Fabrication of ZnS/Porous Silicon Composite and Its Enhancement of Photoluminescence

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ABSTRACT

A ZnS thin film was electrodeposited on the surface of nanopores of porous silicon (PSi) without plugging of the nanopores. And the optical properties of the ZnS/PSi composites were investigated. The PSi was fabricated by anodization of n-Si (100) wafer in HF/EtOH/H₂O solution under constant current conditions. The pore diameter and the porous layer depth of the PSi were 20–80 nm and 8–50 μm , respectively, and they are controlled by variation of the HF concentration and anodization time. Electrodeposition proceeded on the surface of the nanopores (pore diameter, 80 nm) of the PSi under galvanostatic conditions of 0.44–8.85 mA/cm^2 and the aqueous electrolyte solution contained ZnSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and glycerol. The deposited ZnS plugged the nanopores at high current density, whereas at low current density, ZnS was deposited on the nanopore wall without plugging. The photoluminescence (PL) spectra due to the ZnS/PSi composites showed two separate peaks at 430 nm and 530 nm. The PL intensity decreased with increased current density because of the segregation of ZnS on the upper parts of the PSi nanopores. The PL intensity was also enhanced owing to the large surface area of the PSi.

Keywords:

Zinc sulfide, PSi, Anodization, Blue LED, Electrodeposition

1. Introduction

One of the remarkable trends in luminescent material fabrication in recent years is the use of nanocomposites with porous materials that have high specific surface areas. The preparation of functional materials in the mesopores of porous substrates is a popular approach for enlarging surface area. It is expected that nanocomposites with porous materials have high performance as seen in the fields of catalysis[1], gas sensors[2,3] and electrode batteries[4-10].

Since photoluminescence (PL) from porous silicon (PSi) at room temperature was discovered, PSi, which can be fabricated by anodic oxidation in HF-based solution[11,12], has become one of the most attractive porous materials:

where h^+ represents an electron hole of silicon (Si). The diameter of the nanopores, which are formed by anodic oxidation, can be controlled by the resistivity of the Si wafer and/or the various anodization parameters (i.e., HF concentration, current density, reaction time, solvent etc.)[13,14].

When the particle size of nanocrystalline Si decreases to below the Bohr radius, the electron transition occurs without a phonon-like direct band gap owing to the uncertainty principle; consequently, nanocrystalline Si shows visible-light luminescence owing to the quantum size effect.

Therefore, the PSi can emit PL in spite of being an indirect semiconductor because there is nanocrystalline Si in the porous layer[15], and the band gap depends on the particle size of the nanocrystalline Si in accord with the quantum size effect[16-18]. Crystalline Si does not show PL because of the quantum band structure having an indirect band gap of about 1.1 eV and a small

exciton binding energy (below 15 meV)[19]. The ZnO/Si nanopillar composites were fabricated in a previous study, and the composites showed an enhancement of the UV emission intensity at 374 nm compared with the ZnO/Si wafer nanocomposites owing to a remarkable increase in emission area[20].

Zinc sulfide (ZnS) is a direct band-gap semiconductor and is known as a blue photoluminescence material, thus ZnS attracts much attention for applications in UV light emitting diodes (LEDs)[20], electroluminescence panels, light converting electrodes, efficient phosphors in flat panel displays, and solar cells[21]. Particularly, the epitaxial growth of ZnS on substrates is indispensable for LEDs made from ZnS[22,23]. ZnS shows two types of allotropic crystal forms: a cubic and a hexagonal form. The cubic form of ZnS whose lattice constant is 0.541 nm has good lattice matching with Si whose lattice constant is 0.543 nm, hence the ZnS epitaxial thin film can grow on a Si substrate[24]. Furthermore, it can be expected that the emission intensity is enhanced owing to the increase in the area of emission if PSi is used as the substrate instead of a Si wafer[22]. In addition, the deposition of a ZnS thin film on three-dimensional structured substrates would be suitable for enhancement of emission intensity. When a high-dimensionally structured phosphor is designed, it is desirable to have a structure that is illuminated by the excitation beam to the maximum area possible; however, few studies have sought to characterize the effect of substrate structure (e.g., porosity and pillar depth) on the PL intensity. In previous studies by Xu et al.[25], a ZnS thin film was deposited onto a Si nanopillar surface by hydrothermally etching, and white PL was observed which contained blue band PL from Si-NP and green band from ZnS. However, the PL intensity was not so high, because the Si nanopillar array do not have large surface area. Furthermore, from the standpoint of increasing surface area, a porous structure would be preferred to a pillar structure, thus in a previous study by Katiyar et al.[22], a ZnS thin film was deposited on the surface of nanopores of PSi by pulsed laser deposition. However, the porous structure of the PSi became plugged by the ZnS. The growth of a ZnS thin film on a porous substrate, without first covering the pores by a dry treatment process, is difficult because of the long mean free path of the

reactive species[26]. In contrast, a wet process, where the reactants in solution have a short mean free path, allows a high accessibility to the substrates[27-35]. Hence to fabricate ZnS/PSi nanocomposites that retain a porous structure, wet processes such as electrodeposition and liquid phase deposition, originally developed by us, are ideal. Accordingly, in our previous study, a TiO₂ thin film was deposited onto the surface of mesopores of PSi by liquid phase deposition[8]. On the other hand, though it is not clarified still completely, the reaction mechanism of the electrodeposition of ZnS can be considered as follows:

For this study, ZnS/PSi nanocomposites of various pore diameters and porous layer thicknesses were prepared by electrodeposition. Optimization of the reaction conditions for ZnS electrodeposition is a pre-requisite for control of the ZnS/PSi nanocomposite structure. Furthermore, in the case of electrodeposition, the reaction conditions should be optimized not only in terms of the concentration and distribution of reaction species but also to control the electric field distribution in the nanopores of the ZnS. Hence, in this study the concentrations of reaction species and the current density during electrodeposition were optimized in the preparation of the ZnS/PSi nanocomposite structures for remarkable improvement of the PL intensity. The ZnS thin film was electrodeposited on the surface of the nanopores in PSi without plugging of the nanopores and the PL properties of the ZnS/PSi nanocomposites were investigated.

2. Experimental

2.1. Fabrication of n-type porous Si

All chemicals used in this work were of analytical grade. A n-type single-crystal (100) Si wafer, which was purchased from the Shin-Etsu Astech Co., Ltd. (Tokyo, Japan), was used as a working electrode. The resistivity of the Si wafer was 20 m Ω cm, respectively. The Si wafer was cut into pieces of area 2 $\times$ 2 cm² with a diamond cutter, dipped in acetone and degreased ultrasonically for 5 min, removed from the acetone, and dried at room temperature. An electrochemical cell was prepared in a Teflon® vessel as follows. The n-type Si wafer working electrode and a platinum coil-shaped wire counter electrode which was 0.5 mm in diameter were fixed in the electrochemical cell. The reaction area was about 1.1 cm². To remove native oxide layer on silicon working electrode, 5 wt% HF aqueous solution was poured into the cell, and removed after 5 min. A prescribed HF concentration in 1:1 mixture of water and ethanol as an electrolyte solution was then poured into the cell. The electrochemical cell filled with the electrolyte solution was brought to a dark room at room temperature, and anodic oxidation of the Si electrode was performed under galvanostatic condition of 142 mA cm⁻² using high voltage power supply (Matsusada Precision Inc. (Shiga, Japan), HAR-1R300) for the prescribed reaction time. Ultraviolet light at 365 nm from a 200 W Hg-Xe lamp irradiated the sample during the anodization. The electrolyte solutions were removed after the anodic oxidation, and the anodized Si electrodes were succinctly rinsed with deionized distilled water or ethanol and dried in air (as necessary), and were immediately immersed in distilled water or ethanol for 5 min to prevent from the drying of pore inside. The surface morphology and the cross-sectional image of the anodized PSi was observed using a field-emission scanning electron microscopy (FE-SEM; JEOL Co., Ltd. (Tokyo, Japan), JEM6335F), and an acceleration voltage of 15 kV was applied. The surface area and the pore diameter distribution were determined from N₂ adsorption isotherms (Quantachrome Instruments Co., Ltd. (Florida, United States), NOVA 2200e). The Si nanocrystalline size was investigated using a Raman spectrometer (HORIBA, Ltd. (Kyoto, Japan), RAMANOR T-64000). The wavenumber of monochromator was calibrated by silicon plate or powder at 520 cm⁻¹.

2.2. ZnS deposition on n-type PSi by an electrodeposition

The Pt plate of $2 \times 2 \text{ cm}^2$ which was used as a counter electrode was washed with deionized distilled water, degreased ultrasonically with acetone for 5 min and dried at the room temperature. A aqueous solution of $0.01 \text{ mol L}^{-1} \text{ ZnSO}_4 + 0.26 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3 + 0.20 \text{ mol L}^{-1}$ glycerol was used as a ZnS precursor solution. The pH of the ZnS precursor solution was adjusted to 4 by dilute sulfuric acid. To prevent the turbidity by the formation of colloidal sulfur, the precursor solution was prepared immediately before the experiment. An electrodeposition cell was prepared in a Teflon® vessel as follows. The n-type PSi or Si wafer electrode as cathode and the Pt plate as anode were fixed and kept for 30 min in about 30 mL of the ZnS precursor solution at 50 °C, then the constant current was applied by DC power supply (Matsusada Precision Inc. (Shiga, Japan), PLE-650-0.1) or CompactStat-CompactStatPlus (Ivium Technologies B.V. (Eindhoven, Netherlands)), and ZnS was deposited under galvanostatic condition. The current density and the reaction time were $0.4\text{--}8.85 \text{ mA cm}^{-2}$ and 5–120 min, respectively. After the electrodeposition ZnS/PSi composites were rinsed by distilled water and dried in air at room temperature. The cyclic voltammetry (i.e., CV) was carried out in the potential region of $-1.5\text{--}0 \text{ V}$ vs. Ag quasi-reference electrode (i.e., Ag QRE) at a scan rate of 10 mV s^{-1} for 5 cycles using the CompactStat-CompactStatPlus with a Pt electrode as a counter electrode. Currently, we are experimenting in the nonaqueous system in a series of our research, that is, the organic solvent is added and the concentration of the glycerin is increased, hence the Ag QRE was also employed in this research to enable the comparison in a series of our data. It has been confirmed with good reproducibility that the Ag QRE showed lower electrode potential of 0.051 V against Ag/AgCl electrode. The surface morphology and the cross-sectional image of the ZnS deposited PSi was observed by the FE-SEM, and the energy dispersive X-ray spectroscopy (SEM-EDS; JEOL Co., Ltd. (Tokyo, Japan), EX-23000BU) was used to elucidate the distribution of Si, Zn, S, and O of the deposits. The crystalline structures of the deposited ZnS to Si wafer and PSi composites were investigated using an X-ray diffractometer (XRD; Rigaku corp. (Tokyo, Japan), RINT-TTR/S2) equipped with a rotating Cu

anode operating radiation at 45 kV and 200 mA. $2\theta/\theta$ scans were carried out and a scan rate of 10° per minute was applied. Amount of Zn deposited on the porewall of PSi was determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES; HORIBA, Ltd. (Kyoto, Japan), ULTIMA 2000). PSi/ZnS composites electrodeposited for various reaction time were immersed in 10 wt% HF aq. for one month to dissolve all deposited ZnS, then 10 wt% HF aq. was filtrated and diluted by distilled water to a predetermined volume.

2.3. Evaluation of optical properties of ZnS/PSi composites

The photoluminescence(PL) spectra and the photoluminescence excitation(PLE) spectra was investigated using a spectrofluorometer (JASCO corp. (Tokyo, Japan), FP-6500). The light source was Xenon lamp of 150 W and the scan speed of 100 nm min^{-1} , the PMT voltage of 350 V, the scan range were used in the 400-900 nm. The excitation wavelength was 300 nm in PL spectra measurements, and the emission wavelengths were 430 and 530 nm in PLE spectra measurements. For the time-resolved measurements, the excitation and emission wavelengths were fixed at 300 nm and 430 nm, respectively. The room temperature PL lifetime measurements were performed by the time correlated single photon counting technique using a FluoroCube 5000-U (HORIBA JOBIN YVON S.A.S. (Longjumeau, France) equipped Xenon lamp as light source.

3. Results and discussion

3.1. Optimization of preparation conditions for n-type PSi

First, the PSi was prepared from n-type Si wafers of resistivity $0.02 \text{ } \Omega \text{ cm}$ and $1.5 \text{ } \Omega \text{ cm}$ using various HF solutions containing 1:1 mixtures of water and organic solvents (i.e. methanol, ethanol, 1-propanol, and DMF) at current densities of 142 mA cm^{-2} and 12.7 mA/cm^{-2} , respectively. In the case of the Si wafer whose resistivity was $1.5 \text{ } \Omega \text{ cm}$, the shape of the formed pores was not circular but cruciate, irrespective of the type of organic solvent. Meanwhile, in the case of the wafer of resistivity $0.02 \text{ } \Omega \text{ cm}$, circular nanopores were formed on the surface, and the pore diameter and

number density decreased with decreased dielectric constant of the organic solvent. A low dielectric constant solvent such as propanol tended to be adsorbed on the hydrophobic surface of the Si wafer, the surface being covered by Si-H groups[36], thus it became difficult to etch the Si wafer surface by anodic oxidation[37]. The PSi was prepared from the n-type Si wafer of resistivity 0.02 Ω cm by anodization using a HF solution in a 1:1 mixture of water and ethanol, because the diameter and the depth of the nanopores formed by anodic oxidation were readily controlled by the HF concentration and the anodization time. The surface morphologies by FE-SEM of the PSi, prepared from the Si wafer (resistivity, 0.02 Ω cm) by anodization at 142 mA cm⁻² and with an anodization time of 4.2 min using electrolyte solutions of various HF concentrations in a 1:1 mixture of water and ethanol, are shown in Fig. S1. The nanopore diameter increased with decreased HF concentration; that is, the diameters were about 20, 50, 60, and 80 nm for HF concentrations of ≥ 28.5 , 20.4–25.8, 17.6, and 14.8 mol L⁻¹, respectively. Thus, the nanopore diameter can be controlled by judicious selection of the HF concentration of the electrolyte solutions. The effect of the anodization time on the surface morphologies by FE-SEM of the prepared PSi in HF (14.8 wt%) electrolyte solutions are shown in Fig. S2. The diameters of the nanopores were almost constant for an anodization time of 2 min or more and where a clear pore structure was formed, so it can be concluded that it was not possible to control the nanopore diameter by variation of anodization time. However, the porous layer thickness, which is the nanopore depth of the PSi, increased almost linearly with increased anodization time, as shown in Fig. S3. Fig. 1 shows the effect of the porous layer thickness on the PL intensities and PL peak positions of the prepared PSi. All of the prepared PSi exhibited orange PL regardless of differences in particle size of the Si nanocrystallites[38,39]. The PL peak position shifted to a longer wavelength region with increased anodization time because of Si oxidation. The nanocrystalline Si has a SiO_x shell[40] because the material is readily oxidized, and the interface level is formed at the interface between Si and SiO_x. The excited electron is trapped at the interface, then the electron has transitioned to the valence band, hence the PL peak position has not shifted regardless of the decrease of the nanocrystalline Si size after an anodization time of 4 min[39].

Meanwhile, the PL intensity increased considerably for 3 min of anodization (with a local maximum at 3 min of anodization) and, thereafter, the nanocrystalline Si size decreased considerably. The increase of the PL intensity resulted from an increase in the number density of nanocrystalline Si[41]; however, the PL intensity decreased after 3 min of anodization, regardless of the generation of nanocrystalline Si at the openings of the nanopores. This result suggested that the depth of penetration of the excitation beam was limited. After 3 min of anodization, the excitation beam did not reach the tips of the nanopores where the nanocrystalline Si was generated, and a part of the nanocrystalline Si was dissolved by HF in the upper porous layers. As a result, the number density of nanocrystalline Si in the area illuminated by the excitation beam decreased, hence the PL intensity decreased.

3.2. Preparation of ZnS/PSi nanocomposites by electrodeposition

The CV curves of the Si wafer and the PSi whose nanopore diameter was 80 nm were recorded in the ZnS precursor solution and are shown in Fig. 2. A large anodic peak was observed at about -0.3 V for the PSi, whereas this anodic peak was absent for the Si wafer. In addition, it can be considered that the oxidation reaction of Si hardly occurred because SiO₂ is an insulator. The CV measurement started at -0.2 V (vs. Ag QRE) (No. 1 in Fig. 2(a) and (b)) to 0 V (vs. Ag QRE), and then the cathodic scan from 0 V (vs. Ag QRE) to -1.5 V (vs. Ag QRE) was carried out. The E° value of the electrode reaction of Eq. 2 is -0.763 V (vs. SHE), the Ag/AgCl electrode shows higher electrode potential of 0.222 V, and the Ag QRE showed lower electrode potential of 0.051 V against Ag/AgCl electrode as described in section 2.2. Therefore, the reductive reaction of Zn²⁺ to metallic Zn starts at about -0.93 V (vs. Ag QRE, i.e., $-0.763 - 0.222 + 0.051 = -0.934$) (No. 2 in Fig. 2(a) and (b)). The reductive reaction of Zn²⁺ to metallic Zn progresses gradually because the electric conductivity of Si wafer and PSi is low to -1.5 V (vs. Ag QRE) as the end of the cathodic scan. This metallic Zn was observed the XRD patterns after the end of the cathodic scan (No. 3 in (a) and (b)) in the fifth cycle of CV as shown in Fig. 2(c). The metallic Zn formed on the electrode reacts with S

and forms ZnS thin film as Eq. 4. The metallic Zn on the Si wafer rapidly forms ZnS thin film, whereas the formation rate of ZnS thin film in the nanopores is relatively slow, hence the excess metallic Zn exists in the nanopore. The excess metallic Zn in the nanopores oxidizes into Zn^{2+} when the anodic scan. The oxidation peak shifts to the higher electrode potential region, because this oxidation reaction also progresses gradually.

An adequate diffusion rate for the reaction species into the nanopores is important for the preparation of sufficient amounts of the ZnS/PSi nanocomposite by electrodeposition. To confirm the effect of diffusion of the reaction species into the nanopores, a ZnS thin film was deposited onto the surface of nanopores by electrodeposition of three types of PSi as follows: (1) dried PSi after etching, (2) immersion in water for the PSi after etching, and (3) immersion in ethanol for the PSi after etching. The current density and the deposition time were 0.88 mA cm^{-2} and 90 min, respectively. The surface morphology and cross-sectional images by FE-SEM and the EDX line profiles for Si, Zn, S, and O for the prepared ZnS/PSi nanocomposites are shown in Fig. S4. A larger amount of ZnS was deposited on all substrates compared with the Si wafer substrate owing to dielectric saturation on the porous electrode surface. It is difficult for the electrolyte solution to permeate through the dry hydrophobic nanopores, thus Zn and S mainly existed on the dried PSi surface, as shown in Fig. S4(a). In the case of the PSi, which was immersed in water or ethanol, Zn and S were distributed throughout the whole nanopore network. It can be assumed that when the nanopores were filled with solution, the ion diffusion paths formed between the ZnS precursor solution and the inside of the nanopore walls. Zn and S were distributed uniformly in the PSi, which was immersed in ethanol in contrast to that for water. It can be estimated that when a polar solvent is mixed with water, the polar solvent can also form hydrogen bonds, and as a result diffusion of the ions in the pores is accelerated in such mixed solvents.

To confirm the effect of the current density on ZnS electrodeposition, ZnS was electrodeposited onto the PSi of pore diameter 80 nm at various current densities for 90 min. The top view and the cross-sectional FE-SEM images and EDX line profiles for the prepared ZnS/PSi

nanocomposites are shown in Fig. 3. At a low current density of 0.88 mA cm^{-2} , nanopores on the PSi substrate remained after electrodeposition for 90 min, and Zn and S were distributed over the insides of the nanopores. However, at a high current density in excess of 4.42 mA cm^{-2} , the nanopores were plugged by ZnS, which deposited onto the PSi substrate. Furthermore, Zn and S were present only on the top surface of the porous layer because the deposited ZnS plugged the nanopores and inhibited the diffusion of the reaction species into the nanopores. The amount of O atoms in the upper part of the nanopores (i.e., the areas surrounded by the yellow dotted line in Fig. 3) was less than that in the lower part of the nanopores because of the reduction of Zn^{2+} by cathodic bias. Metallic Zn can be confirmed from the XRD patterns of the ZnS/PSi nanocomposites, as shown in Fig. 4. It can be concluded that metallic Zn existed mainly on the upper part of the nanopores as a result of the O atom distribution and the XRD patterns, and this suggested that the current density tended to be concentrated in the upper part of nanopores. The ZnS of the cubic form whose lattice constant is 0.541 nm has good lattice matching with Si whose lattice constant is 0.543 nm, hence it can be estimated that ZnS grew epitaxially in the nanopores of the PSi.

The ZnS was electrodeposited on the PSi at 0.88 mA cm^{-2} for various electrodeposition times, the pore diameter of the PSi being 80 nm and the porous layer thickness being $27 \text{ }\mu\text{m}$ (i.e., anodization time, 4.2 min). The amount of Zn deposited was dependent on the electrodeposition time and this was studied by ICP-AES, as shown in Fig. S5, where the amount deposited increased linearly with electrodeposition time. The effect of electrodeposition time on the surface morphology and the cross-sectional images by FE-SEM and the EDX line profiles are shown in Figs. S6 and 5, respectively. The nanopores were not plugged by the deposited ZnS even for relatively long electrodeposition times, and Zn and S were distributed throughout the whole nanopore network. At first, Zn and S were deposited in a gradient manner from the top surface to the tip of the nanopore for 15–60 min, then they were uniformly deposited throughout the whole nanopore surface for 60–90 min, and finally they were mainly deposited on the lower parts of the nanopores. The porous layer thickness was controlled by the anodization time, as described in section 3.1, and the surface

morphologies and cross-sectional images by FE-SEM and the EDX line profiles are shown in Figs. S7 and S8, respectively. The nanopores were not plugged, irrespective of the porous layer thickness, and Zn and S were distributed throughout the whole nanopore network. In the case of the PSi whose porous layer thickness was 34 μm (i.e., anodization time of 6 min), the amount of O atoms in the upper part of the nanopores (i.e., area surrounded by yellow dotted line in Fig. S8) was less than that in the lower part of the nanopores because of the reduction of Zn^{2+} by cathodic bias. The reduction of Zn^{2+} is confirmed by the decrease in the amount of O atoms in the upper part of the nanopores. The XRD pattern in Fig. 6 shows the existence of metallic Zn for the ZnS/Psi nanocomposite prepared from the PSi substrate, which had a relatively thick porous layer of 32 μm . This was because a high voltage was applied on top of the porous layer, which was relatively thick, and the PSi was used as the substrate owing to the higher resistivity of the porous Si layer compared with the bulk Si. The surface morphologies and cross-sectional images by FE-SEM and the EDX line profiles as a function of pore diameter are shown in Fig. 7. ZnS was distributed throughout the whole nanopore network for the PSi substrates whose pore diameters were > 30 nm, whereas ZnS was mainly deposited onto the top surface of the nanopores and plugged the nanopores of the PSi substrates whose pore diameters were 20 nm. To prevent the inhibition of ion diffusion by the reaction species into the nanopores through plugging of the nanopores, appropriate controls for ion diffusion and ion transport at the solid-liquid interface on the porous layer surface were desirable.

3.3. PL optical properties of ZnS/PSi nanocomposites

The PL spectra of the ZnS/PSi nanocomposites prepared from the PSi substrates with pore diameters of 20, 50, and 80 nm are shown in Fig. S9. The good reproducibility has been confirmed for the PL properties as well as the deposition of a ZnS thin film. It can be estimated that it is owing to the preparation of PSi having uniform pore diameter and the stable electrodeposition reaction. The reactivity of the Si-H termination is high, however, the electrodeposition reaction is a surface reaction, therefore when a pore inner wall is covered with a deposit once, the reactivity of the Si-H

termination is not reflected onto the electrodeposition reaction, consequently, the surface composition in PSi nanopores and the reproducibility of the electrodeposition can be controlled. The pore diameter was controlled by the HF concentration of the electrolyte solution as discussed in section 3.1, and the porous layer thickness was 27 μm (i.e., anodization time of 4.2 min). The ZnS/PSi nanocomposite prepared from the PSi with a diameter of 80 nm showed the strongest PL intensity in the wavelength range from 400–900 nm, and had a peak luminescence at 430 nm. Meanwhile, the PL intensity due to the ZnS/PSi nanocomposite prepared from the PSi with a diameter 20 nm was very low, because the emission surface area of the PL was insufficient to realize a strong PL intensity because of the plugging of the nanopores. It can be assumed that the increase of the surface area of the ZnS thin film owing to a uniform deposition throughout the nanopore surface was essential to sustain the high PL intensity. The effects of the electrodeposition current density on the PL spectra of the ZnS/PSi (prepared from PSi of pore diameter 80 nm) and the ZnS/Si wafer nanocomposites are shown in Fig. 8, respectively, and these PL spectra show two separate peaks at about 430 nm (blue band) and about 530 nm (green band). The electrodeposition time was 90 min for both nanocomposites. As can be seen from the inset plot in Fig. 8, the PL intensity at 430 nm due to the ZnS/PSi nanocomposites considerably decreased with an increase in current density for values $< 1.5 \text{ mA cm}^{-2}$, and the PL intensity gradually decreased with further increases in current density. The following two factors are thought to account for the decrease of the PL intensity: (1) a decrease of the emission surface area of the PL region as a result of ZnS deposition, and (2) a decrease of ZnS, a phosphor, due to reduction to Zn metal. As discussed in section 3.2, ZnS was mainly deposited on the top surface of the porous layer and Zn^{2+} was reduced to Zn under the high electrodeposition current density. When the current density was 0.44 mA cm^{-2} , ZnS was uniformly deposited throughout the whole nanopore surface and metallic Zn was not observed. The ZnS/PSi nanocomposites showed very high PL intensity compared with the PSi/Si wafer composite, and this indicated that an increase of emission surface area was a pre-requisite for achieving a high PL intensity. The PL decay curves and the time-resolved measurement of PL

intensity are shown in Fig. S10. The PL intensity decreased monotonously with increases in the electrodeposition current density; however, the trends for the PL decay curves were similar, regardless of the current density. The ZnS/PSi nanocomposite prepared at the lowest current density of 0.44 mA cm^{-2} showed a particularly long PL life time for both the blue and green bands. The PL intensity increased with increased radiation time. The PL by the ZnS/PSi nanocomposite, which was electrodeposited at 0.44 mA cm^{-2} , had a very long life time, thus the excited electrons were accumulated in a conduction band, and, as a result, polarized light was emitted after a long radiation time. The current-voltage (I-V) curves for the PSi and ZnS/PSi nanocomposites are shown in Fig. 9. When a positive bias was applied to the ZnS side, the band diagram for the ZnS/PSi nanocomposite would be expected to be as the inset scheme of Fig. 9. The conduction band of the PSi has a higher energy level than that of ZnS, thus the direction of energy transfer is from the PSi to the ZnS. The S/Zn ratio was estimated by SEM-EDX quantitative analysis, which was carried out by extraction of the porous layer from the cross-sectional FE-SEM images. The average S/Zn ratio was almost constant at about 0.4 regardless of the electrodeposition current density, so the ZnS in the ZnS/PSi nanocomposites had a large amount of S atom deficits. The impurity level derived from a S atom deficit is located 0.62 eV below the conduction band of ZnS[42], and the energy difference between the impurity level and the valence band was about 2.88 eV (430 nm). This energy difference is near to the energy that corresponded to the peak wavelength of the PL spectra from the ZnS/PSi nanocomposites, therefore this result indicated that the blue PL band of the ZnS/PSi nanocomposite originated from the transition between the impurity level caused by the S atom deficit and the valence band.

The effects of the polarization angle on the PL spectra of the PSi and ZnS/PSi nanocomposites are shown in Fig. 10. The PSi was prepared from monocrystalline Si, so the Si nanocrystalline in the PSi is anisotropic, hence the PL from the PSi is also anisotropic[43]. Therefore, when the polarizing filter was turned in front of the detector, the PL intensity from the PSi drastically changed owing to its anisotropy. However, in the case of the ZnS/PSi nanocomposite,

the intensity of the blue PL band at 430 nm was not influenced by rotation of the polarizing filter, although that of the green PL band at 530 nm was remarkably influenced, hence this result indicated that the green PL band originated from the nanocrystalline Si in the ZnS/PSi nanocomposite. In a previous study by Katiyar et al., the emission wavelength from the Si/ZnS interface was around 530 nm[22]. Hence, it can be concluded that the green PL band of the ZnS/PSi composites observed in this study was derived from the transition between the PSi/ZnS interface level and the valence band. Fig. 11 shows the PL spectra of the ZnS/PSi composites prepared from the PSi substrates, which have various porous layer thicknesses (a), and the effect of the porous layer thicknesses on the PL intensities for the PSi at 650 nm and the ZnS/PSi nanocomposites at 430 nm (b). The relationship between the porous layer thicknesses and the PL intensities for the ZnS/PSi composites was very similar to that for the PSi. The increase of the PL intensity of ZnS/PSi for anodization times up to 3 min was caused by the increase in the emission surface area. It can be estimated that the amount of ZnS deposited in the region illuminated by the excitation beam decreased because of the further increase of the porous layer thickness after an anodization time of 3 min. Furthermore, ZnS was reduced to metallic Zn because the high voltage was applied only at the top surface of the porous layer because of the increase in the porous layer thickness. These results strongly suggested that it was important not only to ensure a high surface area for emission, but also to consider the depth of illumination by the excitation beam. The effects of the ZnS electrodeposition time on the PL spectra are shown in Fig. 12. The PL spectrum shows a single peak at 630 nm before the electrodeposition, but two separate peaks are revealed at 430 and 530 nm after electrodeposition. The amount of Zn deposited, which was determined by the ICP-AES, increased linearly with increases in the electrodeposition time. In contrast, the increase of the PL intensity was not monotonous; the PL intensity increased gradually and linearly for an electrodeposition time of 70 min, then the PL intensity increased considerably between 70–80 min, and, thereafter, the PL intensity was almost constant. Although the gradual and linear increase of PL intensity resulted from an increase in the amount of ZnS deposited, the result suggested that the increase of PL intensity resulted not only

from the increase in the amount of ZnS deposited, but also for other reasons. As shown in Fig. 5, while the PL intensity increased gradually and linearly, the ZnS was deposited from the top surface to the tip of the nanopores, then the ZnS was deposited uniformly on the whole nanopore surface during the phase when there was a dramatic increase in the PL intensity. The increase of the surface area of the ZnS thin film owing to the nanoporous structure, which originated from the PSi, was thought to be the reason for the sudden increase of the PL intensity. After the deposition time of 80 min, the ZnS was mainly deposited on the lower part of the nanopores; however, the depth of this deposition area was lower than the illumination depth of the excitation beam, hence the PL intensity became constant. These results were strongly supported by the correlation between the ZnS distribution in the nanopores and the PL intensity, and it is suggested that the substantial deposition of ZnS thin film in the nanopores was a key factor for the increase of PL intensity.

4. Conclusions

A ZnS thin film was deposited on the surface of PSi nanopores by electrodeposition and the remarkable improvement of the PL intensity by the enhancing surface area of emission region using the PSi substrates. The PSi was prepared from an n-type Si wafer of resistivity $0.02 \text{ } \Omega \text{ cm}$ by anodization using HF solution in a 1:1 mixture of water and ethanol. For PSi, which was immersed in a 1:1 mixture of water and ethanol, Zn and S were distributed throughout the whole nanopore network, and the nanopore diameter was observed to increase with decreases in HF concentration. The porous layer thickness, which is the nanopore depth in the PSi, increased almost linearly with increased anodization time. At a low current density of 0.88 mA cm^{-2} , the nanopores on the PSi substrate remained after an electrodeposition time of 90 min, and Zn and S were distributed over the inside of the nanopores. In contrast, at a high current density, $> 4.42 \text{ mA cm}^{-2}$, the nanopore was plugged by ZnS, which deposited onto the PSi substrate. Zn and S existed only on the top surface of the porous layer because the deposited ZnS plugged the nanopores and inhibited diffusion of the reaction species into the nanopores. Metallic Zn existed mainly on the upper part of the nanopores

because the current density tended to be concentrated in the upper section. The ZnS was electrodeposited at 0.88 mA cm^{-2} for various electrodeposition times onto the PSi whose pore diameter was 80 nm and the porous layer thickness was 27 μm . It was observed that the nanopores were not plugged by the deposited ZnS even for long electrodeposition times and Zn and S were distributed throughout the whole nanopore network. ZnS was mainly deposited onto the top surface of the nanopores and plugged the nanopores of the PSi substrates whose pore diameter was 20 nm. Appropriate controls for ion diffusion and ion transport at the solid-liquid interface of the porous layer surface are desirable to prevent inhibition of ion diffusion of the reaction species into the nanopores as a consequence of the plugging.

The PL spectra due to the ZnS/PSi nanocomposite showed two peaks at 430 and 530 nm. The PL intensity was increased because of an increase of the emission surface area of the PL region by the deposition of ZnS, and an increase in ZnS, as a phosphor. The PL by the ZnS/PSi nanocomposite, which was electrodeposited at 0.44 mA cm^{-2} , had a very long life time, hence the excited electrons were accumulated in a conduction band and as a result, polarized light continued to be emitted long after irradiation stopped. The PL intensity decreased with increased current density because of the segregation of ZnS on the upper part of the PSi nanopore, and the PL intensity was enhanced owing to the large surface area of the PSi. The blue PL band emitted by the ZnS/PSi nanocomposites originated from the transition between the impurity level of the S atom deficit and the valence band. The intensity of the blue PL band at 430 nm was not influenced by rotation of the polarization filter; however, that of the green PL band at 530 nm was remarkably influenced, hence the green PL band originated from nanocrystalline Si in the ZnS/PSi nanocomposite. Therefore, it can be concluded that the green PL band of the ZnS/PSi composites observed in this study was derived from the transition between the PSi/ZnS interface level and the valence band. The increase of the PL intensity of ZnS/PSi up to an anodization time of 3 min was caused by the increase in the surface area of emission. After an anodization time of 3 min, the amount of ZnS deposited in the region that can be illuminated by the excitation beam decreased

because of the further increase in the porous layer thickness. Thus it was important not only to increase the emission surface area, but also to take into consideration the depth of illumination of the excitation beam. The correlation between the ZnS distribution in the nanopores and the PL intensity was confirmed, and the substantial deposition of ZnS thin film in the nanopores was essential for securing the increased PL intensity.

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Figure captions

Fig. 1. The effect of porous layer thickness on the PL intensities and the PL peak positions at 650 nm due to PSi, which was prepared from an n-type Si wafer. The resistivity of the Si wafer and the anodization conditions are as shown in Fig. S3.

Fig. 2. CV curves at a scan rate of 10 mV s^{-1} of the Si wafer without nanopore (a) and the PSi with nanopore diameter of 80 nm (b) observed in the ZnS precursor solution (i.e., $0.01 \text{ mol L}^{-1} \text{ ZnSO}_4 + 0.26 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3 + 0.20 \text{ mol L}^{-1}$ glycerol) and XRD patterns of the Si wafer (Ag and Pt were used as reference and counter electrodes, respectively) and the PSi after the end of the cathodic scan (No. 3 in (a) and (b)) in the fifth cycle of CV (c).

Fig. 3. Surface morphologies (top) and the cross-sectional images by FE-SEM and EDX line profiles of Si, Zn, S, and O for the prepared ZnS/PSi nanocomposites (bottom) by electrodeposition at various current densities for 90 min. The nanopore diameter of the PSi used was 80 nm (anodized in HF (14.8 wt%) in a 1:1 mixture of water and ethanol). The amount of O atoms in the upper part of the nanopores (i.e., the area surrounded by a yellow dotted line) was decreased.

Fig. 4. XRD patterns for the Si wafer and the ZnS/PSi nanocomposites electrodeposited at various current densities for 90 min. The other electrodeposition conditions were as shown in Fig. 3.

Fig. 5. The influence of electrodeposition time on the cross-sectional images of FE-SEM and EDX line profiles. The electrodeposition conditions are as shown in Fig. S5.

Fig. 6. XRD patterns of the ZnS/PSi composites prepared from the PSi substrates of various porous layer thicknesses. The porous layer thickness of the PSi substrates was controlled by etching time. The electrodeposition conditions are as shown in Fig. S5.

Fig. 7. Surface morphologies (top) and cross-sectional images of pore diameters as revealed by FE-SEM and EDX line profiles (bottom). Electrodepositions were carried out at 0.88 mA cm^{-2} for 90 min using PSi with porous layer thickness of $27 \text{ }\mu\text{m}$ (anodization time, 4.2 min). The pore diameter can be controlled by the HF concentration of the electrolyte solution in anodization as shown in Fig. S1.

Fig. 8. The effect of the electrodeposition current density on the PL spectra of the ZnS/PSi nanocomposites prepared from PSi with pore diameter of 80 nm (a) and the ZnS/Si wafer nanocomposites (b). Both nanocomposites were prepared by electrodeposition under galvanostatic conditions for 90 min. The inset plot shows the dependency of the PL intensity (430 nm) of the ZnS/PSi nanocomposites on current density.

Fig. 9. Current-voltage (I-V) curves for the PSi and ZnS/PSi nanocomposites. The inset scheme at the bottom right shows the band diagram of the ZnS/PSi nanocomposite. Current density for electrodeposition: (1) no electrodeposition (PSi); (2) 0.44 mA cm^{-2} ; (3) 0.88 mA cm^{-2} ; (4) 2.65 mA cm^{-2} ; (5) 4.42 mA cm^{-2} .

Fig. 10. Effects of polarization angle for the PL spectra of the PSi (blue) and the ZnS/PSi nanocomposites prepared from the PSi of pore diameter 80 nm (red). Electrodeposition was carried out at 0.88 mA cm^{-2} for 90 min using PSi porous layer thickness of $27 \text{ }\mu\text{m}$ (anodization time, 4.2 min). The inset shows the scheme for PL spectrometry with a polarizing filter.

Fig. 11. PL spectra of the ZnS/PSi nanocomposites prepared from PSi substrates of various porous layer thicknesses and pore diameter of 80 nm (a), and the effect of porous layer thickness on the PL intensities by PSi (at 650 nm) and ZnS/PSi (at 430 nm) nanocomposites (b). Electrodeposition was

carried out at 0.88 mA cm^{-2} for 90 min. The relationship between the porous layer thickness of the prepared PSi and the anodization time is shown in Fig. S3.

Fig. 12. The effect of electrodeposition time on the PL spectra for ZnS(a) and the PL intensities at 430 nm. The ZnS/PSi nanocomposites were prepared from PSi pore diameter of 80 nm. Electrodeposition was carried out at 0.88 mA cm^{-2} using PSi of porous layer thickness $27 \text{ }\mu\text{m}$ (anodization time, 4.2 min). Electrodeposition time: (1) 0 min (PSi); (2) 5 min; (3) 15 min; (4) 30 min; (5) 45 min; (6) 60 min; (7) 90 min; (8) 120 min.

Figure 1

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