

## Study of optimization of Al/a-SiC:H Schottky diodes by means of annealing process of a-SiC:H thin films sputtered at three different hydrogen flow rates

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### Abstract

The aim of the present work is to study the optimization of the electrical and optical properties of a-SiC:H Schottky diodes using thermal annealing process to a-SiC:H thin films in the range from 300°C up to 675°C. The films were deposited onto c-Si(n) using the rf sputtered method at three different hydrogen flow rates, 9sccm, 14sccm, and 20sccm. Subsequently, Al dots evaporated onto a-SiC:H in order to form Schottky contacts. The measurements of logI-V characteristics have shown that the Al/a-SiC:H Schottky diodes are optimized at 550°C, 575°C, and 600°C, for hydrogen flow rates 9 sccm, 14 sccm and 20 sccm respectively. At these temperatures the logI-V curves are linear for more than seven orders of magnitude, and the majority carriers are transported by thermal emission mechanism. The measurements of optical response of these diodes present two maximum values (>70%), one in the range from 550nm up to 625nm and the other at 850nm which are attributed to Al/a-SiC:H junction and to a-SiC:H/c-Si(n) heterojunction, respectively. From the overall study of the electrical and optical measurements of the Schottky diodes it is concluded that at hydrogen flow rate 20 sccm and annealing temperature 600°C is achieved the optimum Al/a-SiC:H Schottky diode. This result is in full agreement with the properties of the a-SiC:H.

**Keywords:** Thermal Annealing, Optical Sensor, Electrical Properties, Schottky Diode.

### 1. Introduction

Amorphous hydrogenated Silicon Carbide (a-SiC:H) is widely investigated for various applications, such as solar cells [1], photo sensors [2], MISiCFETs [3], color sensors [4], flame sensors [5], Schottky diodes [6], and LEDs [7]. The properties of the above devices are influenced by the material quality of the a-SiC:H thin films, which can be optimized by preparation conditions [8-10], as well as by preparation technique [10]. Further improvement of the a-SiC:H thin films quality has been reported by using thermal annealing process in the temperature range from 450°C up to 650°C [12-14]. In this temperature range the silicon-hydrogen bonds start breaking and a rearrangement of bonds take place in the network of amorphous semiconductor leading to higher quality of amorphous material. Taking into account previous research work the annealing temperature in which is achieved the optimum material quality,  $T_{aopt}$ , depends on hydrogen flow rate. More specifically, as the hydrogen flow rate increases from 9sccm to 20sccm,  $T_{aopt}$  increases from 550°C up to 600°C. It would be very interesting to optimize the above microelectronic devices by annealing a-SiC:H thin films for different hydrogen flow rates.

On the other hand, even though the most important microelectronic device is the Schottky diode, there are very few works [7,15] on this topic using a-SiC:H. In a previous work it has been reported that for hydrogen flow rate

20sccm and annealing temperature of 600°C, the electrical properties and the optical properties of the Al/a-SiC:H Schottky diodes present very attractive behavior for many applications.

The present work is a contribution to this particular direction and more specifically, Al/a-SiC:H Schottky diodes are fabricated using the optimum a-SiC:H thin films sputtered in three different hydrogen flow rates. The experimental results show that as the hydrogen flow rate increases from 9 to 20 sccm, the electrical and optical properties of the Schottky diodes are modified, reflecting mainly the electrical and optoelectronic properties of the a-SiC:H thin films.

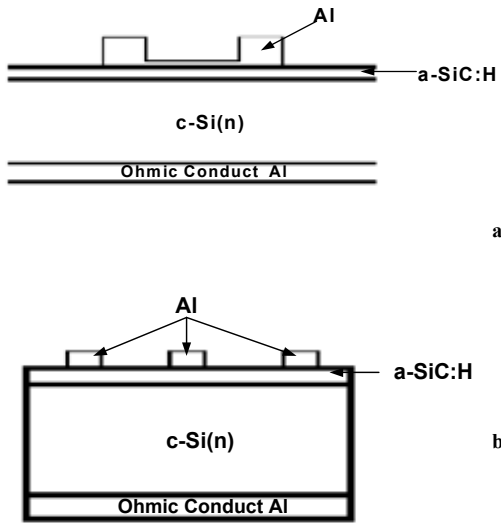
### 2. Experimental

The a-SiC:H thin films were deposited by r.f. sputtering on n-type c-Si ( $\rho=5-10\Omega\text{cm}$ ) substrates. The target used was 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  $5 \times 10^{-7}$  Torr, before the introduction 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  $5 \times 10^{-3}$  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 [8], leading to

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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 675°C for 1 hour. At each temperature the samples were encapsulated in quartz tubes, which were evacuated down to a pressure  $10^{-2}$  Pa. The annealing process was terminated at 675°C, because for higher  $T_a$  we observe complete degradation of the properties of the Al/a-SiC:H Schottky diodes, as it has been reported in our previous work [16]. After the annealing process, ohmic contacts were formed by evaporating Al on the back side of c-Si(n). Then the a-SiC:H surface of the a-SiC:H/c-Si(n) samples was carefully cleaned, sequentially, in trichloroethylene, acetone and methanol, and finally they were flushed with high purity de-ionized water. Finally, the above samples were placed in a high vacuum evaporator (pressure lower than  $2 \times 10^{-6}$  Torr), where aluminum dots (1mm in diameter) were deposited on the amorphous thin films forming the Al/a-SiC:H Schottky diodes. Figure 1(a) shows the typical structure of the Al/a-SiC:H Schottky diodes used for the electrical measurements in the present work.



**Fig.1** (a) Typical structure of the Al/a-SiC:H Schottky diode. (b) Typical structure used for the measurements of the spectral response of the Al/a-SiC:H Schottky diode.

In order to study the optical response of the Al/a-SiC:H Schottky diodes, it was used the optimum material quality of the amorphous material, i.e the a-SiC:H thin films annealed at 550°C, 575°C and 600°C for hydrogen flow rates 9sccm 14sccm and 20 sccm , respectively. Typical structure used for the optical measurements of the Al/a-SiC:H Schottky diodes is given in Figure 1(b). The Al electrode on the amorphous thin film had the shape shown in Fig. 1(b). The metal film in the center of the circular disc was very thin ( $\leq 20$  Å), in order to be transparent to the incident light, whereas at its circumference it was much thicker (about 5,000 Å) to allow for the connection of electrodes. To get this form of Al, the as-deposited Al dots were chemically etched using the photolithography process with very low and controllable etching rate [17]. The thickness in the circular disc was measured using Talystep of  $10\text{Å}$  accuracy. The photoresponse measurements of the structures Al/a-SiC:H /c-Si(n) were carried out in the range from 350nm up to

1000nm, using chopped light with a frequency of 100Hz and reverse applied voltage 2V.

### 3. Results and Discussion

#### a) Electrical Properties

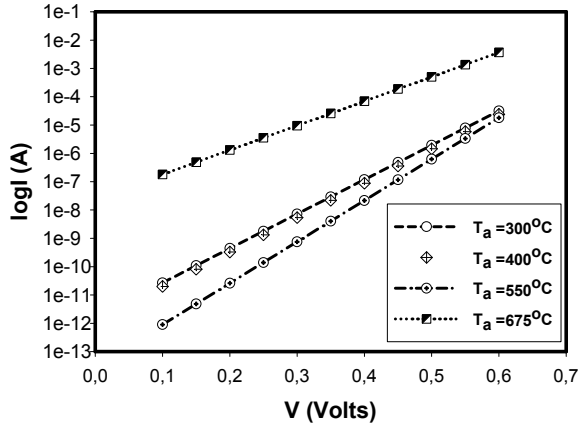
The experimental results of forward room temperature logI-V curves of Al/a-SiC:H Schottky diodes for different annealing temperatures show that the relation between current – voltage (I-V) can be expressed by the relation

$$I = I_s [\exp(qV/\eta kT) - 1], \text{ or} \quad (1.a)$$

$$I = I_s \exp(qV/\eta kT) \text{ for } V > 3kT/q, \quad (1.b)$$

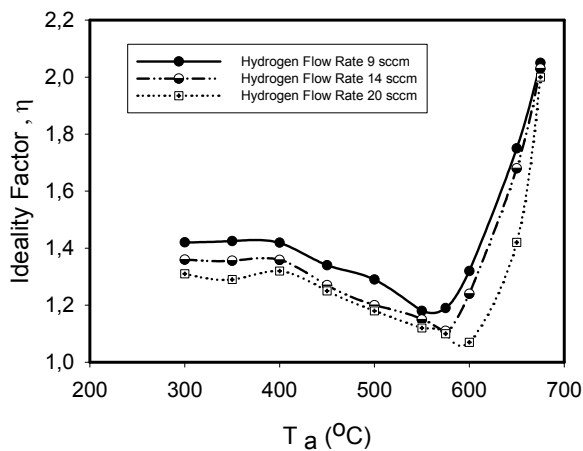
where I is the forward current,  $I_s$  the saturation current, q the magnitude of electronic charge, V the applied forward bias voltage,  $\eta$  the ideality factor, T the absolute temperature of measurement and k Boltzmann's constant. Typical results for hydrogen 9sccm are given in Figure 2. As it is clear from this figure, the annealing temperature does not affect the logI-V curves when  $T_a$  is up to 400°C. For  $T_a$  in the range from 450°C up to 550°C, the logI-V characteristics seem to be optimized, presenting linear relation for up to seven orders of magnitude. However, for higher values of  $T_a$  up to 675°C, the annealing process deteriorates the logI-V curves. According to previous published works [11,12] this overall behavior of logI-V curves of the Al/a-SiC:H Schottky diodes with the annealing temperature is attributed to the fact that up to 400°C there is no one change in the composition of the amorphous alloys as well as in the amorphous network and, consequently, the logI-V curves remains unchanged. In the range of  $T_a$  from 450°C up to 550°C, some silicon-hydrogen bonds, in too small concentration, start breaking and a rearrangement of bonds takes place in the network of amorphous semiconductor leading to higher quality of amorphous material. As a result the logI-V curves show the optimum electrical properties at  $T_a = 550^\circ\text{C}$  with the logI-V characteristics to present linear relation up to seven orders of magnitude. As  $T_a$  increases, much more silicon - hydrogen bonds break and the hydrogen atoms release creating network voids and dangling bonds, that deteriorate rapidly the properties of the a-SiC:H thin films [16] as well as the electrical properties of the Schottky diodes. Qualitatively, the same behavior with  $T_a$  is also observed and for the electrical properties of the Al/a-SiC:H Schottky diodes, where the a-SiC:H thin films were sputtered in hydrogen flow rate 14 sccm and 20 sccm.

Based on the slope of forward logI-V plots, the values of the ideality factor  $\eta$  of the Al/a-SiC:H Schottky diodes were derived for different  $T_a$  and for three different hydrogen flow rates and the results are presented in Figure 3. It is obvious from this figure that for hydrogen flow rate 9 sccm, the ideality factor,  $\eta$ , of Al/a-SiC:H Schottky diodes is constant with annealing temperature up to 400°C and equal to  $1.42 \pm 0.04$ , showing that the annealing process of the a-SiC:H films in this range of  $T_a$  does not affect the ideality factor of these diodes. For higher  $T_a$  up to 550°C, the ideality factor decreases, reaching to a minimum value of  $\eta = 1.18 \pm 0.04$ . After that, the value of  $\eta$  increases rapidly with the increase of  $T_a$ , and it becomes almost two (2.05) at  $T_a = 675^\circ\text{C}$ . This dependence of  $\eta$  on  $T_a$  is in agreement with the above analysis concerning to the quality of the a-SiC:H thin films with the annealing process.



**Fig.2** Typical room temperature forward current-voltage characteristics of Al/a-SiC:H Schottky diodes at different annealing temperature  $T_a$  of the a-SiC:H films, for hydrogen flow rate 9sccm.

More specifically, for  $T_a$  in the range from 450°C up to 550°C, the optimization of the material properties leads to lower values of  $\eta$  since the dominant transport mechanism of the majority carriers seems to be the thermionic emission [6,11]. For the case of  $T_a > 550^\circ\text{C}$ , when the hydrogen release creating dangling bonds and voids formation, recombination seems to be the dominant transport mechanism [11]. Qualitatively, a similar behavior also presents the Al/a-SiC:H Schottky diodes for the case that the amorphous thin films were sputtered in hydrogen flow rate 14 sccm and 20 sccm. It is interesting to notice that as the hydrogen flow rate increases, the optimum material quality is achieved at higher values of  $T_a$ , reflecting exactly the properties of the a-SiC:H [11]. Also, it is obvious that the values of  $\eta$  are greater for hydrogen flow rate 9sccm than that of 20 sccm, which can be explained from the fact that as the hydrogen flow rate increases at suitable  $T_a$  more qualitative material can be obtained.



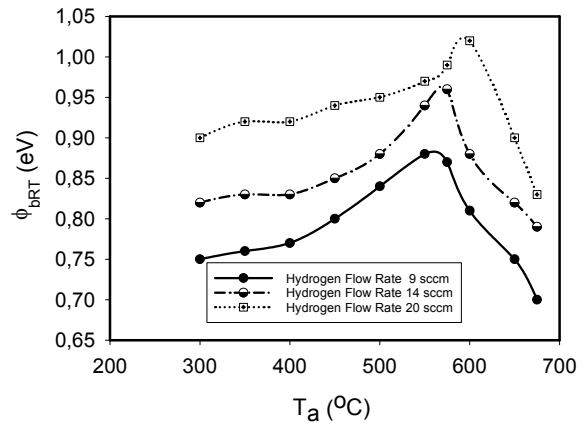
**Fig.3.** The ideality factor,  $\eta$ , of Al/a-SiC:H Schottky diodes as a function of annealing temperature,  $T_a$ , of the a-SiC:H films and for three different hydrogen flow rates.

From the intersection of the  $\log I$  versus  $V$  straight line with the  $\log I$  axis and the reasonable assumption that the dominant transport mechanism is the thermionic emission [6,11], the values of the apparent barrier height at room temperature,  $\phi_{\text{bRT}}$  have been derived using (eq.2) and the experimental value of  $A^{**} = 10\text{A}/\text{cm}^2\text{K}^2$  for n-type a-SiC:H [6].

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$$I_s = sA^{**}T^2 \exp(-\phi_{\text{bRT}}/kT) \quad (2)$$

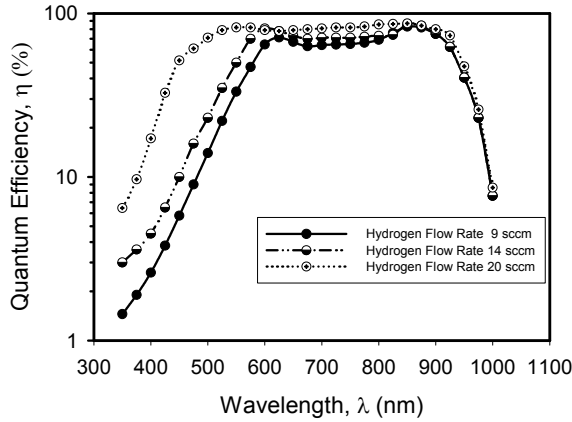
where  $I_s$ , is the saturation current,  $s$  is the device area and  $A^{**}$  the Richardson constant. Figure 4 shows the values of the apparent barrier height at room temperature,  $\phi_{\text{bRT}}$ , of Al/a-SiC:H Schottky diodes, as a function of annealing temperature of the a-SiC:H thin films and for three different hydrogen flow rates. As it is obvious from this figure, for the case of hydrogen flow rate 9sccm, the value of  $\phi_{\text{bRT}}$  is independent of the annealing temperature, for  $T_a$  up to 400°C, whereas from 450°C up to 550°C it presents an increase by about 0.12 eV, reaching to a maximum value equal to  $0.83 \pm 0.04$  eV at  $T_a = 600^\circ\text{C}$ . For further increase of  $T_a$  up to 675°C, the value of  $\phi_{\text{bRT}}$  decreases by 0.22 eV. This overall behavior of  $\phi_{\text{bRT}}$  is also reflects the dependence of the material quality on  $T_a$ , since as the compensation of dangling bonds is achieved to an optimum degree, the value of the apparent barrier height presents higher values [11]. Similar results have also been observed in Metal/a-Si:H Schottky diodes [18]. As the hydrogen flow rate increases from 9sccm to 20 sccm, the dependence of  $\phi_{\text{bRT}}$  on  $T_a$  presents a similar behavior. However the critical value of  $T_{\text{opt}}$  increases with the increase of hydrogen flow rate.



**Fig.4** The room temperature apparent barrier height,  $\phi_{\text{bRT}}$ , of Al/a-SiC:H Schottky diodes as a function of annealing temperature  $T_a$  of the a-SiC:H films and for three different hydrogen flow rate.

### b) Optical Properties

For the study of the optical response of the Al/a-SiC:H Schottky diodes included in the structures Al/a-SiC:H/c-Si(n), these structures are presented in Fig 1(b). In these cases, the rf sputtered a-SiC:H thin films were deposited in three different hydrogen flow rates, 9sccm, 14 sccm 20sccm, and there were annealed at 550°C, 575°C and 600°C, respectively. These annealed thin films of a-SiC:H present the optimum material quality [16] as well as the optimum electrical properties of the Al/a-SiC:H Schottky diodes, as it has been presented above. Figure 5 shows the experimental results of the measured quantum efficiency of the above Al/a-SiC:H Schottky diodes included in the structures Al/a-SiC:H/c-Si(n), in the range of wavelengths,  $\lambda$ , from 350nm up to 1000nm for three different samples.



**Fig.5** Quantum efficiency,  $\eta$  of the Al/a-SiC:H Schottky diode included in the Al/a-SiC:H/c-S(n)/Al structures as a function of the wavelength,  $\lambda$ , for three different hydrogen flow rates, of the a-SiC:H films.

As it is clear from Figure 5, the measured quantum efficiency for the case of 9sccm exhibits two maximum values, one varied from 550nm up to 600nm depending on the hydrogen flow rate and the other at  $\lambda=850$ nm. Both of these two maxima are attributed to the existence of the Al/a-Si:H Schottky junction and the a-SiC:H/c-Si(n) isotype heterojunction, respectively. It is important to refer that the potential barrier of the isotype heterojunction has not been detected in the electrical measurements since it is much lower than that of the Schottky one and with the same polarity. The position of the maxima are slightly smaller to the respective energy band gap,  $E_g$  of a-SiC:H and c-Si(n), according to the relation [19]:

$$\lambda = \left( \frac{1.24}{E_g} \right) \mu\text{m} \quad (3)$$

The measured quantum efficiency,  $\eta_{\text{measured}}$ , is the total result of the spectral response of both junctions, Al/a-SiC:H,  $\eta_1$ , and a-SiC:H/c-S(n),  $\eta_2$ :

$$\eta_{\text{measured}} = \eta_1 + \eta_2 \quad (4)$$

It should be referred that the photosensitivity of a-SiC:H and c-Si present different spectra [20,21] and the a-SiC:H/c-Si(n) junction was determined to be an almost one sided junction [22], since the effective density of states of a-SiC:H [14] is greater more than two orders of magnitude than the donors concentration of c-Si[22]. Taking the above remarks into account, the measured quantum efficiency in the range of wavelengths from 350nm up to 600nm is approximately equal to  $\eta_1$ , ( $\eta_{\text{measured}} \cong \eta_1$ ). On the other hand, the total quantum efficiency in the range of wavelengths from 700nm up to 1000nm is approximately equal to  $\eta_2$  ( $\eta_{\text{measured}} \cong \eta_2$ ). It is remarkable that the position of the first maximum shifts to lower values of wavelength ( from 550nm to 625nm) since the energy band gap of the a-SiC:H thin films decreases from 2.1eV to 1.94eV, as the hydrogen flow rate decreases from 20sccm to 9 sccm. Also it is interesting to notice that the maximum values of the quantum efficiency are greater than 70%. From the experimental results of Figure 5 for  $\lambda=500$ nm, where the spectral response is due only to the Al/a-SiC:H Schottky junction, the values of diffusion length of a-SiC:H holes,  $L_p$ , have been calculated by using

the following expression [19] and the results are presented in table 1:

$$\eta_{\text{measured}} = (1 - R) \left( 1 - \frac{\exp(-\alpha w)}{1 + \alpha L_p} \right), \quad (5)$$

where  $w$  is the thickness of depletion region width in a-SiC:H of the Al/a-SiC:H junction,  $R$  is the incident light reflectance of the Al surface, and  $\alpha$  is the a-SiC:H absorption coefficient. The values of diffusion length of the holes,  $L_p$ , in a-SiC:H as a function of  $T_a$  were calculated taking into account our previous results on the effective density of states  $N_{\text{eff}}$  of a-SiC:H as a function of  $T_a$  [14], as well as of the absorption coefficient [12]. The reasonable assumption was made that the reflectance is  $\cong 10\%$  [24]. As it is clear from this table, the Al/a-SiC:H Schottky diodes with the amorphous thin film sputtered in hydrogen flow rate in 20 sccm and annealed at 600°C present the optimum optical properties with the value of  $L_p$  being greater than the other two cases, which is in agreement with the photosensitivity results of the same films [12].

**Table 1**

Hydrogen Flow Rate	Annealing Temperature	Diffusion Length, $L_p$ (Å)
9 sccm	550°C	6100
14 sccm	575°C	6500
20 sccm	600°C	7450

Finally, primary results on Al/a-SiC:H Schottky diodes with different thickness of the amorphous semiconductor greater than the value of  $L_p$ , show a loss mechanism in the optical spectra, confirming the validity of the calculated values of  $L_p$ .

#### 4. Conclusions

In the present work it was studied the optimization of the electrical and optical properties of Al/a-SiC:H Schottky diodes included in the structure Al/a-SiC:H/c-Si(n) by thermal annealing of a-SiC:H thin films sputtered at three different hydrogen flow rates. The experimental results show that:

The electrical properties of the Al/a-SiC:H Schottky diodes are optimized at 550°C, 575°C and 600°C for hydrogen flow rate 9sccm, 14sccm and 20sccm, respectively, reflecting the properties of the annealed a-SiC:H.

For  $T_{\text{aop}}$ , the electrical properties of the Al/a-SiC:H show that the dominant transport mechanism is thermionic emission as well as the linear relationship of  $\log I-V$  holds for more than seven orders of magnitude.

The optical response of the Al/a-SiC:H/c-Si(n) structure presents two maximum values, the first in the range from 550nm up to 625nm, which is attributed to Al/a-SiC:H junction, depending strongly on the hydrogen flow rate and the other at 850nm, which is attributed to a-SiC:H/c-Si(n) isotype heterojunction.

The evaluated values of diffusion length of a-SiC:H thin films as well as the electrical properties of Al/a-SiC:H Schottky diodes suggest that at hydrogen flow rate 20 sccm and annealing temperature 600°C, the optimum electrical and optical properties of these diodes are achieved.



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