

Photoluminescence Stability of Polymer-Coated Porous Silicon

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Abstract

The photoluminescence stability of the porous silicon produced by laser-induced etching of silicon has been studied. We have employed a method to improve the PL stability of the porous structure. The porous structure was coated by a thin polymer layer, which is transparent to the visible light emitted by the Si nanocrystallites. The porous structure was not affected by the polymer layer and the size of the consistent silicon nanocrystallites does not reduce with the aging time. It has been observed that the polymer treated PS samples are chemically stable and that leads to improve the photoluminescence stability of the porous silicon with aging time.

استقرارية الانبعاث الضوئي للسليكون المسامي المكسو بطبقة بوليمرية

الخلاصة

في هذا البحث تمت دراسة وتحسين استقرارية الانبعاث الضوئي للسليكون المسامي المنتج بعملية القشط المحتث بالليزر.

تم اكساء سطح السليكون المسامي المستخدم في البحث بطبقة رقيقة من مادة بوليمرية شفافة للضوء المرئي المنبعث من حبيبات النانوسليكون.

لقد وجد بان استقرارية الانبعاث الضوئي للسليكون المسامي المستخدم قد تحسنت كثيرا بوجود طبقة بوليمرية، حيث ان هذه الطبقة مستقرة كيميائيا وتمنع تأكسد سطح السليكون المسامي.

1. Introduction

Crystalline silicon has considered as an essential material in the electronic industries, but its application is limited in optoelectronics due to its indirect band gap which makes the material inefficient light emitter [1]. The discovery of intense visible photoluminescence at room temperature from silicon nanocrystallites and porous silicon has attracted a great interest last decade [2-5]. Much effort has been focused on the control of the light emission properties and the stability of the electro and photoluminescence of the consistent silicon nanocrystallites [6-8].

Porous silicon (PS) is a complex network of pores separated by thin walls consisting silicon nanocrystallites of different sizes [9]. Usually, PS is

fabricated by electrochemical etching of silicon wafer in HF acid [10-11] that gives broad photoluminescence (PL) band characteristics due to the large nanocrystallites distribution. Photochemical etching by laser [12-17] provides an alternative method to produce and control the size and the emission characteristics of PS. The photoluminescence from silicon nanocrystallites is often attributed to quantum confinement effect. The quantum confinement model suggests that electron confinement within the nanometer size crystallites leads to enlarge the band gap and also blue shift the band gap toward the visible region [18]. However, other model was explained the photoluminescence from silicon nanocrystallites as a result of

chemical compounds formation at the porous surface [19].

The freshly prepared porous silicon is hydrogen passivated and contains essentially no oxygen and exposure to ambient air results in progressive modification of hydride surface and oxidation of PS [20]. With large surface-to-volume ratio in nanometer sized crystallite, the surface effects become more enhanced as the size of the nanocrystallite decreased. Therefore, the atmospheric storage of porous silicon leads to form an oxide layer at the porous surface. In particular, oxygen atoms at the surface critically modify the electronic structure of silicon nanocrystallites [21-23]. The atmosphere-stored porous samples exhibits unstable photoluminescence emission where the PL intensity decreases drastically with aging time accompanied by the blue shift of PL spectra.

Many authors [24-27] have studied the photoluminescence stability of porous silicon produced by electrochemical etching. Q. Chen et al [24] have prepared porous silicon by hydrothermal etching of silicon in a furnace and studied the PL instability. While, D. Zhu et al [25] have studied the stability of the iron-passivated of electrochemically etched porous silicon and found that a stable PL peak of energy ~ 1.8 eV could be observed from those samples. Their samples show only small changes in mean nanocrystallite sizes after one year indicating that the PL degradation was very slow. Moreover, C. Chen et al [26] have reported that when porous silicon samples prepared by electro chemical etching passivated by gold (Au-passivated), strong and stable red photoluminescence have been observed after three months.

Aim of this paper is to improve the photoluminescence stability of porous silicon samples prepared by laser-induced etching process throughout coating the porous silicon surface with a transparent polymer layer.

2. The experimental work

Porous silicon was prepared by laser-induced etching of n-type silicon with resistivity of $10 \Omega \text{ cm}$. The silicon wafer was immersed in HF acid of 40% concentration and irradiated with Nd:YAG laser (wavelength $1.06 \mu\text{m}$). The laser beam was focused by a lens to produce power density of 20 W/cm^2 . The experimental set up is shown in Fig. 1. The porous silicon samples have been prepared for irradiation time of 60 minutes.

The coating solution is made when a polymer (polymethyl methacrylate PMMA) was dissolved in a chloroform, then, the polymer solution has been put at the surface of the freshly prepared PS and the samples were subjected to a heat treatment in a furnace of about 40°C for half an hour. The polymer layer thickness was nearly $200 \mu\text{m}$ and this layer was transparent to the visible light emitted from the PS layer. The treated samples were investigated under optical microscope. We have observed that the polymer layer has covered the PS surface and filled the pores of the porous structure as shown in Fig. 2.

3. Results and discussion

The PL degradation with a blue shift of the peak position subsequent to the normal preparation of the porous silicon is believed to originate from the chemical instability of the porous silicon surface [1].

We have studied the PL degradation of our freshly prepared PS samples when those samples are stored

in the air. Fig. 3 shows the PL spectra of the freshly prepared PS sample as a function of number of days of exposure to air. Fig. 3 (a) shows the spectrum of peak position at 1.9 eV with a full width at half maximum (FWHM) of 300 meV. After the sample was exposed to atmosphere for 40 days, the spectrum shown in Fig. 3 (b) indicates the PL peak position at 1.95 eV with a smaller (FWHM) of about 240 meV. Furthermore, with an increase in the number of days for exposure in air, the PL peak position monotonically shifts toward higher energies and the (FWHM) becomes smaller as shown in Fig. 3 (c) and (d). After exposing the sample in air for 120 days, the PL peak almost disappears as shown in Fig. 3 (e).

We have examined the PL emission of the polymer-coated porous samples and we found that although there was a slight decreasing in the PL intensity due to the weak light absorption within the polymer layer. The PL degradation can be stopped by this technique since there is no variation for more than five months after preparing the samples.

We have recorded the PL spectra with an excitation energy of 2.41 eV (wavelength of 514.5 nm for an argon-ion laser). The laser light of this photon energy has a very small depth of penetration in the porous structure (0.2 μm) [28] and this helps to study the effect of the polymer layer on the PS surface since the polymer layer is transparent to visible light. Figure 4 shows the PL of the polymer treated porous samples. The freshly prepared PS samples PS is given in the curve (a), while (b),(c),(d) and (e) represent the PL emission of the fresh polymer treated sample and after 40, 70 and 120 days, respectively. The PL intensity is almost the same for the polymer treated sample when this sample stored in the

atmosphere for more than four months and that indicates that there is no degradation where the polymer layer prevents the oxide layer formation. Moreover, in contrast with untreated porous silicon, no blue shift in the PL peak position has been observed for the polymer coated PS sample and that means the Si nanocrystallite size have not affected by the polymer layer and no oxide layer was formed at the PS surface. Figure 5 shows the relation between the experimentally observed PL peak position as a function with the aging time. This technique provides a clear evidence to the origin of the PL in silicon nanocrystallites and supports the quantum confinement model. Otherwise, we would not get any photoluminescence after the polymer coating if the origin of the PL was the chemical compounds.

The quantum confinement model [29] has been used to fit our experimental PL spectra to estimate the silicon nanocrystallite size. Table-I gives values the mean nanocrystallite size (L_0) and the experimentally observed PL peak position and FWHM for the freshly prepared and the polymer-coated PS samples. The value of (L_0) decreases with the exposure time which indicates the nanocrystallite size reduction due to the oxide layer formation, while this value remains almost the constant when the PS sample coated with polymer.

4. Conclusions

It has been found that atmospheric storage of freshly prepared porous silicon does alter the PL behavior and it changes the PL peak position from 1.9 to 2.2 eV, while the PL intensity reduces drastically. Polymer coating of porous silicon could effectively stop the PL degradation. Stable photoluminescence without blue shift toward higher energies has been

observed for these samples. This study provides further evidence to support the quantum confinement model and it is clearly implied that the luminescent process does not relate to the surface complexes and arises from the silicon nanocrystallites. This technique implies that the structure of the polymer-deposited PS is more resistant to the external environment and the oxide layer formation.

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Table caption

Table-I: The experimentally observed PL peak position and FWHM of PL for the polymer coated porous silicon with the theoretically calculated mean

nano-crystallite size using the quantum confinement model.

Figure captions

Figure 1: The experimental set up of the laser-induced etching process.

Figure 2: Micrograph of the optical microscope for the polymer coated porous silicon.

Figure 3: The PL spectra of porous silicon prepared by laser-induced etching and stored in atmosphere as a function of the aging time.

Figure 4: The PL emission of the laser etched silicon sample recorded with the photon energy of 2.71 eV, (a) PL of the freshly prepared PS sample and (b) PL of the fresh polymer treated PS sample and (c), (d) and (e) after 40, 70, and 120 days, respectively. The dotted curves represent the experimentally observed data while solid lines represent the fitting curves using a quantum confinement model.

Figure 5: The relation between the PL peak position with aging time for PS and polymer coated PS.

Table-I

Sample	Aging time (day)	PL peak position (meV)	FWHM (meV)	L_0 (Å)
	Fresh	1.90	300	25.2
	40	1.95	240	24.4
	70	2.00	220	23.8
	90	2.10	200	22.8
	120	2.20	180	21.4
Polymer coated PS	Fresh	1.90	300	21.2
	40	1.92	290	21.0
	70	1.92	290	21.0
	120	1.92	290	21.0

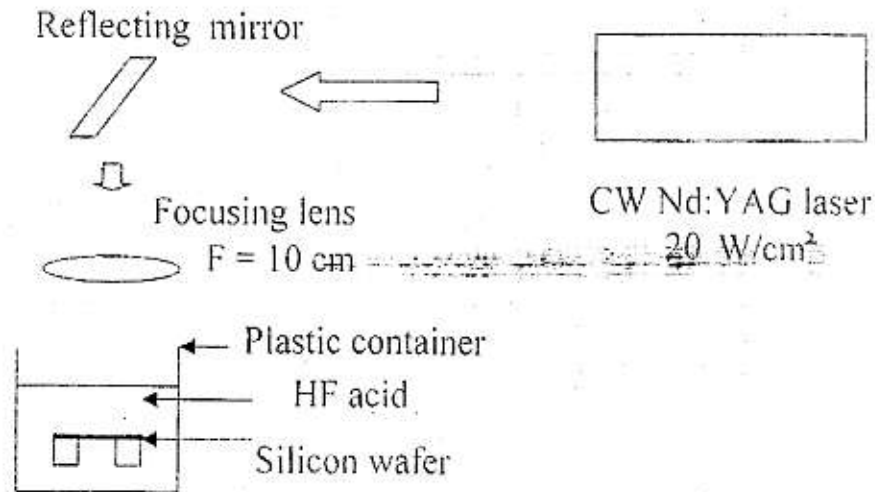


Fig.1

Fig.2

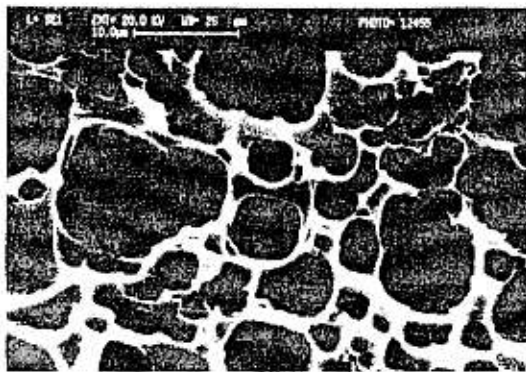


Fig. 4

Fig.3

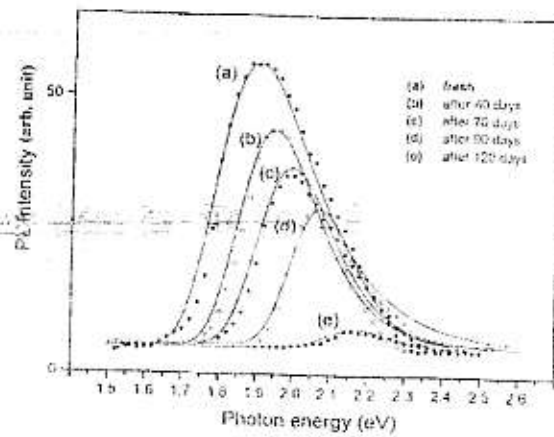


Fig. 5

