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New Si-based multilayers for solar cell applications

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Abstract

In this article, we have fabricated and studied a new multilayer structure Si-SiO$_2$/SiN$_x$ by reactive magnetron sputtering. The comparison between SiO$_2$ and SiN$_x$ host matrices in the optical properties of the multilayers is detailed. Structural analysis was made on the multilayer structures using Fourier transform infrared spectroscopy. The effect of specific annealing treatments on the optical properties is studied and we report a higher visible luminescence with a control over the thermal budget when SiO$_2$ is replaced by the SiN$_x$ matrix. The latter seems to be a potential candidate to replace the most sought SiO$_2$ host matrix.

Introduction

The third generation of solar cells aims at reducing the cost and at improving the efficiency. Thin film solar cells based on silicon nanostructures is one of the most researched system to achieve such a target [1-3]. Ever since the discovery of the visible luminescence of the porous Si by Canham [4] various research groups have exploited the room temperature photoluminescent nature of silicon by fabricating different kinds of Si-based nanostructures. The luminescence is attributed to the quantum confinement of carrier in Si-nanoclusters (Si-nc) [5-8]. Among the methods of obtaining the Si nanostructures we cite electrochemical etching [4,9], fabrication of silicon dots by plasma sputtering technique [10], and multilayer approach [8,11,12].

The important part of the ongoing research involves Si-nc embedded in an amorphous matrix such as SiO$_2$, SiN$_x$, or amorphous silicon. Though Si-nc embedded in SiO$_2$ is the most common structure, the problem of carrier injection in this matrix comes as a major drawback owing to the large band gap of SiO$_2$. Hence the replacement of SiO$_2$ by other dielectric matrices with smaller bandgap turns out to be a solution. SiN$_x$ matrix meets up these requirements and hence Si-nc embedded in SiN$_x$ matrix has become a material of choice in the recent past. In this article, we develop a new multilayer composition silicon-rich silicon oxide (SRSO)/SiN$_x$ to overcome the insulating nature of SiO$_2$ by taking advantage of the reduced bandgap in SiN$_x$. Using SiN$_x$ as the host matrix favors the electrical conductivity of carriers while we still maintain the quantum confinement as done with the SiO$_2$ matrix. This study aims at fabricating and comparing the light emission properties of three different kinds of multilayer compositions: (a) SRSO/SiO$_2$, (b) SRSO/SiN$_x$, (c) SiN$_x$/SiO$_2$. Such a study is important to understand the influence of host matrices on the Si-nc and consequently to achieve an optimized solar cell device in the future.

Experimental details

Three kinds of multilayer structures were fabricated on 2" Si wafer by reactive magnetron sputtering comprising 50 patterns of SRSO/SiO$_2$, SRSO/SiN$_x$, and SiN$_x$/SiO$_2$. We define the gas flow rate as $r_g = f_g/(f_g + f_{Ar})$ where f_g represents the N or H$_2$ gas flow and f_{Ar} represents the Argon gas flow. The SiO$_2$ sublayer was fabricated by sputtering the SiO$_2$ cathode under pure Ar plasma. Reactive magnetron sputtering, an approach developed by our team, was used for the fabrication of SRSO sublayers. It takes advantage of the oxygen reducing capacity of hydrogen when introduced into the Ar plasma [8]. The hydrogen-rich plasma favors Si excess in the SiO$_2$ sublayer. Besides this in order to facilitate a higher incorporation of Si in the matrix, both SiO$_2$ and Si cathodes were used to fabricate the SRSO sublayer. The powers of SiO$_2$ and Si were maintained as 7.4 and 2.2 W/cm^2, respectively. The hydrogen rate r_H was maintained at 50% while the total flow $f_g + f_{Ar}$ was fixed at 10 sccm. The pressure in the chamber was chosen as 3 mTorr. Thus the SRSO/SiO$_2$ multilayer structure was deposited by an alternative reactive sputtering under hydrogen-rich plasma for the SRSO layer and pure Ar plasma for the SiO$_2$ sublayer. The SiN$_x$ layer was

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fabricated by sputtering the Si cathode and simultaneously introducing nitrogen into the Ar plasma. The nitrogen rate r_N was kept at 10% while the total flow rate was fixed at 10 sccm. The pressure in the chamber was chosen as 2 mTorr for SiN_x layers. The temperature of deposition was maintained at 500°C for all the cases. The thickness of the SRSO sublayer was fixed to be 3.5 nm in order to be within the quantum confinement regime. In order to understand the influence of SiN_x matrix, two different thicknesses of the SiN_x sublayer (3.5 and 5 nm) were chosen.

The FTIR spectra of these samples were recorded in absorption configuration using Nicolet Nexus spectrometer at Brewster's angle (65°). The photoluminescence (PL) spectra of the annealed samples were obtained in the visible range using Jobin Yvon monochromator in the wavelength range 550-1100 nm. The excitation wavelength of 488 nm (Ar laser) was used for measurements.

Results and discussions
FTIR spectroscopy
Figure 1 shows the FTIR spectra obtained for the non-annealed $SRSO/SiO_2$, SiN_x/SiO_2, and $SRSO/SiN_x$ multilayers. The spectra were recorded at the Brewster angle of 65° that enables the detection of the LO_3 mode of silica at about 1250 cm^{-1} in addition to the TO_3 mode located near 1080 cm^{-1}.

In $SRSO/SiO_2$ around 1225 and 1080 cm^{-1} we notice the LO_3 and TO_3 peak from the Si-O stretching, the TO_4-LO_4 doublet between the 1100-1200 cm^{-1} and the TO_2-LO_2 asymmetric stretching of Si-O from SiO_2 at 810 and 820 cm^{-1}, respectively [13]. The presence of Si-nc is attested by the intensity of the LO_3 peak which is representative of the Si-O bond at the interface [14]
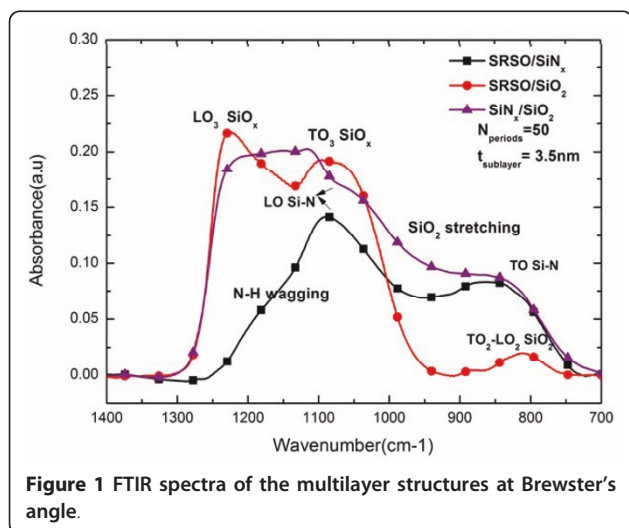
between silicon and silica while the TO_3 vibration mode at about 1080 cm^{-1} is the signature of the volumic silica.

The SiN_x/SiO_2 film has a broad peak in the 1250-950 cm^{-1} region which can be due to the contributions of both LO and TO modes from SiO_2 and Si-N stretching mode [15-17]. The absorption band located around 860 cm^{-1} could be attributed to the Si-N asymmetric stretching mode.

In the case of $SRSO/SiN_x$ films, the shoulder around 1190 cm^{-1} may be due either to N-H bond [16,18] or to a contribution of the LO_3 mode of Si-O-Si bonds at 180° [13]. Such a result is the signature of the Si nanoparticles formation within either the SiN_x [19] and/or the SRSO sublayer [13]. Between 1050 and 1070 cm^{-1} lies the LO peak of a-$Si_xN_yH_z$ from Si-N as it has been observed in the SiN_x/SiO_2 spectrum adding the contribution of the TO Si-O mode.
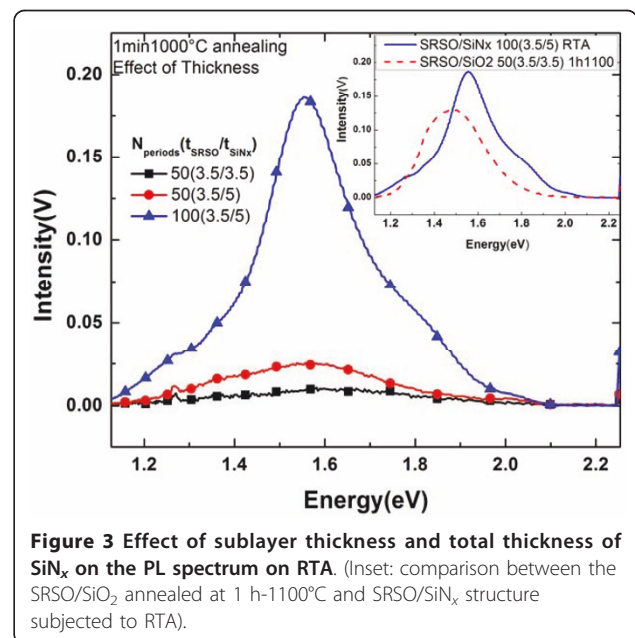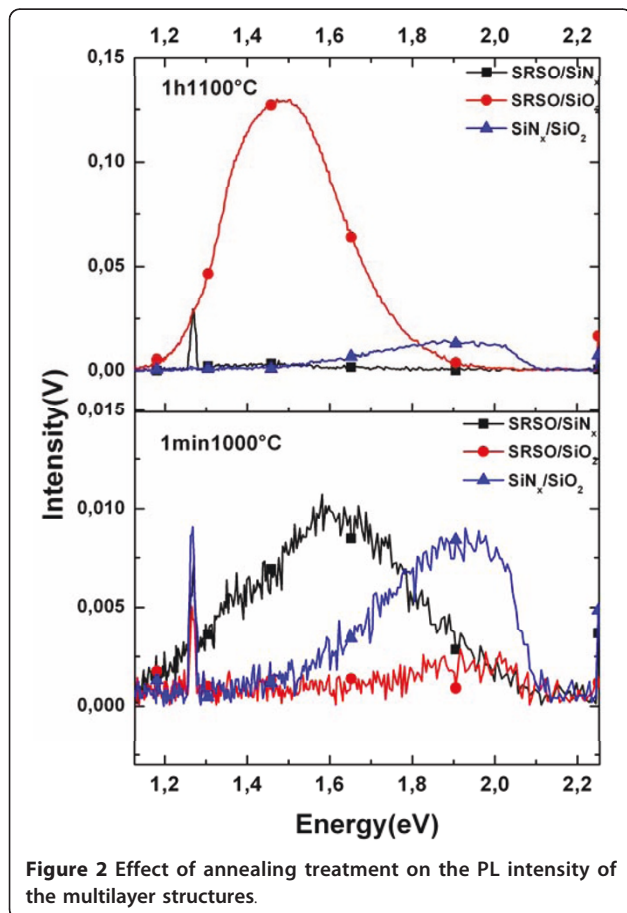
PL spectra
The PL emission spectra of the annealed multilayer structures were measured using 488 nm excitation wavelength and the spectrum was recorded in the visible range. Two different annealing treatments were chosen for the study–1 min-1000°C (rapid thermal annealing–RTA) and 1 h-1100°C under N_2 atmosphere, the latter being the classical annealing treatment used for recovering defects in SiO_2 matrix to favor luminescence from Si-nc [3]. Figure 2 shows the effect of the annealing treatment on the PL intensity of the three kinds of multilayer structures. All the curves are normalized to a total thickness of 100 nm. Since the number of periods and the sublayer thickness remains the same for each of these films, i.e., $N_{periods}(t_{sublayer1}/t_{sublayer2}) = 50(3.5/3.5$ nm), it becomes possible to make a comparative analysis from the PL spectrum of these three different multilayer structures. The interference effect in PL intensity has been investigated by the method proposed by Holm et al. [19] for all the spectra presented in this article. This method gives us the PL intensity versus layer and substrate parameters (refractive indices, thicknesses). We assume and homogenous density of emitting centers, an average refractive index within the thickness of multilayer. For measurements on Figure 2 no important change in PL has been found due to interference.

It can be noticed from the spectrum that when the multilayers are subjected to the classical annealing treatment of 1 h-1100°C, there is no emission from the $SRSO/SiN_x$ while the $SRSO/SiO_2$ structure shows a strong PL signal and has a wide range of emission spectrum. At the same time, it is interesting to note a very weak PL signal in the case of SiN_x/SiO_2. The PL peaks appear in a region usually related to the optical transitions in the SiO_2 matrix due to the presence of defects [3,17]. The lower part of Figure 2 shows the PL

Figure 1 FTIR spectra of the multilayer structures at Brewster's angle.

spectrum recorded after annealing the multilayer structures for 1 min at 1000°C (RTA). The response of the multilayers to this annealing treatment shows almost a reversed trend of what was observed in the case of classical annealing treatment. It can be noted that the SRSO/SiN$_x$ has the highest intensity. No PL emission has been recorded from the SRSO/SiO$_2$ system. We may note from the figures that the luminescence peak arising from the SiN$_x$/SiO$_2$ structure around 1.9 eV is the same whatever the annealing temperature. The fitting of the PL curve recorded from the SRSO/SiN$_x$ film evidences the presence of two emission bands centered at 1.65 and 1.37 eV. Though this result is interesting and shows the possibility of exploiting SRSO alternated with the SiN$_x$ sublayer to achieve a control over the thermal budget, it also has to be mentioned that the PL intensity obtained is one order of magnitude lower than the emission of SRSO/SiO$_2$ subjected to classical annealing. Hence, two methods of fabrication were attempted with the aim of increasing the PL intensity: (i) increasing the SiN$_x$ sublayer thickness to 5 nm and (ii) doubling the number of periods, i.e., fabricating 100 periods of 3.5 nm SRSO alternated with 5 nm SiN$_x$. Figure 3

shows the effect of the aforesaid fabrication methods on the PL spectrum of the SRSO/SiN$_x$ multilayers. All the spectra have been normalized to 100 nm thickness for comparison. The interference effect in PL intensity has been also investigated by the previously mentioned method PL intensity from both 50 periods multilayers should be decreased by about 15%, in order to take into account the enhancement effect due to maxima of interference. The first method adopted reveals that the SiN$_x$ thickness has some significant contribution toward the luminescence. There is a slight change in the emission wavelength from 1.59 eV with 3.5 nm SiN$_x$ sublayer to 1.55 eV in the case of 5 nm SiN$_x$ sublayer. Irrespective of the number of periods deposited, for a given sublayer thickness the wavelength of emission peak remained constant. It is interesting to note that the emission intensity increases with the SiN$_x$ thickness. This result motivated toward trying out the second method mentioned and it can be noticed that the PL signal increases 7.4 times when the number of (3.5 nm)SRSO/(5 nm) SiN$_x$ pattern is increased from 50 to 100. For that case one can notice is the presence of a small peak between 1.90 and 1.65 eV and another one around 1.5 eV. The inset in Figure 3 shows a comparison between the SRSO/SiO$_2$ annealed at 1 h-1100°C and SRSO/SiN$_x$ structure subjected to RTA. One can notice that the emission peak from the SRSO/SiN$_x$ system shifts in the visible region and this is one of the advantageous aspects for the solar cell application. It is very interesting to note that the SRSO/SiN$_x$ annealed for a very short time of 1 min at 1000°C is 1.43 times more intense than the SRSO/SiO$_2$ structure annealed for a

Figure 2 Effect of annealing treatment on the PL intensity of the multilayer structures.

Figure 3 Effect of sublayer thickness and total thickness of SiN$_x$ on the PL spectrum on RTA. (Inset: comparison between the SRSO/SiO$_2$ annealed at 1 h-1100°C and SRSO/SiN$_x$ structure subjected to RTA).

long time of 1 h and at higher temperature. Accounting for the interference effect, we can infer that SRSO/SiN$_x$ exhibits higher PL intensity than SRSO/SiO$_2$. Thus, it can be seen that a replacement of the SiO$_2$ sublayer by the SiN$_x$ sublayer and alternating it with the SRSO sublayer not only favors luminescence but paves way to achieve a control over the thermal budget.

Discussion

The PL spectra of the SRSO/SiN$_x$ subjected to two different annealing treatments show that the quenching of the PL signal after an RTA can be attributed to the non-radiative defects either at the interface of Si-nc and the SiO$_2$ matrix or within the SiO$_2$ matrix itself which traps the photon arising from the recombination of the exciton within the Si-nc. On the contrary, it can be seen that the SiN$_x$ sublayer favors luminescence even if this later could be attributed to the defects in the matrix. Noticing the shift in emission peak from 1.9 to 1.6 eV in the case of SiN$_x$/SiO$_2$ and SRSO/SiN$_x$, respectively, it can be said that the sandwiching of SRSO between SiN$_x$ instead of SiO$_2$ sublayers not only favors luminescence but also exhibits luminescence in a region attributed to the emission from Si-nc. This implies that though at this temperature SiN$_x$ shows a defect-related PL, when alternated with SRSO, the emission from Si-nc becomes dominant.

On the other hand, the quenching of PL in classically annealed SRSO/SiN$_x$ is quite surprising as several authors have noticed an increase of the PL signal either from SRSO or SiN$_x$ after such annealing. It also should be noted that the 'SRSO sublayer' fabricated under the same conditions and alternated with SiO$_2$ sublayer has a high emission. Hence one can conclude that the presence of the SiN$_x$ sublayer quenches the PL. This can be attributed either to the coalescence of Si clusters at such an annealing treatment thereby overcoming the quantum confinement regime or to the non-radiative defects at the interface between SRSO and SiN$_x$ or in SiN$_x$. The increase of the PL emission when increasing the number of layer could be the result of H diffusion during the deposition process which favors the recovering of the defects and the Si nanoparticles formation. Such a hypothesis is supported by the presence of N-H bonds revealed by FTIR experiments in the non-annealed multilayers and that can be attributed to the Si-nc formation [17]. Another explanation could be the increase of strain with the number of layer that favors the Si-np formation resulting in an increase of the Si-np density and hence in the PL emission. However, the comparison in the inset of Figure 3 of the two types of multilayers demonstrates the advantage to replace the SiO$_2$ sublayer by the SiN$_x$. HRTEM experiments are in progress to understand the optical behavior of these multilayers.

Conclusion

The multilayers were fabricated using the sputtering technique and the FTIR spectrum revealed its characteristic peaks. Although SiO$_2$ is the most sought host matrix, we evidenced the interest of replacing it with the SiN$_x$ matrix. A higher intensity of PL emission was obtained for RTA when SiN$_x$ matrix was used whereas from the SiO$_2$ matrix there was no considerable intensity at such an annealing treatment. We have achieved comparable intensity of emission within one minute of annealing and at a lesser temperature, in comparison to the classical annealing treatment that is done for longer time and slightly higher temperature. We also observe an increase in the PL emission with increase in the number of periods. High-resolution electron microscopy experiments are in progress to understand the effect of the annealing process on the achieved optical properties. This set of above-mentioned results paves the way for the fabrication of novel structures for solar cell device applications similar to the one recently reported by Di et al. [20].

Authors' contributions
RPN fabricated the multilayers under investigation and carried out the characterization studies.CD and JC made significant contribution to the optical properties and interference effect. FG conceived of the study and participated in the coordination and writing of the manuscript. All authors read and approved the final manuscript.

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