Annealing Effects on PECVD-grown Si rich aSiNx Thin Films

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Abstract

We report on the effect of the annealing temperature (range 600-1100°C) on amorphous silicon-rich nitride films deposited by PECVD at 300°C. The evolution of Raman spectra, room temperature photoluminescence, and optical absorption has been investigated on samples with different stoichiometry. Evidence of partial phase separation, with silicon-rich and nitrogen-rich regions, in the as-grown material has been inferred, with the thermal treatments inducing further reorganization of the two phases. Nucleation of silicon nanocrystals has been detected only after the highest temperature treatment on the sample with larger silicon content.

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1. INTRODUCTION

A great deal of interest is nowadays focused on silicon nanostructures because of their emission properties in the visible range at room temperature, which could lead to promising applications for optoelectronics devices [1]. Indeed, even if silicon has an indirect gap and low PL efficiency, significant light emission is observed from silicon nanocrystals, where the selection rules for optical transitions, deriving from translational symmetry, are broken, and at the same time non-radiative rates are reduced [2]. Moreover, due to quantum confinement, the enlargement of the gap moves the light emission to the visible range.

Along with the emission properties, the absorption of Si nanostructures might prove useful. The possibility of engineering new materials with tailored band gap, which absorb photons in dedicated energy ranges, by assembling Si quantum dots within appropriate dielectric matrices, can be exploited in the photovoltaic field, to implement the so-called third generation tandem solar cells [3]. Si nanoparticles embedded in a matrix, as a consequence of their...
luminescence properties could also in principle be adopted in solar devices for a more efficient use of high energy photons through a down-conversion process [4,5].

Here, the possibility of producing such kind of material (in particular Si QDs in silicon nitride matrix) by Plasma Enhanced Chemical Vapor Deposition (PECVD) followed by mild temperature annealing is investigated, in view of a possible implementation of such innovative materials within classical thin film silicon architectures on low cost substrates. Amorphous Si-rich silicon nitride films have been deposited by PECVD at 300°C. After deposition, a series of annealing treatments has been performed at increasing temperature values. Changes of photoluminescence, optical, and microstructural properties have been investigated, searching for evidence of thermally induced nucleation of Si quantum dots in the material.

2. EXPERIMENTAL

Silicon nitride films have been grown by PECVD at 13.56 MHz on quartz and c-Si substrates using silane and nitrogen as reactant gas sources at fixed pressure, power and temperature (500 mTorr, 0.3 W and 300 °C respectively). In a previous work, optical and photoluminescence properties vs. [N2]/[SiH4] gas flow rate ratio of as-grown samples have been investigated [6]. Here, two gas flow ratios (40, 150) have been selected in order to have samples with different refraction index values and then different silicon content. The thickness of the films, evaluated with a step profiler, has been kept around 200 nm. Short post-deposition annealing treatments have been applied using a rapid thermal annealing furnace in nitrogen flow. Increasing annealing temperatures (T_a) and, correspondingly, shorter times have been set [(600°C, 10 min); (700°C, 10 min); (800°C, 5 min); (1050°C, 3 min)]. The highest temperature has been applied again two more times consecutively for a total of 7 min, reaching 10 min in the overall at 1050°C. A final annealing step at 1100°C for 1 hour in N2 atmosphere in a conventional tube furnace has been also performed.

Absorption spectra have been extracted from optical reflectance and transmittance measured with a UV-Vis-NIR Perkin Elmer λ-900 spectrophotometer. The refraction index of the films has been evaluated from the interference fringes in the transmittance spectra located around 600-700 nm. Photoluminescence (PL) emission at room temperature has been excited by using the 325 nm line of a He-Cd laser source. 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. The incident power was kept low to avoid crystallization and distortion of the spectra due to laser heating. The PL measurements have been performed on samples grown on c-Si substrates, while the films deposited on quartz plates have been devoted to Raman characterization and UV-visible absorption spectroscopy.

3. RESULTS AND DISCUSSIONS

It is well known that the refractive index, n, of SiNx can be customized by varying the stoichiometry through an adjustment of the reactant gas source flow rates: Larger silicon content in the sample can be expected when the N₂ flow rate is decreased, due to the larger silane partial pressure in the precursor gas mixture [6]. The refraction index evaluated in the 600 – 700 nm range (see Table 1) is 1.89, which according to literature should mean roughly a stoichiometric sample [7], for the film grown with more nitrogen (called sample S in the following), and 2.18, typical of silicon rich silicon nitride, in the other case (called sample NS in the following).

Table 1 Deposition conditions and properties of the as-grown samples (refraction index, n, photoluminescence peak position, E_PL, bandgap energy, E_g, evaluated through Tauc’s plot, energy corresponding to α = 10³ cm⁻¹, E_α).

| Sample | [N₂]/[SiH₄] | n  | E_PL (eV) | E_g (eV) | E_α (eV) |
|--------|-------------|----|-----------|----------|----------|
| S      | 150         | 1.89| 2.0       | 3.1      | 2.90     |
| NS     | 40          | 2.18| 1.85      | 2.5      | 2.34     |
The two as-grown samples show room temperature photoluminescence peaked at 2 eV and 1.85 eV, for the S (in principle stoichiometric) and NS (non-stoichiometric) films respectively (see fig. 1 and Table 1). The hypothesis of inhomogeneous growth of silicon nanostructures in the silicon nitride matrix in this deposition regime has been previously proposed, with different Si cluster sizes and density according to the precursor gas flow ratio [6], as firstly reported in ref. [8]. Quantum confinement of excitons in such silicon dots could then explain the PL emission, with the PL peak blueshift caused by the dot size reduction. On the other hand, the systematic PL evolution with controlled changes in stoichiometry can be also interpreted within the band-tail states model [9]. In this case the luminescence is ascribed to radiative recombination of carriers that thermalize in the conduction and valence band tails, and the PL peak shifts following the enlargement of the bandgap when the concentration of alloying N atoms is raised. Such interpretation has also been applied to non-homogeneous films composed of a mixture of silicon-rich phase, having lower gap, and nitrogen-rich phase, having higher gap [10]. In this picture the carriers, essentially spatially localized in low gap domains, would recombine through the band tail states of the silicon-rich phase.

The evolution of the normalized PL intensity with T_A is shown in Fig. 1. A redshift is observed with the increase of T_A up to 800°C essentially only for sample NS. Above this temperature the PL of sample NS is quenched, while in sample S the PL is preserved, slightly blueshifted (the intensity after the treatment at 1100°C is, however, very low). In general, the intensities in our experiment cannot be quantitatively compared, but qualitatively there is a reduction after the higher temperature treatments (above 700°C). The differences observed for the two samples might be related to the different silicon content, with sample S only mildly Si rich.
As for the optical properties of the two samples, it should be noted that sample NS, that contains more silicon, is more absorbent (fig. 2a), as expected since, using less N₂ in the feedgas, part of the weakly absorbing Si-N bonds are replaced by strongly absorbing Si-Si bonds \([11]\). The gap energies evaluated through the Tauc procedure \([12]\) are reported in Table 1. Sample S, in principle stoichiometric, shows stronger absorption than Si₃N₄ \([13]\), with a spectrum shifted towards lower energy. This result might reveal the presence of some structural inhomogeneity within the material, according to ref. \([11]\). However, the hydrogen incorporated in the material might contribute to lower the refraction index \([7]\).

The variation of the absorption spectra after the annealing steps is shown in Fig. 2 a and b. In both cases, as \(T_a\) is raised (up to 1050°C), the band-gap energy decreases and the films become increasingly more absorbent. This could be an effect, especially for lower \(T_a\) values, of hydrogen release from the film, but also of a rearrangement of Si-Si and Si-N bonds \([10]\). After the treatment at 1100°C an inversion is observed in the medium energy range for sample NS, which is a signal of a different structural change making the material less absorbent.

The lower PL intensity after repeated annealing steps and the PL quenching in the NS sample for \(T_a\) above 800°C could be related to the large number of Si and N dangling bonds in the material, after the break of Si-H and N-H bonds in the process of hydrogen desorption, providing for non-radiative recombination channels \([10]\). As for the light emission mechanism, in the band-tail recombination picture the band-gap decrease would be an easy explanation of the PL redshift with \(T_a\) (up to 800°C). It should be said that roughly estimating the rising edge of absorption through the parameter \(E_03\) (energy at which the absorption coefficient is equal to \(10^3\) cm⁻¹), a rather large difference between the band-tail states and PL peak energy is present for our samples (Table 1). This is, however, not uncommon, with the deepest states involved in radiative recombination of photoexcited carriers after thermalization. The Stokes-shift or the static disorder model are typically invoked to explain the difference between absorption and emission data \([9]\).

The Raman spectra for sample NS after the subtraction of the substrate contribution is shown in Fig. 3. Before the annealing treatments just some signature of the presence of Si-Si bonds (bump around 480 cm⁻¹, which is the TO mode of amorphous silicon) is present in the spectrum. Appreciable changes in the Raman spectra appear only after high temperature annealing: the Raman signal strongly increases after 3 min and more after 10 min of treatment at 1050°C (the spectra have been recorded under the same conditions), while after the final step at 1100°C the intensity decreases again and a sharp peak at \(\sim 515\) cm⁻¹ appears. The spectra for sample S are not shown because no clear features are present, even after the high temperature treatments, due to the lower silicon content and the high transparency that makes the signal too low with respect to the substrate contribution.

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**Fig. 3 – Raman spectra of as-grown and annealed sample NS.**
Note that, apart from the spectrum taken after the annealing at 1100°C, the 480 cm\(^{-1}\) peak is broad and strongly asymmetric, with a tail extending towards the lower wavenumbers. The broadening of the TO mode can be explained in terms of increased disorder due to the presence of N atoms within silicon aggregates [14]. Moreover, there is most probably a contribution from the asymmetric Si-N bond stretching mode, usually located around 420-440 cm\(^{-1}\) [15].

The increase of Raman intensity after the high temperature treatment (1050°C) can be read as a structural change within the material with an increase of Si-Si bonds, probably due to a rearrangement of bonds towards a phase separated structure. Presence of silicon rich aggregates (with amorphous structure) in the film is plausible, and in minor degree is plausible even in the as-grown film. A mixture of a silicon-rich phase and a phase containing more nitrogen, as proposed in ref. [10] could be a possibility, compatible also with the PL measurements, as already discussed.

The formation of Si nanocrystals allows to explain the inversion in the trend of the absorption coefficient changes (fig. 2b), with reduced values at medium energies (2.7 - 4 eV). On the other hand, the absence of photoluminescence in sample NS after the formation of Si nanocrystals might be explained as due to the presence of a large amount of non-radiative defects.

Summarizing, phase separation, partially present already in the as-grown material, in the form of silicon-rich regions embedded in a phase containing more nitrogen, is favored by the annealing treatments at medium temperatures, but the formation of pure silicon aggregates in a matrix close to Si\(_3\)N\(_4\), accompanied by formation of small Si nanocrystals (~ 2 - 3 nm), has been obtained only after the 1 hour treatment at 1100°C, where both temperature and duration might have played a role. The influence of the structural changes on the optical properties has been evidenced, while the mechanisms governing the photoluminescence remain still unclear. The band-tail states model is compatible with all the results. At the same time, it can be argued that the presence of silicon-rich domains in a matrix containing more nitrogen implies carrier confinement in the lower gap regions. With appropriate dimensions for the aggregates the quantum confinement effect could, then, explain the luminescence [8].

In this case the PL redshift with increasing \(T_a\) values would be related to the enlargement of the aggregates. As for the absence of photoluminescence in sample NS after the final annealing step, the crystalline and amorphous Si clusters, revealed through Raman analysis, might not be separate, but rather could be merged in too large regions for quantum confinement to come into play. Finally, the slight PL blueshift observed with sample S after the final annealing step might have to do with the structural change in the Si aggregates [10], even if we have not been able to reveal the phase transition through Raman and optical data for this sample.

4. CONCLUSION

The possibility of producing Si QDs in silicon nitride matrix by PECVD followed by mild temperature annealing has been investigated in view of possible application within third generation photovoltaic devices. Amorphous Si-rich silicon nitride films have been prepared by PECVD at 300°C. After deposition, a series of annealing treatments has been performed at increasing temperature values. Photoluminescence, optical and microstructural properties have been investigated after each step, searching for evidence of thermally induced nucleation of Si quantum dots in the material. With annealing, hydrogen desorption and bond rearrangements occur in the material, probably composed of silicon-rich regions and a phase containing more nitrogen. The sample with larger silicon content shows partial crystallization of Si aggregates only after the 1 hour treatment at 1100°C, when also complete phase separation occurs. The estimated average dimension of the nanocrystals is 2.6 nm. The structural changes clearly influence the optical properties of the material that becomes increasingly more absorbent with lower band-gap energy after the various thermal treatments, because of hydrogen release and increment in Si-Si bonds. The formation of silicon nanocrystals within the material is also evident in the absorption properties. Finally, the
mechanism explaining the photoluminescence emission is not easy to sort out. An interpretation in terms of the band-tail states model could work. Quantum confinement in silicon-rich regions could be another option. Both models are compatible with the PL peak redshift with increasing annealing temperature (up to 800°C), explained in terms of the reduced band-gap energy in the band-tail state picture and with dot enlargement in the quantum confinement approach.

References

[1] L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzò, F. Priolo, Nature 408 (2000) 440, and references therein.
[2] A.P. Alivisatos, Science 271 (1996) 933.
[3] G. Conibeer, M. Green, E.-C. Cho, et al., Thin Solid Films 516 (2008) 6748–6756.
[4] V. Svreck, A. Slauj, J.-C. Muller, Thin Solid Films 451-452 (2004) 384.
[5] J.F. Lelievre, H. Rodriguez, J. de la Torre, et al., Proc. 21st European PV Solar Energy Conf., Dresden (2006), p. 1456.
[6] L.V. Meraldo, P. Delli Veneri, E. Esposito, E. Massera, I. Usatii, C. Privato, Mater. Sci. Eng. B 159-160 (2009) 77.
[7] E. Dehan, P. Temple-Boyer, R. Henda, J.J. Pedroviejo, E. Scheid, Thin Solid Films 266 (1995) 14.
[8] N.-M. Park, C.-J. Choi, T.Y. Seong, S.-J. Park, Phys. Rev. Lett. 86, No. 7 (2001) 1355.
[9] F. Giorgis, L. Buttari, L. Pavesi, Phys. Rev. B 61 (2000) 4693.
[10] M. Molinari, H. Rinnert, M. Vergnat, J. Appl. Phys. 101, 123532(2007).
[11] Z. Yin, F.W. Smith, Phys. Rev. B 42 (1990) 3658.
[12] J. Tauc, in Optical properties of solids, ed. By F. Abeles, North Holland, Amsterdam, 1970.
[13] E.D. Palik, Handbook of Optical Constants of Solids, vol. I, 1985.
[14] Y. Wang, R. Yue, H. Han, X. Liao, J. Non-Cryst. Solids 291 (2001) 107.
[15] V.A. Volodin, M.D. Efremov, V.A. Gritsenko, S.A. Kochubei, Appl. Phys. Lett. 73 (1998) 1212.
[16] J. Zi, H. Buscher, C. Falter, W. Ludwig, K. Zhang, X. Xie, Appl. Phys. Lett. 69 (1996) 200.