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Original Article

Low residual stress in hydrogenated amorphous silicon-carbon films deposited by low-temperature PECVD

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ABSTRACT

Low residual stress in hydrogenated amorphous silicon-carbon ($a\text{-Si}_x\text{C}_{1-x}\text{:H}$) films prepared by plasma-enhanced chemical vapor deposition (PECVD) at temperature range of 100–200 °C was obtained. Profilometry, Fourier transform infrared (FTIR) spectroscopy and atomic force microscopy (AFM) measurements were carried out to characterize the films. The residual stress of each deposited film was calculated using profilometry measurements and the Stoney equation. The results showed that the residual stress decreases as the power density is reduced, or the temperature or the silane/methane ratio are increased. There is a deposition pressure at around 750 mTorr at which low residual stress is promoted. The residual stress showed a correlation with the carbon incorporation in the form of C-H_n molecules. The residual stress depends on the deposition regime: assisted either by silane radicals (also known as “silane starving plasma” (SSP)) or by both silane and methane radicals. Considering that the carbon incorporation under SSP regime is more controlled, there is a higher probability of having low residual stress in this regime. In agreement with the characterization, the most favorable PECVD parameters were selected to obtain $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films with low residual stress (below 100 MPa) within the temperature range (100–200 °C). These results are useful in areas such as flexible electronic devices, implantable devices, microfluidic systems, and microelectromechanical systems, among others, in which the materials and the parameters of fabrication are degraded or modified by temperature above 200 °C.

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1. Introduction

The ever-increasing innovative areas such as flexible electronic devices, implantable devices, microfluidic systems, and microelectromechanical systems (MEMS) require materials deposited at a temperature below 200 °C and with low residual stress [1–5]. One possible candidate to fulfill these requirements is hydrogenated amorphous silicon-carbon ($a\text{-Si}_x\text{C}_{1-x}\text{:H}$), whose properties can be modified in wide ranges depending on the carbon/silicon ratio, as well as the hydrogen content [4–9]. Among its most outstanding characteristics are high mechanical and thermal stability, high electrical resistivity, transparency to sunlight, and resistance to the corrosion and the wear [9–12]. Some works have already set the optimum deposition parameters to obtain $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films with specific properties [2,4,13,14]. Furthermore, its biocompatibility has already been proved, which enable it to be incorporated in bio-MEMS as a structural and functional material [14]. $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films have been obtained using deposition techniques such as sputtering, laser ablation, molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), hot wire chemical vapor deposition (HTCVD), and plasma-enhanced chemical vapor deposition (PECVD) [15]. Among these deposition techniques, $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ deposited by PECVD is a good option because the deposition can be carried out at low temperature (100–400 °C) and the residual stress may be tuned with deposition parameters such as power density, pressure, temperature, and precursor gas flow ratio [2,16].

Several structural and compositional aspects of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ deposited by PECVD have been studied in advance. Low-temperature PECVD $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ forms a tetrahedral amorphous structure of silicon and carbon atoms, with hydrogen atoms occupying the dangling bonds originated during deposition [17]. Its structure and composition are closely related to the deposition regime. Using silane (SiH_4) and methane (CH_4) as precursor gases, if the power density is selected in such a way that only reactive species of SiH_4 are formed and not the reactive species of CH_4 , the deposition works under the regime known as “silane starving plasma” (SSP). In this regime, the carbon incorporation is carried out by CH_4 molecules reacting with the SiH_4 radicals [8]. Conversely, if CH_4 radicals are formed during deposition, then they can directly react with the surface without the mediation of SiH_4 radicals. The characteristic spectrum of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ from Fourier transform infrared (FTIR) spectroscopy is also well understood. For example, it is known that the shift of the peak at 2090 cm^{-1} towards higher frequencies depends on the type of film, namely Si-rich or C-rich film. In Si-rich films, this shift is due to the bonding of two hydrogen atoms to silicon atoms, whereas in C-rich films it is caused by the increase of the number of carbon atoms surrounding silicon atoms with only one bonded hydrogen atom [17].

Hydrogen dilution and hydrogen incorporation into the $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films impact their structure and residual stress. High hydrogen dilution during deposition avoids the incorporation of carbon in graphite-like form, reducing the dissolution and cytotoxicity of the material and improving its quality [14]. With respect to the residual stress, the hydrogen incorporation causes compressive stress in as-deposited $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films,

and it can be changed to tensile stress desorbing hydrogen by thermal annealing of the films [18–20]. However, this strategy must carry out at temperatures higher than the deposition temperature, modifying the properties of the as-deposited films and reducing their range of application, particularly when materials included in the fabrication process are susceptible to higher temperatures [1,4]. Windischmann [18] investigated the residual stress in films deposited in the temperature range of 200–400 °C, obtaining films with high compressive stress about -1 GPa without thermal annealing. Iliescu et al. [2] reported as-deposited films with improved residual stress from -30 to 15 MPa in the deposition temperature range of 300–350 °C. This temperature range is still not within the range that is required for the applications mentioned above.

In addition to incorporated hydrogen, another factor involved in the generation of residual stress is the oxidation of the films. Although the PECVD processes do not include oxygen gas, once the films are drawn from the chamber, oxygen and water vapor in the environment oxidize them. As result, an increase of the absorption peak at 1000 cm^{-1} , associated with vibrations of both C–H_n groups and Si–O bonds, is observed in the FTIR spectra of the films. Some other works have already studied this phenomenon. Deku et al. [16] found that $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films deposited at low temperatures and power are highly susceptible to oxidation and temporal residual stress variation, which reduces their applicability as encapsulation material for implantable devices. As a possible solution to this problem, Jousseume et al. [21] treated the as-deposited $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films with H_2 plasma. The treatment stopped the oxidation and stabilized the residual stress with time. They associated this result with passivation of reactive species in the films. Additionally, Vasin et al. [22] found that carbon clusters and nanovoids in the amorphous network of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films promote their oxidation.

Considering all previous findings, this work aims to find out the deposition parameters resulting in low residual stress (less than 100 MPa) in $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films deposited at low temperatures (100–200 °C). To achieve this, a set of deposition processes with different pressure, power density, temperature, and precursor gas flow ratio was carried out. Finally, an explanation about how these deposition parameters result in a structural arrangement in the film favorable to obtain the desired low residual stress is presented in section 4.

2. Methods

2.1. Deposition parameters of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films

Deposition processes of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films were carried out in an ultra-high-vacuum multi-chamber PECVD system (MVSys-tem Inc.), which operates at a radio frequency of 13.56 MHz . All $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films were deposited with precursor gases of silane (SiH_4) diluted at 10% in hydrogen (H_2) and methane (CH_4), onto 2947-Corning glasses and p-type (100) silicon substrates. H_2 in SiH_4 gas flow and argon (Ar) were used as carrier and diluent gases. Gas flows of CH_4 and Ar were fixed at 10 and 100 sccm , respectively. Considering that the compatibility with the fabrication processes increases when

Table 1 – Deposition parameters of the PECVD processes and deposition rate.

PECVD process	Pressure (mTorr)	Power density (mW/cm ²)	T (°C)	X _{CH₄}	Deposition rate (nm/min)
Pr-01	300	16.7	120	0.83	7.08 ± 0.14
Pr-02	450	16.7	120	0.83	7.74 ± 0.17
Pr-03	750	16.7	120	0.83	11.22 ± 0.62
Pr-04	900	16.7	120	0.83	16.94 ± 0.33
Pr-05	1100	16.7	120	0.83	20.64 ± 0.58
Po-01	1100	8.3	120	0.83	12.71 ± 0.19
Po-02	1100	13.3	120	0.83	18.61 ± 0.35
Po-03	1100	25.0	120	0.83	17.86 ± 0.45
Po-04	1100	33.3	120	0.83	15.46 ± 0.25
T-01	1100	16.7	100	0.83	18.37 ± 0.15
T-02	1100	16.7	150	0.83	18.71 ± 0.21
T-03	1100	16.7	170	0.83	16.49 ± 0.26
T-04	1100	16.7	200	0.83	14.98 ± 0.32
F-01	1100	16.7	120	0.80	19.39 ± 0.26
F-02	1100	16.7	120	0.77	19.08 ± 0.16
F-03	1100	16.7	120	0.74	16.94 ± 0.24
OP-01	750	8.3	100	0.74	10.99 ± 0.14
OP-02	750	8.3	150	0.74	9.30 ± 0.20
OP-03	750	8.3	200	0.74	5.60 ± 0.18

low deposition temperatures are used, temperatures in the range of 100–200 °C were selected [1,4,12]. Methane-silane gas flow ratios ($X_{CH_4} = CH_4/(CH_4 + SiH_4)$) in the range of 0.74–0.83 were chosen. A wide range of deposition pressure from 300 to 1100 mTorr was selected. Low power densities from 8.3 to 33.3 mW/cm² were defined to obtain low reactive species of CH₄. All the deposition processes are shown in Table 1. The deposition processes labeled as OP-01, OP-02, and OP-03 come from an optimization procedure.

2.2. Characterization of the α -Si_xC_{1-x}:H films

The characterization of the deposited α -Si_xC_{1-x}:H films was carried out using profilometry, Fourier transform infrared (FTIR) spectroscopy and atomic force microscopy (AFM) measurements. The DektakXTL stylus profiler manufactured by Bruker Corporation was used to measure the thickness of the films; the spectrophotometer Vector 22 manufactured by Bruker Corporation was used to obtain the FTIR spectra; the AFM Nanoscope IIIA MultiMode head was used to study the surface morphology of the films; the surface profiler KLA Tenkor P-7 was used to measure the surface profile of the Si substrates before and after α -Si_xC_{1-x}:H depositions. Although the measurements of thickness and roughness of the films by profilometry and AFM are direct, the measurement of other parameters such as bond density (N) and curvature deflection by FTIR spectroscopy and profilometry, respectively, required data processing.

An approximate value of the densities of Si-H, Si-C, and C-H_n bonds can be calculated from the FTIR spectra. The area under the curve for the respective peak in the FTIR spectrum is related to the bond density [4,23]. For bonding types such as Si-H, Si-C, and C-H_n, the bond density (N_b , where b can be SiC, SiH, CH, CH₂ or CH₃) is given by:

$$N_b = A_b \int \frac{\alpha(\omega)}{\omega} d\omega = A_b I_b \quad (1)$$

where ω is the frequency of oscillation, $\alpha(\omega)$ is the absorption coefficient, I_b is the integrated absorption, and A_b is the inverse absorption cross section for each bond type [4]. Inverse absorption cross sections of 2.13×10^{19} , 1.4×10^{20} , 3.85×10^{21} , 3.85×10^{20} , and 3.65×10^{20} were used for Si-C, Si-H, C-H, C-H₂, and C-H₃ bonds vibrating at 780, 2090, 2880, 2920, and 2950 cm⁻¹, respectively [8,24–26]. The deconvolution of the data from FTIR measurements was done in OriginPro 8 by using the tool Fit Multi-peaks and fitting them to Gaussian curves. An example of this procedure is shown in Fig. 1.

Average residual stress (σ_a) is calculated from profilometry data. Profiles of 4-cm length and 5-μm resolution were obtained for each substrate before and after deposition by rotating the substrate and passing through its center. A 5th order polynomial was fitted to the data and used to calculate the radius of curvature ($R(x)$) for each point given by ref. [27]:

$$R(x) = \frac{[1 + (dy/dx)^2]^{3/2}}{d^2y/dx^2} \quad (2)$$

where y is the height of the substrate and x is the position. The residual stress ($\sigma(x)$) for each point is given by the Stoney equation [28]:

$$\sigma(x) = \frac{1}{6R(x)} \frac{E}{1-\nu} \frac{t_s^2}{t_f} \quad (3)$$

where t_s is the substrate thickness, t_f is the film thickness, E is the Young's modulus of the substrate (1.805×10^{11} Pa for (100) silicon substrate at 300 K) and ν is the Poisson's ratio (0.22 for silicon substrate). Finally, σ_a was calculated for each deposited α -Si_xC_{1-x}:H film averaging the stresses obtained through the profiles. MATLAB software was used to implement the mathematical procedure.

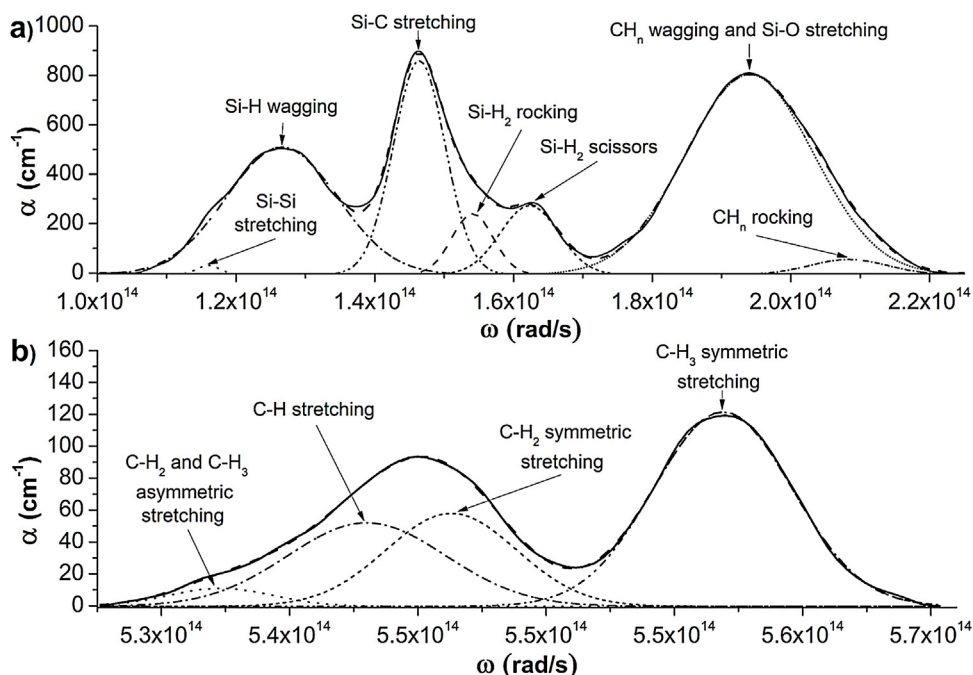


Fig. 1 – Deconvoluted FTIR spectrum for the α - $\text{Si}_x\text{C}_{x-1}\text{H}$ film prepared by PECVD at 13.56 MHz, 13.3 mW/cm², 1100 mTorr, 120 °C, and $X_{\text{CH}_4} = 0.83$. a) Deconvolution of the peak at 780 cm⁻¹ corresponding to Si-C stretching vibrations, and b) deconvolution of the peaks in the band from 2800 to 3000 cm⁻¹ corresponding to C-H_n stretching vibrations (n = 1, 2, 3).

3. Results

3.1. Surface morphology

The thickness of each film reported in Table 2 is the average of four measurements on steps formed using photolithography and dry-etch with tetrafluoromethane (CF₄) plasma. The plasma etching was carried out using a micro-RIE system 800 Series-RIE manufactured by Technics. The root mean square roughness (R_q), the average surface roughness (R_a), and the peak-valley height (R_y) of the films deposited on the silicon substrate were calculated by the AFM software in an area of $2 \times 2 \mu\text{m}^2$. The arithmetic averages of the absolute values of R_q , R_a and R_y were calculated from 4 scans and reported in Table 2 along with their standard deviations (SD).

3.2. Structural arrangement

The FTIR spectrometer was set in absorbance mode in middle infrared from 500 to 3500 cm⁻¹. The absorption spectra were normalized by the corresponding thicknesses and the assignments of the peaks in the spectra are listed in Table 3. According to the results in Fig. 2a, as the pressure goes from 300 to 1100 mTorr, the peaks at 670, 780, and 2090 cm⁻¹ decrease, while the peak at 1000 cm⁻¹ increases. In the case of Fig. 2b, the same effect happens as the power density goes from 8.3 to 16.7 mW/cm². However, the trend towards increasing of the peaks at 670, 780, and 2080 cm⁻¹ changes from 16.7 to 33.3 mW/cm². The opposite trend is observed in Fig. 2c as deposition temperature goes from 100 to 200 °C. In Fig. 2d, the peaks at 670 and 2090 cm⁻¹ increase as the SiH₄ flow is

increased, and the peak at 1000 cm⁻¹ is strongly reduced as X_{CH_4} changes from 0.83 to 0.74. In all these spectra a shifting of the peak at 2090 cm⁻¹ to higher frequencies is observed as the peak at 1000 cm⁻¹ increases. This behavior is consistent with C-rich films in which the number of carbon atoms surrounding silicon atoms increases. Although the spectra of the films from the optimization processes are similar, an increase in the absorbance peaks in the band 2800–3000 cm⁻¹ can be observed in Fig. 3 as the deposition temperature increases. All these findings can be corroborated based on densities of Si-C, Si-H, C-H, C-H₂, and C-H₃ bonds (N_{SiC} , N_{SiH} , N_{CH} , N_{CH_2} , and N_{CH_3}) presented in Table 4, which were calculated following the procedure described in section 2.2. The peak at 1400 cm⁻¹ gives evidence of the good quality of the films by formation of a diamond-like structure.

3.3. Residual stress

Following the procedure described in Section 2.2, the residual stresses of the films were calculated, and the results are showed in Fig. 4. The behavior of the residual stress versus deposition pressure reaches a minimum at 750 mTorr (Fig. 4a). The residual stress increases as the power density increases from 8.3 to 33.3 mW/cm² (see Fig. 4b), whereas it decreases as the temperature increases from 100 to 200 °C (see Fig. 4c). According to the results in Fig. 4d, the residual stress in films deposited with X_{CH_4} in the range of 0.74–0.80 is lower than -150 MPa. However, a strong change in stress residual is observed in the film deposited at X_{CH_4} of 0.83, reaching residual stress of -400 MPa. The residual stresses of the films deposited using the optimized parameters are plotted in Fig. 5 as a function of the deposition temperature. The resid-

Table 2 – Thickness (t_f), average surface roughness (R_a), root mean square roughness (R_q), and the peak-valley height (R_y) of the silicon substrate (c-Si) and the α -Si_xC_{1-x}:H thin films deposited by PECVD at 13.56 MHz.

PECVD process	t_f (nm)	R_a (nm)	R_q (nm)	R_y (nm)
c-Si	$(300 \pm 25) \times 10^3$	0.44 ± 0.04	0.54 ± 0.05	5.91 ± 2.63
Pr-01	283	0.71 ± 0.14	0.89 ± 0.18	7.23 ± 1.54
Pr-02	310	0.64 ± 0.07	0.87 ± 0.09	8.53 ± 1.98
Pr-03	449	0.50 ± 0.03	0.62 ± 0.04	4.82 ± 0.30
Pr-04	678	0.60 ± 0.04	0.76 ± 0.05	6.03 ± 0.21
Pr-05	826	0.76 ± 0.10	0.97 ± 0.17	8.45 ± 3.61
Po-01	509	0.54 ± 0.04	0.67 ± 0.05	5.31 ± 0.35
Po-02	745	0.56 ± 0.02	0.70 ± 0.03	5.49 ± 0.45
Po-03	714	0.67 ± 0.07	0.84 ± 0.09	7.05 ± 0.35
Po-04	618	0.84 ± 0.09	1.07 ± 0.11	9.52 ± 1.41
T-01	735	0.70 ± 0.05	0.89 ± 0.08	8.37 ± 1.84
T-02	749	0.60 ± 0.03	0.75 ± 0.03	5.91 ± 0.34
T-03	660	0.51 ± 0.02	0.64 ± 0.02	5.37 ± 0.81
T-04	599	0.53 ± 0.05	0.66 ± 0.06	5.00 ± 0.46
F-01	776	0.74 ± 0.74	0.93 ± 0.93	7.60 ± 7.60
F-02	763	0.72 ± 0.08	0.93 ± 0.10	7.66 ± 0.55
F-03	678	0.86 ± 0.08	1.12 ± 0.08	9.10 ± 0.65
OP-01	439	0.98 ± 0.15	1.31 ± 0.29	10.85 ± 2.74
OP-02	372	0.74 ± 0.09	0.99 ± 0.21	9.66 ± 2.44
OP-03	224	0.59 ± 0.05	0.75 ± 0.07	6.86 ± 1.24

ual stress slightly increases as the deposition temperature increases, which is opposite to the behavior plotted in Fig. 4c.

4. Discussion

We analyzed the results of this study based on two mechanisms: formation of reactive species in the plasma and reaction rate of reactive species on the deposition surface, as well as two variables: residence time of species and surface passivation with hydrogen. Remembering the two deposition regimes mentioned in Section 1, the mechanism of deposition is defined by the deposition regime, which in turn depends on the power density. Therefore, the residual stress of the films must be closely related to both the deposition regime as well as the two variables mentioned above, which are set according to the other deposition conditions (pressure, temperature, X_{CH_4} , and hydrogen dilution). The first important objective is to find out the power density value from which the deposition no longer works under SSP regime. Previous works have reported different power densities along with specific deposition parameters to obtain SSP regime. For example, Solomon et al. reported SSP regime at power densities lower than 300 mW/cm^2 based on the behavior of the deposition rate as X_{CH_4} increases [30]. Hsu et al [4] reported 50 mW/cm^2 and low residence time as a set up for SSP regime. In this study, we use the results obtained in films deposited under different power densities. According to the results in Fig. 2b and Table 4, there are a remarkable increase in the intensity of the absorption peak at 1000 cm^{-1} and the density of C-H_n bonds, respectively, as the power density goes from 8.3 to 13.3 mW/cm^2 . It indicates that in our reactor probably methane radicals are already forming at 13.3 mW/cm^2 . Accordingly, we conclude that the power density value must be around 8.3 mW/cm^2 for the deposition to take place under the SSP regime. This conclusion is very important in the analysis of results that will be given below because the depositions of most experiments

Table 3 – Bonding configuration assignment of the absorption peaks in the infrared spectra of α -Si_xC_{1-x}:H films.

Assignment	Wavenumber (cm^{-1})	References
Si-H wagging	670	[10,23,24,29]
Si-C stretching	740–800	[4,8,10,23,24]
Si-H ₂ bending	845, 895	[23,28]
CH _n wagging/rocking	1000–1100	[23,24,29]
Si-O stretching	1000	[26]
Si-CH ₃ bending	1250	[4,10,23,24]
CH ₂ sp ³ bending	1400	[23]
Si-H _n stretching	2090	[4,8,10,24]
C-H _n sp ³ stretching	2860–2960	[4,8,10,23,29]

were carried out at power densities above 8.3 mW/cm^2 . Then, the resultant films were obtained by reaction of both silane and methane radicals.

Considering that the films corresponding to the results in Fig. 4a were deposited out of the SSP regime and under high X_{CH_4} , reactive species from both silane and methane were formed in the plasma. However, minimums of C-H and C-H₃ bond densities and residual stress are observed at deposition pressure of 750 mTorr (see first five rows of the fourth and sixth columns in Table 4 and Fig. 4a). Therefore, the residual stress behavior must be related to the formation and reaction of CH₄ radicals. At pressure lower than 750 mTorr, the concentration of CH₄ radicals is slightly promoted, whereas at a pressure higher than 750 mTorr, the time for the reaction of CH₄ radicals increases. In both cases the result is higher densities of C-H and C-H₃ bonds. Hence, 750 mTorr was considered as optimum deposition pressure for low density of C-H and C-H₃ bonds and low residual stress. The results of surface roughness support this statement. The R_q of the film deposited at 750 mTorr is the minimum. The deposition rate, instead, increases progressively with the increase in pressure of the

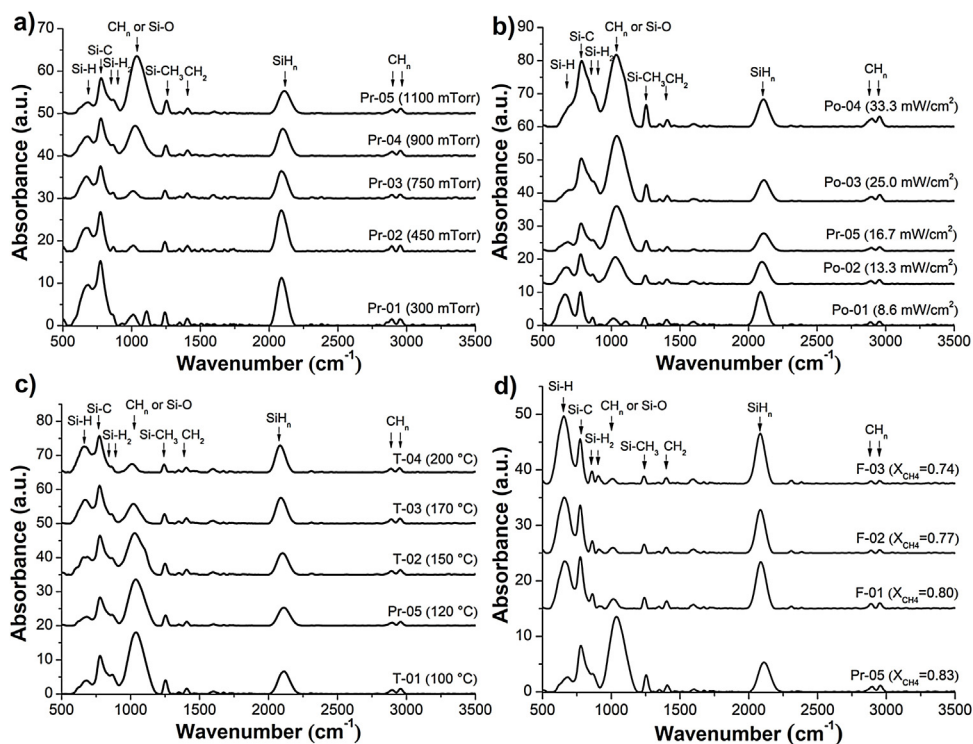


Fig. 2 – FTIR spectra of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films deposited by PECVD at 13.56 MHz and by varying the deposition parameters. a) Films deposited at 16.7 mW/cm², 120 °C, $X_{\text{CH}_4} = 0.83$, and different pressure in the range of 300–1100 mTorr; b) films deposited at 1100 mTorr, 120 °C, $X_{\text{CH}_4} = 0.83$, and different power density in the range of 8.3–33.3 mW/cm²; c) films deposited at 1100 mTorr, 16.7 mW/cm², $X_{\text{CH}_4} = 0.83$, and different temperature in the range of 100–200 °C, and d) films deposited at 1100 mTorr, 16.7 mW/cm², 120 °C and different X_{CH_4} in the range of 0.74–0.83.

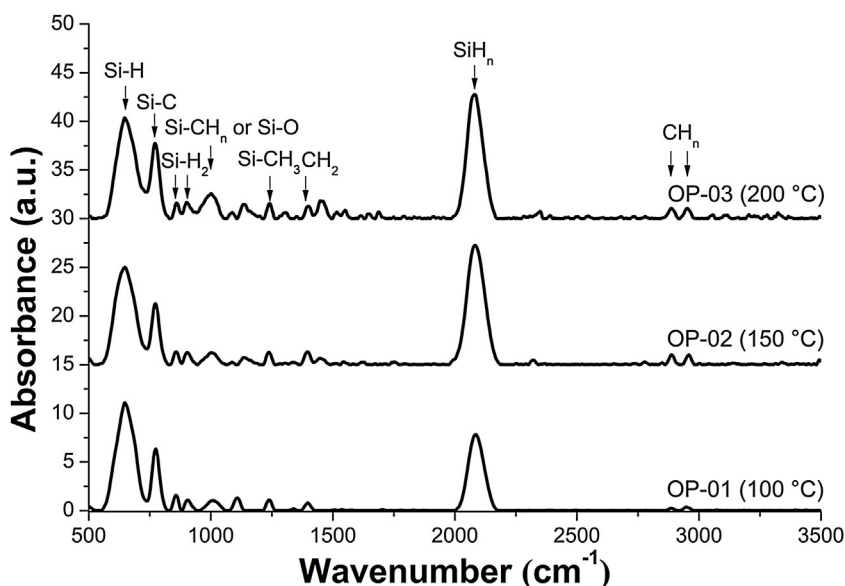


Fig. 3 – FTIR spectra of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films deposited by PECVD at 13.56 MHz, 8.3 mW/cm², 750 mTorr, $X_{\text{CH}_4} = 0.74$, and temperatures of 100, 150 and 200 °C.

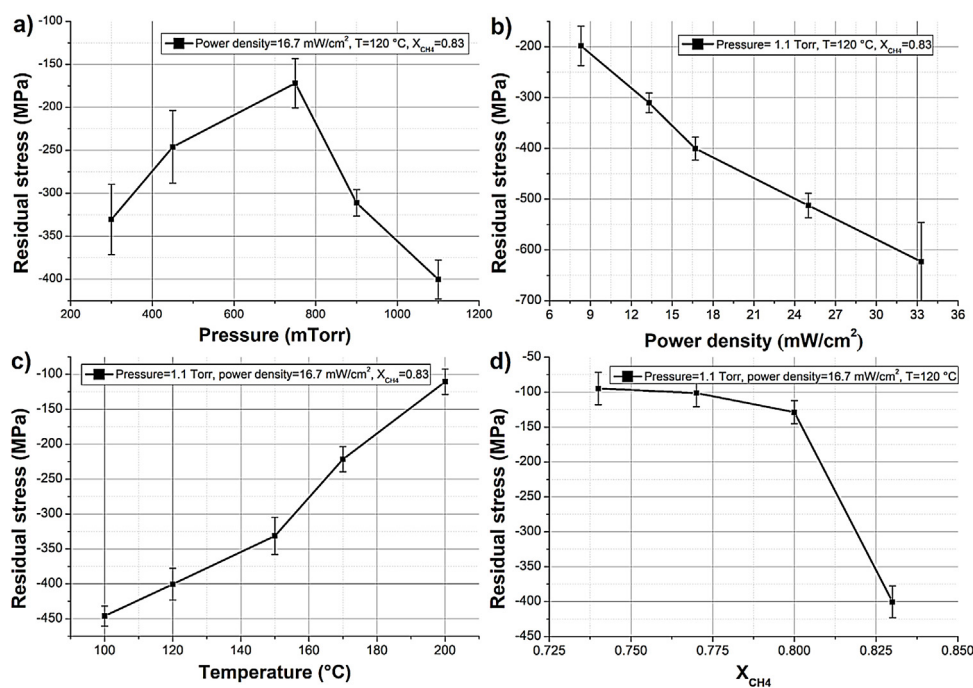
chamber. This is due to lower desorption of reactive species as a result of the lower kinetic energy of Ar ions [2].

In correspondence with the results in Table 4, as the power density increases, a higher concentration of CH₄ radicals is

promoted and more C–H_n groups are incorporated by direct reaction with the surface atoms. This explanation agrees with the progressively higher deposition ratio obtained by increasing the power density. As can be seen in Table 2 and Fig. 4b, the

Table 4 – Densities of Si–C (N_{SiC}), Si–H (N_{SiH}), C–H (N_{CH}), C–H₂ (N_{CH_2}), and C–H₃ (N_{CH_3}) bonds obtained from FTIR data processing of the spectra of the α -Si_xC_{1-x}:H films.

PECVD process	N_{SiC} (bond/cm ³)	N_{SiH} (bond/cm ³)	N_{CH} (bond/cm ³)	N_{CH_2} (bond/cm ³)	N_{CH_3} (bond/cm ³)
Pr-01	1.95×10^{21}	6.67×10^{21}	5.12×10^{21}	2.77×10^{20}	7.37×10^{20}
Pr-02	1.31×10^{21}	5.72×10^{21}	4.13×10^{21}	1.14×10^{19}	5.05×10^{20}
Pr-03	1.09×10^{21}	3.91×10^{21}	3.06×10^{21}	1.08×10^{20}	4.12×10^{20}
Pr-04	1.18×10^{21}	4.18×10^{21}	3.52×10^{21}	1.50×10^{20}	5.86×10^{20}
Pr-05	1.13×10^{21}	3.68×10^{21}	3.62×10^{21}	7.94×10^{19}	5.68×10^{20}
Po-01	1.15×10^{21}	6.01×10^{21}	1.69×10^{21}	2.41×10^{20}	4.76×10^{20}
Po-02	1.15×10^{21}	4.42×10^{21}	2.78×10^{21}	2.61×10^{20}	5.35×10^{20}
Po-03	1.61×10^{21}	4.24×10^{21}	4.49×10^{21}	1.80×10^{20}	9.66×10^{20}
Po-04	3.00×10^{21}	5.48×10^{21}	1.01×10^{22}	4.67×10^{20}	1.77×10^{21}
T-01	1.40×10^{21}	4.49×10^{21}	3.31×10^{21}	2.12×10^{20}	7.40×10^{20}
T-02	1.43×10^{21}	4.17×10^{21}	3.85×10^{21}	1.06×10^{20}	6.67×10^{20}
T-03	1.58×10^{21}	4.66×10^{21}	5.59×10^{21}	9.37×10^{19}	6.86×10^{20}
T-04	1.70×10^{21}	4.60×10^{21}	5.92×10^{21}	1.53×10^{18}	5.52×10^{20}
F-01	1.17×10^{21}	5.05×10^{21}	3.16×10^{21}	1.23×10^{20}	4.65×10^{20}
F-02	1.09×10^{21}	4.42×10^{21}	1.48×10^{21}	3.32×10^{19}	2.27×10^{20}
F-03	9.73×10^{20}	5.27×10^{21}	1.45×10^{21}	3.43×10^{19}	2.12×10^{20}
OP-01	6.50×10^{20}	4.10×10^{21}	7.46×10^{20}	2.49×10^{18}	1.35×10^{20}
OP-02	6.99×10^{20}	7.21×10^{21}	3.52×10^{21}	3.59×10^{18}	3.20×10^{20}
OP-03	9.38×10^{20}	6.85×10^{21}	3.97×10^{21}	2.99×10^{19}	4.00×10^{20}

**Fig. 4 – Residual stress of α -Si_xC_{1-x}:H films deposited by PECVD at 13.56 MHz versus a) pressure, b) power density, c) temperature and d) X_{CH_4} during depositions.**

resulting effect is higher both surface roughness and residual stress. Taking into account that the processes corresponding to the results in Fig. 4c were carried out under the same pressure, power density, and X_{CH_4} , a relationship between the residual stress of the films and the formation of reactive species in the plasma and their subsequent reaction on the surface is unlikely. In this case, the residual stress behavior seems to be the result of a better chemical ordering and a lower formation of weak bonds as deposition temperature increases, which are expected effects. A higher temperature favors the

mobility of reactive species on the surface during the deposition process and their binding in sites energetically more stable. It has already been predicted the formation of weak bonds of C–H in H–C–H bridge configuration in as-deposited films [31]. We believe that these weak bonds increase in the deposition temperature range of this study and gives rise to higher hydrogen desorption after deposition, increasing the dangling bonds and the subsequent oxidation of the films (this will be discussed further later). Although at higher temperature, the incorporation of hydrogen is expected to be lower

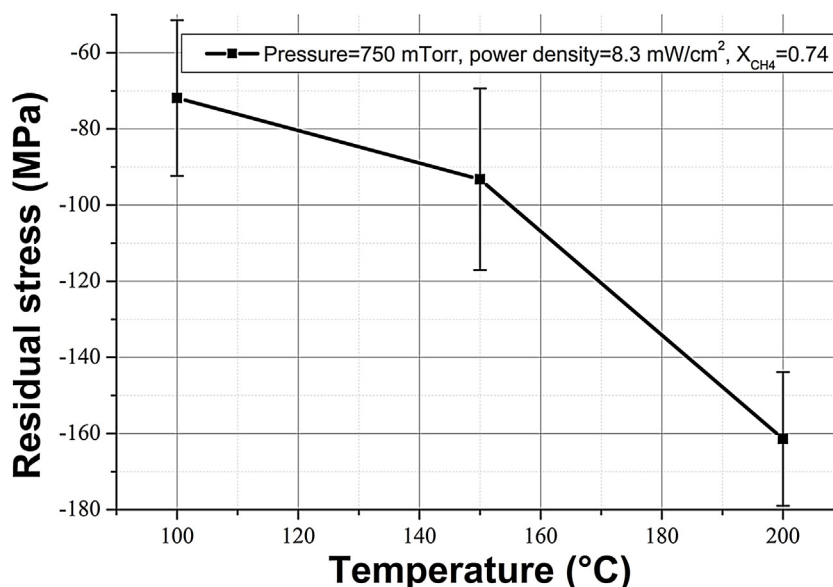


Fig. 5 – Residual stress of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films deposited by PECVD at 13.56 MHz, 8.3 mW/cm², 750 mTorr, $X_{\text{CH}_4} = 0.74$, and temperatures of 100, 150, and 200 °C.

[32], the results do not allow to assert something about it. As can be seen in Table 4 and Fig. 2c, the bond density of C–H₂ and the intensity of the peak at 1000 cm⁻¹ in the FTIR spectra increase as the deposition temperature decreases. Considering that oxygen, as well as hydrogen, is an impurity inside the amorphous network, the resulting effect is lower compressive stress as temperature increases. The trend towards lower R_q as the temperature increases (see Table 2) agrees with the greater mobility of the reactive species on the surface at higher deposition temperature.

X_{CH_4} is one of the deposition parameters more widely used to tune the properties of $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films [2,8,10]. In this work, the main change in residual stress is observed in Fig. 4d as X_{CH_4} goes from 0.80 to 0.83. Seemingly, at X_{CH_4} higher than 0.80 the reactions of CH₄ radicals with the surface are enhanced. As can be seen in Table 4, the higher X_{CH_4} promotes higher bond densities of C–H_n groups in the films, which is an expected result. Again, gathering information in Table 4 and Fig. 4d, higher residual stress is obtained in the films with higher bond densities of C–H_n groups. In general, lower deposition rate, roughness, and density of Si–H bonds are obtained at higher X_{CH_4} , which is consistent with the lower concentration of silane radicals being absorbed by the surface.

In accordance with the presented analysis, out of the SSP regime, there are deposition parameters (i.e., 750 mTorr of pressure, 200 °C of temperature, and 0.74 of X_{CH_4}) under which low residual stress is promoted. Also, one can see that the bond densities of C–H_n groups, which were obtained from FTIR band of 2800–3000 cm⁻¹, highlight a certain correlation with the residual stress. According to this statement and the obtained results, the best way to obtain low both bond densities of C–H_n groups and residual stress is depositing under SSP regime and inhibiting reactions of CH₄ radicals on the surface using the other deposition parameters (pressure, temperature, and X_{CH_4}). Following this conclusion, the three last deposition

processes in Table 1 were proposed in order to obtain residual stress below 100 MPa. According to Fig. 4, the goal was achieved at deposition temperatures of 100 and 150 °C. Under SSP regime, lower temperature yields lower residual stresses in the films, which verifies experimentally the results suggested by Hsu et al. [4]. Although one could expect a higher residual stress at 100 °C, under SSP regime the probability of reactions between silane radicals and methane molecules is lower at low temperature, decreasing the bond densities of C–H_n groups, as well as the compressive stress by incorporation of impurities in the amorphous network. Fig. 6 shows the residual stress versus bond densities of C–H_n groups for the films deposited under SSP regime. According to Fig. 6, the compressive residual stress increases as the bond densities of C–H_n groups increase.

Joining together the previous works presented in Section 1 about oxidation of the $a\text{-Si}_x\text{C}_{1-x}\text{:H}$ films, it is likely that an increase in bond density of C–H_n groups leads to formation of carbon clusters, more reactive species, nanovoids in the amorphous network (low-density films), and consequently to the oxidation and the increase of residual stress after film deposition [16,21,22,26]. Therefore, one could expect not only lower oxidation and residual stress, but also fewer aging effects in films with low C–H_n bond densities. Although this work did not include studies about aging of the films, there is reported information that corroborate it. Deku et al. [16] reported that films deposited at 150 °C have a greatest oxidation over time. According to the FTIR spectra reported by Deku et al., one can also see that the peaks in the band of 2800–3000 cm⁻¹ are more pronounced for the film deposited at 150 °C than for the films deposited at higher temperatures, which is consistent with what is stated here. In our case, the $a\text{-Si}_x\text{C}_x\text{:H}$ film deposited at 100 °C under SSP regime had the lowest densities of C–H, C–H₂, and C–H₃ bonds, the lowest intensity of the peak at 1000 cm⁻¹, and correspondingly, the lowest residual stress.

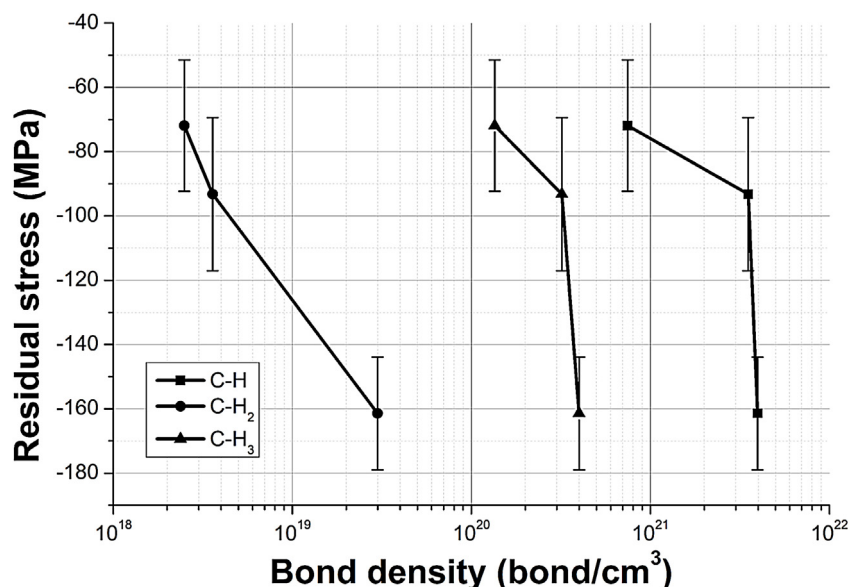


Fig. 6 – Residual stress versus densities of C–H, C–H₂ and C–H₃ groups in α -Si_xC_{1-x}:H films deposited by PECVD under “silane starving plasma” regime at 13.56 MHz, 8.3 mW/cm², 750 mTorr, X_{CH₄} = 0.74, and temperatures of 100, 150, and 200 °C.

Further studies would be oriented to evaluate the stability of the residual stress with the time after film deposition.

5. Conclusions

In summary, depositions of α -Si_xC_{1-x}:H films by PECVD were carried out at a temperature in the range of 100–200 °C in order to find out the optimum deposition parameters yielding low residual stress. A correlation between the bond density of C–H_n groups and residual stress in the films was found. The low bond densities of C–H_n bonds results in low residual stress. According to the results, the SSP regime promotes low bond densities of C–H_n groups, and therefore low residual stress. However, most of the films were deposited through surface reactions involving both SiH₄ and CH₄ radicals in order to know the deposition parameters that inhibits the surface reactions with CH₄ radicals. The residual stress curves versus pressure, power density, temperature, and X_{CH₄} gave as optimal parameters 750 mTorr, 8.3 mW/cm², 200 °C, and 0.74, respectively. The assumptions were also supported through other parameters such as deposition rate, surface roughness, and bond densities of Si–H and Si–C calculated from FTIR spectra of the α -Si_xC_{1-x}:H films.

Additionally, α -Si_xC_{1-x}:H films were deposited under the SSP regime and at different temperatures to obtain lower residual stress. The results showed lower residual stress as the deposition temperature is reduced from 200 to 100 °C, thus achieving the lowest residual stress at the lowest temperature of this work. Apparently, SSP regime and low-temperature yield lower bond densities of C–H_n groups, and then lower hydrogen incorporation, less clusters, less nanovoids and less reactive species in the as-deposited films, which would be responsible of the lower oxidation and residual stress of the films. Under these conditions, residual stress lower than 100 MPa can be obtained avoiding annealing processes and

additional treatments, matching the low-temperature PECVD processes to the specifications of applications such as flexible electronic devices, implantable devices, microfluidic systems, and MEMS.

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