

Effects of 9-cyanoanthracene and anthracene adsorption on the photoluminescence of porous silicon

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Abstract

The photoluminescence of porous silicon can be modified sensitively by surface adsorption of different kinds of molecules. A quite different effects of 9-cyanoanthracene and anthracene adsorption on the photoluminescence of porous silicon were observed. The adsorption of 9-cyanoanthracene induced the photoluminescence enhancement, while anthracene adsorption resulted in photoluminescent quenching. An explanation of the interaction of adsorbates with surface defect sites of porous silicon was suggested and discussed. © 1998 Elsevier Science S.A.

Keywords: Chemical adsorption; Porous silicon; Photoluminescence

1. Introduction

Since Canham [1] discovered the room temperature visible photoluminescence from porous silicon (PS), it has caused considerable interest both theoretically and for potential applications such as optoelectronic devices, optical information storage materials, solar energy conversion and chemical sensors [2,3]. Owing to the photoluminescence of PS being strongly sensitive to molecular adsorption, the effects of surface adsorption on photoluminescence of PS have attracted much attention in the surface chemical studies. Recent reports showed that the photoluminescence of PS can be quenched by a series of adsorbates, including organic solvents, amines, aromatic compounds, metal salts and hydroxide ions etc. [4–9]. But little work has been directed at photoluminescence enhancement by adsorbates until now. In this letter, we report photoluminescence enhancement of PS by the adsorption of 9-cyanoanthracene (9-CA) which is compared with the adsorption of anthracene (An) which led to quenching of the photoluminescence. This study may provide a great deal of insight into surface chemistry of PS which has technological potential in chemical sensor applications and better understanding of photoluminescence mechanism.

2. Experimental details

The PS samples were prepared by anodic etching of *p*-Si (B-doped, (100), 1.0 Ω cm) at a current density of 30 mA/cm² for 10 min in a 1:1 solution of HF (40 wt.%): ethanol followed by chemical oxidation in HNO₃ solution [10]. After HNO₃ oxidized the PS samples were rinsed sequentially in deionized water and ethanol, then dried in a stream of dry nitrogen, and separated into two parts for adsorption of 9-CA and An. The photoluminescence measurements were performed using a microscope (BH-2) with a 488.0 nm line Ar⁺ laser as excitation source. A double-grating monochromator (JY-HPD-2), a photomultiplier (GaAs cathode) and a photo-counter system were used for collecting and detecting the fluorescent light. The samples with and without adsorbates fixed in a measuring tube were excited at the same point, monitoring with the microscope. Adsorption of 9-CA or An molecules were carried out by immersing the PS samples in 5 ml of 5 × 10⁻³ mol/l acetone solutions of 9-CA or An for 5 min, then were dried in the air. The adsorption spectra of acetone solutions that were used to wash the adsorbed PS samples were measured by HITACHI 557 UV-visible spectrometer. Fourier transform infrared (FTIR) spectra were taken by Nicolet Magna IR 750 spectrometers. All the measurements were performed at room temperature.

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3. Results and discussion

The photoluminescence spectra of PS with and without adsorption of 9-CA are shown in Fig. 1a. From this figure we can see that the adsorption of 9-CA resulted in an increase of the photoluminescence intensity to 120% of the initial value and a red shift of the PL peak wavelength. The photoluminescence reverted to original intensity and wavelength when 9-CA adsorbed sample was rinsed with pure solvent (acetone solution). This result was reproducible and can be repeated with other PS samples. Fig. 1b shows the photoluminescence quenching by adsorption of An which led to a decrease of the PL intensity to 75% of the initial value and returning to the origin, after rinsing with acetone solution. The adsorption of both 9-CA and An on the single crystal silicon (c-Si) surface without induction of PL response were also shown in Fig. 1a and b.

In order to demonstrate the 9-CA and An molecules adsorbing on the PS sample surface, the absorption spectra of rinsing acetone solution were measured. In these spectra, the strong peaks in the 350–410 nm and 330–380 nm regions corresponding to the characteristic absorption peaks of 9-CA and An respectively were observed. Fig. 2 shows a comparison of the absorption spectra between the rinsing solution of 9-CA adsorbed sample and acetone solution contained 9-CA. As observed from Fig. 2 there is no absorption at wavelength longer than 420 nm, so 9-CA cannot be excited by PL excitation wavelength (488 nm) to produce a light emission longer than 500 nm. Therefore, the enhancement of PL intensity in 9-CA adsorbed sample is not attributed to the light emission of 9-CA itself. In the case of An, the PL intensity decrease does not stem from the competitive absorption of An in the excited light (488 nm), since An cannot absorb light at wavelength longer than 400 nm. The distinct effects of chemical adsorption on the photoluminescence of PS between anthracene and cyano substituted anthracene are attributed to the interaction of adsorbates with the PS surface, implying that the photoluminescence of PS can be modified sensitively by surface adsorption of different kinds of molecules.

For understanding the photoluminescence enhancement and quenching mechanism, the influences of adsorbed 9-CA and An on FTIR spectra of PS were studied. The results are illustrated in Fig. 3. As seen from Fig. 3, no obvious changes are observed in the FTIR spectra of PS before and after surface adsorption of 9-CA and An, especially in the HSi ($\text{Si}_a\text{O}_{3-a}$) ($a \leq 3$) layer absorption bands between 2000 and 2300 cm^{-1} [11]. This means that the HSi ($\text{Si}_a\text{O}_{3-a}$) ($a \leq 3$) layer of PS surface is unaffected by surface adsorption of 9-CA and An. From the combination of results from FTIR and absorption spectra, it was confirmed that the PL changes by 9-CA and An adsorption were not caused by the formation of new compounds.

The quite different influences of adsorbates studied on the photoluminescence of PS can be interpreted as follows. The structural difference between 9-CA and An is in the existence

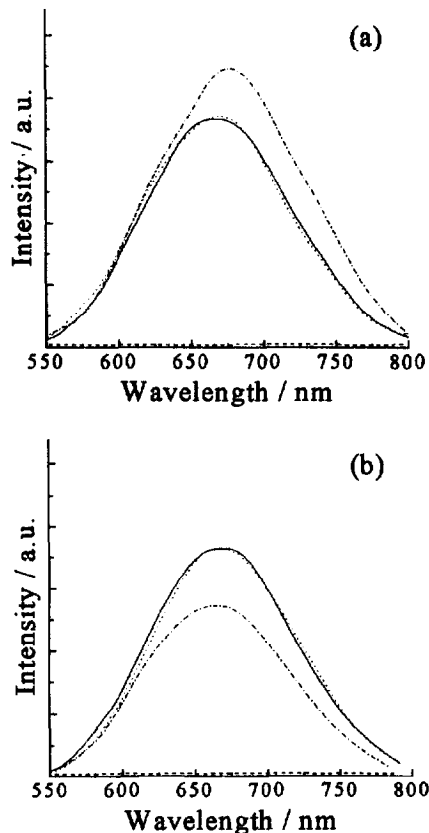


Fig. 1. The photoluminescent spectra of PS modified by organic molecules 9-CA (a) and An (b), — blank, --- adsorbed, ... washed, - - - 9-CA or An on c-Si.

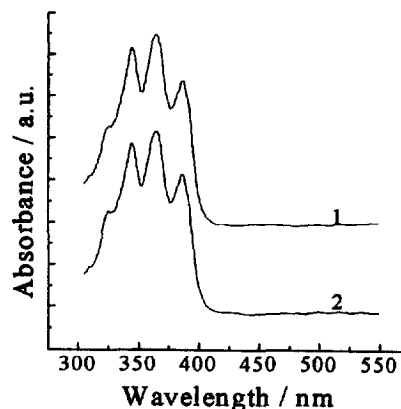


Fig. 2. Absorption spectra of 9-CA (1) in rinsing acetone solution, (2) in pure acetone solution.

of a stronger electron-withdrawing cyano substituent on the anthracene ring of 9-CA molecule. Therefore, 9-CA, known as an electron acceptor can interact with surface defect sites of PS which acted as nonradiative recombination centers to compose the charge-transfer complex like an exciplex, causing the decrease of nonradiative recombination centers and the enhancement of the photoluminescence intensity of PS. Contrary to 9-CA adsorption, An can act as electron donor and electrons can transfer from An to PS surface resulting in a quenching of photoluminescence of PS by recombination with the photogenerated holes at the PS surface.

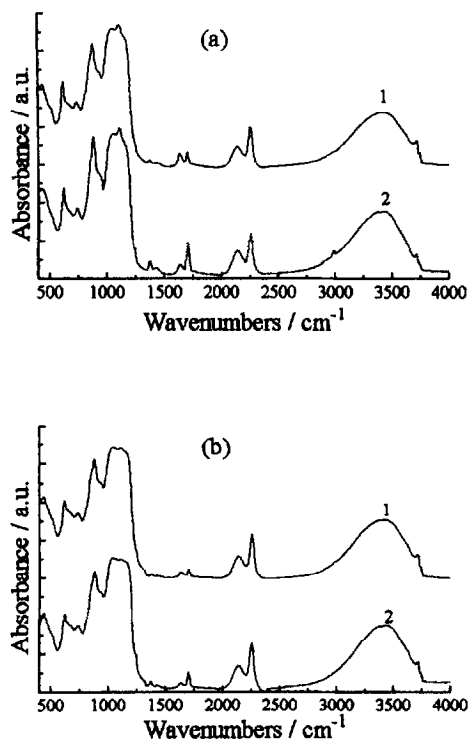


Fig. 3. FTIR spectra of PS modified by organic molecules 9-CA(a) and An(b) (1) before adsorption, (2) after adsorption.

4. Conclusion

Aspect of the surface reactivity of HNO_3 oxidized porous silicon was revealed by the effect of surface adsorption on

the enhancement and quenching of photoluminescence. Further studies on other adsorbates are underway with a view to clarifying the origin of these effects.

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