

Luminescence of black silicon

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Abstract. Room temperature visible and near-infrared photoluminescence from black silicon has been observed. The black silicon is manufactured by shining femtosecond laser pulses on silicon wafers in air, which were later annealed in vacuum. The photoluminescence is quenched above 120 K due to thermalization and competing nonradiative recombination of the carriers. The photoluminescence intensity at 10K depends sublinearly on the excitation laser intensity confirming band tail recombination at the defect sites.

Keywords: band tail recombination, black silicon, laser spectroscopy, luminescence, optical communication, photoluminescence, quenching, recombination, silicon photonics.

1 INTRODUCTION

Silicon is the most widely available semiconducting material, since it is the second most abundant material on earth after oxygen. Silicon has been the material of choice for the microelectronics industry for more than half-a-century [1] since it is a relatively inexpensive, and well understood material for producing microelectronic devices [2]. Silicon based electro-photonic integrated circuit (EPIC), i.e., optoelectronic IC (OEIC) [3] is the natural evolution of the microelectronic IC with the added benefit of photonic capabilities.

Although silicon photonics is less well developed as compared to the direct bandgap III-V semiconductor photonics; silicon is poised to make a serious impact on the optical communications [4]. Silicon, with a near-infrared indirect bandgap of 1.1 eV is transparent in the optical communication wavelengths greater than 1.1 μm , and is a suitable high refractive index optoelectronic group IV material. Therefore, silicon photonics [5] is experiencing a rapid growth, [6] which is in part driven by the need for low cost photonic devices [7] and the need for high speed intrachip communication [8,9]. Recent progress in silicon photonics is being heralded by the observation of first the Raman gain [10,11] then stimulated Raman scattering (SRS) [12] in a crystalline silicon waveguide, SRS “lasing” first in pulse [13,14] modulated [15] and later in CW [16] silicon Raman “lasers,” and finally the hybrid silicon Raman “laser” [17]. Additionally, silicon modulators [18,19] have been developed first using a metal-oxide-semiconductor (MOS) capacitor [20], a Mach-Zehnder [21] configuration, SRS [22], and a microring [23] configuration. Recently, a silicon microring based wavelength converter has been realized [24]. Racetracks [25], microrings [26], waveguides with feedback [27, 28], and microspheres [29] are some of the resonator geometries pursued for silicon lightwave circuits (SLC's). With well established CMOS processing techniques, it will be possible to integrate lasers, waveguides, modulators, switches, wavelength converters, and photodetectors into silicon motherboards [30] for long haul, metro, local area, interchip, and even intrachip optical communication applications [31].

However, most of these discrete or integrated optoelectronic devices are fabricated using crystalline silicon. Black silicon [32] is a relatively novel material, which is obtained by femtosecond [33] or nanosecond [34] laser processing of crystalline silicon surfaces in the presence of a halogen containing gas such as SF₆ or a variety of ambient gases such as Cl₂, N₂, air [35], H₂S, H₂ [36], and SiH₄ [37], or immersed in water [38], or coated with other group VI elements (chalcogens) such as selenium and tellurium [39]. In this process the flat, mirror-like surface of a silicon wafer is transformed into a forest of microscopic spikes.

Black silicon has increased absorbance of approximately 90% from the near-ultraviolet to the near-infrared [40]. This absorbance resulted in high sensitivity infrared photodetectors [41], high quantum efficiency avalanche photodiodes (APDs) [42], and high sensitivity infrared photodiodes [43]. Additionally, black silicon has potential applications such as magnetizeable biodetectors [44], superhydrophobic surfaces [45], and microfluidic devices [46]. Regular arrays of black silicon has been produced for other potential device applications [47]. Black silicon also exhibits visible and near-infrared luminescence [48]. In this paper, we are reporting on the temperature and laser intensity dependence of the visible and near-infrared photoluminescence from black silicon in order to fully characterize and optimize the material in the pursuit of obtaining novel nanophotonic devices.

2 SAMPLE FABRICATION AND MORPHOLOGY

Black silicon samples, which are used in our experiments, are manufactured by shining a series of very short, very intense laser pulses at a silicon surface in air. In the presence of the laser light, air reacts with the silicon surface and etches away some of it, leaving a pattern of conical spikes behind. The spiked surface is strongly light-absorbing: the surface of silicon, normally gray and shiny, turns deep black; hence the name black silicon.

Ordinarily, silicon absorbs a moderate amount of visible light, but a substantial amount of visible light is reflected as well, and infrared and ultraviolet light are transmitted through silicon or reflected from it with very little absorption. Spiked silicon surfaces, in contrast, absorb nearly all light at wavelengths ranging from the ultraviolet to the infrared.

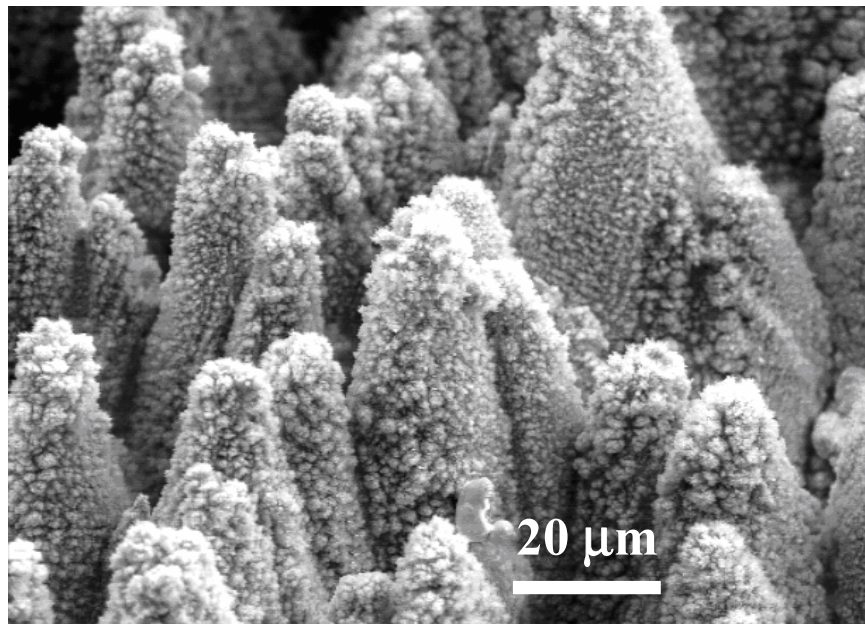


Fig. 1a. Low resolution SEM of the black silicon surface.

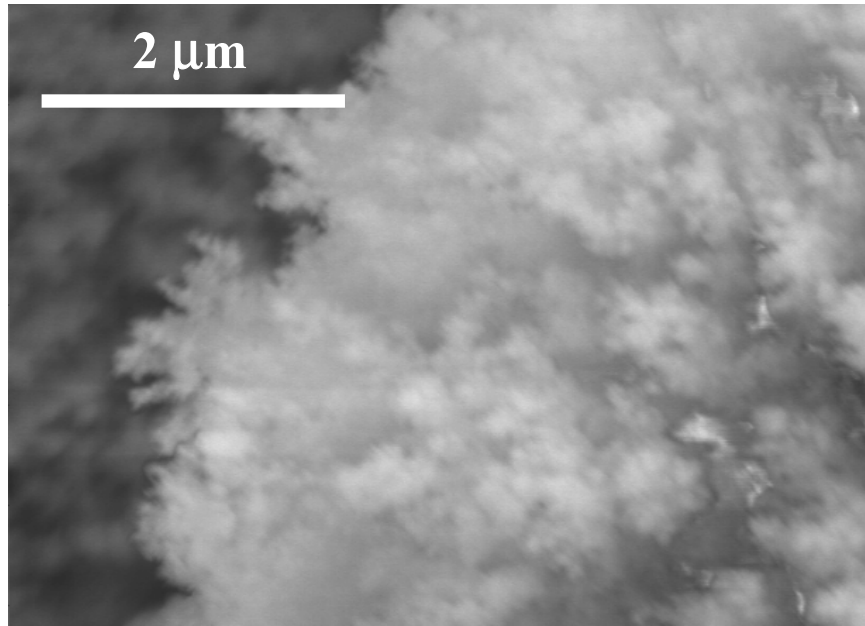


Fig. 1b. High resolution SEM of the black silicon surface.

In the femtosecond laser etching setup, the laser is aligned so that it is incident perpendicular to the (111) silicon wafer surface. An x-y translation stage was used to scan the (111) silicon wafer surface with the focused laser beam. The laser used was a Ti:sapphire pulse laser, with 100 fs pulse duration, 800 nm wavelength, 1 kHz repetition rate, and 22 kJ/cm² fluence. After laser microstructuring, the black silicon sample was annealed at 900° for 3 hours in vacuum.

Scanning electron microscopy (SEM) has been performed on the black silicon samples to characterize the morphology of the surface and to analyze origin of the luminescence. Figure 1 shows SEM pictures of the black silicon surface. Tens of micrometers tall blunt conical microstructures are observed. These microstructures are covered with dendritic nanostructures roughly 10–100 nm in size, which disappear upon annealing. Room temperature visible and near infrared luminescence has previously been observed in these annealed samples [48].

3 EXPERIMENTAL PHOTOLUMINESCENCE SETUP

Figure 2 shows a schematic of the experimental photoluminescence (PL) setup. The black silicon sample is attached to copper holder, which is placed in a closed cycle cryostat system. The closed cycle cryostat system is used to control the sample temperature from 10 K to 300 K. The pump laser is the second harmonic of a multimode Nd:YAG laser operating at a wavelength of 532 nm with a pulse duration of 10 ns and a repetition rate of 10 Hz. The pump laser is incident on the sample at an angle of incidence of 17°. The PL signal is collected with a telescope through a holographic notch filter operating at 532 nm. The collected PL signal is imaged onto an optical fiber bundle, which acts as the entrance slit of the spectrometer, whose output is fed to a sensitive GaAs photomultiplier tube (PMT). A lock-in-amplifier operating at 10 Hz provides the necessary electronic gain to the PMT output in phase with the laser pulse. The digital oscilloscope is used for monitoring and optimizing the PMT signal. All of the measurement and test devices are computer controlled and the data is acquired digitally.

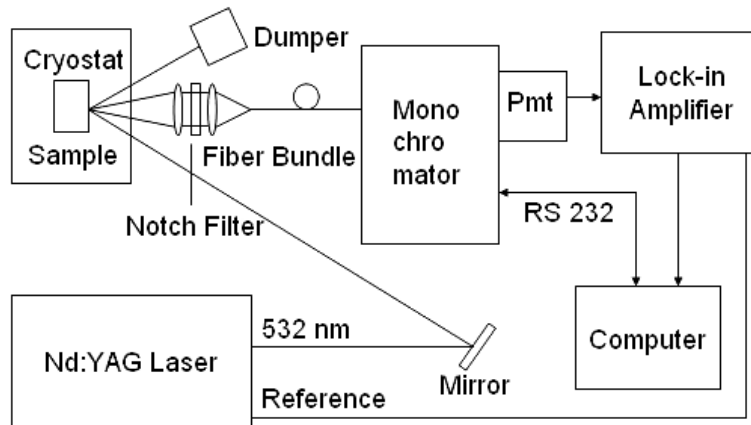


Fig. 2. The schematic of the experimental setup.

4 TEMPERATURE DEPENDENCE OF THE LUMINESCENCE

Figure 3 shows the PL spectra of the black silicon measured in the 550 - 850 nm wavelength and in the 10 – 300 K temperature range at a constant excitation laser intensity of 0.1 W cm^{-2} . A broad PL band centered at 630 nm ($E_p = 1.968 \text{ eV}$) at 10 K is observed. The PL spectra have approximately Gaussian lineshapes. The noise in the PL spectra is due to the intensity fluctuations of our multimode pulse Nd:YAG laser operating at 532 nm. The PL intensity decreases with increasing temperature indicating that there is a quenching process through nonradiative recombination [49].

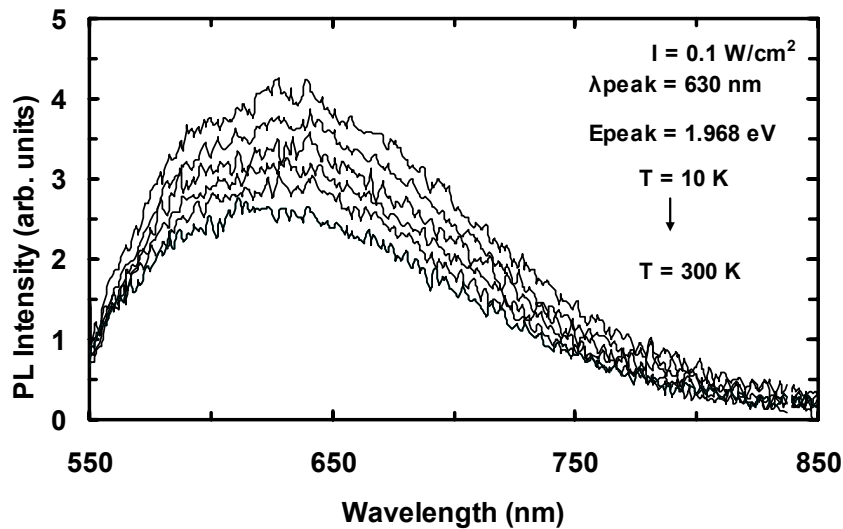


Fig. 3. PL spectra of black silicon in the 10 - 300 K range.

The variation of the PL intensity with respect to temperature is plotted in the Fig. 4. In the 10 - 120 K range, the PL intensity decreases slowly. Above 120 K, however, the PL intensity decreases at a larger rate due to thermal quenching by nonradiative recombination processes

[50]. The thermal quenching is associated with the mobility induced quenching of the band tail states. These band tail states of black silicon are associated with the presence of structural defects and impurities [51].

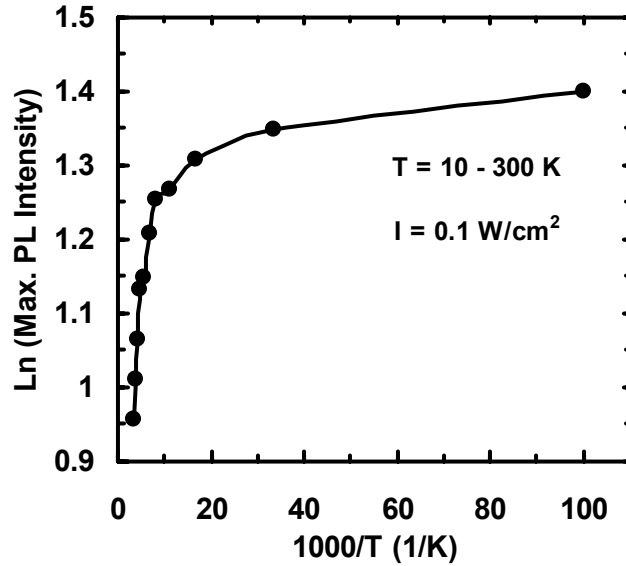


Fig. 4. Temperature dependence of black silicon PL intensity at the emission band maximum. Intensive quenching starts at 120 K.

5 INTENSITY DEPENDENCE OF THE LUMINESCENCE

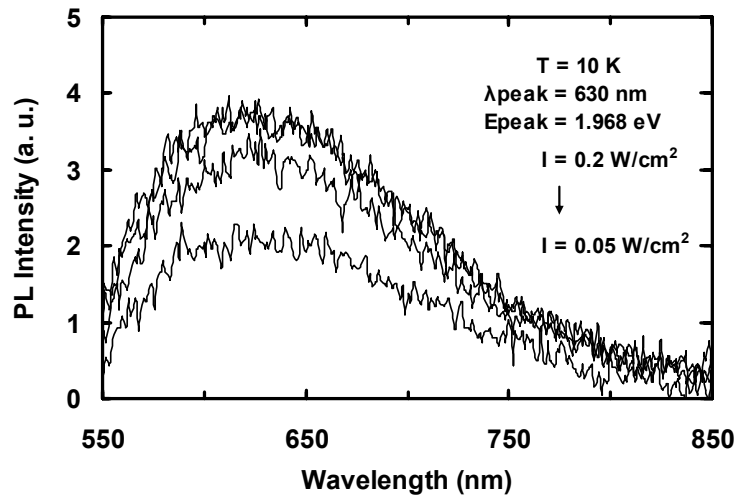


Fig. 5. PL spectra of black silicon at 0.05 – 0.2 W cm⁻² laser intensities at 10 K.

Figure 5 shows the PL spectra for different laser intensities at 10 K. As the laser intensity is increased the PL intensity increases. The intensity variation of the emission band versus the excitation laser intensity at $T = 10$ K is investigated and plotted in the Fig. 6. The experimental data can be fitted by a simple power law, $I \sim L^\gamma$, where I is the PL intensity, L the excitation laser intensity, and γ a dimensionless exponent. It was found that, the PL intensity increases sublinearly (i.e., $\gamma = 0.44$) with respect to the excitation laser intensity. For an excitation laser photon with an energy exceeding the band gap energy, the coefficient γ is generally $1 < \gamma < 2$ for exciton emission; and $\gamma \leq 1$ for free to/from bound or bound to bound state recombination [52]. Thus, the obtained value of $\gamma = 0.44$ at 10K suggest that the PL in black silicon is due to bound to bound band tail recombination.

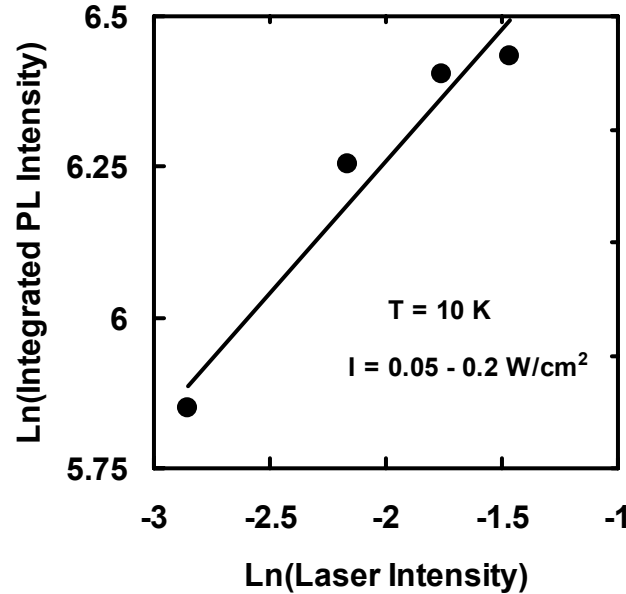


Fig. 6. Dependence of black silicon integrated PL intensity versus excitation laser intensity at 10 K. The solid curve gives the theoretical fit using Eq. $I = L^\gamma$.

CONCLUSIONS

Photoluminescence (PL) properties of black silicon were studied at room temperature and at low temperatures. The PL intensity decreases with increasing temperature. Intensive quenching due to increased carrier mobility and nonradiative recombination starts at 120K, indicating that the PL is due to band tail recombinations in the defect states. Additionally, the sublinear variation of the PL intensity versus the excitation laser intensity at 10 K indicates that the PL is due to bound to bound state recombination at these band tail defect sites. The visible and near-infrared PL spectrum of the black silicon makes it a promising novel material for short haul optical communication applications.

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