

Optimization of process parameter for synthesis of silicon quantum dots using low pressure chemical vapour deposition

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Abstract. Si quantum dots-based structures are studied recently for performance enhancement in electronic devices. This paper presents an attempt to get high density quantum dots (QDs) by low pressure chemical vapour deposition (LPCVD) on SiO₂ substrate. Surface treatment, annealing and rapid thermal processing (RTP) are performed to study their effect on size and density of QDs. The samples are also studied using Fourier transformation infrared spectroscopy (FTIR), atomic force microscopy (AFM), scanning electron microscopy (SEM) and photoluminescence study (PL). The influence of Si–OH bonds formed due to surface treatment on the density of QDs is discussed. Present study also discusses the influence of surface treatment and annealing on QD formation.

Keywords. Annealing; AFM; LPCVD; thin film; quantum dot.

1. Introduction

According to Knoss (2009), quantum dots (QDs) are small devices that contain tiny droplets of free electrons and hence the energy levels in QDs are quantized due to quantum confinement. Semiconductor QD represents nanoscale system with few electrons confined in semiconductor host crystal, thus when excited, they emit light at a characteristic wavelength. Wavelength of light emitted depends on size of the dots. The importance of semiconductor QDs lies primarily in their tunability and sensitivity to external parameters as electrons are confined in all the three dimensions. As a result, they have properties in between bulk semiconductor and discrete molecules. QDs show quantum confinement effect and Coulomb blockade effect which is responsible for excellent optical and electrical properties. Owing to the above properties, QDs are used in LEDs (Soon *et al* 2009), diode lasers (Grundmann *et al* 1998), solar cells (Adachi 2007), sensors (Zhao *et al* 2009) and as floating gate in flash memory cells (Geller *et al* 2008). The reliability of devices depends on controlling size of QD and obtaining their uniformity. There are different techniques like hot wire chemical vapour deposition (Pant and Russell 2001), low pressure chemical vapour deposition (Makihara *et al* 2005), plasma enhanced chemical vapour deposition (Mercaldo *et al* 2009) by which Si QDs can be deposited on SiO₂ substrate. Wiesmann *et al* (1979) reported that *a*-Si:H can be formed by cracking silane gas molecules on hot tungsten foil. Matsumura (1986) used silane and hydrogen gas mixture to obtain Si thin film and Pant and Russell (2001)

studied effect of process parameters on Si QD. Recent studies indicate use of LPCVD for Si QD deposition (Miyazaki *et al* 2000; Makihara *et al* 2005). Earlier work carried out in this area is to improve density, reduce size and increase the uniformity of QD formed. In the present investigation, Si QDs are prepared by LPCVD using very low pressure of the order of 0.2 torr to deposit uniform silicon thin film on SiO₂ substrate at 550 °C. Optimization of surface treatment is carried out to increase the density of Si QDs. Comparative study of luminescence property of QDs formed and its dependence on the size and density are also discussed. Moreover, effect of RTP on size of QD after surface treatment and prior to LPCVD is studied.

2. Experimental

2.1 Initial sample preparation

4" *p* type Si wafer of (100) orientation, 4–7 Ω cm resistivity and polished on one side was taken initially and cleaned. The polished wafers were then oxidized to form SiO₂ by dry oxidation at 1000 °C in O₂ and H₂ atmosphere with gas flow rate 6000 and 8000 sccm, respectively for 20 min at atmospheric pressure.

2.2 Surface treatment

SiO₂ substrate was subjected to surface treatment in order to form Si–OH bonds which further acted as nucleating sites for deposition of QDs. To optimize surface treatment, SiO₂ substrate was dipped into 0.1, 0.3 and 0.5% HF solution for

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Table 1. FTIR peak position of Si–O–Si stretching in different samples dipped in HF solution of different concentration for varying time and their ellipsometry results.

Sr. No	% HF solution	Dipping time (s)	Original thickness (nm)	Thickness after surface treatment (nm)	FTIR peak position (cm ⁻¹)
1.	0.1	5	14.6~14.9	14.5	1070.98
		15		14.3	1071.15
		30		13.0	1070.80
		60		14.6	1070.98
2.	0.3	5	13.9~14.4	12.59	1070.75
		15		13.5	1070.91
		30		13.0	1068.53
		60		11.7	1070.91
3.	0.5	5	14.6~14.9	14.7	1070.99
		15		13.6	1068.22
		30		13.2	1070.93
		60		11.4	1068.03

Table 2. Various processes carried out on SiO₂ substrates.

Sample code	Treatment before LPCVD	Treatment after LPCVD
Sample 1	Without surface treatment	Without annealing
Sample 2	Without surface treatment	Argon annealing
Sample 3	1% HF dip for 5 s	Without annealing
Sample 4	1% HF dip for 5 s	Argon annealing
Sample 5	0.5% HF dip for 30 s	Without annealing
Sample 6	0.5% HF dip for 30 s	Argon annealing
Sample 7	0.5% HF dip for 30 s, RTP	Argon annealing
Sample 8	0.5% HF dip for 30 s RTP	Without annealing
Sample 9	0.5% HF dip for 30 s	RTP
Sample 10	0.5% HF dip for 30 s, RTP	RTP

5, 15, 30 and 60 s followed by rinsing in deionized water to form Si–OH bonds on SiO₂ substrate (table 1). Surface-treated samples were annealed at 850 °C using RTP (AS-ONE 150, ANNEALSYS) for 5 min to study its effect on the number of Si–OH bonds.

2.3 *a*-Si thin film deposition by LPCVD

Surface-treated samples are transferred for LPCVD (Ultech furnace) to deposit *a*-Si film at 550 °C for 30 min at 0.2 torr pressure and 80 sccm gas flow rate of silane. Amorphous thin film of 10 nm thickness was obtained which was then subjected to annealing/RTP to convert it into QD.

2.4 Final heat treatment

The *a*-Si thin film was (a) annealed at 850 °C for 20 min and (b) annealed at 850 °C using RTP for 5 min to obtain Si QDs. Experimental details to prepare set of samples with varying heat treatments before and after LPCVD are given in table 2.

Figure 1 shows flow diagram of the experiment carried out in present work.

2.5 Characterization techniques

Si–OH bonds formed after surface treatment were observed using FTIR (Spectrum BX II, Perkin Elmer). Ellipsometry (SE 800, SENTECH) was used to measure the initial thickness of SiO₂ film formed after oxidation as well as the final thickness of film after HF treatment for different time periods. The images of Si QD were taken by SEM (6400 SEM, JOEL) and AFM (Dimension 3100 AFM, VEECO) and QD size distribution was studied by Auxiovision release 4.6.3 image analyser software. PL study was carried out with PC spectrofluorophotometer (RF 5301, Shimadzo).

3. Results and discussion

3.1 Optimization of surface treatment

The effect of surface treatment on number of Si–OH bonds observed using FTIR and reduction of thickness using ellipsometry is shown in table 1.

3.1a FTIR results: A broad band observed at 3550–3740 cm⁻¹ corresponds to O–H stretching and a weak peak between 1490 and 1560 cm⁻¹ corresponds to O–H bending (Suquet 1989). A strong peak at ~1070 cm⁻¹ indicates the presence of Si–O–Si stretching (Gencer Imer et al 2010). A weak peak at ~810 cm⁻¹ corresponds to Si–O bending (Mestanza et al 2006) and at ~590 cm⁻¹ shows the presence of out of plane Si–O stretching (Suquet 1989). Thus it confirms the formation of Si–OH bonds after surface treatment.

As the etching time and concentration of HF increases, the number of Si–OH bonds on substrate increases as

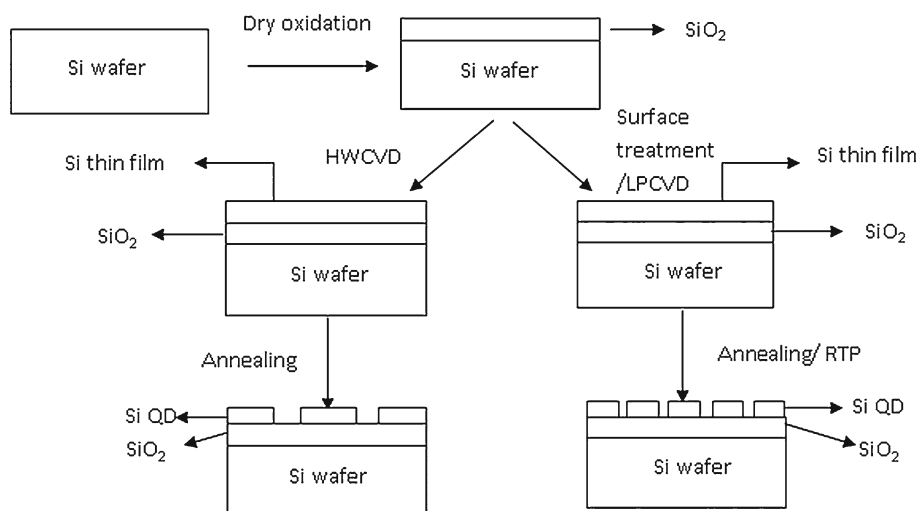


Figure 1. Experimental procedure for fabrication of Si QD.

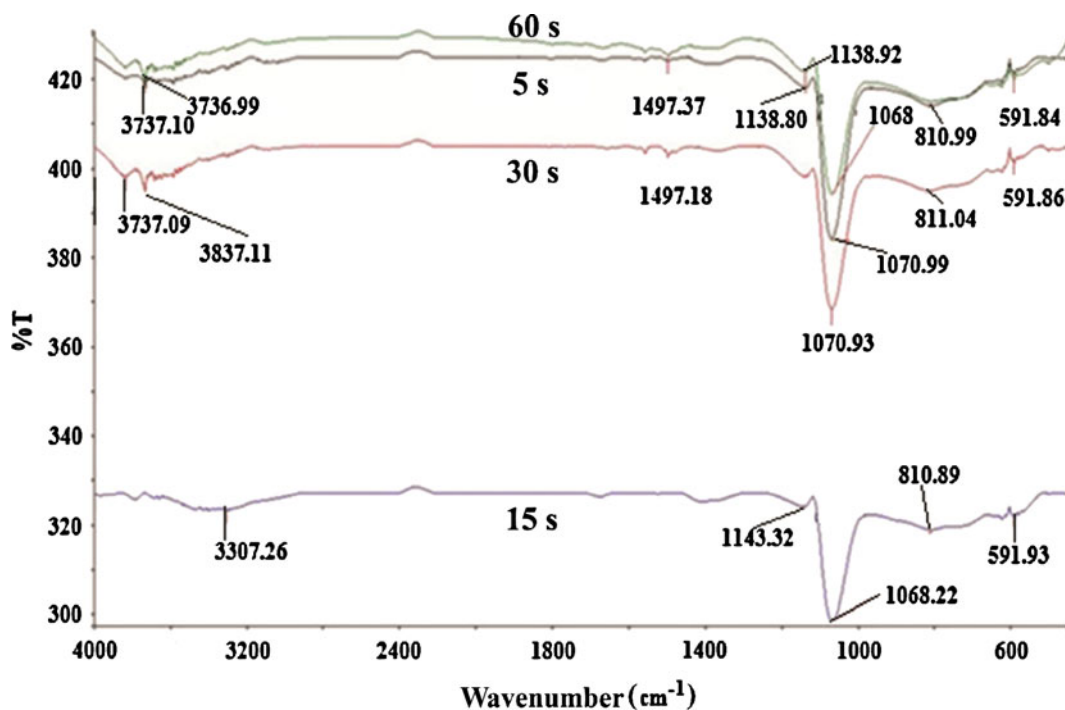


Figure 2. FTIR spectra of wafer dipped for 5, 15, 30 and 60 s in 0.5% HF solution.

indicated by broad peak in between the frequency range 3550 and 3730 cm^{-1} shown in figure 2. Reaction taking place on surface due to HF treatment is given below.



According to above chemical reaction, it is easier to break O-H bonds (bond energy 103.5 kcal/mol) (Mazen *et al* 2003) in comparison with the high energy Si-O bond (193.5 kcal/mol) (Mazen *et al* 2003) resulting in high density of nucleation sites. The broad band indicates presence of bridged silanol and shoulder at $\sim 3740\text{ cm}^{-1}$ indicates isolated silanol. Vicinal silanol are transformed into bridged silanol when bonded

together by hydrogen bonds (Mazen *et al* 2003). The strong peak at $\sim 1070\text{ cm}^{-1}$ indicates Si-O-Si stretching. As the thickness of SiO₂ thin film decreases, the peak at 1070 cm^{-1} shifts towards lower wavelength confirming results obtained from ellipsometer. Observed shift is due to change in Si-O-Si bond angle occurring due to stresses in SiO₂ film (Mazen *et al* 2003). As explained by Mazen, the intrinsic stresses are generated at Si-SiO₂ interface due to molar volume expansion of Si in SiO₂ due to which stresses are minimum on SiO₂ surface and increases at Si-SiO₂ interface. With HF treatment, the surface is chemically attacked thereby decreasing the thickness of film and exposing the stressed region.

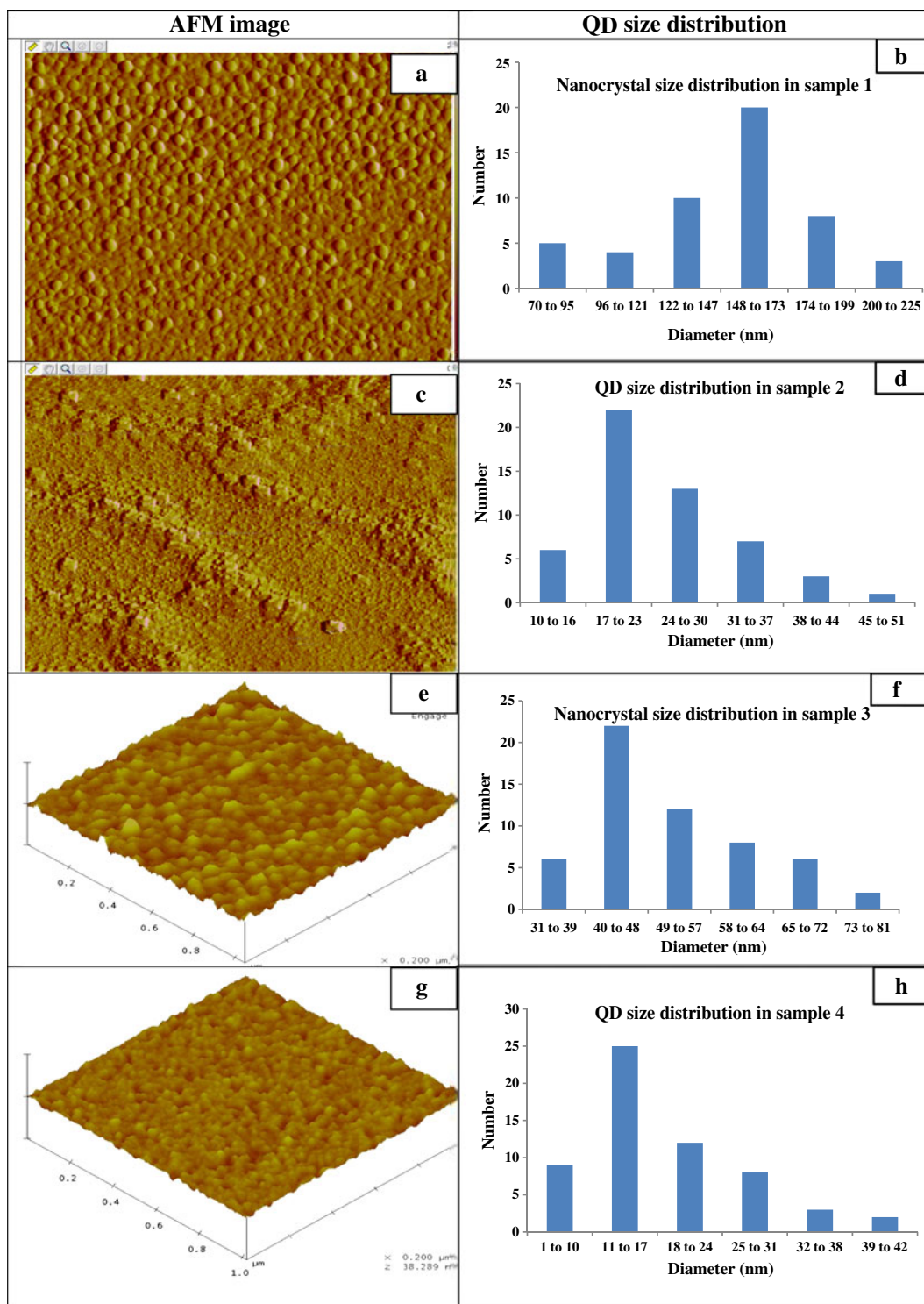


Figure 3. (a) AFM image of sample 1: no treatment + LPCVD + without annealing; (b) nanostructure size distribution in sample 1; (c) AFM image of sample 2: no treatment + LPCVD + annealing; (d) QD size distribution in sample 2; (e) AFM image of sample 3: HF treatment + LPCVD + without annealing; (f) nanostructure size distribution in sample 3; (g) AFM image of sample 4: HF treatment + LPCVD + annealing and (h) QD size distribution in sample 4.

3.1b *Ellipsometry results:* Mostly in the present study, it is observed that as the thickness of SiO₂ thin film decreases, the peak at 1070 cm⁻¹ shifts towards the low wavelength side.

Table 1 shows ellipsometry results and FTIR peak position of Si–O–Si stretching for different samples dipped in HF solution of different concentrations for varying times. In general,

as the film thickness decreases, FTIR peak shift is expected towards lower wavelength but this is not observed in present case (table 1). This mismatch observed could be due to difference in thickness of deposited layer. The optimized concentration of HF used for surface treatment is 0.5% HF applied for 30 s on SiO₂ surface due to which the maximum formation of Si–OH bonds takes place as seen by sharp peak at 3737.09 cm⁻¹ associated with isolated silanol bonds.

3.2 AFM images

3.2a *Effect of annealing on formation of QD:* To understand the effect of annealing on HF treated and non-treated on SiO₂ surface, a separate study is carried out as shown in table 2 for samples 1, 2, 3 and 4. AFM images of samples 1, 2, 3 and 4 are shown in figure 3(a, c, e and g), respectively while figure 3(b, d, f and h) are in the form of histograms

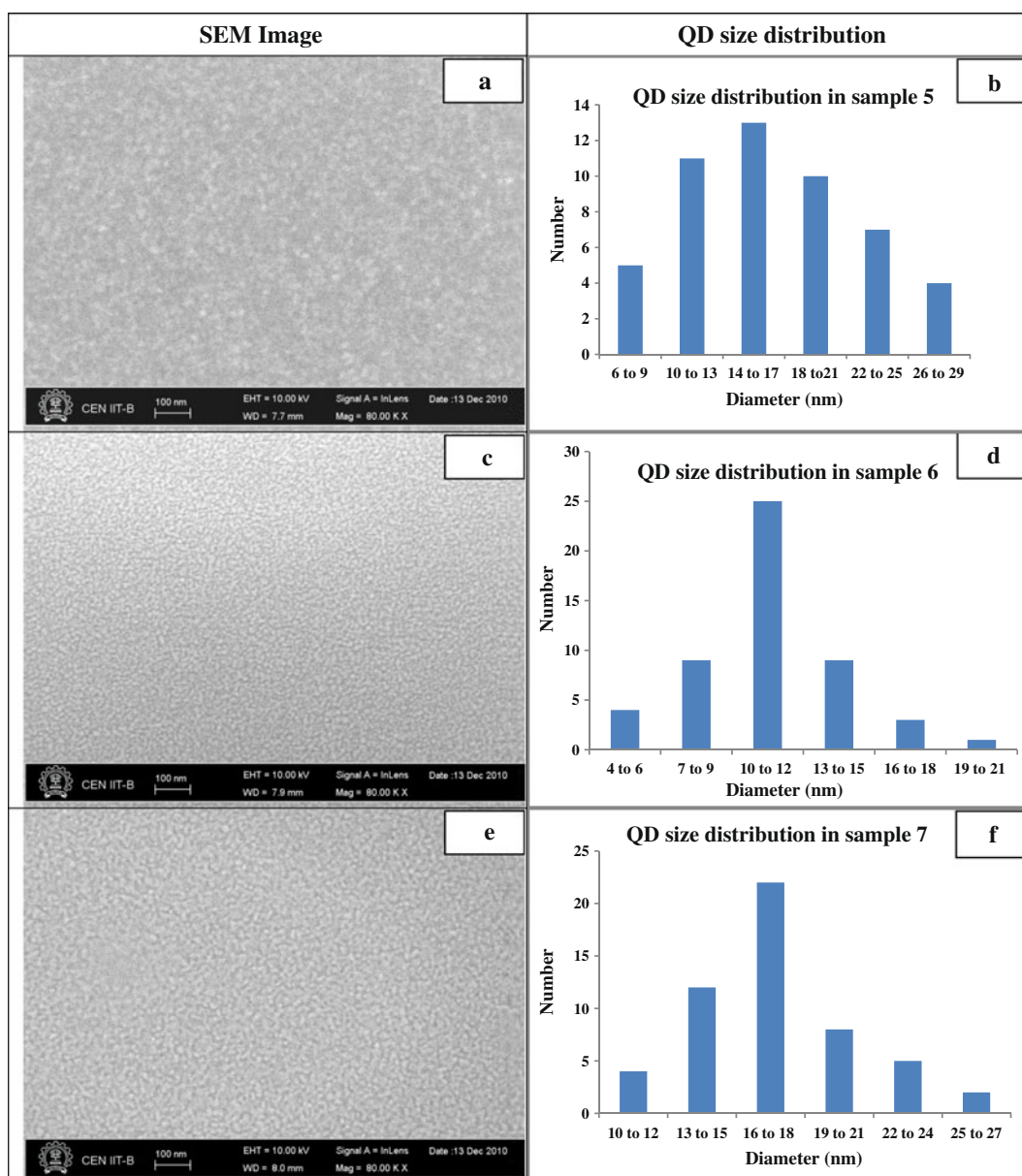


Figure 4. (a) SEM image of sample 5: HF treatment + LPCVD + without annealing; (b) QD size distribution in sample 5; (c) SEM image of sample 6: HF treatment + LPCVD + Ar annealing; (d) QD size distribution in sample 6; (e) SEM image of sample 7: HF treatment + RTP + LPCVD + Ar annealing; (f) QD size distribution in sample 7; (g) SEM image of sample 8: HF treatment + RTP + LPCVD + without annealing; (h) SEM image of sample 9: HF treatment + LPCVD + RTP and (i) SEM image of sample 10: HF treatment + RTP + LPCVD.

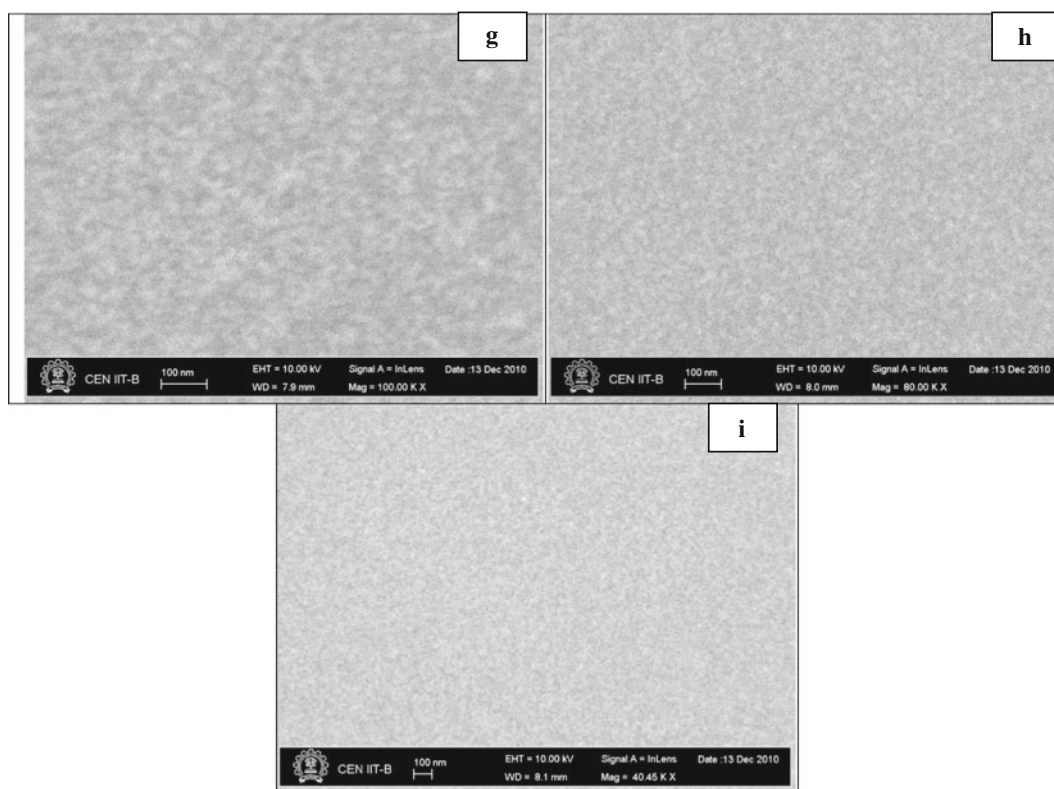


Figure 4. (contd.)

showing distribution of QDs/nanocrystal. Sample 1 is without surface treatment and annealing showing nanostructure having dimension above 100 nm (figures 3a and b). In sample 2, argon annealing is done without prior HF treatment on SiO₂ substrate. QDs formed in sample 2 have dimension in the range of 17–21 nm (figures 3c and d). Processing of sample 3 includes prior HF treatment to SiO₂ film while Si thin film deposited is not annealed resulting in the nanostructure formation in the range 40–48 nm (figures 3e and f). Finally, for sample 4 which is surface treated and annealed, QD dimension in the range of 11–7 nm (figures 3g and h) is obtained. The combined effect of surface treatment and annealing resulted in the reduction of QD size. Surface treatment has produced high density Si–OH bonds which acts as nucleation sites for deposition of Si and further annealing results in recrystallization to form high density homogeneous Si QD throughout the surface.

3.3 SEM results

3.3a Effect of annealing on formation of QD: Figure 4(a, c and e) shows SEM images of samples 5, 6 and 7, while figure 4(b, d and f) are the respective QD size distribution histograms of these samples. The dimensions of QD formed in sample 5 are in the range of 10–30 nm (figures 4a, b) which could be due to absence of annealing treatment while in sample 6, the majority QD size are found to be of 10 nm (figures 4c, d) by annealing after LPCVD. The reason for small size obtained is explained above using AFM results. It is

observed that RTP prior to LPCVD results in increase in size of Si QD which is nearly 16–18 nm in case of sample 7 (figure 4(e and f)). Reason could be due to RTP, number of Si–OH bonds gets reduced due to the removal of water molecules resulting in the decrease of nucleation sites and hence small increase in the size of QD.

3.3b Effect of RTP on formation of QD: SEM images of samples 7, 8, 9 and 10 are shown in figure 4(e, g, h and i), respectively. It is observed that RTP prior to LPCVD (sample 7) can be used to control the density and size of QDs. Annealing is not done for sample 8 resulting in large size of QD formed in comparison with other samples (figure 4(g)). RTP carried out after LPCVD in case of samples 9 and 10 is not enough to convert Si thin film into discrete QD (figure 4(h and i)), this may be due to less time available for recrystallization for rearrangement of Si atoms.

Thus, sample undergoing argon annealing after LPCVD results in uniform QDs as compared to sample undergoing RTP after LPCVD. But RTP prior to LPCVD can be used to get required size and density of QD.

3.4 Photoluminescence spectra of sample

3.4a Effect of annealing on formation of QD: When samples 5 and 6 are excited with wavelength of 352 nm (figure 5), emission spectrum is observed at wavelengths of 388, 438 and 471 nm in the former which indicates varying QD

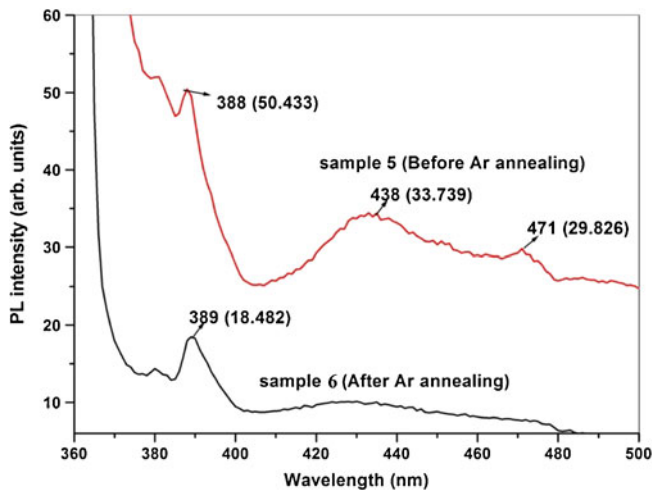


Figure 5. PL spectrum showing effect of Ar annealing on size distribution of QD.

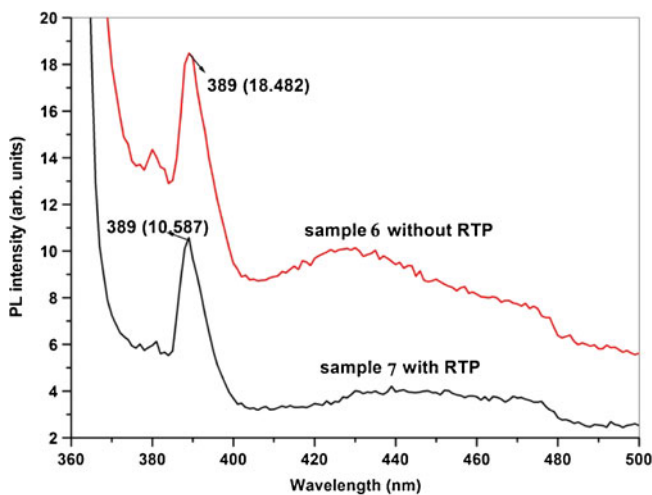


Figure 6. PL spectrum showing effect of RTP on density of QD.

size distribution since the sample is not annealed, whereas latter shows emission only at 389 nm indicating uniform-sized QD. This can be confirmed from QD size distribution histograms of samples 5 and 6, respectively (figures 4b and d). In case of sample 5, majority QD formed are in the range 10–13, 14–17 and 18–21 nm corresponding to emissions at 388, 438 and 471 nm wavelength. In case of sample 6, majority of QD are in the range 10–12 nm and hence shows emission only at 389 nm. Overall larger QD (>20 nm) gets converted into smaller dimension in the range 10–20 nm because of re-crystallization at high temperature annealing. Annealing decreases the stress developed during the deposition of Si thin film on SiO₂ substrate.

3.4b Effect of RTP on formation of QD: The photoluminescence spectra (figure 6) of samples give similar information as SEM images (figures 4c and d). PL intensity of sample 6 is greater than sample 7 which indicates that the

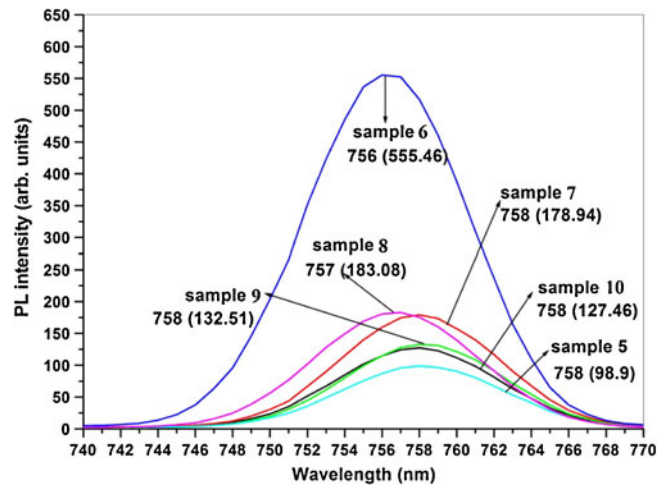


Figure 7. Comparative photoluminescence study of samples prepared by LPCVD (excitation wavelength: 500 nm).

density of QD in sample 6 is higher than sample 7. The decrease in density due to RTP in case of sample 7 is because of decrease in Si–OH bonds/silanol groups which acts as nucleation site for formation of Si QD. Adjacent silanol gets converted into Si–O–Si and water molecule resulting in the reduced nucleation sites which in fact decreases density of QD. As the quantity of QDs increases, the number of electron hole pair recombination on silicon surface also increases (Qin and Jia 1993) which increases the intensity of PL spectra. Blue shift is observed due to decrease in wavelength in case of sample 6 which indicate decrease in QD size in comparison with other samples (figure 7). The smallest QDs of dimension 10–12 nm are formed in case of sample 6 (figures 4c and d) which is similar to results obtained by Fauchet (1996).

4. Conclusions

Surface treatment given to SiO₂ substrate develops Si–OH bonds which act as nucleation sites to increase the density of Si. Argon annealing results in small size uniform QDs. RTP decreases the density and increases the size of QD as compared to that obtained by annealing. The blue shift observed in PL spectra indicates the decrease in size of QD. The emission spectra observed in red frequency region indicates that quantum confinement takes place in sample and confirms the formation of Si QD. Hence QDs fabricated using present process can be adopted in electronic devices manufacturing for performance enhancement.

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