Amorphous silicon carbide thin films deposited by plasma enhanced chemical vapor deposition at different temperature for hard environment applications

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Abstract: PECVD technology was used for deposition of a-SiC:H films at different temperature from SiH_4 and CH_4 gas mixture. A P-type silicon wafer with resistivity 2-7 Ωcm and (100) orientation was used as the substrate for the growth of SiC films. Irradiation of samples by fast neutrons with fluence $1.4x10^{14}$ cm^{-2} was used. Raman band feature intensity decreasing after neutron irradiation. The measured currents after irradiation are greater (up to 100 times) than the current before irradiation for all samples.

Keywords: silicon carbide, plasma deposition, neutron irradiation

1. Introduction

Silicon carbide has attracted much interest for wide range of applications. With its wide band gap, excellent thermal properties and large bonding energy, silicon carbide films are ideal for optoelectronic blue and ultra-violet wavelength emissions operating at high power levels, high temperatures and caustic environments. The significance of this material follows from the fact that its electrical and optical properties can be controlled by varying the carbon, silicon and hydrogen composition of the film. Most researches in the a-SiC passivation layer formation for the silicon solar cells have been confined in a-SiC:H. The silicon heterojunction (SHJ)-emitter system consisting of an a-Si:H(i)- and/or a-SiC:H (n)-layer was examined regarding the influence of the layer thickness on the solar cell parameter and the pseudo fill factor. The best efficiency of 18.5% (independently confirmed) was realised with a single layer a-SiC:H(n) emitter with a thickness of 11 nm [1]. PECVD technique offers an attractive opportunity to fabricate amorphous hydrogenated SiC films at intermediate substrate temperatures and it provides high quality films with good adhesion, good coverage of complicated substrate shapes and high deposition rate [2, 3]. The a-SiC:H thin films deposited by PECVD as protective coatings for harsh environment applications were investigated [4]. Radiation hardness of SiC Schottky diodes has been analyzed after 24 GeV protons and 1 MeV neutrons irradiation [5].

In this paper, PECVD is used for deposition of a-SiC:H films using silane and methane as reactants. The structural properties were investigated by RBS, ERD, IR and Raman methods. FT-IR and Raman spectroscopy was used before and after neutron irradiation. The effect of irradiation by neutrons on film electrical properties was studied by measurement of the I-V characteristics.

2. Experiment

A P-type silicon wafer with resistivity 2-7 Ωcm and (100) orientation was used as the substrate for the growth of SiC films in parallel plate plasma reactor. Technological parameters for samples were: gas mixture was (SiH_4-4 sccm, CH_4-20 sccm) and substrate temperature was for sample P1(200 ^oC), P2(250 ^oC), P3(300 ^oC) and P4(350 ^oC), respectively. Concentration of species in the films were analyzed using RBS and ERD analytical method simultaneously [6]. Chemical composition were analyzed 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. The IR spectra were measured from 4000 to 400 cm^{-1}. Raman measurements of SiC layers were performed by using a Thermo Fisher Scientific DXR Raman microscope with 532 nm laser. The thickness and refractive index were determined by spectroscopic ellipsometry. For this purpose a SpecEl-2000 spectroscopic ellipsometer (400 - 900 nm) manufactured by Micropac, software Scout from Wolfgang Theiss and an O'Leary–Johnson–Lim (OJL) model was used. Irradiation of samples by fast neutrons with fluence $1.4x10^{14}$ cm^{-2} in IREN facility at JINR Dubna was used. The circular electrodes of Au (120 nm thick) as a non-ohmic contacts with diameter 1.2 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 (~260 nm thick). Metal systems were thermally evaporated in a dry high-vacuum system. The electrical properties of SiC films 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 discussion

An example of plasma optical emission spectrum generated by a SiH_4 and CH_4 glow discharge is shown in Fig.1. When fabricating a-SiC:H film from SiH_4 and CH_4, it is known that the $I(CH^*)$ and $I(SiH^*)$ ratio, $I(CH^*)/I(SiH^*)$, is in a proportional relationship to the ratio of the numbers of C and Si atoms inside the film.

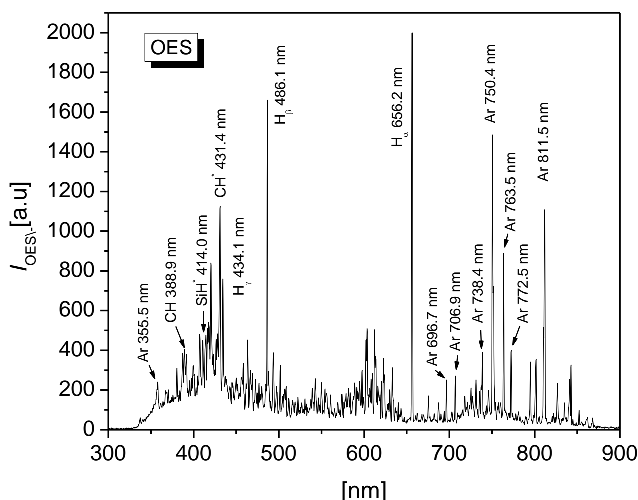

Fig. 1 Optical emission spectrum of SiH_4 and CH_4 glow discharge at 10 Pa with small amount of Ar for actinometry method.

The measured and simulated RBS spectra for samples P1-P4 are shown in Fig.2 and ERD spectra are shown in Fig.3. RBS and ERD analysis indicated that the films contain silicon, carbon, hydrogen and small amount of oxygen and nitrogen.

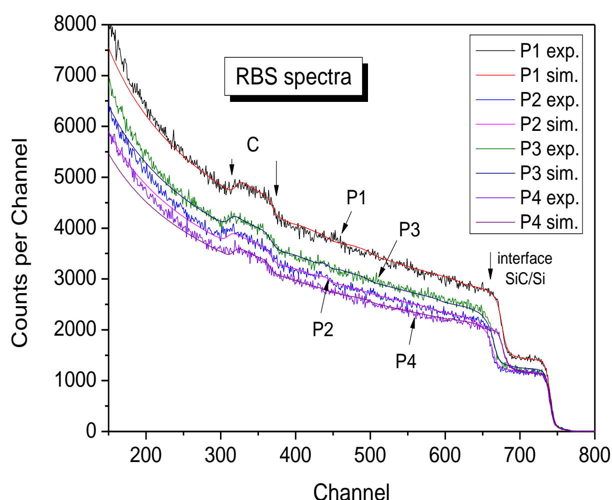

Fig. 2 Experimental and simulated RBS spectra of the silicon carbide films for samples P1, P2, P3 and P4.

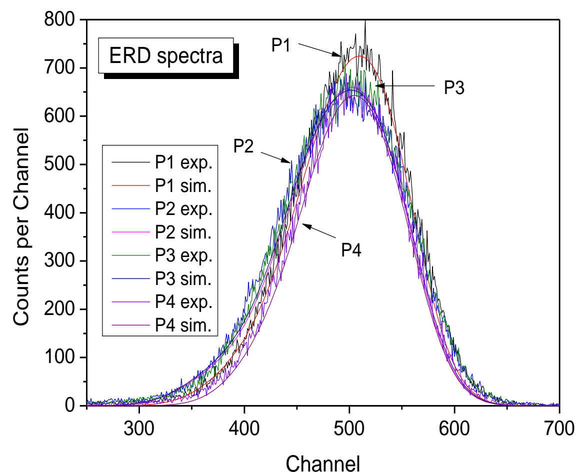

Fig. 3 ERD spectra of the silicon carbide films for samples P1, P2, P3 and P4.

The concentrations of species of samples are presented in Table. 1. From the concentration results we can conclude that the concentration of hydrogen decrease with increase deposition temperature. Thickness and refractive index are also presented in Table 1. The refractive index change in the range of 2.49 to 2.56 and these results can be explained by very small influence of deposition temperature on the change value of refractive index.

Table 1 Concentration of main species in SiC films determined by RBS and ERD and measured thickness and refractive index by spectroscopic ellipsometry.

Sample	Si (at.%)	C (at.%)	H (at.%)	N (at.%)	O (at.%)	Thick. (nm)	Refr. n
P1	34	35	27	1-2	2-3	137	2.52
P2	34	35	27	1-2	2-3	135	2.49
P3	35	36	25	1-2	2-3	139	2.56
P4	36	36	23	1-2	2-3	134	2.52

Figure 4 show infrared spectra before (P) and after irradiation (Pirr) by neutrons of films P1-P4, that is typical for a-SiC:H film. From the IR spectra of P1-P4 film we could determine the following vibration frequencies: the band at 2800 to 3000 cm^{-1} is attributed to stretching vibration of the CH_n group in both the sp^2 (2880 cm^{-1}) and sp^3 (2920 cm^{-1}) configurations. The band at 2100 cm^{-1} is due to SiH_m stretching vibrations. The absorption bands from 1200 to 1500 cm^{-1} are due to bending and scissoring modes of CH_2, CH_3, $Si(CH_3)$, and $C(CH_3)$. The signals occur between 930 and 1200 cm^{-1} which are superposition of several C-H, Si-O and Si-N vibrations [7,8]. No significance effect on the IR spectra band features after neutron irradiation was observed. Only side shoulders occur be-

tween 550 cm^{-1} and 700 cm^{-1} show small differences in the IR spectra before and after neutron irradiation. We proposed that the neutron fluence $1.4x10^{14}$ cm^{-2} is not enough to change dramatically concentration of bonds which influence shape of measured IR spectra.

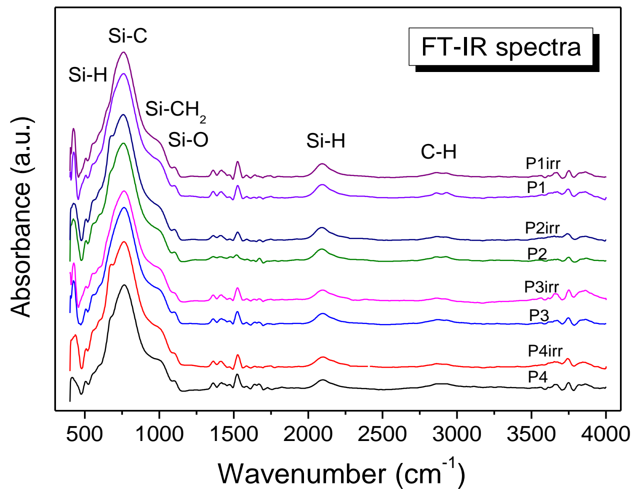

Fig. 4 Infrared spectroscopy results before and after neutron irradiation for all films P1-P4.

Figure 5 shows Raman spectra of the SiC film on silicon substrates for sample P3 before and after neutron irradiation which is typical for all samples. The spectrum was collected under ambient conditions using the 532 nm laser. An essential part of these spectra originates from the silicon substrate, especially the intensity of the lattice vibration at 520 cm^{-1}. The Raman band between 930 cm^{-1} and 990 cm^{-1} is created by acoustical and optical phonon modes of cubic or one of the hexagonal polytypes of SiC. The peak broadening is related to the damping of phonon modes due to the short range ordering of SiC crystallites

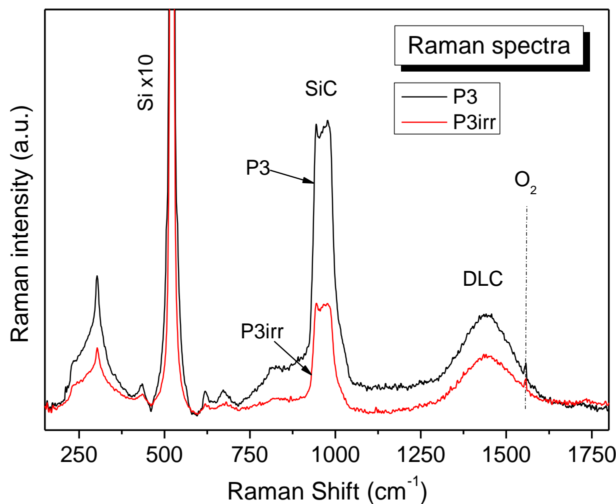

Fig. 3 Raman spectroscopy results before and after neutron irradiation for samples P3and P3irr.

and the effects of surroundings having Si, as well as C-clusters [9]. The peak at around 1565 cm^{-1} is caused by the oxygen since the measurements were carried out in the atmosphere. The Raman band between 1300 cm^{-1} and1700 cm^{-1} is assigned to diamond like carbon (DLC) [10]. It is also observed relatively weaker band around 830 cm^{-1} which is typical for amorphous SiC structure [7]. From the Raman spectra after irradiation we can see decreasing Raman intensity for all band features. In the case of SiC and DLC bands, it can be explain by the breaking of SiC and CC bonds to create Si and C clusters. Figure 6 show *I-V* characteristics before and after irradiation of samples with neutrons of fluence $1.4x10^{14}$ cm^{-2} in the semi-logarithmic (a) and in the logarithmic (b) scale, respectively. The display of both scales is important because the log-log plot shows in detail the low bias voltage region while the higher bias voltage region is better demonstrated in the log-lin scales. The positively biased circular non-ohmic 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. No rectifying effect was observed in the measured *I-V* characteristics. *I-V* dependencies in figure 4 have almost linear behavior in the bias voltage region below 0.02 V, then they have a tendency to sublinear shape between 0.03 and 0.6 V for all samples before irradiation. At bias voltages over 0.6 V the current rises up practically reaching the linear current limit at a bias of 1V. The measured forward current reaches values 9 nA - 90 nA and the reverse current reaches values 9 nA – 60 nA, respectively at a bias of 0.01 V for different samples. The measured current of the SiC films fall down with higher deposition temperature up to 300 °C and at 350 °C measured current rise up. This effect can be explained by the change of graphite like carbon concentration in the films because the concentration of carbon is practically the same. We propose that the other species have very small influence on the conductivity in presented range of deposition temperature. After irradiation with neutrons *I-V* dependencies have linear behavior with a tendency to sublinear (saturation) at about 0.2 V. The measured currents after irradiation of the samples are greater (up to 100 times) than the current before irradiation for particular samples. The higher measured current after irradiation might be due to breaking of the most slightly bonded Si-H and C-H bonds therefore creating more dangling bonds and so increasing number of defect centers in the films responsible for the higher measured current [3]. The hydrogen is most efficient moderator because the neutron can lose up to all its energy in a single collision with a hydrogen nucleus. Futhermore, irradiation of a-SiC:H films with neutrons results in increase of sp^2 C=C bonds, i.e. the carbon in the films tended to graphitization. In general, the

graphitization of carbon led to the decrease of resistivity.

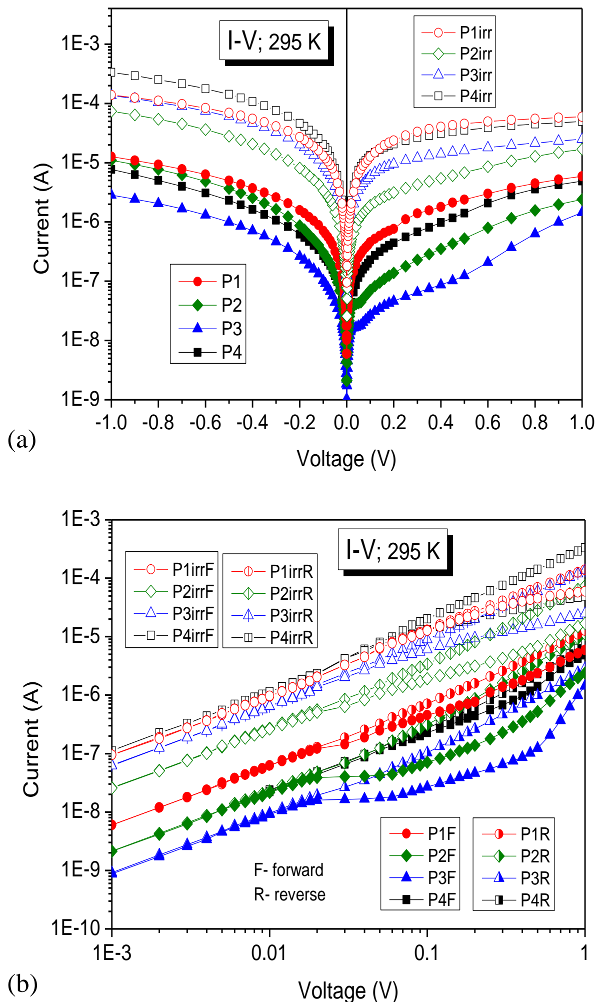

Fig. 6 I-V characteristics of structure Au/SiC/Si/Al –samples P1-P4 before and after irradiation with neutrons of fluence $1.4x10^{14}$ cm^{-2} in the semi-logarithmic (a) and in the logarithmic (b) scale, respectively.

4. Conclusions

We have investigated the structural and electrical properties of SiC films prepared by plasma enhanced chemical vapor deposition at different temperature before and after irradiation by neutrons. The RBS results showed that the concentrations of Si and C in the SiC films were changed a little with the change of deposition temperature. The concentration of hydrogen was decreased with increasing deposition temperature in the range from 27 to 23 at.%. The films contain a small amount of oxygen and nitrogen. FT-IR results of SiC films showed the presence of Si-C, Si-H, C-H and Si-O bonds. No significance effect on the FT-IR spectra band features after neutron irradiation was observed. Raman spectroscopy results showed decreasing of Raman band feature intensity after neutron irradiation. Electrical results showed no rectifying effect in the measured I-V characteristics before and after irradiation with neutrons. I-V curves before irradiation are linear at low voltages, with a slight tendency toward a superlinear shape. Deviation toward the superlinear shape starts for all samples at a bias voltage higher than 0.03 V. After irradiation with neutrons the I-V dependencies have linear behaviour with a tendency to sublinear shape over 0.08 V. The measured currents after irradiation are greater (up to 100 times) than the current before irradiation for all samples.

5. Acknowledgement

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