



Silicon–carbon films deposited at low substrate temperature

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Abstract

Films composed of Si crystallites embedded in an amorphous silicon–carbon matrix have been deposited at low temperature by PECVD onto Corning glass and SnO₂:F coated glass substrates. An increase of RF power from 15 to 100 W reduces the silicon crystalline fraction and enhances the carbon content in the amorphous material, causing the crystalline to amorphous phase transition. SnO₂ coated glass substrate enhances the nucleation of silicon grains and the optical absorbance in the wavelength range of ≈ 300 –1000 nm decreases with increasing the RF power.

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1. Introduction

Hydrogenated microcrystalline silicon–carbon ($\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$), composed of submicron Si crystallites dispersed in an amorphous silicon–carbon matrix, is a promising material for device applications [1–3]. Indeed, these alloys have higher electrical conductivity, optical transparency, dopant activation and long-term stability as compared with the amorphous counterpart [4–6]. The doped material has been mainly used as window layer in solar cells [6,7], while the undoped material, less developed until now, can be potentially used as active layer for multiple junction solar cells, UV photodetectors and LEDs.

Device fabrication needs low substrate temperature to avoid damaging of either the substrate or the interfaces. It has been reported that p-type $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ can be grown only in moderate temperature zone (180–200 °C) [6], whereas undoped $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ can be prepared in the 200–400 °C range at low power with high hydrogen dilution [8].

In this paper the effects of RF power on the properties of hydrogenated microcrystalline silicon–carbon films, deposited at low substrate temperature (250 °C) by silane + methane gas mixtures highly diluted in hydrogen, have been investigated in the 15–100 W range. Since many devices such as solar cells, LEDs, color sensors are fabricated using transparent conductive oxide (TCO) substrates [9], the trend of the silicon grain nucleation on commercial SnO₂:F substrates as a function of RF power has been also explored and compared with that obtained on Corning glass.

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2. Experimental procedures

Hydrogenated silicon–carbon films were deposited in a high vacuum plasma enhanced chemical vapor deposition (PECVD) system capacitively coupled to a RF generator of 13.56 MHz at the substrate temperature of 250 °C. For each sample films were deposited on different substrates simultaneously: Corning 7059 glass, commercial SnO₂:F coated glass (Asahi type U) and <100> c-Si, for different characterizations. Films were grown by silane (SiH₄) and methane (CH₄) gas mixtures highly diluted in hydrogen (H₂). In all the depositions the pressure, the total gas flow rate, the methane fraction $[\text{CH}_4]/([\text{SiH}_4] + [\text{CH}_4])$ and the hydrogen dilution, $[\text{H}_2]/([\text{SiH}_4] + [\text{CH}_4])$, were fixed at values of 226 Pa, 300 sccm, 0.50 and 250, respectively. Several films were deposited varying the RF power, w , from 15 to 100 W (RF power density range 0.098–0.65 W/cm²).

Dark conductivity, σ_d , and photoconductivity, σ_{ph} , under white light of 100 mW/cm² (AM1 conditions), were measured at room temperature in coplanar configuration using a Keithley 617 electrometer. The optical transmission and reflection spectra in the 200–2500 nm range were collected using a dual beam Perkin Elmer Lambda 900 spectrophotometer. From these spectra the thickness and the absorbance of films were determined. Raman spectra were obtained in the 200–2000 cm^{−1} range using a Micro-Raman Renishaw spectrophotometer equipped with a cooled CCD detector and an argon laser excitation at 514.5 nm. PL spectra were obtained at room temperature by exciting the samples with the 514.5 nm line of an argon laser at a power density of 25 mW/mm². The emitted light was collected in a single monochromator with a focal length of 20 cm coupled to a cooled back illuminated CCD camera.

A DME DS95-50 atomic force microscope was used operating in air at an average temperature of 23 °C and relative humidity of 40–50%. All measurements were performed in AC-mode, using silicon tips with a tip radius <10 nm, produced by NanoWorld PointProbe. The lateral and vertical accuracy of the instrument were checked using ultra sharp silicon gratings produced by NT-MDT.

The elemental composition was evaluated with ion beam analysis using the HVEC 2.5 MeV and the CN 7 MV Van de Graaff accelerators at INFN-Laboratori Nazionali di Legnaro. Rutherford backscattering (RBS) with α -particle at 2.2 MeV energy was used to evaluate the silicon dose, while nuclear reaction analysis using the ¹²C(d,p)¹³C reaction with deuterons at 1.05 MeV was used to give the carbon content across all the film thickness. Since these measurements, we can show the carbon to silicon percentage $C/(C + \text{Si})$, relative to the overall film. Furthermore, the hydrogen atomic percentage was obtained with elastic recoil detection analysis (ERDA) using α -particles at 2.2 MeV at a recoil angle of 30°.

3. Results and discussion

The RF power w affects the optical, electrical, structural and radiative properties of hydrogenated silicon–carbon films [8,10].

With increasing w a transition from crystalline to amorphous phase occurs as shown in Fig. 1 by the Raman spectra of the samples deposited on Corning glass. For films deposited at $w < 35$ W, the most relevant peak in the spectra is due to the Si–Si TO mode centered at around 520 cm^{−1}, revealing the presence of silicon crystallites [11]. For samples deposited at $w \geq 35$ W the peak of crystalline silicon disappears and the spectra consist of a broad component at around 480 cm^{−1} related to the amorphous phase. Neither SiC nor C crystallites have been detected, therefore films are composed of Si crystallites embedded in an amorphous matrix. An evaluation of crystalline volume fraction, f , can be obtained, with some caution, by the ratio of the integrated scattering intensity of the crystalline phase to the total scattering intensity

$$f = I_c / (I_c + I_a),$$

where I_c and I_a are the areas of Gaussian peaks at 520 and 480 cm^{−1}, respectively [12]. The crystalline volume fraction decreases from 56 to 41% in the 15–25 W range.

Since the results of ion beam analysis it was found that carbon content, $x = C/(C + \text{Si})$, and the hydrogen concentration, $H/(H + \text{Si} + C)$, in the 15–100 W range increase from 0.014 ± 0.002 to 0.19 ± 0.03 and from 0.09 ± 0.01 to 0.38 ± 0.06 , respectively (see Table 1).

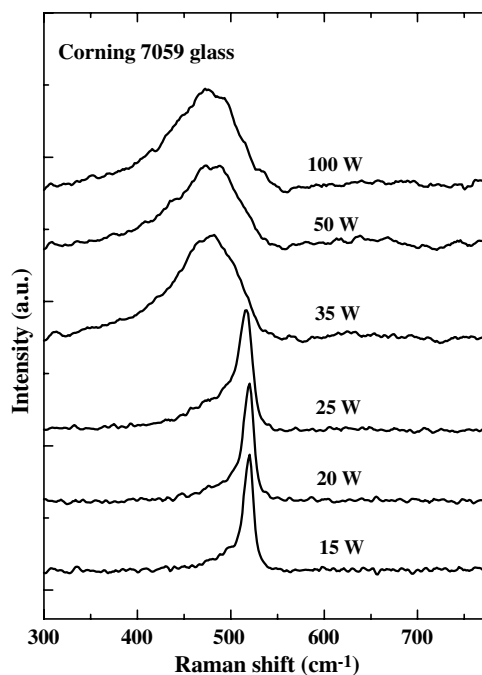


Fig. 1. Raman spectra of samples deposited on Corning 7059 glass substrates at different RF power.

Table 1
Properties of the silicon carbon films as a function of RF power w

w (W)	x	H	σ_d ($\Omega^{-1} \text{ cm}^{-1}$)	σ_{ph} ($\Omega^{-1} \text{ cm}^{-1}$)	ρ (nm)
15	0.014 ± 0.002	0.09 ± 0.01	5.7×10^{-4}	6.0×10^{-2}	17
20	0.025 ± 0.003	0.10 ± 0.01	4.0×10^{-4}	2.0×10^{-2}	–
25	–	–	1.8×10^{-5}	3.3×10^{-4}	–
35	0.049 ± 0.006	0.13 ± 0.02	3.0×10^{-7}	6.9×10^{-6}	11
50	0.115 ± 0.015	0.28 ± 0.04	2.4×10^{-8}	3.0×10^{-6}	0.44
100	0.19 ± 0.03	0.38 ± 0.06	1.0×10^{-11}	6.2×10^{-8}	0.56

Carbon content, $x = C/(Si + C)$, by RBS and NRA; hydrogen atomic fraction, $H = H/(Si + C + H)$, by ERDA; dark conductivity, σ_d , photo-conductivity, σ_{ph} , rsm roughness, ρ , by AFM.

The bond configurations were determined by the analysis of IR absorption spectra, reported elsewhere [10]. The main interesting region is in the $500\text{--}1000 \text{ cm}^{-1}$ range. This region can be considered the superposition of four vibration modes: the Si–H wagging/rocking at 640 cm^{-1} , the Si–C stretching at $760\text{--}780 \text{ cm}^{-1}$, the Si–H bending at $800\text{--}900 \text{ cm}^{-1}$ and C–H wagging at 1000 cm^{-1} [13]. The SiC concentration, N_{SiC} , can be evaluated by the integrated area of the deconvoluted band at 780 cm^{-1} , using $2.13 \times 10^{19} \text{ cm}^{-2}$ as calibration factor [13]. N_{SiC} increases with increasing w as shown in Fig. 2 where also x trend is reported. These results allow to state the amorphous phase consists of hydrogenated silicon–carbon and the N_{SiC} is correlated to the carbon content in the film.

AFM measurements, carried out on samples deposited at different w are displayed in Fig. 3. The topographic images of samples deposited at 15 and 35 W present the occurrence of protrusions of clusters of grains emerging from the surface in the direction of growth. The cluster dimension decreases with increasing w , indicating a lowering of the crystallinity degree according to Raman results. The topographic images of samples deposited at 50 and 100 W exhibit a surface structure consistent with the lack of long-range order expected in amorphous samples. The behaviour of the surface structure as a function of w can be quantified by the root-mean-square (rms) surface roughness, ρ , listed in Table 1. ρ is a relevant parameter because it is related to the diffusive light scattering that can reduce

the reflectance of the material in the infrared spectrum. For the investigated films ρ decreases with increasing w , however for samples deposited at lower w the roughness assumes the typical values of microcrystalline silicon films [14].

From the above data analysis it results that the increase of RF power leads to the increase of carbon content and hinders the crystallite formation according to Ref. [15]. The dark conductivity, σ_d , and the photo conductivity, σ_{ph} , were measured (see Table 1) to gain information on the electrical properties of these alloys. Both quantities decrease very steeply increasing w , approximately 8 and 6 orders of magnitude. The worsening of the electrical properties is due to the combined effect of the decrease of crystalline volume fraction and the increase of carbon content. Microcrystalline films with dark conductivity from 5.7×10^{-4} to $1.8 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ were grown in the 15–25 W range.

It is known that TCO substrates are commonly used in many devices (solar cells, LEDs, etc.) [7]. For this reason, the effects of a commercial $\text{SnO}_2\text{:F}$ substrate on the Si grain nucleation and on the optical properties of $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ were investigated, varying the RF power from 15 to 100 W.

Fig. 4 shows the Raman measurements of the films deposited on this kind of substrate. All the spectra present the peak ascribed to TO vibration of c-Si, except for the spectrum of samples deposited at 100 W that consists of a broad component at 480 cm^{-1} related to the amorphous phase. By comparing the spectra of Fig. 4 with those of films deposited on Corning glass (Fig. 1) it can be inferred that the SnO_2 substrate favours the growth process of microcrystalline films up to 50 W even if with a tensile stress as indicated by the shift of 520 cm^{-1} peak towards low energy [16]. The crystalline volume fraction varies from 56 to 17% in the 15–35 W range.

Carbon content of films deposited on SnO_2 substrate were not measured, however, some information about it can be obtained by PL spectra performed at room temperature and plotted in Fig. 5. Indeed, with increasing RF power the shift of the PL peak position and the increase of the PL peak intensity indicate that more carbon is incorporated in the films [17,18]. It appears that, also for films deposited on $\text{SnO}_2\text{:F}$ substrates, the decrease of crystallinity is accompanied with the increase of carbon content.

In order to investigate the optical properties of silicon–carbon films deposited on $\text{SnO}_2\text{:F}$ substrates the absorbance spectra of these films were determined by means of the R/T measurements. Fig. 6 shows the absorbance spectra in the $200\text{--}1000 \text{ nm}$ range of wavelength. The samples deposited in the 15–35 W range have approximately the same spectra, while for $w > 35 \text{ W}$ a lowering of the absorbance as a function of the RF power in the wavelength range of $\approx 300\text{--}1000 \text{ nm}$, can be appreciated. These trends can be explained taking into account that the optical absorption of $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ films is controlled by the crystallinity degree and the carbon content in the amorphous

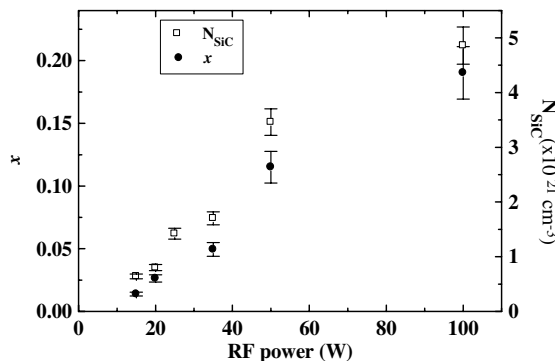
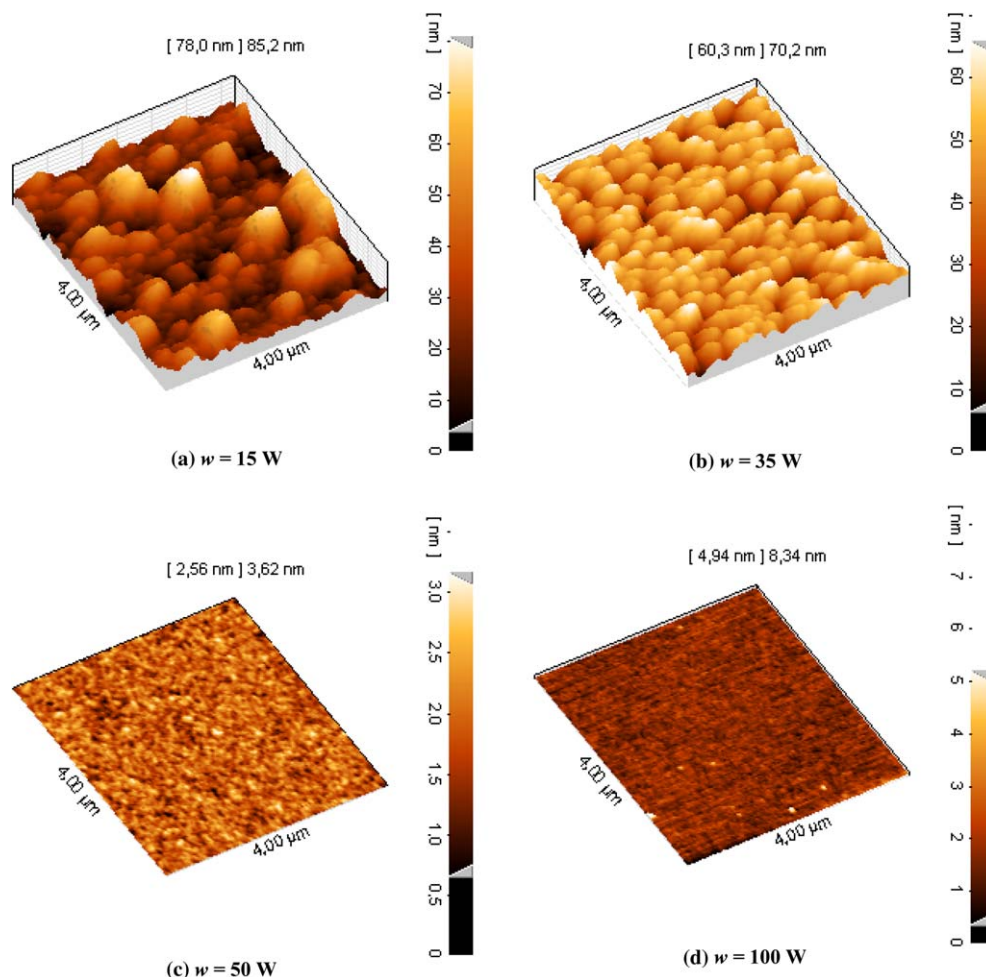
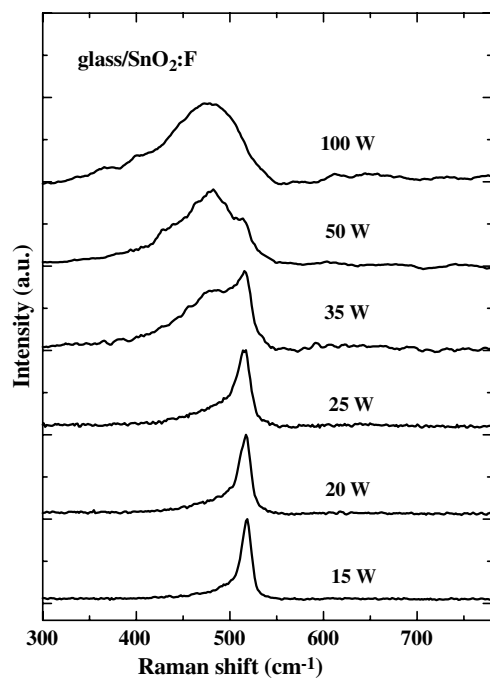
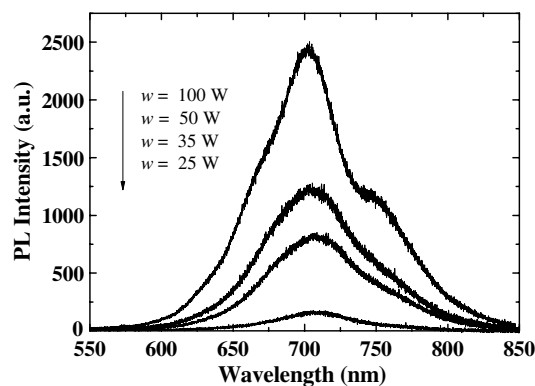


Fig. 2. Carbon content x and SiC bond concentration N_{SiC} vs. RF power.

Fig. 3. Topographic images of samples deposited at different RF power w .Fig. 4. Raman spectra of samples deposited on glass/SnO₂:F substrates at different RF power.Fig. 5. PL spectra of samples deposited on glass/SnO₂:F substrates at different RF power w .

phase [10,16]. Indeed, the increase of crystalline fraction produces a decrease of the optical absorbance spectra in the UV–VIS region and an increase in the NIR region. On the other hand, the increase of carbon content influences the absorbance mainly in the UV–VIS region lowering the spectra. In the $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ alloys the reduction in the crystallinity degree is always coupled with increasing carbon content, therefore it can be hypothesized that, in

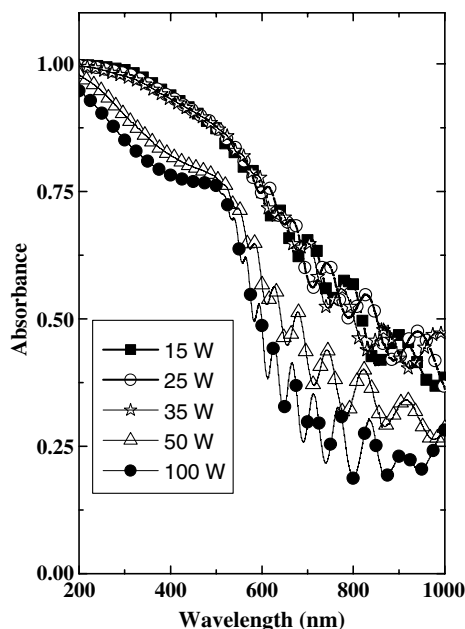


Fig. 6. Absorbance spectra in UV–VIS–NIR region for samples deposited on glass/SnO₂:F substrates at different RF power.

the 15–35 W range, the effect of the moderate reduction in crystallinity on the absorption is balanced by the effect of the increase of carbon content. For $w > 35$ W a marked decrease of the crystalline fraction combined to the enrichment of carbon content in the amorphous phase leads to a lowering of the optical absorbance in a wide range of the UV–VIS–NIR region. Similar trends of the optical properties as a function of RF power were obtained for $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ films deposited on Corning 7059 glass [8,10].

The possibility of varying in the UV–VIS–NIR region the optical absorption properties of $\mu\text{c-Si}_{1-x}\text{C}_x\text{:H}$ at low deposition temperature, makes this material suitable for device applications such as stacked multijunction solar cells [19], color sensors [20] and solar blind UV detectors [21].

4. Conclusions

Hydrogenated silicon–carbon films have been grown in a PECVD system at low substrate temperature (250 °C) by silane + methane gas mixtures highly diluted in hydrogen varying the RF power from 15 to 100 W.

The RF power appears to control the microcrystalline to amorphous phase transition. The increase of RF power reduces the crystallinity degree and enhances the carbon

content in the films leading to a deterioration of the electrical properties. Films with higher dark conductivity (5.7×10^{-4} – $1.8 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$) can be deposited in the 15–25 W range.

The nucleation of silicon grain is enhanced growing on SnO₂:F coated glass substrate and microcrystalline silicon–carbon films can be obtained in the 15–50 W range. The absorbance spectra can be lowered in the wavelength range of ≈ 300 –1000 nm increasing w .

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