Photoluminescence lifetime in porous silicon

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Abstract
Lifetime of photoluminescence emitted by porous silicon has been investigated by using pulsed nitrogen laser as excitation source. This research also involved sample preparation. This in itself necessitated software and hardware development to enable interfacing and data logging using PC.
Orange and orange/red photoluminescence emitted from porous silicon samples have been studied at temperatures (77 - 295) K. The photoluminescence decay was intrinsically nonexponential at different temperatures. The photoluminescence lifetime, defined as 1/e times the initial intensity, decreased as emission energy increased, and increased with decreasing temperature. The time evolution of photoluminescence lifetimes τ_1 and τ_2 for orange porous silicon sample has been investigated.

Keywords: Photoluminescence lifetime, Photoluminescence decay, Porous Silicon, Lifetime evolution

Introduction
The interest in strong visible photoluminescence (PL) from porous silicon has initiated many studies on the specific recombination processes in this material. In particular, almost all the published lifetime measurements reveal a complicated nonexponential decay which varies with the detection wavelength and sample preparation [1-7]. PL offers the possibility of a lifetime detection after pulsed excitation, and this can be analysed to give measurements of the sum of radiative and nonradiative rates [8, 9]. The experimental results in most cases have been interpreted in terms of the quantum confinement model originally proposed by [10].
A detailed study is reported on the PL lifetime of orange and orange/red porous Si samples as a function of PL emission energy. These are compared with each other at different temperatures and on ageing. Different regions on the samples might exhibit different PL efficiency, but the lifetimes were very reproducible.

Measurements and results
In this work porous silicon samples prepared by using the electrochemical etching method of (100) *p*-type, boron-doped silicon wafers of resistivity of (1 - 5) Ωcm and (0.3 - 0.35) mm thickness [11]. A schematic diagram showing the experimental configuration is presented in figure 1. The sample was mounted in a liquid nitrogen cooled cryostat allow variation of temperature from (77 – 295) K via a temperature controller. The excitation beam passed through the entrance window and the resulting PL emerged from the exit window. The sample holder within the cryostat was angled so that the incident excitation radiation impinged on the sample at ~ 60° to the normal. The PL collection optics detected radiation emitted from the sample at ~ 30°, this prevented any directly reflected radiation emerging from the exit window and getting into the collection optics. The PL and scattered and excitation light was collected by means of a convex lens, which brought it to a focus on the entrance slit of the monochromator. Here cut-off filters were used to remove the unwanted excitation light, allowing only the PL to enter the monochromator.
In the monochromater, the wavelength selection was achieved by means of a diffraction grating, the angle of which determined the wavelength of the light appearing at the exit slit. It was possible to scan manually through the desired wavelength range. The PL at the exit slit was picked up by an appropriate photomultiplier, which had to have a high sensitivity in the spectral region of interest. The resulting signal was fed into a digital storage oscilloscope, along with a reference signal from the pulsed nitrogen laser, and then processed by a PC. The PL pulse could be displayed in tabular form on the printer and stored on the PC for future reference.
The excitation source used for these experiments was a pulsed nitrogen laser (337.1 nm). The laser output intensity could be controlled with neutral density filters and by varying the laser beam diameter by using a variable output aperture. The laser beam was focused on the sample by means of a convex lens.

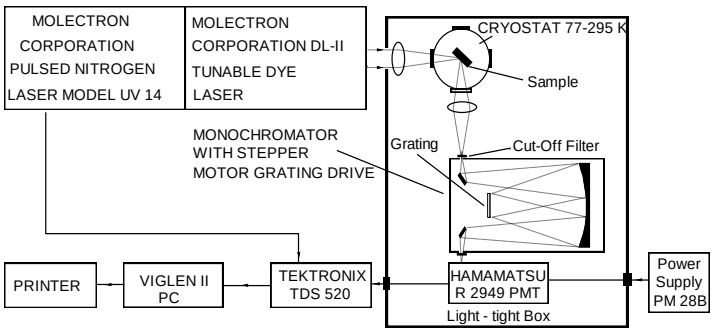

Figure 1 A schematic diagram for the experimental configuration of the PL lifetime system.

The PL decay profiles of porous silicon samples at different temperatures were detected following pulsed excitation. Figure 2 shows the PL decay for orange/red porous silicon as a function of PL intensity for several fixed energies in the visible spectrum region. The spectra were measured at different temperatures between room temperature and liquid nitrogen temperature. The PL lifetimes for all porous silicon samples, defined as 1/e times the initial intensity of PL decay, decreased as PL emission energy increased, and increased with decreasing temperature [12, 13]. The PL decay was corrected for detection efficiency. In figure 2 the axes are displaced to separate the curves and every PL decay curve shown here is a result of summation and averaging of 16 decay pulses using a digital oscilloscope. In general the main feature of all PL decay curves for all emission energies is a nonexponential response, the decay shortening rapidly with increasing sample temperatures and PL emission energies (i.e. confinement) [14-17], since the higher energy components decay faster than the lower energy components, that also supports the hypothesis that the distribution of crystallite sizes produces the wide PL spectrum [18]. The ultra-small size of the silicon particles should confine the electrons and holes. The strong quantum confinement may enable efficient radiative recombination in these silicon nanoparticles [19]. Clearly from figure 2, the PL decay is much slower and noisier at lower detection energies. This behaviour is similar at lower temperatures to that at room temperature although the decay times are much slower (lengthening of the PL decay is observed at lower temperatures). The increases of PL decay towards lower temperatures are a result of reduced nonradiative recombination at low temperatures [2, 20, 21]. The low nonradiative recombination rate is probably caused by surface passivation and exciton localisation by quantum confinement [22]. Nonradiative channels have been introduced by oxidation of the silicon surface whereas silicon dangling bonds are likely candidates for the nonradiative centres [23]. Silicon dangling bonds have been identified in porous silicon by several experimentalists [24]. The dangling bonds are situated either on the surface of nanoscale units or on the interface between nanoscale units and silicon oxide layer covering them [25].

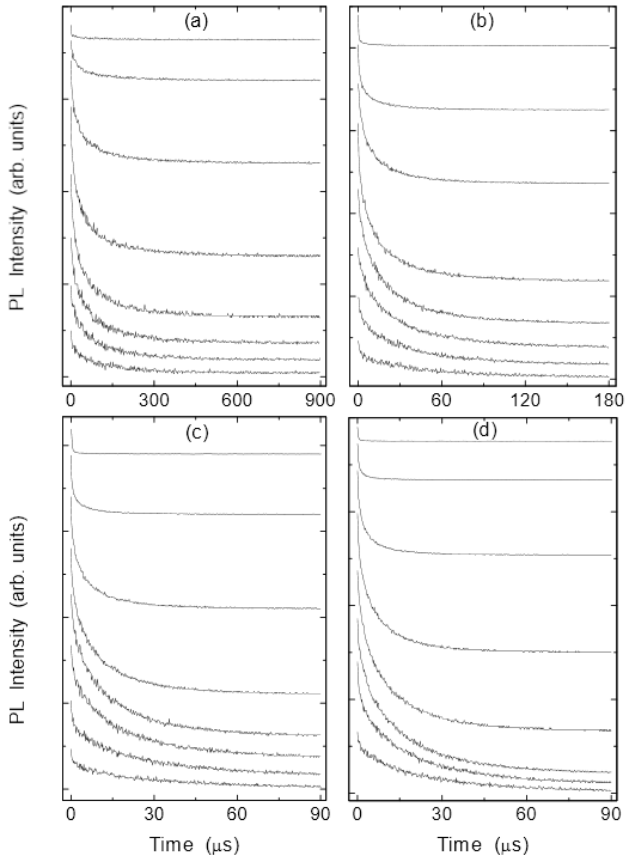

Figure 2 PL decays of orange/red porous silicon sample at 77 K (a), 150 K (b), 220 K (c) and 295 K (d) at various PL emission energies. The PL emission energies from the top to the bottom are 2.53 eV, 2.39 eV, 2.26 eV, 2.14 eV, 2.03 eV, 1.94 eV, 1.88 eV and 1.77 eV, respectively. The ordinatescale is in arbitrary units for each curve, and the zeros have been adjusted for clarity

The decay can be described by two exponential processes with two emission components of different lifetimes, i.e., a faster decay with lifetime τ_1, and slower decay with lifetime τ_2, and can be fitted very well using a stretched exponential [26-29].

$$I = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$$

Where I_1 and I_2 are constant. The parameters τ_1 and τ_2 characterise the PL decay rate. Stretched exponentials can, for example, results from the random walk of carriers on a finite distribution of desecrate sites in real space, as in amorphous silicon. Regardless of the details of the physical mechanisms, there are well-known producers to define an average or most probable lifetime and this is the lifetime that is usually quoted in the literature [18, 30]. The PL lifetimes of the porous Si samples were determined using *Origin* software.

Evolution of lifetime

The time evolution of PL lifetimes τ_1 and τ_2 for orange porous silicon sample are summarised in figures 3 and 4 respectively. In each figure, there are six groups of curves, each one corresponding to certain sample age. The PL lifetime was calculated for different temperatures between (77 – 295) K. One can observe both lifetimes, τ_1 and τ_2, decrease with increasing temperature and PL emission energy [3, 6, 13, 18,].

Figure 3 shows that τ_1 for the as-prepared orange porous silicon sample at 77 K decreases dramatically in the PL emission energy range (1.85 - 2.0) eV, and then increases to a peak in the PL emission energy range (2.1 - 2.4) eV. The decrease in τ_1 becomes smaller with the time evolution of the porous silicon sample. The presence of these features in the lifetime spectra reflects the complex nature of the emitting material [31]. As the temperature increases, the dramatic decrease in τ_1 (i.e. in the energy range (1.85 - 2.0) eV) becomes less evident and it nearly disappears at room temperature for all sample ages.

The behaviour of τ_2 at 77 K in figure 4 differs from that of τ_1 especially for the as-prepared sample. There are weak features for sample of ages 2 hr, 13.5 hr and 3.5 days at 2.14 eV, 2.1 eV and 2.14 eV respectively. For the other temperatures τ_2 just shows a steady decrease with increasing PL emission energy, except for the as-prepared sample at 150 K, where there is a weak feature in the PL energy range (1.9 - 2.2) eV. As already stated the PL intensity consists of two decaying components, so the spectral distribution of the total PL emission results from the competition between these two components during relaxation after excitation [9].

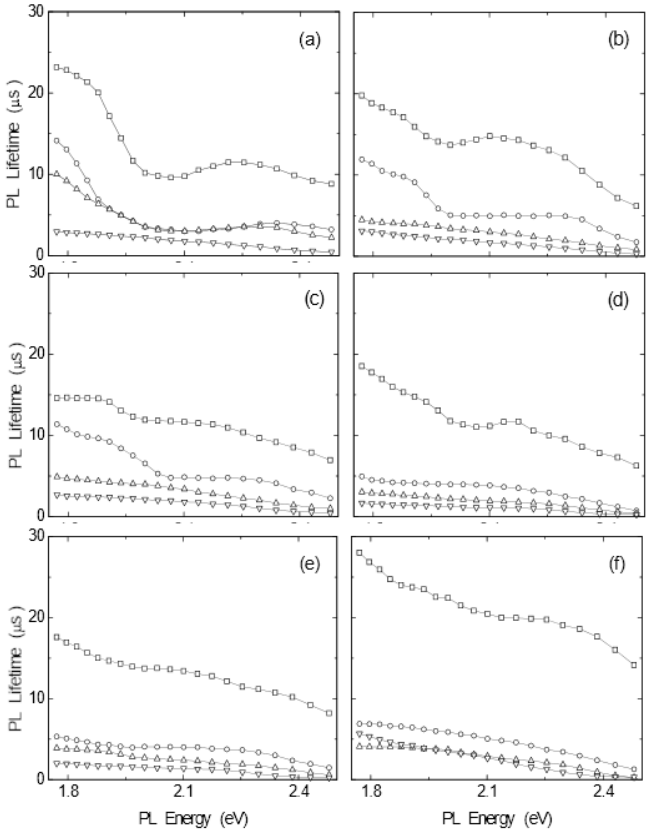

Figure 3 PL lifetime (τ_1) for the decay at various PL emission energies for orange porous silicon sample: as prepared (a), 2 hr after preparation (b), 13.5 hr after preparation (c), 3.5 days after preparation (d), 6.5 days after preparation (e) and 40 days after preparation (f); taken at temperatures, 77 K (□), 150 K (○), 220 K (Δ) and 295 K (∇).

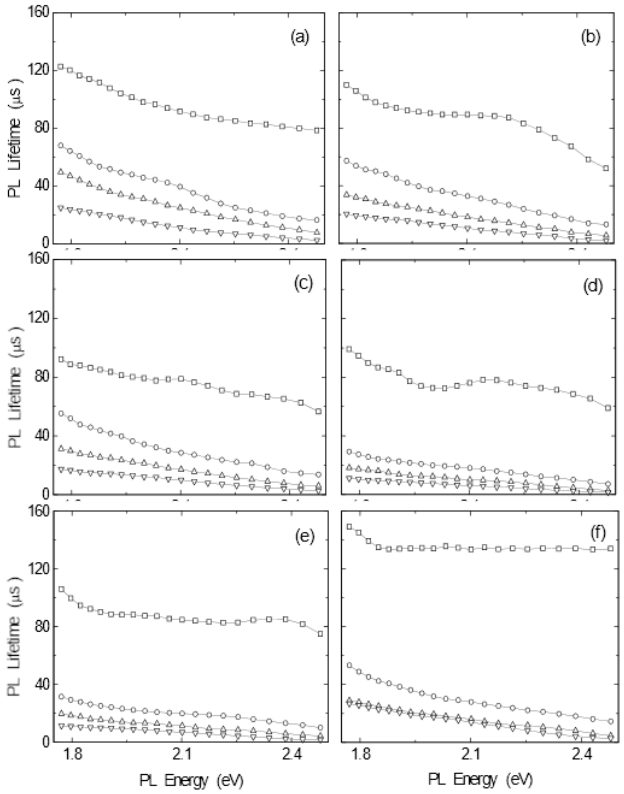

Figure 4 PL lifetime (τ_2) for the decay at various PL emission energies for orange porous silicon sample: as prepared (a), 2 hr after preparation (b), 13.5 hr after preparation (c), 3.5 days after preparation (d), 6.5 days after preparation (e) and 40 days after preparation (f); taken at temperatures, 77 K (□),150 K (○), 220 K (Δ) and 295 K (∇).

Discussion

It is found that the PL decay described by two exponential processes with two emission components. The PL decay decreased as the emission energy increased and increased with decreasing temperature, this is lead to longer PL life time for both fast and slow decays (τ_1 and τ_2 respectively). The nonexponential behaviour of PL decay spectra at all temperatures can interpreted as a superposition fast and slow PL decay processes or the competition between the two decay components.

More features observed in the PL energy spectrum of the as prepared sample, and these features become weaker as the age of the sample increases. It is found that the room temperature measurements, the behaviour of τ_1 for all graphs is similar, which decreases nearly linearly with increasing emission energies within lifetime values, except the curve that corresponds to the sample after 40 days aging, which has with higher values in the energy range (1.7 - 2.48) eV.

It is also found that τ_2 of PL energy curve for 40 days ageing has longer lifetimes at lower temperature has higher lifetime than other curves and is independent of the emission energy in the range (1.85 - 2.48) eV.

Conclusion

The ultra-small size of silicon particles can confine the electrons and holes, and the strong quantum confinement should enable efficient radiative recombination silicon nanoparticles. The PL life time depends greatly on the temperature and on the emission energy; this is may be due to the widening of the band gap of sample. The presence of features in the lifetime PL energy spectra attributed to the complex nature of the emitting material in porous silicon samples.

The increase in τ_1 with decrease in temperature of all these porous silicon samples could be due to the lack of phonons which allow nonradiative recombination paths. The observation of structure in the lifetime as a function of energy suggests the existence of more than one luminescence centre.

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العمر الكلي للتألق الضوئي في السليكون المسامي

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قسم الفيزياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

الملخص

تمت دراسة العمر الكلي للتألق الضوئي المنبعث من السليكون المسامي باستخدام ليزر النتروجين الومضي كمصدر تهيج. تضمن هذا البحث تحضير عينات، وكذلك استلزم تطوير برامجيات واجهزة مختبرية لربط الحاسوب الشخصي مع اجهزة القياس لغرض تسجيل البيانات باستخدام الحاسوب الشخصي.

درس التألق الضوئي ذو اللون البرتقالي واللون البرتقالي المحمر المنبعث من عينات السليكون المسامي عند درجات حرارة مختلفة تتراوح بين (77 – 295) كلفن. لقد وجد بان انحلال التألق الضوئي كان غير اسيا عند درجات الحرارة المختلفة. يعرف العمر الكلي للتألق الضوئي بانه، **1/e** مضروبا بالشدة الابتدائية، ويتناقص هذا العمر كلما ازدادت طاقة الانبعاث ويزداد بانخفاض درجة حرارة العينات. لقد تم حساب عمري التألق الضوئي τ_1 و τ_2 المنبعث من عينات السليكون المسامي الباعثة للضوء البرتقالي لعينة لم تتعرض للظروف الجوية المختبرية ثم تعرضت بعد ذلك لفترات زمنية مختلفة للظروف الجوية المختبرية الطبيعية.