



Deposition and annealing temperature effects on silicon carbon nitride chemical, structural and optical properties

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Abstract:

Crystalline silicon carbon embedded in amorphous silicon carbon nitride have been deposited by micro-wave plasma assisted chemical vapour deposition in HMDSN/H₂/Ar mixture by varying the deposition temperature. The deposited films have been analysed before and after annealing in Ar gas at different temperatures. The films structure and grains size have been determined by X-ray Diffraction (XRD). The films crystallinity increases and the SiC nanocrystallites embedded in the amorphous SiCN average grains size increases from 2 to 9 nm when the deposition temperature increases. The number of SiN and SiC bonds obtained by Fourier Transform Infrared (FTIR) also increase when the deposition temperature increases. High photoluminescence intensity observed in the visible decreases when the annealing temperature increases correlated probably with the SiCN nano particles and SiC nanocrystallites size and density.

Keywords: CVD; SiCN; Annealing temperature; Photoluminescence; XRD; FTIR; SEM.

1. Introduction

SiCN thin films are interesting materials combining properties of hard SiC and wide band gap SiN [1]. They have been used in many cases as hard material for wear resistance [2]. They have good resistance

to oxidation at high temperature and can be used as hard antireflection and passivative coating for solar cells [3]. SiCN has also field emission properties [4]. SiC nanocrystallites embedded in SiCN thin film are promising material due to the possibility of varying their band gap.

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So, they can be used for blue or UV optoelectronic devices such as high temperature photodetectors and High temperature sensors. Many works have been done to prove the advantages of such a material due to the wide possibility of varying the band gap between that of the pure SiC (2,3 eV) and that of SiN (5 eV). For example, Chen *et al.* [5] have proved that the optical band gap of SiCN can decrease from 4 to 3.3 eV when the carbon content in the film increases from 0 to 25 %. Bulou *et al.* [6] have also proved the possibility of Band gap decreasing when the carbon bonds increase. Otherwise, annealing SiCN film is a good way to control photoluminescence (PL) emission by controlling the SiC nanocrystallites embedded in the amorphous SiCN film [7]. In this work, we synthesized amorphous SiCN thin film containing SiC nanocrystallites by chemical vapor deposition assisted by micro-wave plasma in HMDSN/H₂/Ar gas mixture. We investigated the effects of the deposition temperature and the annealing temperature of the film's chemical, structural and optical properties. We tried to correlate films optical properties to the film crystalline structure and chemical bonds.

2. Experiment

SiCN thin films have been deposited using a micro-wave plasma assisted chemical vapour deposition (MPACVD) reactor in a

CH₄/Ar gas mixture and hexamethyldisilazane (HMDSN) vapour. The deposition process and the substrate treatments have been presented and detailed elsewhere [6, 8]. The films deposition parameters are: gas flow rate 50 Standard Cubic Centimeters per Minute (sccm) H₂, 25 sccm Ar and 0.1 g L⁻¹ HMDSN, deposition pressure 50 mbar and micro wave power 500 W. The deposition silicon substrate temperature has been varied from 350 °C to 600 °C. After deposition, the films have been annealed (fast annealing) under Ar gas at different temperature from 700 to 1100 °C. We tried another way of annealing (low annealing) in vacuum at 900 °C. According to Du *et al.* [9] it's better to anneal in H₂ gas and Xu *et al.* [10] preferred N₂ as annealing gas but in our case, we choose an inerte gas such as Ar to avoid an eventual interaction or chemical reaction during the annealing process. The surface morphology and the film thickness have been observed and measured by an Hitachi S-4800 Scanning Electronic Micrograph. The films structure is studied by XRD. Fourier Transform Infrared (FTIR) BRUKER EQUINOX 55 spectrometer was used to analyse the film chemical bonds in the range 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹. The photoluminescence of the films is analysed by a 325 nm Cd-He laser.

3. Results and discussion

3.1 Surface morphology

The SiCN thin films have been deposited at different temperature varying from 350 °C to 600 °C. The Figure 1 presents the top and cross section view obtained by SEM of two different films deposited at 400 °C and 600 °C. The Figure shows that the film deposited at low temperature has an amorphous like surface. The film is composed of big particles surrounded by nanometric particles less than 50 nm. Otherwise, the film deposited at 600 °C is only composed of nanometric particles and seems denser than that deposited at 400 °C. The nanocrystallite particles size increases and the growth seem to be oriented when the deposition temperature increases. The thickness of the films has been measured by the SEM cross-section view images. The films deposited at 350 °C, 400 °C, 450 °C, 500 °C and

600 °C have thickness equal to 580 nm, 550 nm, 525 nm, 500 nm and 430 nm, respectively. The thickness decreases as the deposition temperature increases which can be explained by the densification of the film. The spherical particles like cauliflowers observed in low temperature deposition films disappear and particles take forms like nano-crystalline particles with size increasing as deposition temperature increases. As explain by Bulou *et al.* [6], the cauliflower like morphology of films deposited at low temperature is due to the less mobility of radicals at the surface of the film at low temperature deposition. The film densification is probably due to the decreasing of the size of the cauliflower like particles and the increasing of the size of the nanocrystallites ones.

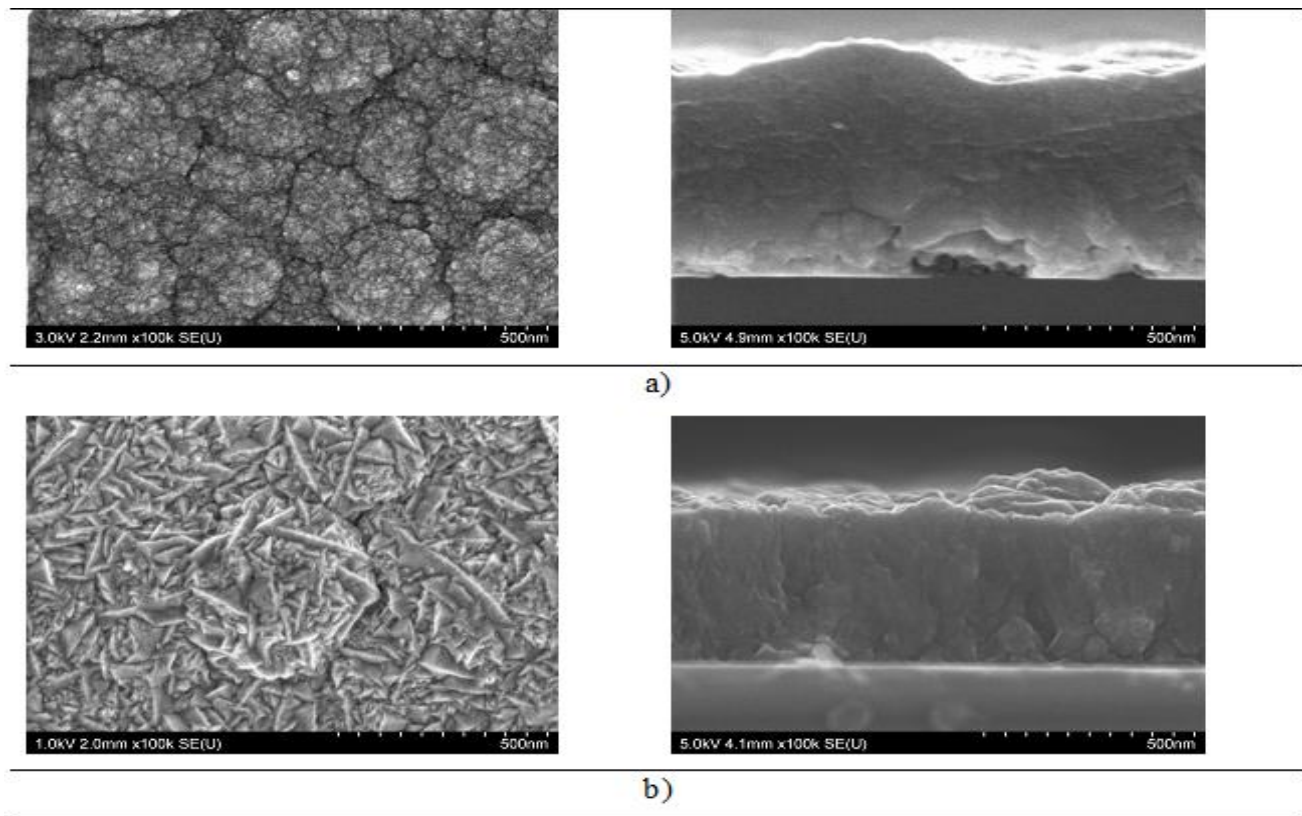


Fig. 1. Top and cross section view micrographs of films deposited at a) 400 °C and b) 600 °C.

3.2 Chemical bond characterization

The films chemical bonds have been studied by FTIR while varying the deposition and annealing temperature. Before annealing films, FTIR analyses have been made on the films deposited 1 year sooner and we observed that the films are stable and the chemical bonds have not change compared to the analyses made just after deposition one year ago. The FTIR analyses made on annealed films show an

important absorption between 600 and 1100 cm^{-1} , corresponding to SiN and SiC bonds. This large band has been decomposed into Lorenzian and Gauss peaks. The principal bonds have been reported in the Table 1.

The Figure 2 presents the normalized to thickness FTIR intensity of SiCN films deposited at different temperatures in the range 650-1000 cm^{-1} . The CH and NH bonds have not been presented here because they are not intense.

Table 1

Principal bonds observed in the SiCN film by FTIR

Wave number (cm^{-1})	Vibration mode
450	SiN symmetric stretching
650	SiC elongation
760	SiC in volum
813	SiC stretching
850	SiN asymmetric stretching
1013	SiN asymmetric stretching

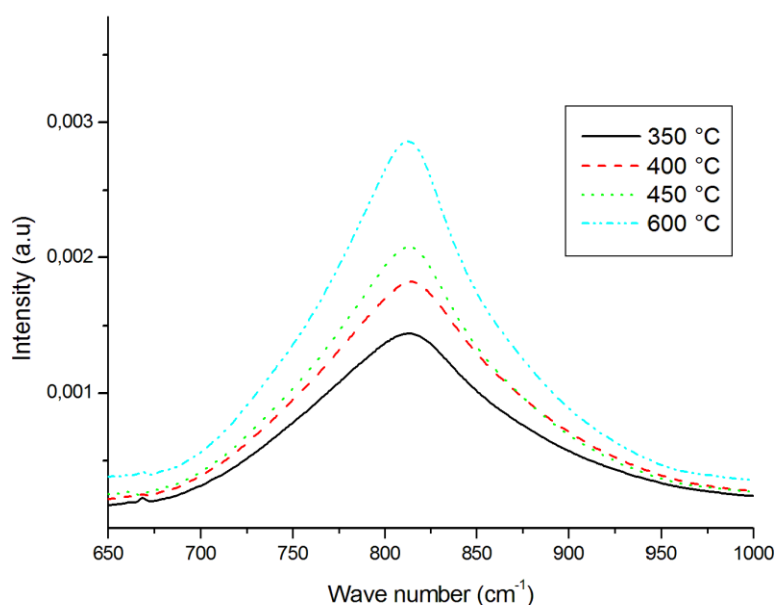


Fig. 2. FTIR spectra in the range 650-1000 cm^{-1} of SiCN films deposited at different temperature.

The Figure 2 shows that the FTIR intensity increases when the deposition temperature increases. The increasing of the intensity when the deposition temperature increases is probably due to the increasing of the absorption coefficient of the films. According to Chen *et al.* [5], the transmittance of the amorphous SiCN film decreases when the carbon content increases. No significant variation has been observed on the FTIR spectra while varying the annealing temperature.

3.3 Structural characterization

The structural properties of SiCN films deposited at different temperatures have been studied by XRD. The Figure 3 presents the XRD spectra of films deposited at low and high temperature.

This figure shows appearance of diffraction peak, meaning that the amorphous SiCN film contains crystalline phase. The crystalline phase in the films has been identified as SiC-2H phase (MPDS file N°: 1217383). The Figure shows the increasing of the diffraction intensity when the deposition temperature increases. As it has been proved by Xie *et al.* [4], high temperature deposition facilitates the presence of crystalline phases in the amorphous films. The grains size (L) of the crystallites has been determined by analyzing the XRD peak using the Scherrer equation:

$$L = \frac{k\lambda}{\beta \cos(\theta)} \quad (1)$$

$k = 0.9$ a constant; λ the radiation wavelength; β the Full Width at Half Maximum (FWHM) and θ the diffraction angle.

The curve is fitted by the Fityk program [11], which permitted to determine the FWHM, the area and intensity of the peaks. The grains size has been determined by using the peak at $2\theta = 44,9^\circ$ corresponding to the (101) plan, the most intensive peak in the MPDS file N°: 1217383. The Figure 4 presents the evolution of the crystallites grain size as a function of the deposition temperature.

The Figure 4 shows that the SiC nanocrystallites grains size increases as the deposition temperature increases. This increasing is probably due to a coalescence of the crystallites as the deposition temperature increases. No significant evolution has been seen when the annealing temperature increases.

3.4 Photoluminescence

The SiCN films have been analyzed by PL for films deposited and annealed at different temperature. The Figure presents the evolution of the PL intensity as a function of the annealing temperature.

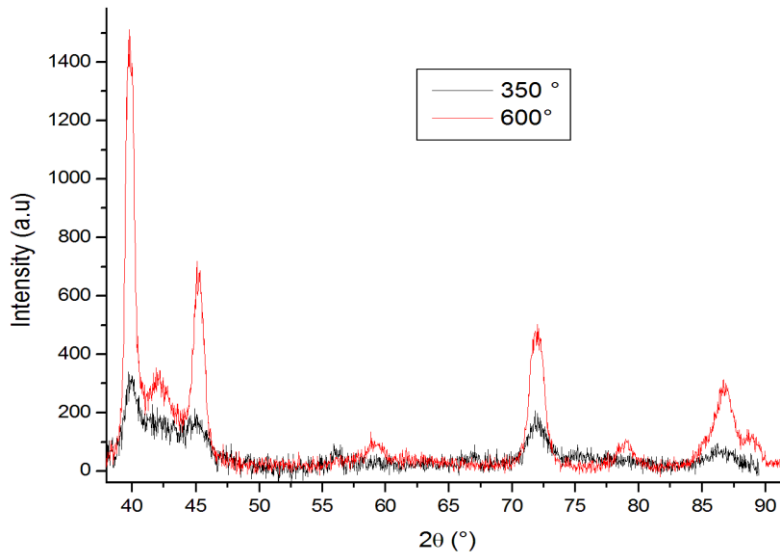


Fig. 3. XRD spectra of SiCN films deposited at low and high temperature.

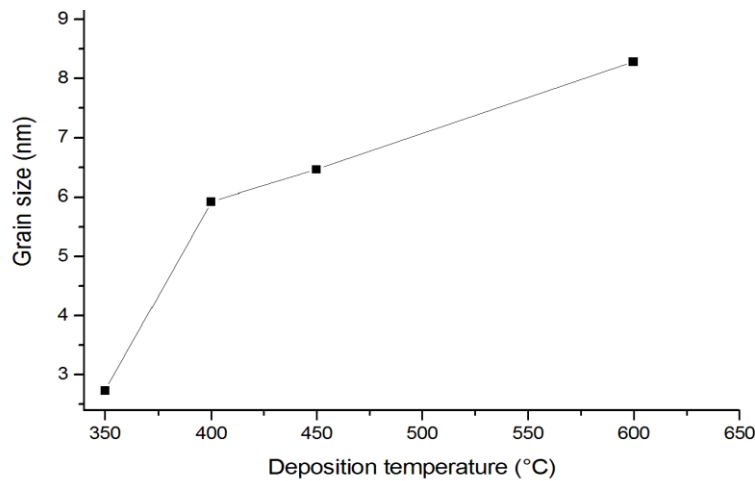


Fig. 4. Effects of deposition temperature of SiCN thin films on the grains size obtained by XRD.

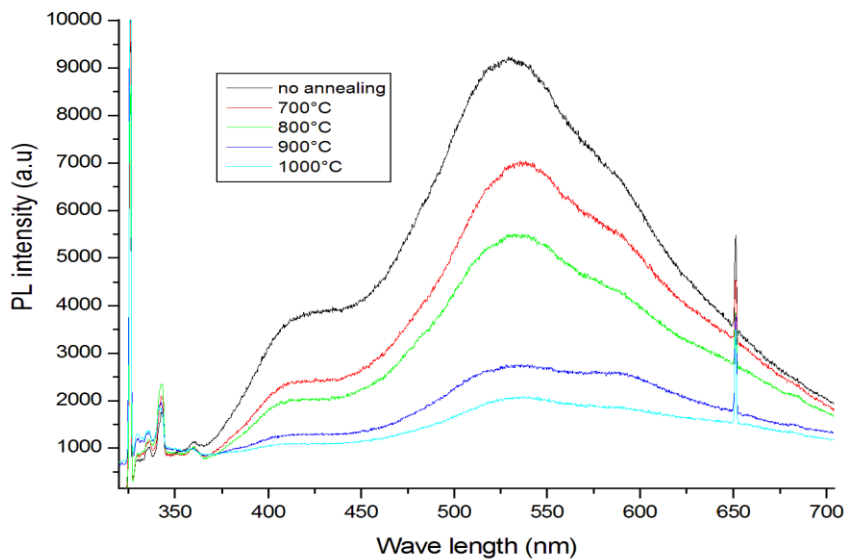


Fig. 5. Annealing temperature effect on the SiCN films PL intensity in the visible.

The peaks at 325 nm and 650 nm are not luminescence from the film but the laser (325 nm) and its frequency multiplication. All the films show a PL large band between 400 and 600 nm that is in many works attributed to the amorphous SiCN nanoparticles and their defaults [12, 9]. The principal peaks observed in the films are situated around 415 nm, 530 nm and 590 nm. The absence of high emission at UV wavelength is probably due to the wavelength of the laser used to illuminate the film as explained by Chen *et al.* [5]. We probably need a lower wavelength (less than 325 nm) to observe effects at lower wavelength. The most intense peaks in our films centered around 530 nm show a blue-shift as compared to that observe by Xu *et al.* [10] around 650 nm in a such film. The intensity of this band is very sensitive to the thickness of the film and to the area of the analyze and complicate the interpretation of the results. The general form of the photoluminescence peaks slightly changes when the deposition or annealing temperature changes. This is probably due to the changing of the structure or the film chemical bonds as mentioned by Du *et al.* [13]. The Figure 5 shows that the intensity of the PL decreases when the annealing temperature increases. According to Ng *et al.* [14] the intensity of the PL peaks increases when the particles agglomerate to form big size particles. That probably means that when we anneal films, the particles disaggregate to form small particles. According to Peng *et al.* [15], intense PL emission occurs near to the bang gap of that of

SiC (2.8 to 3.3 eV) probably when the SiC crystal reach a certain optimum size and number when we vary the annealing temperature. Increasing the annealing temperature increases the PL emission but until a certain temperature and then the PL intensity drastically decreases as it has been observed by Xu *et al.* [10] who find a maximum intensity at annealing temperature of 600 °C. In our case the annealing temperature increases from 600 to 1000 °C, this is probably why the PL intensity decreases when the annealing temperature increases. Otherwise, the PL intensity can also decrease when the film surface become smoother by reducing the states density. As explained in section 3.1 the increasing of the annealing temperature can increase the mobility of particles and the smooth of the film surface. Otherwise, the peaks around 530 nm could probably due to the quantic confinement effect of SiCN nanoparticles or SiC nanocrystallites as mentioned by Du *et al.* [9]. In fact, if we consider an electron confined in a particle with size equal to a , the energy level due to quantic effect is quantified:

$$E = \frac{h^2 n^2}{8ma^2} = \frac{hc}{\lambda} \quad (2)$$

Where λ is the peak wavelength, a , the particle size, n , an integer and h the Planck constant, m the electron mass. The PL wavelength is proportional to the scare of the particle size, so, it shifts to the low wavelength as the particles size decrease. Ma *et al.* [16] have also found a peak around 477 nm in SiCN films and attributed it to incorporated SiC nanocrystallites due to

confinement effects. As mentioned by Xu *et al.* [10], the PL intensity is proportional to the number of emitting particles N :

$$I \propto \sigma \varphi \tau N \quad (3)$$

Where σ , φ and τ are respectively the excitation cross section, the photon flux and the life time are constants for analyses made in the same condition. The intensity increases when the number of appropriate nanoparticles increases. The PL properties can be improved by increasing the nanocrystallites or nanoparticles number or decreasing their size or increasing the Si-C bonds in the film as confirmed by Peng *et al.* [17]. These purposes can be reached by varying the deposition and annealing temperature of the SiCN film.

4. Conclusion

Amorphous SiCN containing SiC nanocrystallites have been deposited by MPACVD in HMDSN/H₂/Ar mixture on silicon substrate at different deposition temperature. The photoluminescence properties of amorphous SiCN containing SiC nanocrystallites deposited and annealed at different temperature have been correlated to the structural and chemical bonds. PL intense emission in the visible has been observed and decreases when the annealing temperature of the films increases. This evolution is probably due to the changing of the nanoparticles size when deposition and annealing temperature vary. This intense emission band in

the visible can be used for example to realise visible diode.

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