

## P-type doping in a-Si<sub>1-x</sub>C<sub>x</sub>:H obtained by PECVD

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In previous works we have pointed out the importance of the so called "silane starving plasma" condition on the optical, chemical and structural properties of a-Si<sub>1-x</sub>C<sub>x</sub>:H obtained by standard radio frequency Plasma Enhanced Chemical Vapor Deposition (PECVD) technique from Silane (SiH<sub>4</sub>) and Methane (CH<sub>4</sub>) gaseous mixtures. We have shown that the *n*-type doping efficiency obtained by Ion Implantation of phosphorous and nitrogen in samples grown in the "starving plasma" condition improves the *n*-type conductivity up to levels close to those obtained in device quality a-Si:H. In this work we study the P-type doping of these PECVD films by adding aluminum and boron, as acceptor impurities, to close to stoichiometry a-SiC:H films grown in "starving plasma condition" with and without H<sub>2</sub> dilution. boron was introduced by ion implantation and aluminum by low temperature thermal diffusion. The results indicate that, even though the attained conductivity levels are not very high, the aluminum doping is more efficient than boron one, in accordance to what has been observed in crystalline SiC material.

### 1. Introduction

In previous works [1,2] we have pointed out the important influence of the so called "silane starving plasma" [3] condition on the optical, chemical and structural properties of a-Si<sub>1-x</sub>C<sub>x</sub>:H obtained by standard radio frequency Plasma Enhanced Chemical Vapor Deposition (PECVD) technique from silane (SiH<sub>4</sub>) and methane (CH<sub>4</sub>) gaseous mixtures. We have shown that in this condition it is possible to obtain almost stoichiometric samples (*x*~0.5), with a chemical order similar to crystalline SiC, and carbon rich material (*x*>0.5), with very high optical gap (*E<sub>o</sub>*~4 eV) and other "diamond like" properties.

In recent works [4] we have obtained an even higher degree of structural and chemical order in the material, by means of hydrogen dilution and higher RF power. The observed chemical and structural order in a-SiC:H grown in "starving plasma" condition is remarkable, since amorphous silicon based alloys exhibit a high degree of disorder, which increases with the alloy element content. This disorder causes a poor carrier mobility and diminishes the doping efficiency, limiting the device applications of a-Si:H alloys. So, the order induced in PECVD a-SiC:H by the "silane starving plasma" regime is a promising characteristic for substitutional doping.

Attending to this, in a recent work we studied the *n*-type doping, by Ion Implantation of phosphorous and nitrogen, of these highly ordered amorphous Silicon-Carbon alloys. There we demonstrated the superior doping efficiency of the material obtained in the "starving regime" when compared with films grown in standard low power regime conditions [5]. The results showed that the "starving plasma" condition improves the *n*-type doping efficiency of the films up to levels close to those obtained in a device quality a-Si:H, the lower activation energy being ~0,12 eV for a nitrogen doped sample which

presents a dark conductivity in the order of 10<sup>-3</sup> (Ωcm)<sup>-1</sup> at room temperature. It was also shown that nitrogen doping efficiency is higher than phosphorous for all the studied samples.

In this work we extend the study to the p-type doping in the same type of highly ordered PECVD a-Si<sub>1-x</sub>C<sub>x</sub>:H grown in starving plasma conditions. We also investigate the influence of the enhanced structural and chemical order, attained by hydrogen dilution and increased RF power on the doping characteristics. It is known, from studies on crystalline SiC, that p-type doping is much more troublesome than n-type doping. Among the studied p-dopants we can mention B, Al, Ga and In, all of them have conducted to p-type material, however the conductivity remained low in most cases.

This is due to a quite high ionization energy of these acceptor impurities, in the 200 to 400 meV range in contrast with the 45 meV ionization energy exhibit by nitrogen as a donor level. Another problem has been the creation of other centers, some of them donor-like, leading to compensation of the generated holes. However, more recently better results with aluminum and boron ion implantation have been obtained. A room temperature conductivity of the order of 10<sup>-4</sup> (Ωcm)<sup>-1</sup>, for aluminum doping, which can be improved to 1 to 0.1 (Ωcm)<sup>-1</sup> range only with heat treatments at temperatures higher than 1600 °C [6]. Another complicated issue is to obtain good ohmic contacts to p-type SiC. Due to the high optical gap (in the order of 3 eV) and to an electron affinity of 3.3 eV, the valence band difference respect to the vacuum level is higher than 6 eV leading to a very high barrier height at the interface with most metals, which have work functions in the 4 to 5.5 eV range [7].

Since the better results have been obtained with aluminum and boron, in this work we consider these two

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doping elements as acceptor impurities. In this way samples grown in “starving plasma” conditions with and without hydrogen dilution, were ion-implanted with boron with energies and doses chosen from experiments with a-Si:H to give constant concentration profiles [8] varying from  $\sim 8 \cdot 10^{16} \text{ cm}^{-3}$  to  $\sim 3,2 \cdot 10^{20} \text{ cm}^{-3}$ . The samples were also aluminum doped through low temperature thermal diffusion experiments. We are considering first ion-implantation and diffusion rather than in-situ doping in order to get a better control of the concentration of the doping species and to guarantee the preservation of the structural properties of the starving condition grown material, since in in-situ doping experiments the influence of the doping gas on the structure of the films must be considered.

## 2. Experimental

The samples studied in this work were grown by standard radio frequency PECVD technique from silane ( $\text{SiH}_4$ ), methane ( $\text{CH}_4$ ) and hydrogen ( $\text{H}_2$ ) gaseous mixtures at  $300^\circ\text{C}$ . Their structural, chemical and compositional properties have been previously reported [1,2,9,10]. The work investigates the effect of ion implantation of boron and thermal diffusion of aluminum in highly ordered a-SiC:H grown by PECVD. The deposition conditions for all the samples are given in Table 1, where their carbon contents (measured by RBS) are also shown.

Table 1 : Deposition conditions of the studied a-Si<sub>1-x</sub>C<sub>x</sub>:H samples. The deposition temperature is  $300^\circ\text{C}$  for all the samples

Sample Type	SiH <sub>4</sub> Flow (sccm)	[CH <sub>4</sub> ] (%)	r.f. Power (mW/cm <sup>2</sup> )	H <sub>2</sub> Flow (sccm)	X
C3680	3.6	80	50	0	0.53
C0480	4	80	50	0	0.47
C0490H	4	90	250	100	0.52

The samples were further implanted at fixed energy, with different doses of boron, to produce total concentrations of  $\sim 10^{16}$ ,  $\sim 10^{18}$  and  $\sim 10^{20}$ , B/cm<sup>3</sup>. Different annealing steps after the ion implantation, necessary to activate the doping elements, were considered. The aluminum diffusion was carried out depositing, by thermal evaporation, a thin aluminum layer followed by a thermal annealing step. The annealing steps analyzed were  $350^\circ\text{C}$  for 4, 8 and 12 hours and  $450^\circ\text{C}$  for 0,5, 2, 4 and 6 hours. The doping conditions are shown in Table 2.

The dark conductivity ( $\sigma_d$ ) and the thermal activation energy ( $E_a$ ) were measured for all the samples in a vacuum cryostat. The current was measured for temperatures varying from 300 K up to 600 K utilizing a Keithley 6517A electrometer. The structural, compositional and optical properties were also characterized by FTIR, RBS, and optical absorption experiments.

Table 2 : Doping conditions of the studied samples

Boron Ion Implantation		
Sample Type	Sample Name	Total Concentration
C3680	P16	$8,0 \cdot 10^{16} \text{ B/cm}^3$
	P18	$5,7 \cdot 10^{18} \text{ B/cm}^3$
	P20	$3,2 \cdot 10^{20} \text{ B/cm}^3$
C0480	B20	$10^{20} \text{ B/cm}^3$
C0490H	B20H	$10^{20} \text{ B/cm}^3$
Aluminum Thermal Diffusion		
Sample Type	Sample Name	Time and Temperature
c3680	Al-4	4 h, $350^\circ\text{C}$
	AL-8	8 h, $350^\circ\text{C}$
	Al-12	12 h, $350^\circ\text{C}$
C0490H	C0490H-Al	30 min, $450^\circ\text{C}$
	c180699-1	2 h, $450^\circ\text{C}$
	c180699-2	4 h, $450^\circ\text{C}$
	c180699-3	6 h, $450^\circ\text{C}$
	c260799	6 h, $450^\circ\text{C}$

## 3. Results and discussion

The main results are summarized in Table 3, which shows the room temperature electrical conductivity ( $\sigma_{RT}$ ) for the studied samples together with the conductivity thermal activation energy,  $E_a$ , and the optical,  $E_o$ .

As it can be appreciated in Table 3, even though many samples presented problems with the metal contacts, both the boron implantation and the aluminum diffusion had a clear effect in the transport characteristics of the samples. As we discussed previously in the introduction, to obtain good ohmic contacts to p-type SiC is a very difficult task, even for crystalline material, and specially for lower doping concentrations, this problem makes difficult to obtain reproducible results, specially for the absolute value of the dark conductivity, since the contribution of the contact resistance is not well evaluated.

Also as most of the samples remained with very low conductivity their value at room temperature is lacking. It is also observed in Table 3, that the optical gap remained unchanged for all the samples except for the one implanted with  $10^{20} \text{ cm}^{-3}$  boron atoms. The effect of the boron implantation on the electrical properties of the samples can be better appreciated in Fig 1. As we can see, in general the electrical conductivity levels were not very high and the activation energies remained high although definitely lower than for the intrinsic sample.

All the curves in Fig.1 are for samples grown without H<sub>2</sub> dilution. Despite the fact that samples grown with H<sub>2</sub> dilution are more ordered, the boron implantation in this

samples lead to important thermal instabilities in the electric conductivity. For increasing temperature the conductivity for this type of samples decreased progressively up to levels near to the intrinsic ones. A possible explanation for this behavior is that substitutional, electrically active, sites for boron are Silicon sites, and in a more ordered material, with Si preferentially bonded to C there exist a lower disponibility of this type of sites. To support this hypothesis, we can consider the infrared spectra for both type of samples, grown with and without H<sub>2</sub> dilution, shown in Fig.2.

Table 3. Room temperature electrical conductivity ( $\sigma_{RT}$ ), conductivity thermal activation energy,  $E_a$ , and the optical,  $E_o$ .

Sample	$\sigma_{RT}$ ( $\Omega\text{cm}$ ) <sup>-1</sup>	$E_a \pm 0,05$ (eV)	$E_o \pm 0,2$ (eV)
c3680	< 10 <sup>-15</sup>	1,2	2,6
P16	< 10 <sup>-15</sup>	0.94	2,6
P18	< 10 <sup>-15</sup>	0.82	2,6
P20	10 <sup>-12</sup>	0,82	2,35
Al-4	~510 <sup>-15</sup>	0.86	2,6
AL-8	~510 <sup>-15</sup>	0.9	2,6
Al-12	~510 <sup>-15</sup>	0.8	2,6
c0490H	< 10 <sup>-15</sup>	1.1	2.6
C180699-1	310 <sup>-12</sup>	0.39	-
C180699-2	810 <sup>-12</sup>	0.35	-
C180699-3	310 <sup>-11</sup>	0.38	-
C260799	10 <sup>-7</sup>	0.17	-

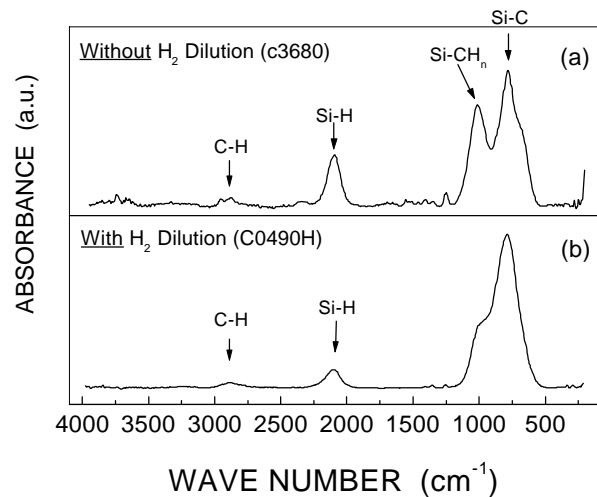


Fig.2. Infrared spectra of samples grown without (a) and with (b) H<sub>2</sub> dilution.

As we can see, samples grown without H<sub>2</sub> dilution exhibit a higher fraction of Silicon bonded to Hydrogen (via Si-H and Si-H<sub>2</sub> bonds), which can be a potential source for Silicon sites to boron to connect. On the other hand, in a lattice with the silicon preferentially connected to Carbon, via strong SiC bonds, the small boron atoms can not find appropriate electrical active sites and, at the low temperatures of our thermal process, just can diffuse or even, out-diffuse from the sample.

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The effect of the aluminum diffusion is depicted on Fig.3. As we can see, the results are much better than the obtained with the ion implantation of boron, leading to an activation energy of ~0,2 eV in the best case, which is very low if we consider that the energy gap of the samples is 2,4 eV and that we are dealing with an amorphous alloy, where it is normally difficult to dislocate the Fermi level position.

Despite the low activation energy, the electrical conductivity remains quite low, being ~10<sup>-7</sup> ( $\Omega\text{cm}$ )<sup>-1</sup> at room temperature and ~10<sup>-6</sup> ( $\Omega\text{cm}$ )<sup>-1</sup> at 570 K. Probably this fact is related with the non-ohmic character of the metal contacts, which as we mentioned earlier is also difficult to obtain even in crystalline SiC. It is important to recall here that, in general, the task of high conductive p-type doping and confident metal contacts to crystalline SiC has not yet been solved [11]. In this way, the results reported here with Al doping are very promising.

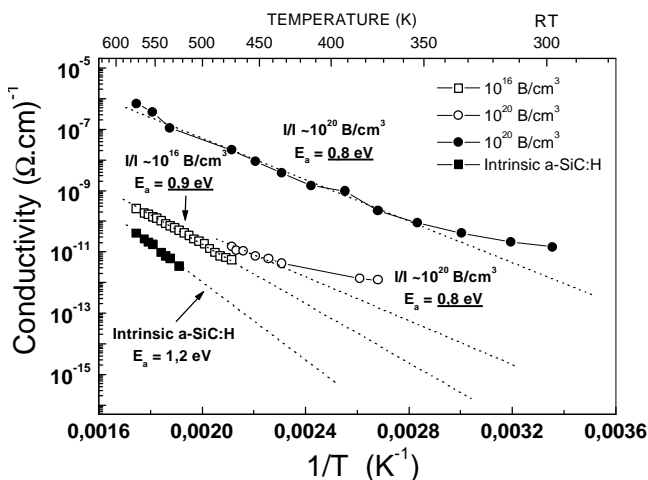


Fig.1 Conductivity vs. 1/T for intrinsic and ion implanted boron samples.

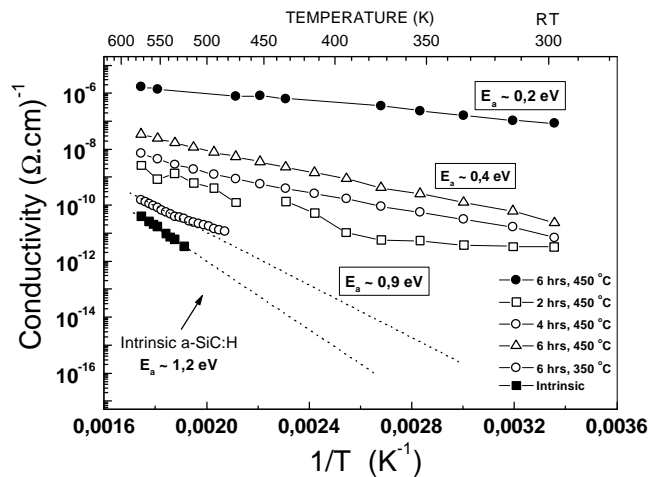


Fig.3 Conductivity vs.  $1/T$  for the intrinsic sample and Al doped.

#### 4. Conclusions

We report the P-type doping of a-SiC:H obtained by PECVD technique. The experiments with low temperature thermal diffusion of Al conducted to better doping effect that ion implantation with boron, and resulted in a very promising dislocation of the Fermi level. The electrical conductivity must be increased and for that it is important to optimize the ohmic character of the electric contact as well as the contact resistivity. Finally, we attribute these results to the superior chemical and structural properties of the a-SiC:H obtained in the so called "starving plasma" condition.

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