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Improved Photoluminescence from Light-Emitting Silicon Material by Surface Modification

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A light-emitting silicon material was prepared by electrochemical etching of n-Si single crystal wafers in a solution of hydrofluoric acid and ethanol. Visible photoluminescence from the silicon was inhomogeneous and decayed rapidly in the ambient laboratory conditions or with photoirradiation. Substantial improvements in photoluminescence which include little-dependent luminescence peak energy with excitation energy variation and longer-lasting room temperature visible photoluminescence were achieved when the surface of photoluminescent silicon material was derivatized with the surface modifier of octadecylmercaptan. Surface modification of the photoluminescent silicon was evidenced by the measurements of contact angles of static water drops, FT-IR spectra and XPS data, in addition to changed photoluminescence. Similar improvements in photoluminescence were observed with the light-emitting silicon treated with dodecylmercaptan, but not with octadecane. The present results indicate that sulfurs of octadecylmercaptans or dodecylmercaptans appear to coordinate the surface Si atoms of LESi and perturb the surface states to significantly change the luminescent characteristics of LESi.

Introduction

We have been interested in electrochemically producing light-emitting silicon (LESi) materials and controlling their luminescent properties.¹⁻³ In this work, we describe significantly improved photoluminescent characteristics from thin porous silicon materials derivatized with surface modifiers of octadecylmercaptan and dodecylmercaptan.

Although the origin and mechanism of recent observations of room temperature visible photoluminescence from porous silicon remains unsolved,⁴⁻⁸ it can be regarded as a good starting point to fabricate optoelectronic devices based on silicon material in the future as far as the phenomenon of strong light emission at the room temperature is reproducible. In the present stage of the development of science in this area, improvement of light-emitting properties of the silicon material should be considered with importance, although electroluminescence has to be eventually shown to be useful. Photoluminescence, which is visible to the naked eye in the dark laboratory conditions, is inhomogeneous and lacks long-term stability,⁷⁻¹⁰ which may present a set of problems in fabricating devices, as is recently described by Jung.¹¹ Improvements in these two aspects of LESi material photoluminescence are the ones we concern in the present work. Previous efforts in this direction were made by heat treat-

ments of porous silicon materials.¹²⁻¹³

Experimental

All the chemicals used were of the best quality available commercially. Si single crystal wafers used in the present experiments were n-type (p-doped, 10-20 $\Omega \cdot \text{cm}$ resistivity) with (100) orientation. The Si surface was anodized in an ethanolic solution of hydrofluoric acid (1 : 1) at 5-7 V versus silver quasi-reference electrode under UV irradiation (Spectronic Co. Model ENF-240C) for 30 min. In our previous work,¹ we have anodized n-type (p-doped, 1.0-2.0 $\Omega \cdot \text{cm}$ resistivity, (100) orientation) samples in the electrolyte solution of the same composition at 1-3 V versus platinum quasi-reference electrode under the same UV irradiation conditions for 20 min. Our present work used the experimental conditions as was described in the above because of the sample availability and convenience. Surface modifications were made by treating the luminescent silicon dried in the nitrogen atmosphere, in the pure thiol atmosphere for one day at 80 $^{\circ}\text{C}$. Surface-derivatized silicon materials thus prepared were washed with ethanol and water to remove unreacted surface modifiers. Because it is known that luminescent properties of LESi strongly depend on the preparation conditions of n- or p-type starting silicon chips, resistivity, current

density, electrolyte compositions, anodization conditions and light illumination levels,¹⁻¹⁴ we checked the reproducibility of our present results by following the experimental sequence; (1) preparation of LESi by electrochemical anodization, (2) measurements of FT-IR spectra and photoluminescence spectra as a function of excitation energy, (3) surface modification, (4) contact angle measurements, (5) doing the above step (2), (6) photoluminescence decay measurements during continuous photoirradiation by using Xe lamp, and (7) the measurements of X-ray photoelectron spectra (XPS). For underivatized LESi materials, the steps of (3) and (5) were omitted. Separate additional experiments were performed for the measurements of contact angles or XPS. The total number of samples prepared is more than one hundred so far. In our experiments, the reproducibility was greater than 90% in producing LESi and about 10% in surface-derivatized LESi.

Electrochemical experiments were performed in a two-compartment cell using conventional three-electrode configuration.¹³ The photoluminescence was measured using Hitachi 650-60 Fluorescence Spectrometer, which operates with Xe lamp power of 150 W. FT-IR Spectra were obtained by employing Shimadzu DR-8501. Thirty to forty scans were collected at a nominal resolution of 3 cm^{-1} for signal averaging. A Rame-Hart NRL Model 100 goniometer was used to measure contact angles of static water drops ($10\ \mu\text{L}$). A Vacuum Science Workshop Scientific Instrument Inc. (Manchester, England) spectrometer equipped with Mg K α X-ray gun was used to obtain XPS data at 1.9×10^{-9} – 5.6×10^{-8} torr at Inter-university Semiconductor Research Center.

Results and Discussion

Because the previous works on LESi clearly demonstrated that the surface Si of LESi network electrochemically prepared was terminated with reactive H atoms,¹⁶⁻¹⁷ we approached the problem of improving the photoluminescent properties of porous silicon by possibly replacing the surface H atoms with stable organic functional groups to restore the hydrophobic surface of silicon wafers as



where X is an atom coordinating to the surface Si (sulfur in the present case) and R is an alkyl group. The strategy of using long-chain alkylthiols to chemically modify semiconductor surfaces was employed for GaAs by Allara¹⁸ and for InP by Woldeck.¹⁹ The idea of utilizing reactive hydrogens at silicon surfaces was applied to form alkyl monolayers covalently bonded to silicon surfaces by Chidsey.²⁰ In our preliminary report on potentiostatic preparation of porous silicon or LESi, we described that LESi surfaces could be modified by octadecylmercaptan, but the supporting experimental results were not presented to show the chemical modification of silicon surfaces by the alkylthiol.¹ In this work, we present the experimental evidences by the measurements of contact angles, FT-IR spectra, XPS and changed photoluminescence of the surface modified LESi with octadecylmercaptan and compare the results with those of as-prepared LESi. To contrast the results, we performed the surface modification experiments by using the two different types of molecular probes; (i) the molecule with the same alkyl chain not having

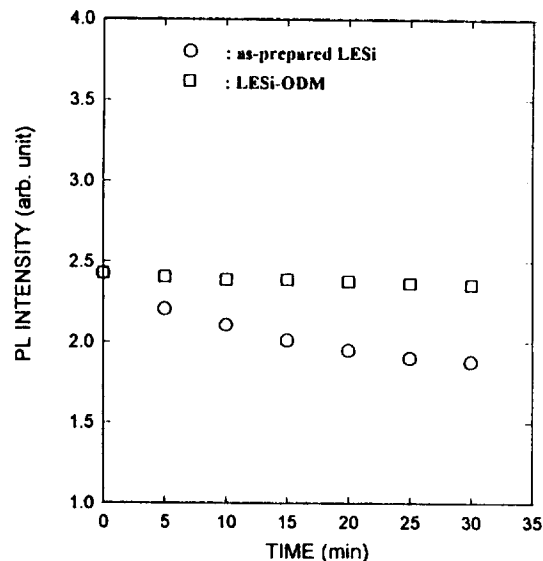


Figure 1. Photoluminescence decay during continuous photoirradiation of (a) as-prepared LESi and (b) modified LESi.

thiol group, octadecane, and (ii) the alkylthiol with a shorter alkyl chain, dodecylmercaptan. The results indicate that sulfurs of octadecylmercaptans or dodecylmercaptans apparently replace reactive hydrogens at silicon surfaces, coordinate the surface Si atoms of LESi and perturb the surface states to significantly change the luminescent characteristics of LESi. For the purpose of our work relevant to LESi, our description centers on and starts from the improved photoluminescence.

Figure 1 shows the normalized photoluminescence decay observed during continuous photoirradiation at 365 nm with a Xe lamp (150 W) of the LESi as-prepared and octadecylmercaptan-covered one. Photoluminescence intensity observed at 645 nm decreased rapidly as a function of time in the case of the unmodified silicon prepared electrochemically from single crystalline silicon wafer, as has been reported by others from the LESi prepared in the similar conditions,¹¹ but visible photoluminescence resisted to decay in the case of the LESi derivatized. These results agree with our previous qualitative observation that strong photoluminescence from the octadecylmercaptan-covered LESi under UV irradiation was visible to the naked eye for months but that no visible luminescence from bare LESi under identical conditions was observable after one month of its preparation.¹

Salient feature of the alkylthiol-modified LESi is shown in Figure 2, where photoluminescence spectra at varied excitation wavelength are shown for the bare and modified LESi. Strong dependence of photoluminescence on excitation energy was observed with LESi as prepared (a) but little dependence was seen with the LESi treated with octadecylmercaptan (b). Direct comparison of the dependence of emission peak energy with excitation energy is shown in Figure 3. Photoluminescence peak energy of the unmodified LESi continuously shifts to longer wavelength as the excitation wavelength becomes longer, but that of the modified LESi remains nearly unchanged. It has been reported that sulfur-doped silicon showed bound-exciton luminescence²¹ and creates new energy levels to generate recombination waves.²² It is also known that chemical treatments with sulfur com-

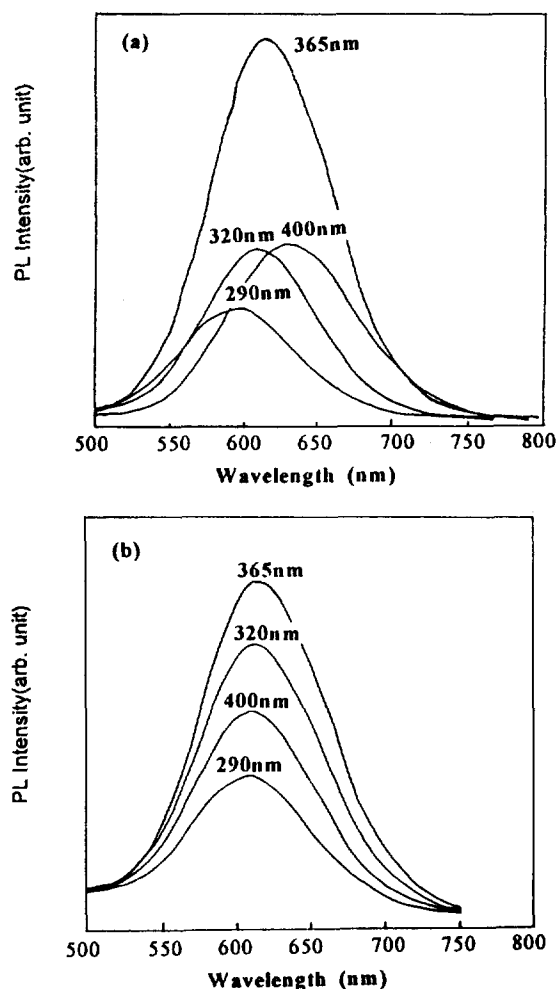


Figure 2. Photoluminescence at different excitation energy. (a) as-prepared LESi and (b) modified LESi.

pounds significantly change surface states in a semiconductor.²³⁻²⁵ In addition, improvements in steady-state photoluminescence signals from GaAs were observed by Lewis when the GaAs surfaces were covered with alkylthiols.²⁶ Thus our observations are favorably comparable to these previous studies on semiconductors by using sulfur compounds, and octadecylmercaptans appear to modify LESi surfaces, passivate dangle bonds of surface Si atoms and change the surface electronic states of LESi to improve photoluminescent properties. We will return to this point later.

We now describe and discuss the experiments on characterization of the surface-modified LESi. A drop of water on the surface-modified silicon did not generate any gas, while the same experiments with unmodified LESi generated unidentified gases as was observed previously.¹ A contact angle ($113(\pm 3)^\circ$) of a static water drop on the LESi covered with octadecylmercaptan, which precisely agrees with that (112°) measured on the surface of the same compound chemisorbed on gold,²⁷ was larger than the one ($87(\pm 5)^\circ$) on the bare LESi. Thus the surface-modified silicon is not covered with reactive H atoms any longer and shows the characteristics of hydrophobic methyl surface, as is described by Whitesides.²⁷ Further characterization of the octadecylmercaptan-covered LESi was performed by infrared spectroscopic

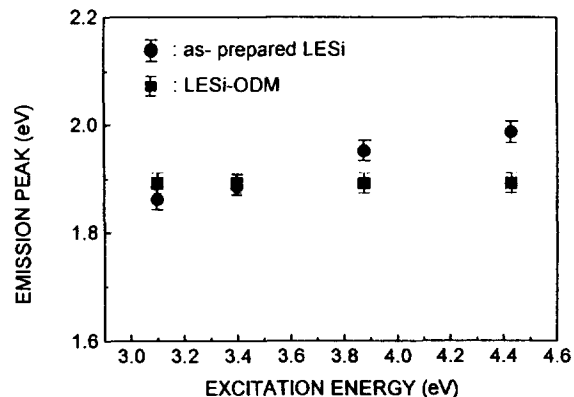


Figure 3. Emission peak energy at excitation energy varied.

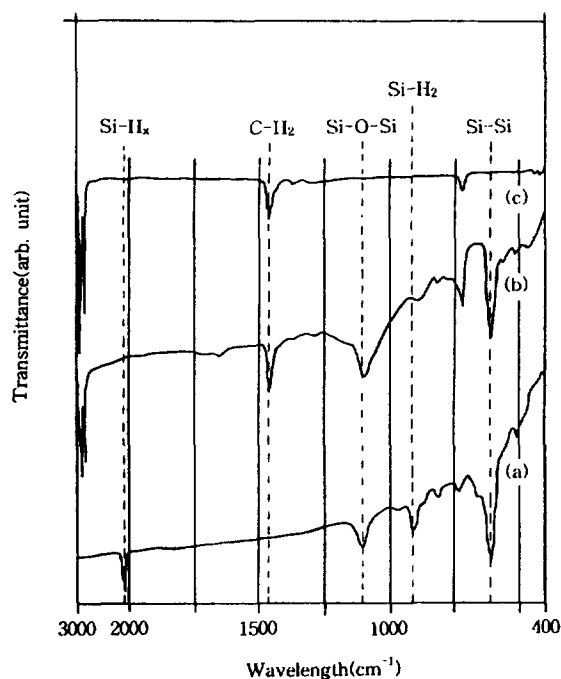


Figure 4. FT-IR spectra of (a) as-prepared LESi, (b) modified LESi and (c) octadecylmercaptan.

method. In Figure 4, FT-IR spectra are shown for a light-emitting silicon as prepared (a), the octadecylmercaptan-covered LESi (b), and octadecylmercaptan (c). Main features of Si-Si and Si-O-Si are found at 620 cm^{-1} and 1107 cm^{-1} ,²⁴ respectively, with the two different LESi samples. Strong aliphatic C(H)_n peaks are observed at 1468 , 2924 and 2953 cm^{-1} with both octadecylmercaptan itself (c) and the octadecylmercaptan-covered LESi (b), while the characteristic peaks originating from Si-(H)_n between 2050 and 2130 cm^{-1} observed with the bare LESi (a) are missing in the FT-IR spectrum of the octadecylmercaptan-LESi (b), indicating that octadecylmercaptans may coordinate the Si atoms exposed on the surface of the LESi matrix. A weak but discernable peak at 472 cm^{-1} observed in the modified LESi (b) may be assigned to S-Si (surface) bond. The wide-scan XPS data showed the strong peaks of Si(2P, 2S), C(1S) and O(1S) from both as-prepared and modified LESi, and did not quantitatively differentiate the modified LESi from as-prepared LESi. It

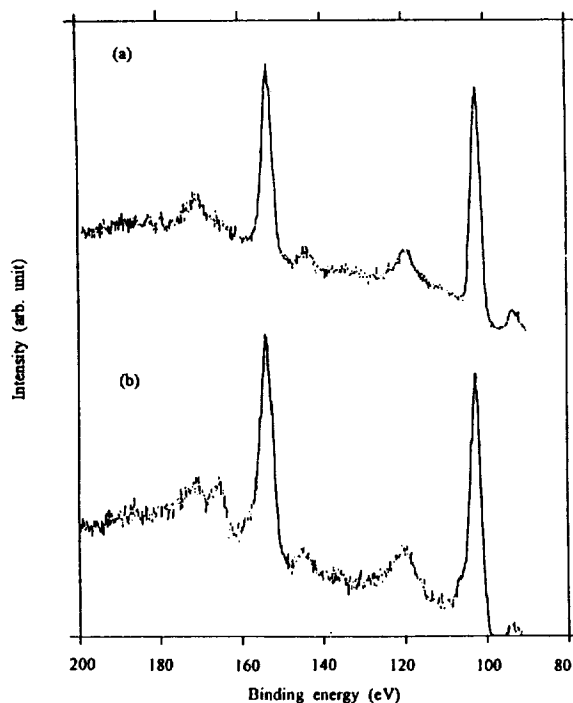


Figure 5. XPS of (a) as-prepared LESi and (b) modified LESi.

has been reported in the previous XPS studies of as-prepared LESi²⁸ that the abundant carbon as well as the elements Si and O were found as in the present work. In Figure 5 are shown XPS data collected in the 0-200 eV region in an effort to determine whether or not sulfur exists on the modified LESi surface. Prominent peaks observed with both as-prepared and modified LESi at 102 and 153 eV are assigned to Si 2P and Si 2S, respectively. A peak at 165 eV observed with the modified LESi, but not with as-prepared LESi, is assigned to sulfur (S 2P).²⁹ The small sulfur (S 2P) peak was expected because the modified LESi was washed with ethanol and water to remove unreacted octadecylmercaptan before XPS experiments (*vide supra*). Therefore, the combined experimental data of contact angles, FT-IR, XPS and changed photoluminescence strongly suggest that sulfurs of octadecylmercaptans appear to replace reactive H atoms and coordinate the Si atoms on the surface of the modified LESi with methyl group exposed to the air, to change the surface states.

Additional experiments were performed to find whether or not the improved photoluminescence characteristics of LESi originated from long alkyl chain or sulfur group by using the different types of molecular probes. First, octadecane, a molecule with the same alkyl chain not having a thiol group, was applied to modify the surface of as-prepared LESi and found not to significantly change the photoluminescent properties of LESi in either homogeneity or stability, as can be expected from that physical replacements of the air contacting LESi surface with simple alkane will not change the surface electronic states of LESi. Second, dodecylmercaptan, an alkythiol with a shorter alkyl chain, was used and proved to produce the modified LESi with long-term stability and homogeneity similar to the results obtained with

the octadecylmercaptan-modified LESi as was described in the above. Thus, the comparative studies of surface modification by different molecular probes demonstrate that the improved photoluminescence can be obtained when LESi is modified with octadecylmercaptan and dodecylmercaptan, and provide an another supporting evidence that sulfurs of the thiols apparently coordinate the surface silicon atoms of LESi, sufficiently perturb the surface electronic states, and significantly improve the photoluminescence of LESi.

Very recently, Laiho and Pavlov reported the spectroscopic scanning tunneling microscopy (STM) data, revealing a peak of the density of electronic states localized at surfaces correlate well with the photoluminescence spectra of LESi samples, and described that surface chemical compounds were expected to influence the photoluminescence, as was found in the present studies, by modifying the structure of the nanoparticles and controlling nonradiative transition probabilities by passivating dangling bonds of LESi.³⁰ The present results may be a good example to show such a change in photoluminescence of LESi by chemical modification of the LESi surface to the extent that Laiho and Pavlov anticipated. Certainly, spectroscopic STM experiments on the LESi modified with octadecylmercaptan and dodecylmercaptan will unveil the direct relationship between the localized density of states and the photoluminescent characteristics of the surface-modified LESi. We also note that the first-principles electronic structure calculations of LESi by Buda *et al.*³¹ showed that quantum confinement and surface effects are responsible for the room temperature visible photoluminescence from LESi, in line with our present results. We expect that the varied band structure of LESi upon surface modification by sulfur will emerge after the first-principles calculations are performed quantitatively. Further collaborative works on chemically modified LESi are in progress.

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A Study of Laminar Flow Torch in Microwave Induced Plasma Atomic Emission Spectrometry

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A comparative study of different torches in the Microwave Induced Plasma is reported. Three types of torches that have been used in this area are characterized and compared with each other. Especially, recently developed laminar flow torches have been optimized in design and analytical performances. The ratio of inner to outer tubes is found to be the most important parameter. As inner tube size increases, recirculating region also increases and consequently, sensitivity becomes better. An optimized laminar flow torch has been coupled to a gas chromatography and examined for halogen compounds. Detection limits are 25 pg s⁻¹ for Cl and 12 pg s⁻¹ for Br. These values are improved over the conventional laminar flow torch.

Introduction

Helium Microwave Induced Plasma (He MIP) has been developed as an element-selective emission detector for Gas Chromatography (GC) and the system has been widely studied by various researchers.¹⁻⁷ In his first paper of GC-MIP, Beenakker⁸ employed simple straight capillary quartz tubes of which diameter ranging from 0.5 to 3.0 mm. The sensitivities reported were in pg s⁻¹ range. However, the plasma tube, capillary flow torch (CFT), frequently suffered from problems such as memory effect, etching of the inner surface of the plasma tube, and wandering of plasma inside the torch. To reduce these problems, Bollo-Kamara⁹ designed a Tangential Flow Torch (TFT) which forced plasma gas to flow through a specially designed glass centersert. Much like

a torch of ICP, TFT could provide a self-centered plasma inside the torch. Plasma did not touch the wall and showed no etching problem. Several workers¹⁰⁻¹³ used TFT in the MIP study with some successes. However, due to a large amount of plasma gas employed (2-10 L/min) for TFT, the sample residence time and consequently, sensitivity is significantly sacrificed.

A recent development in the area of torch design was reported by Bruce *et al.*^{14,15} who employed a laminar flow torch (LFT). A stable plasma was formed by laminar flow of gas, creating a recirculating region separated from the main gas stream. They showed much improvement of detection limits for Cl and Br compared to TFT. When compared to CFT, LFT showed better stability and longer life time. The torch required a water-cooled cavity and was operated