# Plasma enhanced chemical vapour deposition of B-doped silicon carbide thin films for heterojunction application

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**Abstract:** Boron doped silicon carbide a-SiC(B):H films were deposited on N-type Si(100) substrates by means of plasma enhanced chemical vapor deposition (PECVD). Structural properties of films were analyzed by RBS, ERD, FTIR and Raman methods. The electrical properties of structure Al/a-SiC(B):H/Si/Al were determined by *I-V* measurement.

Keywords: B doped silicon carbide film, PECVD, structural and electrical characterization

# 1. Introduction

Silicon carbide is a versatile material utilized in a wide variety of applications. Amorphous alloys of SiC in connection with photovoltaics (PV) are a relatively new subject of investigation. Higher band gap (1.8 - 2.3 eV) of amorphous SiC layers (compared to a-Si:H) lead to a lower parasitic light absorption [1]. PECVD technique offers an attractive opportunity to fabricate amorphous hydrogenated SiC at intermediate substrate temperatures and it provides high quality layers with good adhesion, good coverage of complicated substrate shapes and high deposition rate [2].

In this paper, PECVD technology was used for deposition of B doped a-SiC:H films using SiH<sub>4</sub>, CH<sub>4</sub>, H<sub>2</sub>, 5% B<sub>2</sub>H<sub>2</sub> in H<sub>2</sub> and Ar. Concentrations of elements in films were investigated by RBS and ERD methods. FT-IR and Raman spectroscopy was used for chemical composition analysis. The electrical properties were determined by *I-V* measurement on the prepared structure with metal contacts.

# 2. Experiments

The plasma CVD reactor with parallel plate electrodes was used for films preparation. A N-type silicon wafer with resistivity 5-8  $\Omega$ cm and (100) orientation was used as the substrate for the growth of SiC films. Technological parameters for samples were: substrate temperature was 300 °C and gas mixture was for sample A1 (SiH<sub>4</sub>-5 sccm, CH<sub>4</sub>-30 sccm, 5% B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub>-2 sccm, H<sub>2</sub>-100 sccm, Ar-10 sccm), for sample A2 (SiH<sub>4</sub>-5 sccm, CH<sub>4</sub>-30 sccm, 5% B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub>-8 sccm, H<sub>2</sub>-100 sccm, Ar-10 sccm), for sample A3 (SiH<sub>4</sub>-5 sccm, CH<sub>4</sub>-30 sccm, 5%) B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub>-8 sccm, H<sub>2</sub>-100 sccm, Ar-10 sccm), and for sample A4 (SiH<sub>4</sub>-5 sccm, CH<sub>4</sub>-30 sccm, 5% B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub>-12 sccm, H<sub>2</sub>-100 sccm, Ar-10 sccm), respectively. For all samples were RF power 100 W and pressure 100 Pa. Thickness of films were about 300 nm for RBS, ERD and Raman analyse and about 1000 nm for FTIR and I-V measurement structure. Concentrations of elements in the films were analysed using RBS and ERD analytical method simultaneously. Chemical compositions were analysed by infrared spectroscopy using FT-IR Nicolet 8700 spectrometer in absorption mode and the absorption spectra of used substrate were subtracted from the film spectra. Raman measurements of SiC films were performed by using a Thermo Fisher Scientific DXR Raman microscope with 532 nm laser. The circular electrodes of Al (200 nm thick) as a non-ohmic contacts with diameter 0.5 mm were formed using metal masks on the side with SiC film on each sample. The other side of samples was fully covered by Al ohmic contact (~300 nm thick). The electrical properties of heterojunction structure were determined by I-V measurement at 295 K. An electrically shielded probe station using a computer controlled HP 4140B pA meter/DC voltage source was used for measurements of I-V characteristics of the samples.

### 3. Results and discussions

The measured and simulated RBS and ERD spectra for sample A3 is shown in Fig.1. In Fig. 1(a), RBS spectra are shown leading edge at ~550 ch corresponding to the Si and leading edges around ~450 ch corresponding to SiC/Si interface. The peaks corresponding to C is observed on the profile of the bulk Si at around ~270 ch. In Fig. 1(b), ERD spectra appeared one peak-like profile corresponding to hydrogen with leading edge at approximately ~600 ch. RBS and ERD analysis indicated that the films contain silicon, carbon, hydrogen and small amount of oxygen. Concentrations of elements were practically uniform for all films. Concentration of boron is under concentration limit of RBS method. The small amount of oxygen in the films came from the walls of the reaction chamber as residual oxygen and precursors. Figure 2 shows the FTIR spectrum for A3 film. From the FTIR spectra we could determine the following vibration frequencies: the band at 2800 to 3000 cm<sup>-1</sup> is attributed to stretching vibration of the  $CH_n$  group in both the  $sp^2$  $(2880 \text{ cm}^{-1})$  and sp<sup>3</sup>  $(2920 \text{ cm}^{-1})$  configurations. The band at 2100 cm<sup>-1</sup> appears due to SiH<sub>m</sub> stretching vibrations.



Fig. 1. RBS a) and ERD b) spectra for A3 sample which is typical for all samples.

The band at 780 cm<sup>-1</sup> can be assigned to Si-C stretching vibration. The signals occur between 930 and 1200 cm<sup>-1</sup> which are superposition of several C-H, Si-O and Si-N vibrations. The side shoulder peaking at around 1000 cm<sup>-1</sup> is attributed to the wagging vibration of CH<sub>2</sub> bonded to silicon in Si-(CH<sub>2</sub>)<sub>n</sub>-Si groups. Furthermore, a small shoulder exists around 1100 cm<sup>-1</sup> indicative of the existence of Si-O bonds [3]. Figure 3 shows the Raman



Fig. 2. FTIR spectrum of A3 film which is typical for all films.

spectrum of the A3 film on the silicon substrate. An essential part of this spectrum originated from the silicon substrate, especially the intensity of the lattice vibration at 520 cm<sup>-1</sup>. Raman band between 930 cm<sup>-1</sup> and 990 cm<sup>-1</sup> is created by the acoustical and optical phonon modes of cubic or one of the hexagonal polytypes of SiC [4]. The peak broadening is related to the damping of phonon modes due to the short range ordering of SiC crystallites and the effects of surroundings having Si, as well as C-clusters. The Raman band between 1300 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> is observed for the all samples and is assigned to diamond like carbon (DLC) [5]. It is also observed that all spectra present relatively weaker band at 830 cm<sup>-1</sup>, which is typical for the amorphous SiC structure.



Fig. 3. Raman spectrum for A3 sample which is typical for all samples.

Figure 4 shows measured *I-V* characteristics of samples A1, A2, A3, and A4 in the semi-logarithmic scale at temperature 295 K. The positively biased circular nonohmic contact on the side with SiC film corresponds to the "forward" direction of the I-V characteristic. The negatively biased circular non-ohmic contact corresponds to the "reverse" direction. The measured I-V characteristics of samples A1 and A2 are similar but some quantitative differences are observable. I-V dependencies have almost linear behavior for both polarity of the bias voltage. The measured current of the sample A2  $(1 \times 10^{-9})$ A) is about 100 times greater than the current of the sample A1( $9x10^{-12}$  A) at the bias voltage 5 V. The structures A1 and A2 exhibit any rectification ratio. The measured I-V characteristics of sample A3 is linear in the "forward" direction to the bias voltage 5 V. The "reverse" I-V dependencies are linear in the bias voltage region below 0.05 V then they have a strong tendency to sublinear shape between 0.2 and 2 V. I-V curves of sample A4 are linear at low "forward" voltages, with a slight tendency toward a superlinear shape. Deviation toward the superlinear shape starts at "forward" bias voltage higher than 0.1 V. The I-V dependencies have linear behaviour with clear tendency to sublinear shape

over 0.08 V "reverse" voltage. The measured currents of the sample A4 (2- $6x10^{-9}$  A) are also greater (about 5 - 10 times) than the current of the sample A3 ( $4x10^{-10}$  A) at "reverse" bias voltage 5 V. The structures A3 and A4 exhibit a powerful rectification ratio of  $10^2$  at  $\pm 2$  V of the bias voltage. Results showed, that with increasing flow of 5% B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub> change film behaviour from slightly Ntype to P-type. Measured current and rectification ratio rise up with increasing flow of 5% B<sub>2</sub>H<sub>6</sub> in H<sub>2</sub>.



Fig. 4. I-V characteristics of the A1, A2, A3 and A4 structures.

## 4. Conclusion

We investigated the structural properties of amorphous SiC films doped with boron and electrical properties of heterostructure Al/SiC(B)/Si/Al. The RBS and ERD results showed main concentrations of Si, C and H. Concentration of boron was under concentration limit of RBS method. The FT-IR results of the SiC films showed the presence of the Si-C, Si-H, C-H, and Si-O bonds. Raman spectra showed interesting band intensities SiC 930 cm<sup>-1</sup> and 990 cm<sup>-1</sup> which is created by the acoustical and optical phonon modes of cubic or one of the hexagonal polytypes of SiC and DLC between 1300 cm <sup>1</sup> and 1700 cm<sup>-1</sup>. The measured *I-V* characteristics of samples A1 and A2 are similar but some quantitative differences are observable. The structures A1 and A2 exhibit any rectification ratio. The structures A3 and A4 exhibit a powerful rectification ratio of  $10^2$  at  $\pm 2$  V of the bias voltage. Measured current of structures and rectification ratio rise up with increasing flow of 5%  $B_2H_6$  in  $H_2$  gas mixture.

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## 6. References

[1] D. Pysch, J. Ziegler, J.-P. Becker, D. Suwito, S. Janz, S.W. Glunz and M. Hermle, *34th IEEE Photovoltaic Specialists Conference (PVSC)*, 2009, p. 794.

[2] M. Vetter, C. Voz, R. Ferre, I. Martín, A. Orpella, J. Puigdollers, J. Andreu and R. Alcubilla, *Thin Solid Films*, **511-512**, 290 (2006)

[3] S.W. King, J. Bielefeld, G. Xu, W. A. Lanford, Y. Matsuda, R.H. Dauskardt, N. Kim, D. Hondongwa, L. Olasov, B. Daly, G. Stan, M. Liuh, D. Dutta and D. Gidley, *Journal of Non-Crystalline Solids*, **379**, 67 (2013)
[4] J.K. Seo, Y-H. Joung, Y. Park and W.S. Choi, *Thin Solid Films*, **519**, 6654 (2011)

[5] T. Chen, Y. Huang. D. Yang, R. Carius and F. Finger, *Thin Solid Films*, **519**, 4523 (2011)