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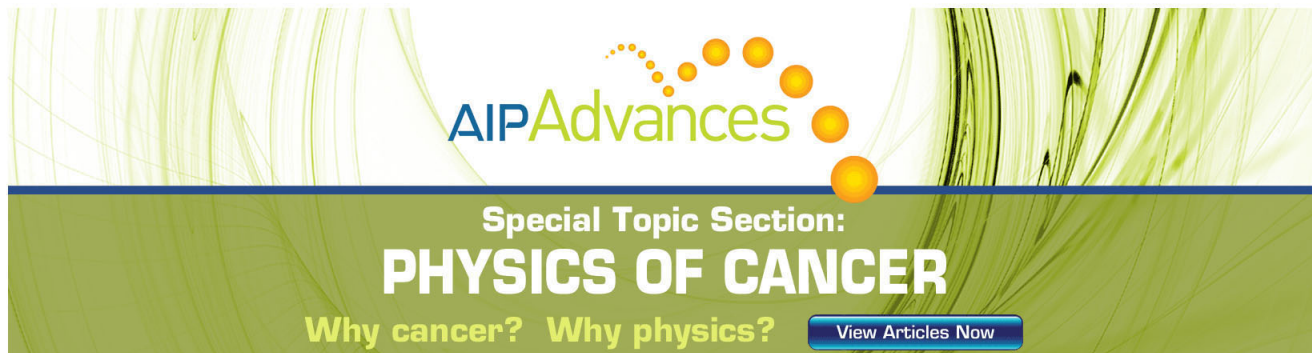
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## Photoluminescence and cathodoluminescence from nanostructured silicon surface

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We report the photoluminescence (PL) and cathodoluminescence (CL) study of nanostructured poly-crystalline silicon surface fabricated by lithography-less, reactive ion etching process. Photoluminescence in visible range at room temperature with peak position between 630 nm and 720 nm is observed without any oxidation or annealing steps. X-ray photoemission (XPS) and Auger electron spectroscopy (AES) revealed the presence of silicon oxide. The observed cathodoluminescence in green and red regions of the visible spectrum are due to nano-scaled tips and their coating with nonstoichiometric silicon oxide. © 2011 American Institute of Physics. [doi:10.1063/1.3648108]

Although the data processing is performed by Si based electronics, the data transferring is done optically primarily using III-V semiconductors.<sup>1</sup> This is due to the fact that Si is a poor light emitter because of its indirect band gap nature. The problem is going to be exacerbated with the information technology industry moving towards optical interconnects for chip-to-chip communication.<sup>2</sup> Hence, silicon-based optoelectronics devices are needed for easy integration to silicon-based circuits. Although porous silicon<sup>3</sup> gives visible photoluminescence (PL) at room temperature, it is very fragile, highly reactive and oxidizes spontaneously in air.<sup>4</sup> Another prominent candidate for visible PL source is silicon nanoclusters embedded in a SiO<sub>2</sub> matrix.<sup>5,6</sup> The mechanisms behind room-temperature PL in Si are the quantization of density of states (DOS) and confinement of the excitons,<sup>7</sup> defect states at the Si/SiO<sub>2</sub> interface,<sup>8</sup> surface trapping<sup>9</sup> and doping effects.<sup>9</sup> However, it is difficult to isolate the relative contribution to PL from defect states and quantum confinement as the contribution from the defect states is related to the size of the nanocrystal.<sup>5</sup>

Black silicon is obtained via a surface modification of bulk silicon that leads to low optical reflectivity and high absorption from visible to infrared wavelength range and thus having a black surface appearance.<sup>10</sup> Black silicon can be produced by wet etching,<sup>11</sup> electrochemical etching,<sup>12</sup> laser ablation of silicon surface,<sup>13</sup> and metal assisted dry etching techniques.<sup>14</sup> Previously developed methods for nanoscale silicon cones structure showed room-temperature PL after thermal oxidation<sup>15</sup> and wet oxidation.<sup>16</sup> Here, we formed the black silicon using a lithography-free reactive ion etching process without using any metal or photoresist mask across the full 4 in. wafer. The nanocone structures are fabricated by simultaneous plasma enhanced reactive ion synthesis and etching (SPERISE) process previously developed by us.<sup>17</sup> As we were using O<sub>2</sub> gas for passivating the Si surface, a thick layer of oxide (heavy oxide) was formed after the fabrication

process. Before carrying out PL experiments, we removed the heavy oxide layers using 10:1 BOE process. We observed room temperature PL without doing any further oxidation or annealing steps on the sample.

Figure 1(a) shows a transmission electron microscopy (TEM) image of the fabricated nanocone structure. The diameter of the cone at the base is about 180 nm and the height varies between 300 and 400 nm. TEM investigation (Fig. 1(b)) revealed that the crystal structures of the cones are free of dislocations and two-dimensional defects (only point defects are expected due to bombardment of low energy ions in RIE process). The inset shows a selective area electron diffraction (SAED) pattern of the nanocone. Figure 1(b) also shows the sub 10 nm tip structure of the nanocone.

We obtained the PL spectra by illuminating the sample with a 442 nm laser source and measuring the luminescence from 500 to 800 nm at room temperature. Figure 2(a) shows the PL spectrum from the sample with an integration time of 300 s. After the deconvolution of the peaks and Gaussian curve fitting, the PL spectrum contains three peaks at 1.73 (718 nm), 1.86 (667 nm), and 1.95 eV (637 nm), respectively. At low temperature (77 K), the peak at 650 nm gets enhanced as compared to peak at 515 nm (Figure 2(b)). The green band (~510-580 nm) is generally attributed to the recombination of carriers at oxygen-related defect centers (“defects related PL”),<sup>4,18-22</sup> and the red band (~635-720 nm) is due to recombination of confined excitons in Si nanocluster (“confinement related PL”).<sup>2,4,20,23</sup> Figure 2(b) shows an increase in intensity for band at 650 nm at low temperature. This can be explained by the quantum confinement of the excited carriers at the tips of the nanocone.<sup>20</sup> At low temperatures, excited carriers are localized at these weak potential wells or traps formed by the defects. At lower temperature, there is reduced probability of non-radiative recombination through defect centers and increased zero phonon recombination probability for electron-hole pair. Hence, the intensity of PL at lower temperature (77 K) is higher as compared to PL at room temperature

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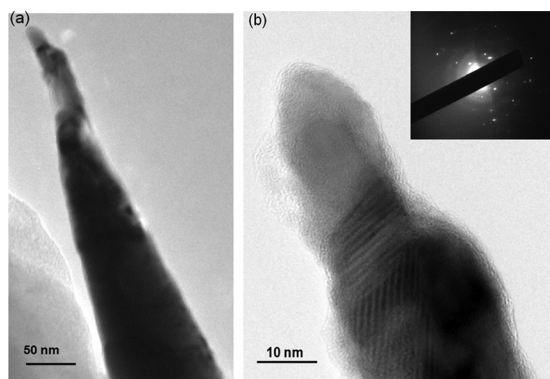


FIG. 1. (a) TEM showing the detailed structure of a single nanocone of the black Si. (b) High resolution TEM of the nanocone structure and the inset showing a SAED pattern of the nanocone.

(300 K). Figure 2(b) shows the peak wavelength of green luminescence band remains unchanged after lowering the temperature, although there is slight increase in intensity. This provides further evidence that the green luminescence band is defects-related PL. Furthermore, with the increase in temperature, the carriers are thermally excited and move to deeper potential well close to band edges. As shown in Fig. 2(c), the band-edge PL intensity is higher than the confinement related PL intensity. Since our system uses Si based detector, we are not able to see the whole band-edge spectrum for Si. Figure 2(d) shows PL spectra for black Si with different excitation energies. We observe a consistent red shift of PL peak with decreasing the excitation energy from 2.8 to 2.33 eV (442–532 nm). The red shift of the PL peak is an indication of defects related PL.<sup>24</sup>

Figure 3(a) shows the cathodoluminescence (CL) spectrum for black Si with an excitation probe current of 25 nA. The measured CL spectra are deconvoluted and fitted to a Gaussian shape. Mainly three Gaussian bands: green, red, and infrared are observed. The green CL band (565 nm or 2.2 eV) is attributed to point defects related to oxygen deficit (Si–Si bond).<sup>25</sup> The observed red band (650–670 nm or 1.9–1.85 eV) is generally assigned to nonbridging oxygen hole centers in oxygen deficient SiO<sub>2</sub> environment<sup>26</sup> or recombination via Si-nanocrystal-SiO<sub>2</sub> interface defects.<sup>27,28</sup> The band at

750 nm (1.65 eV) may also originated from a nonbridging oxygen hole center mostly at Si-SiO<sub>2</sub> interface.<sup>29</sup> The infrared band (1.4–1.6 eV) is attributed to band-band transition in Si-nanocluster.<sup>25</sup> Figure 3(b) shows the variation of CL spectrum with increasing the probe current. The intensity of the CL spectra increases with increase in the probe current. The earlier observed PL peak at 667 nm is also observed in all CL spectra (Fig. 3(b)). The secondary electron image (SEI) and panchromatic CL (panCL) image of the black Si over a 4 μm × 2.67 μm area is shown in Figs. 3(c) and 3(d), respectively. The bright spots are due to the presence of oxide layers on the black Si surface. The luminescence from black Si can be clearly seen from the panCL image.

The presence of oxide layers on black Si surface is further studied using x-ray photoemission (XPS) and Auger electron spectroscopy (AES). Figure 4(a) shows the Si 2*p* and 2*s* XPS spectra for Si, black Si, and black Si with heavy oxide specimen. All the spectra are calibrated with C 1*s* with binding energy of 285 eV. Bulk plasmon peak generally shows as equally spaced satellite structures at higher binding energy side (17.4 eV) of the core peaks.<sup>30</sup> The plasmon peak can be seen for Si and black Si, but not for black Si with heavy oxide. The presence of bulk plasmon indicates that the material in black Si is essentially elemental Si though some broadening is observed for black Si. The Si 2*s* spectrum of black Si with heavy oxide shifts by 2.42 eV as compared to 2*s* of black Si. This is an indication of non-stoichiometric oxide formation on black Si (as it is well known that Si can be oxidized by electronegative elements through several oxidation states (1–4) and the binding energy increase associated with unit increase in oxidation state is ~1 eV).<sup>31</sup> Figure 4(b) shows the Si 2*p* XPS spectrum of Si, Si with native oxide, black Si, and black Si with heavy oxide. The peak with highest binding energy (103.35 eV) is assigned to Si<sup>+4</sup> oxidation state of SiO<sub>2</sub> and the peak with smallest binding energy (99.24 eV) is assigned to Si<sup>0</sup> of the silicon crystal.<sup>32</sup> The inset of Fig. 4(b) shows that with native oxide formation on Si, the Si 2*p* spectrum shifts by around 0.6 eV, which is due to spin-orbit coupling.<sup>32</sup> Hence, Si<sup>0</sup> photoelectron peak has two contributions, Si<sup>0</sup> 2*p*<sub>3/2</sub> with binding energy 98.94 eV and Si<sup>0</sup> 2*p*<sub>1/2</sub> with binding energy 99.54 eV. The Si<sup>+4</sup> peak has similar contributions.<sup>32</sup>

Figure 4(c) shows XPS valence band (VB) spectra for Si and black Si sample. The XPS VB provides useful information about distribution of total DOS of the sample. Hence, any transformation of VB spectrum indicates re-arrangement of the energy spectrum of the electronic states for black Si sample.<sup>33</sup> The Si 3*d* peak is generally situated ~2.4–4.2 eV above the Fermi level and Si 3*s* level is about 11.1 eV above the Fermi level.<sup>34</sup> The rearrangement of DOS on black Si can be clearly seen. The spectrum for black Si shows four main characteristic peaks labeled A–D. Taking into account the positions of Si 3*s* and 3*d* peak and O 2*p* peak from a low energy survey scan, the peak features at A–B–C appear due to strongly hybridized Si 3*d*3*s*–O 2*p* electronic states.<sup>33</sup> This so called XPS VB transition layer<sup>35</sup> gives further indication of migration of oxygen and formation of non-stoichiometric oxide layer on black Si forming Si/SiO<sub>x</sub> (*x* < 2) interface. Figure 4(d) shows the Si KLL Auger spectrum for Si and black Si sample. The intense Auger line (KL<sub>23</sub>L<sub>23</sub>) at 1614–1616 eV (peak-8) is for Si and smaller satellite at 1607–1609 eV (peak-

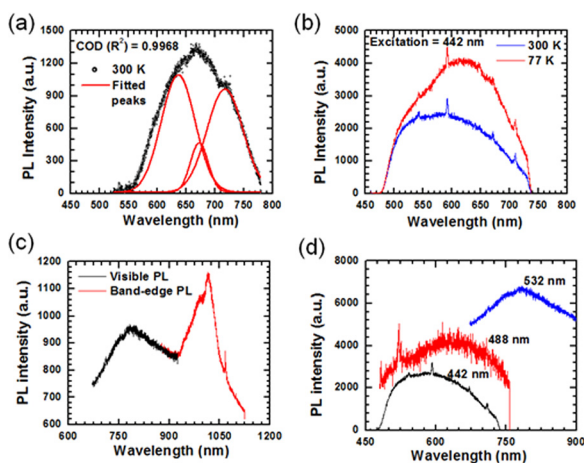


FIG. 2. (Color online) (a) PL spectrum from black Si with excitation laser of 442 nm. (b) PL at 77 K and 300 K using excitation wavelength of 442 nm. The integration time is 300 s. (c) Visible and band-edge PL spectra using excitation wavelength 532 nm. (d) Comparison of PL spectra using excitation wavelength of 442, 488, and 532 nm.



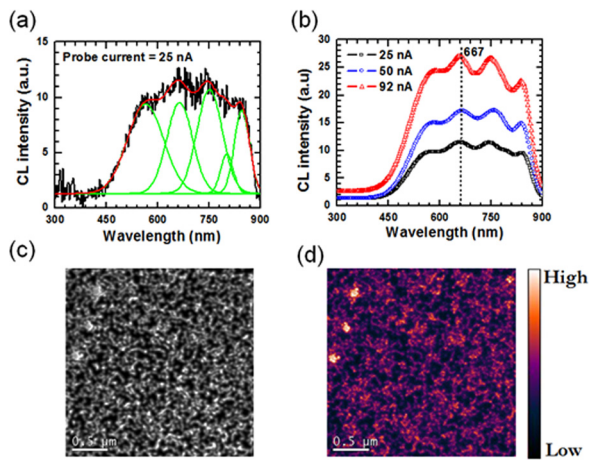


FIG. 3. (Color online) (a) Grating corrected CL spectrum of black Si using probe current of 25 nA. (b) Comparison of CL spectra with increasing the probe current. (c) SEI of the black Si (d) Panchromatic CL image of the same region shown by SEI.

7) is for  $\text{SiO}_2$ .<sup>36</sup> The peaks at 1-3 are due to  $\text{KL}_1\text{L}_{2,3}$  transition and peaks at 4-8 are due to  $\text{KL}_{2,3}\text{L}_{2,3}$  transition.<sup>37</sup> The peaks are shifted to higher kinetic energy for black Si, which is further indication of formation of oxide layers.<sup>38</sup> We believe that nonstoichiometric oxide layer is a necessary condition for PL. The oxygen-defect centers are reported to be located in suboxide structures and the exciton migrates to the defect centers from the absorbing Si grains to produce PL.<sup>39,40</sup>

In conclusion, we observe photoluminescence and cathodoluminescence from crystalline black silicon without additional thermal treatment. The PL and CL study shows three bands: the green band is associated with point defects, the red band is related to the surface and interface defects, and the infrared band can be attributed to the electronic transition between quantum confinement induced widened band gap in the vicinity of the sub-10 nm nanocone tip. Finally, XPS and AES study showed the presence of non-stoichiometric oxide layer forming  $\text{Si}/\text{SiO}_x$  interface states responsible for room-temperature PL and CL. Our results indicate the potential applications of the sharp-tip nanocone black silicon structures in active silicon photonic devices.

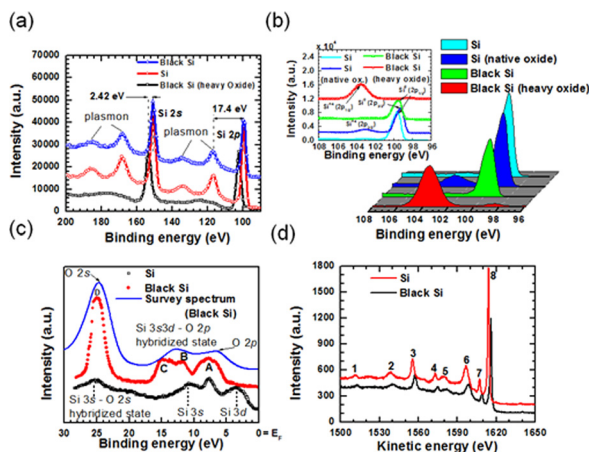


FIG. 4. (Color online) (a) Si 2p and 2s XPS spectra for Si, black Si and black Si with heavy oxide (b) High resolution Si 2p XPS spectra of Si, black Si with and without oxide layer (c) XPS valence band structure of Si and black Si showing variation in density of states (d) AES spectra of Si and black Si.

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