

## Optical Properties of Polymer-Embedded Silicon Nanoparticles

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### ABSTRACT

We seek to use electrically conducting polymers, such as those commonly utilized in polymeric LEDs, as hosts for silicon nanoparticles. The proper design of multilayered devices based on these materials will yield efficient light-emitters in which charge carriers localize and recombine within the nanoparticles. Furthermore, these may combine the flexibility and processability of polymeric LEDs with the reliability of inorganic materials. We have synthesized luminescent silicon nanoparticles and have characterized their photoluminescence (PL) using continuous-wave and time-resolved spectroscopy. These particles have been incorporated into a variety of transparent solid hosts. The photoluminescence obtained from particle-containing poly(methyl methacrylate) (PMMA) matrices is very similar to that of the particles in solution, both in spectral content and PL decay characteristics. However, when incorporated into a variety of conducting polymers, such as poly(N-vinylcarbazole) (PVK), the nanoparticles do not retain their photoluminescence properties. A variety of chemical species have been reported as effective PL quenchers for porous silicon. We believe that these polymers quench the luminescence through similar mechanisms. Protective passivation of the nanoparticle surface is suggested as a strategy for overcoming this quenching.

### INTRODUCTION

Nanocrystalline silicon has received a great deal of attention in recent years as a material that might be easily integrated into silicon wafer processing and utilized for biological and chemical sensing or for light-emitting devices. The well-established effects of the surface termination and the surrounding environment on the silicon photoluminescence (PL) are advantageous for sensing applications, but present a problem for optoelectronic applications requiring stable light emission. One solution is to produce silicon nanoparticles within SiO<sub>2</sub>, for example by implanting Si ions into a glass substrate and thermally annealing the composite. These materials show promise for use as optical devices; optical gain has been reported in nanoparticles produced by this method[1]. An alternate approach is to produce colloidal nanoparticles that can then be incorporated into transparent hosts such as polymers or xerogels.

Various researchers have incorporated luminescent nanoparticles within electrically conducting polymers to yield hybrid electroluminescent devices[2-5]. However, to our knowledge, no study of luminescence from silicon nanoparticles embedded in such materials has been reported. The work presented in this paper is focused on the application of surface modification techniques to silicon nanoparticles produced by high-yield aerosol synthesis as a route toward obtaining such hybrid materials and devices.

## EXPERIMENTAL DETAILS

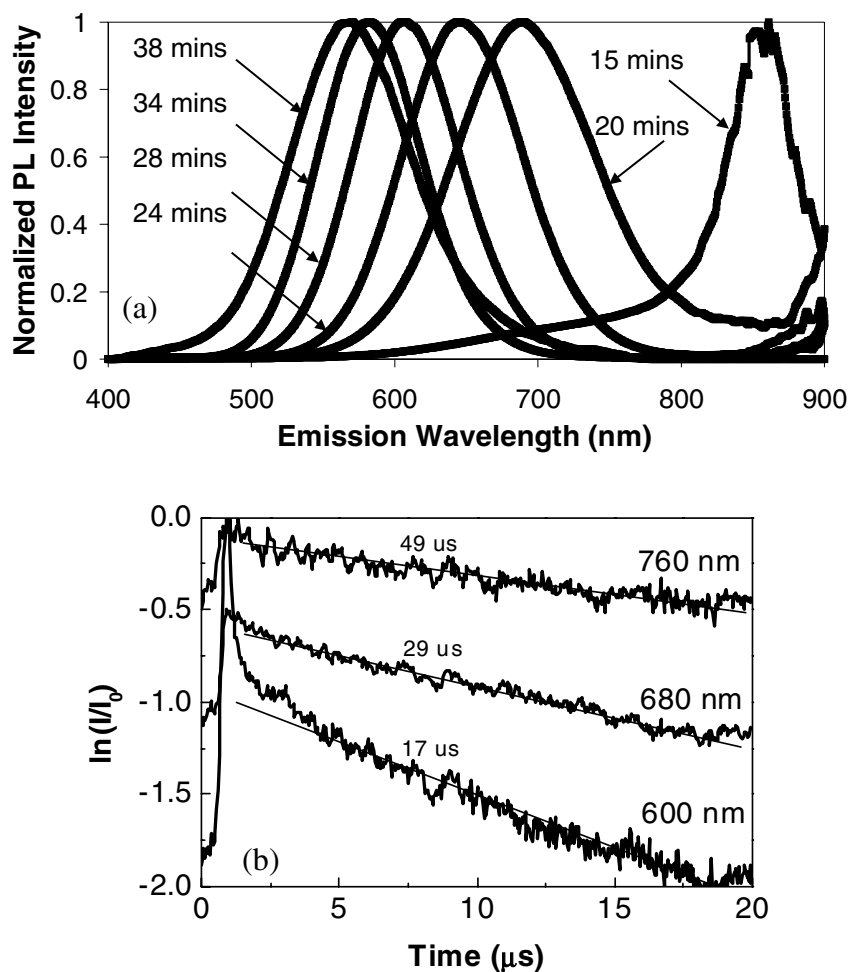
The nanoparticle synthesis procedure has been described in detail elsewhere[6-8]. Briefly, the nanoparticles are synthesized in an aerosol reactor by dissociating silane gas using a CO<sub>2</sub> laser. Helium and hydrogen gas flows confine the reactant mixture, yielding silicon nanoparticles with a mean diameter that can be varied from 5 to 20 nm by controlling the growth conditions. Following the reaction, the nanoparticles are collected on cellulose nitrate membrane filters and dispersed in methanol. The nanoparticles are then etched in solutions containing HF and HNO<sub>3</sub>, which reduces the nanoparticle size and passivates the surface.

Continuous wave (CW) and time-resolved spectroscopic techniques were used to study the basic emission properties of the nanoparticles. Specifically, the CW PL data reported in this work was excited using either a Perkin Elmer LS 50 fluorescence spectrometer (355 nm excitation) or the 351 nm and 364 nm lines of a Coherent Innova 300 Ar<sup>+</sup> laser. The source for the time resolved spectroscopy was 400 nm, ~300 fs, pulses, with repetition rates varying between 9 and 250 kHz, that were generated by frequency doubling the 800 nm, 200 fs pulses output from a Coherent RegA 9000 regenerative amplifier. The time resolved photoluminescence (TRPL) data was collected and recorded using a spectrometer and a C4334 Hamamatsu streak camera. All measurements reported in this work were conducted at room temperature.

## RESULTS AND DISCUSSION

The production method described above generates a high yield of silicon nanoparticles, on the order of 100 mg/hr. The nanoparticle luminescence is similar to that commonly observed from nanocrystalline silicon (including porous silicon), with a luminescence peak that can be varied from about 550 nm to the near infrared by varying the etch conditions, as illustrated in Figure 1a. TRPL measurements of the nanoparticles show emission with multi- or stretched-exponential behavior, and with lifetimes on the order of tens of microseconds, which vary substantially across the emission spectrum. For low energy emission, the decay can be reasonably approximated by a single exponential on long time scales. However, for high energy emission, the decay is more complicated and requires stretched-exponential fitting. The emission decay of a freshly prepared sample is shown in Figure 1b.

When dispersed in most common organic solvents, the PL of the nanoparticles degrades and spectrally shifts with time. To prevent such degradation, the nanoparticles can be embedded in poly(methyl methacrylate) (PMMA). Figure 2 shows the PL spectrum and lifetime of a particular nanoparticle sample both in chloroform solution and when embedded in a PMMA film. The film was prepared by drop-casting a polymer-nanoparticle mixture on a glass slide. The characteristics of the nanoparticle luminescence are not greatly affected by the presence of the polymer. The polymer shields the nanoparticles and prevents degradation of the PL. A second advantage is that these materials facilitate a variety of optical studies that are commonly performed on solid materials but are difficult to perform on solutions.



**Figure 1.** (a) Normalized photoluminescence of nanoparticles after etching for various amounts of time in a 3% HF / 26% HNO<sub>3</sub> / 69% methanol etching solution. (b) PL decay of a typical sample at various emission wavelengths. The plots have been offset for clarity.

PMMA is not an electrically conducting polymer, and therefore it is not suitable for use in electroluminescent devices. Alternative polymer hosts include materials such as poly(N-vinylcarbazole) (PVK), which has been used as a hole-transporting host for a luminescent dye in an LED structure[9], and poly(phenylene-vinylene) (PPV), which is commonly used as the emissive material in polymer LEDs or as a host or hole-transport layer in nanoparticle LEDs. However, the as-produced nanoparticles do not disperse well in most common organic solvents, which is a necessary step in the processing of these polymer films. Further, the PL of unprotected nanocrystalline silicon has been shown by many authors to be severely quenched by the presence of various chemical species, including many amines[10-12]. We have observed such quenching due to the presence of the PVK polymer. Thus, it is necessary to modify the surface of the nanoparticles in order to improve their solubility, and, if possible, to provide some shielding of the surface to prevent PL quenching while not drastically impeding the ability of holes and electrons to be injected into the nanoparticles.

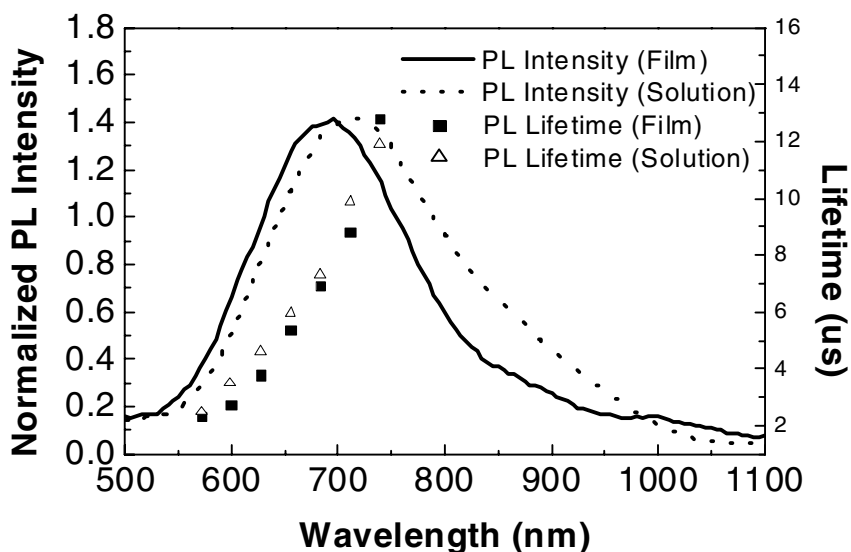
It has been shown that by refluxing silicon nanoparticle dispersions in the presence of octadecene, the nanoparticle surface reacts with the double bond, and the organic becomes bound to the surface[13]. By varying the alkene used, this technique can be used to create organic-capped nanoparticles that form stable dispersions in various solvents. This treatment also serves to stabilize the nanoparticle PL by eliminating the degradation over time observed for the as-produced particles. The detailed results of this treatment on the nanoparticle surface and PL will be reported elsewhere[14].

## CONCLUSIONS

Many variables exist in the development of hybrid electroluminescent materials. To utilize silicon nanoparticles as the emitting species in such devices, it will be necessary to establish a device structure in which the nanoparticles are accessible for carrier injection, while retaining good photoluminescent properties. Effective modification of the semiconductor surface is the first step toward developing useful combinations of these materials.

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**Figure 2.** CW Emission and photoluminescence lifetime (400 nm excitation) of a silicon nanoparticle sample when embedded in PMMA and when dispersed in chloroform solution. The lifetimes were obtained using a single-exponential fit.

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