RADIATIVE RECOMBINATION PROCESSES IN CHALCOGENIDE GLASSES
DEDUCED BY LIFETIME MEASUREMENTS OVER 11 DECADES

T. Aoki\textsuperscript{*}, D. Saito, K. Ikeda, S. Kobayashi, K. Shimakawa\textsuperscript{*}

Dept. of Electronics and Computer Engineering & Joint Research Center of
High-technology, Tokyo Polytechnic University, Atsugi 243-0297, Japan
\textsuperscript{*Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan

The paper presents universality of photoluminescence (PL) mechanisms among chalcogenide- and tetrahedral-amorphous semiconductors. In addition to the previous results (double-peaked lifetime distribution) in PL in the chalcogenide glasses As\textsubscript{2}Se\textsubscript{3}, As\textsubscript{2}S\textsubscript{3} and Se, we found a new component in the lifetime range from 10\textsuperscript{-3} to 10\textsuperscript{2} s by the wide-band quadrature frequency resolved spectroscopy (QFRS) at 3.7 K and above-band gap excitation with generation rates $G$ below ~10\textsuperscript{19} cm\textsuperscript{-3}s\textsuperscript{-1}. We assign it to nongeminate or distant-pair (DP) recombination. All these phenomena are very similar to those obtained in a-Si:H and a-Ge:H. Application of magnetic field on a-As:Se affects PL lifetime distribution in the same way as on a-Si:H, i.e. enhancement of the triplet-exciton component and weakening of the new component, which support the above explanation.

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1. Introduction

Photoluminescence (PL) study of amorphous semiconductors is important for scientific research on electronic gap-states and recombination mechanisms as well as for industrial applications. However, the PL mechanism itself continues to be debated in the amorphous semiconductors.

Quadrature frequency resolved spectroscopy (QFRS) measures PL lifetime distributions and thus gives more detailed information about the PL mechanism [1]. A double-peaked lifetime distribution was found by QFRS for a-Si:H [2,3]. This double-peak phenomenon cannot be explained by the generally accepted radiative tunneling (RT) model for PL [4]. Stachowitz et al. [5] proposed an exciton model to explain the double-peak lifetime distribution in which the short-lived component is attributed to radiative recombination of singlet excitons and the long-lived component, to triplet excitons. Using a specially developed dual phase and double lock-in (DPDL) QFRS for nanosecond lifetime resolution, we discovered at first the double-peaked lifetime distributions in amorphous As\textsubscript{2}S\textsubscript{3} and Se as well as a-Ge:H but a single peak for amorphous As\textsubscript{2}Se\textsubscript{3}, and invoked the exciton model [6-10].

Moreover the QFRS spectra are not really double-peaked, but triple-peaked with a third peak at $\tau_0 = 0.1 \sim 160$ s for PL in both a-Si:H and a-Ge:H under the germinate condition of photocarrier generation rate $G \leq 10^{19}$ cm\textsuperscript{-3}s\textsuperscript{-1} at low temperature [11]. Even well below the germinate condition, the third lifetime peak of $\tau_0$ increased continuously with decreasing $G$, which is one of

\textsuperscript{*} Corresponding author: aoki@ee.t-kougei.ac.jp
characteristic features of distant-pair (DP) or nongeminate recombination [12]. Deducing a quantum efficiency (QE) $\eta_0$ by deconvoluting the QFRS spectra, we demonstrated a sub-linear $G$-dependence of the metastable PL carrier density $n_G = \eta_0 G\tau_0$ as well as its temperature ($T$) dependence in agreement with the light-induced spin density (LESR) results in a-Si:H [11, 13-16]. Thereby we have solved these unsolved problems, i.e. discrepancies between metastable PL carrier density and LESR spin density against $G$ and $T$, and claimed that the DP or nongeminate recombination coexists with the geminate recombination even under the geminate condition.

However, it is still unclear whether the DP recombination coexists in chalcogenide amorphous semiconductors or not. Since chalcogenide glasses are prototype amorphous semiconductors and are closer to structural equilibrium than the tetrahedral amorphous semiconductors. These materials are therefore worth studying to determine whether the PL mechanisms are universal in both the amorphous semiconductors or not, namely whether chalcogenide glasses exhibit similar coexistence of the geminate and nongeminate (DP) recombination processes. This report describes first QFRS observation on such coexistence of excitonic and DP recombination in amorphous As$_2$Se$_3$, As$_2$S$_3$ and Se.

2. Experimental

Films of a-As$_2$Se$_3$ with a thickness of $= 2 \mu$m were prepared by evaporation onto Al substrates followed by annealing at 160 °C for 2 hrs in vacuum. High-purity (99.9999%) bulk g-As$_2$S$_3$ was purchased from Furuchi Chemical Co. and polished on felt with 0.3 µm diamond powder down to a thickness of 0.7 ~ 0.9 mm. Films of a-Se were evaporated onto roughed Al substrates to a thickness of $= 7 \mu$m. The shortest lifetime measured by the DPDL-QFRS technique was 2 ns [8]. Moreover using a digital lock-in amplifier having a low frequency limit of 1mHz in internal reference mode in order to eliminate phase jitter, we expanded the longest limit of lifetime up to 160 s, and moreover the digital-synchronous-filtering function of the lock-in amplifier was adopted in order to reduce noise without wasting a time due to large time-constant for frequency of $\sim 1$ mHz [11].

All the PL experiments were conducted at 3.7 K using low-noise, stabilized semiconductor [640 nm (1.94 eV)], [408 nm (3.04 eV)] and YAG [532 nm (2.33 eV)] lasers. Table 1 presents absorption coefficients $\alpha$ at the three laser photon energies $E_X$, optical bandgap-energies $E_{ex}$ corresponding to $\alpha = 10^4$cm$^{-1}$ and Stokes shift-energies $2W$ for the three chalcogenide glasses, being the same as those of the previous paper [10] except for the coefficients $\alpha$ at 3.04 eV and 4 K deduced by extrapolating the data of Ref.[17-19], and electron-hole (e-h) exchange energies $E_{ex}$ obtained in the previous and present works [10].

A 10 cm grating monochromator with a resolution of $\sim 30$ meV and f/3.0 was placed in the optical path between a sample and the PL detector [Hamamatsu 5509-72 infrared photomultiplier (PMT) having the long-wave length of 1700 nm (0.73 eV)] for dispersed PL QFRS. Spectrally integrated PL in the range from 0.73 to 1.59 eV was detected in f/1.0 optics by the PMT with a 780 nm long-pass filter. Magnetic field effect on the PL lifetime distribution of a-As$_2$Se$_3$ film was investigated by photoexciting the film from back side of a glass substrate and using fiber optics in order to avoid magnetic field disturbance on the PMT.

3. Results and discussion

3.1. a-As$_2$Se$_3$

Chalcogenide glasses exhibit significant PL fatigue [20]; as an example, spectrally integrated PL intensity of a-As$_2$Se$_3$ film during steady state excitations by a 1.94 eV laser light at 3.7 K is shown in Fig.1 as a function of time with various generation rate $G$. Even if $G$ is $10^6$cm$^{-3}$s$^{-1}$ at the sub-band gap excitation of 1.94 eV well below the geminate recombination condition being
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G ≤ 10^{19} \text{cm}^{-3}\text{s}^{-1} for a-Si:H and a-Ge:H [6,14]. PL intensity of a-As_2Se_3 is reduced to ~ 60% of the initial value after ~10 hour irradiation. Hence the QFRS spectra were obtained by selecting the longest limit of lifetime distribution suitable for G, so as to limit the PL degradation within 30%. Since the PL fatigue occurred at 3.7 K is recovered at room temperature, every QFRS measurement was made with restoring a sample to room temperature before each run.

Fig. 1. PL decay of a-As_2Se_3 film during a steady state excitation $E_x = 1.94$ eV at 3.7 K with various generation rates $G$: (1) $G \approx 1.2 \times 10^{13}$ cm$^{-3}$s$^{-1}$, (2) $1.2 \times 10^{14}$, (3) $1.2 \times 10^{16}$, (4) $1.2 \times 10^{17}$, (5) $1.2 \times 10^{18}$, (6) $1.2 \times 10^{19}$, (7) $1.2 \times 10^{20}$, (8) $5.9 \times 10^{20}$.

Fig. 2. QFRS spectra of a-As_2Se_3 film excited at $E_x = 1.94, 2.33$ and 3.04 eV at 3.7 K with $G \approx 10^{16}$ cm$^{-3}$s$^{-1}$ (–•–•–), $10^{17}$ (–□–□–) and $10^{18}$ (– ○–○–). All the peaks at $\tau_T$ are normalized to unity. Inset: enlarged QFRS signals in the range from 10^{-2} to 2 s for the three $G$ at $E_x = 1.94$ eV.

Fig. 2 shows the QFRS spectra for three different $G$ of $10^{16}$, $10^{17}$ and $10^{18}$ cm$^{-3}$s$^{-1}$ for the three PL excitation energies $E_x = 1.94, 2.33$ and 3.04 eV; here all the peaks at $\tau_T$ are normalized to unity. Since a-As_2Se_3 does not possess singlet-exciton state as previously reported, the QFRS spectra
are single-peaked at $\tau_T$, being attributed to triplet exciton [10]. However we can identify conspicuous shoulders around at a lifetime $\tau_0$ longer than $10^{-2}$ s. Although these are recognizable in the previous paper [10], the Fig. 2 taken by the internal reference mode QFRS gives more prominent features. The high PL excitation energy $E_X = 3.04$ eV remarkably enhances the shoulders and a decrease of $G$ enlarges them at all $E_X$; the inset of Fig. 2 indicates a faint lifting of the skirts in the longer lifetime region $\geq 10^{-3}$ s even at the sub-band gap excitation $E_X = 1.94$ eV (Table 1).

Table 1. Optical bandgap-energy $E_{0\alpha}$ corresponding to absorption coefficient $\alpha = 10^\alpha$ cm$^{-1}$ at $\approx 4K$, absorption coefficients $\alpha$ at $E_X = 1.94, 2.33$ and $3.04$ eV at $\approx 4K$, Stokes shifts $2W$ and e-h exchange energy $E_{ex}$ for chalcogenide glasses a-As$_2$Se$_3$, g-As$_2$S$_3$ and a-Se at $\approx 4K$. The data are the same as those of Ref. [10] except for $\alpha$ at $3.04$ eV extrapolated from the data of Refs. [17-19] and $E_{ex}$ obtained at Ref. [10] and this work.

<table>
<thead>
<tr>
<th>$E_{0\alpha}$ (eV)</th>
<th>$\alpha$ (cm$^{-1}$) at 1.94 eV</th>
<th>$\alpha$ (cm$^{-1}$) at 2.33 eV</th>
<th>$\alpha$ (cm$^{-1}$) at 3.04 eV</th>
<th>$2W$ (eV)</th>
<th>$E_{ex}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-As$_2$Se$_3$</td>
<td>2.0 2.8$\times10^3$ 7.0$\times10^4$ 4.0$\times10^5$</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g-As$_2$S$_3$</td>
<td>2.7 2.0$\times10^3$ 2.7$\times10^4$ 9.0$\times10^4$</td>
<td>1.2</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-Se</td>
<td>2.2 2.0$\times10^3$ 3.0$\times10^4$ 3.8$\times10^5$</td>
<td>1.3</td>
<td>0.16</td>
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</tr>
</tbody>
</table>

Fig. 3. QFRS spectra of PL fatigued a-As$_2$Se$_3$ film excited at $E_X = 1.94$ and $2.33$ eV at $3.7$ K with $G \approx 10^{17}$ cm$^{-3}$s$^{-1}$ (\textendash\textemdash) and $10^{18}$ (\textendash\textendash\textendash). All the peaks at $\tau_T$ are normalized to unity. Inset: enlarged QFRS signals in the range from $5\times10^{-3}$ to $5$ s for the two $G$ at $E_X = 1.94$ eV and $2.33$ eV.

The DP or nongeminate recombination predicts that at $E_X$ well above the mobility edge, a photoexcited e-h pair tends to diffuse apart rather than form a geminate pair or exciton during thermalization and occupy separate localized states. Furthermore a decrease of $G$ increases a separation $R$ between a nongeminate e-h pair, which extend the radiative tunneling (RT)
recombination lifetime given by $\tau = \tau_0 \exp(2R/a)$ where $\tau_0$ and $a$ are radiative dipole transition time $\sim 10^{-8}$s and localization length, respectively. Therefore the higher PL excitation energy $E_X$ and the lower generation rate $G$ enhance the DP recombination. After all, the dependence of shoulders on $E_X$ and $G$ suggests the existence of DP or nongeminate recombination in a-As$_2$Se$_3$, although the third peak is rather unclear compared with a-Si:H [11].

The QFRS spectra in the fatigued a-As$_2$Se$_3$ film at $E_X = 1.94$ and 2.33 eV, of which total PL intensity was degraded to $\sim$ 40 % of its initial value, are shown in Fig.3 with all the peaks at $\tau_T$ normalized to unity. The DP component is remarkably reduced for $E_X = 2.33$ eV compared with the $\tau_T$ component, and neither the higher $E_X$ nor a decrease of $G$ raises shoulders so much. This is presumably due to an occurrence of another competing recombination process; a considerable part of distant e-h pairs recombine nonradiatively through light-induced defects and reminders of the DPs recombine through the RT recombination [21].

![Fig. 4](image)

**Fig. 4.** QFRS spectra of a-As$_2$Se$_3$ film for $G \approx 6.5 \times 10^{17}$ cm$^3$s$^{-1}$ at $E_X = 2.33$ eV and 3.7 K, with ($\cdots$) and without ($\cdots$) magnetic field of 0.9 T.

Fig. 4 demonstrates an external magnetic field effect on the PL lifetime distribution of a-As$_2$Se$_3$ at $E_X = 2.33$ eV and 3.7 K. Application of a 0.9 T magnetic field weakens the QFRS signal of the $\tau_D$ component and enhances that of the $\tau_T$ component. Similar effects were observed in a-Si:H, in which the short-lived $\tau_S$ component was independent of magnetic field [22].

Based on the transient PL, Robins and Kastner [23] observed an enhancement of triplet exciton recombination and a decrease of the recombination at time longer than $2 \times 10^{-3}$s for amorphous As$_2$Se$_3$ under a magnetic field. Following them, the results shown in Fig.4 are explained in terms of an excitonic model for the $\tau_T$ components. The three-fold degeneracy of the triplet exciton with a total spin of unity ($S = 1$) is lifted by anisotropic spin-spin interaction and spin-orbit interaction, causing a zero-field splitting in the absence of an external magnetic field. Each of the three eigenstates couples differently with the excited singlet states, allowing relaxation to the singlet ground state on lifetimes specific to each state. Furthermore, Zeeman interaction with the magnetic field mixes the zero-field eigenstates and further separates their energies, thereby changing the lifetime of the triplet exciton. Thus, the enhancement of the $\tau_T$ component under a magnetic field is due to the involvement of triplet exciton recombination in a-As$_2$Se$_3$. A total spin of zero ($S = 0$) of the singlet exciton is responsible for the absence of magnetic field effect on the short-lived $\tau_S$ (singlet exciton) component in a-Si:H as the total spin of $S = 0$ is unaffected by the application of a magnetic field [22].

In the absence of an external magnetic field, the spin directions of distant e-h pairs are completely random, that is, spin polarization is zero because of the lack of correlation in the DPs, where the total spin $S$ is not a good quantum number. When a magnetic field is applied, the spins of
the DP carriers will have finite polarization; spin orientations with magnetic moments along the field are more probable than those opposed to the field [24]. Then, as the spin-aligned state energetically favoured under the magnetic field is spin-forbidden to recombine, the recombination rate will decrease. On the contrary, the formation of a pair in an anti-parallel spin-allowed state is slightly prevented by the magnetic field. Overall, the DP recombination rate will be reduced by the paramagnetism of e-h pairs in the external magnetic field, resulting in the weakening of the shoulder i.e., the $\tau_0$ component seen in Fig. 4.

### 3.2. g-As$_2$S$_3$

Fig. 5 demonstrates QFRS spectra of g-As$_2$S$_3$ excited at 2.33 eV for various temperatures $T$ from 3.7 to 100 K. Here we can see that the long-lived $\tau_T$ component is much larger than the short-lived $\tau_S$ component in contrast to the previous result at 3.7 K and rather the spectrum at 75 K resembles to the previous paper [10]; this is presumably due to insufficiently cooling the sample of which thermal contact to the cold finger was incomplete in the previous experiment. The QFRS spectra are double-peaked and an increase of $T$ enhances the $\tau_S$ component in comparison with the $\tau_T$ component while total QE decreases. This suggests that the short-lived $\tau_S$ component lies in energetically higher states and an increase of $T$ populates the energetically higher state but decreases QE due to nonradiative recombination or thermal quenching. The DPDL-QFRS spectrum of g-As$_2$S$_3$ at 3.7K exhibits a very similar double-peaked structure as that of a-Si:H, while the peak lifetime of $\tau_S \approx 11$ ns in g-As$_2$S$_3$ is very much shorter than that ($\sim \mu s$) in a-Si:H.

![QFRS spectra of g-As$_2$S$_3$](image)

**Fig. 5.** QFRS spectra of g-As$_2$S$_3$ for $G \approx 10^{16}$ cm$^{-3}$s$^{-1}$ and $E_x = 2.33$ eV at various temperatures $T$.

The PL spectra obtained for the quadrature component for 16 kHz corresponding the lifetime $\tau_T = 10$ ms and for 14 MHz corresponding to $\tau_S = 11$ ns are shown in Fig. 6. The PL peak energy associated with the $\tau_S$ component falls at a photon energy = 100 meV higher than that for the $\tau_T$ component. Since the lifetime of $\tau_S = 11$ ns is close to a typical fluorescence lifetime, we confidently assign the $\tau_S$ component to singlet exciton with the e-h exchange energy $E_{ex} = 100$ meV. Note that $E_{ex}$ for g-As$_2$S$_3$ is smaller than that ($\approx 160$ meV) for a-Se [10]. This can be due to the larger Stokes shift $2W$ of a-Se (see Table 1).
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Fig. 6. QFRS spectra of g-As$_2$S$_3$ at 16 kHz corresponding $\tau_T = 10$ ms (●) and at 14 MHz corresponding $\tau_S = 11$ ns (—) with $G \approx 10^{17}$ cm$^3$s$^{-1}$ at $E_x = 2.33$ eV. Peaks are normalized to unity.

Fig. 7(a) presents QFRS spectra of g-As$_2$S$_3$ for two different $G$ of $\sim 10^{17}$ and $10^{18}$ cm$^3$s$^{-1}$ for two $E_x$ of 2.33 and 3.04 eV at 3.7 K with all the peaks at $\tau_T$ normalized to unity. The high PL excitation energy $E_x = 3.04$ eV lifts the skirt at long lifetime side. The effect is enhanced for smaller $G$ of $\sim 10^{17}$ cm$^3$s$^{-1}$ at 3.04 eV but not at a sub-band gap excitation of 2.23 eV (Table I). Thus these results indicate an occurrence of the DP recombination in g-As$_2$S$_3$ similarly as in a-As$_2$Se$_3$. Figure 7(b) shows the normalized QFRS spectra at $E_x = 3.04$ eV and 3.7 K before and after PL fatigue. The DP component is decreased compared with the $\tau_T$ component when the total PL intensity is degraded to $\sim 40$ % of the initial value by 3.04 eV laser-light irradiation. This is caused by light-induced defects as in a-As$_2$Se$_3$.

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**Fig. 7.** (a) QFRS spectra of a-As$_2$S$_3$ film excited at $E_x = 2.33$ and 3.04 eV at 3.7 K with $G \approx 10^{17}$ cm$^3$s$^{-1}$ (●) and $10^{18}$ (—). Peaks at $\tau_T$ are normalized to unity. (b) QFRS spectra of a-As$_2$S$_3$ film at $E_x = 3.04$ eV and 3.7 K with $G \approx 10^{17}$ cm$^3$s$^{-1}$ before (—) and after (●) PL fatigue. Peaks at $\tau_T$ are normalized to unity.
3.3 a-Se

Figs. 8(a) and (b) demonstrate QFRS spectra of a-Se excited at 2.33 and 3.04 eV, respectively; all the data were taken at 3.7 K and normalized by $G$ of $-1 \times 10^{16}$, $-1 \times 10^{17}$ and $-1 \times 10^{18}$ cm$^3$s$^{-1}$ for $E_X = 2.33$ eV (Fig. 8(a)), and by $G$ of $-1 \times 10^{15}$, $-2 \times 10^{18}$, $-5 \times 10^{18}$ and $-1 \times 10^{19}$ cm$^3$s$^{-1}$ for $E_X = 3.04$ eV, respectively (Fig. 8(b)). The short-lived $\tau_S$ (singlet exciton) component in previous paper is beyond the scope in these figures, due to the shortest lifetime of QFRS in the internal reference mode $\sim 1.6 \mu$s.

Fig.8. (a) QFRS spectra of a-Se film at $E_X = 2.33$ eV and 3.7 K normalized by $G \approx 10^{16}$ cm$^3$s$^{-1}$ (---), $10^{17}$ (----) and $10^{18}$ (-----). (b) QFRS spectra of a-Se film at $E_X = 3.04$ eV and 3.7 K normalized by $G \approx 1 \times 10^{18}$ cm$^3$s$^{-1}$ (-----), $2 \times 10^{18}$ (-----), $5 \times 10^{18}$ (-----), $1 \times 10^{19}$ (-----).

In this material, however, we can clearly recognize the third peak at a lifetime $\tau_D$ for $G = 1 \times 10^{16}$ cm$^3$s$^{-1}$ at $E_X = 2.33$ eV (Fig. 8(a)), and for $G = 1 \times 10^{15}$ cm$^3$s$^{-1}$ and $G = 2 \times 10^{18}$ cm$^3$s$^{-1}$ at 3.04 eV (Fig. 8(b)). The third peak is more pronounced at the higher $E_X$. When $G$ is decreased, it grows and shifts to longer lifetime as observed in a-Si:H and a-Ge:H [11]. Therefore, among the three chalcogenide amorphous semiconductors, occurrence of the DP recombination in the a-Se film at low $T$ and low $G$ is most prominent and most analogous to that of the tetrahedral amorphous semiconductors.

4. Conclusions

In the amorphous semiconductors, a-As$_2$Se$_3$, g-As$_2$Se$_3$, and a-Se, we have discovered the new $\tau_0$ component in longer part of lifetime distributions besides the previously observed geminate or excitonic $\tau_g$ and $\tau_e$ components; a-Se film, in particular, exhibits a distinct third peak as observed in QFRS spectra of the tetrahedral amorphous semiconductors. We assigned it to the distant-pair or nongeminate recombination on the basis of its dependence on PL excitation energy $E_X$ and generation rate $G$. PL fatigue reduced the $\tau_0$ component pronouncedly compared with the exciton
component, due to another recombination path induced by light irradiation. Application of a 0.9 T magnetic field on a-As$_2$Se$_3$ film strengthened the triplet-exciton $\tau_1$ component but weakened the $\tau_0$ component, which we explained by spin effect on triplet exciton and paramagnetism of electron and hole DPs in the same way as for a-Si:H. Thus the PL mechanisms at low $T$ and low $G$ are universal among chalcogenide- and tetrahedral-amorphous semiconductors.

In addition, an elevated temperature enhanced the singlet-exciton $\tau_5$ component in QFRS spectra of a-As$_2$S$_3$, while weakening total QE. Hence an electron-hole exchange energy of $E_{ex} = 100$ meV was determined for excitons in a-As$_2$S$_3$ from the PL spectra at the two frequencies corresponding to the lifetimes $\tau_5$ and $\tau_1$.

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