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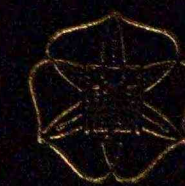


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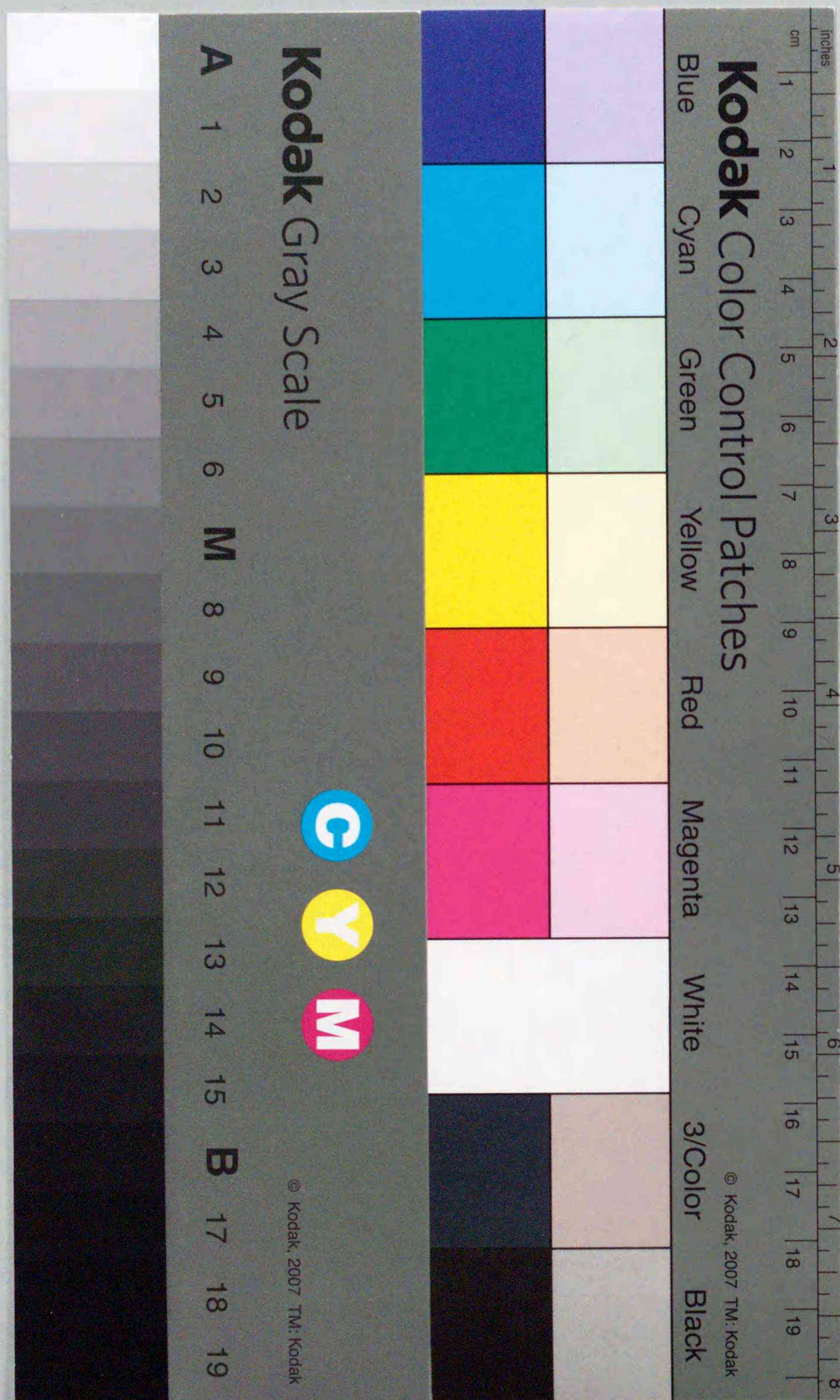
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Hidenori NOGUCHI

Physical Chemistry Laboratory
Division of Chemistry
Graduate School of Science
Hokkaido University



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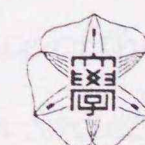
Hidegori NOGUCHI

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Chapter 1

Introduction

Chapter 1

Introduction

1.1. General Introduction

The history of semiconductor photoelectrochemistry is rooted in the 19th century when Becquerel found that an electric current flowed in one of the electrodes immersed in a dilute acid that was illuminated by light (Becquerel effect).¹ The understanding of this phenomenon was not achieved until 1955 when Brattain and Garrett used Ge as the first semiconductor electrode.² As the knowledge of the semiconductor electrochemistry has grown steadily, many reviews and books on this subject have appeared.³ Whereas virtually all of the work in photoelectrochemistry prior to 1970, was of a rather fundamental nature, beginning about 1970 the potential application of photoelectrochemical systems for solar energy conversion and storage was recognized.

In 1972, Fujishima and Honda⁴ showed that the oxidation of water to oxygen occurred at TiO_2 , which is an n-type semiconductor, under illumination at more negative potentials than the standard redox potential of the $\text{H}_2\text{O}/\text{O}_2$ redox couple. The implication was that it might be possible to use sunlight to split water into hydrogen and oxygen. Just after their paper was published, a worldwide search for new alternative energy sources began, and this process, the photoelectrolysis of water, attracted many research groups.⁵

The majority of the research efforts on the photoelectrolysis of water has been made on the use of n-type semiconductors.⁶ All of the n-type materials studied were metal oxides, since they are generally stable against photochemical oxidation. Several oxide semiconductors such as SrTiO_3 ,⁷ KTaO_3 ,⁸ and ZrO_2 ⁹ have been reported to exhibit photoelectrolysis with zero applied bias. However, all these oxides have large bandgaps (3.2-3.5 eV), which result in essentially zero solar absorptivity, i.e., they are not suitable for solar energy conversion. A few experiments have been done on p-type semiconductors.¹⁰ The

relative stability of p-type semiconductors against reductive decomposition is greater than the stability of n-type semiconductors against oxidative decomposition. Non-oxide semiconductors with small bandgaps, such as p-Si^{10(b)}, CdTe^{10(b)} and p-GaP,^{10(c)} appeared to be stable when used as cathodes.

Utilization of a double semiconductor electrode cell in which one electrode is an n-type semiconductor and the second is a p-type semiconductor, and both electrodes are illuminated, became one of the approaches for the photoelectrolysis of water.¹¹ An important advantage of this type of cell is that it allows the photoelectrolysis of water without external bias. The photoelectrolysis of water into H₂ and O₂ at zero external bias under sunlight was demonstrated for the first time with an n-TiO₂/p-GaP^{11(a)} cell. Further studies have been made with n-TiO₂/p-CdTe, n-SrTiO₃/p-CdTe, n-SrTiO₃/p-GaP,^{11(c), (d)} and n-GaAs/p-InP.^{11(e)}

In parallel to the investigations of the photoelectrolysis of water, studies of the conversion of solar energy into electrical energy using semiconductor/liquid junctions were also initiated in the 1970s¹² and a very remarkable conversion efficiency has been obtained with several cells. However, the most severe problem was the stability of the semiconductor electrode. Most semiconductors, having a bandgap lower than about 2 eV, undergo anodic decomposition in aqueous solutions. Only in the case of a few selected redox systems can suppressed the electrode decomposition.¹³ During the last 20 years, several attempts have been made to develop new photoanode materials. One approach was to use semiconducting transition metal compounds, which possess valence bands derived from transition metal d-states¹⁴ such as MoS₂,^{14(a), (d)} MoSe₂,^{14(d), (f)} and WSe₂.^{14(c)-(e)} Other interesting photoelectrochemical cells employed nonaqueous electrolytes.¹⁵ In the case of the n-type Si electrode, the corrosion (SiO₂ formation) was shown to be avoided by using H₂O-free CH₃OH and 10.1 % efficiency for the conversion of light to electricity under air mass 2 (AM2) solar conditions was reported.¹⁶ In the case of other Si-based cells, small Pt islands were deposited on the Si surface across which the current was channeled, whereas the free surface was

covered by a thick oxide layer.¹⁷ The search for the noble materials is still one of the important subjects in this field.

Dye-sensitized semiconductor electrodes were also studied by several research groups as a possible method for extending the spectral response of highly stable but wide bandgap semiconductors in order to increase their utilization of the solar spectrum.¹⁸ The sensitization effect is based on the excitation of dye molecules adsorbed on the semiconductor surface, followed by an electron injection into the conduction band of the semiconductor. In the presence of a suitable electron donor, such as I₃⁻/I⁻, the oxidized dye molecule is reduced back to its initial state. Even during the very early stage of semiconductor electrochemistry research, application to solar cells was suggested.^{18(a)-(c)} However, the photocurrent efficiency with respect to the incident light was less than 1 % due to the fact that the light harvesting efficiency of a single dye monolayer is very small.¹⁸

By use of a porous film consisting of nanometer-sized particles of high effective surface area as a substrate, a high light harvesting efficiency was achieved. Similar means of enhancement are used in nature by stacking the chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structures. In this respect, a very high energy conversion was reported by Grätzel et al.¹⁹ at the TiO₂ porous film electrodes modified with various kinds of dye molecules. Using a Ru complex as the dye, high current efficiencies were obtained with these electrodes.^{19(c)} Recently, they demonstrated that TiO₂ porous film electrodes modified with derivatives of chlorophyll and related nature porphyrins result in high a energy conversion efficiency comparable to those in natural photosynthesis.^{19(c), (d)} An energy conversion efficiency of 10 % modified with Cu chlorophyllin was obtained at 630 nm. The overall energy conversion efficiency of this cell was 2.6 % under simulated sunlight illumination. One of the problems to be solved for dye sensitized systems is the long-term stability of the dye because the oxidized dye formed in the first reaction step may also react with the solvent.

As an extension of the photoelectrochemistry of semiconductors, spontaneous chemical reactions were found to take place where semiconductor particles dispersed in an appropriate electrolyte solution were illuminated. Such reactions are called "semiconductor photocatalysis" or just "photocatalysis". A cathodic reaction using the conduction band electron and anodic reaction using valence band holes take places with the same rate during photocatalysts. Many studies have been carried out from both fundamental and applied standpoints.²⁰

The mechanisms of the semiconductor photoelectrochemical reactions have been inferred by a variety of electrochemical and spectroscopic techniques.²¹ The traditionally employed technique for this purpose include cyclic voltammetry, impedance spectroscopy, and luminescence measurements. During the last 10 years novel in situ techniques such as scanning tunneling microscopy (STM),²² atomic force microscopy (AFM),²³ surface X-ray diffraction (SXRD),²⁴ and the second harmonic generation (SHG)²⁵ have been developed to obtain the information about the morphological and electronic structures of the interface. Also, a direct access to the analysis of the charge transfer reaction at the semiconductor/electrolyte solution interface is now available by utilizing recently developed ultrafast time-resolved laser spectroscopy.²⁶

In the following sections, the basics of semiconductor photoelectrochemistry are briefly reviewed and some results already applied to probe the structure and dynamics of the semiconductor/electrolyte solution are summarized. The formation and properties of porous silicon, which is studied as a new photoelectrode material in this thesis, is briefly reviewed. Finally, the objectives of the present work are stated.

1.2. Semiconductor/Solution Interface

1.2.1. Structure of Semiconductor/Solution Interface²⁷

The semiconductor/electrolyte solution interface is the contact between two

conducting media, therefore, similarities exist with semiconductor/metal contacts. On the other hand, two types of conductors are present at the interface – electrons and ions. Also, the media comprising the interface are in different states – solid and liquid. Therefore, one expects the semiconductor/electrolyte solution interface to possess unique features compared to other types of contacts.

When a semiconductor is in contact with an electrolyte solution and they are in equilibrium, the electrochemical potentials of the two phases should be equal.

$$\overline{\mu}_e^s = \overline{\mu}_e^s$$

where $\overline{\mu}_e^s$ and $\overline{\mu}_e^s$ are the electrochemical potential of an electron in the semiconductor and in solution, respectively. This requires that the Fermi level in the semiconductor be equal to the redox potential in the electrolyte. If the electrochemical potential of the two phases are not equal before contact, then charge transfer involving the majority carriers of the semiconductor must occur. This charge transfer will continue until the electrochemical potentials are equal.

As an example, let us consider an n-type semiconductor/electrolyte solution interface where the Fermi level of semiconductor is above the redox potential of the electrolyte before contact (Figure 1.1). Equilibrium will be established by the transfer of electrons from the semiconductor to the electrolyte. As a result, a space charge

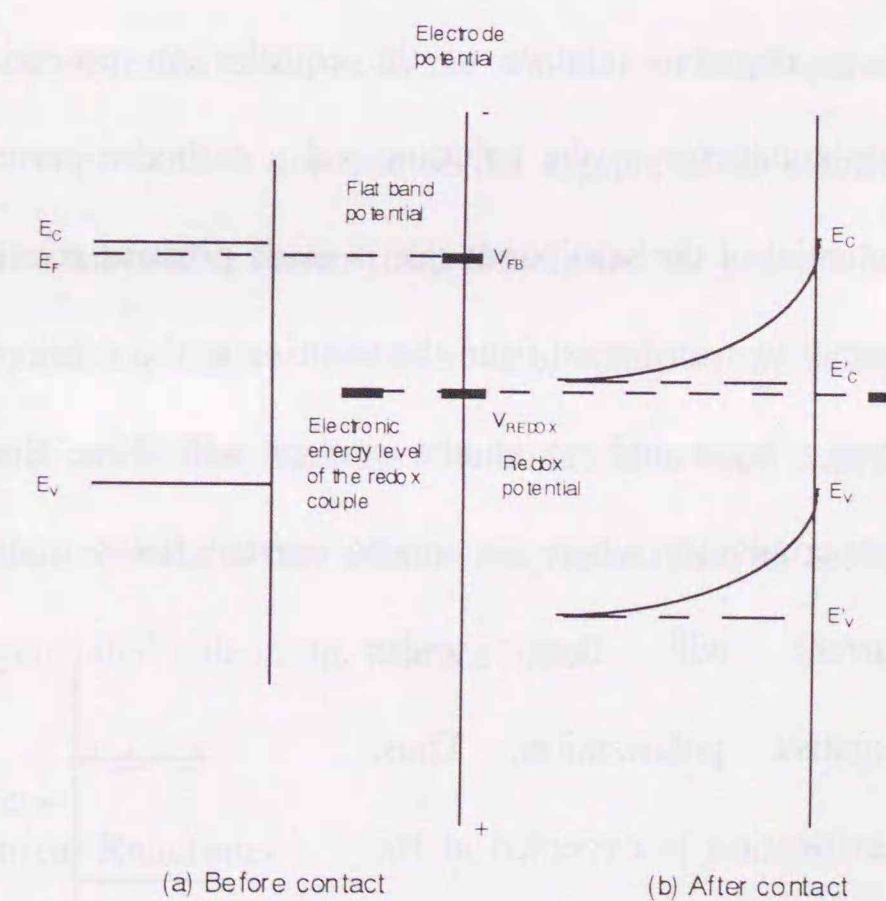


Figure 1.1. Energy diagram of semiconductor/electrolyte solution interface (a) before and (b) after contact. E_c and E_v are the surface energy levels of the conduction band and valence band, respectively, and E'_c and E'_v are those when all the potential drop occurs within the solution.

layer will be formed in the surface region of the semiconductor, which means the formation of an electric field, as indicated by an upward bending of the conduction and valence bands. The magnitude of this band bending corresponds to the potential drop across the semiconductor.

1.2.2. Effect of External Bias on Semiconductor Electrodes²⁷

Figure 1.2 schematically shows the effect of an external potential on the potential distribution at an n-type semiconductor/electrolyte solution interface in an ideal situation, assuming that the potential drop across the Helmholtz layer remains constant. This assumption is valid when the near-surface charge on the semiconductor is not too large. Initially the electrochemical potentials of the counter electrode, redox couple, and the semiconductor are equal. Application of a bias between the semiconductor and counter electrode will result in a separation of the Fermi levels, i.e., the Fermi level of the counter electrode will remain equal to the redox potential. When the potential of the semiconductor is made negative relative to the equilibrium potential, electrons will be transferred from the semiconductor to the solution and a cathodic current flows. On the other hand, when the potential of the semiconductor is made positive relative to the equilibrium potential, electrons cannot be transferred from the solution to the semiconductor due to the existence of the space charge layer and no anodic current will flow. Similar arguments are valid for a p-type semiconductor where an anodic current flows under positive polarization but no cathodic current will flow under negative polarization. Thus, rectification is expected at the semiconductor/electrolyte solution interfaces.

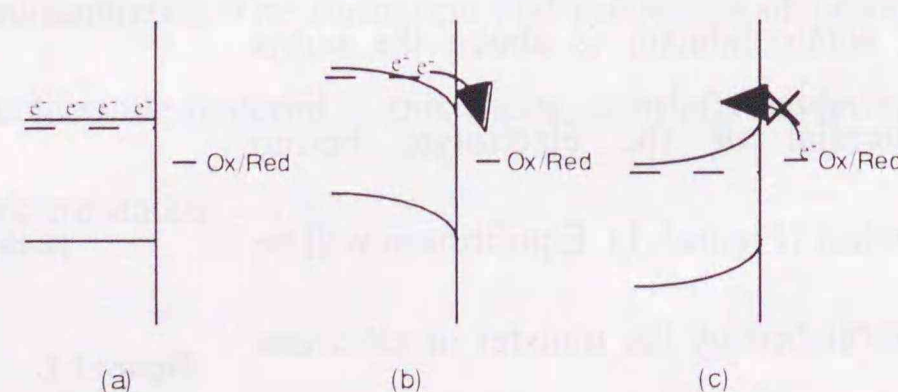


Figure 1.2. Energy diagrams at n-type semiconductor/electrolyte solution interface. (a) in equilibrium, (b) under forward bias, and (c) under reverse bias.

1.3. Photoexcitation of Semiconductor

1.3.1. Generation and Recombination of Electrons and Holes^{27, 28}

Under illumination, semiconductor electrodes absorb the energy of photons to produce excited electrons and holes in the conduction and valence bands. Generally, in semiconductors, photoexcitation significantly increases the density of the minority carriers, but only slightly influences the density of the majority carriers. When the excitation is stopped, recombination of the electron-hole pair occurs and the density of the carriers must return to the equilibrium situation. For the most common case, the excess carrier density exponentially decays with time as $\exp(-t/\tau)$, where τ is the carrier lifetime.

Physically, the recombination processes in semiconductors can be subdivided into two main classes:

- (i) Direct band-to-band recombination.
- (ii) Recombination with participation of impurities and defects.

(i) is a one-step process, which occurs between the electron in the conduction band and the hole in the valence band. (ii) is a two-step process. It consists of the capture of an electron from the conduction band by the empty recombination center (trap center) and the capture of a hole from the valence band by the occupied trap center. However, depending on the energy level of the trap center, the trapped electron can be lost back into the conduction band without recombining with hole. Thus, this trap can be both a trap center and recombination center. Similar arguments are valid at the photogenerated hole in the valence band.

1.3.2. Semiconductor Photoelectrochemical Reactions²⁷

Photoexcited electrons or holes in the space charge layer migrate toward the interface where they participate in cathodic reactions or anodic reactions to provide the current as shown in Figure 1.3. Such a current of the photoexcited electrons or holes is called the photocurrent. The photocurrent of electrons or holes is insignificant when the reacting charge

carriers are the majority charge carriers of which the concentration is only slightly increased by photoexcitation. Whereas, a large photocurrent will flow when the reacting charge carriers are the minority charge carriers of which the concentration is significantly increased by

photoexcitation compared with the minority charge carriers in the dark. Consequently, the photocurrent can be observed only with the reaction in

which the minority carriers participate. Figure 1.4 schematically shows the polarization curves for the photoelectrochemical reactions at n-type and p-type semiconductors in the dark and under illumination.

As shown in Figure 1.4, the photoexcited reaction occurs only when an appreciable electric field exists in the space charge layer. No photocurrent will be observed at the flat band potential because the electric field that is required to separate the photoexcited electron-hole pairs is absent. The photocurrent occurs at any potentials different from the flat band

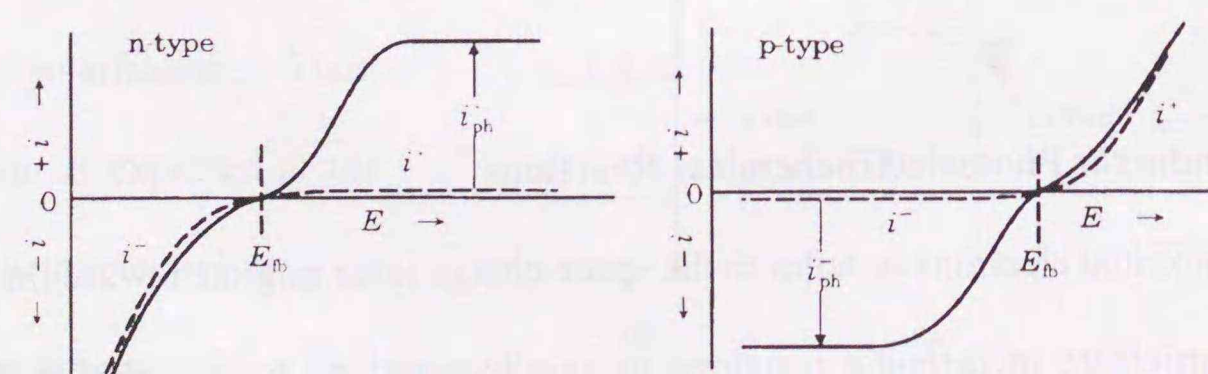


Figure 1.4. Polarization curves for electrode reactions at n-type and p-type semiconductor electrodes in the dark and in the photoexcited state: dotted curve=dark and solid curve=photoexcited; $i^*(i)$ =anodic (cathodic) current in the dark and $i_{ph}(i_{ph})$ =anodic (cathodic) current in the photoexcited states (After Ref. 27).

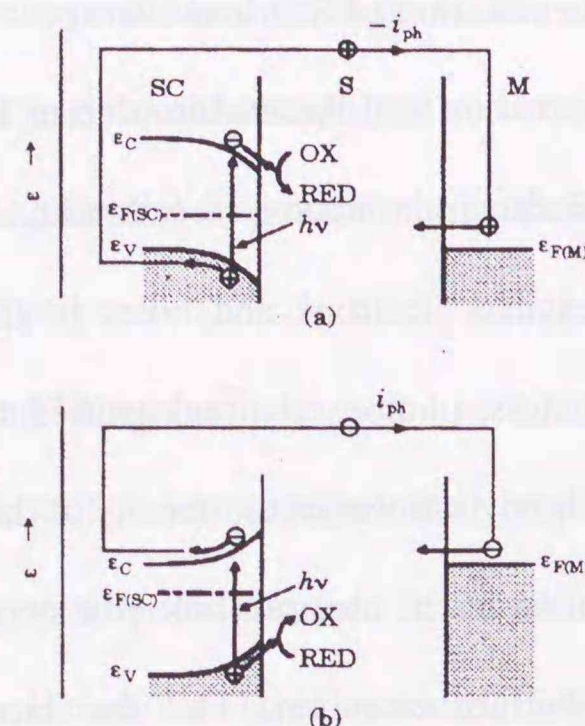


Figure 1.3. Generation mechanisms of photocurrent at semiconductor electrodes. (a) Photoexcited reaction of cathodic electron transfer at p-type semiconductor electrode. (b) Photoexcited reaction of anodic hole transfer at n-type semiconductor electrode. i_{ph} =photocurrent (After Ref. 27).

potential. Therefore, photoelectrochemical reactions may occur at potentials at which the same electrode reactions are thermodynamically impossible in the dark.

1.3.3. Efficiency of Photoelectrochemical Reactions²⁷

The generation and collection of minority carriers is quantitatively described using three characteristic lengths. The width, W , of the space charge layer, the minority carrier diffusion length, L_p , which is determined by the lifetime and the diffusion coefficient of the minority carriers, and the penetration depth of the incident light, $1/\alpha$, which is determined by the absorption coefficient, α . The photocurrent, i_p , is a linear function of the incident photon flux, I_0 , and is given by the Gärtner equation²⁹

$$\Phi = i_p / I_0 = 1 - \{ \exp(-\alpha W) / (1 + \alpha L_p) \}$$

where Φ is the quantum efficiency of the photocurrent generation.

At large values of band bending, most real semiconductor/electrolyte solutions follows the behavior described by the Gärtner equation, but closer to the flat band potential, the photocurrent is usually smaller than expected. The most likely explanation for this is that bulk or surface energy levels are present which assist the recombination of the photogenerated electron-hole pairs as illustrated in Figure 1.5.³⁰ An alternative explanation of the deviation from the Gärtner equation is that illumination results in the development of a surface charge on the semiconductor, which alters the potential distribution across the semiconductor so as to lower the band bending.^{30(b)}

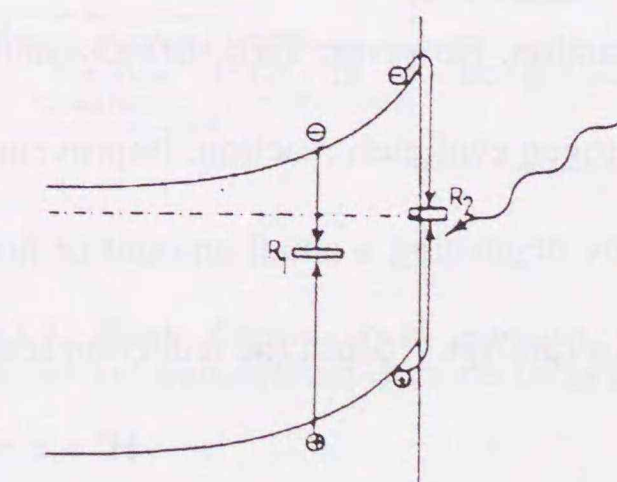


Figure 1.5. Bulk (R_1) and surface (R_2) recombination (After Ref. 30).

potential distribution at the semiconductor/electrolyte solution interface and about the surface states are quite important in order to develop high photo-to-energy conversion systems.

1.3.4. Semiconductor Photocatalysts

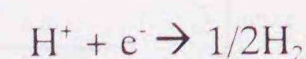
Over the past 20 years, semiconductor suspensions or colloidal solutions have been applied to the degradation of inorganic or organic pollutants.²⁰ A variety of semiconductors have been tested as photocatalysts, but mostly metal oxides, such as TiO_2 , have been used because they are stable in water.

In contrast to semiconductor electrodes, the particles cannot be polarized. Accordingly, the two reactions, reduction and oxidation, always occur simultaneously. Also, in the case of semiconductor particles, the band bending is small and charge separation occurs via diffusion. The quantum efficiency of the reaction depends on the transfer rate of the excited carriers at the interface, the recombination rates within the particles, and the average transit time τ of the excited carriers to move from the interior of the particle to the surface. τ is given by³¹

$$\tau = R^2/\pi^2 D$$

where R is the radius of the particles and D is the diffusion coefficient of the excited carriers.

In many photocatalytic reactions in aqueous solutions, hydrogen evolution is the cathodic reaction. However, TiO_2 , SrTiO_3 , and CdS have very low electrocatalytic activities for the hydrogen evolution reaction. Improvements in the electrocatalytic activities have been attempted by depositing a small amount of noble metal, such as Pt, on these semiconductor particles as a catalyst.³² Since the reduction reaction



very quickly occurs at the Pt site, photogenerated electrons will rapidly move to the Pt surface before it recombine with the holes. Therefore, a high quantum efficiency of the reaction will be achieved.

1.4. Luminescence Properties of Semiconductor Electrodes

The luminescent properties of semiconductor electrodes are known to provide useful information about the electrochemical reactions.^{21(a), (c)} The most common types of luminescence studied in semiconductor physics are photoluminescence (PL), and electroluminescence (EL). Both PL and EL are used to study the luminescence properties of semiconductors in solution. PL is generated by illuminating a semiconductor electrode with light, the energy of which is larger than the bandgap of the semiconductor. The PL intensity is affected by many factors, including the potential distribution in the semiconductor, lifetime of the photogenerated carriers and the surface recombination velocity. By measuring the potential dependence of the PL intensity, these properties can be investigated.

1.4.1. Photoluminescence

PL measurements of semiconductor electrodes can be carried out by combining an ordinary electrochemical system with a light source and detection system. A block diagram of a typical system for luminescence measurements of semiconductor electrodes is shown in Figure 1.6. Lasers provide strong monochromatic light with very good collimation and are most often used

as the light source. When measurements at various excitation wavelengths are required, one may need to use a white light source such as a Xe lamp with suitable interference filters or monochromator to obtain monochromatic light.

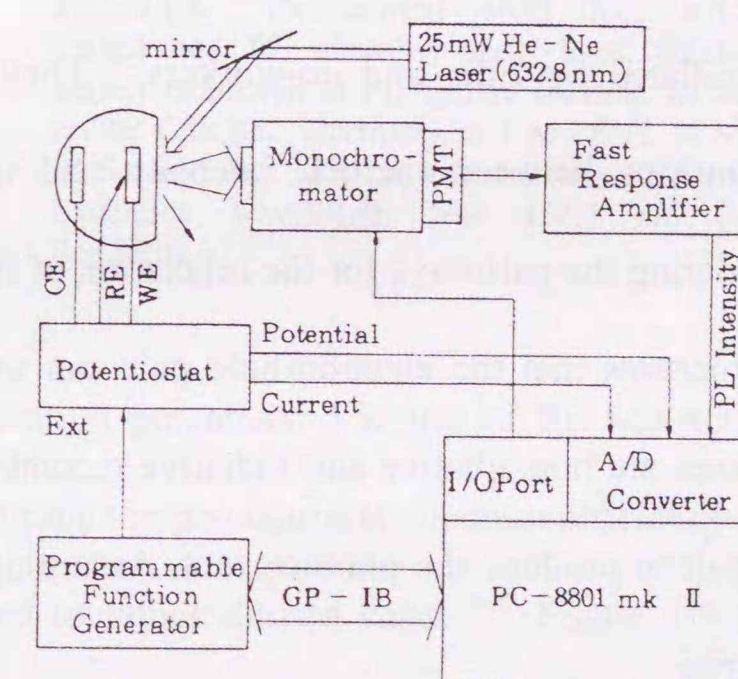


Figure 1.6. Block diagram of an apparatus used for PL measurements of semiconductor electrodes (After Ref. 32).

The early application of PL as a method for understanding the processes at the semiconductor/electrolyte solution interface was reported by Petermann *et al.*³³ They examined the green sub-bandgap PL of n-type ZnO single crystals. They advanced the hypothesis that the photocurrent and PL are directly competing processes. A mirror image relationship between the current-potential and PL intensity-potential was therefore expected. This was indeed experimentally observed to a close approximation (Figure 1.7).

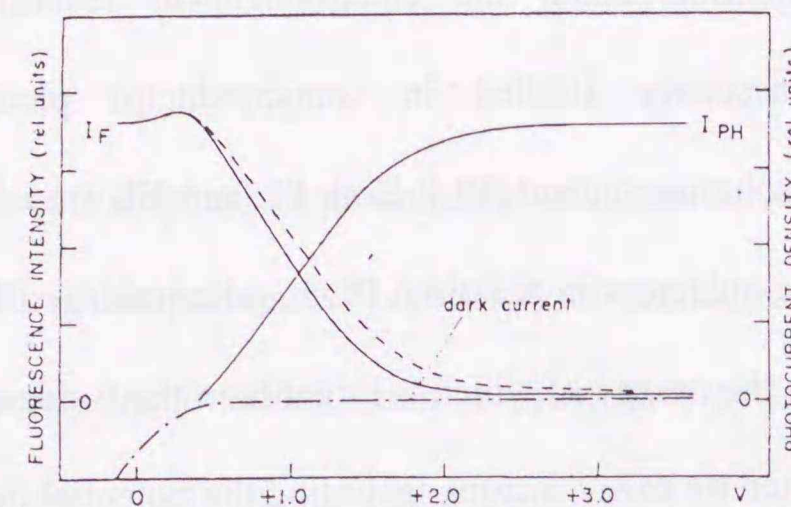


Figure 1.7. Voltage dependence of PL intensity and photocurrent density. Excitation wavelength was 350 nm. The dash line shows the mirror image of the photocurrent density (After Ref. 24).

A major effort in the study of the PL of a semiconductor/electrolyte solution interface was initiated by Ellis and co-workers.³⁴ They proposed a simple model to interpret the relationships between the PL intensity and quantum efficiency of the photocurrent.^{34(b)} Considering the pathways for the relaxation of the excited-state of the semiconductor, that is, the processes that the electron-hole pair can undergo once it is optically generated. These processes are nonradiative and radiative recombination as well as separation of the electron-hole pair to produce the photocurrent. Assuming these are the only processes available, one can write

$$\Phi_x + \Phi_r + \Phi_{nr} = 1$$

These quantities correspond to the quantum efficiency for a photocurrent, the radiative recombination, and the nonradiative recombination, respectively. At the open circuit potentials, there is no current flowing and hence $\Phi_x = 0$ at this potential. The following relationship holds at open circuit:

$$\Phi_{r0} + \Phi_{nr0} = 1$$

If it is assumed that the ratio of the quantum efficiency of the radiative recombination and nonradiative recombination are independent of the potential, i.e., $\Phi_r / \Phi_{nr} = \Phi_{r0} / \Phi_{nr0}$ then one may arrive at the equation

$$\Phi_{r0} / \Phi_r = 1 / (1 - \Phi_x)$$

This is essentially the same result that Petermann *et al.*³³ arrived at, namely, there is an inverse relationship between the photocurrent and PL intensity. Thus inverse relationship was found to be in reasonable

agreement with the experimental results for the $\text{Cd}_x\text{Se}_{1-x}$ system (Figure 1.8).^{34(b)} Reasonable agreement obtained between the Φ_x values calculated from the PL

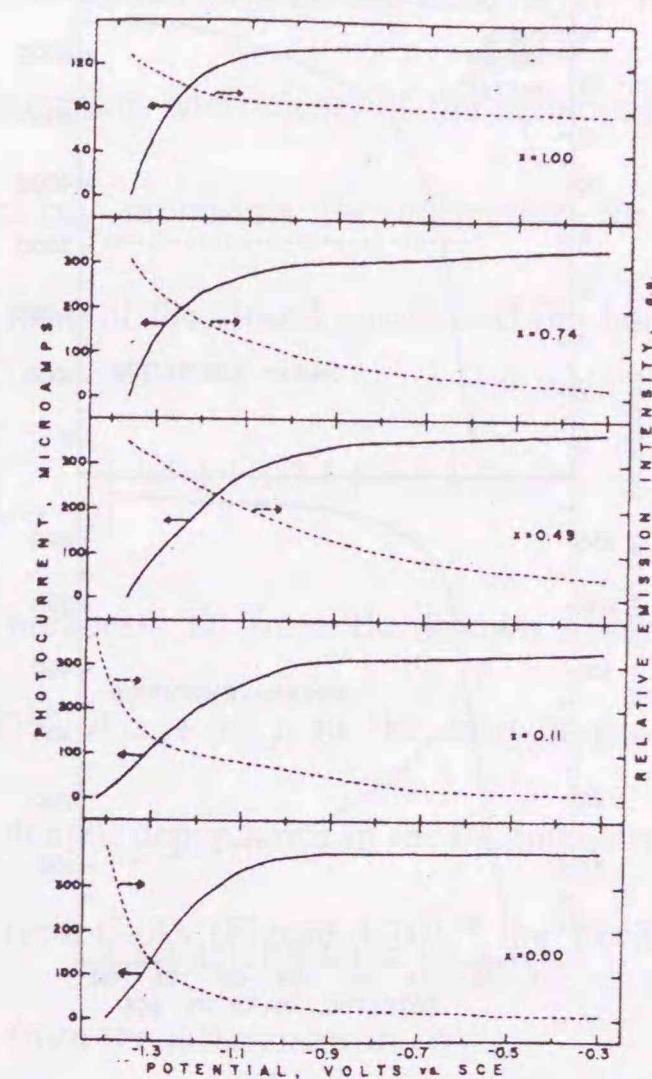


Figure 1.8. Photocurrent (solid lines, left-hand scales) and PL intensity (dash lines, right-hand scales) monitored at PL spectra maxima for single crystal $\text{CdS}_x\text{Se}_{1-x}$ electrodes in 1 M OH⁻/1 M S²⁻/0.1 M S electrolyte solution as a function of potential. Excitation wavelength was 457.9 nm (After Ref.25(b)).

quenching and values measured at the saturation potentials. The use of PL was therefore advanced as an alternative method for determining the photocurrent quantum efficiency.

However, this model can be applied to rather limited cases.³⁵⁻³⁷ Figure 1.9 shows photocurrent-PL intensity-potential curves obtained from the Te-doped CdS/electrolyte solution interface excited at 514.5 and 496.5 nm.³⁵ At the ultra-bandgap wavelength of 496.5 nm, the PL intensity quintuples as the photocurrent declines to zero. With bandgap edge 514.5 nm excitation, the PL intensity is essentially constant over the excursion in potential. In the case of the n-type GaAs electrode (Figure 1.10), quenching of the PL intensity was observed, although in the potential range where the photocurrent saturated.³⁶ Moreover, quenching of the PL intensity became bigger as the excitation wavelength became shorter. In these cases,

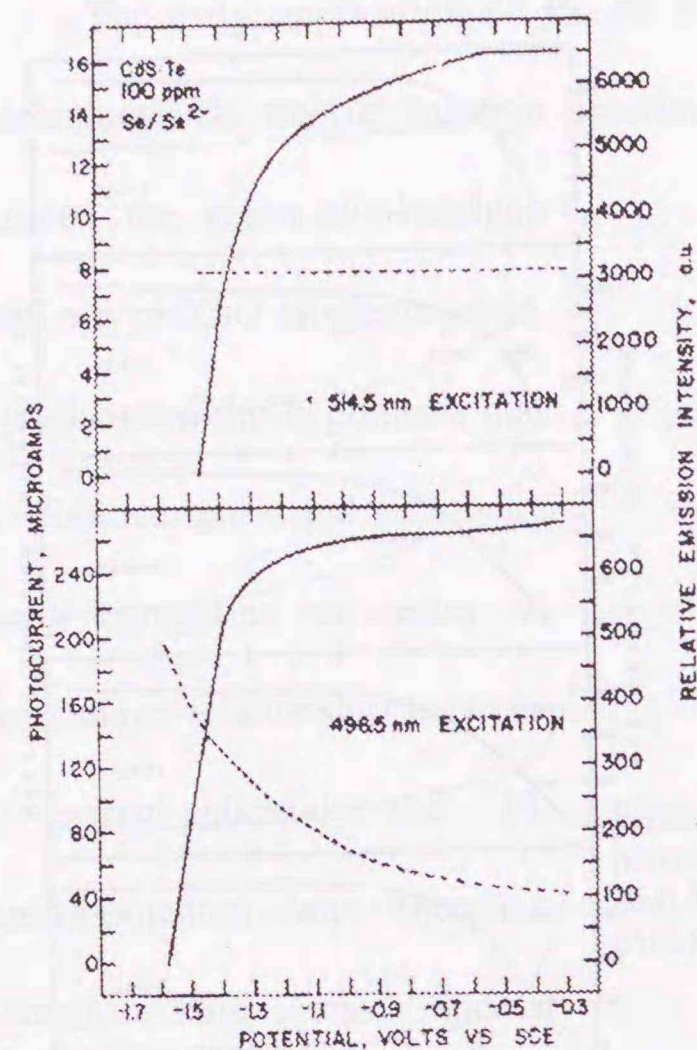


Figure 1.9. Photocurrent (solid line, left-hand scale) and emission intensity (dash line, right-hand scale) monitored at 600 nm vs. potential for a CdS:Te 100 ppm single crystal electrode in 5 M OH⁻/0.117 M Se²⁻/0.001 M Se₂²⁻ electrolyte excited at 514.5 nm (top frame) and 496.5 nm (bottom frame). Electrode potential was swept at 13 mV/s. E_{redox} was -0.96 V vs. SCE (After Ref. 26).

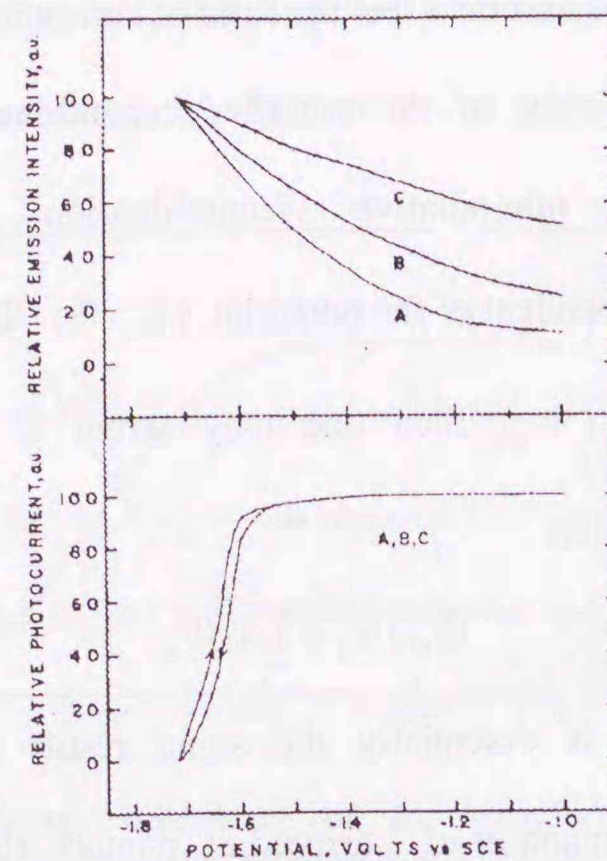


Figure 1.10. Relative photocurrent (bottom panel) and PL intensity (top panel) as a function of potential and excitation wavelength for an n-GaAs in 7.5 M KOH/0.2 M Te²⁻/0.006 M Te₂²⁻ electrolyte. PL intensity was monitored at $\lambda_{\text{max}} = 870$ nm and excitation wavelengths were 457.9, 514.5, and 632.8 nm yielding curves A, B, and C, respectively. PL intensities are relative to open circuit values which have been arbitrarily set at 100 for all three excitation wavelengths. Photocurrents are relative to their values at -1.0 V vs. SCE which have also been arbitrarily set at 100. Electrode potential was swept at 10 mV/s for each excitation wavelength. E_{redox} was -1.13 V vs. SCE. (After Ref. 27).

the "dead-layer model",³⁸ developed by Mettler³⁹ including the effect of surface recombination on the PL intensity, was applied to describe the photocurrent-PL intensity-potential behavior. The essential idea of this model is that there exists a totally nonemissive zone from the surface into the bulk of the semiconductor. This region is treated as being "dead" to luminescence. The thickness of this nonemissive zone is correlated with the extent of the electric field into the semiconductor. Physically, electron-hole pairs formed within this electric field by optical excitation are swept apart more rapidly than the radiative recombination rate. Hence, the luminescence intensity became small. At the flat band potential, the PL intensity, $I_{\text{PL,fb}}$, should be proportional to the incident absorbed light intensity, I_0 . As an electric field is introduced by the applied potential, the PL intensity will be

proportional to $I_0 \exp(-\alpha' D)$, the fraction of light absorbed beyond the dead layer. In this expression, $\alpha' = \alpha_E + \alpha_{\text{PL}}$ with α_E and α_{PL} the absorption coefficients of the semiconductor for the exciting and emitted light, respectively. α_{PL} represents the correction for self-absorption of PL by the semiconductor itself. The ratio of the closed circuit and flat band PL intensities yields

$$I_{\text{PL}}/I_{\text{PL,fb}} = \exp(-\alpha' D)$$

which can be used to calculate the dead-layer thickness, D , from the known absorption coefficient and measured PL quenching. Since $D \ll 1/(\alpha_E + \alpha_{\text{PL}})$, in the case of the CdS electrode excited by 514.5 nm (Figure 1.9),³⁵ no potential dependence in the PL intensity was observed, i.e., $I_{\text{PL}}/I_{\text{PL,fb}} \approx 1$. In the case of the n-type GaAs (Figure 1.10),³⁶ the excitation wavelength dependence of the PL quenching arises from the differences in α_E .

Uosaki *et al.*⁴⁰ applied this "dead-layer model" to the p-GaAs/electrolyte solution interface to evaluate the band edge shift of the GaAs during the hydrogen evolution reaction (HER) under illumination. The transient responses of the PL intensity and spectra were measured when the potential was pulsed from relatively negative in the positive direction. The PL intensity gradually decreased with time, which was accompanied by a quenching of the shorter wavelength part of the PL spectra. Considering the shift in the band edge in the semiconductor under illumination, they proposed a model (Figure 1.11) to explain the

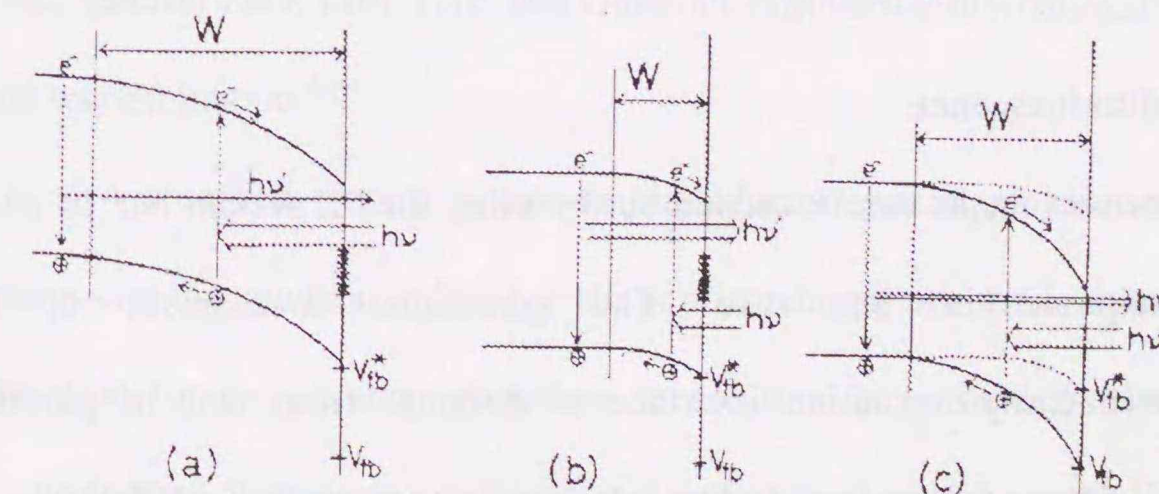


Figure 1.11. Band diagrams of p-GaAs/electrolyte solution interface under illumination (a) at relatively negative potential, (b) at relatively positive potential which is close to V_{fb} , and (c) at the same potential of (b) but after a certain time. V_{fb} is the flatband potential (V_{fb}) under illumination and is ca. -1.0 V in 1 M NaOH and 0 V in 0.5 M H₂SO₄. V_{fb} in dark is -0.35 V in 1 M NaOH and 0.6 V in 0.5 M H₂SO₄ (After Ref. 31).

transient behavior of the PL intensity and spectra.

The potential dependence of the PL intensity of the n-type GaAs electrode under the forward bias conditions was also reported.⁴¹

The PL intensity of the n-type GaAs electrode increased with an increase in the forward bias when the potential was more negative than the flat band potential (Figure

1.12(A)). However, when the GaAs surface was treated by Pt, which has a high activity for the HER, no potential dependence of the PL intensity was observed when the potential was swept in the negative direction (Figure 1.12(B)). The increase in the PL intensity with the increase in forward bias was explained by an accumulation layer formation near the surface caused by a kinetic barrier for the HER. This barrier was removed by Pt modification of the electrode surface, leading to an increase in the HER rate and no accumulation of electrons at the surface, i.e., no increase in the PL intensity under large cathodic bias conditions.

1.4.2. Electroluminescence

EL measurements can be carried out by using the PL system but, of course, no light source is required in this case. The generation mechanism of EL at the semiconductor/electrolyte solution interface is different from that in purely solid state configurations. EL can be generated when minority carriers are injected from the solution into semiconductor under forward bias, in which case there is a high surface concentration of the majority carriers.^{21(b),(c)} For example, when holes are injected into the valence band of an n-

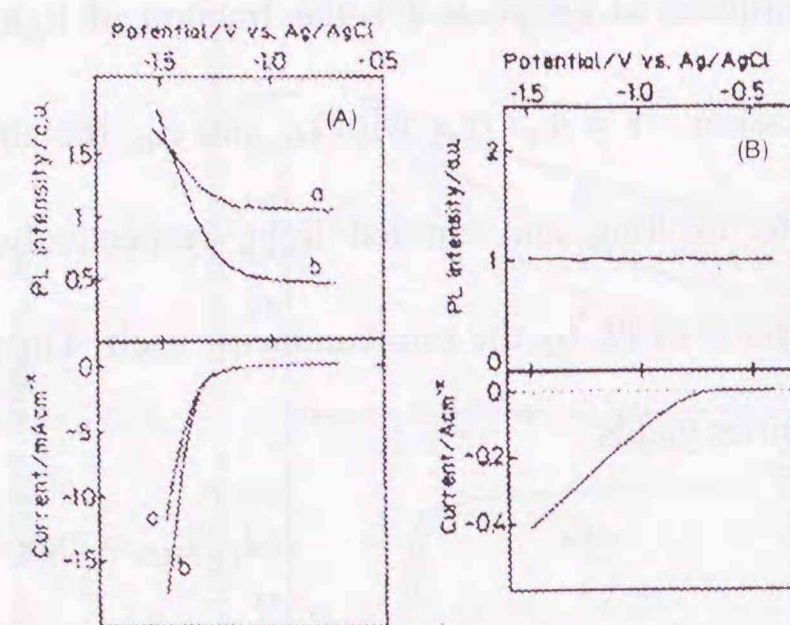


Figure 1.12. (A) Current-PL intensity-potential relations of n-GaAs electrodes in 0.5 M H₂SO₄. Doping density: (a) $1.5 - 5.5 \times 10^{18} \text{ cm}^{-3}$, (b) $0.84 \times 10^{18} \text{ cm}^{-3}$. Sweep rate was 20 mV/s. (B) Current-PL intensity-potential relations of n-GaAs dip treated in 20 mM H₂PtCl₆(pH4) for 60 s. Sweep rate was 20 mV/s (After Ref. 32).

type semiconductor from a species in a solution under cathodic polarization, electrons accumulated near the surface in the conduction band recombine with the injected holes in the valence band, and light is emitted (Figure 1.13). In this case, since recombination mainly occurs near the surface, the information obtained is more sensitive to the surface than that obtained by the PL measurements.⁴²

An extensive study of EL was reported by Gerischer *et al.*⁴³ for several n-type semiconductors (SnO₂, ZnO, CdS, GaP, and GaAs) in an electrolyte solution containing O₂, H₂O₂, or K₂S₂O₈ as oxidants. Reduction currents could generally be observed for the three oxidants with onsets at potentials near and negative of the flat band condition. Observation of EL required potentials negative of the reduction current onset. In the time-resolved measurements, the maximum EL intensity was observed within 0.1 ms after the reduction current started to flow. A decrease in the EL intensity at times up to ca. 0.6 ms after the potential pulse were attributed to a decrease in the surface S₂O₈²⁻ concentration.^{43(b)} With regard to the EL spectra, ZnO, CdS, GaP, and GaAs all exhibited a sub-bandgap emission due to surface state recombination.^{43(b)}

EL is also observed from a p-type semiconductor/electrolyte solution interface if electron injection into the conduction band of the semiconductor occurred, although no report on EL of this kind for p-type semiconductors in solution is available.⁴⁴ However, if the inversion layer is formed at a p-type semiconductor surface under strong cathodic polarization, EL caused by the hole injection should be observed. Uosaki *et al.*⁴⁵ reported EL due to band-to-band recombination at the p-type GaAs/persulfate solution interface for the first time at any

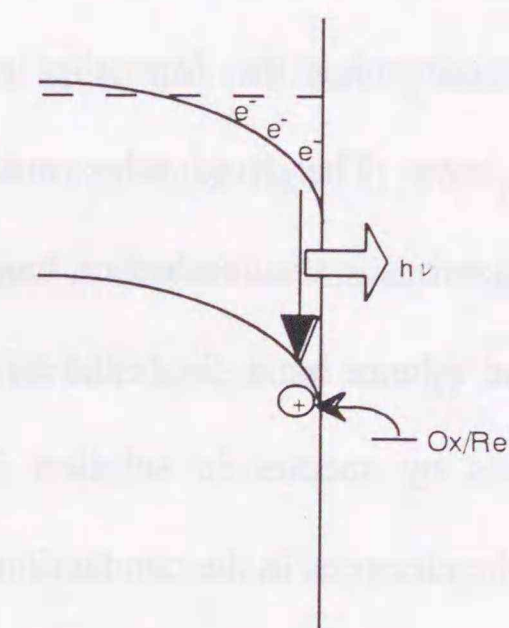


Figure 1.13. EL generation mechanism at an n-type semiconductor/electrolyte solution interface.

p-type semiconductor/electrolyte solution interface, confirming the formation of the inversion layer. The band edge emission requires electrons in the conduction band and holes in the valence band. Since the injection of electrons by species in solution is not possible, the electrons in the conduction band should be created by tunneling from the valence band into the bulk of the semiconductor. Although the holes are the majority carriers in p-type GaAs, the concentration of the hole must be very small under strong cathodic polarization. The holes responsible for EL should be injected by $S_2O_8^{2-}$ and $SO_4^{\cdot-}$ (Figure 1.14).

The use of EL to probe the surface of GaAs during hydrogen evolution led to information on the adsorbed H on GaAs and the effect of Ru on the energy of the surface atoms. Uosaki *et al.*⁴⁶ observed edge emission at p-type GaAs in solution that does not contain hole-injecting species. The electrode was first pulsed to a large negative potential and then pulsed back to the potential close to that at which the bands within the semiconductors are flat.

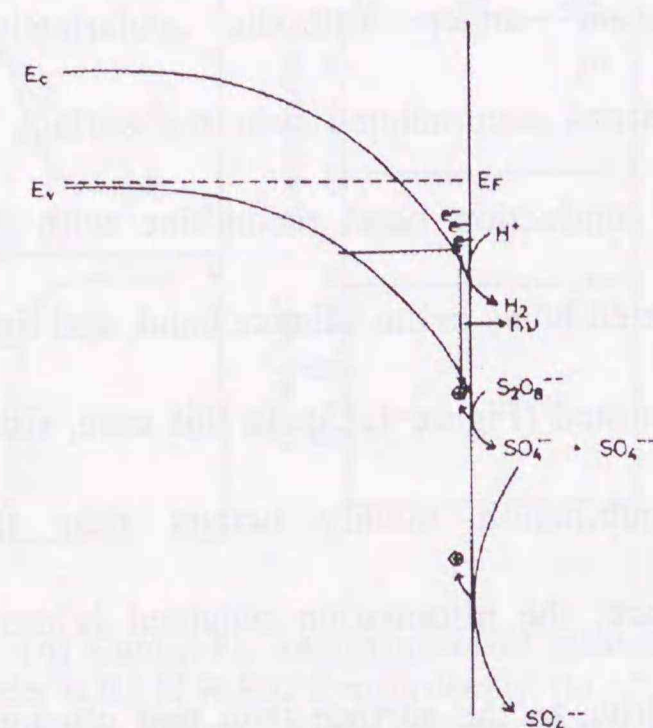


Figure 1.14. Proposed model for hydrogen evolution and EL at cathodically biased p-GaAs (After Ref. 34).

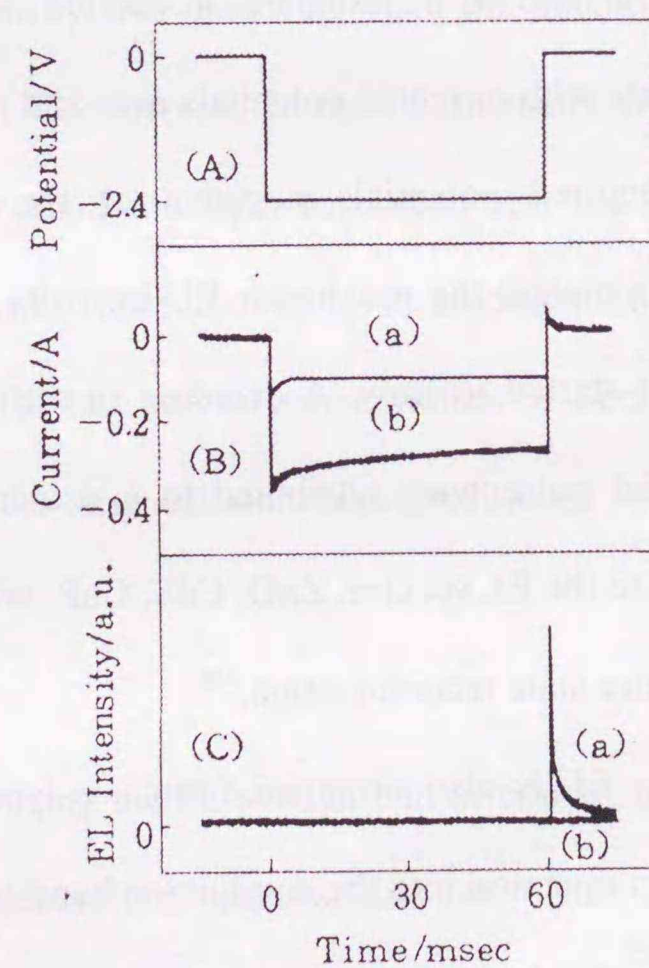


Figure 1.15. Time dependence of current (B) and electroluminescence intensity (C) at p-GaAs single crystal electrode ($Zn: 4.66 \times 10^{18} \text{ cm}^{-3}$) in 0.5 M H_2SO_4 when the potential was pulsed between 0 V and -2.4 V, as shown in (A). (a) Etched electrode. (b) Ru treated electrode (After Ref. 35).

whereupon EL was then detected (Figure 1.15). Thus, adsorbed hydrogen injects electrons into the conduction band upon pulsing the potential near the flat band potential. These electrons recombine with holes in the valence band to produce light. It was possible to conclude that the energy level of the adsorbed hydrogen is above the conduction band edge. They also showed that noble metal treatment of the surface lowers the energy level of the adsorbed hydrogen into the energy gap region.

1.5. Ultrafast Carrier Dynamics in Semiconductors

Electrochemical reactions are heterogeneous chemical reactions, which occur at the electrode/electrolyte solution interface and are accompanied by the transfer of electrons across the interface. Recently, there has been considerable interest in studying the photogenerated carrier dynamics in semiconductors.⁴⁷ However, our understanding of the surface electron transfer reaction is lagging well behind the analogous problem of homogeneous electron transfer reactions. This discrepancy is due to the greater inherent experimental difficulties in studying surfaces. Most of the work on interfacial charge transfer has been conducted using electrochemical approaches to the problem. To access information on the fastest dynamical processes occurring at the surface, i.e., the primary processes, some kind of "jump" experiment is required. These experiments entail a rapid change in one of the reaction parameters (temperature, pressure, electronic state, etc.) on a time scale faster than the dynamics of interest. By probing the subsequent relaxation of the system from this non-equilibrium point, one can obtain information on the fastest processes involved in a reaction mechanism. This time scale requires an all optical approach and the recent development of picosecond and femtosecond time-resolved measuring techniques made available in this respect. In this line of study, the semiconductor serves as the optical switch for turning on the interfacial charge transfer processes. The impulsive non-equilibrium condition, i.e., the "jump", is the photogeneration of electron-hole pairs in the semiconductor.

1.5.1. Ultrafast Time-resolved Absorption Spectroscopy

Studies of fast spectroscopic events in atomic and molecular systems occurring on the picosecond or sub-picosecond time scales generally require short pulse excitation sources to create a population perturbation among discrete energy states and monitor the recovery of the systems toward their equilibrium conditions. With the development of picosecond and femtosecond laser systems in recent years, extensive studies have been carried out on a wide variety of ultrafast processes in physics, chemistry, and biology.⁴⁸

As far as the study of the perturbation state created by the excitation laser is concerned, because of the limited temporal resolution of ordinarily photodetectors, most of the quantitative investigations of picosecond/femtosecond optical processes have employed the pump-probe spectroscopic method (Figure 1.16). In this technique two individual sets of laser pulses of comparable time duration are

incident upon the same region of space of the sample. The absorption of photons from the initially incident pump pulse creates a population perturbation between the two states, i.e., initial and final states, coupled by the radiation. Recovery to the initial (equilibrium) condition following this perturbation occurs on a time scale which is determined by the lifetime of the excited state species. Since the transmission or reflectance of the probe beam from the sample is influenced by the populations of the states perturbed by the pump beam, the recovery of the pump-induced populations

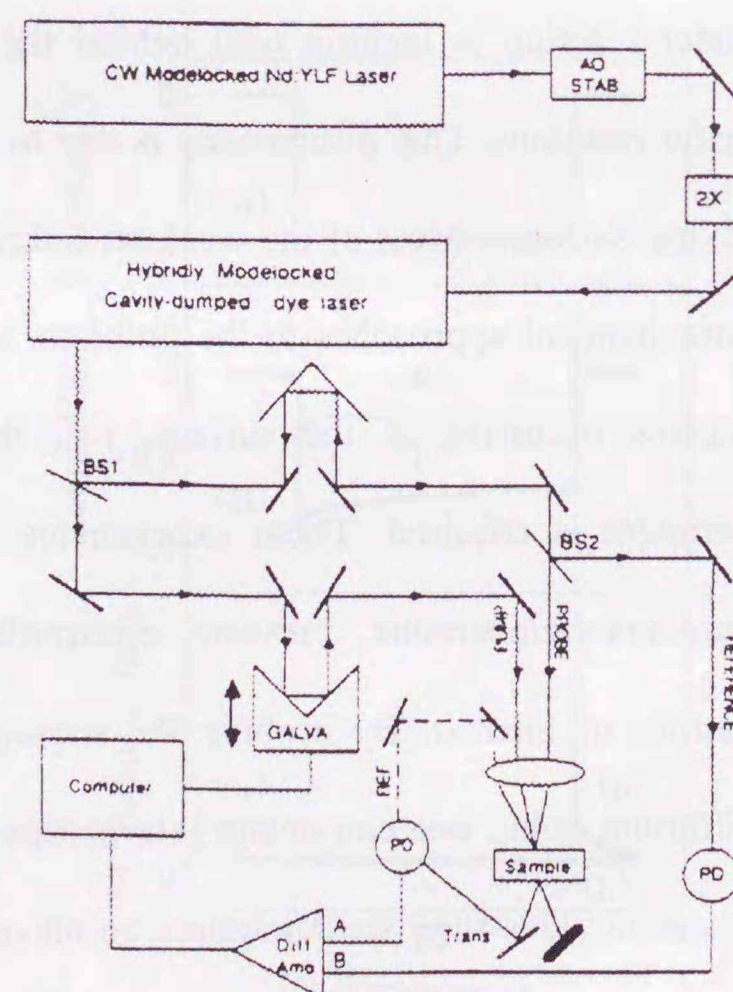


Figure 1.16. Typical experimental setup for one-color pump and probe measurement. A scanning galvanometer was employed as the optical delay line. (After Ref. 36(d)).

toward the equilibrium state can be monitored by delaying the probe pulse in time following pump excitation. Such a time delay is introduced by increasing the optical path length of the probe beam.

1.5.2. Initial Stage of Photoexcited Semiconductor Photocatalysts

Recently, the elementary charge carrier dynamics of nanometer-sized semiconductor particles have been the targets of several ultrafast spectroscopic studies.⁴⁹ The interest in these systems is due to their potential use in technological applications such as photocatalysts. The time scale of the interfacial electron transfer and lifetime of the photogenerated charge carriers in the photocatalysts determine the efficiency of the heterogeneous photochemical reactions. Ultrafast spectroscopic measurements on such nanocluster systems give direct information on the electron transfer and charge carrier lifetimes.

Recent experiments on two of the most studied nanocluster systems, TiO_2 and CdS , reveal that photogenerated electrons become rapidly trapped, and subsequently, most of them undergo electron-hole recombination within the first 50 ps.^{49, 50} In TiO_2 , the recombination was found to obey second-order kinetics,⁵⁰ while for CdS , it was fit to a biexponential with two rates attributed to the geminate and nongeminate recombination.⁵¹ These studies demonstrated that the overall efficiency of the nanocluster as a photoactive species in technical applications strongly depends on the trapping and recombination kinetics at the very early times. The time scale and mechanism for electron trapping is not as well understood. It is generally believed that photogenerated electrons are trapped at the surface of the semiconductor nanoclusters since most of the defects and impurities are at the surface.⁵⁰⁻⁵²

The relation between the dynamics of the charge carrier trapping and the size of the nanoclusters was studied by Cavaleri *et al.* for a colloidal solution of ZnO .⁵³ The early time dynamics for the 3.2 and 6.2 nm diameter nanoclusters are shown in Figure 1.17. The UV (310 nm) pump pulse excites a number of electrons from the valence band to the conduction

band in the cluster. The rise in the absorption at 620 nm was attributed to the electron trapping since the absorption in ZnO in the red (620 nm) region has been assigned to electrons trapped on the nanocluster. The subsequent decay was due to the electron-hole recombination. The trapping time was found to decrease with increasing cluster size. The trapping time extracted from the fits were 70 ± 20 fs and < 30 fs for the 3.2 and 6.2 nm diameter ZnO, respectively. The increase in the trapping rate was consistent with the increase in the number density of the interior atoms which acts as a trap center in the nanocluster.

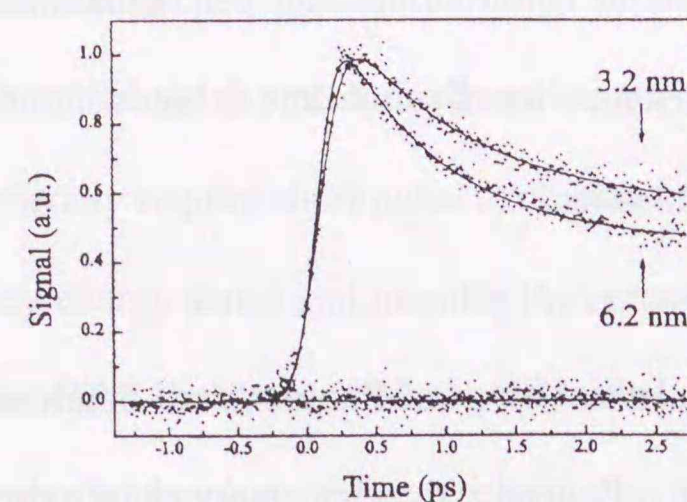


Figure 1.17. Pump-probe absorption data, pump wavelength=310 nm and probe wavelength=620 nm, for the trapping dynamics in 3.2 and 6.2 nm diameter ZnO clusters (After Ref. 42).

Most of the semiconductor nanoclusters utilized in photocatalytic applications are in the form of a powder or opaque suspensions instead of optically transparent colloids. Therefore, time-resolved diffuse reflectance spectroscopy, in which diffuse reflected light of a probe beam from the sample is collected instead of the transmitted light, is a useful method. In this respect, Asahi *et al.*⁵⁴ applied femtosecond diffuse reflectance spectroscopy to a TiO_2 suspension system to investigate the interfacial electron transfer dynamics from photoexcited TiO_2 powder to an adsorbed molecule. Figure 1.18 shows the transient absorption spectra of the TiO_2 powder (diameter: 100 nm) dispersed in water with and without methyl viologen (MV^{2+}) as an electron acceptor after excitation by UV (390 nm) light. Broad absorption spectra extending over the entire visible region due to trapped electrons and holes were observed up to 6 ns accompanied with a slight red-shift in the spectra. This shift in the spectra suggests that at least two kinds of trapped electrons or holes, whose recombination dynamics are quite different from each other, are generated. Other groups also suggested a similar conclusion.⁵⁰

In the case of adding MV^{2+} to a solution, a new absorption band was observed centered around 605 nm. This maximum peak was assigned to the absorption of MV^+ which is generated by a direct electron injection from the excited TiO_2 . Thus, from Figure 1.18, it was proved that the interfacial electron transfer from the photoexcited TiO_2 to the adsorbed MV^{2+} occurs at least in 10 ps.

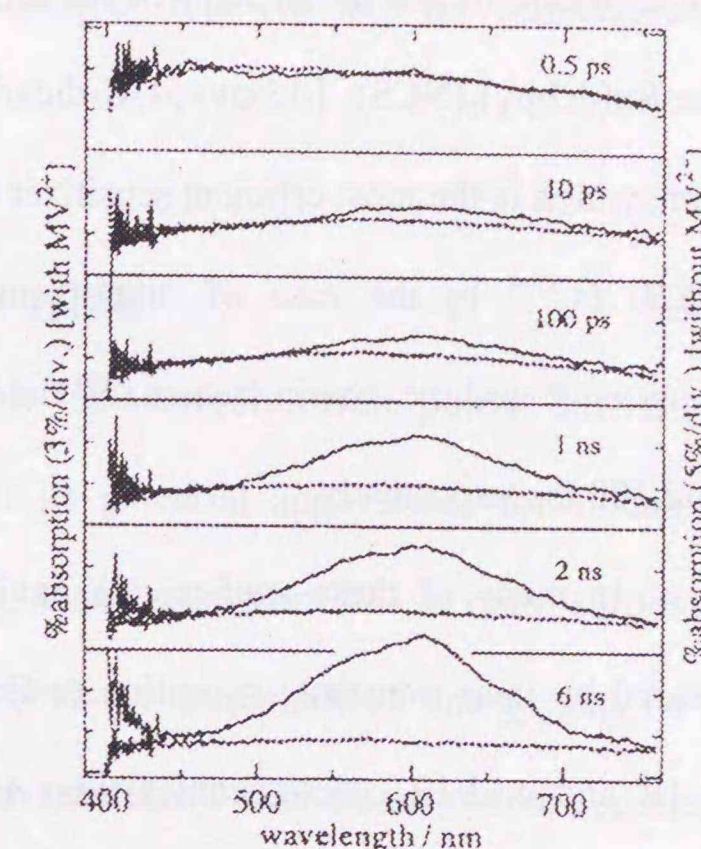


Figure 1.18. Transient absorption spectra of the optically scattering TiO_2 powder (1.5 g/10 ml) dispersed in water of pH 10 without MV^{2+} (dotted lines) and with MV^{2+} (solid lines, $\text{MV}^{2+} = 0.7$ mol/l). Excitation wavelength is 390 nm (After Ref. 43).

1.5.3. Ultrafast Phenomena in Dye-Sensitized Photoelectrochemical Cells

Wide bandgap semiconductors may be sensitized to visible light by the adsorption of dyes to their surface. There is currently considerable interest in the interfacial charge transfer kinetics of such dye-sensitized noncrystalline semiconductors, which is largely due to recent developments in nanocrystalline electrochemical photovoltaic devices.⁵⁵ The function of these devices is based upon electron injection from the photoexcited state of the dye into the conduction band of a semiconductor. Photoelectrochemical solar cells based on dye-sensitized TiO_2 films (Grätzel cell¹⁹) have received much attention in recent years because of their high solar to electric power conversion efficiency. It is generally agreed that a fast electron injection from the sensitizer to the semiconductor might be one of the key factors to achieve a high-energy conversion efficiency.⁵⁵

A detailed understanding of the mechanism and time scale of electron transfer from the surface adsorbed dye to the semiconductor will help to explain the high conversion efficiencies and to further improve them. In this respect, femtosecond laser techniques make it

possible to explore the initial steps of the electron injection and recombination. For example, in the $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ [$\text{dcbpy}=(4,4'\text{-dicarboxy-2,2'-bipyridine})$] (or N3) sensitized TiO_2 system, which is the most efficient sensitizer dye reported to date,^{19(b)} electron injection occurs in <150 fs.^{55(e)} In the case of other sensitizers such as coumarin 343,^{55(f)} a perylene derivative,^{55(g)} and the cyanin system,^{55(h)} the injection time was reported at ca.200 fs, ca. 190 fs, and 100 fs, respectively.

In many of these studies, the excited state dynamics of the dye molecules were measured by their transient absorption or fluorescence decay.⁵⁵ More recently, femtosecond near IR and mid IR spectroscopies were used to study these interfacial electron transfer reactions.⁵⁶ This technique can directly probe the absorption of electrons inside the semiconductors without the complication of broad electronic transitions of the adsorbates. It has been well demonstrated that in bulk⁵⁷ semiconductor materials, conduction band electrons in semiconductors have strong absorption in the infrared region.⁵⁸ Thus, femtosecond IR spectroscopy can probe injected electrons as well as the adsorbate vibrational spectral change. Figure 1.19 shows the transient mid IR signal of the N3 sensitized TiO_2 , Al_2O_3 , and ZrO_2 systems after these samples were excited by a 400 nm femtosecond pump pulse.^{56(f)} Transient absorbance due to the injection of electrons from N3 into the conduction band of a semiconductor was only observed for the N3/ TiO_2 system. From their analysis, the upper limit on the electron injection time was found to be 50 fs. No transient absorbance was observed in the case of the N3/ Al_2O_3 or N3/ ZrO_2 systems. Since the lower level of the conduction band of a semiconductor exists at a higher position than the excited state of N3, in

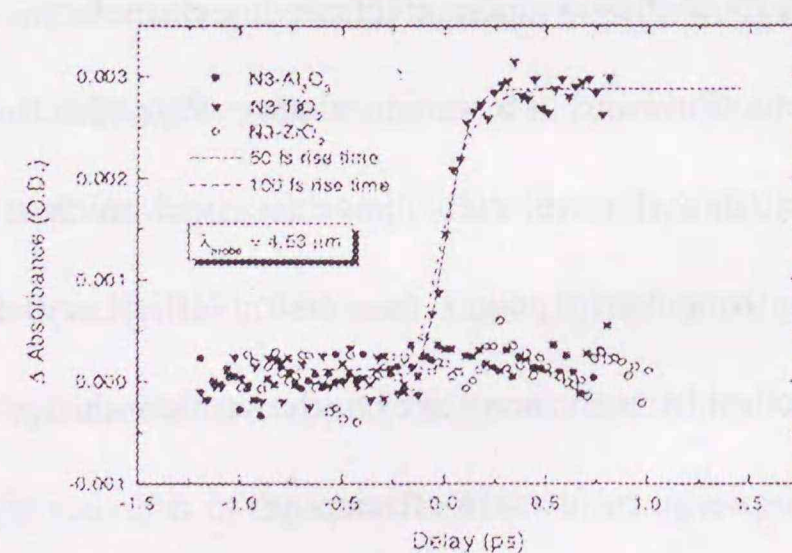


Figure 1.19. Time-resolved infrared absorption data for probe wavelength of $4.9 \mu\text{m}$ following photoexcitation by 400 nm, 100 fs pulses. The rise time indicate an injection time ~ 50 fs (After Ref. 45(d)).

the case of Al_2O_3 and ZrO_2 , any electron injection from N3 into the semiconductor is inhibited.

1.6. Formation and Properties of Porous Silicon (PSi)

The recent discovery of efficient visible light emission from porous silicon (PSi)⁵⁹ has received considerable attention because of its potential applications for silicon-based optoelectronic devices.⁶⁰ This strong visible light emission from PSi is quite surprising in view of the fact that bulk crystalline Si has a relatively small indirect energy gap. At room temperature, its energy gap is about 1.1 eV, which results in a very weak infrared emission.

The origin of visible light emission from PSi is still under debate. One explanation for visible light emission is based on the quantum confinement effect⁶¹⁻⁶³ arising from nanometer-sized Si which is produced during the electrochemical anodizing process. As the characteristic size of a semiconductor is reduced to the nanometer regime, confinement of electron and hole wave functions efficiently increases the bandgap of the material and, hence, the energy of the luminescent photon.⁶² In the case of Si, particle sizes with dimensions below 5 nm produces a blue-shift in the optical bandgap from 1.1 eV into the range of 1.5 to 1.9 eV due to this quantum confinement effect.⁶³ The contribution of chemical species such as siloxene ($\text{Si}_6\text{O}_5\text{H}_6$) to the luminescence has also been pointed out.⁶⁴

1.6.1. Formation of PSi

PSi is typically prepared by anodic etching of Si in HF solution. The conventional methods are to electrochemically anodize bare Si wafers in HF-based solutions in a two-electrode electrochemical cell as shown in Figure 1.20.

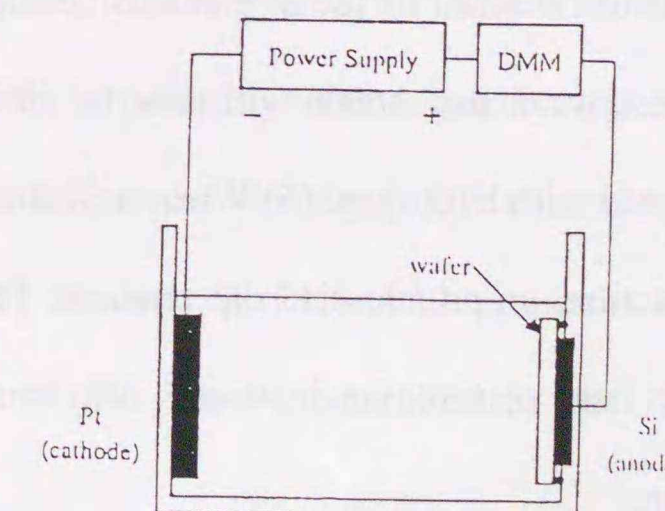


Figure 1.20. Schematic of equipment setup for electrochemical anodization of Si wafer (After Ref. 60(c)).

If the Si is under anodic bias, PSi formation is observed as long as the reaction is limited by the charge supply from the electrode and not by ionic diffusion in the electrolyte. This condition is fulfilled for a current density below a critical value which leads to electropolishing on the Si surface.⁶⁵ The inner surface of PSi was found to be covered with hydrogen.⁵⁵

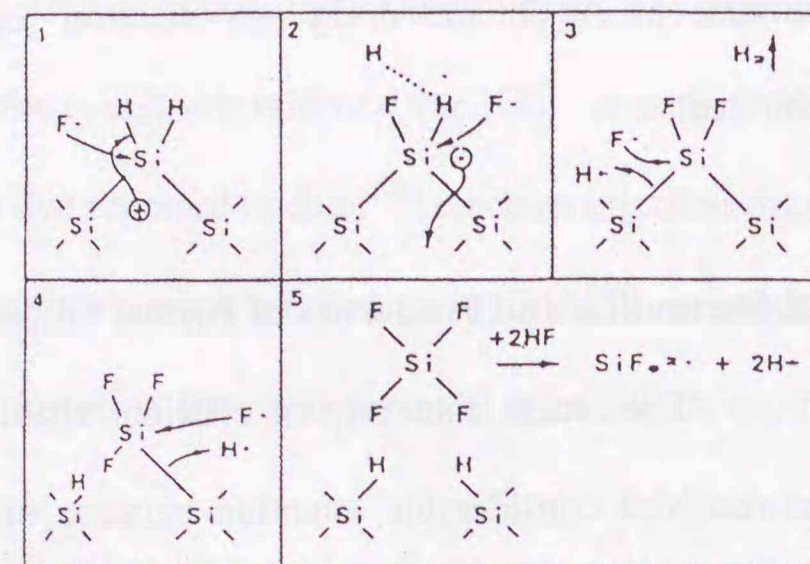


Figure 1.21. Proposed dissolution mechanism of silicon electrodes in hydrofluoric acid associated with porous silicon formation. (1)-(5) indicate the sequence of reaction steps involving F, H, Si, holes, and electrons (After Ref. 63).

From these facts, Lehmann *et al.*⁶⁷ proposed a dissolution mechanism as schematically shown in Figure 1.21. For PSi formation, it is essential that a Si surface terminated by hydrogen is virtually inert against further attack of fluoride ions as long as no holes are available at the Si electrode because the electronegativity of H is about the same as that of Si and the induced polarization is low. (1) If a hole reaches the surface, nucleophilic attack of the Si-H bonds by fluoride ions can occur and a Si-F bond is established. (2) Due to the polarizing influence of the bonded F, another fluoride ion can attack the Si-H bond and a hydrogen molecule is generated along with the injection of one electron into the electrode. (3) Due to the polarization induced by the Si-F bonds, the electron density of the Si-Si back-bond is lowered and these weakened bonds will now be attacked by HF (4) so that the Si surface atom is terminated with hydrogen. (5) When a Si atom is removed from an atomically flat surface by this reaction, an atomic size dip remains. This change in surface geometry will change the electric field distribution in such a way that a hole transfers preferentially occurs at this location.

If the diameter of the remaining Si approaches a nanometer size, the bandgap in this structure increases due to the quantum confinement.⁶⁷ Figure 1.22 shows the band diagram of

the PSi/bulk Si interface. It needs additional energy, E_q , for a hole to penetrate into a wall between the two pores. As a result, the pore walls will be depleted of a hole and therefore, it will become chemically inert against HF whereas the dissolution reaction continues at the pore tip. This process of wall thinning will continue until the energy barrier increases to a value at which a hole can no longer enter the wall and at last, the wall becomes depleted of a hole and dissolution stops. Applying a higher anodic bias to the substrate will increase the energy of a hole and therefore, decrease the diameter of the remaining walls and produce PSi with a larger bandgap.

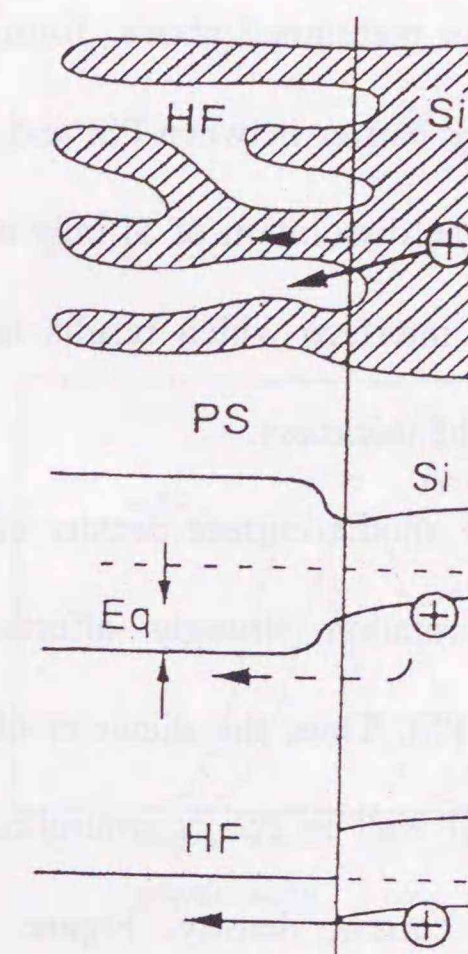


Figure 1.22. Upper part shows a sketch of the interface between PSi and bulk Si. The two possibilities for a hole to cross the interface are marked by arrows. The lower part of the figure shows the corresponding band diagrams. The required energy for a hole to enter the electrolyte via the porous structure (broken arrow) is larger by E_q than the energy that is required to enter the electrolyte directly (solid arrow) (After Ref. 67(a)).

1.6.2. Structure of PSi

The structure of PSi has been extensively studied using SEM,⁶⁸ TEM,⁶⁹ XPS,⁷⁰ AES,⁷¹ XRD,⁷² IR,⁷³ BET,⁷⁴ etc. The morphology of PSi is primarily determined by the etching conditions such as anodic reaction time,⁷⁵ anodic current density,⁷⁶ HF concentration,⁷⁷ presence of light illumination and its wavelength.⁷⁸ To study the PL and EL properties of PSi, it is very important to note that the structure of PSi can be controlled by the etching conditions.

Figure 1.23 shows the relation between the anodic reaction time and the thickness of the PSi.^{75(a)} At a constant current density (i_A), the thickness increases in proportion to the time.

For a higher i_A , the formation rate of PSi increases. As mentioned above, formation of the energy barrier between PSi and bulk Si leads to the dissolution of Si only at the PSi/bulk Si interface which results in the increase of the thickness.

The anodic current density during the PSi formation strongly affects the porosity of PSi. Thus, the diameter of the remaining Si wall in PSi is controlled by the anodic current density. Figure 1.24 shows the dependence of the porosity of PSi on the anodic current density for different HF concentrations.^{76(a)} It seems that the porosity decreases with increasing HF concentration. However, a minimum in the porosity-anodic current density relation appears around 40 mA/cm² for all electrolytes. For higher current densities, the porosity increases with the anodic current density. The high resolution SEM images in Figure 1.25 shows that the PSi has a small particle-like structure, with particle sizes 10 to 50 nm in diameter.^{76(b)} It is clear that the size of these particles varied according to the forming anodic current

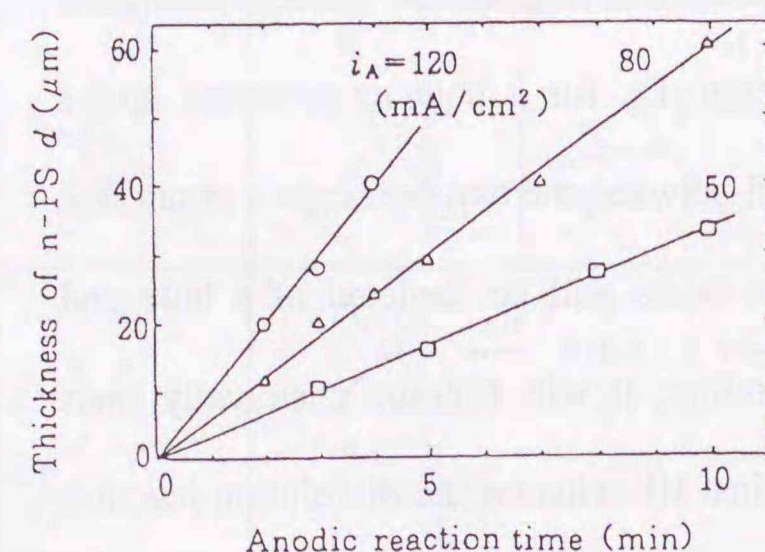


Figure 1.23. Thickness of PSi formed at different current densities as a function of the anodic reaction time (After Ref. 75(b)).

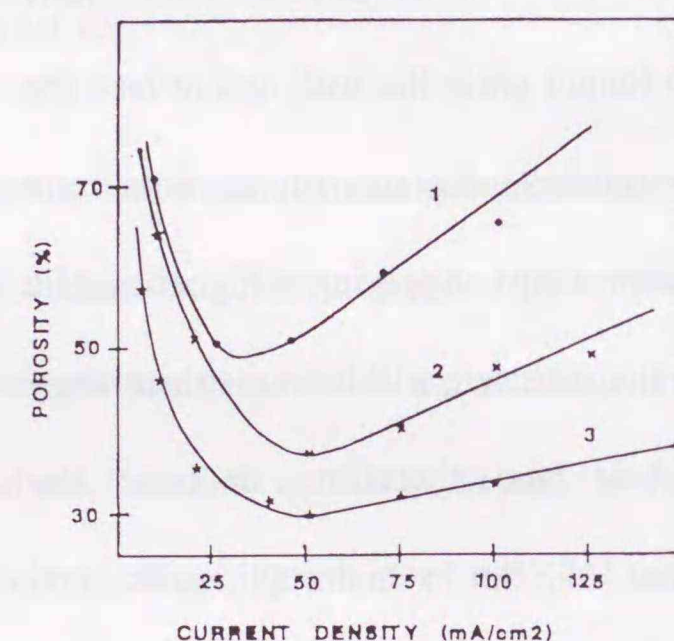


Figure 1.24. Porosity of PSi as a function of the forming current density for PSi in 1: 10 % HF, 2: 15 % HF, 3: 25 % HF (After Ref. 76(a)).

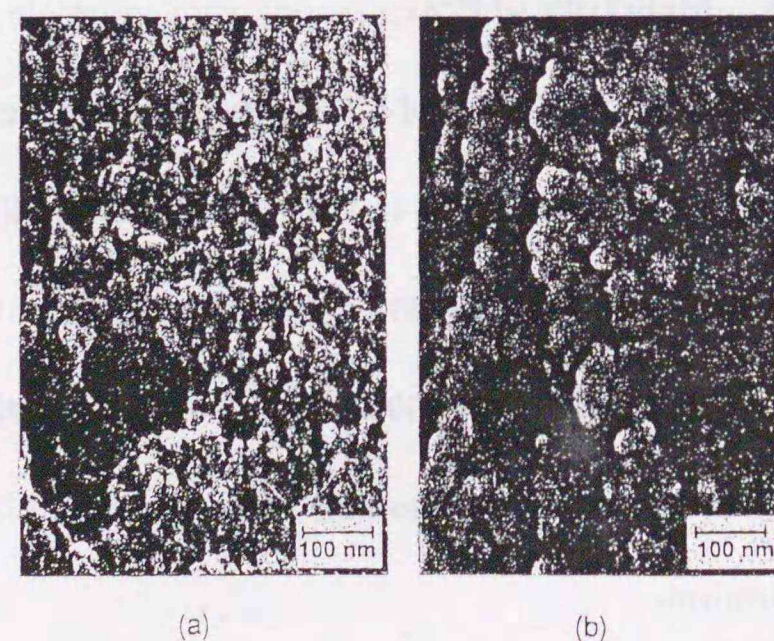


Figure 1.25. Cross sectional high-resolution SEM images of the PSi anodized at current densities of (a) 200 and (b) 25 mA/cm² for 5 min (After Ref. 76(b)).

density and is smaller for the large forming anodic current densities.

1.6.3. Luminescence Properties of PSi

1.6.3.1. PL Properties

Most of the studies reported so far have concentrated on the PL properties of PSi.⁷⁹⁻⁸¹ PSi can be made to emit photons with a peak wavelength varying from the infrared to green, a wavelength range of ca. 900 to 500 nm under short wavelength (from ca. 500 to 300 nm) excitation. Figure 1.26 shows a typical PL spectra from p-type PSi (p-PSi) and n-type PSi (n-PSi) excited by a He-Cd laser beam at room temperature.⁷⁹ Both the red and orange PL emission from p- and n-PSi are stable, reproducible and clearly observable even in daylight. Moreover, the quantum efficiency exceeds ca. 10 %.

Figure 1.27 shows the effect of extended chemical etching in HF solution on the PL from p-PSi.⁵⁹ Clearly, the PL spectra shift to a shorter wavelength with increasing chemical etching time. The PL spectra also show a blue-shift with an increasing anodization current density (Figure 1.28).^{76(b)} According to Herino *et al.*,^{76(a)} the porosity of PSi increases with an increasing anodization current density and, therefore, the behavior of the PL spectra qualitatively reflects the

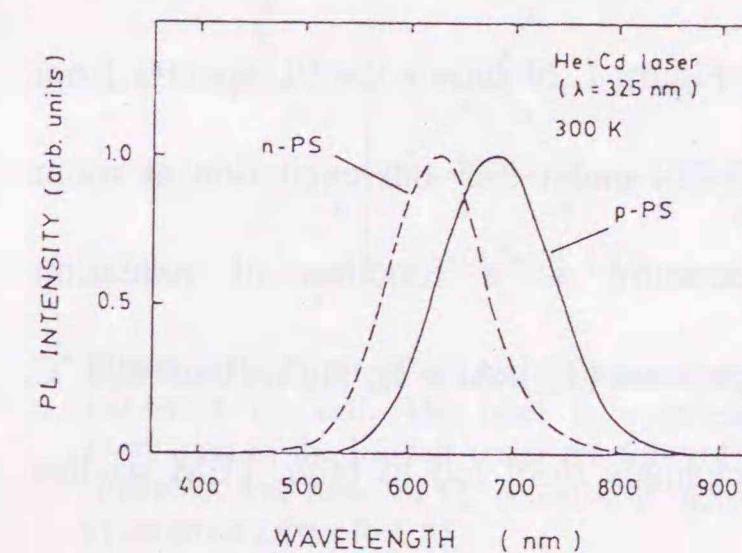


Figure 1.26. Typical room temperature PL spectra of p-PSi (solid curve) and n-PSi (Broken curve) excited by He-Cd laser beam (After Ref. 79).

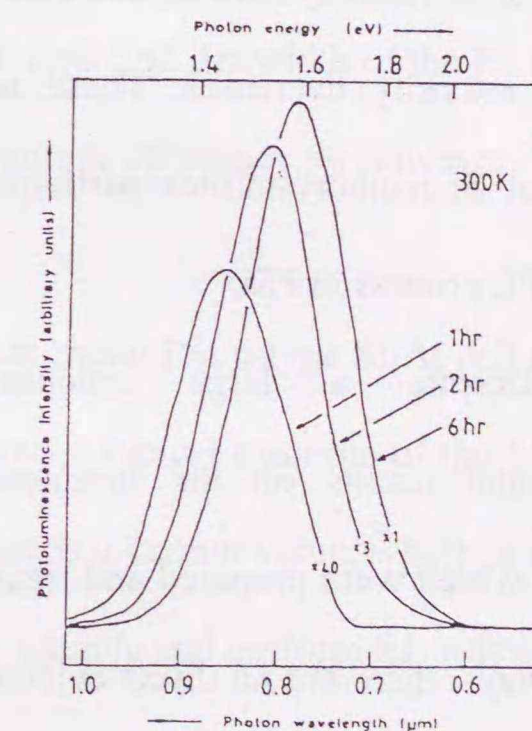


Figure 1.27. Room temperature PL from p-PSi after immersion in 40 % aqueous HF for the times indicated (After Ref. 59).

differences in sample porosity and hence, in the dimensions of the Si nanocrystallites within the PSi.

Kanemitsu *et al.*⁸⁰ also demonstrated that an efficient visible PL can be obtained after the rapid thermal oxidization (RTO) of PSi. Figure 1.29 shows the PL spectra from RTO PSi under 325 nm excitation at room temperature as a function of oxidation temperature (T_{ox}). At a T_{ox} higher than 800 °C, PL changes from red to blue. TEM studies indicated that the number of nanocrystallites decreases rapidly with increasing T_{ox} .⁸² As the number of nanocrystallites decreases, the blue PL intensity decreases. These results imply that Si nanocrystallites participate in the blue PL process in PSi.

Despite a large amount of experimental results on the luminescence from PSi which were prepared and treated in various ways, there are no direct evidence of a correlation between the dimensions of the Si nanocrystallites and the PL spectra.

1.6.3.2. EL Properties

The studies of EL from the PSi/solid interface⁸³⁻⁸⁵ is more important than that of PL as far as technological applications are concerned. In this respect, Richter *et al.*⁸⁵

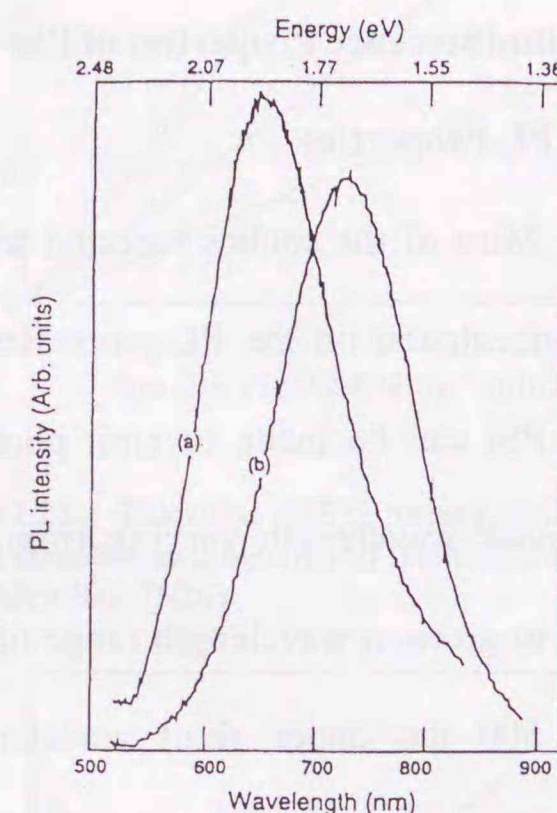


Figure 1.28. PL spectra of PSi anodized at current densities of (a) 200 and (b) 25 mA/cm² for 5 min (After Ref. 76(b)).

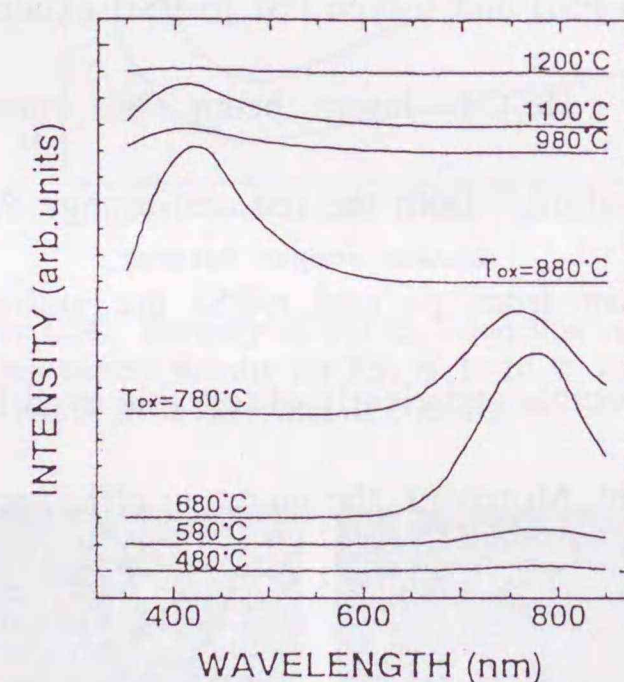


Figure 1.29. PL spectra from oxidized PSi under 325 nm excitation as a function of oxidation temperature (T_{ox}) (After Ref. 80).

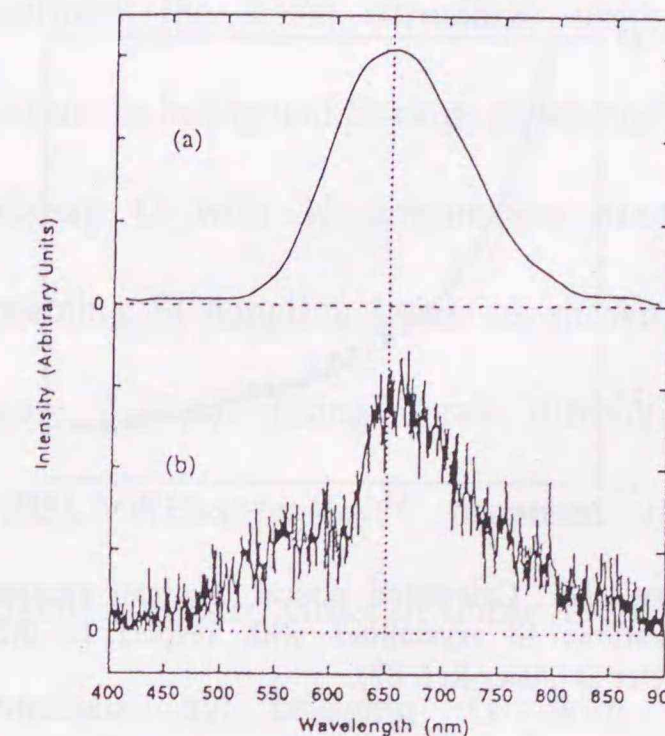


Figure 1.30. Spectra obtained from Au/PSi/n-Si cell. (a) PL and (b) EL (After Ref. 83).

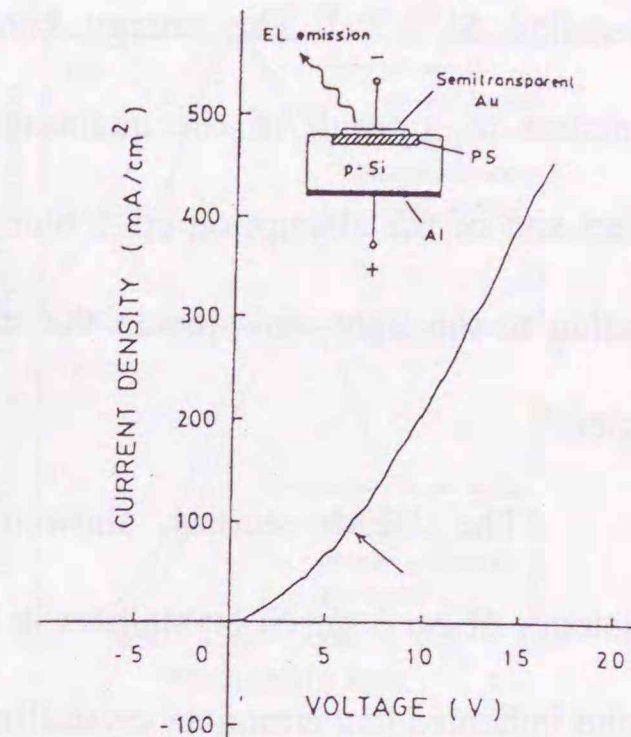


Figure 1.31. Current-voltage characteristics of a PSi-based EL cell. The inset is a schematic illustration of the EL cell under the forward bias condition. The onset of EL emission is indicated by an arrow (After Ref. 85).

demonstrated that a visible EL can be observed by applying a dc or ac voltage to a solid-state contact on top of the PSi. Figure 1.30(b) shows the EL spectrum obtained from the Au/PSi/n-type Si cell at a very high voltage (200 V). The wavelength and linewidth of the PL spectrum (Figure 1.30(a)) agree with the EL spectrum. The quantum efficiency is, however, very low due to the large potential drop at the Au/PSi interface.

Koshida *et al.*⁸⁵ demonstrated that a transparent metal/PSi/p-type Si/Al cell emits EL with a relatively low applied voltage. Figure 1.31 shows a typical example of the I-V curves of the EL cells. When the forward current density exceeds a certain value, which is indicated by the arrow in Figure 1.31 (about 90 mA/cm² at 7 V), a stable and uniform EL was observed.

1.6.4. Mechanism of Visible Light Emission from PSi

1.6.4.1. Quantum Size Effect

Canham was the first to attribute the visible light emission from PSi to the quantum size effect.⁵⁹ The quantum size effect appears if the characteristic diameters of the Si nanocrystals became less than the dimensions of the free-exciton Bohr radius of the bulk

crystallite Si.^{60, 86, 87} The energy bandgap increases as a result of the quantum size effect and of the absorption edge blue-shift leading to the light emission in the visible region.⁸⁸

The TEM studies showed the existence of ca. 3 nm Si crystallites in PSi^{82, 89} and indicated that complete crystallinity is retained in the PSi as shown by the transmission electron diffraction (TED) patterns.

Theoretical calculations indicate that the quantum size effect in crystallite Si wire or dots with diameters less than 5 nm can produce a visible light emission.^{60, 86, 87} Figure 1.32 shows the relation between the calculated optical bandgap and size of the Si crystallite.⁸⁷ It shows that when the sizes range from 0.8 to 4.3 nm, the bandgap varies from 5 to 1.6 eV.

1.6.4.2. Siloxene Derivatives

Siloxene ($\text{Si}_6\text{O}_3\text{H}_6$) is one of the few silicon based materials which show a strong luminescence even at room temperature.⁶⁴ Brant *et al.*⁶⁴ have proposed that this siloxene derivatives are present in PSi and are responsible for the visible luminescence. The three basic structural models of siloxene proposed in the literature are based on sheet-like structures and are illustrated in Figure 1.33.⁹⁰ Kautsky⁹⁰

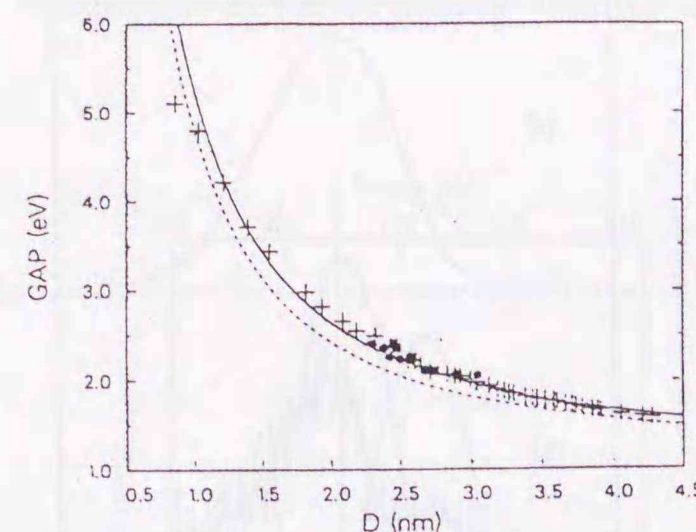


Figure 1.32. Calculated optical bandgap energies for various Si crystallites with respect to their diameter D (After Ref. 87).

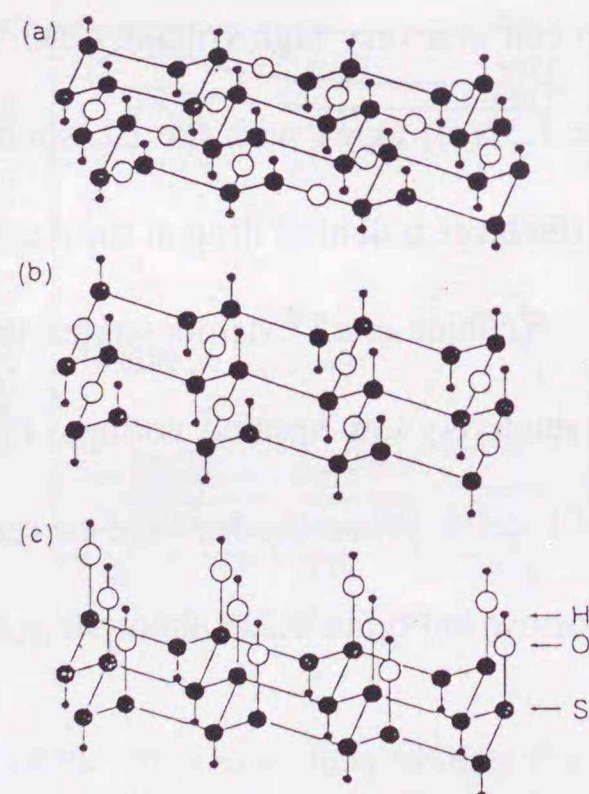


Figure 1.33. Structural models for siloxene ($\text{Si}_6\text{O}_3\text{H}_6$). (a) Monolayers formed by hexagonal Si rings interconnected by oxygen bridges. The fourth bond of Si is terminated by hydrogen. (b) Monolayers formed by linear Si chains interconnected by oxygen, terminated by hydrogen. (c) Si monolayers with alternating OH and H bond terminators (After Ref. 90).

described the basic structural unit of siloxene as hexagonal Si rings connected by bridging O with H termination of the remaining Si dangling bonds as shown in Figure 1.33(a). Using x-ray diffraction (XRD), Weiss *et al.*⁹¹ proposed that siloxene consisted either of linear Si chains connected by bridging O with H termination of the remaining Si dangling bonds as shown in Figure 1.33(b), or Si monolayers with dangling bonds terminated by alternating H and O-H bonds as shown in Figure 1.33(c).

Many parallel characteristics exist between the optical properties of siloxene and PSi. Figure 1.34 shows the typical PL spectra obtained from PSi produced by different etching conditions and from siloxene annealed at 400 °C.⁶⁴ In the case of Figure 1.34(a), etching of PSi performed in HF + HCl solution resulted in a luminescence peak at 690 nm. This is in good agreement with the luminescence of Kautsky siloxene annealed at 400 °C. In Figure 1.34(b), the red luminescence peak at 760 nm was obtained from a PSi after etching in HF. This luminescence agrees with the luminescence of the Wöhler siloxene annealed at 400 °C. The agreement between the light emission from PSi and siloxene strongly suggests a common origin of the luminescence in both cases.

A characteristic feature of the luminescence decay observed in PSi as well as in siloxene is a non-exponential type which becomes faster for shorter wavelengths.⁶⁴ The lifetime was identical for PSi and siloxene and depended only on the sample temperature. Thus, it was clearly demonstrated that recombination processes in both PSi and siloxene are identical.

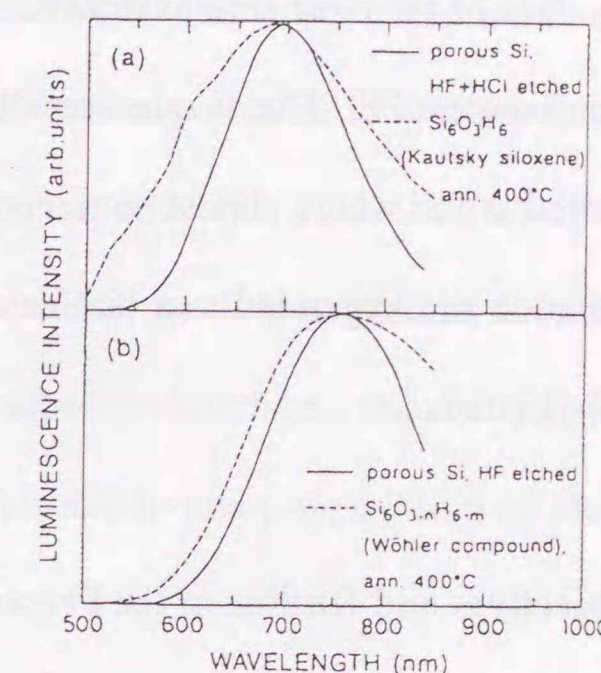


Figure 1.34. Room temperature PL spectra of anodically oxidized PSi and thermally annealed siloxene compounds (After Ref. 90).

One of the most serious drawbacks for this model is that oxygen needs to be present in all luminescent PSi. This is questionable, since other groups have shown that luminescence is observed at PSi where almost no trace of oxygen exists.⁹² It has been also reported that the incorporation of oxygen led to a luminescence degradation, when Si-H bonds were replaced by O-Si-H bonds.⁹³

1.7. Objectives and Outline of the Present Thesis

The objectives of this work are to investigate the optical properties and charge carrier dynamics of semiconductor electrodes and semiconductor photocatalysts using (photo)electrochemical luminescence and recently developed ultrafast time-resolved laser spectroscopic measurements. Luminescence measurements have been widely used for the examination of semiconductors since they provide information about recombination processes that play very important roles in determining the properties of semiconductors. This method is also valuable for the semiconductors under electrochemical conditions to characterize the structure of the semiconductor/solution interface, i.e., charge and potential distribution at the interface. Moreover, in the case of a semiconductor, the lifetime of the electron-hole pairs generated by illumination and also the electron transfer at the semiconductor/solution interface affect the rate of the photoelectrochemical or photocatalytic reaction. Thus, it is clearly desirable to directly observe the electron dynamics with faster time resolution. In order to access information on these fast dynamic processes occurring inside a semiconductor or at the semiconductor/solution interface, ultrafast time-resolved spectroscopy becomes a useful method to solve these problems.

In the present work, porous silicon (PSi), which recently received considerable attention by the discovery of efficient visible light emission, was used to investigate the optical properties and to clarify the mechanism of visible light emission by luminescence measurements under electrochemical conditions. Femtosecond time-resolved spectroscopy

was applied to semiconductor powders and the semiconductor/electrolyte solution interface to investigate the initial stages of electron-hole recombination processes in semiconductors and to determine the interfacial electron transfer reaction, respectively.

In **Chapter 2**, the EL and PL properties of PSi have been studied to clarify the charge transfer reaction at the PSi/electrolyte solution interface, and to consider the mechanism of the visible light emission from PSi for both n- and p-type PSi in an electrolyte solution.

The EL from p-PSi was investigated during the anodic oxidation of PSi in an electrolyte solution. The EL mechanism from p-PSi in an electrolyte solution was proposed by comparing the integrated EL intensity and the consumed Si-H_n species quantitatively determined by the in situ FT-IR measurements.

A voltage-tunable blue-shift in the EL spectra and in the time dependent blue-shift of the EL spectra from an n-PSi were observed in the electrolyte solution containing S₂O₈²⁻ as a hole injector. The change in the emission site from large-sized Si crystallites to smaller-sized ones in the n-PSi layer were considered as the reason for the blue-shift in the EL spectra.

The photoelectrochemical and PL properties of the p-PSi/electrolyte solution interface were investigated. Quenching of the PL intensity accompanied a blue-shift in the PL spectra were observed. These results were explained by considering the dependence of electron accumulation on the conduction band levels in the PSi layers.

In **Chapter 3**, the initial stages of the photoexcited electron-hole recombination processes in various TiO₂ semiconductor powders were investigated using femtosecond time-resolved diffuse reflectance spectroscopy. The observed charge carrier dynamics depending on the nature of TiO₂ powders were discussed in terms of their physical properties. The effects of the excitation wavelength on the ultrafast charge carrier recombination dynamics are shown and discussed with respect to the optical and photocatalytic properties of the semiconductor particles.

In Chapter 4, femtosecond visible pump-IR probe spectroscopy, which is a new in situ technique capable of directly probing the electron transfer processes in semiconductor, was applied to the p-type Si/electrolyte solution interface. The potential dependence on the transient IR absorption was investigated. It was demonstrated for the first time that femtosecond IR spectroscopy is a practicable technique for studying the electron transfer dynamics at the semiconductor/electrolyte solution.

Finally, Chapter 5 summarizes the present results.

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Chapter 2

Photoluminescence (PL), Electroluminescence (EL) and Photoelectrochemical Properties of Porous Silicon (PSi) Electrodes

2.1. Introduction

Since the recent discovery of visible light emission from porous silicon (PSi),¹ many researches on PSi have been carried out by many research groups because of the possible development of Si-based optoelectronic devices.² The electronic properties of bulk silicon cannot explain the above phenomenon as silicon has the indirect bandgap of 1.1 eV. One explanation for the visible luminescence is based on the nanometer-size crystalline structure for PSi.³⁻⁵ This structure can exploit quantum confinement effects which are responsible for bandgap widening into the visible range.³⁻⁵ The contribution of chemical species such as siloxene ($\text{Si}_6\text{O}_3\text{H}_6$) to the luminescence has also been pointed out.⁶

The luminescence properties of the semiconductor/electrolyte solution interface are known to provide useful information of the mechanism of electrochemical reactions as well as the potential distribution at the interface.⁷

In this chapter, electroluminescence (EL) at p-type PSi (p-PSi) in Na_2SO_4 aqueous solution during constant anodic oxidation, EL at n-type PSi (n-PSi) in Na_2SO_4 aqueous solution, containing $\text{S}_2\text{O}_8^{2-}$ as a hole injector, under cathodic polarization, and photoluminescence (PL) and photoelectrochemical properties of p-PSi in Na_2SO_4 aqueous solution were investigated.

2.2 Experimental

2.2.1. Preparation of PSi

Silicon wafers used in the present studies were n-type (1.4-2.0 $\text{ohm}\cdot\text{cm}$) and p-type

(8-12 ohm·cm) single crystals obtained from Shin-Etsu Semiconductor with a (100) surface. The wafers were cleaned first with acetone to remove organic impurities, washed with pure water and then chemically etched in 10 % HF-ethanol solution for 1 min. After ohmic contact was obtained using an In-Zn alloy, the samples were placed in an electrode holder made from Teflon so that only one face of the wafer was exposed (apparent exposed area, 0.283 cm²) (Figure 2.1). Constant current anodic oxidation was carried out in 10 % HF-ethanol solution by using a potentiostat/galvanostat (Hokuto Denko Co., HA-151) in a Teflon cell with a Pt wire as a counter electrode. In the case of n-type Si, constant current anodic oxidation was carried out under illumination with a 30 W halogen lamp (Hayashi Watch-Works Co. Ltd., LA-30) in order to provide holes which are required for the formation of a porous structure. Current density for the porous formation was 5 mA/cm², and the oxidation time was varied from 10 to 1800 s. The as-prepared p-Si was rinsed with purified water and transferred to the spectroelectrochemical cell without exposure to air before the (photo)electrochemical, the EL and the PL measurements to prevent dryness⁸ as well as native oxide growth.⁹

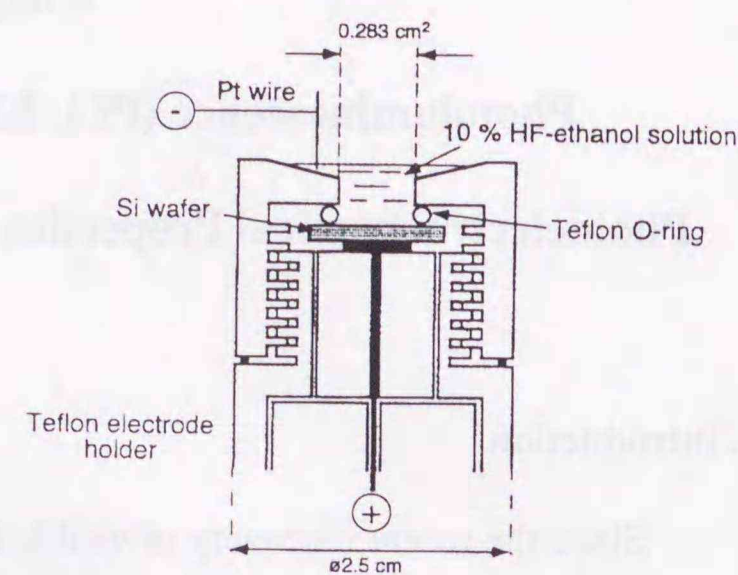


Figure 2.1. Schematic diagram of (experimental setup for p-Si preparation.

2.2.2. AFM and SEM Measurements

A NanoScope II (Digital Instruments) was used for the AFM observation of a p-Si layer prepared from p-Si wafers. All the AFM measurements were carried out in air in constant force mode by an "A-Head" (scan size: 0.7 μm). Microfabricated silicon nitride cantilevers 200 μm long with a spring constant of 0.06 N/m were used. AFM tips integrated with the

cantilevers were also made of silicon nitride and were 4 mm long with nominal radii of less than 40 nm.

A SEM (Hitachi, S-4000) was used for the observation of the surface and cross sectional structures of the p-Si layers with 15 keV electrons.

2.2.3. FT-IR Measurements

p-Si prepared from p-Si wafers were used in the FT-IR measurements. Transmission and reflection FT-IR measurements were carried out by using a Bio Rad FTS30 spectrometer with a mercury-cadmium-telluride infrared detector. Transmission spectra were obtained using a Si wafer etched in HF as a reference. An optical arrangement for in situ reflection FT-IR measurement with specially designed

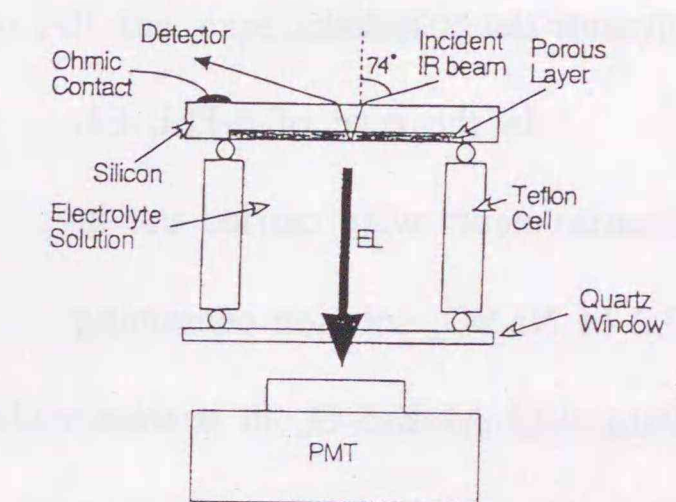


Figure 2.2. Schematic view of the spectroelectrochemical cell for simultaneous measurements of in situ reflection FT-IR and EL.

photoelectrochemical cell which enables simultaneous measurement of EL is shown in Figure 2.2. The incident angle of the IR beam was 74°, since the reflective index of an IR beam at 2000 cm⁻¹ calculated using the Fresnel equation¹⁰ is largest at this angle at a Si/water interface. The EL intensity was simultaneously detected by the EL detection system which is described below.

2.2.4. Electrochemical and EL Measurements

Electrochemical and EL measurements were done in both n- and p-Si. For p-Si, constant current oxidation was carried out in a three electrode glass cell which has an optical window. Ag/AgCl and a Pt wire were employed as a reference and a counter electrode, respectively. Electrolyte solution was prepared using reagent grade Na₂SO₄ (Wako Pure

In the case of n-PSi, EL measurements were carried out in 0.2 M Na_2SO_4 solution containing 0 to 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ in a three-electrode glass cell, which has an optical window. Ag/AgCl (sat.

EL intensity was measured by using a photomultiplier tube (PMT: Hamamatsu Photonics Co. Ltd., R1767). Applied voltage to the PMT was -0.75 kV and the output signal was amplified by using a homemade fast amplifier. The potential and the amplified PMT

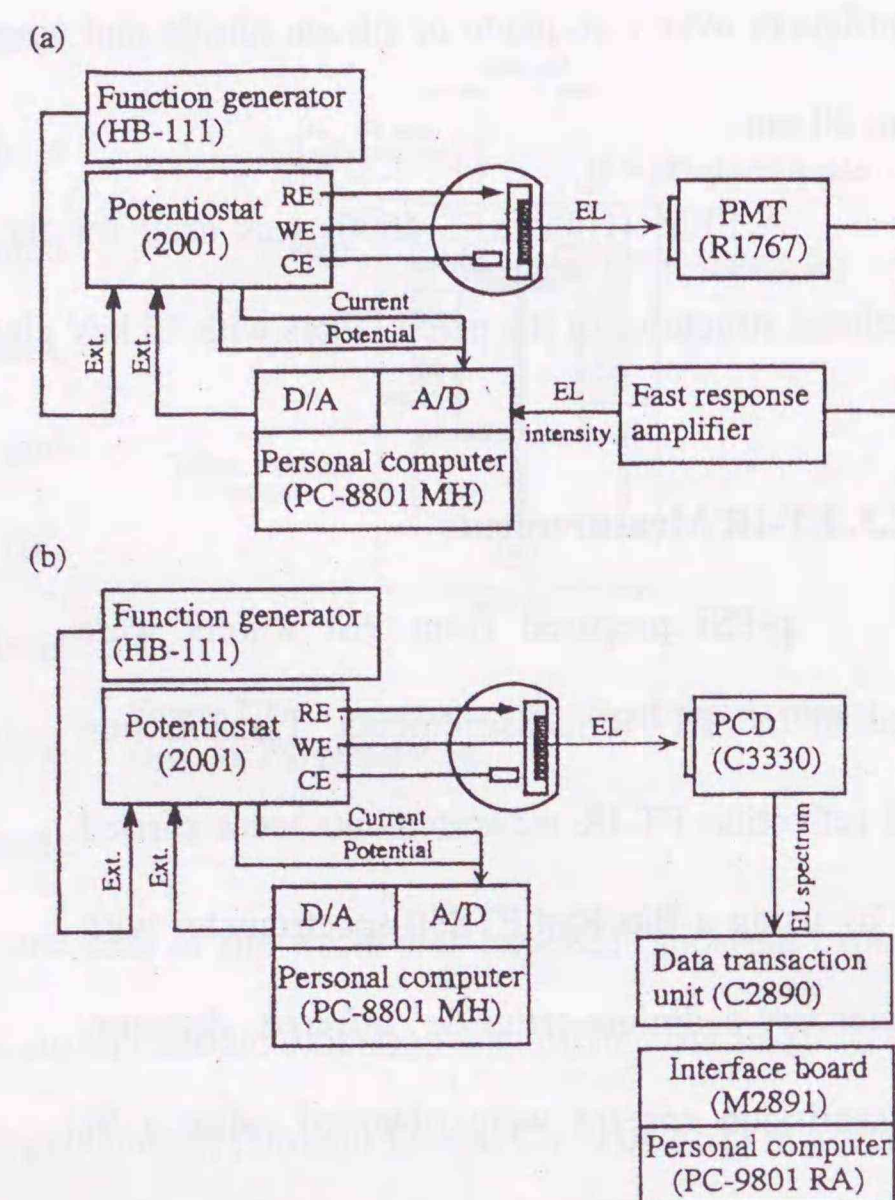


Figure 2.3. Block diagram for (a) the EL measurements and (b) the EL spectra measurements.

2.2.5. Photoelectrochemical and PL Measurements

The experimental setup for the photoelectrochemical and the PL measurements are shown in Figure 2.4. Photoelectrochemical measurements were carried out in 0.2 M Na_2SO_4 aqueous solution in a three electrode glass cell which has an optical window. Ag/AgCl (sat. KCl) and a Pt wire were employed as a reference electrode and a counter electrode, respectively. The electrolyte solution was prepared using reagent grade Na_2SO_4 (Wako Pure Chemicals Co., Ltd.) and Milli-Q water and deaerated by passing high purity nitrogen gas (99.999 %) through it prior to the photoelectrochemical and the PL measurements. Potential was controlled by using a

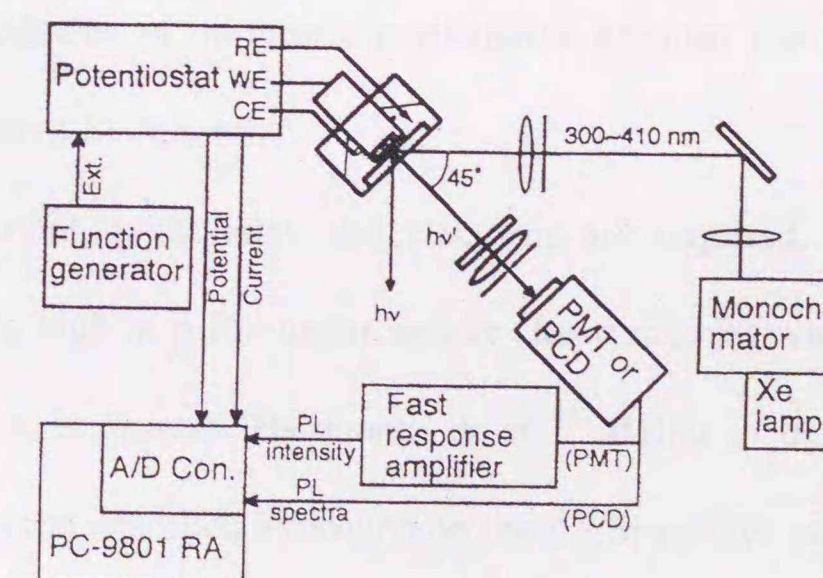


Figure 2.4. Block diagram for the photoelectrochemical and the PL measurements.

potentiostat/galvanostat (Toho Technical Research, 2001) and a function generator (Hokuto Denko Co., HB-111). A monochromatic UV light (from 300 to 410 nm) from a 500 W Xe

lamp (Ushio Electric. Co., Ltd., UXL-500D-O) was employed as an excitation light source. The excitation light intensity was kept constant by adjusting the lamp current to avoid the possible effect of excitation light intensity on the PL property. PL intensity was measured by using a photomultiplier tube (PMT: Hamamatsu Photonics Co., Ltd., R928). A long pass filter (Toshiba Glass Co., Ltd., Y-44), which allows transmission only above 410 nm, was used in order to eliminate the excitation light. The current and PMT output signals were recorded by using a personal computer (NEC Co., PC-9801RA) through a 12 bit AD converter. PL spectra were obtained by using a multichannel detector PCD with an image intensifier (Hamamatsu Photonics Co., Ltd., IMD-C3300) combined with an imaging spectrograph (Jobin Yvon, CP-200; $f=2.9$). The PCD elements were cooled to -20°C . The exposure time was 3 s, and signals were obtained without averaging the PCD response. The optical system is sensitive from 1.4–3.4 eV with a resolution of 4 nm. All the measurements were carried out at room temperature.

2.3. Visible EL from p-Type PSi/Electrolyte Solution Interface

2.3.1. Introduction

Visible EL under cathodically biased n-type PSi in contact with $\text{S}_2\text{O}_8^{2-}$ solution has been reported by several groups.¹¹ The reduction of $\text{S}_2\text{O}_8^{2-}$ by an electron supplied from the conduction band leads to the formation of the very reactive intermediate $\text{SO}_4^{\cdot -}$ in solution¹² which can inject a hole into the valence band of the n-type PSi. Recombination between an electron accumulated at the surface in the conduction band and an injected hole in the valence band results in luminescence of bandgap energy. Bsiesy *et al.*^{11(a)} reported that EL spectra of this system blue-shifted as potential was swept to more negative values.

Visible EL have been also reported at p-PSi. Halimaoui *et al.* demonstrated that EL was observed when p-PSi was anodically oxidized in aqueous electrolyte solution.¹³ A similar observation was actually made by Gee¹⁴ long before the visible PL from p-PSi was reported. He found that visible EL was observed when p-Si, which was treated with 49 % HF solution containing about 0.1 % HNO_3 until a blue interference color was visible, was anodically oxidized in various indifferent electrolyte solutions with constant current. Although he mentioned the film was in the form of amorphous Si, it must be p-PSi. The study of EL properties of p-PSi during anodic oxidation is important particularly because the anodic oxidation is often used to control the size of Si column.¹⁵

For luminescence to be observed, both holes and electrons are required. While surface concentration of holes should be high at p-PSi under anodic (forward) bias when EL is observed, no obvious electron source is present. Halimaoui *et al.*,¹³ Muller *et al.*¹⁶ and Chazalviel and Ozanam¹⁷ suggested that the adsorbed hydrogen on the p-PSi surface acted as an electron injector. Uosaki *et al.* have demonstrated by ex situ XPS¹⁸ and in situ FT-IR¹⁹ measurements that Si-H_n species exist during the EL process but disappear after reaction is ceased at p-PSi.

In this section, it was attempted to correlate the EL properties to the structure of p-

PSi prepared under various conditions by using SEM and AFM measurements and an EL mechanism was proposed by comparing the integrated EL intensity and the amount of the consumed Si-H_n species which was quantitatively determined by the in situ FT-IR measurements.

2.3.2. Results

2.3.2.1. Current-Potential and Current-EL Intensity Relations

Current – potential – EL intensity relations of the p-PSi, which was prepared by constant current (20 mA/cm²) anodic oxidation in a 10 % HF-ethanol solution for 500 s, were galvanostatically measured in 0.2 M Na₂SO₄ (Figure 2.5(a)). A current pulse of 10 s width

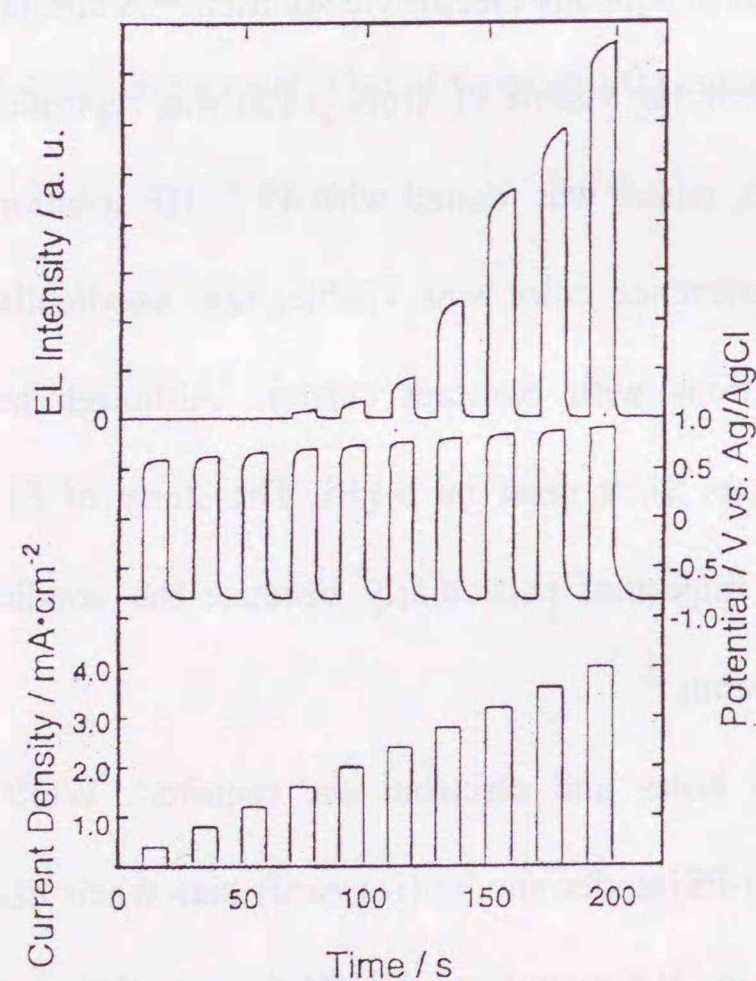


Figure 2.5(a). Time dependence of potential (middle panel) and EL intensity (top panel) at a p-PSi electrode in 0.2 M Na₂SO₄ under pulsed current application (bottom panel). The p-PSi was prepared from the p-Si (B doped, 4.89 - 8.49 × 10¹⁸ cm⁻³; 0.010 - 0.015 ohm·cm) by constant current (20 mA/cm²) anodic oxidation for 500 s in a 10 % HF-ethanol solution.

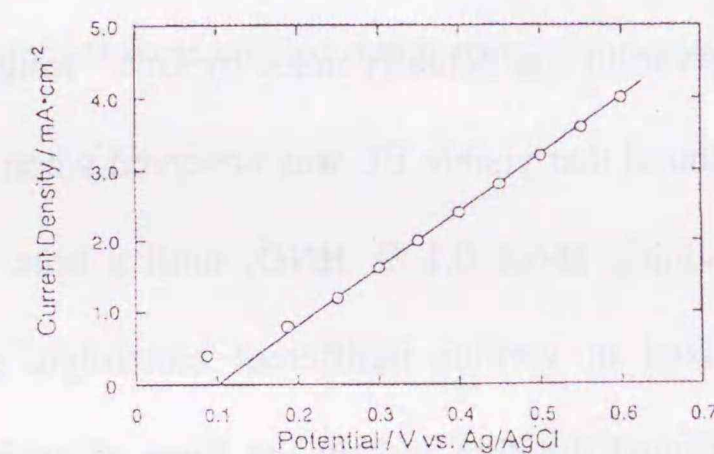


Figure 2.5(b). Current - potential - relation of the p-PSi electrode in 0.2 M Na₂SO₄.

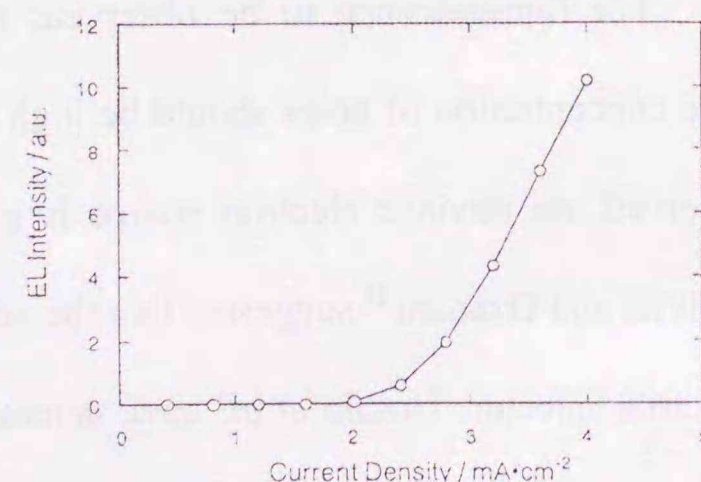


Figure 2.5(c). EL intensity of the p-PSi electrode as a function of current for anodic oxidation in 0.2 M Na₂SO₄. See text for details.

whose time sequence is shown in the bottom panel was applied, and the potential and EL intensity were recorded continuously. Both the potential and the EL intensity changed with time after the current step. Figure 2.5(b) and 2.5(c) shows the current - potential and current - EL intensity relations, respectively, in which mean values of potential and EL intensity obtained at the beginning and the end of the current step were presented. The reproducibility and the signal to noise (S/N) ratio of the EL intensity were lower than those of the potential. The relation between the current and the potential is linear when the potential was more positive than +0.2 V. EL started to increase at 2.0 mA/cm² and the EL intensity was related to the current density almost linearly in the high-potential region as shown in Figure 2.5(c). At high current density, red emission was observed even by the naked eye.

2.3.2.2. Time Dependence of Potential and EL Intensity

Detailed investigations of the time dependence of the potential and EL intensity were carried out by applying constant current to the p-PSi which had been kept at the open circuit potential. Figure 2.6 shows the time course of the electrode potential and the EL intensity at p-PSi samples, which were prepared by constant current (20 mA/cm²) anodic oxidation in 10 % HF-ethanol for 200, 500, and 1000 s, during constant current (2.4 mA/cm²) anodic oxidation in 0.2 M Na₂SO₄.

Although Halimaoui *et al.* reported that there was an induction time before EL was observed unless the porosity of the electrode

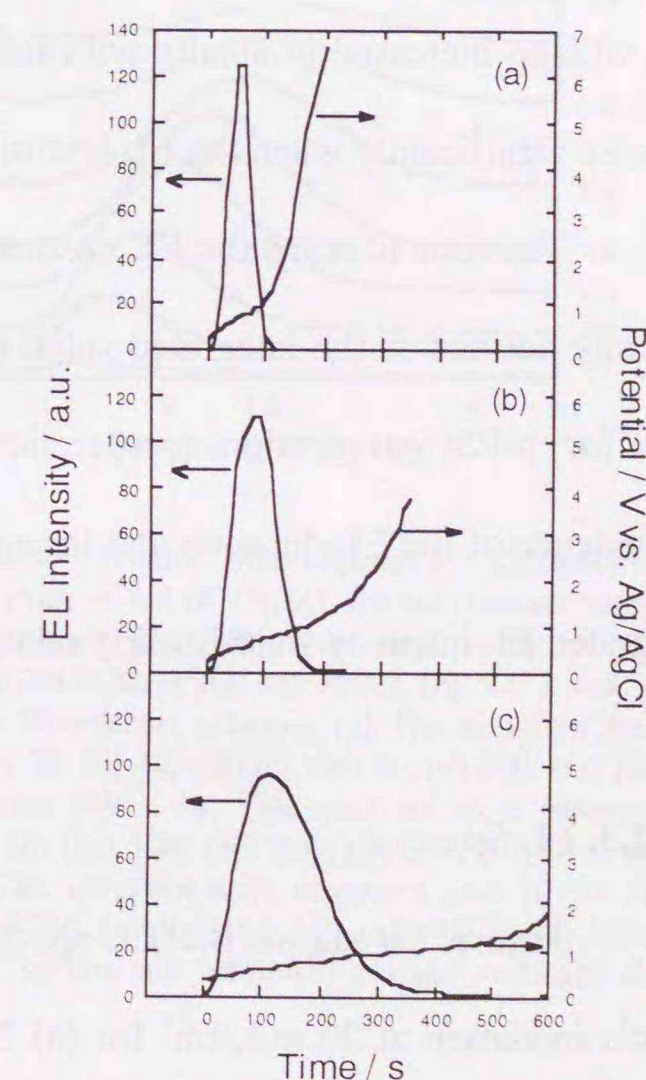


Figure 2.6. Time course of the electrode potential and EL intensity at the p-PSi electrode during constant current (2.4 mA/cm²) anodic oxidation in 0.2 M Na₂SO₄. The p-PSi were prepared by constant current (20 mA/cm²) anodic oxidation for (a) 200 s, (b) 500 s and (c) 1000 s in 10 % HF-ethanol solution.

was very high,¹³ EL was observed as soon as the anodic current started to flow for all cases. This may be because the p-PSi samples were transferred to the electrochemical cell just after the preparation of the porous layer with a pure water droplet and, therefore, the p-PSi surfaces were never dried. It has been known that if the p-PSi surface is dried, permeation of an electrolyte solution into

a porous layer takes tens of seconds, leading to the delay of EL and weakening of the EL intensity.²⁰ The intensity increased rapidly with time, reached a maximum, and then decreased. The voltage increased gradually with time while EL increased and decreased but started to increase significantly when the EL intensity became negligible.

The time to reach the EL maximum, how long EL lasted, and the total integrated EL intensity defined as the integrated value of PMT output over time depended on the oxidation time for p-PSi preparation (preparation time). Figure 2.7 shows the preparation time dependence of the EL duration and the integrated EL intensity. Both the EL duration and the integrated EL intensity were linearly related to the oxidation time.

2.3.2.3. EL Spectra

Figure 2.8 shows the EL spectra of the p-PSi samples, which were prepared by anodic oxidation at 20 mA/cm² for (a) 200, (b) 500, and (c) 1000 s in 10 % HF - ethanol, measured at various times after constant current (2.4 mA/cm²) anodic oxidation in 0.2 M Na₂SO₄. The EL spectra were blue-shifted during the anodic oxidation, confirming the result reported previously.¹³ Figure 2.9 shows the time dependence of the peak energy of the EL at

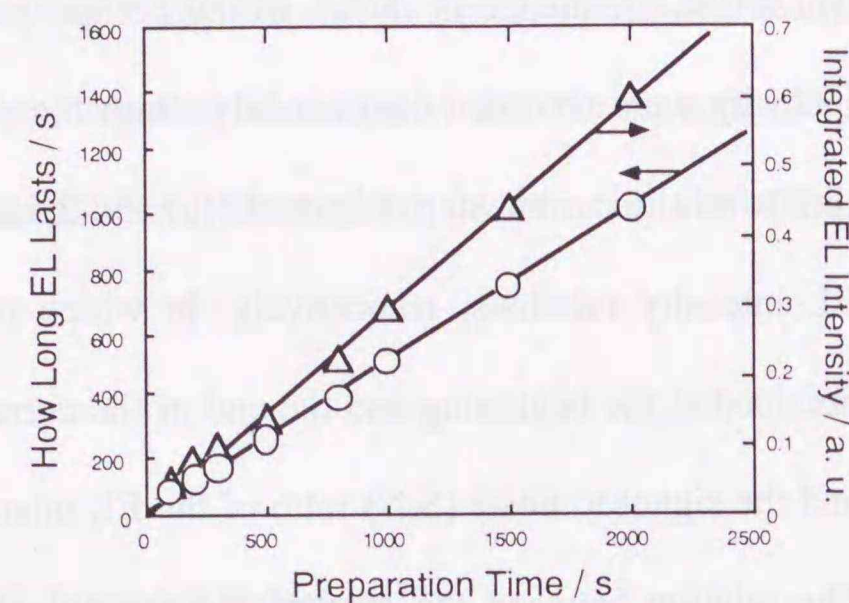


Figure 2.7. EL duration and total integrated EL intensity at the p-PSi electrode as a function of the oxidation time. Currents for preparation and for anodic oxidation in 0.2 M Na₂SO₄ were 20 and 2.4 mA/cm², respectively.

p-PSi prepared under various conditions. The maximum energy of the EL was constant at the p-PSi prepared at a given current density even if the preparation time was different. The peaks of the EL spectra of the p-PSi prepared by anodic oxidation at 20 and at 1 mA/cm² were blue-shifted from ca. 1.45 to 2.0 and 1.84 eV, respectively. The longer the preparation time was, the longer the EL lasted and the slower the blue-shift of EL proceeded.

2.3.2.4. FT-IR Measurements

Figure 2.10 shows the ex situ transmission FT-IR spectra in Si-H_n stretching region before and after EL measurements for p-PSi prepared by the oxidation at 20 mA/cm² for 1000 s with a Si wafer etched in HF as a reference. The

absorption peaks at 2088, 2110 and 2130 cm⁻¹, assigned to Si-H, Si-H₂, and Si-H₃ stretching modes, respectively, were observed at p-PSi before EL measurement.²¹ After EL ceased to be observed, however, no peaks corresponding to Si-H_n bonds were observed but a peak at 1080

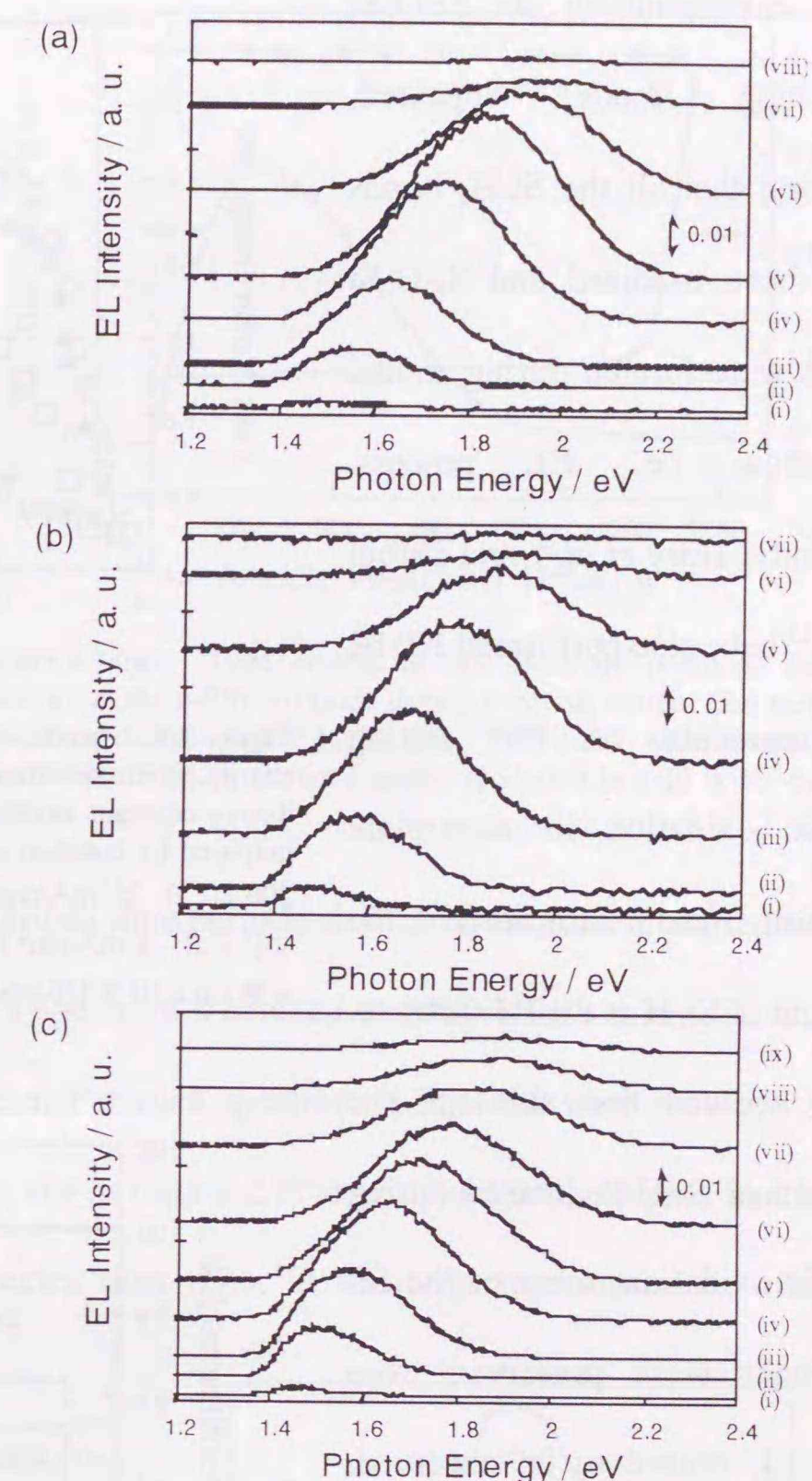


Figure 2.8. Anodic oxidation time dependence EL spectrum of the p-PSi electrode in 0.2 M Na₂SO₄ during constant anodic oxidation (2.4 mA/cm²). The p-PSi were prepared by constant anodic oxidation (20 mA/cm²) for (a) 200 s, (b) 500 s and (c) 1000 s in 10 % HF-ethanol solution. (a) The spectrum were measured after (i) 20, (ii) 40, (iii) 60, (iv) 80, (v) 100, (vi) 120, (vii) 140, and (viii) 160 s. (b) The spectrum were measured after (i) 40, (ii) 80, (iii) 120, (iv) 160, (v) 200, (vi) 240, and (vii) 280 s. (c) The spectrum were measured after (i) 60, (ii) 120, (iii) 180, (iv) 240, (v) 300, (vi) 360, (vii) 420, (viii) 480 s, and (ix) 540 s. Spectra are arbitrarily moved vertically for clarity.

cm^{-1} corresponding to Si-O-Si stretching mode appeared, showing that all the Si-H_n bonds have been oxidized and Si-O-Si bonds were formed during anodic oxidation, i.e., EL process. Recently, Hory *et al.*²² and Dubin *et al.*²³ have also performed FT-IR

measurements of p-Si during anodic oxidation in electrolyte solution and monitored the amount of Si-H at the p-Si surface.

They showed that although the amount of Si-H decreased during anodic oxidation, some of the Si-H bonds were preserved even after EL ceased to be observed, contrary to our results. One reason for this discrepancy should be due to the considerable difference in the constant anodic oxidation current density as Hory *et al.* and Dubin *et al.* performed constant anodic oxidation at 0.5 and 0.2 mA/cm², respectively, but present experiments were performed at 2.4 mA/cm².

The absorption intensities of Si-H_n and of Si-O-Si were followed by use of the in situ

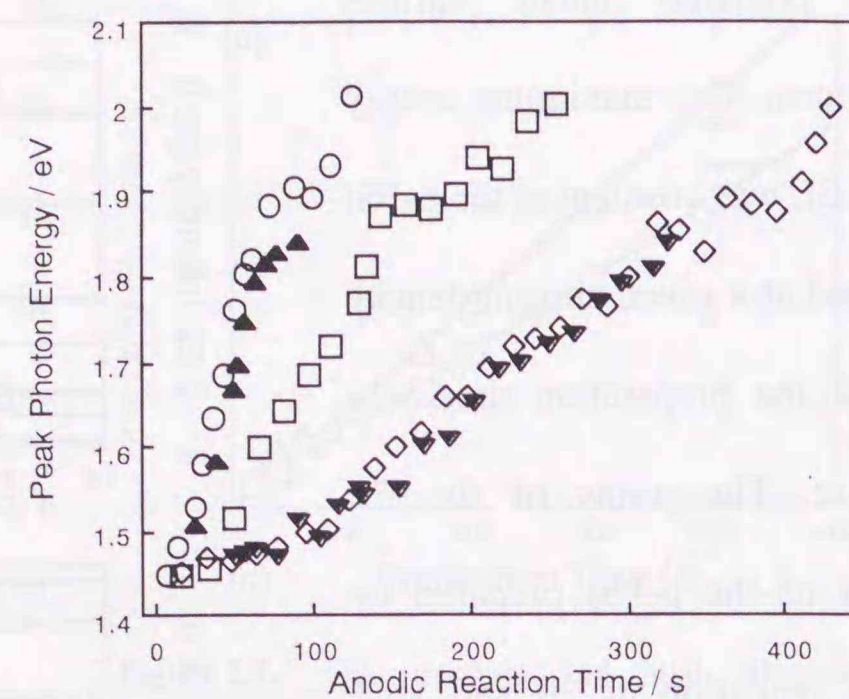


Figure 2.9. Anodic oxidation time dependence of peak photon energy of EL spectrum of the p-Si electrode in 0.2 M Na₂SO₄ during constant anodic oxidation (20 mA/cm²). The p-Si were prepared by constant current anodic oxidation at 20 mA/cm² for 200 s (○), 20 mA/cm² for 500 s (□), at 20 mA/cm² for 1000 s (◇), at 1 mA/cm² for 2000 s (▲), and 1 mA/cm² for 4000 s (▼) in a 10 % HF-ethanol solution.

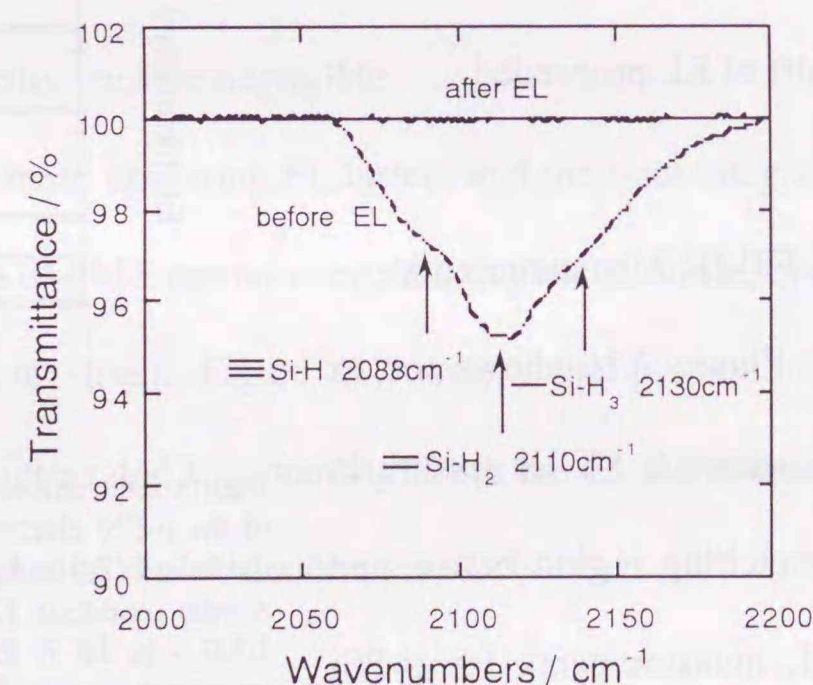


Figure 2.10. Transmission FT-IR spectrum of the p-Si before and after anodic oxidation. The p-Si samples were prepared from the p-Si (B doped, $1.11 - 1.68 \times 10^{15} \text{ cm}^{-3}$; $8 - 12 \text{ ohm}\cdot\text{cm}$) by constant current (20 mA/cm²) anodic oxidation for 1000 s in a 10 % HF-ethanol solution. Si wafer etched in HF were used as reference.

reflection FT-IR technique

during EL process. Figure 2.11 shows the simultaneously measured (a) time course of EL and potential and (b, c) difference IR spectra in (b) the Si-H_n stretching region and (c)

the Si-O-Si stretching region of p-Si prepared by oxidation at 20 mA/cm² for 1000 s. The

difference spectra were obtained at various time periods after constant current started to flow as indicated in Figure 2.11(a), using a spectrum measured at 1000-1120 s when EL was not observed at all as a reference spectrum. For each spectrum, 128 scans were recorded and it took 120 s. Downward and upward peaks in Figure 2.11 correspond to the higher and lower, respectively, amounts of surface species than those at the reference state, i.e., after EL

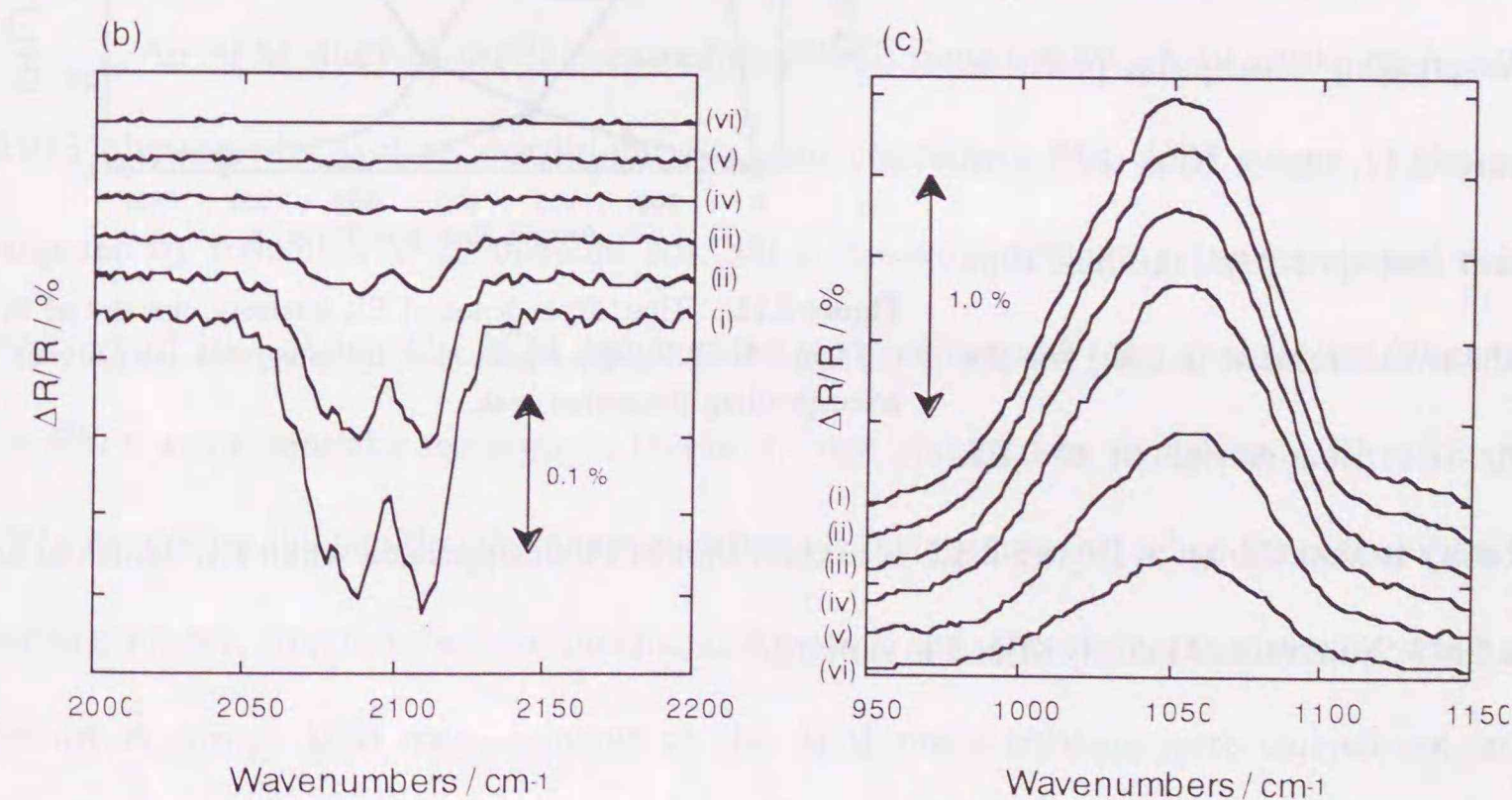


Figure 2.11(b, c). Difference FT-IR spectrum of p-Si electrode in 0.2 M Na₂SO₄ during anodic oxidation in the range of Si-H vibration (b) and Si-O-Si vibration (c). (i) 0 - 120, (ii) 200 - 320, (iii) 400 - 520, (iv) 600 - 720, (v) 800 - 920, and (vi) 1000 - 1120 s after constant current was started to flow as indicated in (a). The p-Si were prepared from the p-Si (B doped, $1.11 - 1.68 \times 10^{15} \text{ cm}^{-3}$; $8 - 12 \text{ ohm}\cdot\text{cm}$) by constant current (20 mA/cm²) anodic oxidation for 1000 s in a 10 % HF-ethanol solution.

measurement. As no Si-H_n species were detected in the transmission IR spectrum after EL was vanished, Figure 2.11(b) really reflects the absolute amount of Si-H_n species. The downward peaks corresponding to Si-H_n at 2088, 2115 and 2130 (shoulder) cm⁻¹ were observed at the initial stage of EL. These peaks decreased gradually with time and disappeared at the end of oxidation of p-PSi (Figure 2.11(b), curve (vi)). At this stage, EL was not observed. The peak intensity of the upward band corresponding to the Si-O-Si stretching band became smaller with time. This means that absorption increased with time, indicating that the formation of the Si-O-Si bond was associated with anodic oxidation. The existence of the upward peak corresponding to Si-O-Si stretching in the period of 1000-1120 s (Figure 2.11(c), curve (vi)) when EL was not observed shows that the Si-O-Si bond was generated even after EL vanished.

Figure 2.12 shows the time course of the amounts of Si-H_n and Si-O-Si species represented by the integrated intensity of the corresponding absorption peaks in Figure 2.11. As it took 120 s to obtain one spectrum, the half time of the measurement is used for the plot. The time course of the EL intensity is also shown in Figure 2.12. It is clear that Si-H_n disappeared when EL vanished and that Si-O-Si increased mainly after EL vanished.

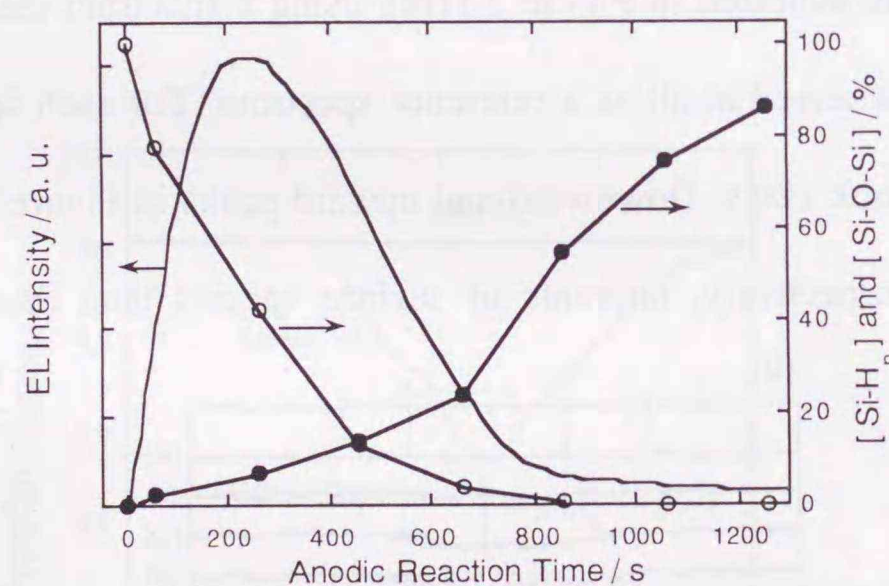


Figure 2.12. Time dependence of EL intensity, amount of Si-H_n (○) and Si-O-Si (●) represented by integrated intensity of the corresponding absorption peak.

2.3.2.5. SEM and AFM Observations

The cross sectional SEM images of p-PSi prepared on PSi (B doped, $4.89 - 8.49 \times 10^{18} \text{ cm}^{-3}$; $0.010 - 0.015 \text{ ohm}\cdot\text{cm}$) by anodic oxidation at 20 mA/cm^2 for various time duration

Table 2.1. Preparation conditions and properties of PSi layer.

Anodic reaction time in preparation / s	200	500	1000	2000	3000	4000
Constant current density in preparation / $\text{mA}\cdot\text{cm}^{-2}$	20	20	20	1	1	1
Number of charges passed in preparation / $\text{C}\cdot\text{cm}^{-2}$	4	10	20	2	3	4
Thickness observed by cross sectional SEM / mm	1.9	4.6	10.2	1.9	2.9	4.1
How long EL lasted / s	120	250	500	120	280	450
Number of charges passed during EL / $\text{C}\cdot\text{cm}^{-2}$	0.29	0.60	1.20	0.29	0.67	1.08
Passivation time / s	130	280	550	170	350	570
Number of charges passed before passivation / $\text{C}\cdot\text{cm}^{-2}$	0.31	0.67	1.32	0.41	0.82	1.37
Calculated charge to oxidize all Si atoms in PS layer / $\text{C}\cdot\text{cm}^{-2}$	2.3	5.5	12.1	2.6	4.0	5.7

showed that the longer the preparation time was, the thicker the p-PSi layer was. The preparation conditions, the thickness observed by SEM, how long EL lasted and charge passed during EL are listed in Table 2.1. In both cases of p-PSi prepared at 20 and 1 mA/cm^2 , the thickness of p-PSi layers was proportional to the anodic charge passed during the preparation, i.e., the preparation time for constant current oxidation as already reported.²⁴

The SEM observation also showed that the thickness of the p-PSi layer was not changed after EL measurement.

An AFM study of p-PSi prepared on PSi (B doped, $4.89 - 8.49 \times 10^{18} \text{ cm}^{-3}$; $0.010 - 0.015 \text{ ohm}\cdot\text{cm}$) by various conditions was also conducted. The AFM image of the p-PSi prepared by oxidation at 20 mA/cm^2 for 200 s showed a relatively regular shaped column structure of $10 - 20 \text{ nm}$. The AFM image of the p-PSi obtained by the oxidation at 20 mA/cm^2 for 500 s was essentially the same as that of the one prepared by oxidation at 20 mA/cm^2 for 200 s except for the fact that the image was less clear. It seems that when the preparation time became longer, structure became mechanically weak and, therefore, the structure was easily destroyed during AFM measurements as the AFM measurements were carried out in the contact mode. Actually the AFM measurement was not possible for the p-PSi prepared by oxidation at 20 mA/cm^2 for 1000 s.

The p-PSi prepared by the oxidation at the lower current density seemed to have a

smaller structure.

2.3.3. Discussion

2.3.3.1. Origin of EL and Oxidation of P-type PSi

As mentioned in the Introduction section, both holes and electrons are required for EL to be observed. While the surface concentration of holes, which are the majority carriers of p-type semiconductor, should be high at p-PSi under anodic bias when EL is observed, no obvious electron source is present in the electrolyte solution used in this study.

As already mentioned, the ex situ transmission FT-IR study (Figure 2.10) showed that the Si-H_n bands observed for as-prepared p-PSi had totally disappeared after the EL measurement was completed, and in situ reflection FT-IR measurements showed that the integrated absorption intensities for the Si-H_n and Si-O-Si stretching vibration decreased and increased, respectively, with time (Figures 2.11 and 2.12). Since the EL intensity represent the number of emitted photons per given time period, i.e., the emission rate, and the IR intensity represent the number of species at a given time, to discuss the role of these species on EL quantitatively, the rate of the generation of Si-O-Si and the consumption of Si-H species should be compared with the EL

intensity. Thus, the differences of the integrated absorption intensities of the two sequentially obtained spectra are plotted against time in Figure 2.13. For example, the points at 260 s were obtained as the difference between the integrated absorption intensities of the spectra (ii), which were obtained between

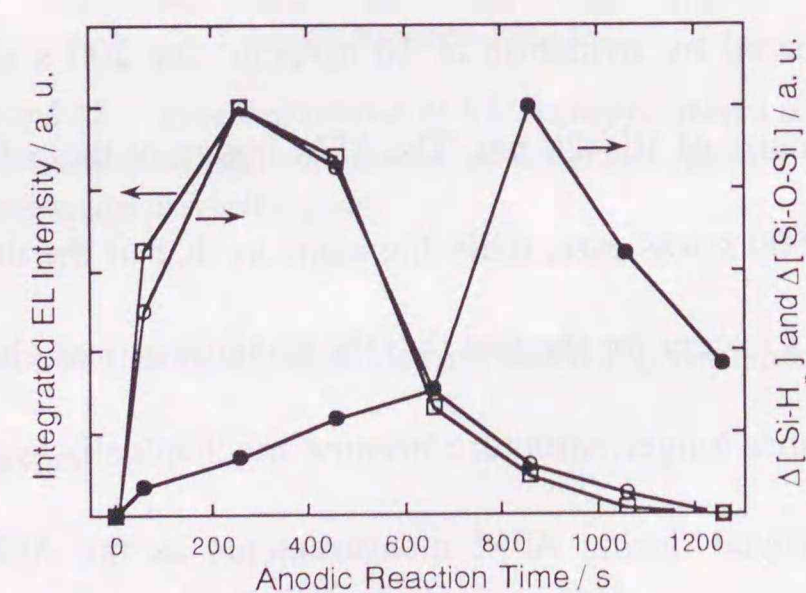
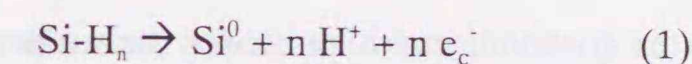


Figure 2.13. Time course of the integrated EL intensity (□), amount of consumed Si-H_n (○), and amount of generated Si-O-Si (●) for 200 s from the data in Figures 2.11 and 2.12. See text for details.

200 and 320 s and were considered to be the spectra at 260 s, and those of the spectra (i), which were obtained between 0 and 120 s and were considered to be the spectra at 60 s, of Figure 2.11. These data reflect the amounts of Si-H_n and Si-O-Si consumed and generated, respectively, during 200 s. Integrated amounts of EL during the same time periods are also shown in Figure 2.13. The time dependence of the integrated EL intensity matches well that of the consumption of Si-H_n. These results and the observations that adsorbed hydrogen at p-GaAs, which is formed as an intermediate during hydrogen evolution under cathodic polarization, can inject an electron into conduction band and short lived EL is observed when potential is pulsed to positive values after cathodic polarization²⁵ strongly suggest that the electron source is the hydrogen species on the surface in this case also. Thus, EL at p-PSi during anodic polarization seems to be generated by the following reactions,



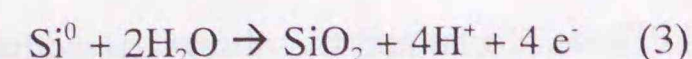
where e_c^- is an electron injected to the conduction band of the p-PSi and h_v^+ is a hole in the valence band of the p-PSi, which is the majority carrier and is accumulated at the p-PSi/electrolyte interface under anodic potential.

There may be a possibility that the decrease of Si-H_n band is due to the destruction of p-PSi structure. The SEM observation, however, clearly showed that the thickness of the porous layers of p-PSi before and after EL measurements were the same as mentioned before. Thus, the decrease of the integrated absorption intensity of the Si-H_n stretching bands was not due to the destruction of the p-PSi layer but due to the consumption of surface hydrogen species as a result of EL reaction.

The observed linear relation between the preparation time and how long EL lasted (Figure 2.7) is the reflection of the linear relation between the thickness and how long EL lasted, since the thickness linearly increased with the preparation time. This is reasonable as the total amount of Si-H_n, which is proportional to the integrated EL intensity, should linearly

increase with the thickness of the PSi layer.

The results that the decrease of Si-H_n took place while EL was observed and that Si-O-Si species increased more quickly after EL ceased to be observed showed that the anodic oxidation reaction that initially took place was reaction (1) followed by the reaction (3), forming Si-O-Si bond.



Since SiO₂ is an insulator, the formation of this species should result in an increase of the potential. The facts that the potential increased gradually while EL was observed and that there was a lag between the time when EL was ceased to be observed and the time when the potential increased sharply support the above mechanism that reaction (1) took place first then reaction (3) followed.

If one assumes that the passivation which causes the sudden increase of the potential occurs because all Si atoms in the p-PSi layer are oxidized to SiO₂, the number of charges passed before the sharp increase of the potential should be equal to the charge required to oxidize the total number of Si atoms in the p-PSi layer by reaction (3) plus the charge to oxidize surface hydrogen species by reaction (1). The charge for the former process can be calculated by assuming that the porosity of the p-PSi prepared at 20 and at 1 mA/cm² are 70 and 65 %, respectively,²⁶ and that the density and atomic weight of Si are 2.3 and 28, respectively. For example, the charge required to oxidized all Si atoms in the p-PSi prepared at 20 mA/cm² for 200 s is calculated to be 1.9 C/cm². Calculated values for samples of various thickness are listed in Table 2.1 and are much larger than the values of the charge actually passed before the passivation. Since the calculated charge does not include the charge for the oxidation of surface hydrogen species due to reaction (1), the actual charge to oxidize all Si atoms in the PSi layer should be much larger. This means that passivation occurs before the oxidation of all the Si atoms in the p-PSi layer, i.e., only a part of the Si atoms in the p-PSi are oxidized before the passivation. Bsiesy *et al.* reported that only 50 % of Si atoms in the p-PSi

were oxidized during EL process in the case of the p-PSi of 65 % porosity.²⁷ This can be explained by considering that oxidation takes place more efficiently near the Si/p-PSi interface and that passivation occurred when the region near the Si/p-PSi interface is totally oxidized so that the rest of the PSi column is electronically isolated from bulk Si phase by this insulating region even when there exist nonoxidized Si atoms in the p-PSi column.

2.3.3.2. Mechanism for Blue-Shift of EL with Time

As described in the Results section, the peak energy of EL spectra blue shifted with time during EL process. If EL in visible region from p-PSi is due to the quantum size effect, EL spectra should reflect the size of Si nanocrystals in the p-PSi layer. In the previous sections, it was described that EL is generated as a result of the oxidation of the surface Si-H_n of the p-PSi and suggested that oxidation takes place more efficiently near the Si/p-PSi interface. Cross sectional SEM images showed that the p-PSi column looks like a circular cone and the size of the Si nanocrystals at the bottom of the p-PSi column is larger than that at the top column, meaning that the bandgap of the Si nanocrystals at the bottom of the p-PSi column is smaller than that at the top column. The larger sized Si nanocrystals at the bottom and the smaller sized Si nanocrystals at the top of the p-PSi column should emit the EL of longer wavelength (lower energy) and shorter wavelength (higher energy), respectively. Thus, the author conclude that major reaction sites at the initial stage of anodic oxidation were near to the PSi/Si interface where the size of nanocrystalline Si is large and, therefore, the energy gap is smaller, and that reaction sites moved gradually to the top of the column where the size of nanocrystalline Si is small and, therefore, the energy gap is larger, with time. The oxidation of large sized PSi also leads to the decrease of PSi size, i.e., the blue-shift of EL.

2.3.4. Conclusion

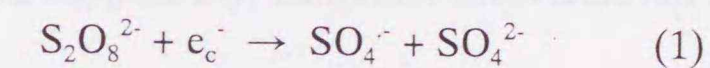
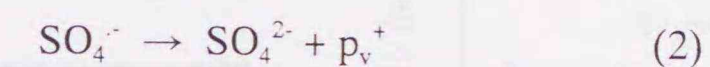
EL from porous Si layer formed on PSi was observed in Na₂SO₄ solution under

anodic bias. EL was observed as soon as constant current started to flow. It increased at the beginning, reached a maximum, and then, decreased with anodic reaction time. The electrode potential gradually increased with oxidation time from ca. 0.8 V vs. (Ag/AgCl) at the beginning to 1.2 V after several hundreds of seconds and increased steeply after EL ceased to be observed. EL spectra were blue-shifted during anodic oxidation, and the rate of the blue-shift was dependent on the preparation condition of the p-PSi. These results were explained by considering the size distribution of nanocrystalline Si in PSi layer. On the basis of the in situ FT-IR study surface hydrogen species were attributed to the electron injector.

2.4. Visible EL from n-Type PSi/Electrolyte Solution Interface: Time-Dependent EL Spectra

2.4.1. Introduction

In previous section, the relation between the chemical nature and EL properties of p-PSi was studied by in situ FT-IR measurements and proved quantitatively that surface Si-H_n species contribute to EL. In the case of n-PSi, EL is obtained when the n-PSi is cathodically biased in an electrolyte containing an electroactive species which can inject holes into the valence band of the semiconductor.¹² It is known that if a negative potential is applied to an n-type semiconductor in a solution containing a hole injector such as S₂O₈²⁻, EL is observed as a result of the following reactions¹²



where e_c^- is an electron in the conduction band of an n-type semiconductor and p_v^+ is a hole injected from SO₄^{·-} to the valence band. This mechanism is expected to explain the visible EL from cathodically biased n-PSi in contact with S₂O₈²⁻ solution. Recently, Kooij *et al.*^{11(b)} investigated the electrochemical characteristics of PSi in acidic S₂O₈²⁻ solution in detail. Compared with results obtained on p-GaAs with p-PSi, they observed no enhancement of the photocurrent, i.e., photocurrent doubling due to the contribution of hole injection from SO₄^{·-}, at p-PSi in the presence of S₂O₈²⁻ under reverse bias conditions. Because a similar effect might be occurring with an n-type electrode in S₂O₈²⁻ solution, they suggested that the reduction of S₂O₈²⁻ at PSi electrodes is not always accompanied by hole injection into the valence band. However, the mechanism of the reduction of S₂O₈²⁻ is still not clear. Thus, quantitative analysis of the application of this EL system to an n-PSi/electrolyte solution interface must be still important. One of the most interesting characteristics in this system is the shift of the EL spectra to higher energy as the potential is scanned or stepped to negative values.¹¹ The author,

however, have found that the spectra of the visible EL from n-PSi in an electrolyte solution containing $\text{S}_2\text{O}_8^{2-}$ blue-shifted with time even when a constant negative potential was applied to n-PSi contrary to the results previously reported.²⁸

The work in this section was carried out to clarify the mechanism of the voltage-tunable blue-shift of the EL from an n-PSi/electrolyte solution interface by employing both potential sweep and potential step methods. The dependence of the intensity and spectra of the EL on electrode potential and $\text{S}_2\text{O}_8^{2-}$ concentrations as well as on time were investigated.

2.4.2. Results and Discussion

2.4.2.1. Current and EL Characteristics Obtained by Potential Sweep Method

Figure 2.14 shows the current - potential and the EL intensity - potential relations of an n-PSi electrode which was prepared by anodic oxidation for 300 s in 0.2 M Na_2SO_4 solution containing 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ measured by sweeping the potential in the negative direction at various scan rates. A cathodic current was observed at potentials more negative than -0.55 V. Limiting current was observed when the scan rate was 20 or 100 mV, but the current increased monotonously within the potential region employed in this study when the potential was scanned at 1000 mV/s. EL was observed at potentials more negative than -1.0 V in

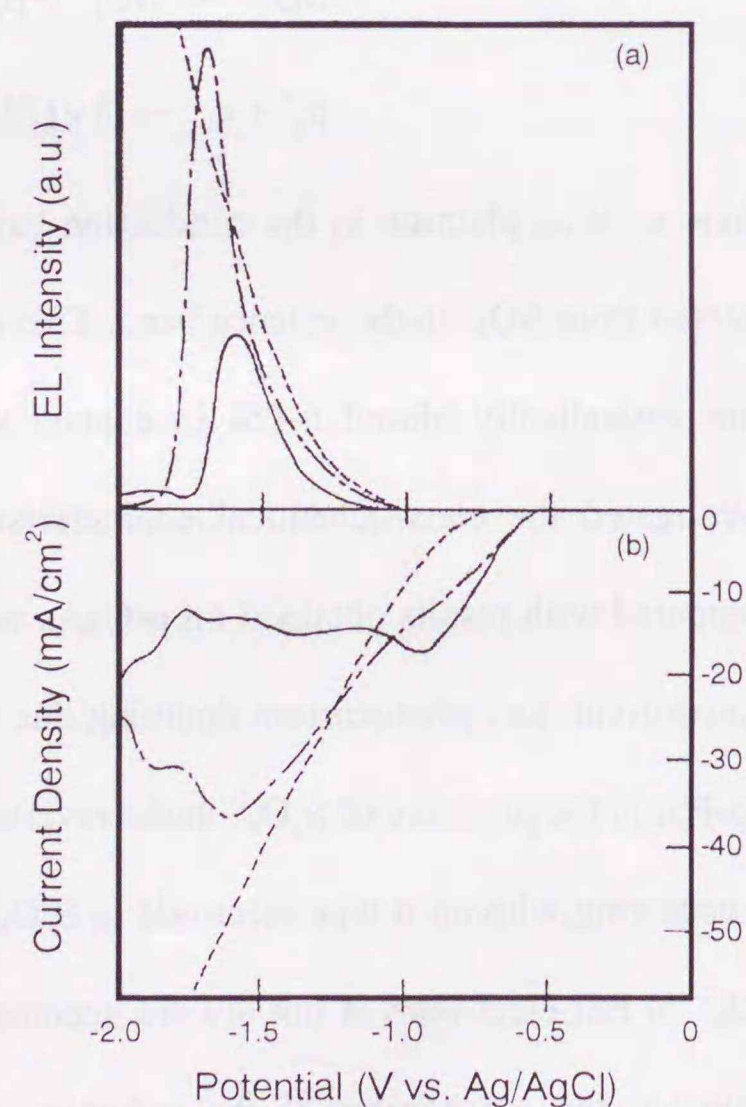


Figure 2.14. (a) EL intensity - potential and (b) current density - potential curves obtained in 0.2 M Na_2SO_4 and 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ solution. n-PSi samples were prepared by anodic oxidation in 10 % HF - ethanol at 5 mA/cm² for 300 s. Potential scan rate was (—) 20 mV/s, (---) 100 mV/s and (.....) 1000 mV/s.

all cases. The EL intensities increased as the potential became negative when the scan rates were 20 and 100 mV/s, reached a maximum at -1.6 V and -1.7 V, respectively and then decreased rapidly after the EL peaks, although the cathodic current still flowed. No EL peak was observed within the potential region examined at 1000 mV/s scan. Although the behavior of both the EL intensity and cathodic current during the potential scan has been reported by several groups,¹¹ they employed only one scan rate. It is clear from Figure 2.14 that when the potential was scanned faster, the limiting values of the cathodic current and the EL intensity became higher for the reduction current and the EL. It was also found that the faster the potential was scanned, the more negative was the peak potential.

Figure 2.15 shows typical EL spectra observed at various negative potentials during a potential scan at 20 mV/s (c.f. Figure 2.14). Because the exposure time of the PCD was 5 s, each spectrum was obtained during the potential scan from -1.0 V to -2.0 V at 0.1 V intervals. The peak energy of the EL spectra was blue-shifted from ca. 1.7 eV at -1.3 V to ca. 2.1 eV at -1.8 V.

After the potential reached -1.8 V, however, the EL spectra were red-shifted (Figures 2.15(e) and 2.15(f)). No potential dependence was observed for the low energy threshold of the EL spectra. The voltage-tunable EL from the n-PSi/electrolyte solution interface has already been reported by several groups¹¹ during a potential scan from -1.0 to -1.6 V. Very recently, Lim *et al.*^{11(f)} have reported that the peak of the EL spectra showed a red-shift at a constant negative potential by repeating the potential application. They attributed this phenomenon to the bandgap lowering caused by the conversion of the predominant Si-H surface bonds to Si-Si

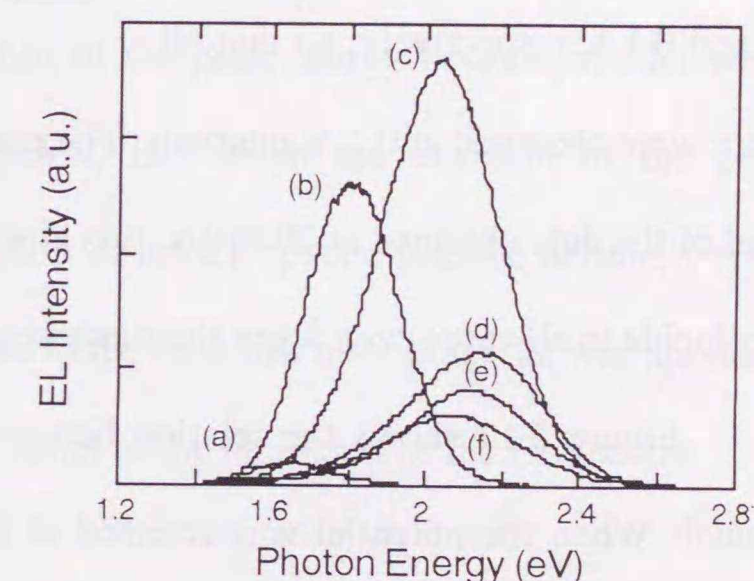


Figure 2.15. EL spectra obtained in 0.2M Na_2SO_4 and 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ solution, during the potential scan from 0 V to -2.0 V, at (a) -1.0 V, (b) -1.2 V, (c) -1.4 V, (d) -1.7 V, (e) -1.8 V and (f) -1.9 V. EL spectra were obtained in 0.1 s. Potential scan rate was 20 mV/s. n-PSi samples were prepared by anodic oxidation in 10 % HF - ethanol at 5 mA/cm² for 300 s.

bonds formed by the destruction of the surface bonds of PSi. The red-shift of the EL spectra during the negative scan observed in our experiments may be related to this effect.

Figure 2.16 shows the EL spectra observed at -1.5 V at various scan rates. The exposure time of PCD for 20, 100 and 1000 mV/s scans were 5, 1 and 0.1 s, respectively, so that all

spectra were observed at 0.1 V intervals. The peak intensity of the EL spectra was normalized to that of the data obtained at 20 mV/s. It is clear that the peak energy of the EL spectrum did not coincide in all cases even when the same negative potential was applied to n-PSi.

Figure 2.17 shows the relation between the peak energy and the applied negative potential. When the potential was scanned at 20 mV/s, the peak energy of the EL spectra increased in proportion to the applied negative potential with a slope of ca. 1 eV/V over a voltage range from -1.2 to -1.7 V, which is close to the value reported in the literature. If the scan rate was increased to 1000 mV/s, however, the peak energy of the EL spectra was almost constant during the negative potential scan.

Previously, Bsiesy et al.^{11(a), (d)} have reported that the peak energy of the EL spectra is proportional to the

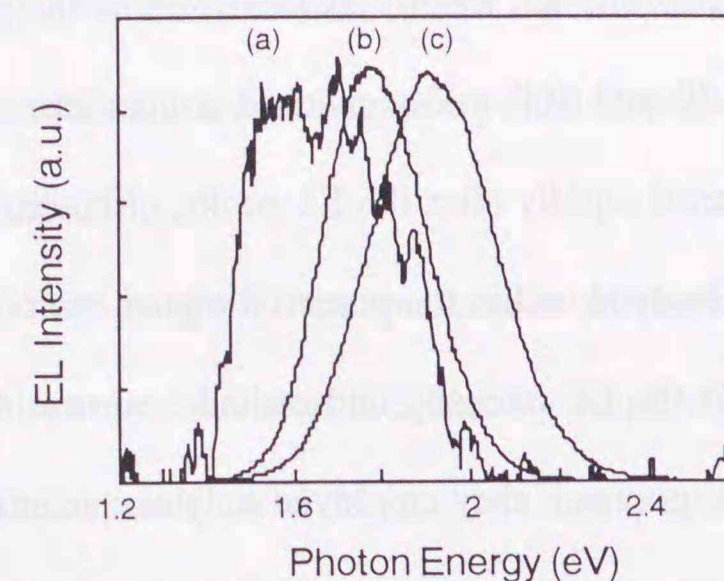


Figure 2.16. EL spectra obtained in 0.2 M Na₂SO₄ and 0.15 M K₂S₂O₈ solution at -1.5 V during the potential scan from 0 V to -2.0 V at a potential scan rate of (a) 1000 mV/s, (b) 100 mV/s, (c) 20 mV/s. EL spectra were obtained in 0.1 s.

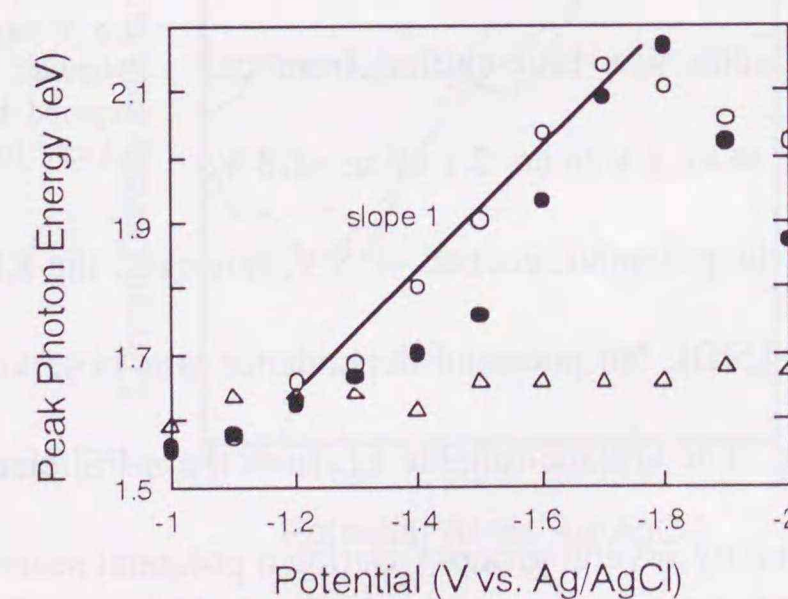


Figure 2.17. The dependence of peak energy on applied potential obtained during the potential scan from 0 V to -2.0 V. Potential scan rate was 20 mV/s (○), 100 mV/s (●) and 1000 mV/s (△).

applied negative potential with a slope of 1 eV/V when the potential was scanned at 25 mV/s. They proposed a model considering a quantum size effect in which an increase in ΔV will be followed by an increase in the energy of emitted photons $\Delta h\nu = e\Delta V$ to explain the blue-shift of the EL spectra. Very recently, however, Lim *et al.*^{11(f)} have reported that this relation between the peak energy and the applied negative potential was very sensitive to the experimental conditions, i.e., the slope will change with the different degrees of PSi surface oxidation by SO₄²⁻. In the present study, hence, as-prepared n-PSi samples were used for EL measurements only once because one EL measurement alters the nature of the PSi layer in certain cases. It is clear from Figure 2.17 that the peak photon energy was not related linearly to the applied potential and that the blue-shift of the peak energy became smaller when the potential scan rate was higher than 20 mV/s, i.e., when the duration of the potential application to n-PSi became short, the blue-shift of the EL spectra became definitely retarded. The present results suggest that the effect due to the time just after potential was applied to n-PSi also plays an important role in the mechanism of the blue-shift of the EL spectra.

2.4.2.2. Current and EL Characteristics Obtained by Potential Step Method

In order to understand the time dependence of the EL in more detail, potential step measurements were carried out. Figure 2.18 shows the time profiles of the EL intensity and cathodic current of n-PSi, which was prepared by anodic oxidation for 300 s, when the potential was stepped from 0 V to a certain negative value in 0.2 M Na₂SO₄ containing 0.15 M K₂S₂O₈. When the pulse limit was -1.5 V or -2.0 V, EL began to be observed just after the potential step, and its intensity increased gradually up to the end of the applied negative pulse. When the potential was stepped to -2.5 V or -3.0 V, however, EL started to occur just after the potential step; its intensity increased dramatically with time, reached a maximum and then decreased rapidly. Actually, similar trends were observed even when the potential was stepped to -1.5 V and -2.0 V if the measurements were carried out over a longer time scale

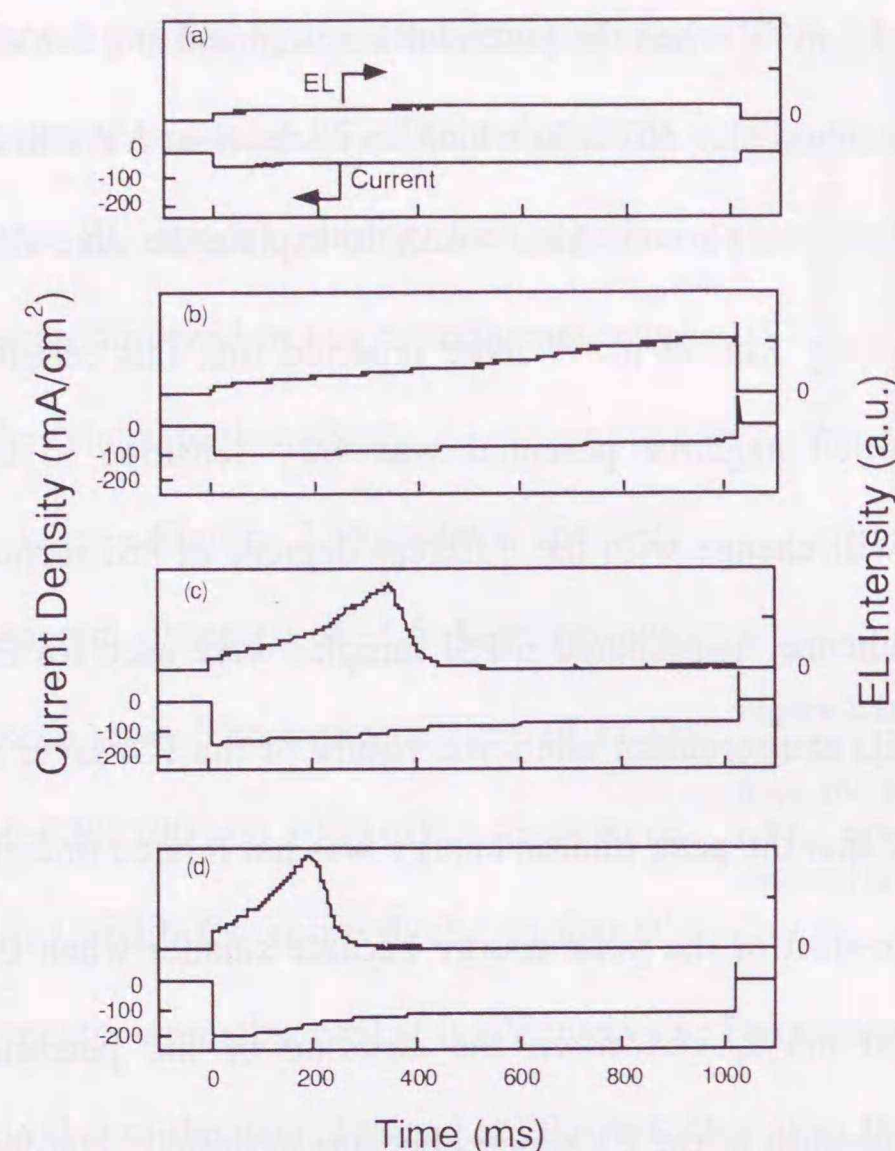


Figure 2.18. Time profiles of EL intensity and current density observed in 0.2 M Na_2SO_4 and 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ solution. n-PSi samples were prepared by anodic oxidation in 10 % HF - ethanol at 5 mA/cm² for 300 s. Potential was stepped from 0 V to (a) -1.5 V, (b) -2.0 V, (c) -2.5 V, and (d) -3.0 V.

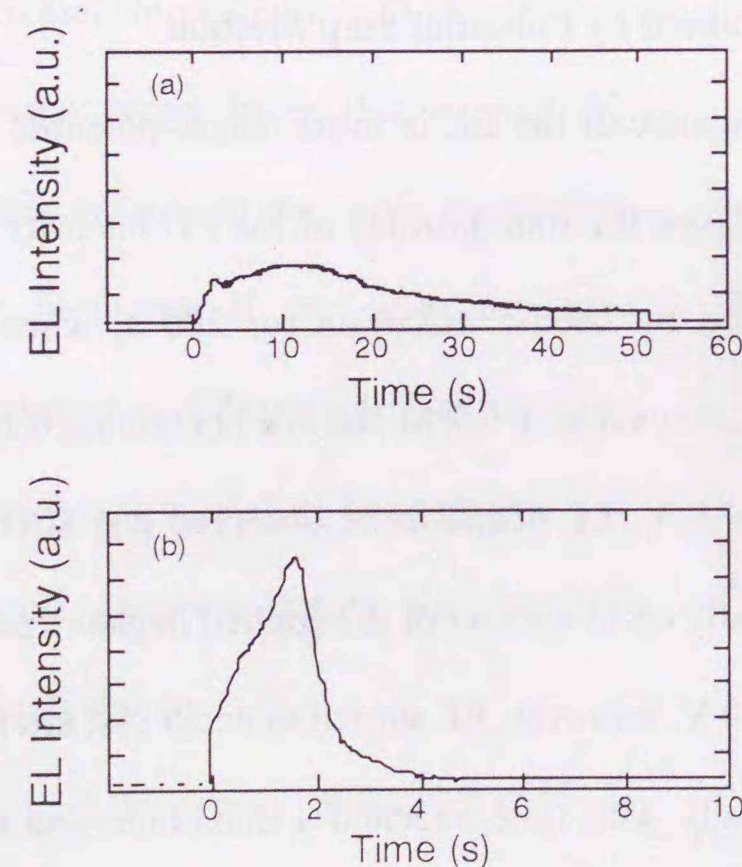


Figure 2.19. Time profiles of EL intensity on a larger time scale to (a) -1.5 V and (b) -2.0 V in Figure 2.18(a) and (b).

(Figures 2.19(a) and 2.19(b)). The more negative the potential was stepped to, the faster the EL maximum appeared. When a negative potential was applied, cathodic current started to flow, decreased gently, showed an inflection point and then decreased gradually. The time when the inflection point in the current time profile appeared was in good agreement with the time when the EL intensity reached a maximum.

Figure 2.20 shows the time profiles of EL intensity and cathodic current in 0.2 M Na_2SO_4 solution containing various concentration of $\text{S}_2\text{O}_8^{2-}$. For all the cases in Figure 2.20, the samples were prepared by anodic oxidation for 300 s and the potential was stepped from 0 to -3.0 V for 1 s. When $\text{S}_2\text{O}_8^{2-}$ was not present in the solution, EL from n-PSi was not observed and the cathodic current reached a steady value almost immediately after the potential step as shown in Figure 2.20(a). When $\text{S}_2\text{O}_8^{2-}$

was present in the electrolyte solution, EL started to occur just after a negative potential was applied. Its intensity increased gradually with time, reached a maximum and decreased rapidly. The time when the EL intensity reached a maximum was in good agreement with the time the inflection point appeared in the current time profile. Concentrations of $\text{S}_2\text{O}_8^{2-}$ in the electrolyte solution influenced the rate of the increase in the EL intensity only slightly but significantly influenced the time to

reach a maximum in the EL intensity time. The time to reach a maximum in the EL intensity profile was delayed, and therefore, the maximum EL intensity was higher as the SO_4^{2-} concentration became higher. As soon as the potential was stepped to a negative value, cathodic current started to flow, decreased gently, showed an inflection point and decreased gradually as already reported in Figure 2.18.

The overall mechanisms of the electrochemical reaction occurring at the n-PSi electrode during the potential step were considered as follows²⁹

1. Mass transport (i.e., $\text{S}_2\text{O}_8^{2-}$ transport) to the n-PSi electrode.
2. Electron transfer at the n-PSi electrode surface. (reaction (1) and (2))
3. Visible light emission. (reaction (3))

In general, mass transport can be achieved by migration, convection or diffusion. In the presence of a strong electrolyte and using a stationary electrode, both of which were used

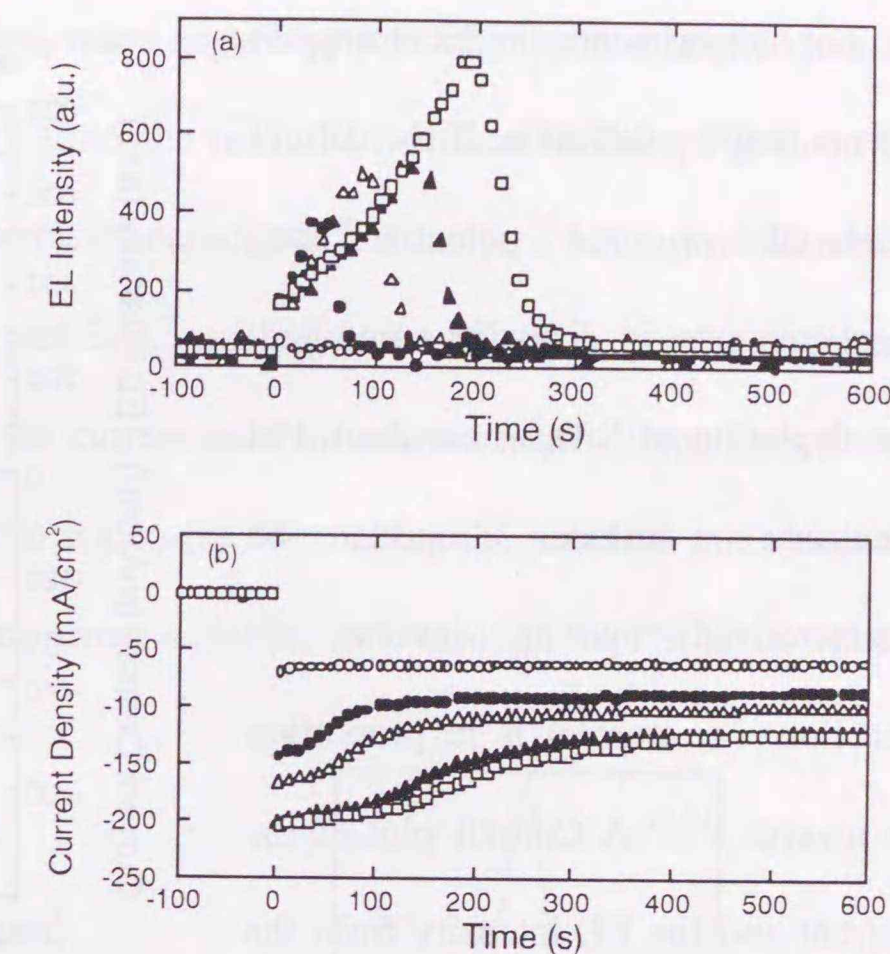


Figure 2.20. Time profiles of EL intensity (a) and current density (b) observed by potential stepping for 1 s from 0 V to -3.0 V. Electrolyte solutions measured were 0.2 M Na_2SO_4 + 0 M ($\square$), 0.05 M ($\bullet$), 0.075 M ($\triangle$), 0.125 M ($\blacktriangle$), and 0.15 M ($\square$) $\text{K}_2\text{S}_2\text{O}_8$ solutions. n-PSi samples were prepared by anodic oxidation in 10 % HF - ethanol at 5 mA/cm² for 300 s.

in our experiments, mass transport occurs only by diffusion. If the current observed in our potential step measurements is diffusion-controlled, the depletion of $\text{S}_2\text{O}_8^{2-}$ near the n-PSi electrode surface must be characterized by an inverse $t^{1/2}$ function, i.e., current is in proportion to inverse $t^{1/2}$.²⁹ A Cottrell plot of the current and the EL intensity from the data in Figures 2.18(c), (d) is shown in Figure 2.21. During the first stage of the potential step (region (a)), however, the current was almost constant although the EL intensity increase gradually. After the maximum of the EL intensity appeared (region (b)), both current and EL intensity were decaying linearly with inverse $t^{1/2}$. Thus, it is clear that EL proceeds by two different mechanisms before (region (a)), and after (region (b)) the EL intensity reached a maximum.

Let us discuss the EL mechanism before a maximum in the EL time profile (region (a)). In this region, EL intensity increased gradually with time just after a negative potential pulse was applied to the n-PSi. In addition, this increase in the EL intensity was almost independent of the $\text{S}_2\text{O}_8^{2-}$ concentration (Figure 2.20(a)). Hence, it is possible to say that in region (a), generation of EL is not limited by the diffusion of $\text{S}_2\text{O}_8^{2-}$ in the electrolyte. The Cottrell plot (Figure 2.21) which did not show a linear dependence of current and inverse $t^{1/2}$ in region (a) may support this speculation. In region (a), thus, the generation of EL is limited by the electron flux supplied from the n-PSi electrode. Recently, Gelloz *et al.*³⁰ reported that the PSi layer in contact with an electrolyte is not always conductive but is also depleted of

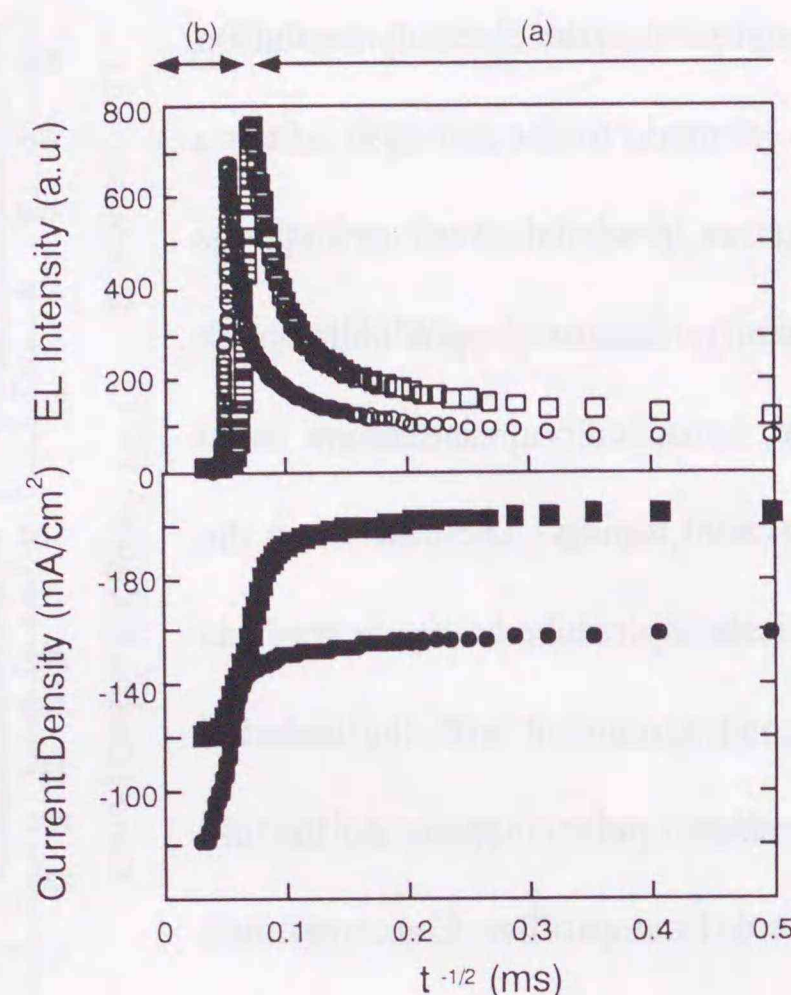
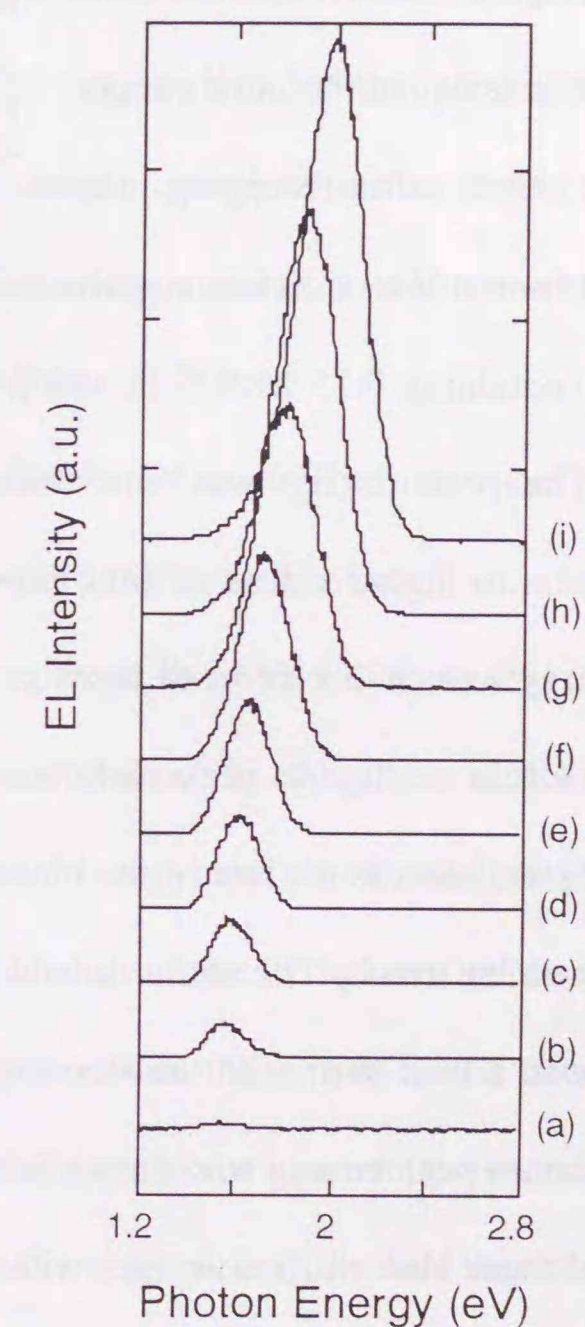


Figure 2.21. A Cottrell plot of the current (-2.5 V(●), -3.0 V(■)) and the EL intensity (-2.5 V(○), -3.0 V(□)) from the data in Figure 2.18(d), (c). See text for details.

free carriers under some conditions. Thus, when negative potential pulse was applied to n-PSi, an electric field will emerge gradually from the n-PSi/Si interface to the n-PSi/electrolyte solution interface due to the high interfacial capacitance.⁶⁰ Finally, a homogeneous electric field through the n-PSi layer will form and $\text{S}_2\text{O}_8^{2-}$ existing in the PSi layer from the beginning of the potential pulse will be reduced by the current until it becomes nearly zero. Thus, the EL intensity increases gradually with time in region (a). By making the potential more negative, the high driving force to build up a homogeneous electric field through the PSi layer will lead to both the time and the rate to reach a maximum in the EL time profile faster.

In the case of region (b), a rapid decrease in the EL intensity after the maximum was observed. In this region, current and inverse $t^{1/2}$ showed a linear relationship which means that when the electrochemical reaction is diffusion-controlled, $\text{S}_2\text{O}_8^{2-}$ is depleted at the surface and eventually SO_4^{2-} also decreases. That is the reason why the EL intensity decreases in region (b).



2.4.2.3. Time Dependent EL Spectra

Figure 2.22 shows the typical time-resolved EL spectra from n-PSi, which was prepared by anodic oxidation for 300 s, obtained every 0.1 s after the potential was pulsed to -2.0 V in 0.2 M

Figure 2.22. Time-resolved EL spectra obtained in 0.2 M Na_2SO_4 and 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ solution, when the potential was stepped for 1 s from 0 V to -2.0 V. EL spectra were obtained at every 0.1 s: (a) 0 - 0.1 s, (b) 0.1 - 0.2 s, (c) 0.2 - 0.3 s, (d) 0.3 - 0.4 s, (e) 0.4 - 0.5 s, (f) 0.5 - 0.6 s, (g) 0.6 - 0.7 s, (h) 0.7 - 0.8 s, and (i) 0.8 - 0.9 s. The n-PSi samples were prepared by anodic oxidation in 10 % HF-ethanol at 5 mA/cm².

Na_2SO_4 containing 0.15 M $\text{K}_2\text{S}_2\text{O}_8$.²⁸

The peak energy and the high energy threshold of the EL spectrum showed a blue-shift during a constant negative potential application, although the low energy threshold was constant (ca. 1.4 eV).

Figure 2.23 shows the relationship between the peak energy and the time after stepping the potential from 0 V to a certain negative value. The data in Figure 2.23 were obtained in 0.2 M Na_2SO_4 containing 0.15 M $\text{K}_2\text{S}_2\text{O}_8$ using an n-PSi sample prepared by anodic oxidation for 300 s. The peak energy was blue-shifted from ca. 1.5 eV observed just after cathodic polarization to higher values as time proceeded. It is interesting to note that the maximum peak energy was ca. 2.1 eV in all cases except for the case when the potential was pulsed to -1.5 V where a negligible peak shift was observed. Clearly, the more negative the applied potential, the faster is the rate of the blue-shift of the peak energy. The high energy threshold showed similar trends. The author would like to emphasize here that the EL spectra from n-PSi showed a blue-shift with time even when a constant negative potential was applied and the maximum peak energy was almost independent of the applied potential. Note that the time region of these blue-shifts coincides with that of the increase in the EL intensity as shown in Figure 2.18.

2.4.2.4. Mechanism for Blue-Shift of EL with Time

The blue-shift of the EL spectra has been reported by several groups under conditions similar to ours. Their explanations for the blue shift were mainly based on

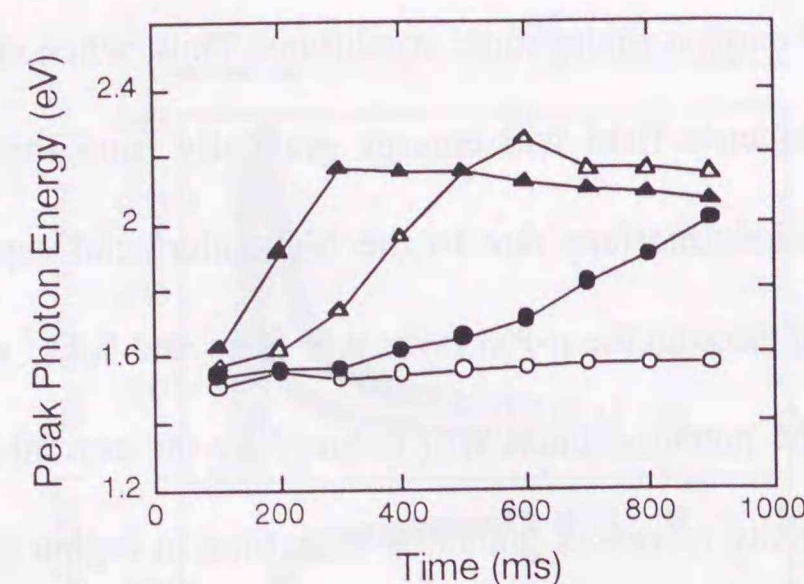


Figure 2.23. The dependence of peak energy obtained from the time-resolved EL spectra with time after stepping the potential. Potential was stepped from 0 V to -1.5 V (○), -2.0 V (●), -2.5 V (△), and -3.0 V (▲). PSi samples were prepared by anodic oxidation in 10 % HF - ethanol at 5 mA/cm² for 300 s.

considering the size distribution of the nanometer-sized Si crystallites, which produce the quantum size effect.

If a visible EL from n-PSi is due to the quantum size effect of the spatial confinement of the charge carriers in the nanometer-sized Si crystallites, the EL spectrum obtained from n-PSi reflects the size distribution of the nanometer-sized Si crystallites in the n-PSi layer and the peak energy of the EL spectrum provides the bandgap energy of the Si crystallites with the most dominant nanometer-size in n-PSi. The fact that the peak energy and the high energy threshold blue-shifted from ca. 1.5 to ca. 2.0 eV and from ca. 1.6 to ca. 2.6 eV, respectively, in all cases suggests that the n-PSi prepared under the present conditions consisted of nanometer-sized Si crystallites with bandgap energies from ca. 1.4 to ca. 2.6 eV (Figure 2.22). Theoretical calculation shows that nanometer-sized Si crystallites with bandgap energies from 1.4 to 2.6 eV have diameters of ca. 4.5 to ca. 2.0 nm.³¹

The crystallites in PSi are reported to be distributed vertically from a smaller size at the PSi/electrolyte solution interface to a larger size at the PSi/Si interface,³² i.e., the bandgap energy is distributed from larger at the top to smaller at the bottom of the PSi layer. The larger-sized Si crystallites at the bottom and the smaller-sized Si crystallites at the top of the PSi layer should emit EL of longer wavelength (lower energy) and shorter wavelength (higher energy), respectively. Thus, the time-dependent blue-shift of the EL spectra can be explained by considering that the rate of the EL generation depends on the size of the Si crystallites in the PSi layer, i.e., the major reaction site at the initial stage of the potential pulse was near the n-PSi/Si interface where the size of the Si crystallites is large, and the fact that the reaction sites moved gradually to the top of the n-PSi layer with the time needed to build up a homogeneous electric field through the PSi layer.

2.4.3. Conclusions

Visible EL from n-PSi in an electrolyte solution containing $\text{S}_2\text{O}_8^{2-}$ was investigated

by potential sweep and potential step methods. By potential sweep measurements, dependence of EL intensity, cathodic current and EL spectra on the scan rate were found. By potential step measurements, the EL intensity was found to increase with increasing cathodic polarization time although the cathodic current decreased. By time-resolved EL spectra measurements, the author found that the EL spectrum was blue-shifted even at a constant negative potential applied to n-PSi. These results were explained by that the emission site changed from larger-sized Si crystallites to smaller-sized ones in the n-PSi layer. The author proposed for the first time a mechanism in which the EL process was dependent not only on the electrode potential but also on the time after the negative potential was applied.

2.5. Photoelectrochemical and PL Properties of p-Type Si/Electrolyte Solution Interface: Potential Dependent PL Spectra as a Result of Size Dependent Quenching

2.5.1. Introduction

Interest in PSi has been stimulated by the discovery of voltage induced wavelength tuning of EL¹¹ and PL.^{11(d), 33} PL measurements are often used to determine the quantum efficiency of photoelectrochemical reactions and to probe potential distributions across semiconductor electrode/electrolyte solution interfaces.³⁴ Thus, one can expect that PL measurements of PSi/electrolyte solution interfaces provides useful information on the nature of PSi. Only few reports on PL of PSi/electrolyte solution interfaces are available and they are on n-PSi in the forward bias condition.^{11(d), 33}

In this section, the effect of a bias voltage on the photocurrent and the visible PL characteristics at a p-PSi/electrolyte solution interface were investigated. When the potential became more negative than ca. -0.6 V, a cathodic photocurrent started to flow and PL was quenched accompanied by a blue shift of the peak wavelength.

2.5.2. Results and Discussion

2.5.2.1. PL from p-Type PSi/Electrolyte Solution Interface

Figure 2.24 shows the typical PL spectra from p-PSi/electrolyte solution interface under various excitation light intensities measured in 0.2 M Na₂SO₄. In this experiment the exposure time for the PCD system was 100 ms and the signal was averaged over ten exposures. The potential was kept constant at -0.5 V during the spectral measurements and the excitation light wavelength was 360 nm. The incident light was passed through several neutral density filters (Toshiba Glass Co. Ltd., ND-25, 50, and 70) to adjust the excitation intensity. The peak wavelength was ca. 660 nm and the full width at half maximum (FWHM) of the PL spectra was ca. 0.48 eV. The change in the excitation light intensity did not affect the shape of the PL spectra but affected the PL intensity. Although PL spectra from the PSi/electrolyte solution interface were reported by Bsiey *et al.*^{11(d)} and Meulenkaamp *et al.*³³ on n-PSi in 1.0

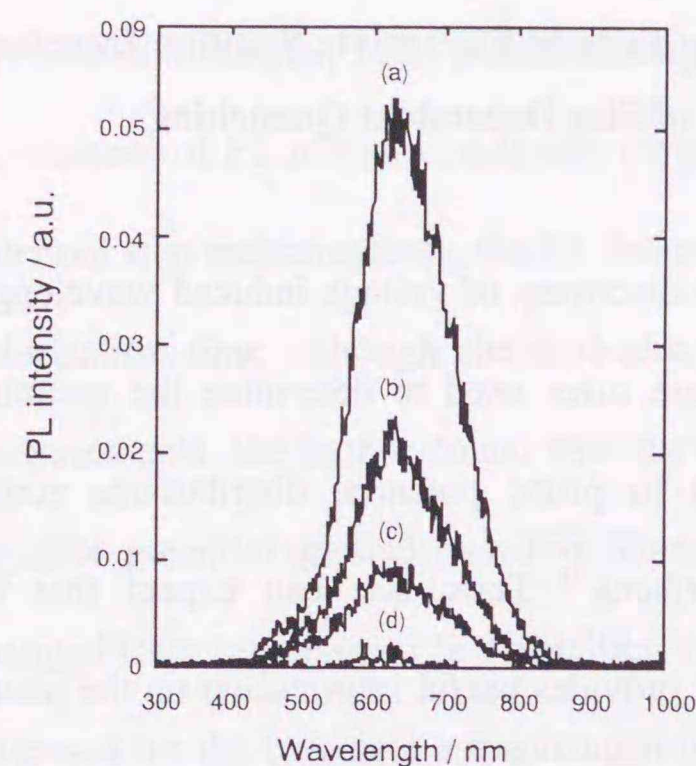


Figure 2.24. PL spectra of p-PSi observed at various excitation intensities in 0.2 M Na₂SO₄ at -0.5 V with the excitation wavelength of 360 nm. The relative excitation intensities were (a) 100, (b) 53, (c) 30, and (d) 4.

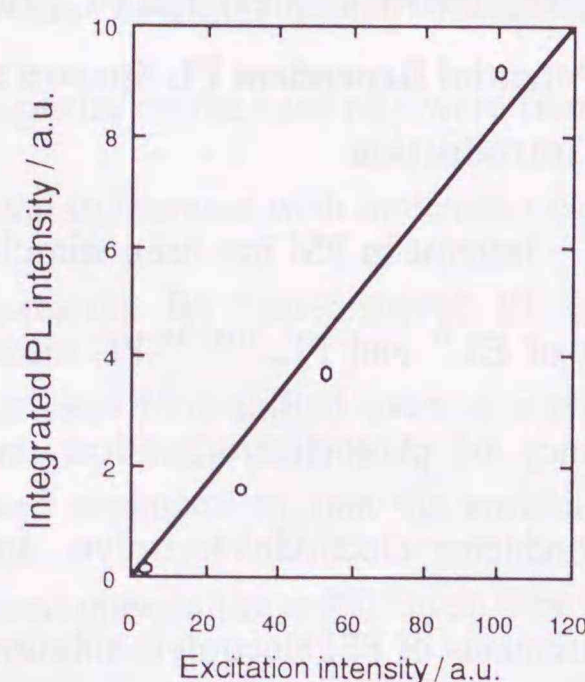


Figure 2.25. The relation between the integrated PL intensity and the excitation intensity. The integrated PL intensity was obtained by the integration of the PL spectra in Figure 2.24 from 300 to 1000 nm.

M H₂SO₄ solution, the peak wavelength was ca. 700 nm. The difference in the PL peak wavelength between our result and those previously reported^{11(d), 33} might be related to the significantly different microstructures of p-PSi and n-PSi.³⁵

Figure 2.25 shows the relation between the integrated PL intensity and the excitation light intensity. It is clear that the integrated PL intensity increases in proportion to the excitation light intensity in the range of the present experiment. This result implies that PL from the p-PSi/electrolyte solution interface is observed as a result of recombination of photogenerated electron-hole pairs.

2.5.2.2. Potential and Excitation Light Wavelength Dependence of PL Spectra

Figure 2.26 shows the PL spectra at various potentials recorded during the potential sweep between 0 and -1.2 V with a sweep rate of 20 mV/s under monochromatic 330, 360, and 390 nm light excitation in 0.2 M Na₂SO₄ aqueous solution. As the excitation light wavelength became longer, the intensity of the emitted light from the p-PSi became smaller. When the potential was swept in the negative direction, a quenching of the PL intensity

accompanied with a blue-shift of the peak wavelength was observed as a result of the selective quenching of the red portion (low energy) of the spectra. No potential dependence was observed, however, for the blue portion (high energy) of the PL spectra. When the potential was swept back in the positive direction, the red portion of the PL spectra gradually recovered. The electrically-induced quenching of the PL intensity from PSi was also reported by Bsiesy *et al.*^{11(d)} and Meulenkamp *et al.*³³ on n-PSi in forward bias condition. Although they demonstrated that the visible PL from an n-PSi/electrolyte

solution interface is reversibly quenched by negative biases due to the quenching of the red portion (low energy) of the PL spectra, little attention has been given to the dependence of excitation light wavelength on voltage tuning of the PL spectra.

The quenching of the red portion increased quite significantly as the excitation light wavelength became longer.

2.5.2.3. Current-Potential and PL Intensity-Potential Relations

Figure 2.27 shows the potential dependence of current and relative PL intensity recorded by sweeping the potential of the p-PSi electrode at 20 mV/s between 0 and -1.2 V in 0.2 M Na₂SO₄ aqueous solution under excitation light wavelengths of 330, 360 and 390 nm.

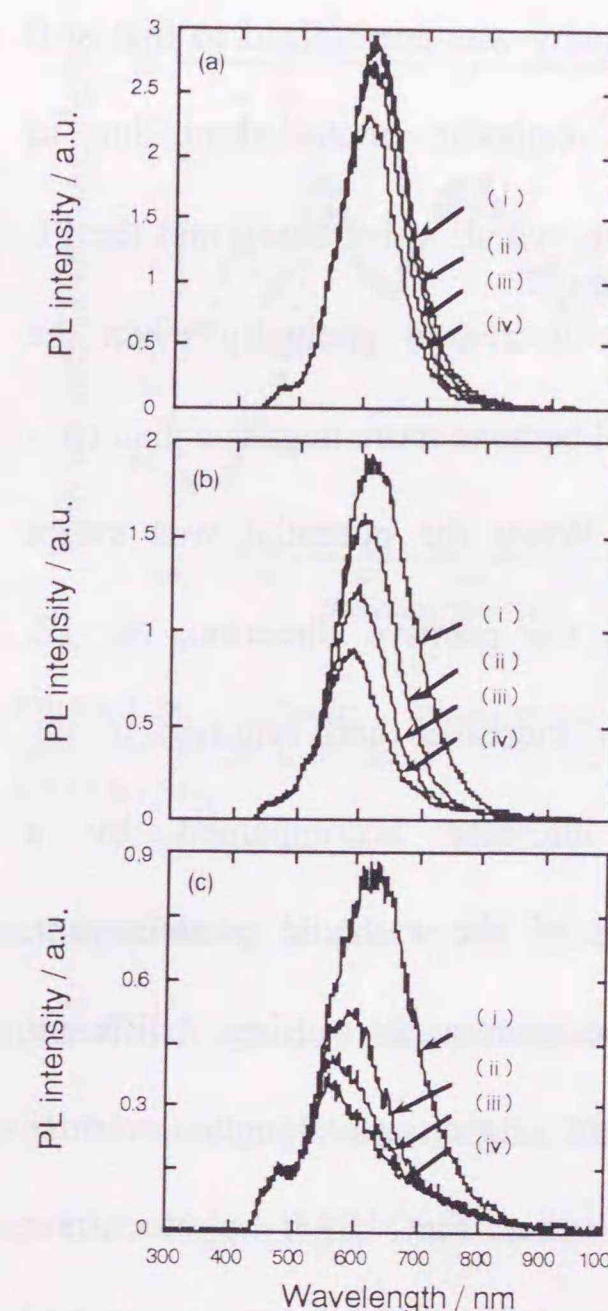


Figure 2.26. PL spectra observed at various negative potentials by sweeping the electrode potential with a sweep rate of 20 mV/s under monochromatic (a) 330, (b) 360, and (c) 390 nm excitation light. The spectra were measured at (i) -0.60 to -0.65 V, (ii) -1.05 to -1.10 V, (iii) -1.10 to -1.15 V, and (iv) -1.15 to -1.20 V.

PL intensity was normalized to that at 0 V. The cathodic photocurrent due to hydrogen evolution increased and the PL intensity decreased gradually when the potential became more negative than ca. -0.6 V. When the potential was swept back in the positive direction, the PL intensity increased and returned to the initial intensity accompanied by a decrease of the cathodic photocurrent. The measurements using different excitation light wavelengths clearly showed that the larger photocurrent flowed and the PL was more quenched by longer wavelength excitation light. Note that the this behavior of the quenching coincides with that of the potential dependence of the PL spectra as shown in Figure 2.26.

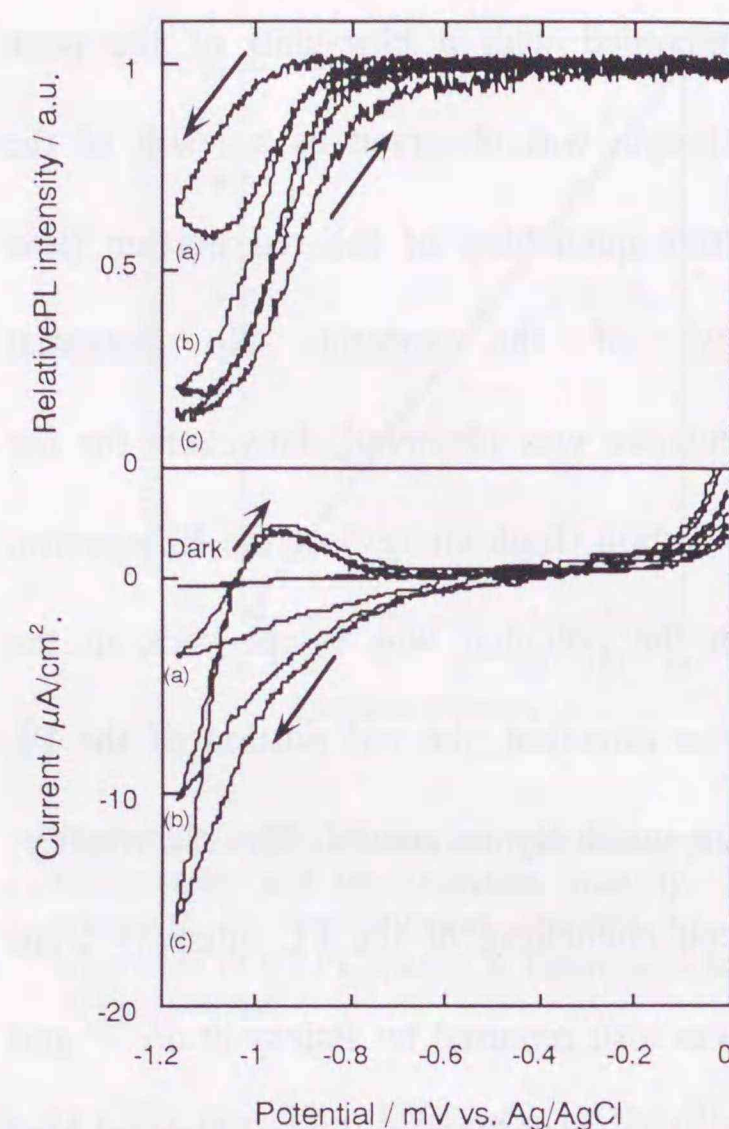


Figure 2.27. Potential dependence of PL intensity and cathodic photocurrent density with a sweep rate of 20 mV/s under monochromatic (a) 330, (b) 360, and (c) 390 nm excitation light. PL intensity (I) was normalized to that of the initial intensity (I_0).

2.5.2.4. Photocurrent Action Spectra at p-Type PSi/Electrolyte Solution Interface

In order to discuss the origin of the photocurrent observed above, i.e., whether the cathodic photocurrent is arising from the Si substrate or from the PSi layer, the cathodic photocurrent action spectra of a p-Si and a p-PSi electrodes at -1.2V were measured as shown in Figure 2.28. The cathodic photocurrent was normalized with respect to the light intensity to eliminate the effect of the excitation light intensity on cathodic photocurrent property. When the excitation wavelengths were longer than 500 nm, the response of the cathodic photocurrent was approximately the same for both PSi and p-PSi (ca. $1.5 \mu\text{A}/\text{cm}^2 \cdot \mu\text{W}$). When the excitation wavelengths became shorter than 500 nm, however, a decrease of the cathodic

photocurrent was observed for the p-PSi, although, it was approximately constant for p-Si. The optical transmission spectra of PSi measured by Koyama *et al.*³⁶ using self-supporting p-PSi layer, the PSi layer is almost optically transparent in the wavelengths longer than 500 nm. Thus, it is possible to say that the decrease of the cathodic photocurrent observed in p-PSi in the excitation light

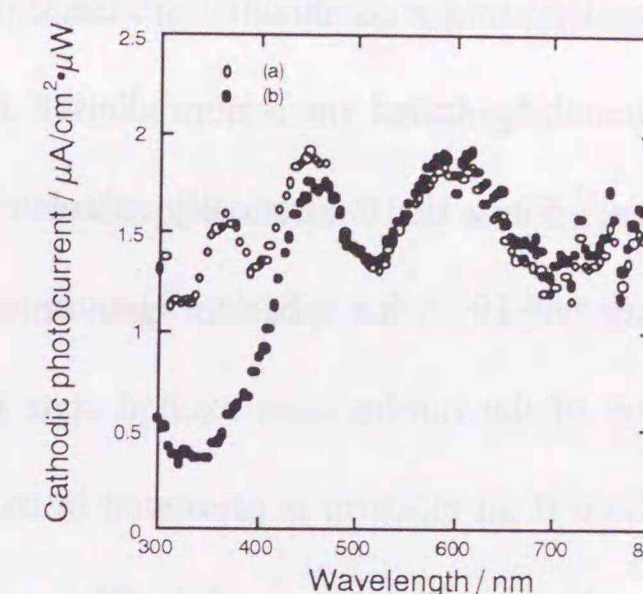


Figure 2.28. Cathodic photocurrent action spectra at the (a) p-Si and (b) p-PSi electrodes in 0.2 M Na_2SO_4 .

wavelength shorter than 500 nm observed in our experiments is due to the absorption of incident photons by PSi layer formed on Si substrate which acts just like a short cut optical filter for Si substrate. Most of the incident photons in the wavelength shorter than 500 nm will contribute to the initial efficient PL as it was observed in Figure 2.27. Only few photons are able to reach the Si substrate and contribute to generate photocarriers. Hence, the author concluded that the cathodic photocurrent observed during the potential scan in Figure 2.27 is arising from the Si substrate.

2.5.2.5. Interpretation of Potential and Excitation Light Wavelength Dependence of PL from p-Type PSi/Electrolyte Solution Interface

Recent investigations of electrically induced quenching of the PL intensity at an n-PSi electrode in forward bias by Bsiesy *et al.*^{11(d)} and Meulenkamp *et al.*³³ have shown that this quenching is related to the changes in potential. Very recently, Peter *et al.*³⁷ have observed a voltage tuning of EL from p-PSi/persulfate solution interface under reverse bias condition where electrons were generated in the substrate by illuminating from the rear of the Si wafer. They also measured the interfacial capacitance of the p-PSi/electrolyte solution and concluded that the electrons accumulated in the PSi layer could be able to generate EL via the reduction

of persulfate and recombine with the injected hole.^{37, 38} They proposed a mechanism of the PL quenching based on a nonradiative Auger recombination of the electron-hole pair or exciton.³⁷ Since the theoretically calculated nonradiative Auger recombination lifetime is of the order of 10^{-9} s for spherical quantum sized Si crystallites³⁹ and is much shorter than the lifetime of the luminescent excited state (ca. 10^{-5} s), the light emission will be completely quenched if an electron is presented in the excited state. They did not, however, discuss the relation between the degree of the PL quenching and amount of photocurrent which is one of the most important parameters to characterize the p-Si/electrolyte solution interface.

The photocurrent action spectra of the p-Si and p-PSi showed that most of the incident photons are absorbed in the PSi layer when wavelength is shorter than 400 nm. Since PL measurements were carried out in this wavelength region, we should consider the mechanism with this fact in mind. The remaining photons reach the Si substrate and generate electron-hole pairs. The photogenerated electrons may be either swept into the confined state in the PSi layer or contribute to hydrogen evolution at Si/electrolyte solution interface, i.e., photocurrent, with the competition of recombination with holes. As the potential becomes more negative, the Fermi level scans across the conduction band levels of the Si nano crystallites toward the smaller size (large bandgap) which leads to a shift in the optical absorption edge to higher energies by accumulation of electrons in PSi layer injected from the Si substrate induced by the electric field in the Si substrate. Therefore, the quenching from the red portion (low energy) of the PL spectra is observed by increasing the negative potential (Figure 2.26). Note that our results are quite analogous with that seen in the previous works with n-PSi/electrolyte solution interface under forward bias conditions.^{11(d), 33}

The excitation wavelengths dependence of the photocurrent and the PL quenching can be explained qualitatively by considering the optical penetration depth of the excitation light wavelength. Longer wavelength light will penetrate deeper in Si substrate and generate more photogenerated electrons. Large population of photogenerated electrons will lead to both

high probability to enter the confined energy states in PSi layer and large cathodic photocurrent at Si/electrolyte solution interface. Hence, quenching of the lower energy portion of the PL spectra becomes faster and the cathodic photocurrent becomes larger in the case of longer excitation wavelength light than in the case of shorter one even at the same potential.

2.5.3. Conclusion

The photoelectrochemical and PL properties of the p-PSi/electrolyte solution interface were investigated. It has been demonstrated that voltage tuning of the PL spectra is observed even at p-PSi/electrolyte solution interface under reverse bias region. A quenching of the PL intensity accompanied by a blue-shift of the peak wavelength, as a result of the quenching of the red portion of the PL spectra, and increased photocurrent were observed by making the potential more negative. The longer the excitation light wavelength, the larger the observed quenching. The experimentally observed results can be explained by considering the dependence of electron accumulation on the conduction band levels in PSi layer, which is in turn related to the Si nano crystalline size.

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Chapter 3

Ultrafast Dynamics of Electron-Hole Recombination Processes in Semiconductor Powders

Chapter 3

Ultrafast Dynamics of Electron-Hole Recombination Processes in Semiconductor Powders

3.1. Introduction

Photoirradiation on semiconducting materials with light, the energy of which is greater than their bandgap, creates pairs of electron in the conduction band and positive hole in the valence band. They react with species adsorbed on the surface or in solution to induce redox reactions, otherwise undergo mutual recombination without substantial chemical reactions. Such redox reactions at solid/liquid or solid/gas interfaces are called "photoelectrochemical" or "photocatalytic" reactions, and are of great importance from both fundamental and applied standpoints.¹ In order to clarify the dynamics and mechanisms of these photocatalytic reactions, conventional time-resolved optical spectroscopic techniques have been applied over the past decades to a large number of transparent colloidal, but not opaque suspension, systems in solution.² The majority of these studies have focused on the electron-hole recombination dynamics in semiconductor particles and photoinitiated electron transfer reactions to and/or from species adsorbed on the particle or in solution. It was reported that such kind of kinetics involving nanometer-sized semiconductor particles are often complex and range from the femtosecond to the millisecond time scale. In contrast, there have been only few optical studies on light scattering materials such as powder and suspensions,³⁻⁷ which are usable to technologically important applications, e.g., photocatalytic detoxification of environmental pollutants.

Diffuse reflectance spectroscopy permitting optical spectroscopic measurements of highly scattering samples, where diffuse light from the sample is detected instead of transmitted light in conventional spectroscopic methods, should be utilized to the photocatalytic reaction system using semiconductor powders. Wilkinson *et al.*⁸ have applied

time-resolved diffuse reflectance (TRDR) spectroscopy to crystal and powder samples for the first time. Several groups have extended this TRDR laser flash photolysis spectroscopy into the picosecond and femtosecond time regimes where the dynamics of molecules adsorbed onto semiconductors and other substrates take place.⁹ Kamat *et al.*^{9(a)-(c)} investigated the dye sensitization processes of TiO₂ and SiO₂ solid substrates by the TRDR spectroscopy. They elucidated the time scale of charge injection into the semiconductor nanoparticles and its dependence on surface coverage. Fox *et al.*^{9(d), (e)} investigated the photooxidation reaction of opaque suspension of TiO₂ powder with several electron donors in solution. Both wavelength and time-resolved measurements were performed on intermediate oxidized species in solution and revealed the mechanism for electron transfer. Recently, femtosecond TRDR spectroscopic measurements were performed to follow up charge carrier trapping and recombination kinetics in TiO₂ nanoclusters.⁴ It was found that photogenerated electrons in the conduction band of TiO₂ are trapped at Ti⁴⁺ site to generate Ti³⁺ within 180±10 fs,^{4(a)} and subsequent recombination in second-order kinetics of trapped electron and hole occurs within 100 ps.⁵ The relationship between the charge carrier dynamics and photocatalytic activity on some TiO₂ photocatalysts were also investigated.⁶

In this chapter, the femtosecond TRDR spectroscopy on TiO₂ powder systems is reported. The observed charge carrier dynamics depending on the nature of TiO₂ powders will be discussed in terms of their physical properties.⁷ On the basis of these fundamental considerations, effect of excitation wavelength on the ultrafast charge carrier recombination dynamics is shown and discussed in relation with the optical and photocatalytic properties of semiconductor particles.

3.2. Experimental

3.2.1. Materials

Four kinds of TiO₂ powders were mainly examined in the present work. JRC-TIO-2,

Table 3.1. Physical properties of TiO₂ powders used in the present experiments.

TiO ₂	crystal structure	primary particle size (nm)	BET surface area (m ² g ⁻¹)
JRC-TIO-2	anatase	400	18
JRC-TIO-5	rutile	640	2.6
P-25 ¹	anatase+rutile	20-60 (21 ²)	50
Idemitsu UF	(amorphous)	15-20	115

¹ P-25 is also supplied from Catalysis Society of Japan as JRC-TIO-4.

² Average size.

and JRC-TIO-5 were supplied by the Catalysis Society of Japan. Degussa P-25 and Idemitsu UF were gift from Nippon Aerosil and Idemitsu Kosan Co. Ltd., respectively. Some of their physical properties are listed in Table 3.1. As a pretreatment for transient diffuse reflectance measurements, these powders were ground thoroughly in an agate mortar without further treatments.

3.2.2. Femtosecond Laser System for the Transient Diffuse Reflectance Spectroscopy

A schematic diagram of the experimental arrangement is shown in Figure 3.1. Train of 100 fs pulses of 1 mJ energy and 1 kHz repetition rate was generated by a regenerative amplifier system (Quantronix, 4812RGA/4823S/C), which was synchronously pumped by a mode-locked YLF laser (Quantronix, 527DP-H). The seed pulses were supplied by a mode-locked Ti: sapphire laser (Spectra-Physics, Tsunami: 3960-L2S) pumped by an argon ion laser (Spectra-physics, BeamLok: 2580C) producing 400 μJ energy, 100 fs pulses centered at 790 nm with a repetition frequency of 82 MHz. The final output of the laser system was split into two beams of almost equal intensity to pump two identical optical parametric generation (OPG)/optical parametric amplification (OPA) systems (Light Conversion Ltd., TOPAS). The 620 nm output beam from one OPG/OPA was mainly used as a probe beam (1.5 μJ/pulse) and

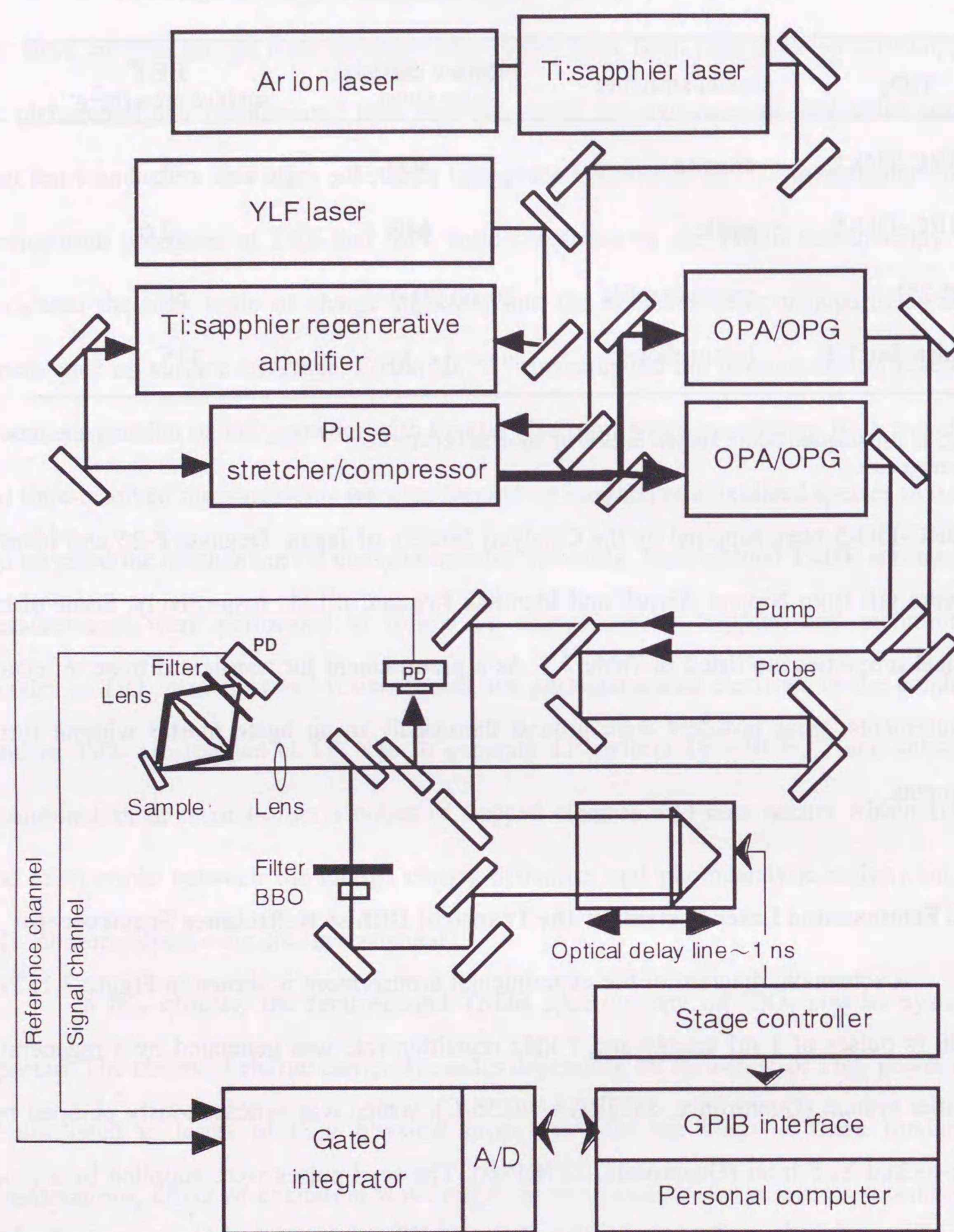


Figure 3.1. Schematic diagram of the femtosecond laser system and the time-resolved diffuse reflectance spectrometer.

a 620 - 820 nm output beam from second OPG/OPA was frequency doubled in a BBO crystal and used as a pump beam (0.1-0.03 $\mu\text{J}/\text{pulse}$). The probe beam was split into two beams. One beam of smaller intensity goes to a reference photodiode (Hamamatsu Photonics Co. Ltd., S2387-66R) and the other goes to a sample and diffusely reflected to a signal photodiode

(Hamamatsu Photonics Co. Ltd., S2387-66R). The pump and probe beams were collinearly focused with focal lens ($f=10\text{ cm}$) and overlapped at the sample. The outputs from the photodiodes were fed into two separate gated boxcar integrators (Stanford Research Systems, SR250), and digitized with 8 bit A/D converter (Stanford Research Systems, SR245). Reflectance data was accumulated and recorded by a personal computer (Digital Equipment Co., VENTURIS FP5100) as absorption, $(R_0-R)/R_0$, where R and R_0 represent the intensity of diffused light from the sample with and without pump beam, respectively. Both R and R_0 were corrected by the reference beam intensity of each probe pulse, and only the absorption for the probe pulse whose intensity is within a given, typically $\pm 5\%$, fluctuation. The delay between the pump and probe pulses was controlled by an optical delay line containing with a translation stage of $1\text{ }\mu\text{m}$ (3.3 fs) resolution and 1 ns maximum delay (Sigma Koki Co., Ltd., AS NET-3/STM-160). Before experiment, zero point of delay, i.e., timing of coincidence of pump and probe beams, was determined by measuring the transient absorption of 1,1'-binaphthyl (Tokyo Kasei Kogyo Co. Ltd., for 310 nm pump) or perylene (Wako Pure Chemical Industries, Ltd., for 350-410 nm pump) dissolved in organic solvent in a quartz cell. Spatial overlapping of two beams was adjusted to be maximum by using also these solutions. All the measurements were carried out at room temperature.

3.3. Results and Discussion

3.3.1. Recombination Dynamics in Various Semiconductor Powders

Figure 3.2 shows representative decay profiles of transient absorption in various TiO_2 powders (P-25, JRC-TIO-2, and Idemitsu UF). It was commonly observed that a pump beam of wavelength at 310 nm induced very rapid (<ca. 250 fs) rise and gradual decay of absorption at 620 nm, as has been reported previously.⁴ The maximum absorption was 1.5 - 4 % irrespective of TiO_2 samples. The recent papers for experiments on TiO_2 colloid or powder systems have reported that photogenerated electrons are rapidly trapped after bandgap

excitation of TiO_2 , and a large fraction of them undergo subsequent electron-hole recombination. It has been shown that these trapped electrons give a broad absorption centered around 500 - 650 nm.¹⁰ On the basis of these considerations, this absorption at 620 nm was also assigned as trapped electrons in TiO_2 . The observed decay

profiles could be fitted by assuming a second-order kinetic equation of,

$$\text{absorption} = \alpha_e \left\{ \frac{[e]_0}{1 + k_r [e]_0 t} + BL \right\} \quad (1)$$

where $[e]_0$, BL, k_r , and t refer to initial concentration of trapped electron just after the pump pulse, base line corresponding to long lived trapped electron, second-order rate constant for electron hole recombination, and delay time.⁵ This is based on the assumption that the trapped electrons disappear by recombination with positive holes in the ps time scale but a part of them remain trapped in the >ns time scale, as the BL.¹⁰ A parameter α_e (cm^3) includes photoabsorption cross section and penetration depth, but seems to be an empirical parameter. The decay profile depended strongly on the pump beam intensity; the intenser the pump beam, the higher the maximum and steeper the decay, but the decay curves were reproduced with almost same k_r value when α is assumed to be constant for a series of measurements. In the subsequent discussion, we assumed, for convenience, α to be unity for all the measurements to calculate the second-order rate constant, k_r .

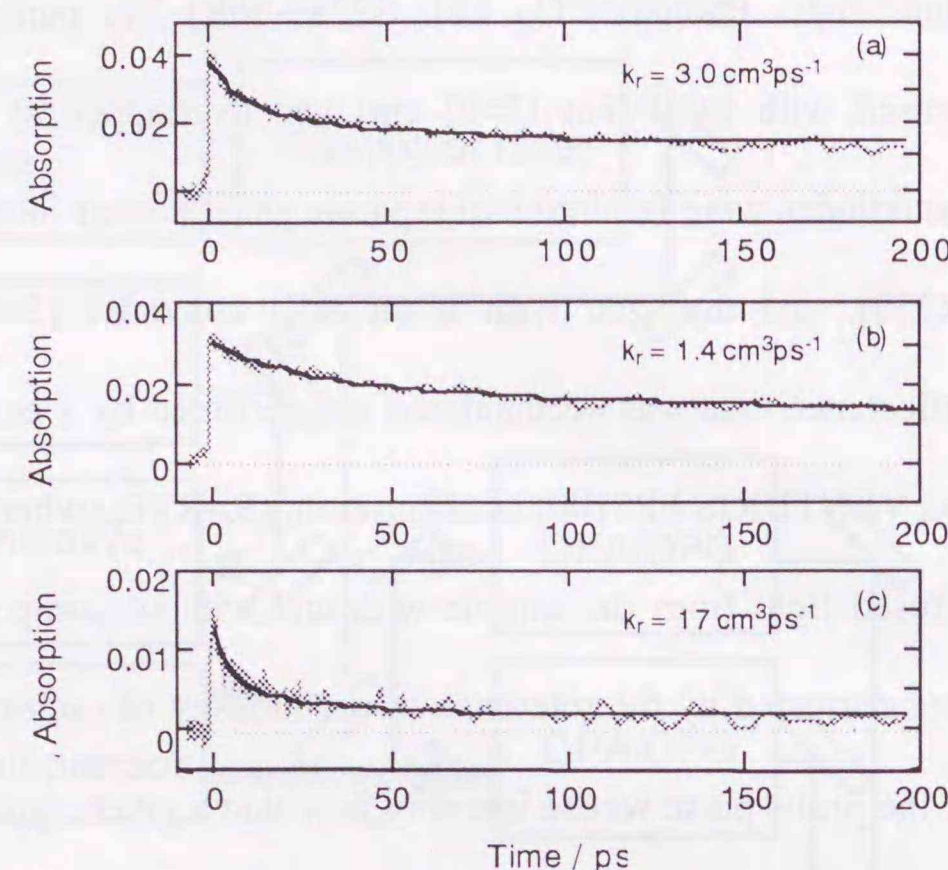


Figure 3.2. Transient absorption decay profiles of TiO_2 powders. $\lambda_{\text{pump}}=310$ nm and $\lambda_{\text{probe}}=620$ nm. (a) P-25, (b) JRC-TIO-2, and (c) Idemitsu UF. Solid lines are the fitting curves with equation 1 (see text).

As clearly seen in Figure 3.2, recombination dynamics depended strongly on the nature of TiO_2 . Among these samples, amorphous TiO_2 (Idemitsu UF) showed the largest k_r ($17 \text{ cm}^3\text{ps}^{-1}$), i.e., the fastest recombination, and anatase TiO_2 (JRC-TIO-2) showed the smallest k_r ($1.4 \text{ cm}^3\text{ps}^{-1}$), i.e., the slowest recombination. Although P-25 is composed of mainly anatase, recombination was faster ($k_r=3.0 \text{ cm}^3\text{ps}^{-1}$) than JRC-TIO-2 which is also composed of same anatase. A good correlation between surface area and k_r was seen among the present TiO_2 powders, i.e., the larger the surface area, the faster the recombination. Considering the absorption coefficient, α , of TiO_2 at 310 nm ($\alpha=6.52 \times 10^{15} \text{ cm}^{-1}$),¹¹ the light penetration depth, L , of incident UV pump was calculated as 0.15 nm, where L is defined as $1/\alpha$, which suggests that most of the photons are absorbed at the surface of the particles. From these results, it is reasonable to conclude that certain surface sites on the TiO_2 induce the fast electron-hole recombination in ps time scale, though further detailed studies are necessary to exclude the participation of other physical properties, e.g., crystallinity, crystal structure, or grain boundaries.

3.3.2. Effect of Excitation Wavelength on Electron-Hole Recombination Processes

Recently, Furube *et al.*^{3(b), 6(a)} reported that faster decay was observed for JRC-TIO-2 than JRC-TIO-4, i.e., P-25. This was in contrast to the present results, in which P-25 showed the decay faster than JRC-TIO-2. One of the possible reason for the discrepancy is difference in the wavelength of pump beam; in the previous report 390 nm light, which corresponds roughly to the bandgap of anatase TiO_2 (3.2 eV), was employed, while in present study was used 310 nm. This suggests the presence of wavelength dependence of the recombination dynamics in TiO_2 powders and the detailed study may give us significant informations. Therefore, the author tried to clarify the wavelength dependence of decay profiles by changing the pump beam wavelength.

As representative TiO_2 samples consisting of rutile and anatase crystallites, JRC-

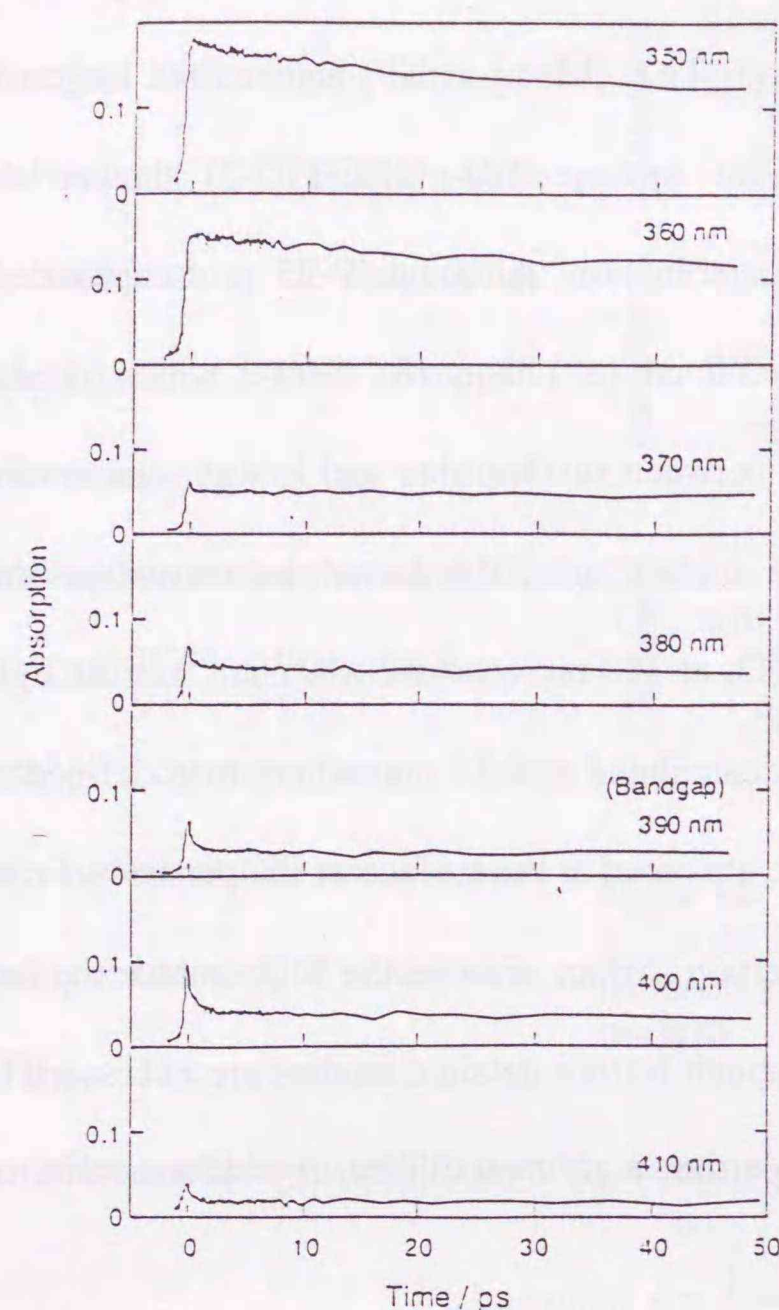


Figure 3.3. Excitation wavelength dependence on transient absorption decay profiles observed at JRC-TIO-2. $\lambda_{\text{probe}}=620$ nm.

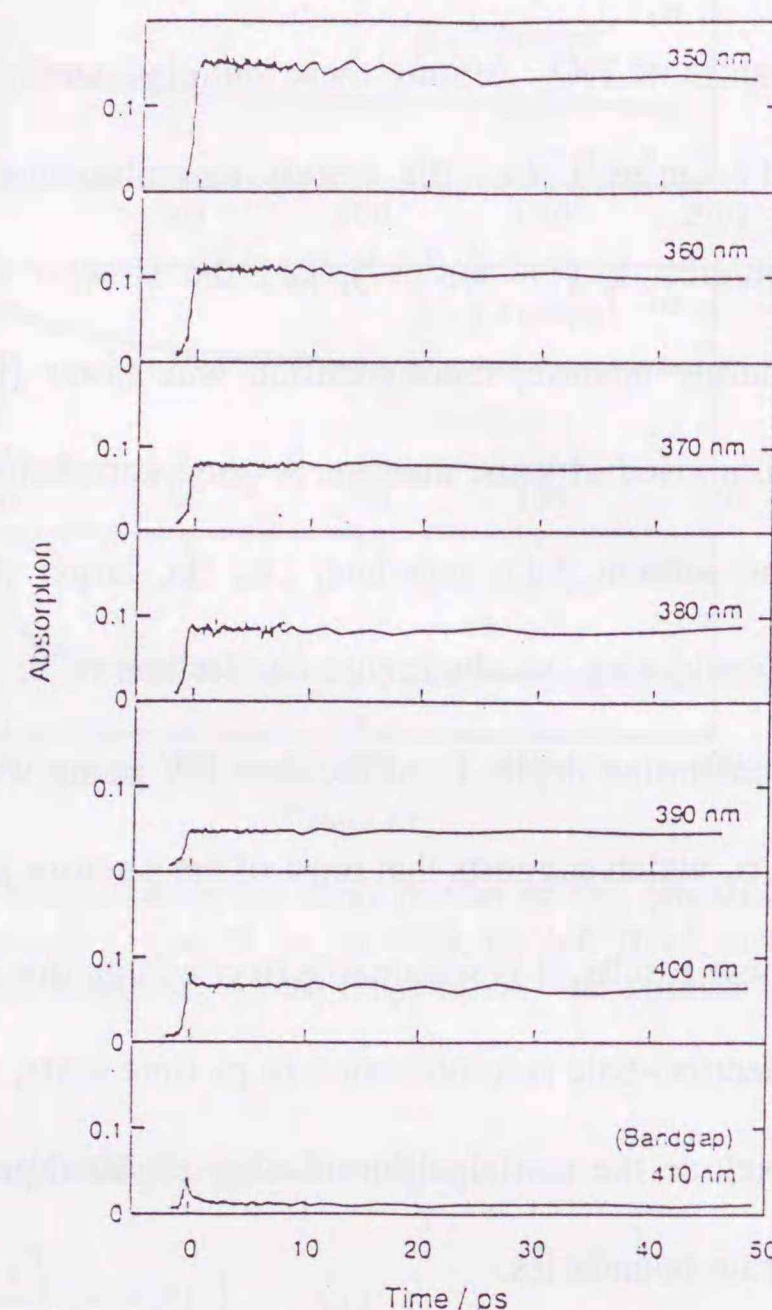


Figure 3.4. Excitation wavelength dependence on transient absorption decay profiles observed at JRC-TIO-5. $\lambda_{\text{probe}}=620$ nm.

TIO-5 and JRC-TIO-2 were used, respectively, to be compared each other. Figure 3.3 shows the time profiles of transient absorption for the anatase powder with various excitation (pump) wavelengths. In the case of 350 and 360 nm pump, rapid (<ca. 1ps) rise of absorption at 620 nm and subsequent gradual decay were observed. This behavior was quite similar to the results of 310 nm pump, as described in the previous section. When the pump wavelength was set longer, 370 to 410 nm, however, very rapid decay in a few ps region after the rise of absorption was observed. Another interesting feature is that almost constant absorption follows the very rapid decay, i.e., negligible decay was observed within the time range examined in this study and the constant absorption became smaller as the pump wavelength

was set longer. It should be noted here that the decay profile reported by Furube *et al.*^{3(b), 6(a)} for JRC-TIO-2 by 390 nm pump, which mentioned above, was almost the same as what we observed at the same pump wavelength. Thus, it has been revealed that the electron-hole recombination dynamics depends strongly on pump wavelength of energy around the bandgap, and will be discussed by comparing with the results for rutile TiO_2 .

There seems to be another notable finding in Figure 3.3. Since the bandgap energy of anatase TiO_2 is 3.2 eV (ca. 390 nm), no absorption was expected when JRC-TIO-2 was irradiated by pump pulse of wavelength longer than 390 nm. However, appreciable absorption was seen at >390 nm pumping. One of the possible reasons which account for this absorption is that two photon absorption process occurs in TiO_2 by intense femtosecond laser pulses.

Figure 3.4 shows the time profiles of transient absorption in rutile TiO_2 powder observed with various pump wavelengths. The behavior with various pump wavelengths was quite similar to that observed with anatase TiO_2 powder; when the pump wavelength was set to 350 or 360 nm, rapid (<ca. 1ps) rise of absorption at 620 nm and subsequent gradual decay were observed. By pumping at the longer wavelength, i.e., 370 - 410 nm, almost constant absorption follows very rapid decay was observed and the constant absorption became smaller along with the pump wavelength. Thus, in the case of rutile TiO_2 , the very rapid decay in the early stage was observed by 400 and 410 nm pump.

While the effect of pump wavelength on electron-hole recombination dynamics was very similar in both TiO_2 powders, difference in the pump wavelength giving the very rapid decay was observed between anatase and rutile crystallites, >370 nm for anatase and >400 nm for rutile. It should be noted that this ca. 30 nm difference in pump wavelength matches quite well with the difference in absorption edge between anatase (3.2 eV=388 nm) and rutile (3.0 eV=413 nm). These results suggest that there is, basically, no difference in electron-hole recombination dynamics between anatase and rutile TiO_2 , i.e., the recombination dynamics do not depend on the crystal structure, if the wavelength dependence are normalized by

using energy relative to their absorption edge.

Although only limited information is available at present to discuss the origin of the rapid decay, it seems reasonable to assume that the near bandgap excitation produces exciton which disappears very rapidly, since the fast decay was observed only when TiO₂ was excited by the wavelength near its bandgap energy⁷. There have been no papers reporting the absorption spectrum of exciton generated in TiO₂ crystals, and therefore, it is difficult to judge whether the absorption at 620 nm is reasonable to be assigned as exciton or not. Any how, two possible mechanisms for the fast decay of exciton can be considered. One is exciton-exciton annihilation, which might be the most possible explanation to observe a very fast decay,¹² and the other is just relaxation of exciton within its lifetime.

Pump intensity dependence was measured for the anatase TiO₂ powder to rationalize one of the two mechanisms. Results are shown in Figure 3.5. The excitation pump wavelength was 390 nm, which is almost the bandgap energy of anatase TiO₂ and the probe wavelength was 620 nm. Pump intensity was adjusted by using a neutral density (ND) filters to be 0.07, 0.05, and 0.06 $\mu\text{J}/\text{pulse}$, which correspond to 4.87×10^{16} , 3.47×10^{16} , and 2.09×10^{16} photons/pulse, respectively. If the anomalous fast decay originates from the exciton-exciton annihilation, the profile should follow a second-order

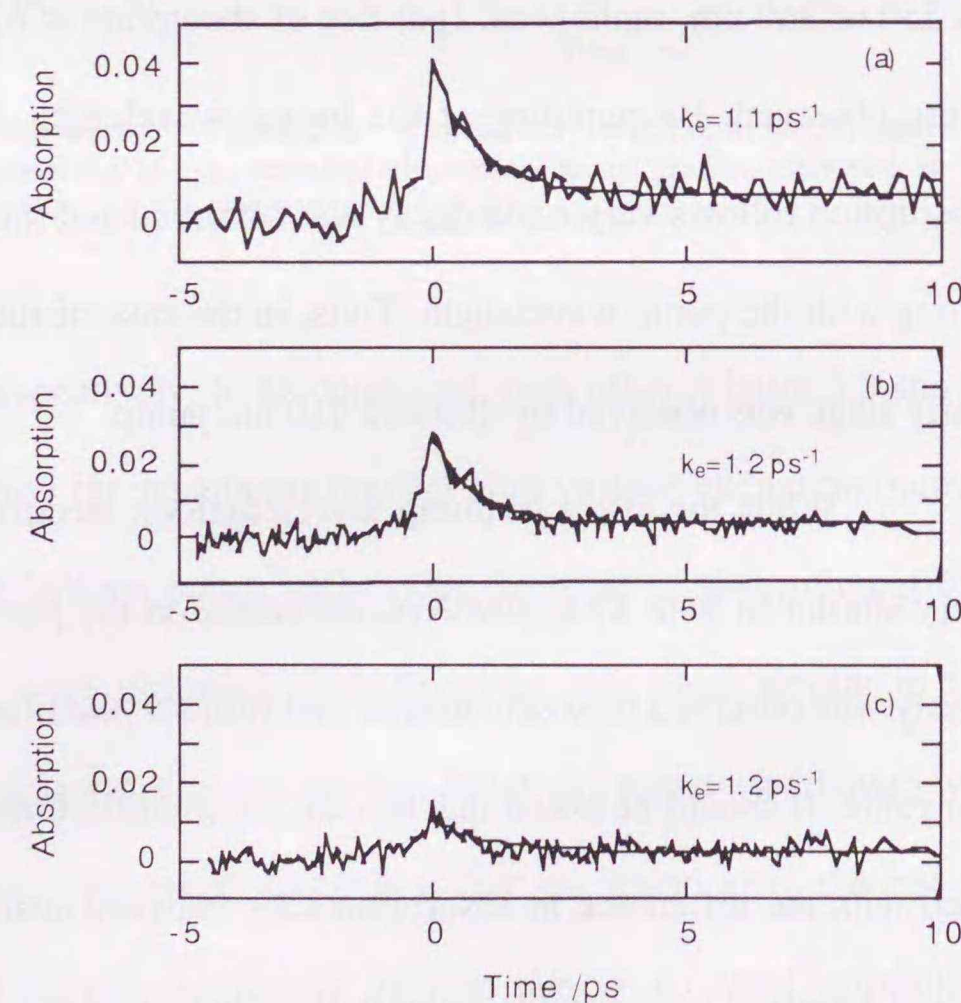


Figure 3.5. Pump intensity dependence on transient absorption decay profiles of JRC-TiO₂. $\lambda_{\text{pump}}=390$ nm and $\lambda_{\text{probe}}=620$ nm. Pump intensity: (a) 0.07 $\mu\text{J}/\text{pulse}$, (b) 0.05 $\mu\text{J}/\text{pulse}$, and (c) 0.03 $\mu\text{J}/\text{pulse}$.

kinetics;

$$\frac{d}{dt}[\text{exc}] = k_a [\text{exc}]^2 \quad (2)$$

where [exc] and k_a refer to concentration of exciton and second-order rate constant for exciton-exciton annihilation, respectively. While if it originates from just the relaxation of exciton, the decay profile could be fitted to a first-order kinetic equation as,

$$\frac{d}{dt}[\text{exc}] = k_e [\text{exc}] \quad (3)$$

where k_e refers to first-order rate constant for electron-hole recombination. By assuming a baseline component, BL, is due to long-lived trapped electron, the present profile is fitted by using eq.(3) as,

$$\text{absorption} = \beta \exp(-kt) + BL \quad (4)$$

rather than with second-order kinetic eq.(2). β and t refer to initial absorption of exciton and delay time, respectively. The parameter β was almost parallel to the pumping intensity. The rate constant k_e was determined to be ca. 1.2 ps^{-1} for all the pump pulse intensities examined. These results strongly indicate that the origin of the anomalous fast decay is due to the relaxation of exciton by itself, not by the exciton-exciton annihilation.

3.4. Conclusion

Femtosecond time-resolved diffuse reflectance spectroscopy on TiO₂ powder systems was carried out in air. It has been shown that the nature of TiO₂ gives differences, especially in rate constant, for electron-hole recombination when the pump wavelength is enough to induce bandgap excitation which was employed. It was suggested that certain surface site on the TiO₂ induces the fast electron-hole recombination in ps time scale. It was also demonstrated that the electron-hole recombination dynamics in anatase and rutile TiO₂ depend strongly on the excitation pump wavelength. Anomalous rapid decay in the first few ps, after a rise of absorption, was observed when TiO₂ was excited by near bandgap energy. Although

there is only limited information at present to discuss the origin of the rapid decay, some possibilities to explain the rapid decay were discussed. It was suggested that this rapid decay originates from relaxation of exciton by itself, not by exciton-exciton annihilation by measuring the pump intensity dependence of the transient absorption decay profile. Since no evidence for the components giving the absorption and its decay, further detail investigation such as probe wavelength dependence, temperature dependence, or time-resolved luminescence measurement are needed to confirm the above-mentioned hypothesis.

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Chapter 4

Direct Observation of Photoexcited Electron Transfer Reaction at Semiconductor/Electrolyte Solution Interface

Chapter 4

Direct Observation of Photoexcited Electron Transfer Reaction at Semiconductor/Electrolyte Solution Interface

4.1. Introduction

Electron transfer (ET) across solid/liquid interface, i.e., electrochemical reaction, is one of the simplest and most important chemical reactions. Not only in the electrochemical systems involved the ET but also plays important roles in other various processes of chemistry as well as biochemistry. Therefore, research on the ET is strongly stimulated by both its fundamental aspects and the applications to practical processes, e.g., industrial electrochemical processes, lithographic processes, and catalytic reactions.¹ However, our understanding on the interfacial ET is lagging behind those of homogeneous ET in solution, due to the greater inherent experimental difficulties, especially by spectroscopy, in studying systems involving interface.

Recently, one approach to overcome this problem was shown by Miller *et al.*² That is picosecond surface restricted transient grating spectroscopy to study the ET reaction dynamics at a semiconductor/electrolyte solution interface. One of the features of this method is that events occurring on the surface can be selectively detected, owing to the effect of semiconductor space charge field on the surface population of reactive charge carriers generated by laser pulse. They applied this technique to an n-type GaAs/KOH aqueous solution interface in the presence of selenium redox couple and observed that trapping of hole by surface states was completed within 1-2 ps.^{2(c)}

To study ET dynamics systematically in the solid/liquid interface, new in situ techniques that are capable to probe "directly" the ET process are needed, since the above mentioned transient grating spectroscopy detects ET with higher resolution in time scale, but "indirectly" which monitor the change of surface charge carriers population as the change of

the refractive index at the surface induced by two above bandgap excitation beam pulse. Femtosecond IR spectroscopy³ possibly provides an solution for the detection of interfacial events because it can directly study the very fast dynamics of electrons in semiconductors. As demonstrated in the studies of bulk semiconductors,⁴ conduction band electrons have strong absorption in the infrared region. Such absorption consist of free carrier absorption,⁵ which is broad and increases with wavelength, intraband transitions⁵ between different valleys (or subbands) within the conduction or valence bands, and absorption of trap states.⁵ Since these IR absorptions reflect characteristics and behavior of electrons inside the semiconductor, they will become a good spectroscopic probe for interfacial ET between semiconductor and liquid. Recently, Lian *et al.*⁶ demonstrated the ability of the ultrafast IR spectroscopy for measuring the rate of interfacial ET between sensitizer molecules and semiconductor nanoparticles in air. Excitation of dye molecules at 400 nm resulted in injection of electron into the conduction band of TiO₂, as observed as an rapid rise of IR absorption in the mid-IR range (1700 - 2400 cm⁻¹). It was reported that the electron injection into TiO₂ occurs within 50±25 fs after dye excitation.^{6(d)}

In this chapter, ET dynamics at photoexcited potential regulated semiconductor/solution interface is investigated by using femtosecond visible pump-IR probe method. This work is the first example to apply femtosecond visible pump-IR probe method to the semiconductor photoelectrochemical systems.

4.2. Experimental

4.2.1. Materials

Silicon wafers used in this study were p-type (B doped, 8 - 12 ohm•cm: 1.11 - 1.68 x 10¹⁵ cm⁻³) single crystals exposing (100) surface obtained from Shin-Etsu Semiconductor. The wafers were cleaned first with acetone to remove organic impurities, washed with pure water and then chemically etched in HF solution for 10 s to remove the surface native oxide. Its

ohmic contact was made with In-Zn alloy to be used as a working electrode.

Electrolyte solution was prepared with reagent grade Na₂SO₄ (Wako Pure Chemicals), KI (Wako Pure Chemicals), I₂ (Wako Pure Chemicals) and Milli-Q water and was deaerated by passing high purity nitrogen gas (99.999 %) thorough it prior to the measurements.

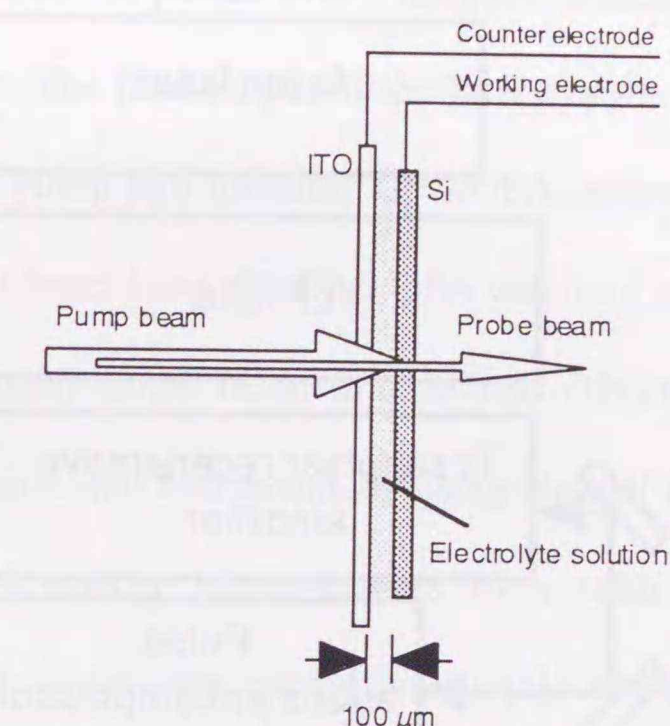


Figure 4.1. Thin layer photoelectrochemical two-electrode cell.

4.2.2. Electrochemical Measurements

Electrochemical measurements were carried out in 0.1 M Na₂SO₄ aqueous solution containing 0.05 M KI + 0.05 M I₂ in a two-electrode thin-layer cell as shown in Figure 4.1 with Si as a working and indium tin oxide (ITO) as both a counter electrode and an optical window for incident visible and IR beams. Two electrodes were separated by using a Teflon spacer and the thickness of the electrolyte solution, i.e., optical path length, was 100 μm. The potential of the working electrode with respect to an ITO was controlled by using a potentiostat/galvanostat (Hokuto Denko, HA-151) and a function generator (Hokuto Denko, HB-111). The current-potential relations were recorded by using an X-Y recorder (Rika Denki, RW-11T). All the measurements were performed at room temperature.

4.2.3. Femtosecond Laser System for the Visible Pump-IR Probe Spectroscopy

A schematic diagram of the experimental arrangement is shown in Figure 4.2. Pulses of 100 fs duration and 400 μJ/pulses centered at 790 nm with a repetition frequency of 82 MHz were generated by a mode-locked Ti: sapphire laser (Spectra-Physics, Tsunami: 3960-

room temperature.

Photoelectrochemical measurements were carried out during the visible pump-IR probe measurements by applying a constant negative potential (vs. ITO) to the p-type Si electrode. Photocurrent induced by 620 nm pump beam was recorded by using X-t recorder (Rika Denki, RW-11T).

4.3. Results and Discussion

4.3.1. Photoelectrochemical Measurements at p-Type Si/Electrolyte Solution Interface

Figure 4.3 shows the current-potential relation by sweeping the potential of p-type Si electrode at 100 mV/s between 0 and -2.0 V in 0.1 M Na_2SO_4 aqueous solution containing 0.05 M KI + 0.05 M I_2 in dark and under pump beam (620 nm) irradiation. Cathodic photocurrent due to reduction of I_3^- to I^- as well as to hydrogen evolution increased gradually as the potential became more negative than ca. -0.7 V. Without illumination, cathodic current was also started to flow around -0.7 V and became large as a result of hydrogen evolution in more negative potentials. Because electron is a minority carrier in p-type semiconductors, no appreciable cathodic current is expected in a negative potential region. One possibility to explain this result is to consider that the valence band electrons in p-type Si electrode contributed in the electrochemical reaction in the dark, i.e., reacting with the redox couple in solution, since the redox potential of I_3^-/I^- (+0.55 V vs. NHE)⁷ is positive enough to lie below the upper energy level of valence band in Si. Another possibility to explain this result is to consider a formation of inversion layer at the surface. If an inversion layer is formed, a tunneling of the valence band electrons to the conduction

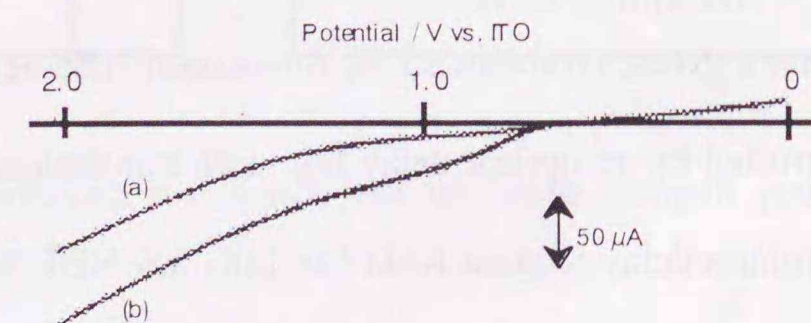


Figure 4.3. Cyclic voltammogram of Si/0.1 M Na_2SO_4 + 0.5 M KI + 0.05 M I_2 (a) in dark and (b) under illumination.

band become possible when the top of the valence band in the bulk is higher than the bottom of the conduction band at the surface.⁸ As a result, electrons tunnel to the conduction band at the surface from the valence band in the bulk and they participate in electrochemical reactions.

4.3.2. Femtosecond Visible Pump-IR Probe Measurements at p-Type Si/Electrolyte Solution Interface

In order to investigate the photoexcited ET dynamics in semiconductor electrode, the visible pump-IR probe spectroscopy was applied to p-type Si/electrolyte solution interface at the negative potential where photocurrent was observed. Since IR beam was used as a probe, it enables direct observation of behavior of electrons in the conduction band of Si.

Figure 4.4 shows the decay profiles of IR absorbance at p-type Si after 620 nm visible excitation. Very rapid rise (< 1 ps) of the absorbance at 4000 nm was induced by the 620 nm pump pulse corresponding to the excitation of valence band electrons into conduction band. The maximum absorbance of ca. 0.15 was observed both in air and for electrolyte solution. In the measurements in air (Figure 4.4 (a)), i.e., without electrolyte solution, decay of the absorbance at 4000 nm

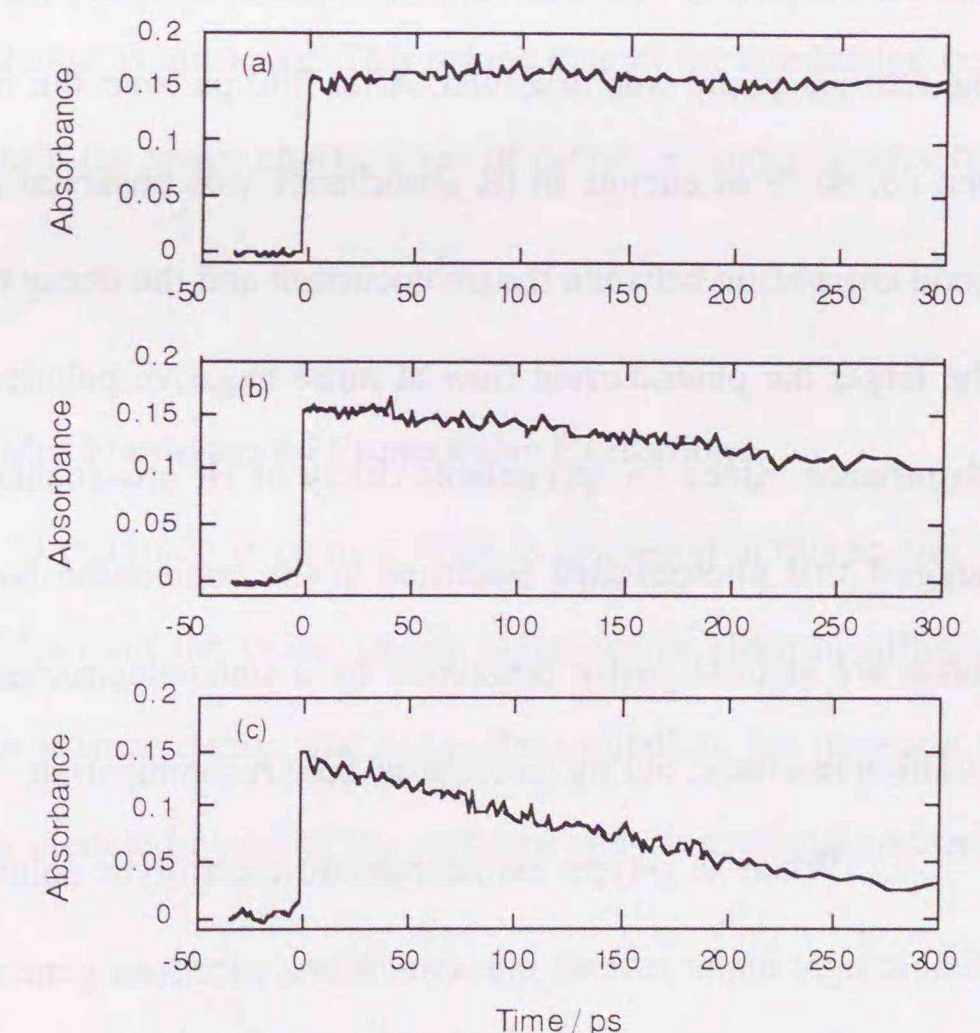


Figure 4.4. Transient IR absorbance decay profiles of (a) p-type Si measured in air and in an aqueous solution containing 0.1M Na_2SO_4 , 0.5 M KI, and 0.05 M I_2 at bias potentials of (b) -1.5 V, and (c) at -2.0 V (see Figure 4.3.). $\lambda_{\text{pump}}=620$ nm, $\lambda_{\text{probe}}=4000$ nm

was not observed within the time range examined in this study. The lifetime of the photogenerated electrons in the conduction band of Si is known to be in the order of ns time scale though it depends on the carrier concentration.⁹ Because Si is an indirect bandgap semiconductor, the relaxation of electrons between conduction and valence bands must be mediated by an intermediate process which conserves momentum, i.e., phonon emission or phonon absorption.⁵ Thus, the transition probability becomes lower than that of direct bandgap semiconductors, e.g., GaAs, InP, InSb.

Different behavior was observed when the Si wafer was immersed in an electrolyte solution. Figures 4.4(b) and 4.4(c) shows the transient IR absorbance profiles measured in 0.1 M Na₂SO₄ aqueous solution containing 0.05 M KI + 0.05 M I₂ as a redox couple. Constant negative potential was applied to the p-type Si electrode. The photocurrent induced by the 620 nm pump pulse was measured during the visible pump-IR probe measurement to be, ca. 90 and ca. 175 μ A, at -1.5 and -2.0 V, respectively. Very rapid rise of IR absorbance induced by the 620 nm pump was observed. After 300 ps from the incidence of the pump pulse, ca. 30 and ca. 80 % of change in IR absorbance was observed at -1.5 and -2.0 V, respectively. A good correlation between the photocurrent and the decay of IR absorbance was observed, i.e., the larger the photocurrent flow at more negative polarization, the larger the decrease of IR absorbance. Since no appreciable decay of IR absorbance was observed in air, these results suggest that photoexcited electrons in the conduction band, generated by the visible pump pulse are at least partly consumed by a photoelectrochemical reaction at the Si/electrolyte solution interface, not by an electron-hole recombination.

When a p-type semiconductor/electrolyte solution interface was illuminated by visible light under reverse bias conditions, electrons generated in the space charge layer move to the semiconductor/solution interface rolling down the potential slope in the space charge layer. The thickness of the space charge layer, W , can be calculated as,¹⁰

$$W = \sqrt{\frac{2\epsilon\epsilon_0\Delta V}{eN}} \quad (1)$$

where ϵ , ϵ_0 , ΔV , e , and N refer to static dielectric constant of the semiconductor, permittivity of vacuum ($\epsilon_0=8.86\times 10^{-14}$ F cm⁻¹), potential drop within the semiconductor, elementary charge ($e=1.60\times 10^{-19}$ C), and doping density, respectively. Use of the reported values for the present Si of $\epsilon=11.7^5$ and $N=1.1 \times 10^{15}$ cm⁻³ enables to calculate W to be 163 and 188 μ m at the potentials of -1.5 and -2.0 V, respectively, if its flat band potential is assumed to be 0 V, although the exact flat band potential is unknown in the present experiments. Light penetration depth, L , of incident visible light into the semiconductor is also an important parameter to know where electrons are photogenerated in the semiconductor, i.e., within the space charge layer or at the deeper part without the band bending. By using an absorption coefficient, α , of Si at 620 nm light ($\alpha=4457$ cm⁻¹),¹¹ L was calculated as 2.24 μ m, where L is defined as $1/\alpha$. Thus, W is larger than α in the present case, even though the exact amount of potential drop within the semiconductor is unknown. This means that all the conduction band electrons were photogenerated within the space charge layer of p-type Si under reverse bias conditions.

4.3.3. Carrier Transport in Si Under Femtosecond Pump Pulse Excitation.

Carrier transport inside a Si electrode in ps time scale is discussed in this section to evaluate the effect of electric field within the space charge layer and/or electron diffusion process in a Si on observed IR absorbance decay. Following the excitation, the transport of electrons in the conduction band is modeled by using the standard one-dimensional transport equation¹² given by

$$\frac{\partial n(x,t)}{\partial t} = n(x,t)\mu \frac{\partial E(x,t)}{\partial x} + \mu E(x,t) \frac{\partial n(x,t)}{\partial x} - D \frac{\partial^2 n(x,t)}{\partial x^2} + G - R \quad (2)$$

where $n(x, t)$ is the density of electrons at time t at x from the surface, D is the diffusion coefficient for electron and μ is its mobility, $E(x, t)$ is the electric field, G and R are the

optical generation and recombination rate of electrons. To apply above eq.(2) to our situation, the following assumptions could be made. First, generation rate G was neglect, since the generation of electrons were complete within the pump pulse duration, i.e., 150 fs. Second, recombination rate R was also neglected due to the fact that no decay in IR absorbance was observed within the time range up to 300 ps (Figure 4.4(a)) when Si was measured in air. Third, electric field $E(x, t)$ was assumed to be constant within the space charge layer where electrons were generated and with time. Thus, eq.(2) becomes:

$$\frac{\partial n(x,t)}{\partial t} = \mu E(x,t) \frac{\partial n(x,t)}{\partial x} - D \frac{\partial^2 n(x,t)}{\partial x^2} \quad (3)$$

Initial concentration of photoexcited electron at x is given by

$$n(x,0) = I_0 \exp(-\alpha x) \quad (4)$$

where I_0 and α refer to number of incident photons and absorption coefficient of the semiconductor. The calculations of eq.(3) with eq.(4) were carried out by using the following parameters: $I_0 = 5.5 \times 10^{17} \text{ cm}^{-2}$, $\alpha = 4457 \text{ cm}^{-1}$, $\mu = 1350 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $E(x, t) = -92^{13}$ and 106 V cm^{-1} at -1.5 and -2.0 V , respectively, and $D = 35 \text{ cm}^2 \text{ s}^{-1}$.¹² Figure 4.5 shows the calculated electron distribution from the Si/electrolyte solution interface up to $4 \mu\text{m}$ into the bulk at -1.5 and -2.0 V after $t = 1, 50$, and 150

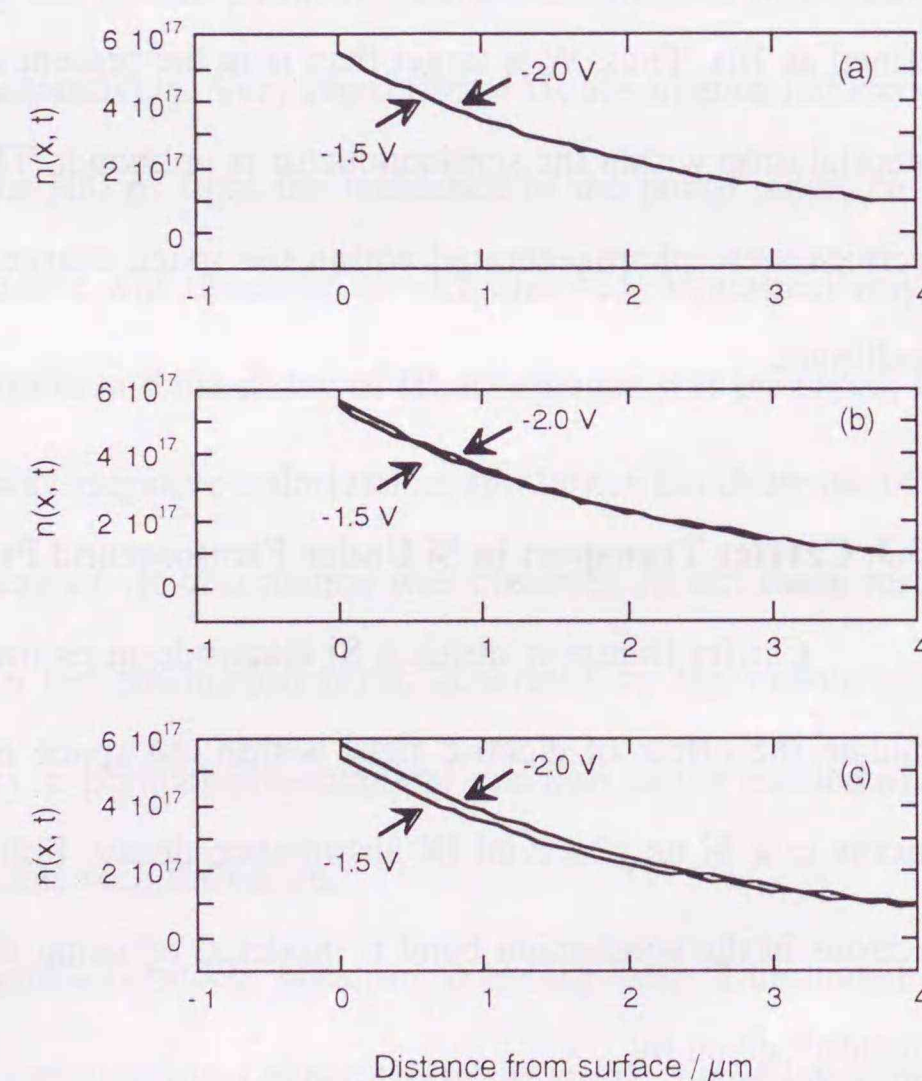


Figure 4.5. Calculated photogenerated electron distribution at -1.5 and -2.0 V for three different times after the excitation. (a) 1, (b) 50, and (c) 150 ps.

ps after the excitation. As the potential becomes more negative, surface concentration of electrons becomes slightly higher within 150 ps due to the transport of the electron by the electric field. In general, however, there was no significant change in electron concentration within 150 ps induced by an electric field or a diffusion inside a Si electrode, while ca. 16 and ca 50 % of change in IR absorption were observed at 150 ps in transient IR profiles at -1.5 and -2.0 V , respectively. Thus, these results lead to the conclusion that the only possibility to observe a decay in IR absorbance is the ET processes at Si/electrolyte solution interface, i.e., $\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$. To confirm this conclusion, more quantitative and detailed studies to determine the ET reaction rate at the Si/electrolyte solution interface are now under progress.

4.4. Conclusion

Visible pump-IR probe transient absorption spectroscopy, which is a new in situ technique capable to probe directly the ET process, was successfully applied to a p-type Si/electrolyte solution interface under potential control for the first time. A very rapid rise of absorbance at 4000 nm due to the excitation of valence band electrons into conduction band was observed by 620 nm pump pulse. Subsequent decrease in the IR absorbance was observed when negative potential was applied to the Si electrode in the electrolyte solution containing I_3^-/I^- redox couple, while no decrease was observed when measured in air. This decrease in IR absorbance is attributable to the consumption of conduction band electrons in electrochemical reaction, giving cathodic photocurrent, at Si/electrolyte solution interface, but not to the electron-hole recombination. At present, reproducibility of the transient absorbance profile was relatively low. By improving the reproducibility, more quantitative and detailed understanding of the dynamics and mechanisms of ET at Si/electrolyte solution interface should be possible.

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- 13 Electric field within the space charge layer at -1.5 and -2.0 V were calculated as ΔV (applied bias) / W (thickness of the space charge layer).

Chapter 5

General Conclusions

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In this thesis, photoeffects on semiconductor and catalysts were investigated by luminescence, photoelectrochemical measurements and transient absorption spectroscopy.

In Chapter 2, luminescence and electrochemical characteristics of porous silicon (PSi) were investigated. It was demonstrated that the photoluminescence (PL) and electroluminescence (EL) measurements of PSi in electrolyte solutions provide much useful information on the recombination processes that play very important roles in determining the mechanism of the visible light emission.

EL from PSi layer formed on p-PSi prepared under various conditions was investigated galvanostatically at various current densities in Na_2SO_4 solution. EL was observed as soon as constant current started to flow. Its intensity increased at the beginning, reached a maximum, and then decreased with time. The electrode potential gradually increased with time from ca. 0.8 V (vs. Ag/AgCl) at the beginning to -1.2 V after several hundreds of seconds and increased steeply after EL ceased to be observed. EL spectra were blue-shifted during the anodic oxidation, and the rate of the blue-shift was dependent on the preparation condition of the p-PSi. This was explained by considering the size distribution of nanocrystalline Si in PSi layer. The time dependence of the integrated EL intensity had a good correlation with that of the amount of Si-H_n species, which was quantitatively determined by the in situ reflection FT-IR measurements. It was concluded that the surface Si-H_n species acts as an electron injector in EL process at p-PSi/electrolyte solution.

A visible EL from n-PSi in an electrolyte solution containing $\text{S}_2\text{O}_8^{2-}$ as a hole injector was investigated by the potential sweep and the potential step methods. By the potential sweep measurements, dependence of EL intensity, cathodic current, and EL spectra on scan rate was investigated. By the potential step measurements, EL intensity increased with

increasing cathodic polarization time although cathodic current decreased. By the time-resolved EL spectra measurements, it was found that the EL spectrum was blue-shifted even at the constant negative potential applied to n-PSi. From these results, it was concluded that the emission site changed from larger-sized Si crystallites to smaller-sized ones in n-PSi layer. It was proposed for the first time the mechanism that EL process was dependent not only on the electrode potential but also on the time after the negative potential was applied.

Potential dependence of the visible PL from p-PSi in 0.2 M Na_2SO_4 aqueous solution was investigated and was compared with that of photocurrent. When the potential became more negative than -0.6 V, cathodic photocurrent was started to flow and PL intensity was quenched. When the potential was swept back in the positive direction, the PL intensity increased and the photocurrent decreased, and both returned to the initial values. The PL spectra measurements showed that the quenching of the PL intensities was accompanied with a blue-shift of the peak wavelength as a result of the selective quenching of the red portion of the PL spectra. The experimentally observed results were explained by considering the dependence of electron accumulation on the conduction band levels in PSi layer, which is in related to the Si nanocrystalline size.

In Chapter 3, femtosecond time-resolved diffuse reflectance spectroscopy was carried out on TiO_2 powder systems in air. It was shown that the nature of TiO_2 gives differences in rate constant for electron-hole recombination. It was suggested that a certain surface site on TiO_2 induce the fast electron-hole recombination in ps time scale. It was also demonstrated that the electron-hole recombination dynamics in anatase and rutile TiO_2 depended strongly on excitation wavelength. Anomalous rapid decay in the first few ps after a rise of absorption was observed when TiO_2 was excited by near bandgap energy. By measuring the pump intensity dependence of the transient absorption decay profile, one possible cause for this rapid decay was relaxation of exciton by it self, not by exciton-exciton annihilation. Although, there is no evidence for the component giving the absorption and its

decay. Further detail investigation such as probe wavelength dependence, temperature dependence, or time-resolved luminescence measurement are needed.

In Chapter 4, it was demonstrated for the first time that a visible pump-IR probe transient absorption spectroscopy, which is a new in situ technique capable to probe directly the electron transfer process, were applied to p-type Si/electrolyte solution interface under potential controlled conditions. A very rapid rise of absorption at 4000 nm due to the excitation of valence band electrons into conduction band induced by 620 nm pump pulse was observed. Subsequent decrease in IR absorption was observed when negative potential was applied to Si electrode, although no decrease was observed in Si measured in air. This decrease in IR absorption suggests that the photoexcited electrons in the conduction band were consumed by an electrochemical reaction at Si/electrolyte solution interface, not by electron-hole recombination. However, reproducibility of the transient absorption time profile was still poor at the present. There remain many questions about the detailed mechanisms of electron transfer at Si/electrolyte solution interface. A more quantitative studies are need to determine the electron transfer rate at the interface.

