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Kojima, Osamu
Ito, Yukako
Kita, Takashi
Shim, Yong-Gu

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Electron transport in a silicon crystal observed by energy transfer luminescence

Osamu Kojima^{1*}, Yukako Ito¹, Takashi Kita¹, and Yong-Gu Shim²

¹*Department of Electrical and Electronic Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan*

²*Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*

Observation of electron diffusion in semiconductor crystals is considerably important to improve device performance. This study investigates electron diffusion based on the observation of luminescence from a cyanine thin film fabricated on a semiconductor substrate. When the backside of the substrate was excited by laser light, enlarged intensity profiles, 20 times larger than the laser spot, were observed. An analysis of the spatial enlargement suggests that the enlargement originated from electron diffusion. This method can be used for analyzing electron transport and contributes to the development of emission devices based on energy transfer.

1. Introduction

Electron transport based on the diffusion and drift is an essential issue that needs to be addressed to improve the efficiency of semiconductor devices. Various methods have been developed to analyze the transport process. For instance, observations of Bloch transport in miniband structures using luminescence from wide well,^{1–4)} time-of-flight methods,^{5,6)} a pump-probe technique,^{7–10)} and theoretical simulations^{11–20)} have been employed to obtain information about the vertical diffusion process. On the contrary, materials having a low oscillator strength make the observation of the transport via luminescence difficult because the signal intensity is dependent on oscillator strength. Moreover, electrical observation requires a p-n junction. The material combination is limited because the fabrication of the p-n junction in wide-gap materials is still not easy. Therefore, a new method is required to observe the electron diffusion process in various solid-state materials.

Recently, we reported the luminescence of a cyanine thin film on a silicon crystal due to energy transfer.²¹⁾ The electrons generated by laser light in the backside of the silicon substrate diffused through the crystal and excited the cyanine thin film via energy transfer in

*E-mail: kojima@phoenix.kobe-u.ac.jp

this report (See Fig. S1 in Supplementary File). Therefore, it becomes possible to observe the electron diffusion process in various materials, e.g., materials having issues associated with the fabrication of the p-n junction and those having a low oscillator strength. To discuss the possibility to use this result as the observation method of electron diffusion, the measurement using well-known material should be demonstrated. In this work, we demonstrate the electron diffusion process in a silicon crystal by observing the luminescence from a cyanine thin film. By exciting the backside of the silicon substrate, we obtained the image maps of the luminescence intensity of the cyanine thin film fabricated on the substrate surface. In comparison with the laser spot, the radius of observed luminescence is considerably large, by approximately 20 times. This radius depends on the excitation intensity; With an increase in the excitation intensity, the radius increases. The radius observed at the surface can be evaluated by considering the electron diffusion. The observed results were discussed based on electron diffusion in silicon.

2. Experimental methods

We used $C_{25}H_{25}IN_2S_2$ (DTTCI), a commercially available cyanine molecule, as the luminescence layer, which was an energy acceptor. Its chemical structure is shown in Fig. 1. A commercial-base p-type Si substrate having a nominal resistivity of $100 - 150 \Omega \cdot \text{cm}$, which acted as an energy donor, was polished to a thickness of approximately $300 \mu\text{m}$. In our trials, the luminescence from the thin film on the p-type substrate was approximately twice as large as that on the n-type substrate, which is the reason we used the p-type substrate. The resistivity corresponds to an impurity concentration of approximately 10^{14} cm^{-3} from the reference.²²⁾ As shown in Fig. 2(a), in which the dependence on the luminescence intensity due to energy transfer on the concentration plotted and the values were normalized by the lowest intensity, the intensity depends on the concentration, because of the impurity scattering. Therefore, in this work, the substrate mentioned above was used. The DTTCI thin film was fabricated on the (001)Si substrate using the layer-by-layer method.^{23–29)} The detail of the sample fabrication is available from the reference.²¹⁾ The thickness of the DTTCI thin film and the separation between the DTTCI film and the substrate were 6.7 nm and 6.0 nm, respectively, which were determined using a spectroscopic phase-modulated ellipsometer (HORIBA Jobin-Yvon UVISEL-TK9017TK).

To obtain the luminescence mapping, a continuous-wave-mode Ti:sapphire laser having a photon energy of 1.650 eV was used as the excitation light source. The luminescence was measured by a 35-cm single monochromator with 2.0-nm resolution; the monochromator was

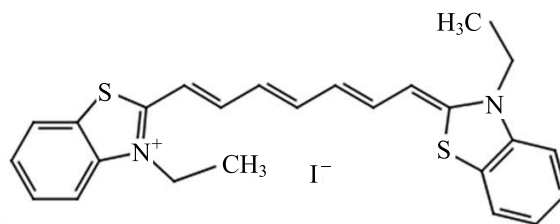


Fig. 1. Chemical structure of DTTCl.

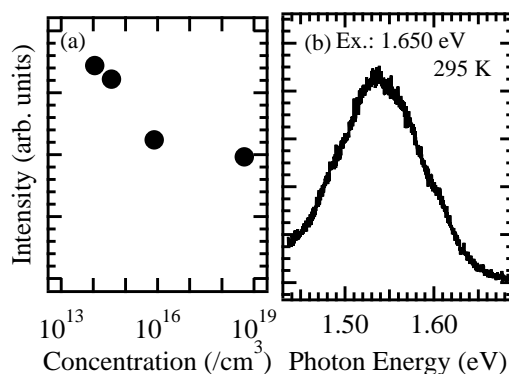


Fig. 2. (a) Normalized luminescence intensity due to energy transfer plotted as a function of impurity concentration. (b) Luminescence spectrum of DTTCl excited by energy transfer.

connected to a charge-coupled device. The laser spot diameter evaluated using a laser beam profiler was $22\ \mu\text{m}$. To measure the luminescence intensity map, the intensity was scanned using an optical fiber (core diameter: $230\ \mu\text{m}$). The scanning step was $100\ \mu\text{m}$. Figure 2(b) shows the luminescence spectrum of the cyanine thin film fabricated on the substrate, where the backside of the substrate was excited. It was confirmed by the excitation energy dependence of the luminescence intensity that the thin film was excited by the energy transfer from electrons inside the substrate.²¹⁾

3. Results and discussion

Figures 3(a)-3(c) show the image maps of peak intensities of the luminescence spectra measured at various excitation intensities. This luminescence was caused by that the electrons generated by light excitation of Si excite the DTTCl molecules through energy transfer during the relaxation process.²¹⁾ The luminescence intensity is indicated by the color bar. The

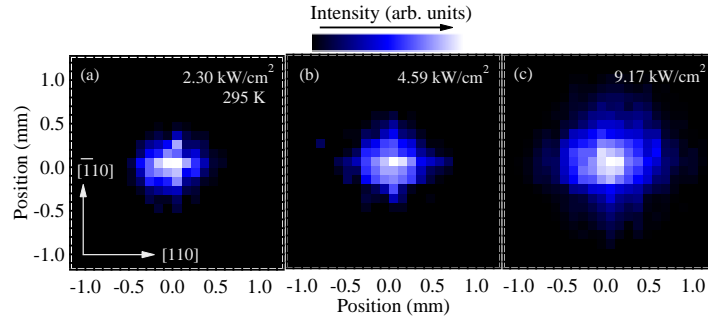


Fig. 3. Image maps of the luminescence intensity observed at various excitation intensities: (a) 2.30, (b) 4.59, and (c) 9.17 kW/cm². Measurements were performed at room temperature.

luminescence spectral waveform did not depend on the observation point.

The radius of the luminescence intensity on the sample surface was larger than the laser spot diameter of 22 μm and increased as the excitation intensity increased. Focusing on the shape of the image, the radii along the $[110]$ and $\bar{[110]}$ directions seem almost same for each image. The radius of the luminescence intensity can be explained based on electron diffusion. Figures 4(a) and 4(b) show the intensity profiles by open circles at the center positions of the image map of Fig. 3(c) along the $\bar{[110]}$ and $[110]$ directions, respectively. Moreover, the profiles along $[010]$ and $[100]$ are indicated in Figs. 4(c) and 4(d), respectively. Because the laser that excited the backside of the substrate has the Gaussian profile, the electron wave packet traveling through the substrate has the same profile. Therefore, it is reasonable to fit the intensity profiles in this analysis using the Gaussian function.

The fitting curves are indicated by dashed curves. The evaluated half-width-at-half-maximum (HWHM) values are listed in Table 1, which slightly varied with the direction. The value for the $[110]$ direction is larger than the others. We speculate the reason of this; the laser polarization affects the propagation. The laser polarization was along with the $[110]$ direction, and the traveling wave packet of carriers may maintain the polarization somewhat because the direction of the electron-hole pair depends on the laser polarization. Therefore, the direction of electric field of light may cause the elongation.

The diffusion dynamics of electrons is discussed based on these values. At first, the diffusion coefficient was estimated. The electron/hole diffusion coefficient is given as $D_{e/h} = \mu k_B T / e$, where μ is the electron/hole mobility, k_B is the Boltzmann constant, T is temperature, and e is the electron charge. In the case of p -type silicon having a doping concentration of 10^{14} cm^{-3} , the hole mobility can be estimated as $500 \text{ cm}^2/\text{V/s}$ from the reference.³⁰⁾ Therefore,

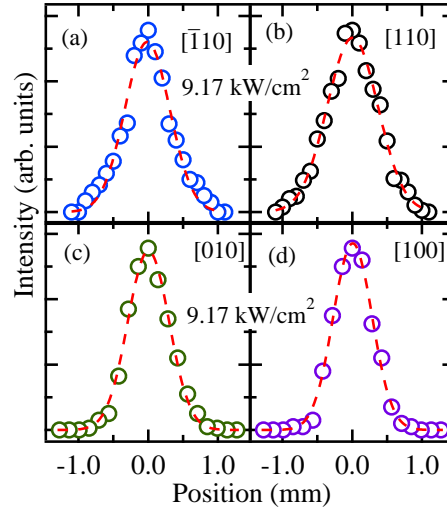


Fig. 4. Intensity profiles at the center positions along the directions (a) $\bar{1}10$, (b) 110 , (c) 010 , and (d) 100 in Fig. 3(c). The dashed curves demonstrate the fitting results.

Table I. Evaluated HWHM values at an excitation intensity of 9.17 kW/cm^2 .

Direction	HWHM (mm)
$\bar{1}10$	0.54 ± 0.04
110	0.60 ± 0.03
010	0.49 ± 0.02
100	0.47 ± 0.02

D_h in the substrate was $1.29 \times 10^{-3} \text{ m}^2/\text{s}$. Here, the electron diffuses faster than the holes and reaches the surface earlier. To obtain the luminescence, both of electron and hole are required. Therefore, we considered that the emission area is limited by the hole diffusion, and the coefficient for hole D_h is used in the discussion.

Next, carrier diffusion is generally described as $\exp(-x/\sqrt{D_{e/h}t})$, where x and t indicate the electron position from the surface and time, respectively. The minority carrier (electron) lifetime in the p -type silicon having a doping concentration of 10^{14} cm^{-3} was estimated as 0.1 ms at room temperature.³¹⁾ Therefore, the electrons can diffuse for $\sqrt{D_h \times 0.1 \times 10^{-3}} = 359 \text{ } \mu\text{m}$ before they vanished.

Here, we assumed that the electrons diffused concentrically, as shown in Fig. 5. Considering that the HWHM values correspond to in-plane diffusion lengths, it is possible to assume a diffusion length of 0.47 mm using a thickness of $300 \text{ } \mu\text{m}$, i.e. $\sqrt{0.300^2 + 0.359^2}$, where 0.359 is the diffusion length estimated above and is considered as the edge of the luminescence

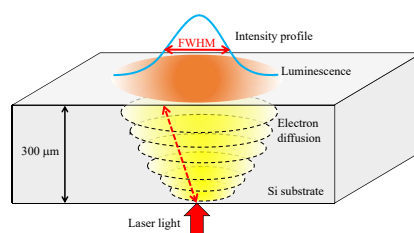


Fig. 5. Schematic showing electron diffusion.

circle. The value 0.47 mm is close to the HWHM values. Considering the coarse measurement step, this coincidence is sufficient to explain the intensity map originating from electron diffusion. The observed radius is larger than the laser profile originates from the wave packet spreading, as mentioned above. The laser profile was Gaussian form, and the luminescence profile was also Gaussian profile; during the diffusion, the Gaussian form was maintained, which supports that the radius enlargement results from the wave packet spreading. Therefore, in this discussion, the parameters for the [100] direction were considered.

The change in the radius with the excitation intensity shown in the image maps is related to the number of generated electrons. The intensity profiles measured by 4.59 and 2.30 kW/cm² were also analyzed (See Fig. S2 in Supplementary File) Although the diffusion coefficient was hardly changed by the excitation intensity, this result seems that the diffusion coefficient depended on the excitation intensity in Fig. 6.

Diffusion dynamics is discussed using the diffusion length, as mentioned above. The cross symbols in Fig. 6 indicate the average values at each excitation intensity. The diffusion lengths estimated using the averaged values mentioned above were 0.45, 0.50, and 0.60 mm at excitation intensities 2.30, 4.59, and 9.17 kW/cm², respectively. Considering the constant D_e and lifetime mentioned above, this dependence corresponds to the dependence of the number of electrons reaching at the surface on the excitation intensity. When the number of electrons increased, the number that the electrons reached the surface increased. This increase was observed as the enlargement of the radius of the intensity map. These results demonstrate that the electron diffused with spreading in-plane directions.

In summary, we observed electron diffusion in the silicon substrate via energy transfer to the cyanine thin films. When the laser light generated electrons at the backside of the substrate,

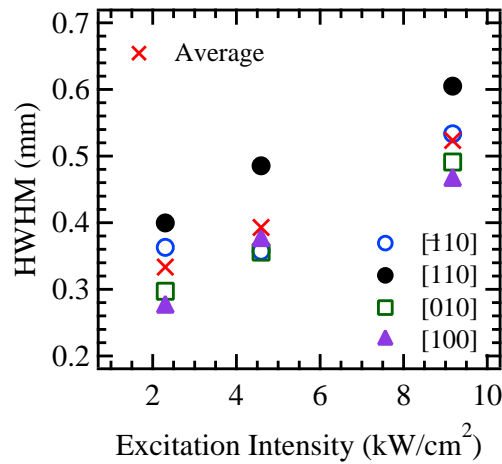


Fig. 6. Evaluated HWHM values from the intensity profiles shown in Fig. 3. The cross symbols indicate the average values at each excitation intensity.

the electrons diffused toward the surface and excited cyanine molecules in the thin film. The analysis of the intensity profile whose size depended on the excitation intensity showed the large electron diffusion in-plane direction. This method can be used for analyzing electron transport. Moreover, in our previous report, the efficiency of luminescence via energy transfer was as low as 10^{-10} . Therefore, the suppression of in-plane spread is the key factor to develop devices using energy transfer.

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