As-associated defect was estimated to be arsenic with two neighboring sulfur atoms in which the unpaired electron occupies the nearly isolated $4p$ orbital of arsenic. From an observation of formation of neutral defects in the pseudobinary system $As_2S_3:Ge_2S_3$, the formation process of neutral defects was proposed on the basis of the nature of chemical bonds involved in the system. The importance of the "weak" intermolecular force was stressed as the definitive factor for the defect formation, especially in the "kinetic" process of solidification.

I. INTRODUCTION

Since the early 1960s, chalcogenide glass semiconductors have been widely investigated because of their potential applications as memory or switching devices.[1,2] Controlling the conduction type (p or n) is essential in most applications of semiconductors in electronic devices. However, any effective improvement in controlling the electrical properties of chalcogenide glasses has not been accomplished. There are two, perhaps related, explanations for the above-mentioned uncontrollability. The first is that the bonding of dopants into the glasses is such that the formation of charged donors or acceptors appears to be inhibited. The insensitivity of electrical properties to impurities is considered to originate from the structural and bonding accommodation of amorphous semiconductors. The second explanation is that a large number of gap states exists in the glasses, which can be related to some structural imperfections. The success of doping in a-Si:H suggests that the first explanation is not always applicable to all kinds of amorphous materials, especially for rigid glasses, such as a-Si and a-Ge, from group IV of the Periodic Table. Therefore, characterization of gap states has been a central topic in the science of amorphous semiconductors.[3]

A physical model of the gap states was first proposed by Anderson[4] with theoretical consideration on the total electronic energy of the system. This model was modified by Mott, Davis, and Street[5] and finally extended and visualized by Kastner *et al.*[6–8] and Fritzsche *et al.*[9,10] as valence-alternation-pair (VAP) model. The most important assumption underlying the physical models is that the structural defects constituting the gap states must be

negatively or positively charged. The electronic energy levels of respective defects were roughly estimated and a number of interesting phenomena observed in chalcogenide glasses were interpreted in terms of the charged-defect model. The model has also been applied to SiO_2 glasses, as discussed by Greaves[11,12] and Lucovsky.[13–15] However, these has been no direct experimental evidence concerning the presence of the charged defects in various amorphous materials. Although this may be partly due to the spectroscopically inactive nature of the defects, it seems necessary to reexamine the VAP model and see if charged defects really exist or are dominant in the glasses.

Recent applications of a-SiO_2 (a-SiO_2:GeO_2) to optical waveguides, dielectric thin layer of metal-oxide-semiconductor device, and optical components for uv region has accelerated characterization of the defects present in the glasses. This is because their optical, electrical, and chemical properties are sensitive to the presence of defects. The most interesting observation is the detection of the Si or Ge E' center (singly occupied dangling bond) and peroxy or oxygen radical, all being electrically neutral defects.[16,17] These are considered to be the fission products of Si—O (Ge—O) bonds in the melts. When we refer to the above-mentioned results, similar kinds of defects would also be expected for chalcogenide glasses; there exists a greater possibility for radical breaking of chemical bonds in "covalent" chalcogenide glasses than in "ionic" oxide glasses in melting states. However, most chalcogenide glasses show no ESR absorption so that all electrons in the system are in spin pairs. One exception can be found in the glasses of a Ge-S system in which well-resolved ESR absorptions are observed.[18]

The formation of neutral defects in a Ge-S system appears to be quite a special case since the VAP theory predicts the charged defects also for Ge-S glasses. However, ESR studies on liquid sulfur and selenium revealed that the melting states are achieved by breaking S—S or Se—Se bonds homolytically and the equilibrium number of broken bonds at a specified temperature follows from the Arrhenius's equation.[19,20] In the preceding paper of this series,[21] it was also confirmed by ESR spectroscopy that the melting state of As_2S_3 glass was achieved by breaking bonds homolytically. The above facts suggest that in most chalcogenide glasses, a number of broken bonds are formed in their melt states. Thus, the formation of neutral defects in Ge-S glasses seems to be reasonable since the equilibrium state before quenching may well be reflected in the resulting glassy states. However, there is very little information concerning the structures, formation mechanisms, and electronic states of such neutral defects in the Ge-S system, partly due to the lack of informative features in ESR spectra.

In this paper the structure of a paramagnetic defect in GeS_2 glass is determined from ESR studies which include the first detection and analysis of a ^{73}Ge hyperfine structure (hfs) in the spectrum. A model for the formation process of a neutral defect in the Ge-S system will be given and its confirmation will be accomplished by predicting the formation of a paramagnetic and electrically neutral defect associated with As in as-prepared Ge-As-S glasses. The As-associated defect was assigned based on an analysis of its ^{75}As hfs. Finally, it will be stressed that the strength of various types of chemical bonds or the cohesive energy of the system, i.e., "molecular and weak" or "continuous network and strong," must be the definitive factor in determining the character of the resulting structural defects in the glasses.

II. EXPERIMENTAL PROCEDURE

A. Preparation of glass samples

Glass samples examined in the present study are in the systems of Ge-S and Ge-As-S having a chemical composition of Ge_2S_3, GeS_2, and GeS_3: $5\,GeS_2$:$1\,As_2S_3$ and $x\,Ge_2S_3$:$(1-x)As_2S_3$ $(x=0-1)$. The glasses were prepared by quenching melts from constituent elements of 99.99% pure Ge, 99.999% pure S and As, respectively. Before preparation, pretreatments were made on both As and S. In particular, elemental As was dehydrated by heating at 350°C under evacuation in order to prevent oxygen-impurity contamination in the glasses. Sulfur was distilled in an evacuated and sealed Pyrex ampoule under a temperature gradient (350°C on the high-temperature side and room temperature on the other side) to remove carbon impurities, since the carbon gave rise to an ESR absorption at $g=2.000$ with linewidth of 3 G. The raw materials were carefully weighed for the desired composition and had a total mass of $\sim 3-5$ g and were placed in a silica glass ampoule of 10-mm inner diameter with 60 mm length. The ampoule was evacuated up to 10^{-4} mm Hg, sealed and heated in an electric furnace at $\sim 850-950$°C

for more than 24 h. During heating, the ampoule containing the glass melt was rocked several times and rotated to obtain a homogeneous glass. Then the ampoule was quenched in ice-water bath. All the glasses were homogeneous and transparent showing the color of yellow to red.

In order to avoid annihilation of paramagnetic defects formed in the glasses, these samples were not thermally annealed after quenching.

B. ESR Measurements

The glass samples were subsequently crushed, placed in a silica tube, evacuated, and sealed. Measurements were carried out on a JEOL FE-2XG (X band, 9 GHz,TE_{011}) ESR spectrometer at 77 K. The saturation of ESR absorptions were observed at a microwave power levels of 0.5 mW for the Ge-associated defect and 1 mW for the S-associated defect, respectively. Therefore, the operating microwave power was suppressed to less than 0.1 mW for all of ESR measurements. The magnetic field and operating microwave frequency were calibrated with a proton NMR marker and a cavity wave meter, respectively. The GeS_2 glass was also γ irradiated so as to enhance the ^{73}Ge hfs. The irradiation was done at 77 K using a ^{60}Co source with a dose rate of 5×10^5 rad/h for 2 h.

III. RESULTS AND DISCUSSIONS

A. Structural determination
of Ge-associated paramagnetic defects in GeS_2 glass.

As was stated in the Introduction, among all of chalcogenide glasses only a bulk glass[18] or evaporated thin film[22] of a Ge-S system shows an intrinsic ESR absorption. In this subsection, a detailed analysis of the ESR spectrum which includes the ^{73}Ge hfs observed in the present work is carried out to determine the structure of Ge-associated defects in GeS_2 glass.

Figure 1 shows ESR spectra of (a) GeS_3, (b) GeS_2, and (c) Ge_2S_3 glasses. As seen in the figure, the spectra changed systematically with changing composition of the glasses; for the glasses of Ge-rich (Ge_2S_3) or stoichiometric (GeS_2) composition, only a simple absorption line at $g=2.01$ was observed, whereas for the S-rich (GeS_3) glass the absorption consists of several features. Apparently the change in the spectra on going from the S-rich to the Ge-rich glasses appears to be discontinuous, but it actually occurred continuously in a narrow composition region. The two characteristic absorptions of spectrum (a) and (b) are simultaneously observed in GeS_2 or slightly S-rich glasses; in spectrum (b), the absorption characteristic to S-rich glass (a) cannot be shown at the same time, since the difference in power saturation level between the absorptions (a) and (b) makes a simultaneous recording impossible.

Structural assignments for absorptions in Fig. 1 were previously carried out by other workers[22-24] based on the
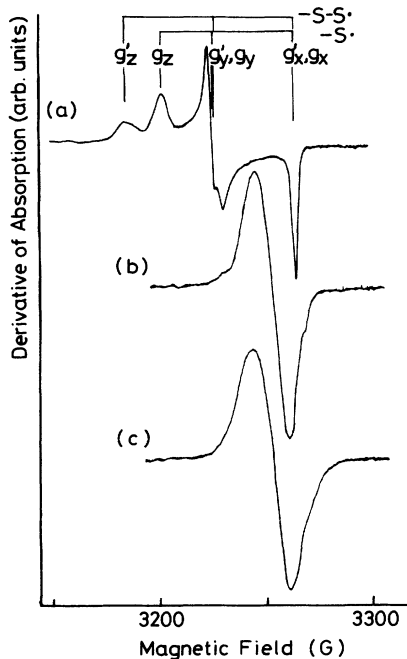
FIG. 1. ESR spectra (9.16 GHz) for glasses of Ge-S system at 77 K. The compositions are (a) GeS_3, (b) GeS_2, and (c) Ge_2S_3. The complex features in spectrum (a) are due to superposition of absorptions of two kinds of sulfur dangling bonds, which are clearly distinguished from each other by the brackets.

FIG. 2. ESR spectra of GeS_2 glass before (a) and after (b) γ irradiation. The dashed line in (a) represents a result of line-shape simulation. A new absorption appeared after irradiation was clearly indicated by an arrow in (b). The label $C_?^?$ was used for abbreviation of the new center in which the coordination number and charged state of the central chalcogen atom was yet unidentified.

analysis of the g tensors. The spectrum of S-rich glass (GeS_3) in (a) was considered to be composed of a superposition of absorptions due to S dangling bonds, —S· and —S—S·.[22] The difference between these two defects is apparent in the anisotropy of their g tensors. As indicated by the arrows in Fig. 1(a), two of the principal g values, g_x and g_y, are similar for —S· and —S—S·, whereas their respective g_z's are significantly different. It was suggested that —S—S· has a larger g_z value than —S·.[23] Although the sulfur dangling bond model has not been experimentally verified by detection of the ^{33}S hfs ($I = \frac{3}{2}$, natural abundance$=0.74\%$), we accept the structure of the defects as sulfur dangling bonds. Hereafter, the different defects are denoted as $C^0_{(1)T}$ or $C^0_{(1)C}$ (C and T mean chalcogen and group-IV element, respectively, and superscript and subscript denote excess charge and coordination number, respectively. T or C in the subscript expresses the neighboring atom(s) of the central chalcogen.

In contrast to the $C^0_{(1)}$ signal, ESR absorptions in (b) GeS_2 and (c) Ge_2S_3 glasses show no characteristic feature useful for determining the structure of the defects. It has been proposed[25,26] that the absorption is due to germanium dangling bonds, since its g value and slightly asymmetrical line shape are comparable to those observed in amorphous germanium and amorphous Si:Ge. Among all of the stable isotopes of germanium atoms, only ^{73}Ge has a nonzero nuclear spin ($I = \frac{9}{2}$) so that one might be able to observe the hfs due to an interaction between an
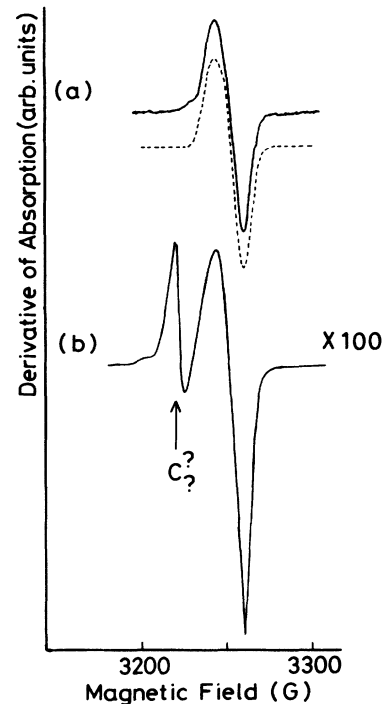
unpaired electron and a ^{73}Ge nucleus in spectrum (b). However, in practice, it is impossible to detect the hfs because of the low concentration of paramagnetic defects in GeS_2 glass (typically 10^{15} spins/gram), the low natural abundance of ^{73}Ge (7.76 at. %), and the high nuclear spin. Thus no definitive identification of the paramagnetic defect species has previously been possible.

In the present work, γ irradiation at 77 K was found to be effective in enhancing the ESR absorption. Figure 2 shows ESR spectra of GeS_2 glass before (a) and after (b) γ irradiation, respectively. The intensity of the absorption at $g=2.01$ was successfully increased by about 2 orders of magnitude after γ irradiation, and a new absorption spectrum appeared at $g=2.03$ which is indicated by an arrow in Fig. 2(b) (hereafter we abbreviate the new absorption as $C_?^?$ and the absorption observed before irradiation as $T^0_{(3)}$, respectively). The absorption $C_?^?$ could be bleached out by annealing the irradiated glass at room temperature for a few minutes, while the absorption of $T^0_{(3)}$ survived with only a slight decrease in its initial intensity just after the irradiation. Thus the γ-induced $C_?^?$ center should differ in its origin from $T^0_{(3)}$ center.

The increase in intensity of absorption $T^0_{(3)}$ implies the possibility of detecting the ^{73}Ge hf lines. Figure 3 shows the ESR spectrum for γ-irradiated GeS_2 glass remeasured
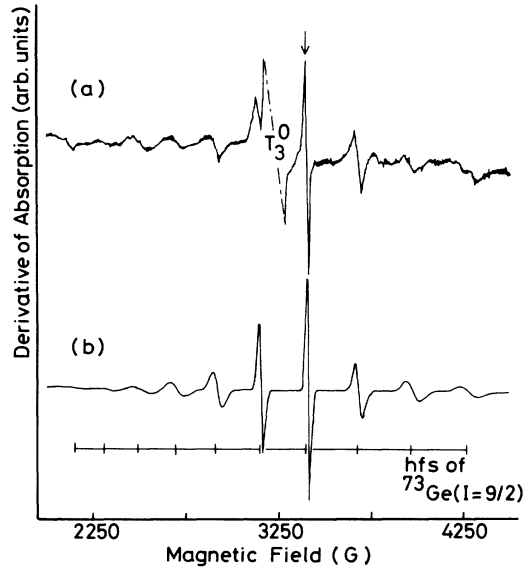
FIG. 3. (a) ESR spectrum of γ irradiated GeS_2 glass remeasured with a wider scanning range and larger spectrometer gain than in Fig. 2. The central absorption at $\simeq 3250$ G observed before irradiation was omitted in this figure. (b) Result of line-shape simulation of absorption in (a). The positions of absorption of hfs due to ^{73}Ge was indicated by the bracket.

with a wider scanning range of magnetic field and higher spectrometer gain than those of Fig. 2. The absorption $T^0_{(3)}$ is omitted in this figure because of its extremely high intensity. As seen in Fig. 3, several absorptions were clearly observed in the magnetic field region of 3250 ± 1000 G where each line seems to be separated from their neighboring absorptions by $\simeq 240$ G. All of these lines decreased their intensities at the same time by annealing at room temperature, in harmony with decreasing of the absorption $T^0_{(3)}$. Furthermore, the intensity ratio

of the absorption line labeled by an arrow to the absorption $T^0_{(3)}$ at the center of Fig. 3 (0.092:1.000) was nearly equal to that of natural abundance of ^{73}Ge to other isotopes having zero nuclear spin (0.076:1.000). Thus it can be assumed that these absorptions are of the same origin and are associated with ^{73}Ge and other germaniums having zero nuclear spin, respectively.

Simulations were carried out to confirm the above assumption and to estimate the ESR parameters of the Ge-associated defect. A detailed procedure of the simulation was described in the literature and in the present case: We utilized a semiempirical but time-saving method established in our previous work.[27] At first, absorption of $T^0_{(3)}$ was taken into account for determination of the g tensor and the result is shown in Fig. 2(a) by the dashed line. The whole shape of $T^0_{(3)}$ could be satisfactorily reproduced. This means that the principal g values are fixed. Secondly, an hf interaction between the unpaired spin and a ^{73}Ge nucleus was added to the spin Hamiltonian. The result of the calculation is shown in Fig. 3(b) in which 10 hf lines due to ^{73}Ge are clearly indicated by the bracket. The agreement between the observed and calculated spectra is sufficiently good and is enough to indicate that the origin of the ESR absorption in GeS_2 glass is a Ge-associated paramagnetic defect. The ESR parameters used in the simulation are listed in Table I as well as those for paramagnetic defects in which an unpaired spin is localized on a group III, IV, or V atom.[28–31]

In order to identify the structure of the defect, the spin density on ^{73}Ge $4s$ orbital (s character, $D_s^2 = A_{iso} / A_{iso}^{free}$, where A_{iso} and A_{iso}^{free} represents the isotropic term of the hf tensor and that of the free atom, respectively) was calculated and found to be 0.28 from the estimated isotropic term of ^{73}Ge hf tensor. Figure 4 shows an empirical relation between the s character and geometrical structure of the paramagnetic defects. Comparing this value with those of paramagnetic defects related to group III, IV, or

TABLE I. ESR parameters for $T^0_{(3)C}$ in GeS_2 glass and defects associated with group III, IV, and V elements in the Periodic Table.

		g tensor		hf tensor (G)		$D_s^{2\,a}$	
^{73}Ge in GeS_2 glass		$g_x = 2.0175$ $g_y = 2.0096$ $g_z = 2.0066$		$A_x = 241$ $A_y = 235$ $A_z = 234$		0.28	

		$g_{\parallel}$	$g_{\perp}$	A_{iso} (G)	A_{an} (G)	D_s^2	Ref.
E' type	B	2.0020	1.9996	216	9	0.26	28
	Al	2.0015	2.0003	354	16	0.25	29
	Si	2.0017	2.0004	420	22	0.24	10
	Ge	2.0008	1.9946	251	9	0.30	27
	P	2.002	1.999	910	60	0.23	30
	As	2.0		748	60	0.22	31
Electron center	Ge	1.9926	1.9976	291	4	0.35	27
	P	2.0013		1300	50	0.33	30
	As	2.0		990		0.29	31

[a]D_s^2 represents s character, the spin density on a s orbital of central atom and is calculated by $D_s^2 = A_{iso} / A_{iso}^{free}$, where A_{iso} and A_{iso}^{free} represent the isotropic term of hf tensor and that of a free atom, respectively.

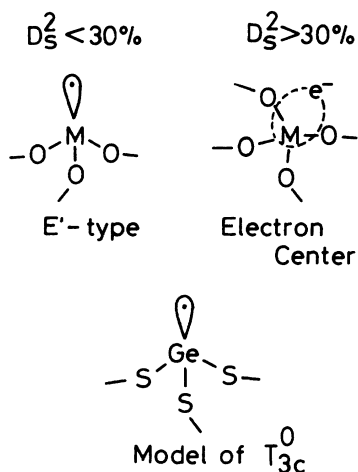FIG. 4. Model structure for paramagnetic defect in oxide glasses and GeS_2 glass.

FIG. 5. Equilibrium reactions in the glass melt of the Ge-S system.

V elements in oxide glasses, we suggest that the structure of $T^0_{(3)}$ in GeS_2 glass is an E' type in which the unpaired spin is localizing on a sp^3-like hybridized orbital of ^{73}Ge as shown in Fig. 4. One of the sp^3-like hybridized orbitals of the Ge is a singly occupied and nonbonding state while the others are in bonding states. The neighboring atoms around the central Ge are expected to be sulfur atoms or germanium atoms but could not be determined, since any information such as super hf interaction with neighboring ^{33}S or ^{73}Ge was not obtained in the present ESR results. From the similarity in the g tensors of the $T^0_{(3)}$ and the E' centers in oxide glasses and from consideration concerning the structure of GeS_2 glass, we strongly suggest that the central Ge of $T^0_{(3)}$ in GeS_2 glass is surrounded by three neighboring sulfur atoms.

B. What controls the formation of neutral defects in chalcogenide glasses

In this subsection we consider why the detection of electrically neutral dangling bonds has been limited only to Ge-S glasses. The singly occupied dangling bonds are undoubtedly present in almost all the liquid chalcogenides, but these are quenched out under the cooling process to a glass in most of chalcogenide glasses. Therefore, we first consider the chemical equilibrium of the thermal decomposition in Ge-S melts as an initial state and second proceed to the discussion on its change under quenching process.

From works on glass structure of the Ge-S system by Raman spectroscopy,[32,33] it is well known that GeS_2 glass (stoichiometric composition) consists of GeS_4 tetrahedra linked together forming a network structure. In the glasses of nonstoichiometric composition, besides the major bonds of Ge—S, homopolar bonds of —S—S— in S-rich (e.g., GeS_3) glasses and $\equiv$Ge—Ge$\equiv$ in Ge-rich (e.g., Ge_2S_3) glasses are formed by excess sulfur atoms and excess germanium atoms, respectively. Figure 5
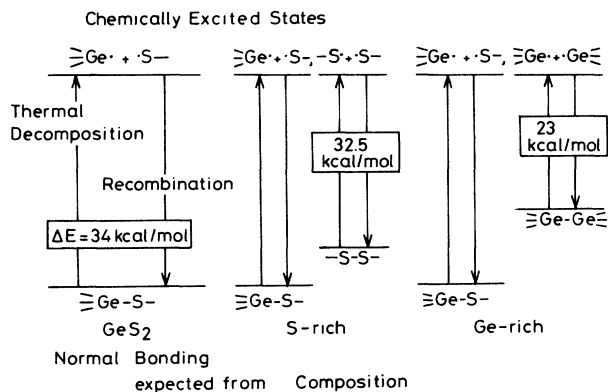
shows thermal equilibria between normal bonding states and thermally excited states in the Ge-S system. As shown in the figure, bonds in the system are assumed to be broken in the excited states. The heats of equilibrium reactions were assumed to be half dissociation energy of each bond; bond-dissociation energies of Ge—S, S—S, and Ge—Ge, were 68, 65, and 46 kcal/mol, respectively, referenced by Arai[34] and originally listed by Myuller and Borisova.[35] Those values seemed to be high, since in our preceding work,[21] the heat of equilibrium reaction for —S—S— $\rightleftarrows$ —S· + ·S— was estimated to be 34 kcal/mol, which was almost half of the above listed dissociation energy of S—S. Thus, as a rule of thumb we took half of the dissociation energy of Ge—S and Ge—Ge as the heat of equilibrium reaction for each bond (though the original work of Myuller, et al. was not available in our library, the disagreements must be due to difference in the method of evaluation).

The fraction of broken bonds (chemically excited states) for GeS_2 glass at 950 °C is calculated to be 8.4×10^{-7}. Using the Boltzmann distribution, $\exp(-\Delta E /kT)$, the concentration of chemically excited states at that temperature is calculated to be 7.4×10^{15}/g for both $\equiv$Ge· and —S·. Assuming the structure of broken bonds for germanium atoms in the liquid state is similar to $T^0_{(3)}$ in the solid glass, the estimated concentration of broken bonds is of the same order of magnitude as the number of $T^0_{(3)C}$ observed in the solid glass. Hence, we suggest that the neutral defects $T^0_{(3)C}$ are formed by rapid quenching of glass melt in which the precursors of $T^0_{(3)C}$ are generated by thermal decomposition of Ge—S bonds in the liquid state. Analogously, the composition dependence of ESR spectra or more specifically the type of defects observed in nonstoichiometric glasses can be understood as follows: The broken bonds of —S· are dominant in S-rich glasses and $\equiv$Ge· in Ge-rich glasses because of the formation of homopolar bonds for the sulfur excess and germanium excess glasses. The homopolar bonds have smaller binding energy than Ge—S bonds so that sulfur atom dangling bonds and $T^0_{(3)}$ are mainly observed in GeS_2 and Ge_2S_3 glasses, respectively.

The proposed process for defect formation is expected to hold also for other chalcogenide glasses, for example, As_2S_3 glass. ESR results have indicated the absence of paramagnetic defects in As_2S_3 glass, whereas a considerable number of radicals exist in the high-temperature melts. Because of the simple ESR absorption line shape, it was difficult to clarify the nature of radicals in the As_2S_3 melt. However, the radicals must be formed by dissociation of As—S bonds to form $=As\cdot$ and $\cdot S$—, since the glass is composed of AsS_3 trigonal pyramids linked together with bridging sulfur atoms. Thus, we must answer the question as to why the radicals are not observed in As_2S_3 glass, but are detected in Ge-S glasses after quenching the melts. A current explanation for the absence of radicals in the glass is that defects in As_2S_3 glass are charged defects such as VAP's that are formed by transfer of an electron localized on the broken bonds during the quenching process. This does not explain the appearance of neutral defects in Ge-S glasses. We assume that the condition for whether the radicals in the melts remain as neutral or charged defects in the glass is related to the rate of recombination between the radicals. The recombination between broken bonds is assumed to occur faster in As_2S_3 melt than that in GeS_2 melt, so that broken bonds remain as paramagnetic defects in GeS_2 glass but do not remain so in the As_2S_3 glass.

The above kinetic explanation must be confirmed, and it is done by detecting a dangling bond on As in as-prepared chalcogenide glasses. It is expected from the assumption that some radical species associated with arsenic or a dangling bond on As should be detected in glasses having moderately low recombination velocity. Then, the glasses of the Ge-As-S system are chosen for detection of As-associated neutral defects. Figure 6 shows
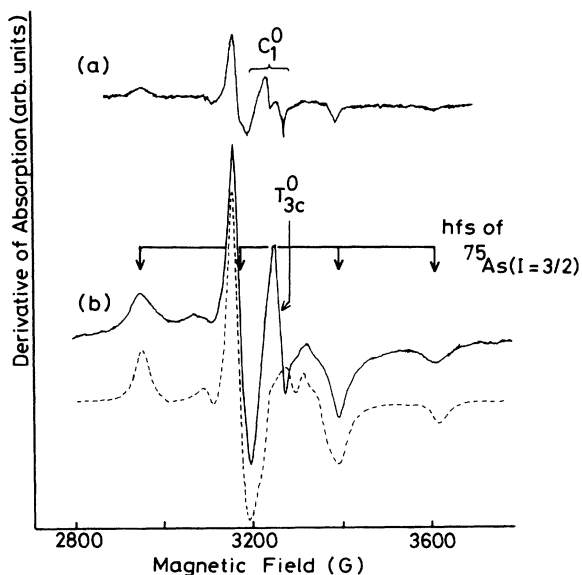

FIG. 6. ESR spectra of as-prepared Ge-As-S glasses: (a), $1\,As_2S_3{:}5\,GeS_2$; (b), $1\,As_2S_3{:}3Ge_2S_3$. The positions of hfs due to ^{75}As were clearly indicated by the bracket. The dashed line in (b) represents the results of line-shape simulation.

ESR spectra of as-prepared (a) $5\,GeS_2{:}1\,As_2S_3$ and (b) $6Ge_2S_3{:}1\,As_2S_3$ glasses, respectively. As seen in the spectrum (a), complicated absorption lines were observed in the magnetic field region of 3200 ± 500 G. The spectrum is a superposition of two absorptions. One spectrum has the complicated features labeled by the brackets in (b) and the other (rough shape is given in the upper portion), which is weak and seen around 3300 G), is the absorption characterized by an anisotropic g tensor. The former absorption is assigned to As-dangling bonds as discussed below, and the latter is assigned to $C_{(1)}^0$ of sulfur atoms (sulfur atom dangling bonds). The absorption of $T_{(3)C}^0$ in simple GeS_2 glass was not observed in this glass.

In the spectrum (b), $T_{(3)C}^0$ was observed as indicated by the arrow while the unidentified absorption in (a) was also observed with increase in its intensity. The center giving this absorption was stable at RT and any reduction of absorption intensity was not observed for a long period. The set of absorptions indicated by the bracket was separated by about 200 G with each other and by annealing the glass at $200\,°C$ for a few hours, the absorptions were bleached out at the same time. These results suggest that the center responsible for the absorption is a single kind of defect species associated with arsenic, showing an anisotropic hf interaction of ^{75}As ($I = \frac{3}{2}$, natural abundance of 100%). Line-shape simulation was carried out to confirm the ^{75}As hfs and to elucidate the ESR parameters of As-associated neutral defect. An hf interaction between an unpaired electron and a single ^{75}As nucleus was assumed in the calculation and the result is shown in Fig. 6(b) by the dashed line. The hole shape of the observed absorption was well reproduced in the calculated spectrum and arises from the large anisotropy in the ^{75}As hf tensor. ESR parameters used in the calculation are summarized in Table II with some of those for organic and inorganic radicals associated with arsenic.[36-39] By assuming that two of the principle values of hf tensor, A_y and A_z have negative signs, the spin density on the $4p$ atomic orbital of arsenic was calculated to be 1.00, thus implying strong localization of the unpaired electron on the arsenic. Figure 7 shows the proposed structure of As-associated paramagnetic defects listed in Table II (note that these defects are produced by uv- or γ irradiation). From a comparison of the ESR parameters of As-associated defect in Ge-As-S glass with those shown in the figure and the estimated spin densities, the structure of our defect was estimated to be that shown at the bottom of Fig. 7, in which an unpaired electron is localizing on nonbonding $4p$ orbital of arsenic having two neighboring sulfurs. Hereafter, we abbreviate this defect as $P_{(2)C}^0$ (P represents a group-V atom or pnictide).

The structure of $P_{(2)C}^0$ can be interpreted as originating from the bond breaking reaction in the Ge-As-S glass melt. In the $5\,GeS_2{:}1\,As_2S_3$ glass, the glass network consists mostly of Ge—S and As—S bonds. Because of the smaller dissociation energy for As—S bonds (61 kcal/mol) than for Ge—S bonds (65 kcal/mol), a larger number of broken $=As\cdot$ than $\equiv Ge\cdot$ bonds should exist in the high-temperature melt so that $P_{(2)C}^0$ is dominant in the resulting glassy state. In the case of $3\,Ge_2S_3{:}1\,As_2S_3$

TABLE II. ESR parameters for $P^0_{(2)C}$ in Ge-As-S glasses and As-associated defects. Here, Ph and Et represent phenyl and ethyl groups, respectively.

	hf tensor (G)			g tensor			D_s^2	D_p^2	Ref.
	A_x	A_y	A_z	g_x	g_y	g_z			
^{75}As in Ge-As-S	221	(−)60	(−)60	2.00	2.053	2.016		1.00	
AsPh$_4$	592.6	505	524.8	1.97	2.014	2.027	0.16	0.28	36
$+$AsEt$_3$	550	280	280	2.00	2.03	2.03	0.11	0.97	37
AsPh$_2$	225	−40	−40	1.999	2.052	2.012		0.96	38
AsO$_2^{2-}$	217	−62	−52	1.999	1.991	2.015		1.00	39
AsO$_4^{-}$	$A_{iso}=990$				2.0		0.29		31
AsO$_3^{2-}$	$A_{iso}=748$,	$A_{an}=60$			2.0		0.22	0.66	31

glass, the sulfur atom deficiency enhances the formation of $\equiv$Ge—Ge$\equiv$ and $=$As—As$=$ homopolar bonds. The dissociation energy for both homopolar bonds is 46 kcal/mol, so that the number of $\equiv$Ge· and $=$As· broken bonds in the glass melt is larger than those in the stoichiometric glass of 5 GeS$_2$:1 As$_2$S$_3$, thus resulting in the increase in total density of the neutral defects.

The detection of the neutral defect $P^0_{(2)C}$ and the change in type of defects with change in glass composition strongly support the proposed process of formation of neutral defects in chalcogenide glasses. It seems to be important to note that the formation and nature of neutral defects in the resulting glasses were governed by the chemical equilibrium of homolytical bond breaking and recombination reactions between the defects in chalcogenide melts.

C. The factor affecting recombination rate of defects in melts

In the preceding section, we interpreted the presence and absence of the neutral defects in Ge-S and As-S glasses. In this subsection the effect of chemical bonding on the recombination rate of the radical species in glasses is discussed.
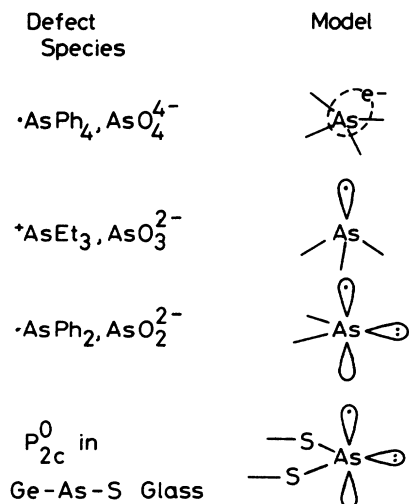

FIG. 7. Structural models for paramagnetic defects associated with arsenic.

The suggestion in the last subsection will be supported experimentally as follows. We assume that the recombination rates of radical species in Ge-S and As-S systems differ from each other. Then the condition of formation of neutral defects is expected to be changed with changing mixing ratio of As$_2$S$_3$ and Ge$_2$S$_3$. Figure 8 shows ESR spectra of X Ge$_2$S$_3$:$(1-x)$ As$_2$S$_3$ glasses, where X varies from 0.125 (e) to 0.875 (a). Two characteristics are noted in the effect of changing composition. As seen in the figure, ESR spectra consist of the superposing absorptions due to $T^0_{(3)C}$ and $P^0_{(2)C}$, varying their relative intensities with compositions of the glasses. This is the first feature. In the glass (a) containing large content of Ge$_2$S$_3$, intensity of the absorption of $T^0_{(3)C}$ was dominant
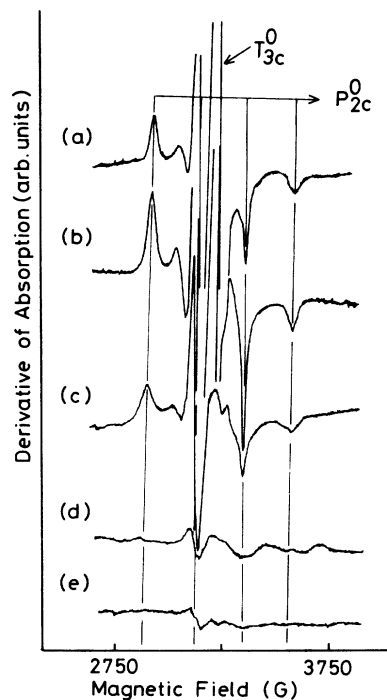

FIG. 8. Changes in ESR spectra for glasses of the system x As$_2$S$_3$:$(1-x)$Ge$_2$S$_3$. The compositions are (a) $x=0.125$, (b) $x=0.250$, (c) $x=0.500$, (d) $x=0.750$, and (e) $x=0.875$. The spectra consist of superpositions of absorptions due to $T^0_{(3)C}$ and $P^0_{(2)C}$, changing their relative intensities with changing the compositions of glasses.

and was omitted in the figure. By increasing As_2S_3 content in the glasses, intensity of the absorption of $T^0_{(3)C}$ was reduced, while that of absorption of $P^0_{(2)C}$ increased, and $P^0_{(2)C}$ was dominant in the glass (c) containing equal amounts of Ge_2S_3 and As_2S_3. The second feature is the change in the total concentration of the paramagnetic species. Further increase in As_2S_3 content reduces the absorption of $P^0_{(2)C}$ in the glasses (d) and (e) and any paramagnetic defect was not observed in the glass without Ge_2S_3, i.e., in As_2S_3 glass.

The above results suggest that the recombination rate of broken bonds in Ge-S system must be smaller than that in As-S system. The origin of the difference in recombination rate between Ge-S and As-S systems can be explained in the following way. Melting points of crystalline GeS_2 and As_2S_3 are 850 and 310 °C, respectively, and these crystals are formed by only Ge—S bonds for GeS_2 (Refs. 40 and 41) and only As—S bonds for As_2S_3.[42] Dissociation energies for each bond are almost the same (68 kcal/mol for Ge—S and 65 kcal/mol for As—S). Then, a large difference in their melting temperature cannot be understood by considering that the melting takes place only through bond breaking. The crystalline structures are very helpful for understanding the melting process in the both crystals. Crystalline GeS_2 consists of GeS_4 tetrahedra linked together with their corners forming a three-dimensional structure and crystalline As_2S_3 consists of two-dimensional layers in which AsS_3 pyramids links together with their corners. Thus melting can occur only by breaking Ge—S bonds in GeS_2, while in As_2S_3, it is possible to be melted by overcoming the interlayer (intermolecular) force. The interlayer forces are generally considered to be much weaker than intralayer forces so that melting occurs at lower temperature in low dimensional and/or molecular solids, such as As_2S_3. The effect of the melting process on the formation of neutral defects in both GeS_2 and As_2S_3 glasses should be taken into consideration. In both glasses, there exist broken bonds ≡Ge· and =As· in their melting states. During rapid quenching, recombination reaction forming the normal bonds, Ge—S and As—S or homopolar bonds ≡Ge—Ge≡ and =As—As= takes place to attain a preferable stable states. The recombination rates are considered to be governed by the structural flexibility of glass above solidification temperature, so that the recombination reaction can easily occur in As_2S_3 glass having molecularlike character in its melting states.

The process and condition for defect formation are then sufficiently understood by the discussion in the last paragraph. It is suggested that the definitive factor for whether the neutral defects are formed in glasses is the nature of chemical bonds in glasses governing the recombination rate of broken bonds in melt.

IV. SUMMARY

In the present work, a process for the formation of neutral defects was proposed on the basis of the nature of chemical bonds involved in the system. The structure of the Ge-associated paramagnetic defect in GeS_2 glass was assigned by the first observation and analysis of the ^{73}Ge hfs to be an unpaired electron localized on a germanium atom which we further suggest is bonded to three neighboring sulfur atoms. The above assignment strongly suggests that the defects are formed as fission products in the melt at high temperature, in which the Ge—S bonds broke homolytically to be ≡Ge· and ·S—. The condition for whether the broken bonds in melt remain in the glass was assumed to be related to the recombination rate between the broken bonds. The first observation and analysis of an As-associated paramagnetic defects in Ge-As-S glasses provides support for our model concerning the mechanism by which these defects form as well as their general nature. It was found that the presence or absence of "weak" intermolecular bondings in the system in question was the definitive factor for the defect formation, especially in the kinetic process of solidification.

One of the important problems remaining is the localized gap states in chalcogenide glasses. The reason is as follows: the neutral paramagnetic defects, needless to say, form a localized states in the midgap. However, most of chalcogenide glasses show no ESR absorptions and the reason for the absence of neutral defects in As_2S_3 glass was discussed in the last section. It seems unlikely to consider the existence of charged defects (VAP's) based on our model for defect formation and then alternative model of gap states must be given. In the following paper[43] we propose an alternative model termed "the interacting lone-pair-electron model" and discuss its electronic structure in detail.

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