In-Situ and Ion Implantation Nitrogen Doping on Near Stoichiometric a-SiC:H Films

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Abstract — **In this work we study the nitrogen n-type electrical doping of a-$Si_{0.5}C_{0.5}$:H films obtained by plasma enhanced chemical vapor deposition (PECVD) utilizing and comparing two doping techniques: *in-situ* (during the material growth) and ion implantation. The *in-situ* doped a-SiC:H films were obtained adding different amounts of N_2 to the precursor gas mixture. For ion implantation four different nitrogen implanted concentrations were studied (between 10^{18} and 10^{21} atoms/cm^3) using multiple energies and doses to define a homogeneously doped layer. The doping experiments are carried out on a-SiC:H samples that present different structural order. The results show that high levels of electrical conductivity can be obtained with ion implantation technique. For *in-situ* technique the doping effect is also observed but must be improved in order to attain higher electrical conductivities. In the best case the room temperature dark conductivity for the sample implanted with 10^{21} nitrogens/cm^3 was ~10^{-7} (Ω.cm)$^{-1}$ and the activation energy was 0.2 eV. For *in-situ* doping the electrical dark conductivity reached values near 10^{-10} (Ω.cm)$^{-1}$ at high temperatures and the activation energy was ~0.6 eV. Despite of the apparent low values of the electrical conductivity, these results are promising because we are dealing with a wide gap material and the doping processes are still not optimized.**

Index Terms — **SiC, doping, PECVD, amorphous semiconductor.**

I. INTRODUCTION

Hydrogenated amorphous silicon carbide alloys (a-SiC:H) grown by plasma enhanced chemical vapor deposition (PECVD) have been widely investigated for application in a variety of electronic devices, mainly as window layer in solar cells [1], as insulator in thin film transistor [2] and as active layer in light emitting diodes [3]. These investigations have mainly explored the possibility of tuning the material optical bandgap. Aiming to improve the properties of those films, we have studied the conditions to obtain close to stoichiometric samples of a-$Si_{0.5}C_{0.5}$:H, with enhanced chemical and structural order, being a real counterpart of crystalline SiC thus, preserving at least part of its notorious properties. This was achieved diluting the precursor gaseous mixture in hydrogen and increasing the RF-power delivered to the discharge [4,5].

For applications in a-SiC:H based devices is desirable to prepare doped films with maximum electrical conductivity. Thin layers of a-SiC:H with appropriate conductivity have been traditionally obtained by *in-situ* doping (during the material growth) by adding either boron (for p-type) or phosphorus (for n-type) to the films. Generally the p-type doping is obtained by adding diborane (B_2H_6) to the precursor gaseous mixture while phosphine (PH_3) is used for n-type doping. The properties of a-SiC:H films doped *in-situ* using gases as the mentioned B_2H_6 and PH_3 have been widely investigated [6,7]. These studies however involve non-stoichiometric alloys that normally are silicon rich material. This is why we study here the doping properties of the stoichiometric a-$Si_{0.5}C_{0.5}$:H with optimized properties that we have developed in previous works.

On the other hand, for planar integrated circuits fabrication doping of selective areas is required. For this, ion implantation is the principal available technique [8,9]. Nevertheless, the creation of a great deal of damage due to the implantation process is the major drawback for this technique. Both, point defects and voids, are originated by the ion bombardment resulting in a significant increase of the density of localized gap states. A feasible method to recover the damage is to perform an annealing process [10,11].

Dopants suitable as donor in crystalline SiC are nitrogen and phosphorus. Due to its low activation energy (~54 meV) nitrogen is more convenient, besides it is low cost and non-toxic [12]. So, in this work we present a detailed study of nitrogen doping in PECVD a-$Si_{0.5}C_{0.5}$:H grown with and without hydrogen dilution in the precursors gaseous mixture to obtain materials with different degrees of structural order. The *in-situ* and ion implantation doping efficiency is studied and compared by electrical measurements.

II. EXPERIMENTAL

The intrinsic a-SiC:H samples to be doped by nitrogen ion implantation were deposited at 320 °C by standard radio frequency PECVD technique from gaseous mixture of silane (SiH_4) and methane (CH_4), with and without dilution in H_2 to obtain samples with different structural order (samples type "c3680" and "c3690H" in Table 1).

Table 1. Deposition conditions of the a-$Si_{1-X}C_X$:H samples at 320 ºC.

Sample Type	SiH_4 Flow (sccm)	[CH_4] (%)	H_2 Flow (sccm)	R.F. (mW/cm^2)	x	
c3680	3.6	80	-	50	0.53	Less Order
c3690H	3.6	90	200	250	0.52	Higher Order

A short description of the deposition conditions is made in Table 1 and a detailed description of the structural prop-

erties and their relation with the depositions parameter can be find in reference [5].

The nitrogen ion implantation experiments were performed according previous simulation by SRIM software and using multiple energies and doses in order to produce a 300 nm thick homogeneously doped layer (see Fig.1). So four final concentration plateaus varying between 10^{18} and 10^{21} cm^{-3} were obtained (see Table 2b). To electrically activate the implanted impurities and to reorder the atomic lattice, we performed a thermal annealing for one hour at 550 °C.
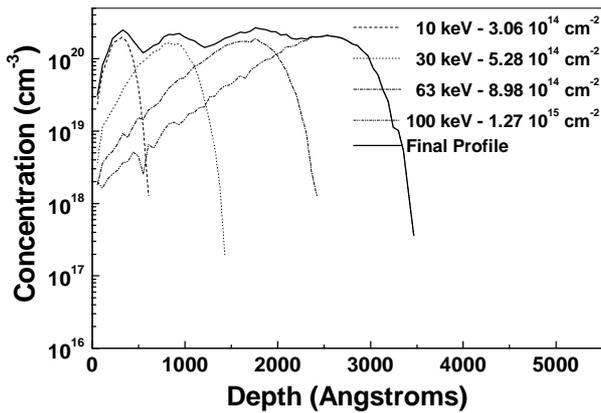

Fig. 1. Nitrogen concentration profile obtained by SRIM software simulation. The curves show the simulation to obtain a constant concentration of 10^{20} impurities/cm^3 up to a depth of ~300 nm.

The *in-situ* nitrogen doping was achieved trough the addition of small amounts of N_2 to the $(SiH_4 + CH_4)$ gaseous mixtures in order to promote the nitrogen incorporation in the a-SiC:H films. In this case, we investigated samples grown in the same conditions of Table 1 to obtain materials with different structural order (types "c3680" and "c3690H" with lower and higher structural order, respectively). The N_2 amount added to the gaseous mixtures is depicted in Table 2a.

Table 2. Doping conditions.

Sample Type	Sample Name	N_2 Flow (sccm)	Sample Type	Sample Name	Concentration (cm^{-3})
c3680	N0.1	0.1	c3680	N18	1.10^{18}
	N0.5	0.5		N19	1.10^{19}
	N1.0	1.0		N20	1.10^{20}
				N21	1.10^{21}
c3690H	N0.1	0.1	c3690H	N18	1.10^{18}
	N0.5	0.5		N19	1.10^{19}
	N1.0	1.0		N20	1.10^{20}
				N21	1.10^{21}

a. *In-situ* doping.   b. Ion implantation doping.

The nature of the chemical bonding in the doped samples was studied by infrared spectroscopy using a FTIR spectrometer (model FTS 40 from BIORAD) between 400 and 4000 cm^{-1}. The optical properties were measured by optical absorption experiments.

The doping effect was evaluated through the dark conductivity (σ) and its thermal activation energy (E_A), which was obtained from current versus temperature measurements.

The current was measured in the 300 to 500 K temperature range using an electrometer Keythley 6517A.

III. RESULTS AND DISCUSSION

A. In-situ doping during the films deposition

The dark conductivity as a function of temperature for the *in-situ* doped samples grown with different nitrogen flow (see Table 2) with and without hydrogen dilution are shown in Fig. 2.a. and Fig. 2.b., respectively.
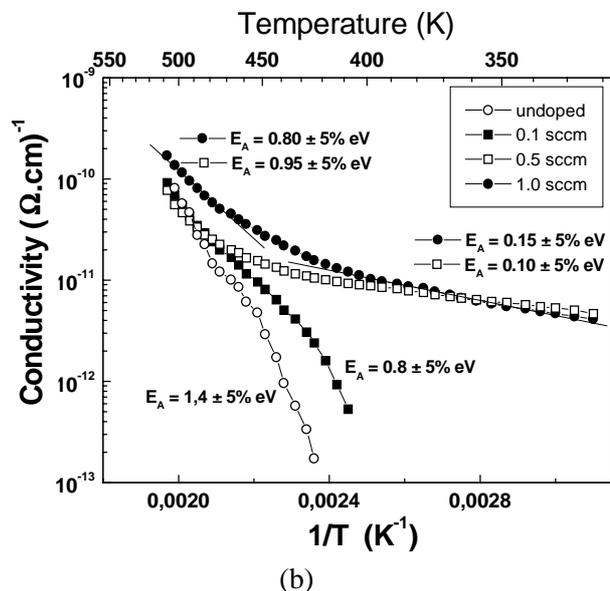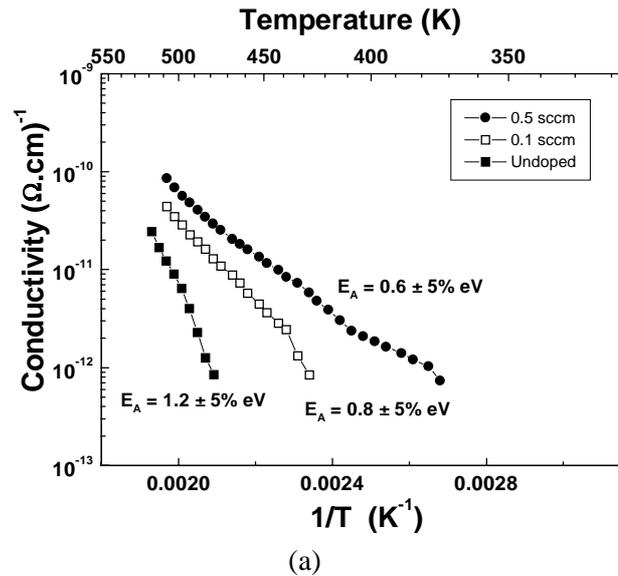

(a)

(b)

Fig.2 – Conductivity versus 1/T for undoped and nitrogen in-situ doping: a) samples type c3680 without H$_2$ dilution and b) samples type c3690H with H$_2$ dilution.

It can be observed in Fig. 2a that the conductivity for samples deposited without hydrogen dilution (c3680 type) presents a more consistent behavior than samples grown with hydrogen dilution, this is, for higher N2 concentration in the gaseous mixture, higher is the electrical conductivity of the films. On the other hand, for samples deposited with

hydrogen dilution (c3690H type, Fig.2b) the results are not so clear and we get evidences of a change in the mechanism of electronic transport as a function of the temperature. In fact, for high temperatures (higher than approximately 460 K) the conductivity of doped and undoped samples tends to be the same. Even more, samples with higher conductivity (grown with 0.5 and 1.0 sccm of N_2) exhibit two conductivity regimes, one with very low activation energy (~0.15 eV) at low temperatures, and another one at temperatures higher than 450 K with activation energy close to 0.9 eV. Furthermore for the sample deposited with 1 sccm nitrogen flow even a third activation energy regime of approximately 0.6 eV for intermediate temperatures can be assigned.
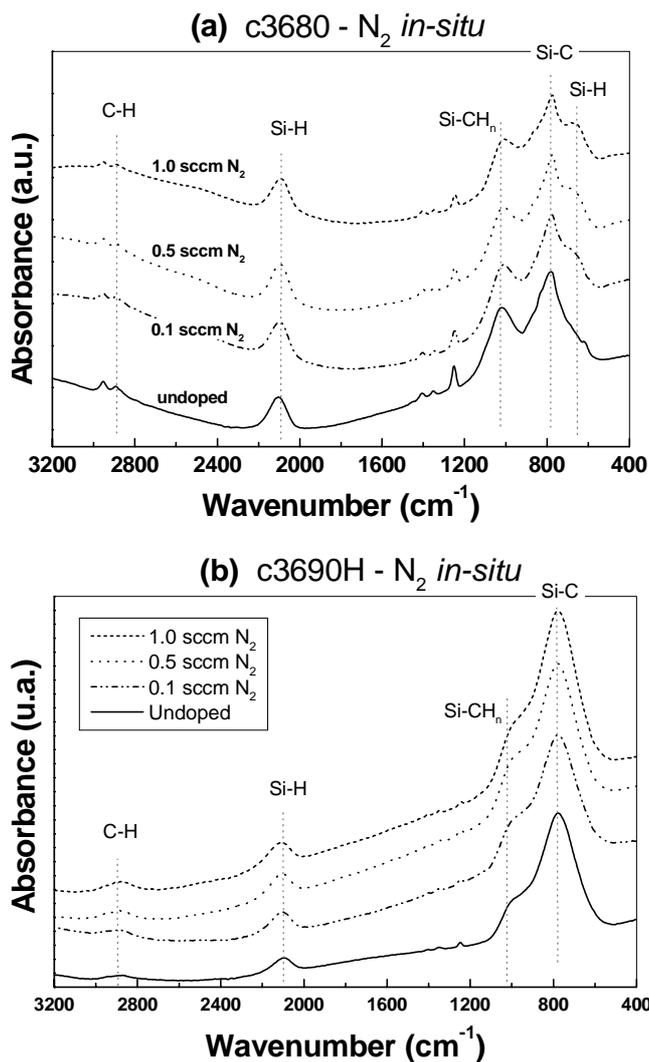

Fig. 3 – FTIR spectra of nitrogen *in-situ* doped samples of (a) c3680 samples type (less structural order) and (b) c3690H samples type (higher structural order).

Despite the particular features exhibited by c3690H type material (grown with H_2 dilution) that needs more studies to be clarified, the observed increase in the electrical conductivity of c3680 type a-SiC:H is consistent with the results reported by Nakaaki and Naito [13] on films deposited using the Glow Discharge technique, and can be attributed to an increase in the doping level (substitutional N incorporation) with the increase in the N_2 gas flow. Finally, the curve for

sample c3680 grown with the higher N_2 gas flow (1 sccm) is not shown in Fig.2a because this sample presented electrical instabilities related to electrical contact problems which prevent the electrical characterization.

In order to verify if the nitrogen incorporation remains at doping levels, thus without changing the materials structure, FTIR spectra and the optical gap of the samples were analyzed. The results from the FTIR measurements on the nitrogen doped and intrinsic samples, c3680 and c3690H type, are shown in Fig. 3 (a) and (b), respectively. As expected the spectra for both undoped samples (0 % nitrogen flow) show the typical features of hydrogenated amorphous silicon carbide, whilst evidencing the chemical and structural order differences. In this way all spectra exhibit the main band at 780 cm^{-1}, related to the Si-C stretching vibration mode, at 1020 cm^{-1} the band related to Si-CH$_n$ vibrations, the C-H stretching band at around 2900 cm^{-1}, and the band around 2100 cm^{-1} corresponding to Si-H stretching vibrations. The samples grown with H_2 dilution, c3690H (Fig. 3b), present less hydrogen incorporation and a more pronounced SiC band, indicating a higher concentration of Si-C bonds, and thus enhanced chemical and structural order [4,5]. On the other hand, for both sample types very small nitrogen induced changes are observed, especially for the more ordered c3690H type material. For the higher utilized nitrogen flow in the samples deposited without hydrogen dilution it is possible to observe a small band appearing at approximately 1000 cm^{-1}, which can be attributed to Si-N modes [14,15]. Also enhanced Si-H vibrations accompanied by decreasing SiC bands can be observed for the highest utilized nitrogen flow.

The optical band gap values, calculated by Tauc's extrapolation technique [16] are plotted in Fig. 4 as function of the nitrogen flow. For both sample types, c3680 and c3690H no significant changes are observed. These FTIR and optical gap results, are indicating that nitrogen incorporation is high enough to insure doping and low enough to avoid significant structural changes in the material.
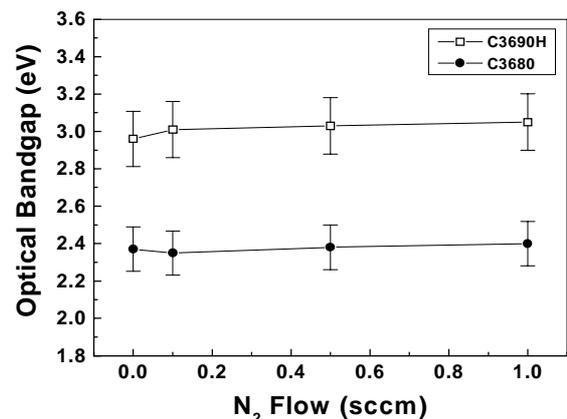

Fig 4 - Optical bandgap of *in-situ* doped a-SiC:H as a function of nitrogen flow added to the gas mixture.

B. Ion implantation doping

Fig. 5 shows the obtained curves of electric conductivity versus temperature for samples of both types of a-SiC:H (c3680 and c3690H) doped with 10^{18}, 10^{19}, 10^{20} and 10^{21}

nitrogens/cm^3. All the samples were submitted to post implantation thermal annealing for one hour at 550 °C. As we can see the doping effect is evident: the higher the implanted concentration is, the higher is the conductivity. We can observe that the doping is more efficient for the samples c3690H, which present an optimized structural order when compared to type c3680 samples. This behavior is specially pronounced for the highest implanted concentration (10^{21} nitrogens/cm^3) that corresponds to our best result: this sample (type c3690H) exhibited a room temperature conductivity of the order of 10^{-7} (Ω.cm)$^{-1}$ and an activation energy of E_A~0.2 eV.
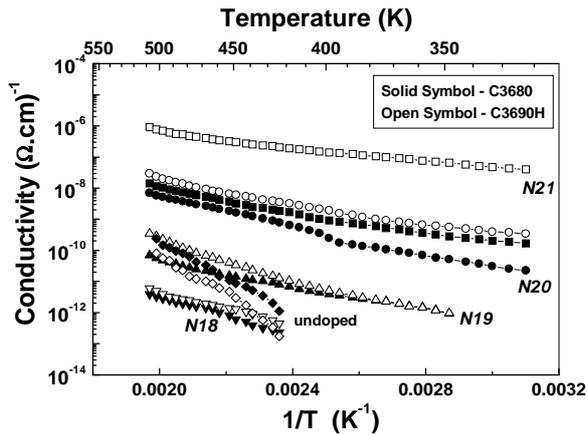

Fig. 5 – Conductivity versus 1/T for undoped and nitrogen ion implantation doping.

Note that high impurity concentration is needed to obtain satisfactory doping levels and even in the best case the nominal current is not very high (~10^{-6} (Ω.cm)$^{-1}$ for high temperatures). On the other hand these values represent an increase in the electrical conductivity of more than six orders of magnitude if compared to intrinsic material, which is extremely insulating and presents a conductivity smaller than 10^{-12} (Ω.cm)$^{-1}$, below the detection limit of our experimental setup.

Fig. 5 also shows no significant difference in the activation energy (E_A) while the electrical conductivity varies strongly with the implanted nitrogen concentration. This can be appreciated in Fig. 6, where the values of E_A extracted from curves in Fig. 5 for both type of samples (c3680 and c3690H) are plotted.

Similarly the *in-situ* doped samples, in order to check eventual structural changes induced by the implantation process, optical absorption measurement and FTIR analyses were carried out. In Fig. 7 we show the infrared spectra of as deposited and implanted with 10^{21} nitrogens/cm^3 samples, of both type of materials. As we can see, the implantation process did not introduce significant variation on the structural properties of the material. In fact, the main effect on the infrared spectra is due to the post implantation thermal annealing (one hour at 550 °C), which induces an increase in the Si-C bonds and H effusion in the films. This is a well known effect of thermal annealing in hydrogenated amorphous silicon alloys and is appreciable just for c3680 type a-SiC:H.
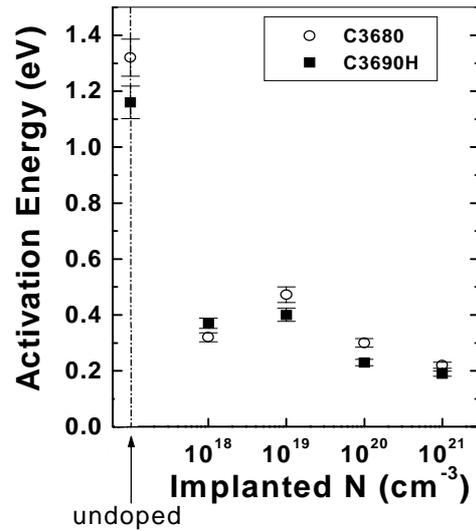

Fig. 6. Activation energy (E_A) as a function of the nitrogen implanted concentration.

In the same way, the implanted nitrogen induces just a small reduction of the optical gap, probably related with damages produced on the atomic network by the ion bombardment [17]. This variation is more significant immediately after the ion implantation but it is strongly reduced by the one hour thermal annealing (at 550 °C) and the final gap reduction is too small to justify the observed increase in several orders of magnitude of the dark electrical conductivity (see Fig. 8).
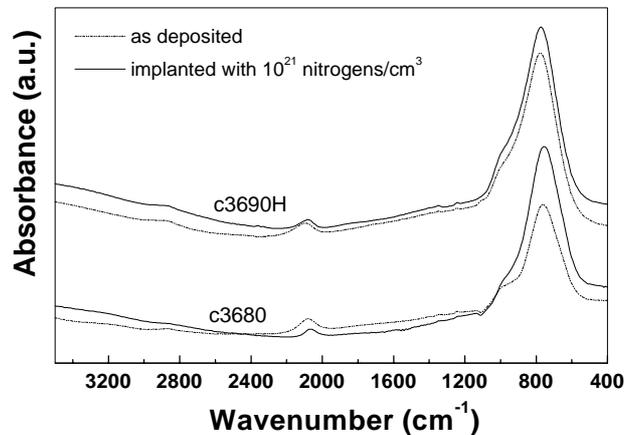

Fig. 7. FTIR spectra of the sample as deposited and doped by ion implantation with concentration of the 10^{21} nitrogens/cm^3 annealed at 550 °C for 1 hour.

Fig. 5 also shows another important result. We can observe that the sample doped at 10^{18} cm^{-3} nitrogens/cm^3 presents a lower dark conductivity than the undoped sample one. This suggests that the "as deposited" a-SiC:H films exhibit a p-type conductivity, and thus need a n-type doping to reach the minimum of conductivity. This "doping compensation" behavior is also observed in intrinsic a-Si:H (but for this material the as deposited films exhibit n-type conductivity) and it is associated to the state distribution inside the pseudo-gap [18]. Probably a similar effect occurs in this PECVD a-SiC:H material, but more detailed studies must be carried out in order to explain this behavior.
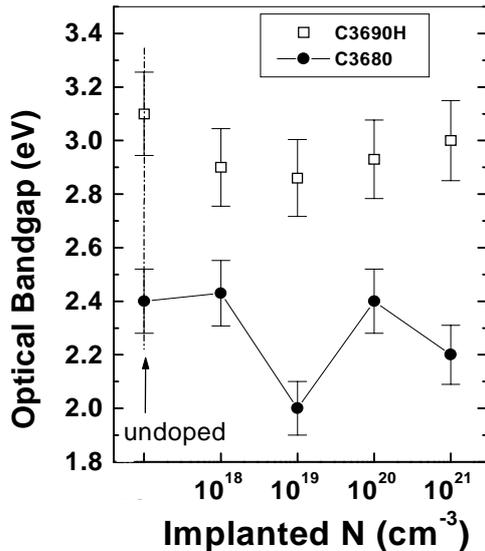
Fig. 8. Optical bandgap as a function of nitrogen implanted concentration. Measured after thermal annealing (1 hour, 550 ^{o}C).

IV. CONCLUSIONS

In this work we study nitrogen n-type doping in two type of stoichiometric PECVD a-SiC:H films, exhibiting different degrees of chemical and structural order. The doping experiments were performed by *in-situ* technique, adding N_2 to the gaseous mixture during the films growth, and by ion implantation.

For *in-situ* experiments better results were obtained with the less ordered c3680 type material, that show an increase of the electrical conductivity consistent with the occurrence of a nitrogen n-type doping process. The electrical dark conductivity for this material reached values in the order of 10^{-10} $(\Omega.cm)^{-1}$ at high temperatures, with an activation energy of ~0.6 eV. On the other hand, the more ordered c3690H type material, in spite of the observed conductivity changes induced by N_2 addition, did not show clear evidences of a doping process and new studies are necessary to clarify its behavior.

For ion implantation experiments, the highest electrical conductivity was the order of ~10^{-7} $(\Omega.cm)^{-1}$ and was obtained for the more order c3690H type material implanted with 10^{21} nitrogens/cm^3 was ~10^{-7} $(\Omega.cm)^{-1}$. The activation energy value for this material was 0.2 eV. Even though the obtained conductivity values are still below device quality, the results are promising because we are dealing with a wide gap material and the doping processes are still not optimized.

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