Picosecond Time-Resolved Linear Polarization Spectroscopy of the Blue-Green Photoluminescence in Vacuum-Annealed Porous Silicon

Norio AKIYAMA, Yoshiaki KIDO and Takahumi ASAHI

Department of Electronic Engineering,

Okayama University of Science,

Ridai-cho 1-1, Okayama 700-0005, Japan

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Abstract

The dynamics of the blue-green photoluminescence (bg-PL) from porous silicon film oxidized in ambient air after vacuum-annealing have been investigated in terms of excitation energy dependencies of bg-PL spectra and of linear polarization P, using picosecond time-resolved polarization spectroscopy under the cavity dumping method. The P depends on the difference between the excitation and PL energies (Stokes shift) and remains constant until 8 ns. The results are explained using a localized exciton model.

1. Introduction

In view of the possible applications of all-silicon-optical devices, it is important to explain the origin of visible photoluminescence (PL) from porous silicon (PSi). PL from PSi can be separated into two characteristic bands with a different PL energy and decay time τ[1-5]: One is a yellow-red PL (yr-PL) band with $\tau \sim 1 \mu$s and the other is a blue-green PL (bg-PL) band with $\tau \sim 10$ ns. For these two bands, many experimental results have been obtained and several models for the luminescence mechanism have been proposed[6]. A yr-PL is observed for as-anodized PSi[6], and the luminescence mechanism in yr-PL has been shown to be related to the hydrogenated nanocrystalline silicon and strongly localized states[7]. A bg-PL sample is usually prepared by rapid thermal oxidation (RTO) at high temperature[4]. In this case, a bg-PL is not immediately observed after oxidation and only appears after aging in ambient air[8]. However, the creation and luminescence mechanisms of bg-PL are not clear.

Recently, using polarization spectroscopy with pulse[1,5] and cw[9] lasers, it was found that bg-PL in PSi has a large linear polarization P, which is defined by $P = (I_{\|} - I_{\perp})/(I_{\|} + I_{\perp})$, where $I_{\|}$ and $I_{\perp}$ are the parallel and perpendicular components of the PL intensity with reference to the linear polarization of incident light, respectively[10].

Time-resolved polarization spectroscopy is a powerful tool for studying radiative and nonradiative relaxation dynamics of PL[11]. In particular, in the case of PL that has

both long and short lifetimes as like PSi, one can obtain accurate information of individual[5].

In this paper, we report that bg-PL is observed by oxidation in ambient air after vacuum-annealing, which plays an important role in hydrogen desorption from PSi. Moreover, using picosecond time-resolved polarization spectroscopy under the cavity dumping method, we report the dependence of time and the excitation photon energy E_{exc} for P of the bg-PL. To explain our experimental results, we propose a luminescence mechanism using a localized exciton model and Si nanostructure.

2. Experimental

PSi layers were prepared by anodic etching in ethanoic HF (mixture is $1 : 1 : 1$ of 47 vol% HF : C_2H_5OH : H_2O). A (100) p-type Si (10 Ωcm) substrate was used for the anode and Pt for the cathode. The anodic etching was carried out with an average current density of 11 mAcm^{-2} for 15 min under visible light illumination. After anodic etching, the sample was kept in the same solution for 5 min. The as-anodized PSi sample appears only as strong yr-PL under 2.96 eV laser excitation.

The bg-PL sample of PSi was prepared as follows: Sample was oxidized in air for 4 min at 150 °C and quenched to room temperature. In the next step, the sample was annealed in a vacuum (2×10^{-6} Torr) for one hour at 200 °C, using a cryostat (Oxford DN 1754) controlled by a temperature controller (Oxford ITC 502). This process was repeated 24 times. Then, PL from the sample was not observed, because most of the hydrogen that passivates the PSi surface is desorbed[12]. We analyzed the spectrum of the Fourier transform infrared (FTIR) on the sample. The infrared absorption bands in the triplet at 2090–2140 cm^{-1}, corresponding to the stretching modes of Si-H$_x$ atomic groups, disappeared by vacuum-annealing. The vacuum-annealed sample was stored for several days in ambient air before measuring. Then, the sample appeared almost as bg-PL. In the spectrum of FTIR, the intensity of the Si-O-Si asymmetry stretching mode located at 1100 cm^{-1} became stronger by keeping in ambient air for several days. Therefore, it is considered that the surface was covered by a SiO or SiO_2 layer. In this paper, we chose a specimen with a film-like area, which is about 12 mm from the top of the etched area.

The experimental setup was the same as in our previous work[5]. For the experiment in the range between 2.70 and 2.99 eV, we used a cavity dumped dye laser (pulse width 8 ps, Stilven 3) pumped with a third-harmonic generator (THG) combined with a second harmonic generator (SHG) from a mode-locked Nd^{3+}: YAG (yttrium aluminum garnet) laser (Coherent Antares 76-s). For the experiment in range between 2.00 and 2.21 eV, we used a cavity dumped dye laser (pulse width 8 ps, Rodamin 6 G) pumped with a SHG from a mode-locked Nd^{3+}: YAG laser. For the experiment at 2.33 and 3.49 eV (pulse width 80 ps), we used an acousto-optic modulator. To avoid the effect of a photo carrier induced by the strong excitation power and the slow decay of the yr-PL band caused by a high repetition rate, we used low excitation power (4 μWcm^{-2}) and slow repetition frequency (3.8 MHz) for the laser pulse.

3. Results ans Discussion

Figure 1 shows typical time-resolved spectra of the bg–PL under E_{exc} 2.96 eV at room temperature, observed as a function of delay time t_d from the excitation laser pulse. The position of the peak energy E_p and the shape of the time-resolved spectra do not change with decay. The decay time at 1/e of the initial intensity of the PL band was about 0.3 ns over the whole band. These results show that the sample aged in ambient air after vacuum-annealing only appears as a bg–PL band. Moreover, we measured the temperature dependence of P for bg–PL band between 77 and 470 K, but found no temperature dependence of P.

Figure 2 shows the PL spectra of PSi at $t_d=0$ under constant excitation photon number and varying E_{exc} between 2.21 and 3.49 eV. The value of the full width at half maximum of the PL spectrum becomes broader with increasing E_{exc} in the direction of the high energy side of the PL-band. The peak intensity of the PL spectrum increases with increasing E_{exc}. The position of E_p of the bg–PL band shifts from 1.93 to 2.55 eV by varying E_{exc}, keeping to the shape at the low energy side of the PL band.

Figure 3 shows a typical time-resolved PL decay and time-dependence of its P for the photon energy E_{ph} at the shoulders of the bg–PL band (1.90 and 2.50 eV). The decay curve of PL is clearly non-exponential. However, after the laser excitation, the time dependence of P at $E_{ph}=1.90$ and 2.50 eV demonstrates that the value of P remains almost at its initial values of about 0.23 and 0.32, respectively, until 8 ns at room temperature. These results show that photo-generated electrons and holes in PSi are localized at the excited states even in room temperature.

Figure 4 shows the E_{exc}-dependence of P in the PL bands. The degree of P at a fixed
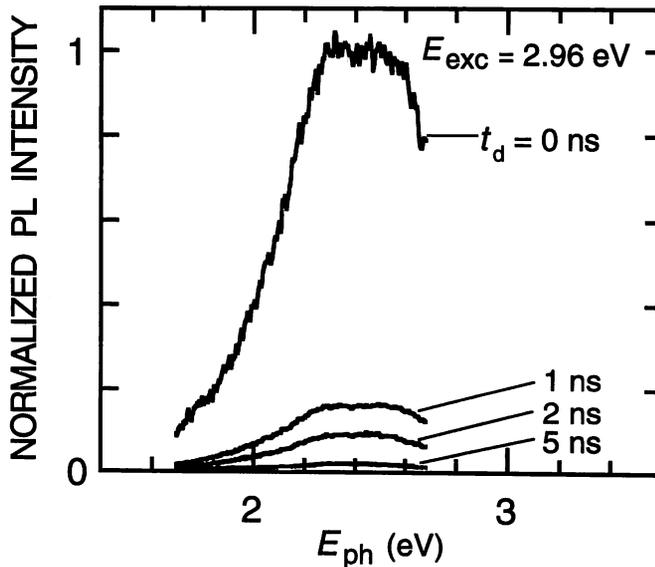

Fig. 1   Typical time-resolved spectra of the bg–PL under 2.96 eV excitation at room temperature were observed as a function of delay time t_d from the excitation laser pulse.
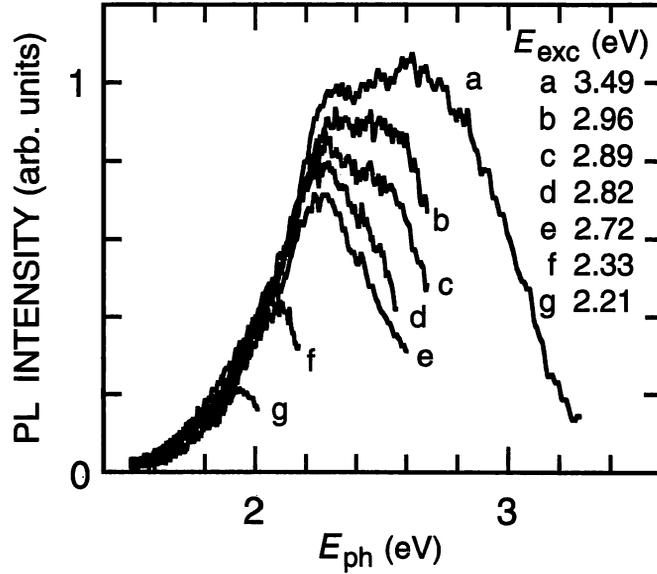
Fig. 2   Relative PL specta of PSi at $t_d=0$ under the E_{exc} range between 2.21 and 3.49 eV.
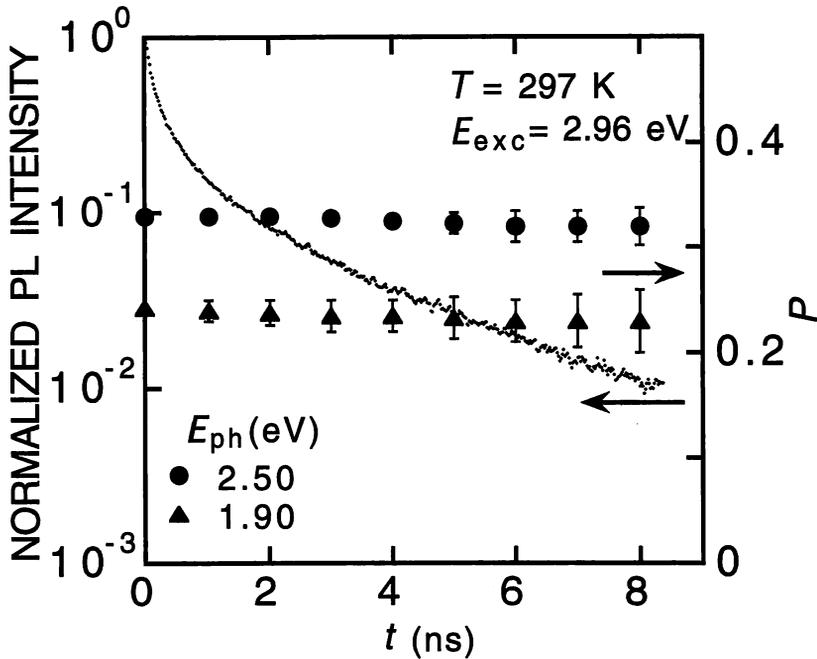

Fig. 3   Time-resolved PL decay is described by dotted lines. Time dependence of P at the shoulders of the bg-PL band 1.90 and 2.50 eV are plotted by closed triangles and closed circles, respectively.

E_{ph} depends largely on the E_{exc}. The maximum value of P for each E_{exc} is 0.32. In our sample, we observed no sample-orientation dpendence of P with respect to the rotation of the sample around an axis normal to its surface. For E_{exc} smaller than 2.33 eV, the
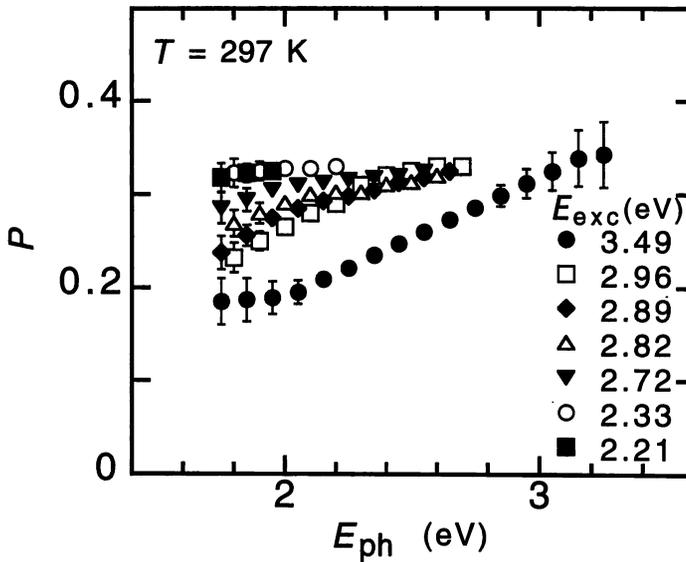
Fig. 4   The values of P in the PL bands for several E_{exc} are plotted as a function of E_{ph}.

value of P is almost constant in the PL band observed by E_{exc}. This suggests that an electron and hole excited at one site recombine radiatively without moving to another site with electron-phonon interaction. Therefore, it is considered that spectrum f in Figure 2 corresponds to a PL related to the lowest energy level, which is estimated to be 2.06 eV.

Figure 5 shows the P for each E_{exc} plotted by Stokes shift $(E_{exc}-E_{ph})$. From the figure, it can be seen that the value of P for the different E_{exc} lies on the same dependence and decreases with increasing Stokes shift. This implies that the reduction of P is caused by the phonon interaction with electrons and holes in the PL band. However, in yr-PL, replotting the E_{exc}-dependence of P with Stokes shift[1,13], the value of P does not lie on the same dependence. This implies that the dynamical process of the yr-PL is different from that of the bg-PL.

In Figure 5, the value of P saturates at 0.32 around no Stokes shift. Such a high P memory of 0.32 is considerd to be caused by the high degree of localized electrons and holes, because the maximum value of P from the ensemble of randomly oriented dipoles is expected to be 0.5[13]. A reduction of P from 0.5 in the Franck-Condon state (FCS) may be related to the spin-orbit interaction[2]. Such a reduction of P in FCS has been found using resonant secondary radiation in the absorption of an F center in alkali halide crystals[11,14].

The bg-PL and its P of PSi prepared by RTO near 1000 °C are similar to our results[9,15], although the bg-PL is obtained by a different preparation of PSi. According to our results, we consider that the bg-PL from PSi prepared by RTO is slowly created by oxidation in ambient air after hydrogen desorption by RTO.

To explain the above experimental results, we propose a localized exciton model as
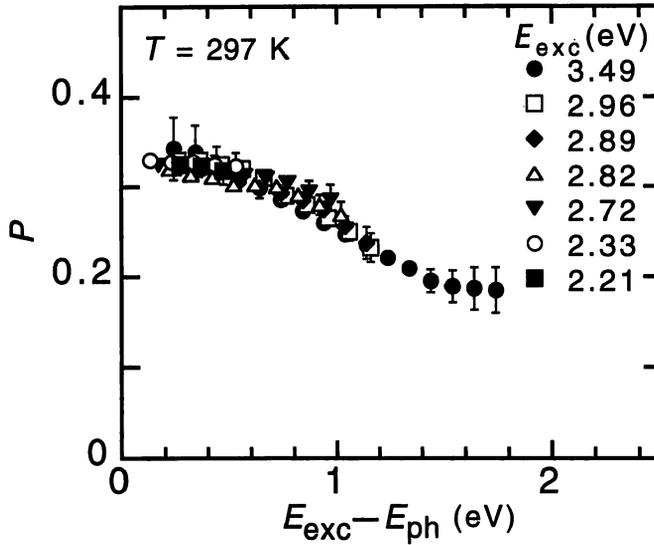
Fig. 5   The values of P in the PL bands for several E_{exc} are plotted as a function of Stokes shift (E_{exc} $-E_{ph}$).

follows: The excited electron relaxes to the bottom of conduction band in X valley and forms an exciton with hole at the top of the valence band at Γ point[16,17]. Moreover, we assume that a created exciton relaxes to a bottom of the potential using a configuration coordinate model for the localized exciton and emits. The size distribution of the silicon nanocrystals creates many energy states of excitons. Therefore, the PL band width also becomes wider with increasing the Stokes shift as reported by Muramatsu[17].

The depolarization bg-PL band is explained by an emission accompanied with a phonon-assisted process. The phonon-assisted process is explained as follows: In the E_{exc} above 2.33 eV, electrons or holes in one potential transfer to a successively lower potential with TO phonon emission during thermalization in the potential minimum, causing PL at multiple potentials. Therefore, the PL band width also becomes wider with increasing the Stokes shift. Moreover, the memory of P is successively lost by transferring the electrons or holes from one potential to another, because the number of participating phonons increases in proportion to the increse in Stokes shift.

In the E_{exc} between 2.21 and 2.33 eV, after the exciton is excited to a potential in PSi, it loses the excitation P memory at FCS immediately and reaches the potential minimum without moving to another potential. Then, it emits after thermalization. In this case, since the phonon does not assist, the value of P is constant over the whole PL band. As in the above results, P decreases with increasing Stokes shift and finally becomes constant.

4. Conclusion

In summary, we revealed that the bg-PL is slowly created by oxidation in ambient air after hydrogen desorption. We studied the bg-PL band using time-resolved polarization spectroscopy under the cavity dumping method. From the results of excitation energy dependence of polarization and the PL band, the origin of the bg-PL band suggested to be due to the localized exciton states which are induced by oxygen. The bg-PL is composed of emissions from the many different nanocrystals. The memory of P is successively lost by transferring the electrons or holes from one potential of the localized exciton state to another. These states are produced by the Si-O bonds at the surface of the nanocrystals or the interface between the silicon nanocrystals and the silicon dioxide.

Acknowledgments

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