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ABSORPTION AND LUMINESCENCE OF HYDROGEN AND OXYGEN PASSIVATED SILICON QUANTUM DOTS

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Silicon (Si) quantum dots (QDs) passivated with oxygen and hydrogen of size 1 nm in diameter are prepared by wet chemical route and electrochemical route respectively. The optical measurements reveal the strong absorption feature around 4.7 eV and weak absorption at 3.4 eV for oxygen passivated Si QDs. Hydrogen passivated Si QDs of the same size show absorption at 4.9 eV. Both the oxygen and hydrogen passivated Si QDs show broad luminescence around 3.9 and 3.8 eV. Films of these QDs, when coated on crystalline silicon solar cells, show an increase in the efficiency of the solar cell by 12 %.

Keywords: IV SEMICONDUCTOR, PHOTOLUMINESCENCE, UV-VIS ABSORPTION, NANOPARTICLES, PHOTOVOLTAICS.

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1. INTRODUCTION

An interest in studying the quantum confinement effects in indirect band gap semiconductors has been triggered by observation of visible radiation from porous silicon by L.T. Canham [1]. Till now most of the work is carried out on Si nanocrystals which are passivated by hydrogen both theoretically as well as experimentally. In realistic situations the structure and chemical environment of Si nanocrystals are extremely complicated [2, 3]. Hydrogen passivated Si nanocrystals of 1-3 nm size are shown to be highly fluorescent and exhibit stimulated emission [4] as well as harmonic generation [5]. Photoluminescence emission (PL) and excitation spectroscopy of hydrogen passivated Si nanocrystals show that they emit from ultraviolet (UV) to red region of the electromagnetic spectrum [6]. Origin of such luminescence is still under debate. It is believed that defect states play an active role. Defects states can arise due to surface and its interaction with other molecules. Very often, in most of the devices Si is found with SiO₂ around it. One of the nanotechnology based device, considered to be the near future contender is single electron transistor (SET). The nature of I-V characteristics for SET is closely related to the surroundings of the silicon nanocrystals at the junction [7, 8].

Effect of small amount of oxygen or hydrogen passivated silicon nanocrystals has been studied computationally [9]. It is observed that the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular

orbital (LUMO) gap is defined in this case by the oxygen in the cluster, however, the first significant absorption is not between HOMO-LUMO states [9]. In another study [10] oxygen was considered in Si = O configuration on silicon surface. It was observed that the energy gap for these nanocrystals showed systematic behavior with respect to size of nanoparticle. The gap was assigned to the oxygen related defect states [10]. Hence it is important to investigate the effect of oxygen on the surface of such nanocrystals. In the present work, we address this issue. Si nanocrystals passivated with oxygen and hydrogen are shown to absorb UV radiation efficiently and emit in UV through visible by virtue of defect luminescence [11]. Thus surface oxygen and hydrogen is playing an important role in optical properties of silicon nanocrystals. The response in the UV region is particularly indicative of the use of these nanoparticles in case of UV detectors and solar cells [12-14].

2. EXPERIMENTAL

Si QDs passivated with oxygen (O) were synthesized by adapting the method suggested by Tilley et al. [15] The preparation route is slightly modified to obtain oxygen capping particularly by varying the ratio of SiCl_4 to LiAlH_4 it was possible to obtain oxygen coating on silicon core. The measurements were carried out by dispersing Si QDs in methanol.

The hydrogen (H) passivated Si QDs were synthesized by the method suggested by Nayfeh et al. [4] Silicon wafers used in experiments are (100) oriented, 1-10 Ω cm resistivity, *p-type*, boron doped silicon wafers. Silicon was laterally anodized in an electrochemical cell under room light illumination. Silicon samples were ultrasonically cleaned in an acetone, and then immersed in hydrofluoric acid (HF) solution for oxide removal and surface passivation. The anodizing solution consisted of mixtures of hydrogen peroxide (H_2O_2), HF, and methanol.

Transmission electron microscopic (TEM) measurements were carried out using a Philips CM200 microscope operating at 200 kV. The samples were deposited on the carbon grid for the TEM image and electron diffraction pattern.

Optical absorption spectra were measured on JASCO V-670 spectrophotometer. For photoluminescence (PL) studies, Perkin Elmer LS55 spectrophotometer was used. The studies were carried out by dispersing them in methanol. The Fourier transform infrared spectra (FTIR) were recorded with the aid of JASCO FT/IR-6100. For FTIR measurements the sample in powder form was mixed with the potassium bromide (KBr) powder in the form of pellets.

3. RESULTS AND DISCUSSION

Fig. 1a shows the TEM image of Si QDs passivated with O and the size obtained is 1.0 ± 0.3 nm. Electron diffraction pattern (Fig. 1b) of these QDs reveals the diffraction rings corresponding to (1 1 1), (2 1 1), and (2 2 0) lattice planes of cubic diamond structure of Si (JCPDS # 27-1402).

The Si bond length calculated from electron diffraction measurements is 2.33 ± 0.01 Å which is short compared to the bulk value. Fig. 1c shows the TEM image of Si QDs passivated with H and the size obtained is 1.1 ± 0.4 nm. Fig. 1d shows the electron diffraction of these QDs. The corresponding bond length is 2.35 ± 0.01 Å. This is close to bulk value of

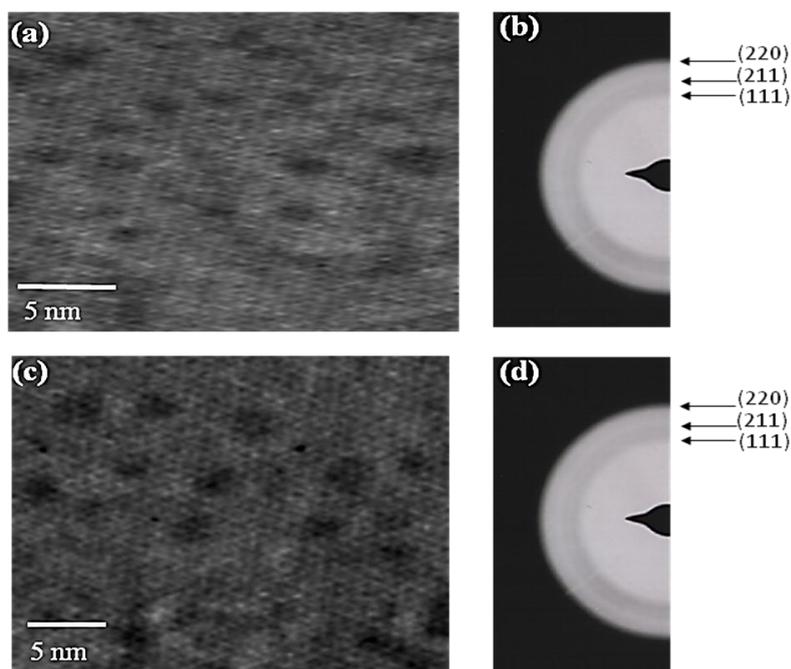


Fig. 1 – (a) TEM image and (b) electron diffraction pattern of O passivated Si QDs. (c) TEM image and (d) electron diffraction pattern of H passivated Si QDs

Si. The comparison between O and H passivated bond lengths show that H passivated are bulk like while O passivated are compressed. Hence the diffraction pattern confirms the presence of core silicon clusters. Thus, we have obtained silicon clusters with fourfold co-ordination engulfed with O and some organic groups for O passivated Si QDs. For H passivated Si QDs, we have obtained silicon clusters with fourfold co-ordination engulfed with H and some organic groups.

The FTIR spectroscopic studies are carried out to examine the chemical composition (Fig. 2a).

The O passivated Si QDs revealed features at 1465 and 1288 cm^{-1} and are attributed to vibrational scissoring and symmetric bending of Si-CH₂ [15]. The peaks at 2852 and 2920 cm^{-1} are due to C-CH₃ symmetric, C-CH₂ asymmetric vibrations respectively [15]. Si-O-Si asymmetric stretching mode is located at 1097 cm^{-1} while Si-OH stretching mode appears at 3425 cm^{-1} [16]. We have verified that on increasing the LiAlH₄ content the Si-O-Si contribution reduces, and ultimately one can obtain 1-heptene coated particles as in Ref. [15].

Similarly for H passivated Si QDs (Fig. 2b) revealed features at 1630 and 2085 cm^{-1} and are attributed to stretching of Si-C₆H₅ and stretching of Si-H [15]. The peaks at 2850 and 2915 cm^{-1} are due to C-CH₃ symmetric, C-CH₂ asymmetric vibrations respectively [15]. Si-OH stretching mode appears at 3425 cm^{-1} which is the most dominant peak [16]. For this sample Si-O-Si vibration is reduced considerably.

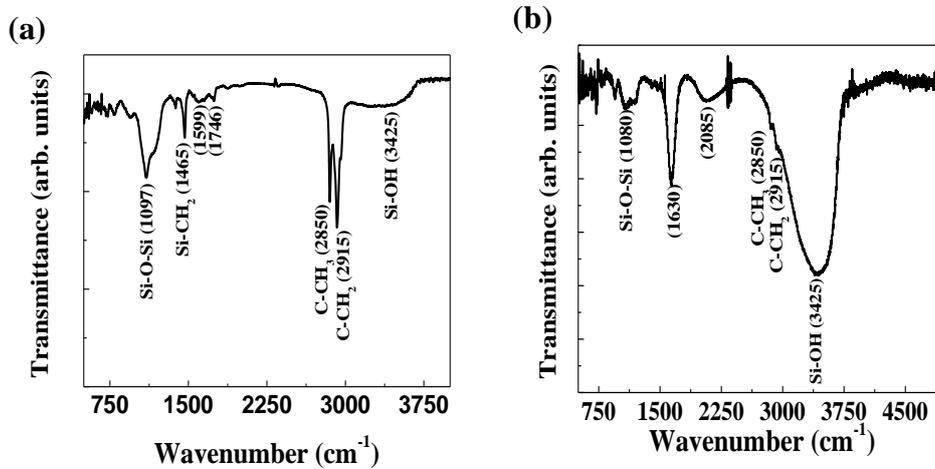


Fig. 2 – FTIR spectra of (a) O passivated, and (b) H passivated Si QDs

Fig. 3a shows the optical absorption of O passivated Si QDs. The spectrum reveals a broad absorption feature at 3.4 eV (370 nm) along with another sharp transition at about 4.7 eV (265 nm) and the low energy transitions at 1.3 eV (978 nm), 1.1 eV (1170 nm), and 1.0 eV (1242 nm) (inset of Fig. 3a).

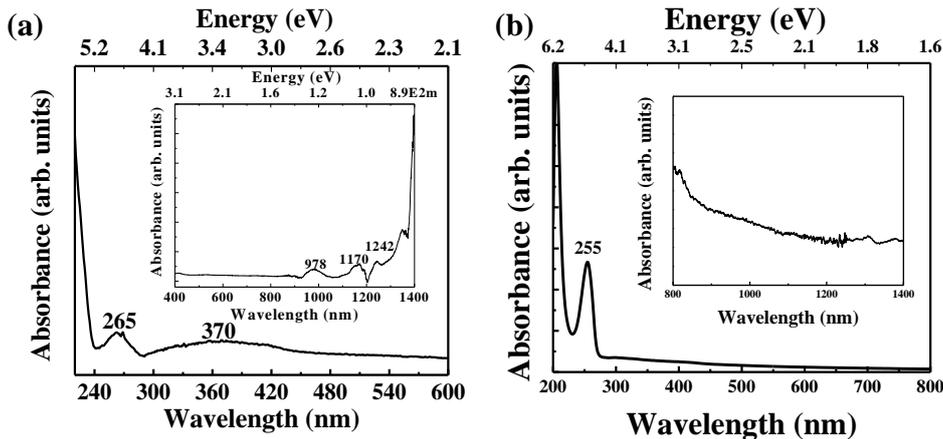


Fig. 3 – Optical absorption spectra (a) O passivated Si, and (b) H passivated Si QDs. All measurements were recorded at room temperature. The inset in (a) and (b) corresponds to the absorption taken at lower wavelength region

Fig. 3b shows the optical absorption of H passivated Si QDs. The spectrum reveals a very sharp transition at about 4.9 eV (255 nm) whereas at low energy region there are no peaks as observed in the O passivated Si QDs (inset to Fig. 3b). The low energy absorption in Si passivated with O indicates presence of states in the same energy range of HOMO-LUMO gap of H passivated Si nanoparticles.

The PL measurement on O passivated Si QDs is shown in Fig. 4a. In this figure excitation energy was varied from 4.5 to 5.0 eV. However, the spectrum remains invariant. This feature is not very common in Si nanocrystals.

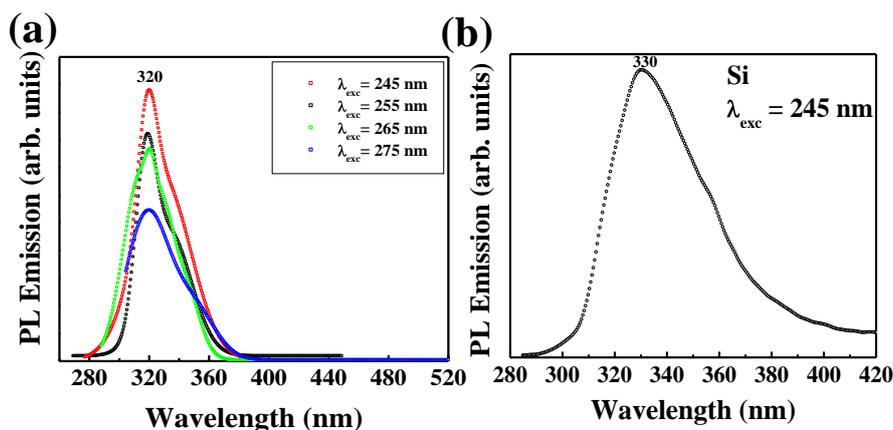


Fig. 4 – PL [excitation energy was varied from 5.0 to 4.5 eV (245-275 nm)] (a) O passivated Si, and (b) PL [excitation energy at 5.0 eV (245 nm)] H passivated Si QDs

In many other studies [18-21] the emission peaks are seen to vary with the excitation energy. This indicates strong role played by the encapsulation. O passivated particles prepared by Belomoin et al. [22] showed a significant shift in the PL emission with excitation energy due to rather complex surface chemistry. Interestingly, the particles prepared in our method do not show such a shift. The pronounced PL peak is centered at 3.9 eV (320 nm) with the full width at half maximum (FWHM) of 50 nm. The position of the PL peak in the present case, is comparable to that reported by Wilcoxon et al. [23] (3.3 eV (380 nm) in case of Si nanocrystals with size less than 5 nm and at 3.4 eV (365 nm) for size of 2 nm). Another hump at 3.4 eV (360 nm) red shifted considerably with respect to the optical absorption feature is also observed. The optical Stokes shift and excitonic exchange splitting cannot account² for such a large shift. In Fig. 4b, the H passivated Si QDs show similar features. The peak occurs at 3.8 eV (330 nm). Above results indicate that a blue shift is obtained for O passivated Si QDs in comparison with H passivated Si QDs. The observed blue shift is due to the compressive strain. This result is consistent with the PL results of Si nano wires reported by Audoit et al. [24] Consequently, the defect levels arising due to the chemical environment are presumed to be active in deciding the luminescent behavior. Thus, luminescence behavior is similar in both the cases although absorption in low energy range is significantly different.

Fig. 5a and b shows I-V characteristic for solar cell under UV lamp and normal solar spectrum. The O and H passivated Si QDs were coated on the surface of the solar cell.

Table 1 and Table 2 shows the parameters of the solar cell obtained for characterization done under UV lamp and solar spectrum. It is interesting to see that the O passivated solar cells show high sensitivity to UV.

This implies that the coating is behaving as a wavelength conversion medium from UV to deep blue making it absorbable in the Si matrix. The Fig. 5(a) clearly shows that the I_{sc} has increased and thereby shows an increase of efficiency by 12 % over the original efficiency. In particular the maximum power point has higher value for O passivated Si QDs coated solar cell for both UV lamp and solar spectrum. The measurements were carried out at room temperature.

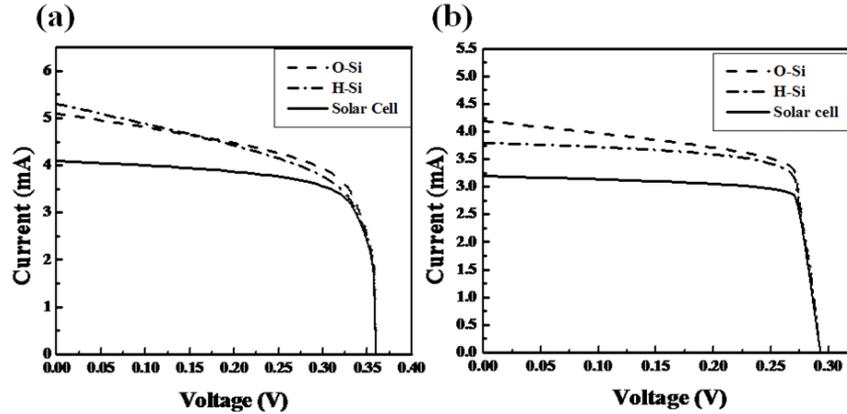


Fig. 5 – *I-V characteristics of the O passivated and H passivated Si QDs by coating it on Si solar cell under (a) UV lamp, and (b) solar radiation (1 Sun)*

Table 1 – *Open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and efficiency of the solar cell under UV and solar spectrum for solar cell (SC), O passivated Si QDs (O-Pass SC) and H passivated Si QDs (H-Pass) on solar cell under solar spectrum*

Under Solar Spectrum	Open Circuit Voltage (V_{oc} , V)	Short Circuit Current (I_{sc} , mA)	Fill Factor (FF)	Efficiency (η , %)
Solar Cell	0.29	3.10	0.91	11.0
O pass SC	0.29	4.21	0.89	12.3
H pass SC	0.29	3.75	0.80	12.1

Table 2 – *Open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and efficiency of the solar cell under UV and solar spectrum for solar cell (SC), O passivated Si QDs (O-Pass SC) and H passivated Si QDs (H-Pass) on solar cell under UV lamp*

Under UV Lamp (330-380 nm)	Open Circuit Voltage (V_{oc} , V)	Short Circuit Current (I_{sc} , mA)	Fill Factor (FF)	Efficiency (η , %)
Solar Cell	0.36	4.12	0.81	11.0
O pass SC	0.36	5.23	0.66	12.4
H pass SC	0.36	5.14	0.61	12.2

4. CONCLUSIONS

In conclusion, Si QDs passivated with O and H of size as small as 1 nm in diameter were synthesized. For O passivated Si the optical absorption spectrum reveals a broad feature at 3.4 eV (370 nm) with another sharp transition at about 4.7 eV (265 nm). While for H passivated Si only a sharp transition at 4.9 eV (255 nm) is observed. The absorption features for O passivated cluster are also observed in infrared region at 1.3 eV (978 nm), 1.1 eV (1170 nm), and 1.0 eV (1242 nm) which are absent in H passivated Si QDs. The interaction of O with Si QDs leads to PL emission close to that of the direct band gap transition of bulk Si. The pronounced PL peak is

centered at 3.9 eV (320 nm) with FWHM of 50 nm. This peak is attributed to direct e-h recombination and is independent of excitation energy. Si solar cells coated with O passivated QDs show a 12 % increase in the efficiency. This is attributed to the UV to lower wavelength conversion due to the QDs.

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