Properties of metal/porous Si composite materials

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1 INTRODUCTION

1.1 Porous silicon and metal/porous silicon

Bulk silicon (Si) is an indirect bandgap material and is not an efficient light-emitting material. However, the porous Si (PSi), which is a nanocrystal assembly, is an efficient light emitter in visible spectrum. This is due to the low dimensionality of the Si nanostructures in the PSi. Thus, this property makes PSi a good candidate as an optoelectronics material. These nanocrystals not only have a widening of the band gap compared with bulk Si, thus shifting the photoluminescence (PL) into the visible, but also are responsible for efficient radiative recombination since the spatial confinement by potential barriers prevents the diffusion of carriers to nonradiative recombination centers. Thus, this makes the PSi the good material for applications in photonics besides micro-electronics.

Porous Si (PSi), which is a nanocrystal assembly, contains the nanometer-sized pores. Because of the nanopores present in PSi, PSi serves as the base material for various other purposes like enhanced catalytic activity of a catalyst for a chemical reaction and sensing applications. This can be achieved by the preparing the metal/PSi composite powders in which the metal nanoparticles are embedded on the surface of the nano-pores present in the PSi structures. The enhanced catalytic activity of the metal nanoparticles is attributed to their increase in the ratio of the surface area to the volume. This topic will be discussed in detail in a separate sub-title when the catalytic activity of Pt/PSi is discussed.

In this experiment, we prepare metal/porous silicon (metal/PSi) by metal-assisted electroless chemical etching. In this thesis paper, two different metal composite nanopowders will be discussed, namely Ag/PSi and Pt/PSi nanopowders.

2. Equipments and measurement techniques
2.1 PHOTOLUMINESCENCE MEASUREMENT (PL MEASUREMENT)

Photoluminescence spectroscopy is a very important tool in semiconductor research, especially for the research and development of the optoelectronic devices. Photoluminescence spectra are collected through Photoluminescence Measurement, which is a nondestructive technique. The photoluminescence spectra are important because they provide the light emission mechanisms for the development of the optoelectronic materials and devices. Besides, PL spectra, also provide the information of the impurities and their concentrations in the materials of interest. PL spectrum is obtained when the excitation energy is larger than the energy gap of the sample materials. Figure 2.1 shows the most commonly observed electronic transitions that are attributed to the photoluminescence of the sample material.

Schematic diagram of the mechanisms of luminescence

(a) Band-to-band recombination
Band-to-band recombination dominates at room temperature but is rarely observed at low temperatures in materials with small effective masses due to the large electron orbital radii.

(b) Exciton recombination
When a photon generates an electron-hole pair, Coulombic attraction can lead the formation of an excited state in which an electron and a hole remain bound to each other in a hydrogen-like state. This excited state is referred to as a free exciton. Exciton recombination is observed with narrow width \((\leq kT)\) at low temperature. Considering the Zeeman effect, we can obtain some information about impurities and defect.

(c) Donor to valence band recombination
(d) Conduction band to accepter recombination

(e) donor-accepter recombination

An electron on a neutral donor can recombine with a hole on a neutral accepter, the well-known donor-accepter (DA) recombination, illustrated in Fig. 2.1(e). The emission line has an energy modified by the Coulombic interaction between donors and accepters

\[
h\nu = E_g - (E_A + E_D) + \frac{q^2}{K_{\infty}r}
\]  

(2.1)

Where, \( r \) is the distance between donor and accepter. The photon energy in eq. (2.1) can be higher than the band gap for low (\( EA + ED \)). Such photons are generally reabsorbed in the sample. The full widths at half maximum (FWHM) for bound exciton transitions are typically \( \leq kT/2 \) and resemble slightly broadened delta functions. This distinguishes them from donor-valence band transitions which are usually a few (\( kT \)) wide. Energies for these two transitions are frequently similar and the line widths are used to determine the transition type.

Fig. 2.2 shows experimental setup for PL measurement. The sample is irradiated by excitation light source from He-Cd or YAG laser. Luminescence from the sample is collected by 7.3 cm and 22.1 cm-focused quartz lenses. Undesirable lights due to the surface scattering are canceled by some color filters. PL is separated by monochromater and detected by charge-coupled device (CCD) equipped Si detectors.
2.2 Scanning electron microscopy (SEM)

An electron microscope utilizes an electron beam to produce a magnified image of the sample. A SEM consists of an electron gun, a lens system, scanning coils, an electron collector, operation system and a display. An electro-optical system and the sample holder are kept in vacuum for reducing the loss of emitted photons due to scattering. The use of electrons has two main advantages over optical microscopes: much larger magnifications are possible since electron wavelengths are much smaller than photon wavelengths and the depth of field is much higher.

In general, it is known that various kinds of photons (e.g. Backscattered electrons, X-ray photons, Auger electrons, and Secondary electrons) are emitted from the sample surface with electron-absorption under the electron beam irradiation [see Fig. 2.3(b)]. X-ray photons are used in the electron microprobe, emitted light is known as cathodoluminescence, and absorbed electrons are measured as electron beam induced current. The image in an SEM is produced by scanning the sample with detecting the secondary electrons. The electron energy is typically 10-30 keV for most samples, but for insulating samples the energy can be as low as several hundred eV.

The nature of the secondary electrons is the emission of valence band electron. Because the emission intensity is small, many electrons generated in deep position of the sample is absorbed immediately, and only an electrons emitted from sample surface can be observed. This fact means
that the emission of secondary electrons is sensitive to the surface shape. Furthermore, the emission intensity with irradiation from diagonal direction is stronger than the vertical irradiation. Therefore, using the secondary electrons is reasonable for producing the image of uneven surface.

The detection system is shown in Fig. 2.4. The secondary photons accelerated by collector come from the left side direction. In detection system, ET-detector developed by Everhart and Thornely is generally used. This detector consists of a scintillator, light-guide, photo-multiplier and preamplifier.
Schematic diagram of ET-detection system.

Fig. 2.4
3. Properties of silver/porous-silicon nanocomposite powders

3.1 INTRODUCTION

Silicon (Si) nanocrystal is a promising material for optoelectronic devices due to efficient visible light emission at room temperature and tunability of emitted light wavelength.\(^1\)\(^2\) A typical Si nanocrystal assembly is porous Si (PSi) which can be prepared by anodic electrochemical\(^3\) or stain etching\(^4\) in a HF-based solution. Recently, a new method for preparing PSi, called metal assisted electroless chemical etching, is developed.\(^5\)\(^-\)\(^10\) This type of etching method is similar to the conventional stain etching, and is simpler than the anodic electrochemical etching. A Si wafer deposited with a thin noble metal film (Au, Pt, and Ag) is immersed in an etchant composed of HF and an oxidizing agent. In this method etch rate is relatively high and resultant PSi shows intense luminescence comparative to anodic PSi luminescence.\(^9\) Moreover, a bare Si wafer can be etched in an ionic metal-contained HF solution, e.g., aqueous solution of AgNO\(_3\) and HF. Using this method, luminescent PSi nanowires are formed on the surface of Si substrate in large areas.\(^11\)

Many researches on preparing PSi based nanocomposites by introducing different materials such as metal into its pores have been reported.\(^12\) A typical method to prepare the nanocomposites is electroless chemical deposition from a reactive solution. The process of this method is to dip PSi in an ionic metal-contained aqueous solution.\(^13\)\(^14\) The metallic ions are reduced at the PSi surface, and then metal layers are formed on it with simultaneous oxidation. Because PSi has a large surface area due to the presence of nanometer-sized pores, the metallic nanocomposites are utilized for catalytic\(^15\) and sensing applications.\(^16\)

Here, we prepare Ag/PSi nanocomposite powders using metal assisted electroless chemical etching and investigate their properties using x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and optical techniques. It was shown that a large amount of PSi powders were produced simply by stain etching metallurgical grade Si powders in aqueous HNO\(_3\) /HF solutions.\(^17\) We use the Si powders as a starting material for metal assisted electroless chemical etching. The powders are wet-etched in an aqueous AgNO\(_3\) /HF solution. Due to chemical redox reaction in the aqueous HF solution with Ag ions, Ag layer is deposited and simultaneously Si layer is dissolved. Such a reaction results in the formation of Ag/PSi nanocomposite powders. From XPS and SEM measurements, the existence of nanometer-sized Ag particles and their aggregates is confirmed on the surface of the wet-etched PSi powders. The Ag/PSi nanocomposite powders show optical absorption due to the surface plasmon excitation in the Ag nanostructures. The photoluminescence PL intensity of the Ag/PSi powders is weaker than that of anodic or stain-etched PSi; however, it is shown that these powders have higher photostability.

3.2 OBJECTIVE

The main purpose of this experiment is to prepare Ag/PSi nanopowder by metal assisted electroless chemical etching and analyze its optical properties, surface morphology and surface
stability by applying various techniques.

3.3 EXPERIMENTAL

The samples were prepared by etching polycrystalline Si powders in an aqueous solution of AgNO$_3$/HF. Metallurgical-grade polycrystalline Si powders (Vesta Ceramics) with mean diameter 3–11 μm were immersed in 18% HF solution and then AgNO$_3$ was added gradually in the solution for 10 min at 30 °C. The concentrations of AgNO$_3$ were varied from 2 to 37 g/L. The total etching time was 60 min. The etching proceeds as follows: First, the metallic atom nuclei are deposited on the surface of Si powders by redox reaction. Then, the metallic nuclei behave as a cathode and their surrounding area acts as an anode, resulting in the etching of the surrounding area. After etching, the powders were filtered out from the etching solution and then dried in room air for 24 h. XPS measurements were performed with an ULVAC-PHI model 5600 spectrometer equipped with a MgK (1253.6 eV) line as x-ray source. The takeoff angle of photoelectrons was at 45°. Si 2p and Ag 3d core levels were examined. The surface morphology of samples was examined by SEM (JEOL JSM-6330F). For PL measurements, the powders were placed on a quartz substrate. The excitation source was the 325 nm line of a He–Cd laser (Kimmon IK3302R-E). The PL spectra were detected by a spectrometer equipped with charge coupled devices (Princeton Instruments PIXIS:100B). Diffuse reflectance measurements were performed by a UV-VIS spectrophotometers (JASCO V-570). All measurements were performed at room temperature.

3.4 RESULTS

3.4.1 Surface state and morphology

Figure 3.1(a) shows a picture of Si powders before and after etching in aqueous HF/AgNO$_3$ solutions at various AgNO$_3$ concentrations. With increasing AgNO$_3$ concentration, the sample colors are clearly changed from black to brown and then gray. The color of the etched powders reflects the degree of the porosity and oxidation, as well as Ag layer thickness on each Si powder surface. To examine the amount of deposited Ag, we removed Ag layer by immersing the etched powders into concentrated HNO$_3$ and then the weight of these powders was measured. Using the weight values of before ($m_1$) and after removal of the Ag layer ($m_2$), we define

\[ r = \frac{m_1 - m_2}{m_1} \]  

(3.1)

Here, $r$ simply represents the weight ratio of the Ag layer to the Ag/PSi composite powders. Figure 2.1(b) shows $r$ as a function of AgNO$_3$ concentration in the etching solution. $r$ increases with increasing AgNO$_3$ concentration and then finally reaches unity. These results suggest that the composition ratio of Ag to PSi in the composite powders can be controlled by changing AgNO$_3$ concentration and at the highest concentration (37 g/L) Si powder is completely dissolved and
SEM images are taken to investigate the surface morphology of the nanocomposite particles prepared in various AgNO$_3$ concentrations. Figure 3.2 shows SEM images of (a) Si and Ag/PSi composite powders etched in (b) 17, (c) 33, and d 37 g/L AgNO$_3$ concentrations. The right-hand images are high-magnification views of (a), (b), (c), and (d). The surface morphology of the synthesized powders is dependent on the AgNO$_3$ concentration. At low concentration, nanometer-sized small particles are observed [Fig. 3.2(e)]. With increasing AgNO$_3$ concentration, the size of the particles increases and, as a result, aggregates of the particles several micrometers in diameter are seen [Figs. 3.2(c) and 3.2(g)]. At the highest concentration (37 g/L), the aggregates become larger the order of ten micrometers in diameter and the rounded-shape aggregates are clearly seen [Figs. 3.2(d) and 3.2(h)]. These particles and aggregates are arising from Ag deposited by redox reaction. The shape of the Ag aggregate is similar to that of Au aggregates deposited on a PSi surface by reductive deposition method. Moreover, the morphology is formed to be quite different from Ag dendrites which are formed on the Si nanowires by metal assisted electroless etching. Although the reason for this difference is not fully understood, the different process of Ag
deposition may occur on Si powders because of their large surface area.

The synthesized powders show an orange emission under UV illumination similar to that of PSi powders prepared by conventional stain etching in an aqueous HNO$_3$/HF solution.\textsuperscript{17} We thus consider the formation of the similar porous layers to that reported in Ref. 14 on our sample surfaces. The PL properties of the samples will be discussed later.

Figure 3.3 shows XPS spectra of Ag/PSi powders in the Si 2p region. AgNO$_3$ concentrations in the etching solutions are 3, 12, 25, and 37 g/L. The clear peak is observed at around 105 eV. This peak corresponds to the photoelectrons from SiO$_2$ together with suboxide layer.\textsuperscript{19} We can also find the small peak at around 99 eV which arises from bare Si (Si–Si). The stronger oxide peak intensity compared to that of bare Si peak indicates that the surface of Ag/PSi powders is strongly oxidized.
The oxide peak intensity decreases with increasing AgNO$_3$ concentrations. The observed decrease in the oxide intensity depending on AgNO$_3$ concentration suggests that the dissolution of Si layer and the formation of Ag aggregates simultaneously occur. It should be noted that at the highest AgNO$_3$ concentration (37 g/L), Si 2$p$ signals completely disappear, indicating that Si is dissolved. This coincides with the results of the weight measurement [Fig.3.1(b)].

![XPS spectra of Ag/PSi powders in the Si 2p region. The AgNO$_3$ concentrations are 3, 12, 25, and 37 g/L.](image)

**Fig. 3.3**

XPS spectra in the Ag 3$d$ regions are shown in Fig. 3.4. The AgNO$_3$ concentrations are (a) 37, (b) 35, (c) 25, and (d) 3 g/L. The peaks at 374 and 368 eV are observed on all samples. These peaks are due to Ag 3$d_{3/2}$ and 3$d_{5/2}$, respectively. As understood from Fig. 3.4, the Ag 3$d$ intensity increases with increasing AgNO$_3$ concentration. This result is in good agreement with those observed in Fig. 3.2.
In the literature, XPS spectra of Ag electrochemically deposited on PSi surface were analyzed in detail. It was shown that the XPS spectra in the Ag 3d region consist of three components, bare Ag (Ag–Ag), oxidized Ag (Ag–O), and bonding between Ag and Si (Ag–Si), and their relative intensities depend on deposition conditions. We analyzed the XPS spectra in the Ag 3d region of Fig. 3.4 by a procedure similar to that used in the literature. We assumed that each peak of Ag 3d_{3/2} and 3d_{5/2} consists of three components, Ag–Ag, Ag–O, and Ag–Si and fitted the experimental XPS spectra with these three components assuming the Gaussian line shape. The chemical shifts in energy position for the Ag–O and Ag–Si components are 2.0 and 1.0 eV with respect to the Ag–Ag peak.
16

Full width at half-maximum value is assumed to be 1.2 eV. The solid lines in Fig. 3.4 show the fitting results. The fits to the data are excellent. This actually indicates the existence of Ag–Si bonds in our samples.

We also plotted Ag–Ag, Ag–O, and Ag–Si components by the solid lines in Fig. 3.4. The relative intensity of each component is strongly dependent on the AgNO₃ concentration. At the lowest concentration (3 g/L) the XPS spectrum consists of the Ag–Ag and Ag–Si components. With increasing AgNO₃ concentration, the Ag–O component appears and finally only the Ag–Ag peak is observed. This dependence is explained as follows: at a low concentration the thickness of Ag layer is very thin, and thus the signal of Ag–Si bond from the Ag/Si interface is prominent. With increasing AgNO₃ concentration reductive reaction of Ag ions dominates, and then the volume of Ag layer increases. Thus, the relative intensity of Ag–Ag and Ag–O components increases. At higher concentration, the Si powder is completely dissolved and Ag–Si signal disappears. Note that at the highest concentration (37 g/L) the Ag–O signal cannot be observed while at a middle concentration its signal is recognized. This may be due to different reactivities of different surface area Ag aggregates against oxidation. At the highest concentration, Ag surface has the lowest reactivity against oxidation because of their small surface to volume ratio of the large Ag aggregates. On the other hand, at middle AgNO₃ concentration, the size of the aggregates is moderate and thus the reactivity is moderately large.

### 3.4.2 Optical Properties

Figure 3.5 shows the diffuse reflectance spectra of the Ag/ PSi powders formed in various AgNO₃ concentrations. The measurements were performed for samples dispersed in water (17, 33, and 37 g/L) or at room air (37 g/L). As a reference, the spectrum taken for Si powders without etching is also plotted in Fig. 3.5. We can see a dip in each spectrum near 400 nm and it shifts toward long-wavelength side and its degree becomes remarkable with increasing AgNO₃ concentration. Furthermore, the clear difference in the dip wavelength is observed between those spectra taken in water and air.

The dip in the diffuse reflectance spectra may originate from the roughness-assisted absorption due to the surface plasmon resonance of Ag nanostructures formed on the PSi surfaces. It is known that the resonance of the surface plasmon absorption depends on a refractive index of a surrounding medium. In the present case, the dip position for the higher refractive index of the surrounding medium (water) locates at a lower-energy side. This can be qualitatively explained by the prediction of the resonance energy position of surface plasmon: \( \omega_{sp} = \omega_p / \sqrt{1 + \varepsilon_s} \), where \( \omega_p \) is the plasma frequency of the metal and \( \varepsilon_s \) is the dielectric constant of a surrounding medium. Furthermore, surface plasmon resonance wavelength is dependent on the metal nanostructure size. Endriz and Spicer showed that the amplitude and energy position of dips in reflectance spectra of Ag films due to the roughness-assisted absorption of surface plasmons increase with increasing the
size of surface roughness. As obtained from SEM measurements (Fig. 3.2), the size of Ag nanostructures formed at higher AgNO$_3$ concentration is larger than that at lower concentration. Therefore, the redshift in the dip wavelength may reflect the change in Ag nanostructure size with the AgNO$_3$ concentration.

To give detailed information on the dip in the diffuse reflectance spectral, we theoretically calculate reflectance spectra for a roughened metallic surface using a model by Elson and Ritchie. Surface plasmons on a perfectly smooth surface of a metal are nonradiative modes and thus cannot be coupled with incident photons normally. For coupling with photons the momentum mismatch between surface plasmons and photons should be compensated. In case of a roughened surface, the compensation occurs due to the scattering of surface plasmon waves at the roughened surface, and it allows coupling of surface plasmons with incident photons. Using the first-order perturbation theory, the probability to excite surface plasmons by a photon incident on a rough metallic surface can be calculated and is expressed as

\[
P_{sp} = \delta^2 \left( \frac{\alpha}{c} \right)^3 \frac{\varepsilon_2^2}{[-(1 + \varepsilon_2)]^2} g(k) \tag{3.2}
\]

where \( \varepsilon_2 \) represents the dielectric constant of metal (Ag) and \( \delta \) is the root-mean-squares height of roughness. \( g(k) \) is the two-dimensional Fourier transform of the autocorrelation function of the surface roughness. If a Gaussian autocorrelation function is assumed, \( g(k) \) is given by

\[
g(k) = \exp\left(-\frac{\pi^2}{4 \sigma^2} k^2 \right)
\]
where $\sigma$ is the correlation length. The wave number $k$ is given by the dispersion relation of surface plasmon

$$k = \frac{\omega}{c} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}$$  \hspace{1cm} (3.4)

To simplify the calculation, we assume that $R_{sp}$ is equal to the amplitude of the spectral dip $\Delta R_{sp}$. Then, the total reflectance spectrum $R$ can be expressed by the equation

$$R = R_{sc} - \Delta R_{sp}$$  \hspace{1cm} (3.5)

Where $R_{sc}$ is relative scattering intensity of incident light. In our calculation, $R_{sc}$ is obtained from the linear baseline fitting of the experimental spectra in the range from 350 to 550 nm. The obtained $R_{sc}$ is shown in Fig. 3.5 by dashed curves. The dielectric constant of Ag ($\varepsilon_2$) is taken from the literature.\(^{24}\)

At first, we fit the reflectance spectra for the samples measured in water (17–37 g/L) to Eq. (3.5) with two fitting parameters, $\sigma$ and $\delta$. In the calculation, the $\varepsilon_1$ value of dielectric constant of the medium is assumed to be 1.77. The calculated $R$ are shown as solid curves in Fig. 3.5. We can see that the experimental dips are well reproduced by our calculated curves. The obtained parameters $\sigma$ and $\delta$ presented in Fig. 3.5, which are connected with the size of the surface roughness, increase with increasing AgNO$_3$ concentration. This tendency coincides with the variation in the Ag nano-structure sizes observed from the SEM images in Fig. 3.2. The degree of surface roughness is also corresponding to those observed in the SEM images.

In fit of the data for the 37 g/L sample measured in air, we used the values of $\sigma$ and $\delta$ which are the same as those measured in water and $\varepsilon_1$ is treated as fitting parameter. Good agreement between the experimental and calculated results is achieved at $\delta=1.63$. The smaller dielectric constant value obtained here is in qualitative agreement with the larger energy of surface plasmon $\omega_{sp}$, although the value is be caused by any structural effect of the Ag aggregates.

Figure 3.6(a) shows PL spectra of Ag/PSi powders at various AgNO$_3$ concentrations. A broad emission band is observed, which is similar to that typically observed in anodic PSi samples formed in HF/alcohol-based electrolytes. With increasing AgNO$_3$ concentration the PL intensity increases, peaking at 9 g/L and then tends to decrease its intensity. The shift in PL peak energy toward higher-energy side is also observed. In Fig. 3.6(b), the PL peak intensity is plotted against AgNO$_3$ concentration. It is understood that the maximum intensity occurs at around 10 g/L and monotonous decrease at higher concentration region (>10 g/L). The increased PL intensity at the lower concentrations and the spectral blueshift suggest the formation of a porous structure on Si powder.
surface and its size reduction. The decrease in the PL intensity at a higher concentration region arises from the destruction of the porous structure (i.e., etching of Si powders). At the highest AgNO$_3$ concentration (37 g/L), no PL emission was observed due to the complete dissolution of Si powders in agreement with the XPS results [Fig. 3.4(a)].

![Graphs (a) and (b)](image)

(a) PL spectra of Ag/PSi powders formed in various AgNO$_3$ concentrations. (b) PL peak intensity of Ag/PSi powders as a function of AgNO$_3$ concentration. The AgNO$_3$ concentrations are varied from 2 to 37 g/L.

Fig. 3.6

PL intensities for Ag/PSi powders synthesized in AgNO$_3$ /HF solution are found to be two orders weaker than that of PSi powders etched in an aqueous HNO$_3$ /HF solution. One reason for this observed lower intensity is due to the absorption of the emitted light by the deposited Ag layers. However, when the Ag layer is etch-removed in an aqueous HNO$_3$ solution, the PL intensity of the sample with the presence of Ag layers is only about 50% of the intensity without Ag. The reason for this much lower PL intensity of the Ag/PSi powders is not fully understood at present.

Finally, we examine the stability of PL emission from Ag/PSi powders under light illumination. Figure 3.7 shows the PL peak intensity for Ag/PSi powders as a function of the illumination time of excitation light (325 nm). For comparison, the data obtained from PSi powders formed in HNO$_3$/HF is shown. We can see much higher photostability of the Ag/PSi powders than that of the conventional PSi powders. The improvement of this photostability is considered to be due to different surface states of Ag/PSi. In the inset of Fig. 3.7, XPS spectra of Ag/PSi and PSi powders are shown. The surface of Ag/PSi powders is heavily oxidized while the surface of PSi powders is predominantly passivated by atomic hydrogen. Because the oxygen bonds are more stable, the oxidized PSi has higher photostability. Another possible reason for the higher photostability is the existence of Ag–Si bonds as observed in the XPS Ag 3$d$ spectra (Fig. 3.4). It has been shown that the photostability of anodic PSi can be improved by the existence of strong Ag–Si bonds.
To clarify these effects, we prepared the following two samples: One is Ag/PSi sample subsequently immersed in an aqueous HNO$_3$ solution [Ag/PSiHNO$_3$] to remove the Ag layers, i.e., Ag–Si bonds. Another one is Ag/PSiHNO$_3$ sample subsequently immersed in an aqueous HF solution to remove any Si oxide layer [Ag/PSiHF]. In Fig. 3.7, the UV illumination time dependence of PL intensity for these two samples is plotted. The photostability of Ag/PSiHNO$_3$ is almost comparable to that of Ag/PSi. From the XPS spectrum in the inset of Fig. 3.7, we can see that Ag/PSiHNO$_3$ powders are slightly oxidized. Because the photostability is not changed by removing the Ag–Si bonds in HNO$_3$ solution, the higher photostability of Ag/PSi compared to PSi is concluded to be due to the existence of oxide overlayer. In Ag/PSi(HF) powders, on the other hand, the extremely high photostability is obtained although the surface oxide layer is completely removed as demonstrated in the XPS spectrum. Thus, the high photostability of Ag/PSi(HF) is due to slightly remained strong Ag–Si bonds on the PSi surface rather than the surface oxide overlayer. However, we observed the decrease in the PL intensity of Ag/PSi(HF) by about one order (data is not shown). This fact suggests that the contribution of Ag–Si bonding-related emission to the total PL emission in the Ag/PSi powders is very low. The photostability of Ag/PSi powders may be improved by performing efficient passivation of Ag/PSi interface.

As shown in the inset of Fig. 3.7 the PSi powders are oxidized by HNO$_3$ treatment for Ag removal. This oxidation results in the change in the PSi powder weight. The thicknesses of oxide layers are
estimated from the XPS data for samples before and after HNO$_3$ treatment using the same procedure as in Ref. 25. The obtained thicknesses of oxide layer for samples before and after the treatment are 18 nm and 190 nm, respectively. From these values, an increase in the weight of the PSi powders after the HNO$_3$ treatment is estimated to be about ten percent. Therefore, the weight ratio of Ag to PSi obtained from Eq. (3.1) may give slightly large values.

3.5 CONCLUSION

We demonstrated the preparation of Ag/PSi nanocomposite powders by metal assisted electroless chemical etching of Si powders in an aqueous AgNO$_3$/HF solution. From XPS and SEM measurements, Ag layer was found to be formed on the Si powder surfaces. The Ag layer consisted of nanometer-sized Ag particles and the aggregates of their particles depending on the concentration of AgNO$_3$. Immoderate etching at higher concentrations of AgNO$_3$ resulted in the decrease in powdered Si volume with increasing Ag layer thickness. The Ag/PSi nanocomposite powders exhibited the optical absorption caused by surface plasmon excitation in the Ag nanostructures on the powdered Si surface. By fitting the experimental optical absorption spectra to the theoretical ones with taking into account the roughness-assisted surface plasmon excitation, the plasmon resonance wavelength was found to be strongly dependent on the etching conditions via the size of the Ag nanostructures. The Ag/PSi powders showed an orange emission similar to that of PSi prepared by anodic or stain etching. The photostability of the Ag/PSi nanocomposite powders was better than the conventionally stain-etched PSi powders. This was considered to arise from stable surface bonds, such as Si–O and Si–Ag. Our simple method to prepare Ag/PSi nanocomposite powders can be applied to the preparation of other metal/PSi systems. Systematic studies on this are now in progress. These metal/PSi nanocomposite systems may have potential usefulness for various applications such as, catalysis and biological sensing.

REFERENCES

4 Properties and enhanced catalytic activities of platinum/porous-silicon nano composite powders (Pt/PSi)

4.1 INTRODUCTION

A typical Si nanocrystal assembly is porous Si (PSi), which can be prepared by anodic electrochemical\(^1\) or stain etching\(^2\) in a HF-based solution. Recently, a new method of preparing PSi, called metal-assisted electroless chemical etching, is developed.\(^3\)-\(^5\) This type of etching method is similar to conventional stain etching and simpler than anodic electrochemical etching. A Si wafer deposited with a thin noble metal film (e.g., Au, Pt, or Ag) is immersed in an etchant composed of HF and an oxidizing agent. In this method, the etch rate is relatively high. Moreover, a bare Si wafer can be etched in an ionic-metal-containing HF solution, e.g., an aqueous solution of AgNO\(_3\) and HF.

Many research studies on the preparation of PSi-based nanocomposites by introducing different materials such as metal into its pores have been reported.\(^6\) A typical method of preparing such nanocomposites is electroless chemical plating from a reactive solution.\(^1\) This method entails dipping PSi in an ionic-metal-containing aqueous solution. Metallic ions are reduced at the PSi surface, and then metal layers are formed on the surface with simultaneous oxidation. PSi has a large surface area because of its nanometer-sized pores and its surface area can be easily varied by adjusting the chemical etching conditions. Thus, the metal/PSi composites are utilized for various applications such as catalysis. Recently, it has been demonstrated that metallic particles in the PSi network fabricated by electroless plating show high catalytic activity for CO oxidation.\(^8\)

In our previous work, a novel method of preparing a metal/PSi composite was developed. Using the metal-assisted electroless chemical etching of Si powders in aqueous HF solution containing a metal-based oxidizer (AgNO\(_3\)), Ag/PSi composite powders were directly obtained. The composition ratio of Ag to PSi and the surface morphology of Ag/PSi powders were found to be determined by the oxidizer concentration. Moreover, the composite showed a stable photoluminescence and surface plasmon resonance absorption of the metal (Ag) nanostructure. The optical properties of the Ag/PSi composite were dependent on the oxidizer concentration, reflecting the change in the morphology of the metal nanostructure. Our developed method\(^9\) can be very useful for application to the catalytic reaction of noble metals such as Pt and Pd since catalytic activity is strongly dependent on the surface morphology of the metallic particles. In this article, we show that Pt/PSi composite powders are directly synthesized using a wet chemical process developed previously.\(^9\) These powders have sufficient catalytic activity even at room temperature. Metallic (Pt) composites of Psi are obtained by immersing Si powders in aqueous HF/PtCl\(_2\) solution. The quantity and size of deposited Pt can be controlled by changing the PtCl\(_2\) concentration. Pt/PSi powders show spontaneous combustion in air/methanol (CH\(_3\)OH) mixture because of the enhanced catalytic activity of Pt/PSi. The catalytic activity is shown to depend on the size of nanostructured Pt particles.
4.2 OBJECTIVE

We examined the surface morphology and PL measurement to confirm the formation of the porous assembly. This is because, unlike the bulk Si, the porous silicon powders show strong luminescence even at room temperature, and the emission efficiency of Si nanocrystals depends strongly on the pore size; smaller the pore size, higher is the emission efficiency.

To investigate the catalytic activity of Pt/PSi powders, the methanol oxidation reaction, which is a combustion reaction, was examined. We also investigated the surface chemistry of these samples by XPS and demonstrate that only Pt nanoparticles, and not nanoparticles of Pt oxide species, are responsible for the enhanced catalytic activity. The catalytic activity of Pt/PSi powders is also found to increase with the ratio of the Pt surface area to its volume.

4.3 EXPERIMENTAL

Pt/PSi samples were prepared by etching polycrystalline Si powders in an aqueous solution of PtCl₂/HF. Metallurgical grade polycrystalline Si powders (Vesta Ceramics) with a mean diameter range of 3–11 μm were immersed in 15% HF solution, and PtCl₂ was then added gradually to the solution for 10 min at 50°C. The etching time was 60 min and the concentrations of PtCl₂ were 0.6, 0.8, and 1.1 g/L. The formation process of Pt/PSi composite powders is as follows. Because of a chemical redox reaction in the aqueous HF solution containing Pt ions, a thin Pt layer was deposited and a Si layer was dissolved. This dissolution led to the formation of PSi powders. Finally, Pt/PSi composite powders were formed. After etching, the samples were dried in room air at room temperature for 24 h. The chemical reaction model for the Pt/PSi formation is outlined below:

\[
\text{Si} + 2\text{H}_2\text{O} + n\text{h}^+ \rightarrow \text{SiO}_2 + 4\text{H}^+ (4 - n) \text{e}^- \\
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \\
\text{Pt}^{2+} + 2 \text{e}^- \rightarrow \text{Pt}
\]

Where, \(n\) : electron

\(h\) : hole

The surface morphology of the samples was examined by scanning electron microscope (SEM; JEOL JSM-6330F). For photoluminescence (PL) measurements, the Pt/PSi powders were placed on a quartz substrate. The excitation source was a 325 nm line of a He–Cd laser (Kimmon IK3302R-E). The PL spectra were measured by a spectrometer equipped with charge-coupled devices (Princeton Instruments PIXIS:100B). XPS measurements were performed with a spectrometer (ULVAC-PHI 5600) equipped with a MgK (1253.6 eV) line as the X-ray source. The takeoff angle of photoelectrons was 45°. In this experiment, we examined the Pt 4f core level.

For catalytic experiments, samples were prepared by mixing 100 mg of silica wool (fiber diameter: 2–6 μm; Daico MFG) with 15 mg of the Pt/PSi sample, and 15 mg of this mixture was put in a glass
tube reactor (0.4 cm in internal diameter and 15 cm in length). The glass tube reactor was supplied with saturated air/CH$_3$OH gas from one end, and the other end was connected to a thermocouple (Type K) to monitor the sample temperature. The saturated air/CH$_3$OH mixture was prepared using a combination of a methanol bubbler and a dry air compressor. The gas flow rate was 13 cm/s. A schematic of the experimental setup used is shown in Fig. 4.2(d).

### 4.4 RESULTS

#### 4.4.1 Morphology

We prepared two different Pt/PSi samples with different drying procedures. One sample was prepared by allowing the powder to dry naturally after etching, without any posttreatment (sample A). The other one was prepared by rinsing the sample in distilled water to remove residues of the etching solution and then drying it in air (sample B). Figures 4.1(a) and 4.1(b) respectively show SEM images of the Pt/PSi powders for samples A and B prepared at a PtCl$_2$ concentration of 1.1 g/L. These images clearly show that the two samples have different morphologies, i.e., sample A has a larger number of pits on its surface than sample B, and the pit size of sample A is larger than that of sample B. This difference indicates that the etching of the powders continues until sample A is completely dry.

Figure 4.1(c) shows the PL spectra of Pt/PSi powders for samples A (solid curves) and B (dashed curves) prepared at PtCl$_2$ concentrations of 0.6, 0.8, and 1.1 g/L. For sample A, a broad emission peak is observed at each concentration. These emission peaks can be attributed to the recombination of quantum-confined excitons in the porous structure. The peak energy shifts to a shorter-wavelength region with increasing concentration, and the PL intensity peaks at 0.8 g/L. The spectral blueshift suggests the formation of a porous structure on the Si powder surface and its size reduction. The decrease in the PL intensity at 1.1 g/L arises from the destruction of the porous structure, i.e., etching of Si powders. This concentration dependence of the PL spectra qualitatively corresponds to the dependence of the PL spectra observed for the Ag/PSi composite powders reported in our previous work.\(^9\)
A broad PL emission band is also observed for sample B, even though its PL intensity and peak wavelength are quite different from those of sample A. The PL intensity of sample B is much lower than that of sample A. Furthermore, the emission band of sample A is located at shorter wavelengths than that of sample B. The PL spectrum of sample B has a weak red-shifted emission peak that results from the large size of the PSi structure since the bandgap energy and emission efficiency of Si nanocrystals depend strongly on the pore size.\(^{11}\)

### 4.4.2 Surface chemistry

To investigate the surface chemistry of Pt/PSi powders, we performed XPS measurements on samples A and B, respectively. The XPS spectra of these samples in the Pt 4f region are shown in Figs. 4.2(a) and 4.2(b). The components at 76 and 73 eV correspond to the spin–orbit split states of Pt, i.e., 4f\(_{5/2}\) and 4f\(_{7/2}\), respectively. The XPS intensity depends on the PtCl\(_2\) concentration for both samples. This indicates that the amount of the deposited Pt layer can be controlled by changing the concentration of PtCl\(_2\). This tendency is also observed in the silver/PSi composite powder prepared by a similar method.\(^9\)
To obtain more information on the PtCl₂ concentration dependence of the oxide state intensity, the XPS spectra were fitted using bare Pt and Pt oxide (PtO and PtO₂) components. The chemical shifts in the peaks of Pt oxides, i.e., PtO and PtO₂, with respect to the peak of bare Pt are 1.3 and 2.7 eV, respectively. The solid curves in Fig. 4.2(a) and (b) show the results of this fitting; the bare Pt and Pt oxide components are shown by dashed lines. It can be seen that the distinguishing feature between samples A and B is that no bare Pt peak is observed for sample A, while modest bare Pt peaks can be observed for sample B. Although the reason for this difference is not yet fully understood, one possible reason is that the large surface area of sample A, which is due to the presence of many pores on it, leads to the high reactivity of Pt toward oxidation. Another possible reason is that, during the drying process, the residual HF solution promotes the oxidation of bare Pt on the Pt/PSi surface of sample A.

Figure 4.2(c) shows the XPS intensity of each Pt oxidation state (Pt, PtO, and PtO₂) normalized by the total Pt 4f intensity as a function of PtCl₂ concentration. The open and solid symbols represent the data for samples A and B, respectively. Dashed curves are just guides to the eye. (d) Schematic illustration of experimental setup for measuring temperature traces of the reactor. A photograph shows the spontaneous combustion of methanol resulting from the catalytic activity of the Pt/PSi powders.

Fig. 4.2
concentration, the relative intensity of the PtO\(_2\) state decreases. In contrast, for sample B, an increase in the PtO\(_2\) intensity is observed, and thus the number of Pt and PtO components decrease. The concentration dependence indicates that, in sample B, the growth of high-quality Pt layers, i.e., metallic Pt layers, is attained at lower concentrations, while in sample A, a metallic layer cannot be deposited.

4.4.3 Catalytic activity

Since the Pt/PSi powders synthesized by us have a nanometer-sized porous structure with Pt nanoparticles on the PSi surface, it is expected that these powders show enhanced catalytic activity for various chemical reactions such as the mineralization of aqueous organic compounds\(^{13}\) and the partial oxidation of alcohols for hydrogen evolution.\(^{14}\) To investigate the catalytic activity of Pt/PSi powders, the methanol oxidation reaction, which is a combustion reaction, was examined. The chemical reaction for this catalytic activity can be outlined as below:

\[
\text{Pt} + \text{O}_2 \rightarrow \text{PtO} \\
\text{PtO} + \text{CH}_3\text{OH} \rightarrow \text{Pt} + \text{HCHO} + \text{H}_2\text{O}
\]

In Fig. 4.2(d), a schematic of the experimental setup used for performing the catalytic reaction is shown. An air/CH\(_3\)OH mixture was flowed in the quartz-wool reactor loaded with Pt/PSi powders (samples A or B) prepared at various PtCl\(_2\) concentrations. For sample B, an intense spontaneous combustion was observed at room temperature, as shown in Fig. 4.2(d). For sample A, on the other hand, no such reaction was observed. Note that for conventional catalysts, external heat (i.e., initial heating) is required for ignition. The temperature required for the catalytic oxidation of alcohol is about 200°C.\(^{15,16}\) It is considered that the enhanced catalytic activity of Pt/PSi is due to the Pt nanoparticles being embedded on a nanometer-sized porous surface. Sample A showed no catalytic activity because of the absence of the bare Pt state [Fig. 4.2(a)]. Pt oxide species are inactive toward methanol oxidation.\(^{13}\) The spontaneous combustion of methanol was also observed in Pt nanoparticles having diameters of several hundred nanometers.\(^{17,18}\)

Figure 4.3 shows the temperature traces for a catalytic reaction of Pt/PSi powders of sample B in the presence of an air/CH\(_3\)OH mixture flow. The air/CH\(_3\)OH flow rate is 13 cm/s. Each trace in Fig. 5(b) shows the catalytic behavior for the first 10 min: an increase in the temperature is seen in the first 5 min when the air/CH\(_3\)OH mixture is passed through the glass tube reactor, and a decrease in the temperature is observed in the last 5 min because of the termination of the flow of the air/CH\(_3\)OH mixture.

In Fig. 4.3, as the concentration of PtCl\(_2\) (\(M\)) increases, the peak temperature increases up to a value of 0.8 g/L, beyond which it decreases. The maximum temperature of the sample formed at \(M = 0.8\) g/L is approximately 330°C. The maximum temperature of the sample at \(M = 1.1\) g/L is
300°C, which is higher than that of the sample at $M = 0.6 \text{ g/L (200°C)}$. Let us consider the dependence of the catalytic activity on $M$. At least two factors are required to determine the degree of catalytic activity: (i) the amount of Pt nanoparticles and (ii) the ratio of the Pt surface area to its volume. The amount of Pt increases with $M$. However, the ratio of the Pt surface area to its volume decreases because of the increase in the particle size. The opposite trends shown by these two factors with increasing $M$ may be responsible for the optimum catalytic activity observed at $M = 0.8 \text{ g/L}$. We verified the catalytic activities of the samples prepared for etching times longer than 60 min. These samples showed higher catalytic activities and had a maximum value for an etching time of approximately 360 min.

Powdered Si having no porous structure but deposited with Pt nanoparticles by electroless plating in PtCl$_2$ aqueous solution shows no enhanced catalytic activity. The temperature trace of such Pt-deposited Si powder in the air/CH$_3$OH mixture flow is shown in Fig. 4.3 (dashed curve). As expected, no catalytic activity (i.e., no increase in the temperature) is observed.

To verify the stability of the catalytic activity of Pt/PSi samples against repeated use, we performed the catalytic reaction five times using the same sample. In Fig. 4.3, the results of this experiment on a sample with a concentration of 0.6 g/L are shown. The catalytic activity of Pt/PSi increased with the number of repetitions. (The maximum temperatures for the first, third, and fifth experiments are about 150, 175, and 200°C, respectively.) One reason for this increase may be the clean sample surface resulting from the surface contaminants being combusted.

---

**Fig. 4.3**

Temperature traces of the catalytic reaction of Pt/PSi powders (solid curves) and Si powders with Pt (dashed curve) in the presence of air/CH$_3$OH flow
4.5 CONCLUSION

XPS analysis revealed that Pt layers were deposited on Si surface together with the formation of a porous structure and that the oxidation state of Pt layers strongly depended on the conditions for the preparation of the Pt/PSi composite powders. The catalytic activity of Pt/PSi composite powders for the spontaneous combustion reaction with mixture of air/CH$_3$OH was found to depend on the oxidation state of Pt present in the sample. It was also determined that unlike bare Pt state, the oxide state of Pt (PtO and P$_2$O) do not play role in the catalytic activity. The Pt/PSi composite powders synthesized in this study may have potential uses in various applications such as to the production of hydrogen from methanol and in a microscale combustor.

REFERENCES
5. Control of random lasing in ZnO/Al₂O₃ nanopowders

5.1 INTRODUCTION

Random laser is a stimulated emission source without any precise external cavities.¹⁻³ Random laser consists of randomly shaped nano- or micropowders, and various luminescent materials such as semiconductor powders (ZnO,⁴ GaAs,⁵,⁶ and ZnSe⁷), solid-state laser materials, and organic molecules.⁸,⁹

In simple language, multiple scattering is the core reason behind the random lasing. Hence, this requires the randomness of the medium which lacks any long order. In the random medium with strong scattering strength, recurrent light scattering event arises. After multiple scattering the light returns to the previous scatterer. The interference of the return light is constructive only at certain frequencies. Therefore, the requirement for constructive interference of backscattered light selects the resonant frequencies. At or above the threshold lasing excitation power density (Pₜₚ), which is the minimum power density at which the lasing occurs, this multiple scattering leads to the increase in the population of the excited state so that the population inversion takes place, and consequently the stimulated emission occurs.

Because of its simplicity and low cost, the random laser is an attractive candidate for use in various light-emitting devices.³ However, in contrast to the case of the conventional lasers, the control of lasing emission wavelength in case of random lasers remains a challenge due to their simplicity. Some strategies for the control of the random lasing wavelength were proposed, e.g., controlling the Mie resonance by changing the sizes of scatterers,¹⁰ and modifying the gain curve by adding a light absorber.¹¹ Note that these reports describe the control of the characteristics of organic-dye random lasers with incoherent feedback.¹,¹⁰,¹¹

In this experiment, we demonstrate the control of random lasing characteristics of semiconductor nanopowders (ZnO) with coherent feedback by the inclusion of dielectric nanopowder scatterers of Al₂O₃.

5.1 OBJECTIVE

In this experiment we demonstrate that the random lasing wavelength of ZnO/Al₂O₃ nanopowders can be controlled by varying the weight fraction of Al₂O₃ to ZnO (f₃) in the sample. Specifically, we induce a blueshift in the lasing wavelength of the sample with increase in f₃. We also show that the random lasing characteristics, like lasing wavelength and threshold excitation power density (Pₜₚ), can be well explained by a theoretical model based on the photon-transport mean free path (lₘₚₚ).

5.3 EXPERIMENTAL

The size of ZnO and Al₂O₃ were 230 and 300 nm respectively. These nanopowders were mechanically mixed, and a thin film of the mixture was formed on a silicon substrate. The thickness of the samples was ~1 mm. The weight fraction of Al₂O₃ to ZnO (f₃) of the mixture samples was
varied from 0 to 100. Random lasing experiments were performed using a frequency-tripled light pulse of 355 nm from a Nd:YAG laser with a pulse duration of 5 ns. The excitation area was \( \sim 0.17 \) \text{mm}^2. All measurements were performed at room temperature.

5.4 RESULTS

5.4.1 Blueshift of lasing wavelength

As shown in Fig. 5.1, the wavelength of the lasing emission clearly depends on weight fraction of \( \text{Al}_2\text{O}_3 \) to \( \text{ZnO} \) (\( f_w \)). With increasing \( f_w \), the lasing wavelength shifts toward a shorter wavelength side. Also, as the lasing occurs simultaneously at wider range of wavelengths, we calculate the mean lasing wavelength (\( \lambda_{\text{mean}} \)) for each sample separately and the maximum shift of \( \lambda_{\text{mean}} \) observed in this study is \( \sim 4.0 \) nm. The sharp spike-like peaks appearing in the emission spectra fluctuate from pulse to pulse and this fluctuation is a typical feature of random lasers.\(^{12}\)

![Photoexcitation emission spectra of ZnO/Al\(_2\)O\(_3\) nanopowders with various values of the weight fraction \( f_w \). Excitation power density is 1450 kW/cm\(^2\).](Fig.5.1)
In Fig. 5.3, the mean lasing wavelength ($\lambda_{\text{mean}}$) is plotted as a function of $f_w$ (solid squares, left axis). $\lambda_{\text{mean}}$ decreases with increasing $f_w$. This result clearly shows that the random lasing wavelength can be controlled by changing $f_w$.

To confirm the dependence of the scattering strength on weight fraction of $\text{Al}_2\text{O}_3$ to ZnO ($f_w$), the photon-transport mean free path length ($l_{mf}$), which is the average distance a wave travels before its direction of propagation is randomized, is calculated. The $l_{mf}$ gives the measure of scattering in the medium; higher its value, lower is the scattering strength. The mathematical model to calculate $l_{mf}$ is outlined below based on the literature.\textsuperscript{13–15}

$$ l_{mf} = \frac{\lambda_{\text{me}}} {2\pi W (n_{\text{eff}})} $$

(5.1)

Where, $\lambda_{\text{me}}$ is the wavelength of scattered light and $W$ represents full width at half maximum of the coherent backscattering peaks.\textsuperscript{13} $\overline{R}(n_{\text{eff}})$ is calculated as below.\textsuperscript{15}

$$ \overline{R}(n_{\text{eff}}) \equiv \frac{1 - R(n_{\text{eff}})\begin{bmatrix} 1 - 0.2R(n_{\text{eff}})\end{bmatrix}} {1 - 0.2R(n_{\text{eff}})} $$

(5.2)

$$ R(n_{\text{eff}}) = \frac{3C_2 + 2C_1}{(3C_2 - 2C_1 + 2)} $$

(5.3)

$$ C_n = \int_0^{\pi/2} r(\theta, n_{\text{eff}}) \sin \theta \cos^n \theta d\theta, $$

(5.4)

Where, $r(\theta, n_{\text{eff}})$ is the Fresnel reflection coefficient averaged over the polarization of the boundary at given at a given incident angle $\theta$.\textsuperscript{16,17} $r(\theta, n_{\text{eff}})$ depends on the effective refractive index ($n_{\text{eff}}$) and is calculated using Maxwell-Garnett theory\textsuperscript{18} as below.
\[ n_{\text{eff}} = \left( \frac{(1-f)n_m^2 + \sum f_i \beta_i n_i^2}{1-f + \sum f_i \beta_i} \right)^{1/2} \]  \hspace{1cm} (5.5)

\[ f^i = \sum_{i=1}^{i=2} f_i \]  \hspace{1cm} (5.6)

\[ \beta_i = 3n_m^2/(n_i^2 + 2n_m^2) \]  \hspace{1cm} (5.7)

\[ f_1 = f/(1 + f_w d) \]  \hspace{1cm} (5.8)

\[ f_2 = f d/(1 + f_w d) \]  \hspace{1cm} (5.9)

Where, \( i = 1 \) for ZnO; \( i = 2 \) for Al\(_2\)O\(_3\)

\( n_i \): Refractive index of the \( i \)th inclusion

\( f_i \): Volume fraction of the \( i \)th inclusion

\( n_m \): Refractive index of the surrounding medium, which is air in this case

\( d \): Ratio of mass density of Al\(_2\)O\(_3\) to ZnO

Also, in our case, the following is true.

\( n_1 = 2.3 \)

\( n_2 = 1.76 \)

\( n_m = 1 \)

\( f = 0.6 \)

\( d = 0.71 \)

\( W = 0.2 \text{ rad}^{15} \)

In Fig. 5.3, the inverse of the calculated photon-transport mean free path length (\( l_{mf} \)) is plotted as a function of the weight fraction (\( f_w \)). The value of \( 1/l_{mf} \) decreases, i.e., the scattering strength decreases as \( f_w \) increases.

### 5.4.2 Blueshift analysis

One possible reason for the dependence of lasing wavelength on weight fraction of Al\(_2\)O\(_3\) to ZnO (\( f_w \)) is the modification in the extent of self absorption by ZnO nanopowders as a result of the addition of Al\(_2\)O\(_3\). In the lasing process, a certain amount of the scattered light can be re-absorbed if the emission and absorption occurs in a pronounced manner in the case of the short wavelengths, longer light path length, or in other words, greater light-scattering strength may lead to redshift of the laser emission. The inset of Fig. 5.3 shows the absorbance spectrum of ZnO nanopowders. It can be easily understood from this spectrum that the optical absorbance is higher in the shorter wavelength region.
In the literature, the peak shift of photoluminescence spectra of dye molecules by modifying the self-absorption strength with the addition of scatterers in the luminescent medium was reported. Therefore, one can expect that the self-absorption effect can lead to a peak shift in the photoluminescence spectra even though excitation power is below the lasing threshold ($< \sim 160$ kW/cm$^2$). Figure 5.4 shows the peak wavelength of the emission spectra under no lasing excitation as a function of $f_w$. Examples of these emission spectra are shown in the inset of Fig. 5.4. The blueshift with increasing $f_w$ can be clearly observed. However, the shift of $\sim 1.9$ nm is smaller than that of the lasing wavelength, which is $\sim 4.0$ nm [Fig. 5.2]. Although this difference is not fully understood at present, the larger shift corresponding to the laser wavelength may be because coherent light has a longer path length, and therefore, it is absorbed to a greater extent than spontaneous light.

![Graph showing peak wavelength as a function of weight fraction](image)

Mean of the peak lasing wavelength as a function of the weight fraction of $f_w$. The solid curve is the inverse of the calculated photon-transport mean free path ($l_{mf}$) (right axis) vs. $f_w$. Inset shows the absorbance spectrum of ZnO nanopowders.

Fig. 5.3
5.4.3 Relationship of lasing parameters

Finally, the dependence of the lasing threshold power density ($P_{th}$) on weight fraction of Al$_2$O$_3$ to ZnO ($f_w$) is examined. In Fig. 5.5(a), the lasing emission intensity is plotted against the excitation power density for different $f_w$. The lasing threshold excitation power density ($P_{th}$) is found to depend on $f_w$. This dependence of $P_{th}$ on $f_w$ is considered to be related to the change in photon-transport mean free path length ($l_{mf}$). With increasing $f_w$, the effective refractive index of ZnO/Al$_2$O$_3$ decreases, and as a result, $l_{mf}$ changes (increases). In Fig. 5.5(b), $P_{th}$ is plotted as a function of the calculated $l_{mf}$ for $f_w$ ranging from 0 to 100. $P_{th}$ increases with increase in $l_{mf}$. The dependence of lasing threshold power density ($P_{th}$) on photon-transport mean free path length ($l_{mf}$) was reported in the literature.$^{20,21}$

In the literature,$^{20}$ the dependence of lasing threshold power $P_{th}$ on $l_{mf}$ was explained by a simple equation, $P_{th} = A \sqrt{l_{mf}}$, where A is a constant. Here, in the experiment, the best fit, which is represented by the solid line, is obtained with $A=800$. This good fit suggests that the reason for the variation in $P_{th}$ with $f_w$ [Fig. 5.5(a)] is mainly the change in $l_{mf}$.

Peak wavelength in ZnO/Al$_2$O$_3$ emission spectra as a function of $f_w$ when the excitation power is substantially below the lasing threshold power (100kW/cm$^2$). The inset shows examples of the emission spectra for $f_w=0$ and 20.

Fig. 5.4
In conclusion, this experiment demonstrates that the change in the lasing wavelength of ZnO/Al$_2$O$_3$ nanopowder random laser can be achieved by varying weight fraction of Al$_2$O$_3$ to ZnO ($f_w$), in the sample. This change was found to be due to the modification in the extent of self-absorbing by ZnO resulting from the addition of Al$_2$O$_3$ scatterers. The controllability of lasing wavelength makes random lasers attractive for potential applications in identifications makers, displays, etc.

REFERENCES

6. Investigation of photoluminescence decay characteristics in metal/porous-silicon system.

6.1 INTRODUCTION

The luminescence decay characteristics, in various materials are known to be strongly modified by metal nanostructures. This is caused by the electromagnetic interactions between the host materials and metal particles via excitation of the surface plasmons in the nanostructures. This type of modifications has been observed in a wide variety of materials, such as semiconductor nanocrystals and organic molecules.

The primary purpose of this research is to investigate the modification of photoluminescence decay characteristics due to thin Au nanoparticle deposition on porous silicon (PSi), which is a typical nanocrystalline Si assembly. The motivation for the present research is that there are only few works on the PL decay characteristics of nanocrystalline Si modified by metal nanostructures. This is because the nanocrystalline Si usually shows a complex decay process due to the broad distribution of radiative and non-radiative decay rates caused by the phonon-assisted recombination processes and also fluctuation of Si nanoparticle size and morphology.

6.2 OBJECTIVE

In present work, we investigate the modification of photoluminescence decay characteristics of Si nanocrystals due to very thin metal films. First, the decay curves were analyzed by taking the distribution of the decay rates into consideration. Second, we examined the emission wavelength dependence of the decay rates.

6.3 EXPERIMENTAL

Thin porous Si (PSi) layer of ~75 nm thickness was formed by the conventional anodic etching on the Si substrate and then, gold thin layers were deposited on this PSi by Vacuum Evaporation Deposition Technique. The mass thicknesses of gold is 1.0, 2.5, 5.0 nm. A schematic diagram for sample is shown in the Fig. 6.1.

![Sample for Au/PSi](image)

6.4 Results

To analyze the decay curves, we used two decay functions. One is lognormal distribution function, equation (6.1). Another one is the stretched exponential function, equation (6.2), which is usually used for the fitting of decay curve of porous silicon. We try to fit the decay curves of porous silicon...
samples with both of these functions and found that both of the equations result in the best fit, as shown in the Fig. 6.2(a) and (b). This is because, the values of the reduced Kai square, $\chi^2_R$, which represents the goodness of fit, is close to unity in both cases.

However, as shown in the Fig. 6.3, only the lognormal distribution function results in the perfect fit for Au/porous-silicon (Au/PSi sample).

Decay function with lognormal distribution of decay rates

\[
I(t) = I(0) \int_0^\infty \phi(\gamma) \exp[-\gamma_{mf} t] d\gamma
\]

\[
\phi(\gamma) = \left[ \int_0^\infty \phi(\gamma) \right]^{-1} \exp \left[ -\ln^2(\gamma/\gamma_{mf})/w^2 \right]
\]

\[
w = \sinh^{-1}(\Delta\gamma/2\gamma_{mf})
\]

(6.1)

Stretched exponential decay function

\[
I(t) = I(0) \exp[-(\gamma_{st} t)^\beta]
\]

(6.2)

$\gamma_{mf}$: Most frequent decay rate

$\Delta\gamma$: Width of $\phi$

$\gamma_{st}$: Decay rate of stretched decay

$\beta$: Stretching factor

Fig. 6.2
We compare the decay curves for porous silicon/Au (Au/PSi) sample with that of only porous silicon sample. Figure 6.4(a) shows the comparison. We can see that the decay time becomes faster by the deposition of gold. From the decay fitting with the lognormal distribution function, we can obtain the distribution of decay rates. Figure 6.4(b) shows this distribution for the sample with and without gold. The distribution becomes wider by the deposition of Au.

The mean value of decay rate was calculated by the width and peak of distribution. These values are mean decay rates calculated for the sample with and without gold. The mean value of decay rate increases by a factor of about 10.

\[ \gamma_{\text{mean}} = \gamma_{\text{mf}} \exp\left[3/4 \sinh^{-1} \left(\Delta \gamma / 2 \gamma_{\text{mf}}\right)^2\right] \]

Fig. 6.3

We compare the decay curves for porous silicon/Au (Au/PSi) sample with that of only porous silicon sample. Figure 6.4(a) shows the comparison. We can see that the decay time becomes faster by the deposition of gold. From the decay fitting with the lognormal distribution function, we can obtain the distribution of decay rates. Figure 6.4(b) shows this distribution for the sample with and without gold. The distribution becomes wider by the deposition of Au.

The mean value of decay rate was calculated by the width and peak of distribution. These values are mean decay rates calculated for the sample with and without gold. The mean value of decay rate increases by a factor of about 10.

Fig. 6.4

Figure. 6.5(a), shows that the decay rates for both the sample with gold layer and without gold layer depend on the emission wavelength. Moreover, Fig. 6.5(b), which is the plot of normalized decay rates for various gold layer thickness, demonstrate that the decay rates show the wavelength
dependence on the thickness of gold layer. The decay rates increase with increasing the wavelength, and the rates are higher for the sample with thicker Au films.

\[
\gamma_{\text{norm}} = \frac{\gamma_{\text{metal}}}{\gamma_{\text{air}}}
\]

6.5 CONCLUSION

It was found that the deposition of gold film on the porous Si (PSi) leads to much wider decay rate distribution with its peak shifted toward longer decay rate side. And the decay curves, strongly modified by Au, showed remarkable non-single exponential feature, and were well fitted by lognormal distribution function of decay rates.