Characteristics of silicon nanocrystals obtained by thermal annealing of amorphous low pressure chemical vapor deposition SiN_x (x=0.12) thin film

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Abstract— **The formation of silicon nanoclusters embedded in amorphous SiN_x matrix is of great interest for optoelectronic devices such as solar cells and nanoelectronics such as thin films transistors (TFTs). In this work, we investigate the properties of silicon nanocrystals formed in annealed low-pressure chemical vapor deposition in situ nitrogen doped silicon thin film (SiN_x). Structural, optical and electrical characteristics of the thin film were studied by scanning electron microscopy (SEM), Raman spectroscopy, photoluminescence (PL) and four-point probe measurement. The results revealed a crystalline volume fraction of the annealed film exceeded 63 %, with a dominance of silicon nanocrystallites having the sizes within the range 2-4 nm and density ~$1.09.10^{12}$ /cm^2. The electrical characterization has shown a good conductor behavior of silicon nanocrystals thin film. The PL spectrum, highlights that photoluminescence of film originates from quantum confinement effects.**

Keywords-component; Silicon nanocrystals; Crystallinity; conductivity; Photoluminescence.

I. INTRODUCTION

In recent years, much research exists to improve and developed the use of silicon nanostructures embedded in an amorphous matrix in the field of optoelectronics and nanoelectronics [1-4]. These applications require an improvement of the optical and electric properties of thin films by the intermediary of quantum confinement in Silicon nanocrystals (Si-NCs) [5-7]. In this context, nanocrystalline silicon has been the subject of scientific and technological interest because of its outstanding properties such as higher electrical conductivity and greater doping efficiency [8]. In addition, the optical band gap of Si-NCs can easily be tailored to absorb sufficient amount of solar radiation, by controlling the size and density of silicon nanocrystals [9-11]. The electrical conductivity which is controlled by the crystallinity level in terms of crystalline volume fraction and crystallites size, has been widely considered of the most crucial parameters for TFT and solar cell applications [12 - 16]. A high conductivity in the film leads to better voltages and to lower series resistance in photovoltaic (PV) devices. The lower resistance results in higher fill factors in PV devices [17]. A high electrical conductivity provides high transductance of Si-NCs TFT_s and thus high performance nanoelectronic devices can be designed [18].

In this work, we deal to characterize Si-NCs formed in annealed amorphous SiN_x thin film obtained by low-pressure chemical vapor deposition (LPCVD) using a mixture between (Si_2H_6) and (NH_3). Disilane and ammonia gas mixture offers the possibility to realize different types of materials between the silicon nitride and amorphous silicon, and hence it is possible to introduce low nitrogen content necessary to obtain high silicon crystallites concentration with smaller sizes. Indeed, the excess of silicon in films allows high silicon crystallites concentration after heat treatment while the nitrogen atoms increase the disorder in the silicon network during the film deposit phase in one hand and suppress the crystallites growth during the thermal annealing process, in the other hand [19].

II. EXPERIENCE

The deposit of amorphous SiN_x (x = N/Si) thin film (thickness around 200 nm) was carried out in a conventional hot-wall, horizontal, LPCVD furnace by using Si_2H_6 and NH_3 gaseous mixture, on 10 cm, (111), oxidized (about 120 nm of oxide) silicon wafers. The deposition pressure P and the temperature deposition T were respectively fixed to 200 mTorr and 465 °C. The nitrogen content (x=0.12) was measured by ellipsometry and energy dispersive X-ray spectrometry. The film thickness was measured by ellepsometry and checked by profilometry. Thermal annealing process was performed at 1050 °C during 1 h into a conventional furnace under nitrogen (N_2) ambient.

Scanning electron microscopy (SEM) analysis of the sample was done using Philips model XL 30. The grain size distribution (GSD) and the crystalline volume fraction X_c were determined via image-processing techniques. Raman spectroscopy analysis has been carried out using a LabRAM

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Jobin -Yvon spectrometer. The excitation wave-length was the 488 nm line of an Argon laser in the backscattering configuration. The laser spot on the sample was kept at a power density low enough to avoid temperature effects (about 6 mW over the sample). The conductivity measurements of the film studied in this work, is deducted by measuring the square resistance using a probe 'Jandel', the point of this probe are aligned and spacing's. The PL was measured using a laser excitation source wavelength of 355 nm. The laser beam has a power density of 3.27 mW and a spot diameter of few mm and a resolution of 6.8 nm.

III. RESULTS AND DISCUSSION

SEM measurements were performed. Figures 1 and 2 depict, respectively, the SEM image and GSD of film annealed at 1050 °C during 1 h.

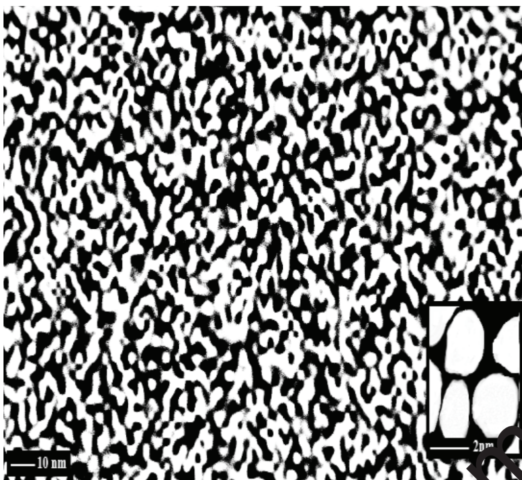

Figure 1: SEM image of $SiN_{0.12}$ after heat treatment at 1050 °C for 1 h.

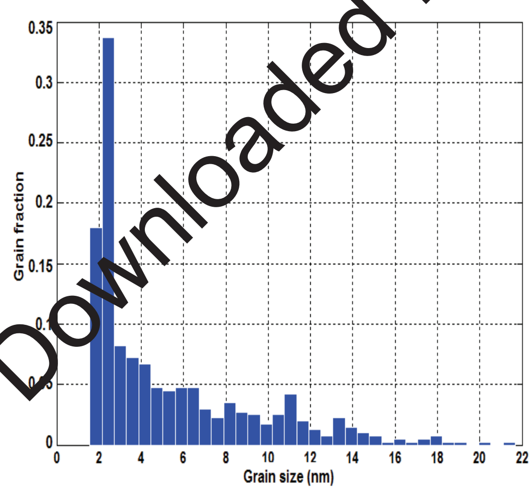

Figure 2: Histogram of grain size distribution of $SiN_{0.12}$ film annealed at 1050 °C for 1 h.

The SEM image shows clearly the crystallization of film characterized by the existence of nanocrystalline silicon (bright regions) in contrast to the amorphous matrix (dark regions in SEM image). As shown in the inset, each cluster consists of subgrains and amorphous phase between the grains. The grain size distribution and the crystalline fraction are determined by image analysis using the wavelet edge detection method [20]. The equivalent diameter g of a grain is obtained using the following expression [21]:

$$g = 2\sqrt{A/\pi} \quad (1)$$

Where A is the surface of a grain.

The crystalline fraction X_c is calculated using the following expression [22]:

$$X_c = \left(\frac{S_{crystallites}}{S_{crystallites} + S_{amorphous}} \right)^{3/2} \quad (2)$$

Where $S_{amorphous}$ and $S_{crystallites}$, represent the total crystalline area and the total amorphous area, respectively.

We calculate an average silicon crystallites size of 4.59 nm and a crystalline volume fraction X_c = 63 %. Through the analysis of GSD, it may be noted that 48 % of nanocrystallites have sizes within the range 2-6 nm, among this proportion, 85 % of the crystallites have sizes within the range 2-4 nm and density ~1.09.10^{12} /cm^2.

The formation of Si-NCs in the film after 1050 °C annealing can bee also confirmed by Raman spectrum as shown in figure 3.

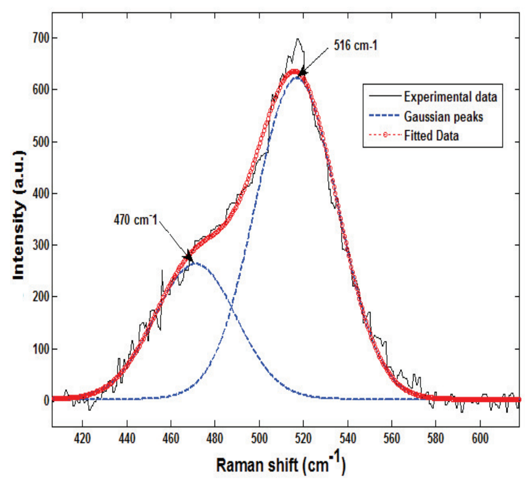

Figure 3: Deconvolution of Raman spectrum of $SiN_{0.12}$ film annealed at 1050 °C for 1 h.

The Gaussian deconvolution of experimental spectrum can be decomposed into two bands (figure 3). The Raman band observed at 470 cm^{-1} corresponds to the amorphous silicon. This band has been interpreted by the presence of small amorphous silicon clusters [23, 24]. The band centered at 516 cm^{-1} can be assigned to the crystalline silicon [24]. This clearly indicates the presence of the crystalline phase in the annealed SiNx thin film. The band associated with the crystalline silicon is shifted by 4 cm^{-1} with respect to the observed peak in the monocrystalline silicon (520 cm^{-1}). Generally, more the shift is significant; more the size of nanocrystals is small. This shift is related to phonon confinement in nanocrystals [25-26].

Note that the peak characteristic of Si-NCs is more intense than that of amorphous silicon showing a formation of a significant portion of nanocrystalline silicon in the annealed thin film. Quantitative estimation of X_c can be performed via the two Gaussian components by using the following formula [27]:

$$X_c = I_c / (I_c + \eta * I_a) \quad (3)$$

Where I_c is the Gaussian integration intensity related to crystalline composition, I_a is the integration intensity related to amorphous composition in Raman spectrum and $\eta = 0.88$ represents the fitted factor. The X_c extracted from Raman spectra is equal to 70 %. The slight difference of this value, comparing it with the data provided by SEM analysis (a difference of 7 %) can be attributed to the specificity of measurement and calculation of each method.

The conductivity value of film after heat treatment, deduced from the resistivity measurement carried out using the four-point probe method, is found to be $3.9 \cdot 10^{-1}\ \Omega^{-1}cm^{-1}$. This high value of conductivity show the high electrical quality of the obtained silicon nanocrystals film.

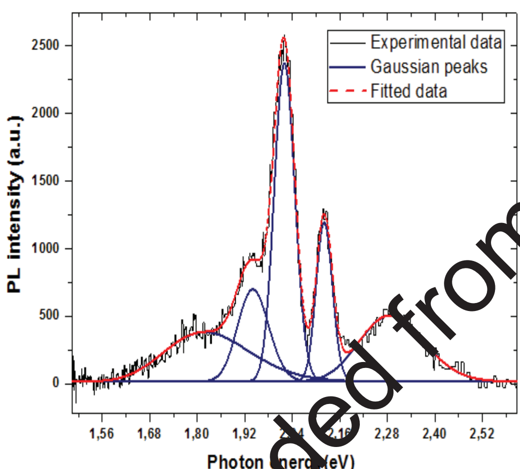

Figure 4: PL spectrum of SiN_{x} film annealed at 1050 ° C for 1 h with deconvoluting Gaussian peaks.

The PL spectrum of SiN_x film as a function of photon energy is plotted in figure 4. This spectrum shows a large luminescence energies band of 1.56 eV to 2.52 eV, with a maximum at 2.02 eV. Gaussian deconvolution of the PL spectrum clearly identifies five peaks of different energies, namely, a peak characterized at 1.97 eV related to the quantum dots in the amorphous silicon [28]. Thus, this peak can be considered to have originated from the amorphous phase contained in the silicon clusters as shown in figure 1. The peaks at energies of 1.92 eV, 2.02 eV, 2.13 eV and 2.28 eV are associated with Si-NCs quantum dots (Si-NCs QDs) due to the quantum confinement effect [28, 31]. Therefore, these peaks can be assigned to the luminescence from the crystalline phase. The PL spectrum of our film is marked by the quantum confinement effect. No PL peaks related to radiative defects were observed, probably due to the low nitrogen content introduced during the film deposit [32] in one hand and to the high temperature annealing in the other hand [33].

By using the expression proposed by Kim et al [34], it is possible to access to the size of silicon nanocrystallites knowing their luminescence energies by the following formula:

$$E_C = 1.13 + 13.9 / d^2 \quad (4)$$

Where d is a diameter of nanocrystals.

We calculate a nanocrystallites size of 3.48 nm,3.72 nm, 3.95 nm and 4.20 nm, corresponding to the PL energy 2.28 eV, 2.13 eV, 2.02 eV and 1.92 eV, respectively. Indeed, these four sizes are in the range of crystallites having the largest proportion as it has been provided by the SEM data.

IV. CONCLUSIONS

In this work, different characterization techniques were used to investigate the Si-NCs formation and properties. Results show the formation of Si-NCs after heat treatment of amorphous SiN_x, characterized by high electrical conductivity and a large crystalline volume fraction in which the largest proportion of silicon crystallites have the lowest sizes. The PL shows a broad band luminescent associated with the Si-NCs QDs. The various properties characterizing the optical and electrical behavior of the formed Si-NCs offer to the studied material large potential applications in optoelectronic and nanoelectronics fields.

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