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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/H_2O 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 $ZnSO_4$, $Na_2S_2O_3$ 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.

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:

$$Si + 4h^+ + 6HF \rightarrow SiF_6^{2-} + 6H^+ \quad (1)$$

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

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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 TiO_2 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:

$$Zn^{2+} + 2e^- \rightarrow Zn^0 \ (E^\circ = -0.763\,\mathrm{V}\ \text{vs. standard hydrogen electrode (i.e., SHE)}) \quad (2)$$

$$(3\text{-}1)\ S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O \ (E^\circ = +0.50\,\mathrm{V}\ \text{vs. SHE})$$

$$(3\text{-}2)\ H_2SO_3 + 4H+ + 4e^- \rightarrow S + 3H_2O \ (E^\circ = +0.45\,\mathrm{V}\ \text{vs. SHE})$$

$$Zn + S \rightarrow ZnS \quad (4)$$

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 mΩ cm, respectively. The Si wafer was cut into pieces of area $2 \times 2\,\mathrm{cm}^2$ 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 $1.1\,\mathrm{cm}^2$. 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 $142\,\mathrm{mA\,cm^{-2}}$ 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 N_2 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 $520\,\mathrm{cm}^{-1}$.

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

The Pt plate of $2 \times 2\,\mathrm{cm}^2$ 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 $0.01\,\mathrm{mol\,L^{-1}}\ ZnSO_4 + 0.26\,\mathrm{mol\,L^{-1}}\ Na_2S_2O_3 + 0.20\,\mathrm{mol\,L^{-1}}$ 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 $0.4\text{–}8.85\,\mathrm{mA\,cm^{-2}}$ 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 −1.5–0 V vs. Ag quasi-reference electrode (i.e., Ag QRE) at a scan rate of $10\,\mathrm{mV\,s^{-1}}$ for 5 cycles using the CompactStat-CompactStatPlus with a Pt electrode