Screening of optical-phonon–hole interaction by photogenerated carriers in the layered semiconductor gallium selenide

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The time-resolved photoluminescence kinetics of GaSe has been measured at room temperature. The rise time of the spontaneous-emission band is within the response time of the picosecond laser pulse duration and streak camera ($\lesssim 20$ ps) when the photogenerated carrier density is below 5×10^{18} cm^{-3} and increases to a measurable value when the carrier density is above 5×10^{18} cm^{-3}. The increase in the rise time of the spontaneous-emission band arises from the screening of nonpolar optical-phonon emission from hot photogenerated carriers due to high photogenerated carrier density. On the other hand, the rise time of the stimulated-emission band is not time resolved with increasing picosecond laser pulse intensity.

INTRODUCTION

Gallium selenide is a layered semiconductor with interesting optical and electrical properties. The valence electrons of GaSe are strongly coupled to the lattice vibrations which are perpendicular to the layer plane.[1] In the previous report on the measurements of the time-resolved absorption spectroscopy,[2] we have observed the photogenerated hot carriers in GaSe relax to the bottoms of bands with the emission of nonpolar optical phonons $A_1^{(1)}$ ($=16.7$ meV). We found that the deformation potential between the holes and the nonpolar optical phonons $A_1^{(1)}$ is reduced by five times when the photogenerated carrier density reaches 10^{19} cm^{-3} as compared with the deformation potential at 3×10^{17} cm^{-3}. The reduction of the deformation potential was speculated in that report to be due to the screening effect of the phonon emissions from high density of photogenerated hot carriers.

In this Communication, we continue our research on GaSe and measure the time-resolved photoluminescence from GaSe excited by a picosecond laser pulse at room temperature. In the photoluminescence of GaSe at high picosecond laser pulse excitations, two emission bands were observed[3]: a spontaneous emission component with wavelength less than 640 nm and a stimulated emission component with wavelength longer than 640 nm at room temperature. The spontaneous emission arises from the exciton-carrier scattering emission at low excitation intensities and the electron-hole plasma emission at high excitation intensities. The Mott transition from the exciton state to the plasma state occurs at photogenerated carrier density of 3×10^{17} cm^{-3}. By measuring the rise time of photoluminescence subsequent to picosecond laser pulse excitation, we can support our speculation and measure the slowing of the photogenerated carriers. The rise time of the stimulated emission band is within our time resolution. However, the rise time of the spontaneous emission band is within our time resolution when the photogenerated carrier density is less than 5×10^{18} cm^{-3} and increases when the photogenerated carrier density is above 5×10^{18} cm^{-3}. This increase in rise time supports our previous speculation concerning the screening of hot carrier relaxation in highly photoexcited semiconductors and quantitatively fits the theory[4] of Yoffa.

EXPERIMENTAL SETUP

A second harmonic (527 nm) of Nd: glass laser pulse of 8-ps duration was used to excite a gallium selenide sample. The luminescence was collected by a Hamamatsu streak camera with 100-μm slit, analyzed by a temporal analyzer and a computer. It was necessary to use 100-μm slit in order to detect the luminescence which limits the time resolution to 20 ps. A narrow band filter at 620 nm was used to select the spontaneous emission and a Hoya R-64 filter was used to select the stimulated emission above 640 nm with Corning 3-67 filters. The excitation area on the sample is ~2.6 mm^2. The polarization of the incident light is normal to the c axis of GaSe. The optical transmission of GaSe was measured to be $\sim40\%$ of 700 nm which is less than the direct band-gap energy. This means that only 40% of the incident light intensity will be absorbed to create the electron-hole pairs. The optical-absorption constant at 530 nm is 2×10^3 cm^{-1} at room temperature.[5] The carrier densities generated optically at different excitation intensities were estimated using the above parameters.

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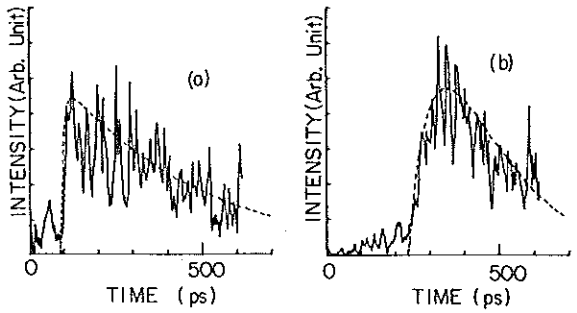

FIG. 1. Time-resolved photoluminescence of the spontaneous emission with $610 \leq \lambda \leq 630$ nm from GaSe excited by a picosecond laser pulse at room temperature. (a) $N = 4.8 \times 10^{18}$ cm^{-3}, $\tau_r \sim 10$ ps. (b) $N = 1.4 \times 10^{19}$ cm^{-3}, $\tau_r \sim 90$ ps.

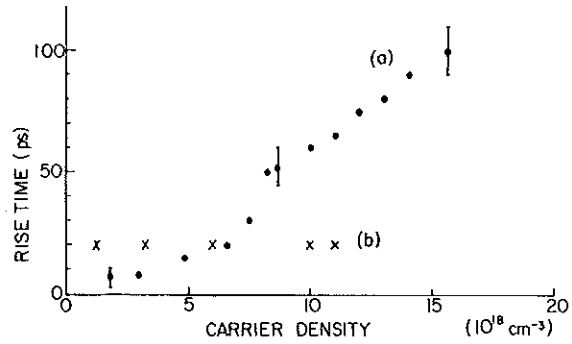

FIG. 3. Rise time of the (a) spontaneous emission (circles) and (b) stimulated emission (crosses) from GaSe at room temperature as a function of the photogenerated carrier density.

EXPERIMENTAL RESULTS

Time-resolved photoluminescence spectra for spontaneous emission component with wavelength of 610 to 630 nm from GaSe at room temperature is displayed in Fig. 1. We used $I(t) = A\,[\exp(-t/\tau_d) - \exp(-t/\tau_r)]$ to fit the profile of the time-resolved emission kinetics, where τ_d and τ_r are the decay and rise times of the emission, respectively. In Fig. 1(a), the rise and decay times are 10 and 400 ps, respectively, for the carrier density of $\sim 5 \times 10^{18}$ cm^{-3}. In Fig. 1(b), the rise and decay times are 90 and 150 ps, respectively, for the carrier density of 1.4×10^{19} cm^{-3}.

Time-resolved photoluminescence for stimulated emission component with wavelength longer than 640 nm from GaSe at room temperature is displayed in Fig. 2. In Fig. 2(a), the rise time is 20 ps, and the decay time is ~ 100 ps for carrier density of 6×10^{18} cm^{-3}. In Fig. 2(b), the rise time is ~ 20 ps, and the decay time is ~ 50 ps, for the photogenerated carrier density $\sim 1.0 \times 10^{19}$ cm^{13}.

The rise times at different photogenerated carrier densities for both spontaneous and stimulated emission are plotted in Fig. 3. The rise time of the spontaneous emission increases from within time resolution to 100 ps when the carrier density increases from $\sim 1.8 \times 10^{18}$ to $\sim 1.6 \times 10^{19}$ cm^{-3}. However, the rise time of the stimulated emission remains the same ≤ 20 ps from $\sim 1 \times 10^{18}$ to $\sim 1.1 \times 10^{19}$ cm^{-3}.

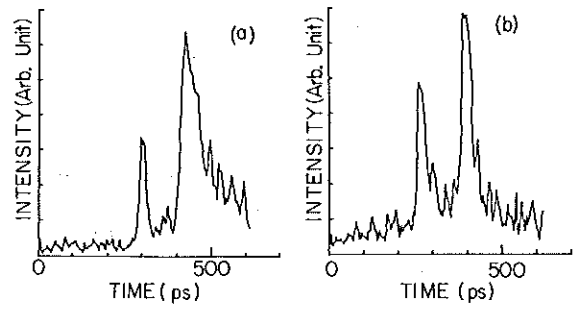

FIG. 2. Time-resolved photoluminescence of the stimulated emission with $\lambda \geq 640$ nm from GaSe excited by picosecond laser pulse at room temperature. (a) Photogenerated carrier density $N = 6.0 \times 10^{18}$ cm^{-3}, $\tau_r \leq 20$ ps; (b) $N = 1.0 \times 10^{19}$ cm^{-3}, $\tau_r \leq 20$ ps.

DISCUSSION

The spontaneous emission arises from electron-hole plasma[3] since the photogenerated carrier density from $\sim 1 \times 10^{18}$ to $\sim 1.6 \times 10^{19}$ cm^{-3} is greater than carrier density 3×10^{17} cm^{-3} for Mott transition. As shown in Fig. 3(a), the rise time of the spontaneous emission component from GaSe at room temperature remains within the time resolution of the excitation-detection system when the photogenerated carrier density is smaller than $\sim 5.0 \times 10^{18}$ cm^{-3} and increases when the photogenerated carrier density is larger than 5.0×10^{18} cm^{-3}. This increase of the rise time can be attributed to the screening of high density of photogenerated carriers on the relaxation of hot photogenerated carriers.

The dominant relaxation process of the hot photogenerated carriers in GaSe is the emission of nonpolar optical phonons $A_1^{\prime(1)}$ ($= 16.7$ meV) from the holes.[2] From the theory developed by Yoffa,[4] the emission rate ν of nonpolar optical phonons from hot carriers inside semiconductors is proportional to $[1 + (N/N_c)^2]^{-1}$, where N is the carrier density and N_c is the critical carrier density which is equal to

$$\frac{\epsilon_0 \hbar}{8\pi e^2}\left(\frac{2m_l^* \omega}{\hbar}\right)^{3/2}\left(\frac{1}{\beta m_l^*}\right)^{1/2}.$$

The emission rate ν remains constant when the carrier density N is much smaller than the critical carrier density N_c and decreases when the carrier density N is larger than N_c. In GaSe, ϵ_0, the static dielectric

constant, is 10.6 when the polarization of the incident light is normal to the c axis[6]; m_l^* is the effective mass of hole, which is $0.5m_0$ on the direct band gap[7]; e is the electronic charge which is 4.8×10^{-10} esu; $\hbar\omega$ is the $A_1^{(1)}$ phonon energy; $\beta\equiv1/kT_e$, and T_e is the carrier temperature. When the carrier temperature is higher, the value of N_c becomes larger. The critical density N_c is $\sim2\times10^{18}$ cm^{-3} when the electronic-hole temperature T_e is $\sim$400 K and N_c is $\sim4.8\times10^{18}$ cm^{-3} when $T_e\sim2000$ K. At the temperature decay rate[2] of 30 K/ps from time-resolved absorption kinetic measurements, the temperature will drop from 2000 to 400 K during the rise time of spontaneous photoluminescence of 60 ps for photogenerated carrier density $\sim10^{19}$ cm^{-3}. Eight to nine phonons are emitted by each hole. During the rising period of the time-resolved spontaneous emission, both the carrier temperature and density decrease. Since it is difficult to extract the carrier temperature and density simply from the time-resolved emission, we did not include the exact time rate of change into our fitting process. According to the Yoffa's theory, the emission rate of phonons from relaxing holes is

$$\nu\propto1/\{1+[N(t)/N_c(t)]^2\}\ .$$

Because N_c is proportional to the square root of carrier temperature, both $N(t)$ and $N_c(t)$ decrease monotonically with time. We believe that ν will be close to a constant during the relaxation process of holes. This can be seen in the Fig. 2 of Ref. 2, where the carrier temperature decreased at almost a constant rate ($\sim$30 K/ps). Since the change rate of carrier temperature is linearly proportional to the phonon emission rate ν from relaxing holes, ν will be close to a constant for a given $N(0)$. Therefore the inverse of the rise time of the spontaneous emission should be proportional to the emission rate ν of phonons from relaxing holes. The initial carrier density $N(0)$ was determined by the experimental parameters and the initial carrier temperature[2] was estimated to be $\sim$2000 K when the sample was irradiated by a 530-nm light. In Fig. 4, the inverse of the rise time at various carrier densities is plotted. The values of $\nu\propto1/[1+(N/N_c)^2]$ are also plotted for $N_c=4.8\times10^{18}$ cm^{-3} at $T_e=2000$ K. These values fit the experimental results well when the carrier density is above 5×10^{18} cm^{-3}. Until subpiscosecond work is performed with higher time accuracy, fitting the data to a more appropriate theoretical expression and taking into account of changing N_c with T_e is not warranty at this time.

The emission rate ν at 10^{19} cm^{-3} and $T_e=2000$ K is about $[1+(10^{19}/4.8\times10^{18})^2]^{-1}\simeq0.2$, or five times smaller than the unscreened value 1. From the time-resolved absorption spectroscopy of GaSe, we found the deformation potential between the holes and the nonpolar optical phonons is reduced five times[2] when the initial photogenerated carrier density

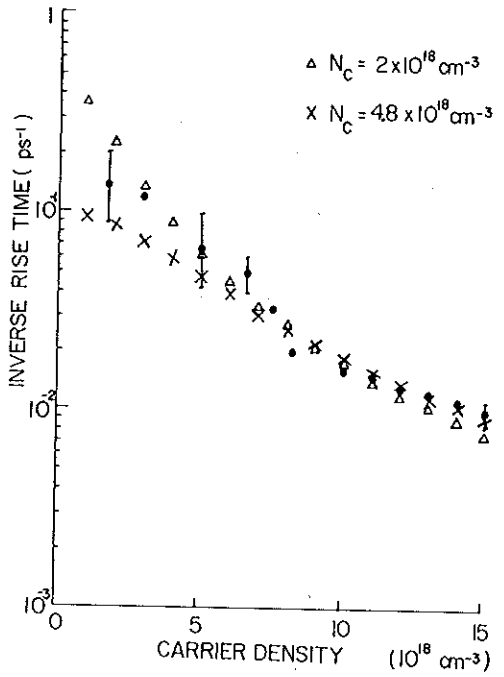

FIG. 4. The inverse of the rise time at various photogenerated carrier density (circles). The cross dots represent $\nu=A/[1+(N/N_c)^2]$ where $A=0.1$ and $N_c=4.8\times10^{18}$ cm^{-3}. The triangles represent ν, $A=0.45$ and $N_c=2\times10^{18}$ cm^{-3}.

is $\sim10^{19}$ cm^{-3}, and the energy of each pair of electron and hole decays at a rate proportional to the square of the deformation potential.[2] This energy decay rate would be about twenty-five times smaller than the unscreened value. Since the rise time is less than 20 ps which is the resolution of our measuring system when the carrier density is below 5×10^{18} cm^{-3}, it is impossible to know whether the inverse of rise time will increase above 0.1 ps^{-1}. It is therefore impossible to know experimentaly whether the emission rate ν at 10^{19} cm^{-3} will be twenty-five times smaller than the unscreened value. In Fig. 4, the values of $\nu\propto1/[1+(N/N_c)^2]$ are also plotted with $N_c=2\times10^{18}$ cm^{-3}. In this case, the value of ν at $N=10^{19}$ cm^{-3} would be twenty-five times smaller than the unscreened value. These values do not fit the experimental results as well as compared with that of $N_c=4.8\times10^{18}$ cm^{-3} above 1.5×10^{19} cm^{-3}. There may be three reasons to account for this difference of emission rate ν at 10^{19} cm^{-3}: one is that the carrier density of 10^{19} cm^{-3} and carrier temperature of 2000 K from time-resolved absorption spectroscopy measurements could be off from the exact values. The second reason is that this sample is a layered semiconductor, therefore the theory of Yoffa probably should be modified to account for this change to obtain a different value of N_c by a factor of 2. The third reason may be that the unscreened de-

formation potential is smaller than[8] 6.6 eV/Å by a factor of 2, therefore the emission rate is about five times smaller at photogenerated carrier density 10^{19} cm^{-3}.

As shown in Fig. 3(b), the rise time of the time-resolved stimulated emission remains within the time resolution of the laser pulse with increasing photogenerated carrier density. This implies that the rise time of the stimulated emission is extremely fast.

In conclusion, we measured the time-resolved photoluminescence kinetics of GaSe at room temperature. The rise time of the spontaneous emission is within the resolution of the laser pulse when the photogenerated carrier density is below 5×10^{18} cm^{-3} and increases above 5×10^{18} cm^{-3} in agreement with Yoffa's theory. The rise time of the stimulated emission remains within the resolution of the laser pulse with increasing photogenerated carrier density. One should extend these measurements and measure the phonon emission rate at lower carrier density using subpicosecond laser techniques. Furthermore, the subpicosecond absorption kinetic measurements should be extended as a function of photogenerated carrier density.

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