PECVD IN-SITU GROWTH OF SILICON QUANTUM DOTS IN DIELECTRIC MATRIX FOR THIRD GENERATION PHOTOVOLTAICS

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Abstract

Silicon nanostructures have interesting possible applications in third generation photovoltaics. The fabrication techniques for Si quantum dots in dielectric matrix usually involve a high-temperature post-deposition annealing. Here we report on the spontaneous growth of silicon quantum dots in silicon nitride films by plasma enhanced chemical vapour deposition (PECVD) at 300°C using two different gas mixtures. Room temperature photoluminescence (PL) has been observed, and tuning of PL emission has been demonstrated by adjusting the gas flow rates. The effect of the strongly absorbing Si nanostructures in the silicon nitride matrix on the absorption properties has been also investigated.

1. Introduction

At present the multiple-junction approach to Third Generation PV concepts seems to be the most mature strategy to obtain efficiencies exceeding the Shockley-Queisser limit, since already used in spacecraft PV applications and in amorphous silicon thin-film modules.

The strategy of realizing an all-silicon tandem cell based on the use of artificially nanoengineered silicon is intensively studied [1-4]. Silicon quantum dots can be grown by several methods. A well-established approach, which allows also for improved size uniformity, consists in depositing of alternating layers of stoichiometric matrix (such as silicon oxide, nitride or carbide) and a silicon-rich form of the same material and subsequent annealing of the films at high temperature (≥1100°C) [1-4]. However, quantum confinement effect has been reported also in silicon nanostructures spontaneously grown in silicon nitride by PECVD at 300°C in-situ (with no need of post-deposition high temperature annealing) [5, 6].

Our idea is to test this route as a possible way to realize innovative materials for photovoltaics. The use of an abundant, non-toxic and not-too-expensive material, such as silicon, on one side, and thin film deposition techniques on the other, makes this approach, in principle, compatible with large scale implementation of photovoltaics. In addition, a low temperature process allows for use of low cost substrates and classical thin film silicon solar cell architecture. Essentially, tuning of energy gap in a useful range, appropriate absorption coefficient and relatively high electrical conductivity values have to be demonstrated, in order to have a suitable absorber layer. Also the down-converter potentialities of this material, as a consequence of the luminescence properties, deserve to be explored [7, 8], for the eventual straightforward implementation of this innovative concept within industrial crystalline and multicrystalline solar cells, where SiN_x is already largely used as antireflection coating.

In this paper, we present our results for two series of non-stoechiometric silicon nitride samples obtained via PECVD at low temperature (300°C) by using two gas mixtures. Structural, optical, and photoluminescence properties are discussed. Indirect evidence of spontaneous formation of amorphous Si quantum dots is reported.

2. Experimental

Silicon nitride films have been grown by Plasma Enhanced Chemical Vapour Deposition (PECVD) at 13.56MHz on glass, quartz and c-Si substrates using two different gas mixtures: silane and nitrogen in one case and silane and ammonia diluted in nitrogen in the other. The two types of samples will be called nitrogen-type and ammonia-type (or N_2-type and NH_3-type), respectively, in the text. The electrode configuration consists of a 13 x 13 cm^2 powered electrode and an 11 x 11 cm^2 substrate carrier as the grounded electrode. The inter-electrode distance is kept at 17 mm, and the gas supply is of simple cross-flow geometry.

The effect of changes in gas flow rates has been explored in low power regime (0.3 W). The substrate temperature has been set to 300°C. For the first type of samples a 0.2 sccm SiH_4 flow rate has been used, whereas the N_2 flow rate has been varied in the range 8 - 180 sccm. In the other case, a fixed flow rate for SiH_4 and N_2 (2 sccm and 40 sccm, respectively) and a variable flow rate for NH_3 in between 1.5 and 9 sccm have been used. For both types of samples the large N_2 flow rate serves to dilute the gas mixture, while its change in the first case and the variable NH_3 flow rate in the other case allow controlling silicon content in the layers. Depending on the deposition conditions, growth rate values in between 0.4 and 0.7 Å/s have been obtained for the samples grown with N_2. Larger values, in between 1.2 and 1.5 Å/s have been obtained in the other case, due to the larger silane flow rate and the use of ammonia, easy to dissociate. The thickness of the films, evaluated with a step profiler, has been kept around 200 nm.

The refraction index of the films has been evaluated by using a Jobin-Yvon UVISEL phase-modulated ellipsometer. Absorption spectra have been extracted from optical reflectance and transmittance measured with a UV-VIS-NIR Perkin Elmer λ-900 spectrophotometer. Raman spectra have been obtained using a Renishaw inVia Reflex Raman microscope functioning in backscattering configuration using the 514 nm line of an Ar^+ laser. PL emission at room temperature has been excited by using the 325 nm line of a He-Cd laser source. The photoluminescence spectra were collected by an optic guide and registered in the VIS range by a calibrated CCD spectrometer (OCEAN-OPTICS S2000). The PL and ellipsometric measurements have been performed on the samples grown on c-Si substrates, while the films deposited on glass or quartz plates have been subjected to structural characterization and UV-visible absorption spectroscopy.

3. Results and discussion

It is well known that absorption coefficient and refractive index of SiN_x can be customized by varying the stoichiometry through a simple adjustment of the deposition conditions. Larger silicon content in the sample can be expected when N_2 or NH_3 flow rate is decreased, due to larger silane partial pressure in the precursor gas mixture. Our samples deposited on glass/quartz substrate change from highly transparent to yellowish color when lowering the nitrogen flow rate. Correspondingly, the refraction index at 633 nm varies from 1.9, typical of stoichiometric PECVD hydrogenated silicon nitride [9], to 2.3, typical of silicon rich silicon nitride, thus evidencing increasing silicon content in the films.

All the samples show room temperature luminescence in the visible range. The PL spectra are characterized by one clear emission peak (a double peak is observed only for the sample grown with the highest N_2 flow rate), with much stronger intensity registered for NH_3-type samples (inset to Fig. 1b). The evolution of PL peak position and integrated PL intensity is shown in Figs. 1 and 2, respectively. When changing the stoichiometry of the films, a blue-shift is observed for decreasing silicon content, realized by increasing the N_2 flow rate (a) or the NH_3 flow rate (b).

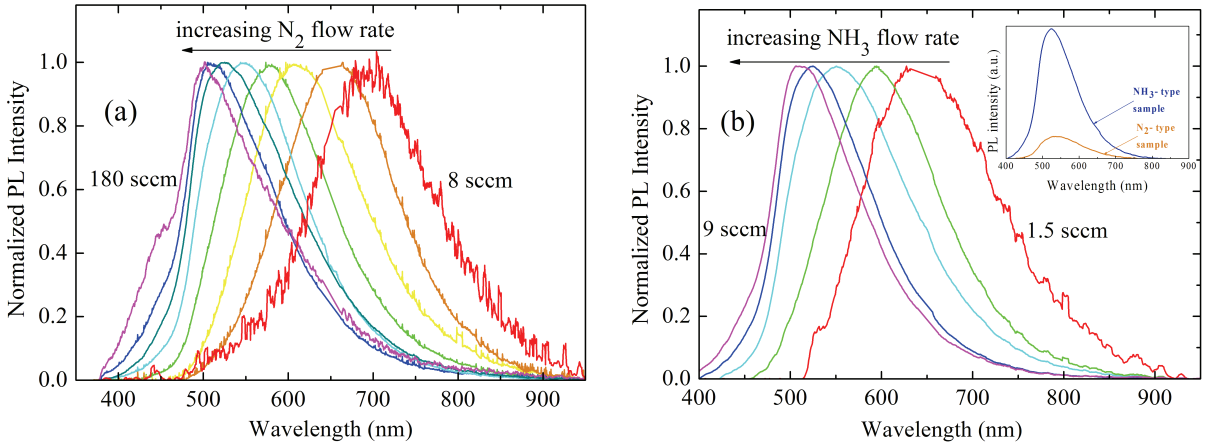


Fig. 1. Normalized PL spectra for N_2-type (a) and NH_3-type (b) samples. Inset: comparison of samples with maximum PL intensity within each series (same measurement conditions).

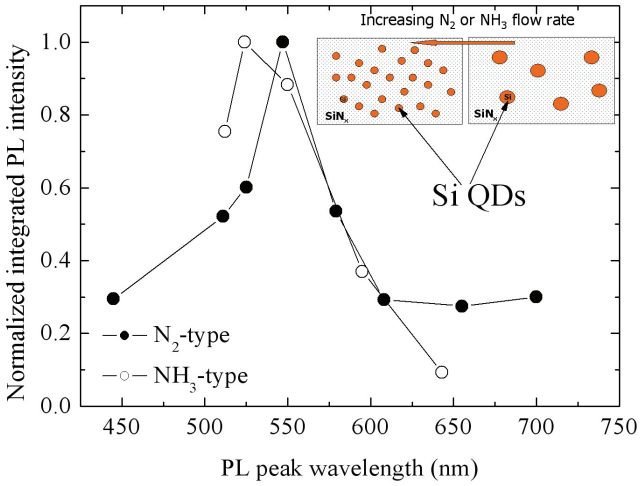


Fig. 2. Normalized integrated PL intensity for N_2-type (solid symbol) and NH_3-type (open symbol) samples. Inset: Schematic of the in-situ growth of Si QDs with different gas flow rates.

The origin of PL in SiN_x films is still an object of debate. The freely controllable dependence of the PL peak position on nitrogen or ammonia flow rate should rule out the possibility of PL emission from radiative defects in the silicon nitride matrix observed around well defined energy values [10].

It has been claimed that inhomogeneous growth, with spontaneous aggregation of Si quantum dots in silicon nitride matrix, is promoted in the low deposition rate regime by formation of Si dangling bonds acting as nucleation sites [11]. In particular, the increase of N_2 or NH_3 flow rate (at fixed SiH_4 flow rate) influences size and density of Si QDs by enhancing the creation of such sites, and then favouring the realization of densely packed but smaller silicon clusters around them (inset to Fig. 2). In this picture, the PL peak blueshift with increasing N_2 or NH_3 gas flow rate (Figs. 1a and 1b) can be interpreted as an evidence of the enlargement of the energy gap of the Si dots as their size decreases.

On the other hand, the presumed variation of dot density as the deposition conditions are varied (as an effect of varied number of nucleation sites) can give an explanation to the observed change of the PL peak intensity (Fig. 2). Less intense luminescence is indeed found

with samples grown with low N_2 or NH_3 flow rate in the mixture (condition for having few nucleation sites during the film growth). Larger intensities are found for intermediate values, while for higher flow rates the response decreases again: with very low silane partial pressure and many Si dangling bonds there are not enough Si atoms that can aggregate around all the nucleation sites [8].

Finally, the explanation in terms of quantum confinement effect could fit our case. Direct evidence of presence of quantum dots by TEM analysis in samples obtained with similar growth conditions has indeed been reported in literature [5, 6].

The presence of a large number of silicon dangling bonds, when high N_2 flow rate is used, could explain the presence of the double luminescence peak observed in Fig. 1a for the sample grown with the highest N_2 flow rate (180 sccm), where the peak around 500 nm (~2.5 eV) could be associated to radiative recombination at metastable silicon dangling bonds located about midgap [10]. The highest energy peak could be related to very small silicon dots; however, the large intensity of the 2.5 eV peak implies a very defective material.

We have employed Raman spectroscopy to obtain information about the presence of silicon nanocrystals within the silicon nitride matrix (Fig. 3). Crystalline structure, favoured by the extra hydrogen dissociated from the NH_3 gas, has been reported for samples grown with ammonia [6]. In our case, a broad asymmetric band around the same wavenumbers is observed for both types of samples. The spectra can be deconvoluted with a contribution around 450 cm^{-1}, assigned to the asymmetric Si-N bond stretching mode, and another contribution slightly above 480 cm^{-1}, due to localized phonon modes in amorphous silicon [12]. Possible presence of amorphous dots can then be deduced in both cases. Since the same region of the visible spectrum is spanned by the PL peak when N_2 or NH_3 flow rate is varied (Figs. 1 and 2), and no difference in structural properties can be evidenced, presumably the same dot sizes have been reproduced using the two gas mixtures in these conditions.

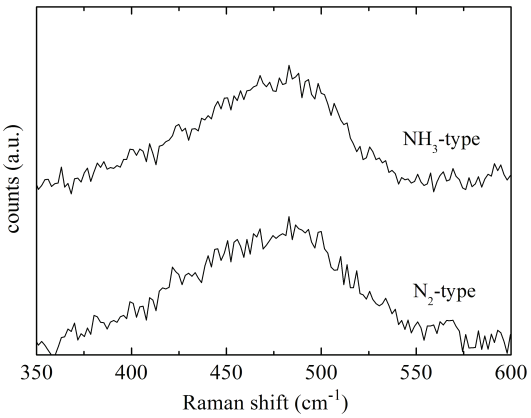


Fig. 3. Raman spectra of N_2-type and NH_3-type samples with similar PL peak energy.

While the PL evolution is similar for both types of samples, the intensity is much stronger in the ammonia-type case (inset to Fig. 1b). The enhanced luminescence has been related to the extra hydrogen available during the growth process when NH_3 is used in the gas mixture [6]. The effect of this extra hydrogen would be to more efficiently passivate nonradiative defect centers at the surface of the silicon dots.

The presence of strongly absorbing Si nanostructures in the silicon nitride matrix should also manifest in the optical absorption spectra. If phase separation into strongly absorbing Si regions in transparent silicon nitride matrix is assumed, as opposed to a random bonding picture, where Si-Si and Si-N bonds are homogeneously dispersed throughout the alloy, enhancement of the low energy optical absorption and drastic reduction of the energy gap is predicted [13].

The two types of samples are characterized by similar absorption properties. In general, the absorption of our films decreases in magnitude and shifts towards higher energies as the silicon content in the films is reduced (Fig. 4), as expected since the weakly absorbing Si-N bonds gradually replace the strongly absorbing Si-Si bonds. Two absorption spectra for each type of samples are shown in the figure, characterized by similar refraction index (2.0

and 2.3) and photoluminescence response (PL peak energy, E_{PL}, around 1.90 and 2.35 eV). The experimental data are reported together with the absorption curves of a 200 nm thick PECVD grown a-Si:H film and tabulated Si_3N_4 [14], shown for reference. The curves look almost the same, with a behaviour in between the a-Si:H and tabulated Si_3N_4 curves. With $n \sim 2.0$, not far from stoichiometric case ($n \sim 1.9$ for hydrogenated material), the absorption spectra are already very different from the Si_3N_4 curve. The main difference is in the low energy side of the spectrum, where the curve seems to be pulled toward the a-Si:H spectrum. Using E_{02}, the energy value at which the absorption coefficient is 10^2 cm^{-1}, as an estimate of the absorption rising edge of the material, a value very close to the PL peak energy is obtained in all cases (the average difference is $E_{02} - E_{PL} \sim 250$ meV) (Fig. 4 and ref. [15]). This result can be interpreted as an effect of the presence of Si nanostructures in the material.

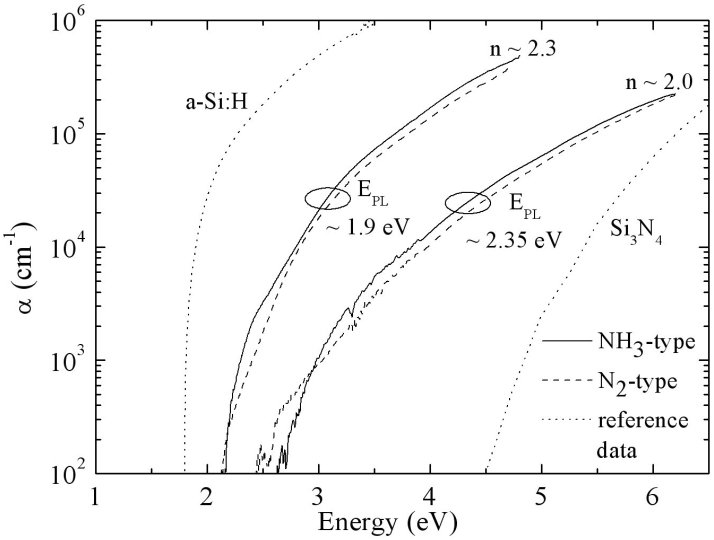


Fig. 4. Absorption coefficient for N_2 (dashed lines) and NH_3-type samples (solid lines) characterized by similar refraction index, n, and PL peak energy, E_{PL}. The absorption curves of a PECVD grown a-Si:H film, and tabulated Si_3N_4 [14] are also shown for reference (dotted lines).

4. Conclusions

Silicon rich silicon nitride films have been deposited by plasma enhanced chemical vapour deposition (PECVD) at low temperature (300°C) using two different gas mixtures, composed of silane and nitrogen with and without ammonia. Visible photoluminescence (PL) is observed in all cases, and tuning of PL emission is demonstrated by adjusting nitrogen or ammonia flow rates. Shift and intensity evolution of the PL spectra are ascribed to size and density change of silicon quantum dots spontaneously formed in the silicon nitride matrix, while the deposition parameters are varied. Presence of amorphous silicon aggregates can be inferred through Raman spectroscopy for both types of samples. Optical absorption spectra are also influenced by the inhomogeneous structure of the material with the strongly absorbing silicon nanostructures pulling the rising edge towards low energy. The main difference between the two types of samples is the much stronger PL observed for ammonia-type layers, most probably caused by improved passivation of nonradiative defect centers at the dot-matrix interface, thanks to the extra hydrogen available during the material growth. Moreover, in this case the films are grown at an interestingly higher deposition rate. Such results contribute to give strength to the low temperature in-situ method for growing Si nanostructures, with some ad-

vantages when using silane, nitrogen and ammonia as process gases. We want to stress that the absence of a post-deposition annealing makes this growth technique very powerful for the application of nanostructured materials within multilayered devices, such as innovative solar cells. In particular, third generation concepts would be feasible also on low cost substrates.

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