Photoluminescence lifetime distributions of chalcogenide glasses obtained by wide-band frequency resolved spectroscopy

T. Aoki a,*, S. Komedaori a, S. Kobayashi a, T. Shimizu a, A. Ganjoo b, K. Shimakawa b

a Department of Electronics and Computer Engineering & Joint Research Center of High-Technology, Tokyo Institute of Polytechnics, Atsugi 243-0297, Japan
b Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan

Abstract

Photoluminescence (PL) lifetime distributions for amorphous arsenic chalcogenides g-As2Se3 and g-As2S3, and amorphous selenium a-Se, are obtained for the first time using a quadrature frequency resolved spectroscopy (QFRS) technique modified for nanosecond resolution. The g-As2S3 and a-Se chalcogenides exhibit double-peak lifetime distributions, whereas the lifetime distribution of g-As2Se3 peaks uniquely at around $10^{-4}$ s, which is consistent with earlier results. PL fatigue is found to reduce the intensity of PL but not affect the observed PL lifetimes. A self-trapped exciton model is adopted to explain the experimental results, providing reasonable mechanisms for the two-component lifetimes and associated phenomena. For a-Se, singlet–triplet exchange energy of $\approx 160$ meV is estimated.

PACS: 61.43.Dq; 78.55.Ap; 71.35.Gg

1. Introduction

Photoluminescence (PL) measurements are useful for investigating electronic gap-states and recombination processes in amorphous semiconductors. However, the PL mechanism itself continues to be debated. To clarify the PL mechanism in more detail, PL lifetime distributions have been measured by time resolved spectroscopy (TRS) and quadrature frequency resolved spectroscopy (QFRS). QFRS is superior to TRS because TRS requires intense light pulses to achieve a sufficient signal-to-noise ratio, which in many cases breaks the geminate recombination conditions. PL lifetimes were first studied by QFRS for a-Si:H, which was found to have a bimodal lifetime distribution [1,2]. This double-peak phenomenon cannot be explained by the generally accepted radiation tunneling (RT) model for PL [3]. Stachowitsch et al. [4] proposed an exciton model to explain this double-peak lifetime distribution in which the short-lived component is attributed to radiative recombination.
of singlet excitons, and the long-lived component is assigned to triplet excitons. The present authors also discovered this PL double-peak for a-Ge:H by QFRS [5]. However, the short lifetime of around $10^{-6}$ s observed for both a-Si:H and a-Ge:H is inconsistent with the singlet-exciton lifetime of $10^{-9}$ to $10^{-8}$ s in usual fluorescence. As a further detailed investigation, the authors recorded the PL lifetimes of these materials with nanosecond resolution using a specially developed dual phase, double lock-in (DPDL) wide-band QFRS technique, and confirmed that the PL lifetime distribution is bimodal with peaks at $\sim 10^{-6}$ and $\sim 10^{-3}$ s [6]. Chalcogenide glasses are prototype amorphous semiconductors and are closer to structural equilibrium than tetrahedral amorphous semiconductors. These materials are therefore worth studying to determine whether chalcogenide glasses exhibit a similar double-peak lifetime distribution in spite of the earlier reports for the lifetime distributions obtained by TRS in some chalcogenides, since QFRS can guarantee the geminate conditions and record an approximate lifetime distribution without tedious deconvolution. This report describes the technique developed to record PL lifetimes on the nanosecond scale by QFRS (wide-band DPDL-QFRS) and the implications of the lifetime distributions obtained for g-As$_2$Se$_3$, g-As$_2$S$_3$ and a-Se.

2. Experimental

High-purity (99.9999%) bulk g-As$_2$Se$_3$ and g-As$_2$S$_3$ were purchased from Furuuchi Chemical and polished on felt with 1-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 about 7 μm. Films of a-As$_2$Se$_3$ were also made by evaporation onto Al substrates followed by annealing at 160 °C for 2 h in vacuum. The PL lifetime distribution was measured by the wide-band DPDL-QFRS system developed by the present authors with a PL lifetime resolution of 0.3 ns [6]. The resolution was confirmed using a $10^{-6}$ mol/l aqueous solution of Rhodamine 6G, which has a fluorescence lifetime of 4 ns [7]. All the PL experiments were conducted at 4.3 K using a low-noise, stabilized semiconductor [640 nm (1.94 eV)] and YAG [532 nm, 2.33 eV] lasers. A 10 cm-diameter f/3.0 monochromator with resolution of ~30 meV was placed in the optical path between the sample and the PL detector (photomultiplier) for dispersed PL. As these chalcogenide glasses exhibit remarkable PL fatigue as a result of PL excitation during QFRS measurements in the lifetime range of ns to 0.1 s [8], the excitation intensity was maintained at a sufficiently low level to limit PL degradation to 15% at the expense of a higher signal-to-noise ratio. In particular, QFRS measurements prior to PL fatigue were made at a generation rate of $G \leq 10^{18}$ cm$^{-3}$s$^{-1}$ so as to preserve the geminate conditions.

3. Results

The PL lifetime distribution of g-As$_2$Se$_3$ excited by 1.94 eV light is shown in Fig. 1(a), normalized with respect to the generation rate $G$. This sample exhibits a single lifetime peak at $\sim 4 \times 10^{-5}$ s, and this distribution was also observed for the evaporated films of a-As$_2$Se$_3$. The figure also shows the lifetime distribution of PL fatigue under 1.94 eV irradiation at 6.7 mW/cm$^2$ for 60 min. The distribution is similar, with a total PL intensity decrease of 75%. When excited at 2.33 eV, the lifetime distribution the peak lifetime shifted to $\sim 7 \times 10^{-5}$ s both before and after PL fatigue. The total PL intensity decrease due to fatigue under 2.33 eV irradiation at 3.5 mW/cm$^2$ for 5 min was 80% (Fig. 1(b)).

The double-peak PL lifetime distribution of a-As$_2$S$_3$ excited at 1.94 eV is presented in Fig. 2(a). The distribution consists of a weak short-lived of $\sim 3 \times 10^{-9}$ s and a long-lived component of $\sim 10^{-4}$ s. The ratio of short-lived to long-lived component $\sim 0.15$ was obtained from the deconvolution mentioned earlier [6]. When the a-As$_2$S$_3$ sample was excited at 2.33 eV, the shape of the lifetime distribution changed with an enhanced short-lived component and a much weaker long-lived component but the two peaks did not shift (Fig. 2(b)); the ratio of short-lived to long-lived component significantly increased to 1.6. The PL lifetime distribution of g-As$_2$S$_3$ fatigued under 2.33 eV irradiation at 13 mW/cm$^2$ for 40 min remained...
unchanged except for a 75% decrease in PL intensity.

The PL lifetime distribution of a-Se excited at 1.94 eV, as shown in Fig. 3(a), includes two peaks, at \( \sim 2 \times 10^{-7} \) and \( \sim 6 \times 10^{-4} \) s with the ratio of short-lived to long-lived component of \( \sim 0.13 \). These peaks did not shift when the sample was fatigued under 1.94 eV irradiation at 3.9 mW/cm\(^2\) for 120 min, but the PL intensity decreased by 1/3. When photoexcited at 2.33 eV, the short-lived component became prominent at \( \sim 2 \times 10^{-7} \) s, and the long-lived component weakened and shifted to \( \sim 1 \times 10^{-4} \) s (Fig. 3(b)), where the ratio also increased to \( \sim 1.6 \). When fatigued at this irradiation energy at a dose of 9.6 mW/cm\(^2\) for 20 min, the PL intensity dropped by \( \sim 98\% \), although the features of the distribution did not change (Fig. 3(b)). In all experiments, only the PL intensity of the lifetime distributions obtained by total-light QFRS was affected by PL fatigue; other features such as peak positions were not affected.

The PL spectra obtained for the dc component, the quadrature component for 250 Hz corresponding to the long lifetime of 0.64 ms, and the quadrature component for 700 kHz corresponding to the short lifetime of 0.23 \( \mu \)s under 1.94 eV excitation at \( G \approx 1.1 \times 10^{17} \) cm\(^{-3}\)s\(^{-1}\) are shown in Fig. 4. Although the PL spectra could not be
obtained below 0.75 eV due to the long-wavelength cutoff of the photomultiplier (~1.7 μm), the PL peak associated with the short-lived component falls at a photon energy ~200 meV higher than that for the long-lived component.

4. Discussion

At first glance, the PL lifetime distributions of the three chalcogenide glasses appear to vary markedly. However, as is seen in Table 1, this is partly due to the different bandgap energies and absorption coefficients with respect to the PL excitation energies of 1.94 and 2.33 eV. As g-As2Se3 has an energy gap of ~2.0 eV at 4.3 K, carriers are excited near the bandgap at both 1.94 and 2.33 eV, giving rise to the single lifetime peak at ~4–7×10^{-5} s. This coincides with the TRS results for PL in g-As2Se3, in which PL is generally accepted to originate from triplet excitons [10,11]. The TRS of PL in crystalline As2Se3 has also revealed a single-peaked lifetime distribution centered at ~10^{-4} s, and optically detected magnetic resonance (ODMR) results have predicted a singlet–triplet exchange splitting of 1.8 eV, by which the singlet state merges into conduction band and the singlet excitonic emission is eliminated [12].

The PL lifetime distributions for g-As2S3 present well-defined double-peak structure with the short lifetime ~10^{-9} s and the long lifetime ~10^{-4} s for 1.94 and 2.33 eV excitations.

The long-lived component of ~10^{-4} s is attributed to the triplet exciton in agreement with a

---

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>𝐸₀ (eV)</th>
<th>𝑎(1.94 eV) (cm⁻¹)</th>
<th>𝑎(2.33 eV) (cm⁻¹)</th>
<th>2𝑊 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-As₂Se₃</td>
<td>2.0</td>
<td>2.8 × 10³</td>
<td>7.0 × 10⁴</td>
<td>0.9</td>
</tr>
<tr>
<td>g-As₂S₃</td>
<td>2.7</td>
<td>2.0 × 10⁻¹</td>
<td>2.7 × 10¹</td>
<td>1.2</td>
</tr>
<tr>
<td>a-Se</td>
<td>2.2</td>
<td>2.0 × 10⁻¹</td>
<td>3.0 × 10²</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig. 3. PL lifetime distributions for a-Se at 4.3 K, normalized by G: (a) excited 1.94 eV with G = 1.1 × 10^{15} cm⁻³ s⁻¹ (○) before and (●) after PL fatigue; (b) excited at 2.33 eV with (○) G = 4.2 × 10^{17} cm⁻³ s⁻¹ before PL fatigue and (●) G = 6.9 × 10^{19} cm⁻³ s⁻¹ after PL fatigue. PL fatigue is so large as to reduce PL intensity by one-two hundredths. Hence plots (●) are magnified by 100.

Fig. 4. PL spectra for dc (○), 250 Hz (long-lived) (●) and 700 kHz (short-lived) (×) components for a-Se excited at 1.94 eV with G = 1.1 × 10^{17} cm⁻³ s⁻¹.
report by Higashi and Kastner [13]. Those authors did not observe a nanosecond component, but Murayama et al. did observe a nanosecond decay in g-As$_2$S$_3$ by TRS [14]. The exciton model is therefore favorable as it offers a simple explanation of the bimodal lifetime distribution, attributing the short-lived component to a singlet exciton with a normal lifetime of $\sim 10^{-9}$ to $10^{-8}$ s and the long-lived component to triplet exciton [4]. The difference between the ratios of short- to long-lived component for g-As$_2$S$_3$ excited at 1.94 and 2.33 eV can be also favorably explained by the exciton model. As the singlet state is higher than the triplet state due to singlet–triplet exchange energy, the singlet states are more populated under photoexcitation at 2.33 eV or higher, thereby enhancing the short-lived component.

The PL lifetime distributions for a-Se also have well-defined bimodal structures (Fig. 3). However, the short lifetime is $\sim 10^{-7}$ s, which significantly exceeds the expected singlet-exciton PL lifetime of $\sim 10^{-9}$ to $10^{-8}$ s. This difference can be explained by introducing a self-trapped exciton into the model. The PL photon energy is lower than the excitation energy in amorphous semiconductors, known as Stokes shift, and generally lower still in chalcogenide glasses [15]. Photoexcitation generates an electron–hole pair in these materials, which turns into a self-trapped exciton with energy lower than the photon energy, giving rise to the Stokes shift. Electron is usually self-trapped in chalcogenides glasses, with a contracted electron orbit $a_E$ and hole is weakly bound to the self-trapped electron with orbit $a_H$ much larger than $a_E$. Thus, self-trapping introduces a Stokes shift and the discrepancy in the orbital sizes $a_E$ and $a_H$. The recombination rate of singlet excitons is consequently reduced by $(a_E/a_H)^3$ which gives a lifetime of the order of $10^{-7}$ to $10^{-6}$ s [16,17]. Selenium possesses smaller bandgap compared to g-As$_2$S$_3$ as is seen in Table 1, which results in larger hole orbit $a_H$. On the other hand the Stokes shift $\sim 1.3$ eV for PL in a-Se is rather large against the bandgap energy $E_g$ (Table 1). Street showed a proportionality of PL peak energy to $E_g$ for various chalcogenide glasses, but a-Se does not obey the same proportionality [18]. This large Stokes shift suggests deeper self-trapping of photoexcited electrons, resulting in smaller electron orbits $a_E$. Therefore the singlet recombination rate reduced by $(a_E/a_H)^3$ would then give $\sim 2 \times 10^{-7}$ s in contrast to that of g-As$_2$S$_3$ ($\sim 3 \times 10^{-9}$ s). Although PL in g-As$_2$S$_3$ exhibits the Stokes shift $\sim 1.2$ eV, a short lifetime is $\sim 3 \times 10^{-9}$ s close to normal singlet-exciton lifetime, which suggests that there is little appreciable difference between $a_E$ and $a_H$.

The short-lived component of a-Se remarkably increases compared with the long-lived one when excitation is changed from 1.94 to 2.33 eV similarly as g-As$_2$S$_3$. Here again, the singlet–triplet exchange energy is responsible for the ratio of the short- to long-lived component increased by $\sim 10$. This explanation is supported by the data in Fig. 4, which reveals that the PL spectrum for the short-lived component is $\sim 200$ meV higher than that for long-lived component. This energy difference is reasonably attributed to the exchange energy $E_X$ in a-Se. $E_X$ can obtained more precisely by assuming that the PL spectra of the two components are Gaussian functions shifted relatively by $E_X$. The spectrum of the short-lived component divided by that of the long-lived component gives a straight line with respect to photon energy on a semi-logarithmic scale as shown in Fig. 5. The slope $S$ of the line gives an $E_X$ of $\sigma_0 S/2 \log_{10} 2$, where $2\sigma_0$ is the full-width of half-maximum of the PL spectrum. Here, $2\sigma_0 \approx 0.36$ eV for a-Se, giving an $E_X$ of $\sim 160$ meV.

![Fig. 5. Plots of the ratio of short-lived to long-lived component as a function of photon energy $h\nu$ in semi-logarithmic scale for PL in a-Se excited at 1.94 eV.](image)
5. Conclusion

The DPDL-QFRS technique developed by the present authors, with nanosecond resolution in a geminate recombination regime, was used to obtain detailed PL lifetime distributions for the chalcogenide glasses g-As$_2$Se$_3$, g-As$_2$S$_3$ and a-Se. Double-peak lifetime distributions were observed for g-As$_2$S$_3$ and a-Se similar to those observed for a-Si:H and a-Ge:H. PL fatigue was found to have little effect on the lifetime distributions except for the PL magnitude. A self-trapped exciton model reasonably explains the two-component lifetime distribution and PL Stokes shift in these amorphous chalcogenides, with the short-lived and long-lived components attributed to singlet and triplet excitons, respectively. The enhancement of short-lived component in g-As$_2$S$_3$ and a-Se under higher energy excitation is interpreted as due to single-triplet exchange energy. The single-peak PL lifetime distribution for g-As$_2$Se$_3$ is explained as due to absence of a singlet exciton, similar to the case of c-As$_2$Se$_3$. The observed difference between the short lifetimes of g-As$_2$S$_3$ and a-Se is attributed to a difference between the orbital sizes for electrons and holes in the self-trapped exciton. Finally, an exchange energy of ~160 meV was determined for a-Se from lifetimes of the short- and long-lived PL components.

Acknowledgements

The authors thank the Japan Private School Promotion Foundation for financial aid. This work was also financially supported by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References