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INTRINSIC AND PHOTON-INDUCED DEFECTS ASSOCIATED WITH Ge IN OPTICAL FIBER

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Résumé - Les mesures de champ hyperfin sur le Ge$^{73}$ ont montré que les défauts d'irradiation induits dans des fibres de silice dopées au germanium sont bien du type E' (30 %) et tétraédrique (35 %). La relaxation thermique des fibres irradiées permet de suggérer que la formation de groupement OH par diffusion de l'hydrogène atmosphérique est une réaction catalysée par les défauts E'.

Abstract - Structural models for darning- and radiation-induced defects associated with Ge were confirmed to be E' type and spherical tetrahedron from the spin density on Ge, 30% and 35%, respectively, estimated from hfs due to $^{73}$Ge. From the observation of thermal relaxation of radiation-induced center to Ge-E', the loss-increase due to OH formed on the reaction of a fiber with hydrogen molecule diffused from atmosphere was explained as the E'-catalyzed formation of OH groups.

I - INTRODUCTION

It has been established that light transmittance of an optical wave-guide is seriously reduced by OH groups as an impurity and color centers formed by fiber-drawing or ionizing radiation. Four types of paramagnetic centers localized on a Ge were detected for Ge-doped silica fiber /1/. One was observed in as-prepared fiber and the remaining three were in irradiated fibers. The one observed before irradiation was thought to be a E' type defect(Ge-E') and the three others observed after irradiation were suggested to have similar structure, one difference arising from the number of second neighboring Ge ion around the Ge carrying an unpaired spin. It is, however, extremely difficult to distinguish each defect in terms of the number of second neighbor-Ge atoms from the results of conventional ESR. In a present work we state the detection of the hfs due to $^{73}$Ge in the Ge associated centers induced by drawing or γ-irradiation of Ge-doped silica fiber. Possible structural models for these defects will be given by analyzing the hf tensors estimated from ESR lineshape simulation. The structure of precursor and formation process of these defects will also be discussed on the basis of an observation of their thermal bleaching behavior.

II - EXPERIMENTS

Sample used in this work was a silica based fiber doped with 30 mol% GeO$_2$ drawn at 45m/min from a preform fabricated by the VAD process. The fiber of 200 μm diameter was cut into a piece each having 100mm length and 400 pieces of the fiber were used for ESR measurement. Isotope enrichment was also carried out to ascertain the hfs due to $^{73}$Ge. The batch of the composition 10 GeO$_2$:90 SiO$_2$(total weight =100mg) in which $^{73}$Ge was concentrated to 95% was melted with hydrocarbon-oxygen flame and allowed to cool to RT to form a glass. All samples were subjected to γ-ray from a $^{60}$Co with the total dose of 1Mrad at 77K. ESR measurements before and after irradiation were carried out at the temperature ranging from 77K to 300K on a JEOL...
PE-3X spectrometer. The magnetic field and operating microwave frequency were calibrated with proton NMR marker and cavity wave meter, respectively.

III - RESULTS and DISCUSSION

1. Intrinsic Ge-E' center: Figure 1(A) shows an ESR spectrum of unirradiated VAD fiber measured at RT. As seen in the figure, the spectrum was primarily composed of three absorption lines labelled by a), b) and c), respectively. The lineshape and intensity of a) near 2500G, which is strong and broad, changed with temperature of measurements or from sample to sample, and the identification of absorption a) has not been finished. It was reported that sharp but weak signal c) was due to heavy metallic ion impurity in γ-irradiated GeO2 glasses /1/. However, the concentration of these heavy metallic ions in VAD fiber is extremely low so that the signal c) should be intrinsic to VAD fiber. The central absorption b) was identical to Ge(III) center reported by Friebel e.t.al., though the concentration of the center was markedly higher. As in many earlier works, we assumed that the absorption b) of fig.1(A) was due to an E' type defect associated with Ge having zero nuclear spin. Then, there must be ten hf component lines due to 73Ge. On the basis of the following three observations we concluded that the absorption c) in fig.1(A) is one of the hf component lines. (1) The intensity ratio of absorption b) and c) in fig.1(A) was almost agreed with the ratio of the natural abundances of even Ge(1=0) and 73Ge(1=9/2). (2) As seen in fig.1(A), two additional absorptions indicated by arrows were clearly observed at the higher magnetic field than that of signal c). These three absorptions are expected to be hf component lines of 73Ge since the splitting width among them was nearly equal. (3) In 73Ge enriched GeO2:SiO2 glasses, these three absorptions were also observed, though their apparent intensity was relatively low because the total amount of the enriched sample is very small. To estimate ESR parameters for the center giving hfs due to 73Ge, computer simulation was carried out and the result was shown in fig.1(B). The ESR parameters used in the simulation were summarized in table 1 with those of E'-analogue associated with group III, IV or V element. The spin density on a 77Ge 4s-orbital, C\(_g^s\) was calculated to be \(\approx 50\%\) which was almost in accordance with C\(_g^s\) for other E' type centers. Therefore, structural model of Ge-E' center, in which the unpaired electron mainly localizes on a Ge with three neighboring oxygen forming a trigonal pyramid, was confirmed by detecting and analyzing the hfs due to 73Ge.

2. Radiation-induced Center: After γ-irradiation at 77K, ESR measurements were carried out at 77K without intervening warm-up. Figure 2 shows an ESR spectrum of γ-irradiated VAD fiber. On the both sides of the strong absorption at 3300G, which is omitted from the figure, ten absorption lines were clearly observed. These ten lines were ascertained to be hfs of 73Ge by detecting the same absorptions in γ-irradiated 10GeO2:90SiO2 glass. It was noticed that the center responsible for the spectrum in fig.4 is not identical with Ge-E' center, since the spectral features of Ge-E' center didn't appear in fig.2. The results of simulations are shown in the same figure by the dashed lines. The ESR parameters used in the simulation for the radiation-induced center associated with Ge are summarized in table 1. The difference between Ge-E' and the radiation-induced center is clearly visible in their spin densities on a Ge 4s-orbital, C\(_g^s\). We propose a structural model of the radiation-induced center as that the unpaired electron is mainly localizing on a Ge with four neighboring oxygens forming a rather symmetric coordination sphere, which is responsible to increase in spin density on Ge. It has been already confirmed that the radiation-induced center is formed by trapping an electron on GeO\(_4\) tetrahedron from the observation of similar absorption in 10GeO2:90SiO2 glass doped with a small amount of Ge\(^{73}\) after photo excitation /8/. Hereafter we abbreviate the center to as GEC (germanium electron-trapped center).

3. Thermal relaxation of GEC to Ge-E' center: Figure 3 shows the ESR spectra of γ-irradiated 10GeO2:90SiO2 glass after annealing at room temperature under vacuum for 1 year. Though the total spin concentration was decreased by an order of magnitude, it was surprising that Ge-E' center grew up in the spectra (the signal was originally possessing only features due to GEC). In fig.3, both Ge-hfs' of Ge-E' and GEC are clearly observed. They can be distinguished by their characteristic resonance fields indicated by brackets in the figure. Possible models for the conversion of GEC to Ge-E' center are shown in fig.4(a),(b) and (c). In model (a), an excess electron in GEC...
transfers to a positively charged Ge with three neighboring oxygen($\text{Ti}^{3+}$). This model
assumes that the positively charged Ge initially exists in the glass. Because of the
stability of Ge-$E'$, an excited electron should be trapped on the pre-existed
positively charged Ge forming Ge-$E'$ center under an irradiation. In this case, the
formation of GEC must be suppressed. Therefore, the process (a) can be neglected.
In process (b), Ge-$E'$ center is generated by detaching an oxygen from the coordinating
sphere of GEC. In this case, a negatively charged non-bridging oxygen($\text{Cr}^{2-}$) is
simultaneously generated. This process is identical to the proposed relaxation
process of radiation induced centers localized on P in alkali- or alkaline earth-
phosphate glasses, where the electron trapped center on P relaxes into $E'$ type center of
P on thermal annealing /9/. In the third model (c), a negatively charged GEC is
assumed to be stabilized by a proton. Upon thermal annealing, the GEC relaxes into
Ge-$E'$ through detaching an oxygen, the $\text{O}^{-}$ ion, the another product, forming -OH group
by capturing $H^{+}$. The $H$-assisted model is devised as an analogue of the relaxation
process of photo-induced radical from $\text{SiH}_{4}$ in Xe matrices. The process (c) may be
experimentally evidenced by detecting an increase in OH content with increasing Ge-$E'$
center but this was not conducted in this work. At present we have no additional and
experimental evidences which prefer the process (b) or (c). The process (c) may be
suggestive when we notice the enormous increase in the intensity of OH bands around
1.4 $\mu m$ for Ge-doped silica fibers annealed at above 100°C after exposing it to $H_{2}$
atmosphere /10/. On this treatment ESR intensity of Ge-$E'$ decreased simultaneously,
but the decrease was a few order of magnitude smaller than the increase of OH
concentration and tends to saturate. The reaction mechanism may be tentatively
explained in a following way;

\begin{align*}
\text{intrinsic Ge-$E'$ + $H_{2}$ + GeO}_{4} & \rightarrow 3\text{Ge-H + GEC/H}^{+} \\
\text{The reaction is initiated by thermally activated reaction of Ge-$E'$ with } H_{2} \text{ as shown in fig.4(c'). The remaining } H^{+} \text{ reacts with } \text{GeO}_{4} \text{ group giving rise to the formation of GEC. As aforementioned, GEC successively relaxes into Ge-$E'$ and T-OH;}
\end{align*}

\begin{align*}
\text{GEC} & \rightarrow \text{Ge-$E'$ + T-OH} \text{ Net reaction is expressed as}
\end{align*}

\begin{align*}
H_{2} + 3\text{Ge-O-T} & \rightarrow 3\text{Ge-H + HO-T} \\
\text{This reaction seems to be Ge-$E'$ catalyzed hydrogenation of } 3\text{Ge-O-T} \text{ structure. The products are 3Ge-H and OH groups and the concentration of Ge-$E'$ remains unchanged. As discussed above, it is important to clarify the behavior of hydrogen in an analysis of defects in silica fiber. Further investigations are ongoing.}
\end{align*}

Table 1 - ESR parameters for $E'$-type defects and GEC

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<th>$g_{\parallel}$</th>
<th>$g_{\perp}$</th>
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<th>$A_{\text{an}}$</th>
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* this work
Fig. 1 - (A) ESR spectrum of as-drawn silica fiber containing 30 mol% GeO₂. Three absorptions labelled by a), b) and c) are explained in the text. (B) Calculated spectrum for ⁷³Ge-E' center.

Fig. 2 - ESR spectrum of γ-irradiated silica fiber containing 30 mol% GeO₂ (solid line). Ten hf lines due to ⁷³Ge are clearly noted. The calculated spectrum for the hfs is denoted by the dashed line.
Fig. 3 - ESR spectrum of γ-irradiated $^{73}\text{GeO}_2$:$\text{SiO}_2$ glass after annealing at RT for 1 year. The resonance fields of hfs' due to $^{73}\text{Ge}$ of Ge-E' and GEC are indicated by the brackets.

Fig. 4 - Formation process and structure of GEC and its thermal relaxation process resulting a formation of Ge-E' center.

REFERENCES