

# Optical properties of silicon nanoparticles: Influence of etching, surface oxidation and surface functionalization

Anoop Gupta<sup>\*</sup>, Christof Schulz<sup>\*\*</sup> and Hartmut Wiggers<sup>\*\*\*</sup>

<sup>\*</sup>Institute for Combustion and Gasdynamics (IVG), University of Duisburg-Essen,  
47048 Duisburg, Germany, [anoop.gupta@uni-due.de](mailto:anoop.gupta@uni-due.de)

<sup>\*\*</sup>Institute for Combustion and Gasdynamics (IVG) and CeNIDE, University of Duisburg-Essen  
47048 Duisburg, Germany, [christof.schulz@uni-due.de](mailto:christof.schulz@uni-due.de)

<sup>\*\*\*</sup>Institute for Combustion and Gasdynamics (IVG) and CeNIDE, University of Duisburg-Essen  
47048 Duisburg, Germany, [hartmut.wiggers@uni-due.de](mailto:hartmut.wiggers@uni-due.de)

## ABSTRACT

In this study, we investigated the optical properties of silicon nanoparticles (Si-NPs) after surface etching, surface oxidation and surface functionalization process. Surface etching of as-prepared Si-NPs with hydrofluoric acid causes a blue shift in their emission spectrum. We observed that the air oxidation of orange emitting freshly etched Si-NPs transforms them to blue luminescing particles. Surface functionalization of etched Si-NPs was achieved by a liquid phase hydrosilylation. Despite of having similar size, the etched Si-NPs show a shift in their emission spectrum after surface functionalization with organic molecules. It is observed that the magnitude of shift depends on the time of functionalization.

**Keywords:** silicon nanoparticles, photoluminescence, surface functionalization

## 1 INTRODUCTION

Silicon has elicited an intense scientific attention because it acquires novel optical properties at the nanometer scale, enabling the possibility of manufacturing new generation optoelectronic devices based on silicon [1]. It is believed that the increased photoluminescence (PL) emission from silicon nanostructures arises from the quantum confinement effects [2, 3]. Despite of showing high PL efficiency, the surface oxidation of silicon nanomaterials has been a major hindrance in the realization of their full-fledged industrial applications. It is observed that the passivation of silicon surface with an organic shell bound through Si-C bonds show increased resistance to surface oxidation [4, 5]. A variety of techniques have been employed to functionalize the surface of silicon with organic molecules including radical initiation, photochemical activation with UV light and thermally activated hydrosilylation [6].

Because the physical properties of nanomaterials are very sensitive to their surface composition, the realization of silicon nanomaterial based optoelectronic devices can not be accomplished without proper understanding the effects coming along with surface modification. In this paper,

we study the influence of etching, surface oxidation and surface functionalization on the optical properties of Si-NPs.

## 2 EXPERIMENTAL

Si-NPs with a diameter of about 5 nm were synthesized in a microwave plasma reactor via pyrolysis of silane (SiH<sub>4</sub>). The details of particle synthesis have been discussed earlier [7, 8]. The surface etching of Si-NPs was carried out with hydrofluoric acid (HF). In a typical experiment, about 5 ml of HF was added to a dispersion of 20 mg of Si-NPs in 2 ml of methanol. The surface functionalization of freshly etched Si-NPs was accomplished via liquid phase hydrosilylation. For this purpose, the freshly etched Si-NPs were immersed in alkene and the dispersion was exposed to UV radiation ( $\lambda = 254$  nm) or heated in an oil bath at 120°C (used to synthesize the material discussed in Fig. 5). The PL measurements shown in figure 5 was recorded using a diode laser as an excitation source operated at a wavelength of 405 nm, whereas all other measurements were carried out using a Perkin-Elmer LS 50 fluorescence spectrometer with 350 nm excitation wavelength. All PL measurements were performed at room temperature.

## 3 RESULTS AND DISCUSSION

As-prepared Si-NPs were stored under ambient conditions and therefore their surface is covered with an amorphous oxide layer [9]. The oxide from the surface of as-prepared Si-NPs was removed by etching them with HF inside a glove box under inert conditions. Figure 1 shows the PL emission spectra of as-prepared and freshly etched Si-NPs. We find that etching of Si-NPs with HF causes a small blue shift in their emission spectrum, which indicates that the core size of Si-NPs is slightly reduced [10]. The PL spectrum of etched Si-NPs was recorded directly after the etching and we did not observe any signature of surface oxide in their FTIR spectrum, therefore, the blue shift can not occur by oxidation of Si-NPs. It is reported that in Si-NPs transition from Si to SiO<sub>2</sub> occurs through a sub-oxide layer, which results in some leakage of the wavefunction [11]. We believe that the as-prepared Si-NPs emit at larger

wavelength with respect to freshly etched sample due to leakage of the wavefunction to their surrounding oxide layer.

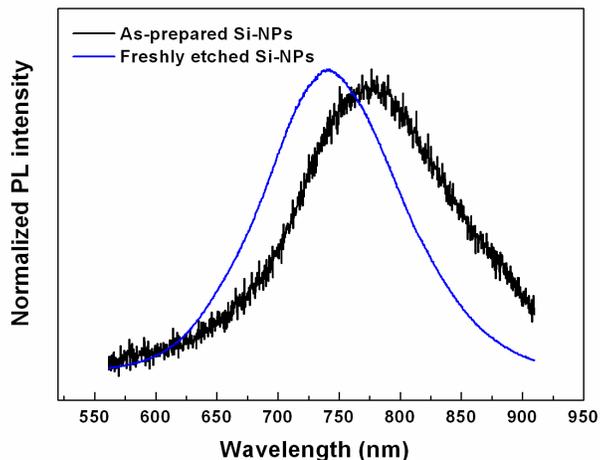


Figure 1: Normalized PL spectra of as-prepared and freshly etched Si-NPs.

The surface oxidation of Si-NPs deteriorates their optical properties and is well studied in the past [12-14]. It is reported that oxidation introduces lots of nonradiative defects (for example, dangling bonds and vacancies) at the interface between the silicon core and the surrounding oxide shell. These nonradiative defects quench the PL emission of Si-NPs [14]. We also studied the oxidation of etched Si-NPs and found similar results [15]. However, during the oxidation of orange luminescing etched Si-NPs, the increased intensity of blue emission ( $\lambda = 420$  nm) was observed together with diminishing intensity of the main peak ( $\lambda = 616$  nm). Figure 2 shows the time dependent PL emission of initially orange luminescing, etched Si-NPs in air. It is reported that the defects, such as nonbridging oxygen hole centers and dual coordinated silicon within the silica matrix are responsible for the blue emission [16-19]. We believe that the blue luminescence from Si-NPs with its increasing intensity with time is originating from these defects inside the silicon oxide shell. This effect might be due to the rising concentration of such defect centers during the preceding oxidation process.

In order to prevent the surface of Si-NPs against oxidation, the freshly etched Si-NPs were functionalized with organic molecules. A complete surface coverage of functionalized Si-NPs with organic molecules was not observed because attached organic ligands on the silicon surface provide an increasing steric hindrance for the further attachment of organic molecules during functionalization [4, 9, 20]. We observed a drastic increase in the PL stability of etched Si-NPs in air after their surface functionalization. Figure 3 shows the PL spectra of dodecyl terminated Si-NPs in air. No change in the PL intensity of Si-NPs was observed after 13 days of storage in air; however, there was only a slight red shift in the emission spectrum.

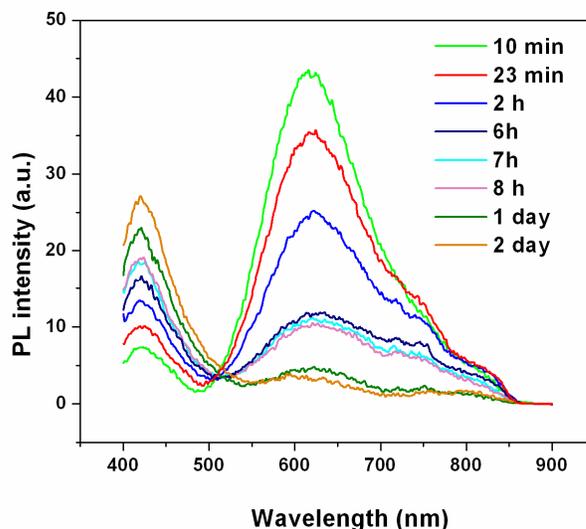


Figure 2: Time dependent PL spectra of etched Si-NPs in air.

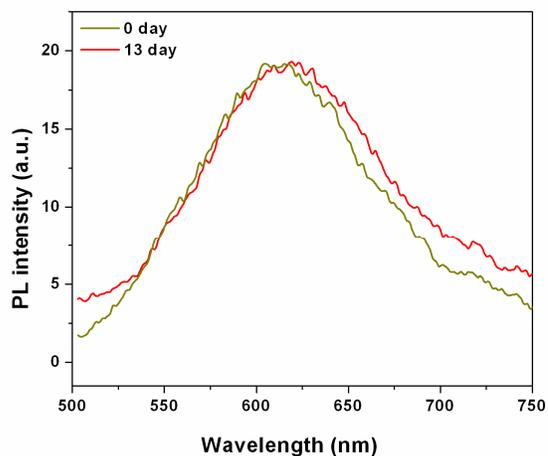


Figure 3: PL spectra of dodecyl terminated Si-NPs in air.

The covalent attachment of organic ligands on the surface of Si-NPs provides long-term air stability, however, it does not preserve the original emission of freshly etched sample. Figure 4 shows the PL spectra of Si-NPs before and after their surface functionalization with dodec-1-ene. The initially yellow luminescing, freshly etched Si-NPs change their color from yellow to orange after the surface functionalization. Rogozhina et al. [21] also observed the red shift after modification of Si-NPs (size  $\sim 1$  nm) surface with butylamine. Reboredo and Galli [22] did ab initio calculations on silicon cluster and they found that the HOMO and LUMO gap of silicon cluster decreases when the hydrogen from the surface of silicon cluster is replaced by alkyl groups.

## 4 SUMMARY

We observed a shift in the PL emission of Si-NPs after etching and surface functionalization process. The surface oxidation of etched Si-NPs either completely quenches their emission and/or gives rise to blue luminescence. The PL stability of Si-NPs in air can be drastically increased by surface functionalization.

## ACKNOWLEDGEMENTS

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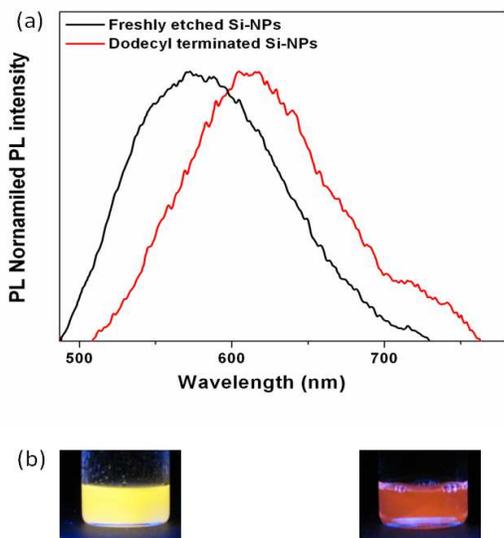


Figure 4: (a) Normalized PL spectra of freshly etched and dodecyl terminated Si-NPs. (b) Chloroform dispersion of freshly etched (left) and dodecyl terminated Si-NPs (right) under UV illumination.

We find that the shift of functionalized Si-NPs with respect to freshly etched samples can be altered by changing the functionalization time. Si-NPs functionalized for longer time show higher surface coverage of organic ligands on their surface as well as larger shift compared to particles functionalized for shorter time [9]. Figure 5 shows the PL emission spectra of Si-NPs functionalized with dodec-1-ene for 2h and 5h. The emission spectrum of Si-NPs functionalized for 2h is red shifted of about 10 nm after 3h of further surface functionalization.

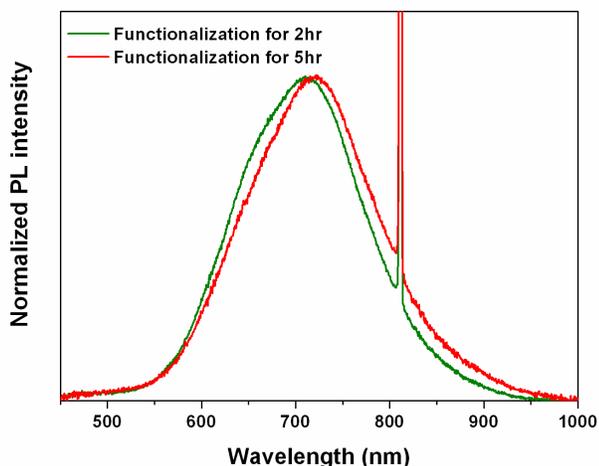


Figure 5: Normalized PL spectra of Si-NPs after 2h and 5h of surface functionalization with dodec-1-ene. The sharp peak at 810 nm originates from the second harmonics of the laser wavelength.

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