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Thermal annealing effects on the optical and electrical properties of a-SiC:H thin films sputtered at different hydrogen flow rates

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In this paper we study the effect of annealing process on the optical and electrical properties of the a-SiC:H thin films sputtered at three different hydrogen flow rates 9 sccm, 14 sccm and 20 sccm. Optical transmission measurements have shown that the optical band gap, E_g, is affected by thermal annealing when T_a>575 °C, due to emission of hydrogen bonded to silicon. For hydrogen flow rate 9 sccm, the evaluation of the optical and electrical measurements have shown that for 400 °C<T_a≤ 550 °C the quality of the a-SiC:H thin films presents a reasonable improvement, with the optimum result been achieved at T_a = 550 °C remaining there up to 575 °C. This behavior is attributed to the relaxation of the strain in the amorphous network. Further increase of T_a causes emission of hydrogen bonded to silicon, leading to rapid deterioration of the properties of the amorphous semiconductor. As the hydrogen flow rate increases from 9 sccm to 20sccm, the optimum material quality is achieved at higher T_a, since the emission of a small quantity of hydrogen enables additional relaxation in the amorphous network. Finally, the maximum values of photosensitivity of the annealed a-SiC:H thin films (≅1500) in combination with the corresponding values of E_g make these films very interesting for applications as optical sensor devices and solar cells.

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1. Introduction

Since the first preparation of a-SiC:H films by Anderson and Spear [1], an increasing research interest has been pointed out on this material, for the production of a large variety of materials with interesting properties (wide optical band gap, mechanical strength, and photoluminescence) that can be tailored according to the needs of several different technological applications. As a result, nowadays a great number of applications are based on a-SiC:H thin films, such as solar cells [2], optical sensors [3], color sensors [4], flame sensors [5], Schottky diodes [6] and TFTs [7]. All these years the main target of the research works has been the optimization of these devices mainly by the improvement of the a-SiC:H quality, that implies lower density of gap states and structural defects. This has been achieved by changing the deposition parameters [8,9] or by varying the atomic ratio C/Si [8]. Additionally, quality improvement of a-SiC:H can be achieved by thermal annealing in the temperature range from 450 °C up to 650 °C [10-15], when the silicon-hydrogen bonds start breaking and a rearrangement of bonds take place in the network of amorphous semiconductor. It has been found that the optimum material quality depends on annealing temperature up to a critical value, which depends on the preparation technique. Taking into account that the improvement of a-SiC:H quality is due to the rearrangement in the amorphous network [15,16], since the crystallization process takes place at too high annealing temperatures [13,14], it would be interesting to study the effect of annealing temperature on the optical and electrical properties of the amorphous material deposited at different preparation conditions.

The present work is a contribution to this particular direction and more specifically, it is studied the effect of thermal annealing, in the temperature range from 300 °C up to 775 °C, on the electrical and optical properties of rf sputtered a-SiC:H thin films for three different hydrogen flow rates, 9,14 and 20 sccm. The experimental results have shown that the optimum material quality is achieved at different annealing temperatures, from 550 °C up to 600 °C, as the hydrogen flow rate varies from 9 sccm to 20 sccm.

2. Experimental

The a-SiC:H thin films were deposited by r.f. sputtering on Corning Glass substrates and on n-type c-Si (ρ=5-10Ωcm) substrates. As a target we used poly-SiC of constant composition (C 66 wt% and Si 34 wt%) and of 99.8% purity. The r.f. power was 250W and the target to substrate distance was 5.5 cm. The sputtering chamber was evacuated to a pressure lower than 5×10^{-7} Torr, before the piping of Argon. During the deposition, the flow rate of argon and hydrogen was 9, 14 and 20 sccm, and substrate temperature (T_s) was 160 °C, 140 °C, and 120 °C respectively. The pressure in the sputtering chamber was 5×10^{-3} Torr. Under these deposition conditions the dangling bonds of a-SiC:H thin films are compensated to an optimum degree as we have found in a previous work [9] leading to an optimization of electrical and optoelectronic properties of a-SiC:H.

The as deposited a-SiC:H films were annealed in the temperature range from 300 °C to 775 °C for 1 hour. At each temperature the samples were encapsulated in quartz tubes, which were evacuated at a pressure of the order 10^{-5} Torr. The annealing process was terminated at 775 °C because at this temperature the films started to peel from the substrates.

The optical measurements of the a-SiC:H thin films in the range from 400 nm up to 700 nm were carried out by a single beam spectrophotometer using samples deposited on the Corning Glass substrates. The Fourier transform infra-red (FTIR) measurements were carried out in the range of 2.5 –25 μm using a double beam spectrophotometer and samples deposited on crystalline Si substrates.

After the annealing process, electrodes, for the dc conductivity measurements, were formed by vacuum evaporation of Al on samples sputtered on Corning Glass substrates. A co-planar gap configuration was used for the conducts. The I-V characteristics of Al/a-SiC:H/Al structures represent the resistance of a-SiC:H thin films, since the contacts resistance was found negligible.

The dark dc conductivity measurements were carried out using a cryostat, evacuated below 10^{-4} Torr, in the temperature range from 20 °C up to 220 °C. For the dc photoconductivity measurements at room temperature the samples were illuminated under AM1 (100 mW/cm^2) conditions.

3. Results and discussion

A series of optical transmission measurements of a-SiC:H thin films in the range from 400 nm up to 700 nm was carried out using the Lambert-Beer law:

$$T=T_o e^{-\alpha d}, \tag{1}$$

where d is the film thickness and T, T_o the film-substrate and the substrate transmittance respectively. The values of absorption coefficient, α, were obtained as a function of photon energy. Published results [8,9] have shown that the absorption coefficient of a-SiC:H thin films and the photon energy are associated by the relation [17]:

$$\alpha h\nu=B^2(h\nu - E_g)^2, \tag{2}$$

where h is Planck's constant, ν is the radiation frequency, E_g the optical band gap, and B is the slope of the graphs $(\alpha h\nu)^{1/2}$ versus hν, which hinges on the amorphous material degree [8,17]. The values of E_g as well as B were obtained by fitting such absorption data to the above expression (2).

Fig. 1 shows the optical energy band gap of the a-SiC:H thin films as a function of annealing temperature for three different hydrogen flow rates, 9, 14 and 20 sccm. As it is clear from Fig. 1, the optical energy band gap of the a-SiC:H films for hydrogen flow rate 9sccm is independent of the annealing temperature for T_a ≤450°C, whereas from 450 °C to 575 °C may have a slight decrease, since it is within experimental error. This value (2.00eV) of E_g is the same as that of the as deposited (T_s=160 °C) a-SiC:H thin films [9]. For T_a >575 °C up to 725 °C, E_g decreases rapidly by 0.42eV, and it remains almost constant for values of T_a up to 775°C. Since the emission of hydrogen bonded to carbon as well as the crystallization process of the a-SiC:H starts at higher values of T_a (>800 °C) [8, 12,14], this behavior of E_g versus T_a can be attributed to the emission of hydrogen bonded to Si, as it will be discussed below. A similar dependence of the optical band gap on annealing temperature holds for hydrogen flow rates 14 and 20 sccm.

Fig. 2 shows the dependence of the slope of the optical spectra, B, on T_a for three different hydrogen flow rates. It is obvious from this figure that for hydrogen flow rate 9 sccm the slope B remains constant up to 400°C, it increases slowly with the increase of T_a up to 550 °C, and it remains constant up to 575 °C. For higher annealing temperatures, B decreases rapidly up to 725 °C and remains invariant up to 775 °C. Taking into account that high values of B imply low degree of disorder in the amorphous material and vice-versa [8,9,17], it is clear from this figure that the annealing process affects the disorder of the amorphous material when T_a is over than 400 °C and the optimum material quality is achieved at T_a = 550 °C. Since the emission of hydrogen bonded to silicon occurs over than 575 °C (see Fig. 4), this matter can be attributed to relaxation of the strain in the amorphous network, which leads to a reduction of gap states concentration, improving the electrical and optoelectronic properties of a-SiC:H [8]. For T_a >575°C, where the emission of hydrogen bonded to silicon takes place (see Fig. 4), B decreases rapidly due to voids formation in the a-SiC:H thin films, deteriorating the electrical and optoelectronic properties of the films [8,10,15]. From the same figure it is obvious that as the hydrogen flow rate increases from 9 to 20 sccm, the maximum of B is shifted from 550 °C to 600 °C. This result is possibly due to the fact that the a-SiC:H films deposited at hydrogen flow rate 20 sccm present higher strain in their network [15] in comparison with those of 9 sccm and their optimum quality is achieved in combination with a weak hydrogen emission that takes place at 600 °C (see Fig. 4). This emission is necessary for the optimum compensation of dangling bonds and structural defects in the amorphous network. It is important to note that as it has been found in previous research works [8,9,18] the variation of B is not so sensitive with the disorder in a-SiC:H, in contradiction with the quality parameters derived from the electrical measurements, as we will see later.

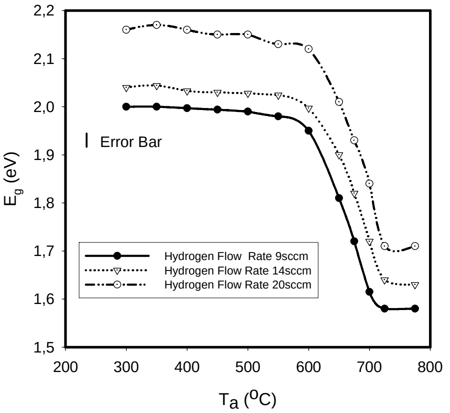

Fig. 1. Optical energy band gap E_g of a-SiC:H films as a function of the annealing temperature, T_a, for three different hydrogen flow rates.

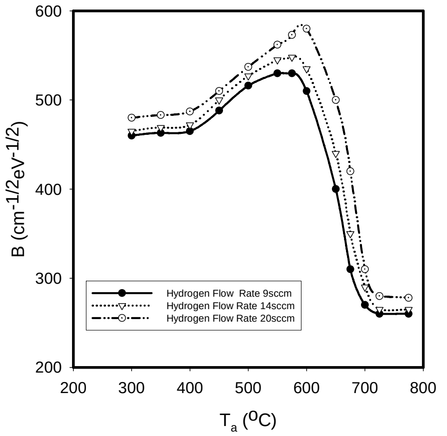

Fig. 2. The slope of the optical spectra, B, of a-SiC:H films as a function of the annealing temperature, T_a, for three different hydrogen flow rates.

The infrared (IR) spectra of a-SiC:H thin films in the range of 2.5-25 μm for various annealing temperatures from 300 °C up to 700 °C and for three different hydrogen flow rates have shown three absorption bands, at 780cm^{-1}, 2050 cm^{-1} and 2890cm^{-1}, which they are attributed to stretching vibration mode Si-C [19], Si-H$_n$ [20], and C-H$_n$ [21], respectively. The variation of hydrogen concentration in a-SiC:H thin films has been evaluated from the absorption band at 2050 cm^{-1} , because this band presents intensive dependence on T_a in the range from 600 °C up to 775 °C, whereas the other two bands do not show any detectable dependence in the above range of annealing temperatures.

Fig. 3 shows typical results from IR measurements in the range of 1900-2200 cm^{-1} for various annealing temperatures from 300 °C up to 700 °C and for hydrogen flow rate 9 sccm. As it is clear from this figure, the maximum of the absorption spectra remains almost constant with the increase of T_a up to 575 °C, and it decreases in the range from 600 °C up to 700 °C, indicating a decrease of hydrogen bonded to silicon for T_a >575 °C.

The values of hydrogen bonded to silicon have been evaluated from the absorption band at 2050 cm^{-1} as a function of T_a and for three different hydrogen flow rates, 9sccm, 14sccm and 20 sccm, by using the relation [8,18]:

$$N_H = A\int \frac{a(k)}{k}dk \qquad (3)$$

where k is the wave number, α(k) the IR absorption coefficient and A is a constant equal to 1.4×10^{20}cm^{-2} [8,18]. The results are presented in Fig. 4.

It is obvious from Fig. 4 that independently hydrogen flow rate, the concentration of hydrogen bonded to silicon as a function of T_a is almost invariant up to 575 °C and then it decreases rapidly up to 700 °C. This overall behavior of N_H on T_a is qualitatively similar with E_g, suggesting that the emission of hydrogen bonded to silicon is mainly responsible for the decrease of the optical band gap by ≅0.42eV in the range of T_a from 600 °C up to 700 °C.

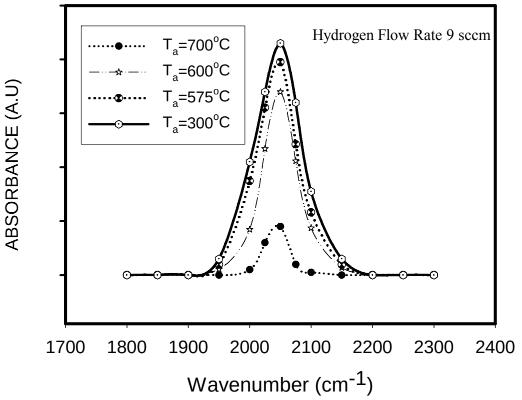

Fig. 3. FTIR absorption band for Si-H$_n$ stretching mode of a-SiC:H films as a function of the wavenumber at hydrogen flow rate 9 sccm and for various annealing temperatures, T_a.

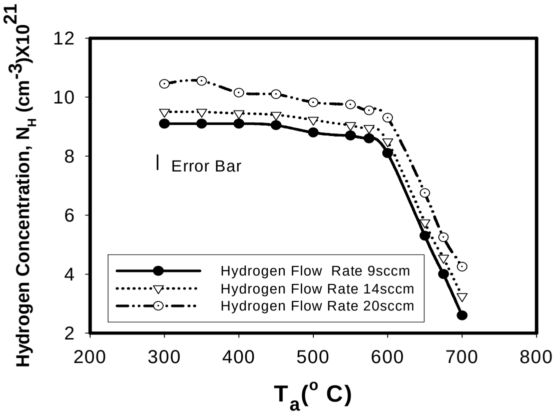

Fig. 4. Hydrogen Concentration bonded to Silicon N_H of a-SiC:H films as a function of the annealing temperature, T_a, for three different hydrogen flow rates.

Fig. 5 shows typical results for the temperature dependence of dark dc electrical conductivity, σ_D, in the range from 20 ^oC up to 220 ^oC of the a-SiC:H samples, for various annealing temperatures and for hydrogen flow rate 9 sccm. Taking into account that previous works [3,9] have shown that the rf sputtered a-SiC:H thin films exhibit n-type conductivity, it is obvious from this figure that the dark dc electrical conductivity increases exponentially with the absolute temperature of measurement, T, according to the relation [8]:

$$\sigma_D=\sigma_o \exp[-(E_C-E_F)_{T=0}/kT] \qquad (4)$$

where $(E_C-E_F)_{T=0}$ is the energy difference between the edge of conduction band, E_C, and the Fermi level E_F at T=0 K, σ_o is a factor independent on T, and E_a is the conductivity activation energy defined by the relation:

$$E_a=(E_C-E_F)_{T=0} \qquad (5)$$

From the slope of the graphs $\log\sigma_D$ versus 1/T, and using the relation (4) the conductivity activation energy has been calculated. Fig. 6 shows the conductivity activation energy versus annealing temperature from 300 ^oC up to 775 ^oC for three different hydrogen flow rates. It is obvious from this figure that, for hydrogen flow rate 9 sccm, the conductivity activation energy of the a-SiC:H thin films qualitatively presents a similar dependence on T_a as the slope B. More specifically, E_a is almost independent of the annealing temperature for temperatures up to 400 ^oC and it is equal to 0.58 eV. For higher annealing temperatures, the conductivity activation energy increases, reaching to a maximum value 0.75 eV at T_a =575 ^oC. Taking into account that the a-SiC:H thin films are undoped, the increase of E_a with T_a (up to 550^{o}C) reveals decrease of gap states due to higher compensation degree of dangling bonds and structural defects in the films [8,9] and, consequently, the maximum value of E_a indicates the optimum material quality [6,7,13,15]. For further increase of T_a (>575 ^oC), E_a decreases rapidly, reaching to a minimum value of 0.23 eV at T_a=725 ^oC, and then it remains constant up to 775 ^oC, indicating degradation of the material quality and, more specifically, formation of voids [8,14]. For as much as that the emission of hydrogen bonded to silicon occurs over than 575 ^oC, this overall behavior of E_a is attributed to the existence of two different processes. More specifically, for annealing temperatures from 400 ^oC up to 550 ^oC, a relaxation of the strain in the amorphous network appears taking place, improving the electrical and optoelectronic properties of the amorphous semiconductor [8,9, 15]. In the range from 550 ^oC up to 575 ^oC, E_a remains constant, since no other structural changes are expected. For T_a> 575 ^oC, the emission of the hydrogen bonded to silicon causes formation of voids in the amorphous network, deteriorating rapidly the quality of a-SiC:H thin films. As the hydrogen flow rate increases, from 9 to 20 sccm, there is a shift in the corresponding maximum of E_a versus T_a curves towards higher annealing temperature (from 550^{o}C to 600^{o}C). This result can be explained taking into account that the films deposited at hydrogen flow rate 20 sccm contain higher hydrogen concentration in comparison with that of 9 sccm, which causes higher strain in the amorphous network [15] and, consequently, a weak emission of hydrogen bonded to silicon enables additional improvement of the material quality.

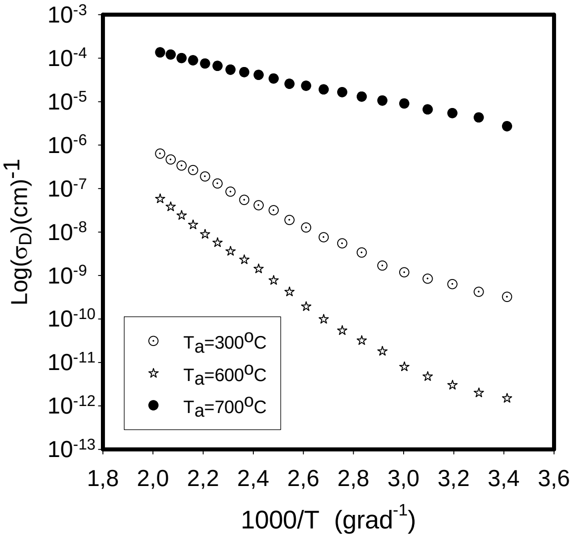

Fig. 5. Dark dc electrical conductivity, σ_D, of a-SiC:H thin films as a function of $10^3/T$, at hydrogen flow rate 9sccm for various annealing temperatures, T_a.

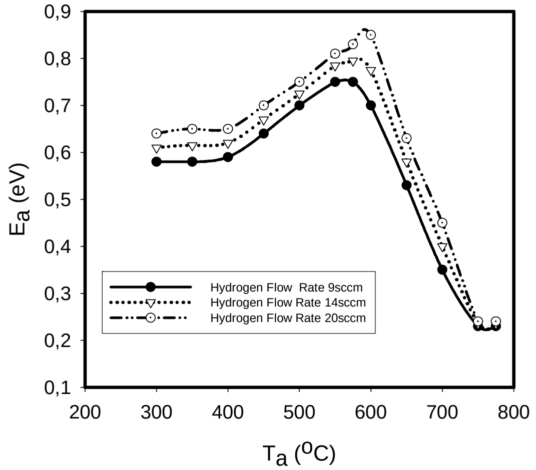

Fig. 6. Conductivity activation energy, E_a, of a-SiC:H thin films, as a function of the annealing temperature, T_a for three different hydrogen flow rates.

Finally, Fig. 7 shows the photosensitivity expressed by the ratio $\sigma_{Phot}/\sigma_{DRT}$ versus T_a and for three different hydrogen flow rates, where σ_{Phot} is the room temperature dc photoconductivity. It is obvious from this figure that the ratio $\sigma_{Phot}/\sigma_{DRT}$ qualitatively presents a similar dependence on T_a as B and E_a. More specifically, for hydrogen flow rate 9 sccm, the ratio is almost constant up to 400 ^oC and equal to 80. In the range from 450 ^oC up to

550 °C, the photosensitivity increases presenting a maximum value 850 at 550 °C and it remains constant up to 575 °C. For further increase of T_a up to 700 °C, the photosensitivity decreases rapidly down to 10. Also, as the hydrogen flow rate increases from 9 to 20 sccm the maximum value of $\sigma_{Phot} / \sigma_{DRT}$ is shifted at higher T_a (=600 °C). These results are in excellent agreement with the results of optical and dc dark conductivity measurements, supporting the previous analysis. It should be referred that these maximum values of the photosensitivity (up to 1500) in combination with the corresponding values of the optical band gap of the a-SiC:H thin films, are very interesting for fabricating high sensitivity optical sensor devices in the blue region of the optical spectrum as well as low cost high efficiency solar cells.

Finally, as it is clear from Fig. 7, for a given T_a the photosensitivity presents higher values as the hydrogen flow rate increases from 9 sccm to 20 sccm. This behavior is possibly related to higher compensation degree of dangling bonds as the hydrogen flow rate increases even though it causes higher strain in the amorphous semiconductors [8]. Also, the above-described behavior of photosensitivity is possibly related to the values of E_g, (see Fig. 1) and the spectrum of AM1 illumination, since the films deposited at higher hydrogen flow rate can absorb more photons with higher frequency, contributing more carriers to the photoconductivity.

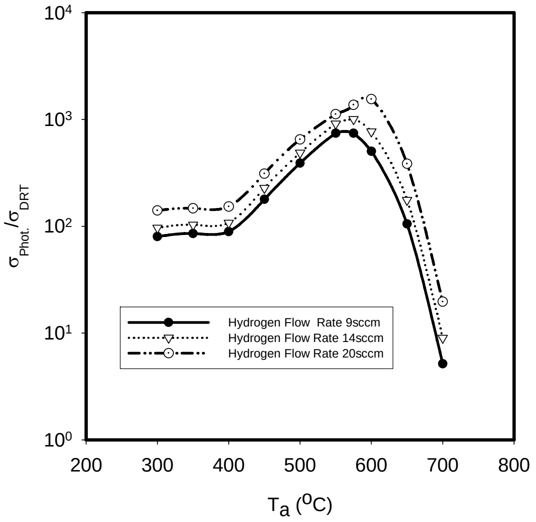

Fig. 7. Photosensitivity, $\sigma_{Phot} / \sigma_{DRT}$, of a-SiC:H thin films, as a function of the annealing temperature, T_a , for three different hydrogen flow rates.

4. Conclusions

In the present work the effect of thermal annealing on the optical and electrical properties a-SiC:H thin films deposited at three different hydrogen flow rates was studied in order to be achieved the optimum material quality. The main conclusions are:

a. Independently the hydrogen flow rate, the optical band gap of a-SiC:H thin films is invariant for annealing temperatures up to 575 °C, and subsequently it decreases with further increase of T_a. This behavior is attributed to the emission of hydrogen bonded to silicon.

b. The evaluation of the slope of the optical spectra, the conductivity activation energy as well as the photosensitivity show that for hydrogen flow rate 9 sccm, the quality of the a-SiC:H thin films is invariant for $T_a \leq 400$ °C, whereas for the temperature range from 400 °C up to 550 °C a reasonable improvement occurs to the amorphous material quality, with the optimum quality to be achieved at T_a =550 °C and remaining up to 575 °C. This overall behavior is attributed to the relaxation of the strain in the amorphous network, which starts from 400 °C and it terminates at 550 °C. For further increase of T_a (>575 °C), the phenomenon of hydrogen emission causes rapid deterioration of the properties of the amorphous material.

c. As the hydrogen flow rate increases from 9 sccm to 20sccm, the optimum material quality corresponds to higher values of T_a, 550 °C and 600 °C respectively. This can be explained taking into account that higher hydrogen flow rate causes higher strain in the amorphous network and, consequently, a weak hydrogen emission that takes place at T_a=600°C enables additional rearrangement in the amorphous network.

d. The maximum values of photosensitivity of the annealed a-SiC:H thin films (≅1500) in combination with the corresponding values of E_g make these films very interesting for applications as optical sensor devices and solar cells.

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