18th International Vacuum Congress

Structural and physical characteristics of PECVD nanocrystalline silicon carbide thin films

J. Huran\(a^*\), A. Valovič\(a\), A.P. Kobzev\(b\), N.I. Balalykin\(b\), M. Kučera\(a\), Š. Haščík\(a\), L. Malinovský\(c\), E. Kováčová\(a\)

*Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava, 841 04, Slovakia
\(b\)Joint Institute for Nuclear Research, Dubna, 141980, Russia
\(c\) Institute of Physics, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava, 845 11, Slovakia

*E-mail address: elekhura@savba.sk

Abstract

Nanocrystalline silicon carbide was prepared by PECVD technology in capacitively parallel plate plasma reactor, where both silane and methane were introduced into the plasma reactor. The concentration of species in the SiC films was determined by RBS and ERD. Chemical compositions were analyzed by IR spectroscopy. Film morphology was assessed by AFM. The RBS results showed the main concentrations of Si and C in the films. The concentration of hydrogen was approximately 20 at.\%. IR results showed the presence of Si-C, Si-O, Si-N, Si-H, N-H, C-H, C-N specific bonds. The AFM micrographs revealed the film surface smooth and compact. Results of I-V measurements before and after samples irradiation by neutrons are presented.

© 2012 Published by Elsevier B.V. Selection and/or peer review under responsibility of Chinese Vacuum Society (CVS). Open access under CC BY-NC-ND license.

Keywords: plasma deposition; nanocrystalline silicon carbide

1. Introduction

The next generation of electronic devices may benefit from the development of alternatives to silicon and gallium arsenide based devices. The demands of higher power, radiation hardness, operating frequency, temperature and speed are potentially met by silicon carbide with additional attractive properties such as wide band gap, high breakdown field, high electron saturation velocity and physical strength [1]. In addition to high-temperature applications, SiC has potential for use in high-power and high-frequency [2]. However, SiC has several advantages over other wide-band gap semiconductors at the present time including commercial availability of substrates, known device processing techniques, and the ability to grow a thermal oxide for use as masks in processing, device passivation layers, and gate dielectrics. Furthermore, SiC can also be used as a thin buffer layer for the growth of
diamond films on silicon substrates [3]. For example, a-Si_{1-x}C_{x}:H was used as a wide window material to enhance the conversion efficiency of amorphous solar cell. 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. PECVD technique offers an attractive opportunity to fabricate amorphous hydrogenated N-doped 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 [4]. Recently, Si-rich a-SiC_{x}:H films have attracted new attention in the photovoltaic community, since this material has shown excellent electronic surface passivation of c-Si comparable with thermal SiO_{2} and low temperature amorphous silicon nitride (a-SiN_{x}) passivation [5].

In this contribution the attention has been focused to the properties of silicon carbide films prepared by the plasma enhanced chemical vapour deposition (PECVD) of silane SiH_{4} and methane CH_{4} and is continuation of our work in [6]. The structural properties were investigated by RBS, ERD, IR, PL and XRD measurement techniques. Spectroscopic ellipsometry was used for optical characterization of the film. Electrical characterization was made by I-V measurement technique before and after neutron irradiation of samples.

2. Experimental

Capacitively coupled plasma reactor was used for thin film deposition. The silan and methane were introduced into reactor through the shower head. Both gases were flown vertically toward the substrate on bottom electrode. A n-type silicon wafer with resistivity 2-7 Ω•cm and (111) orientation was used as the substrate for the silicon carbide films. Prior to deposition, standard cleaning was used to remove impurities from the silicon surface, and the 5% hydrofluoric acid was used to remove the native oxide on the wafer surface. The wafer was then rinsed in deionised water and dried in nitrogen ambient. The flow rates of SiH_{4} and CH_{4} gases were 10 sccm and 40 sccm, respectively. The deposition temperature was 450 °C. The concentration of species in the SiC films was determined by Rutherford backscattering spectrometry (RBS). Chemical compositions were analyzed by infrared spectroscopy. The IR spectra were measured from 400 to 4000 cm\(^{-1}\). The hydrogen concentration was determined by the elastic recoil detection (ERD) method. For this purpose the \(^{4}\)He\(^{+}\) ion beam from a Van de Graaff accelerator at JINR Dubna was applied. The energy of \(E = 2.3\) MeV was chosen. For the determination of the hydrogen concentration from the recoiled spectra a computer program has been used. In this program the effects of detector resolution, straggling, and multiple scattering of \(^{4}\)He\(^{+}\) ions and protons in the target and stopper Al foil are included. These corrections improve essentially the agreement between experimental and simulated spectra. Film morphology was assessed by Atomic Force Microscopy. Irradiation of samples by fast neutrons in IREN facility at JINR Dubna was used for radiation hardness investigation. The thickness, refractive index and optical gap were determined by spectroscopic ellipsometry. For this purpose a SpecEl-200 spectroscopic ellipsometer (400 - 900 nm) manufactured by Micropac, software Scout from Wolfgang Theiss and OJL model [7] was used. The electrical properties of nc-SiC:H films were determined by I-V measurement on diode structures.

3. Results and discussion

We prepared SiC film on Si substrate with thickness 580-593 nm, refractive index 2.72 and optical band gap 2.18-2.22 eV. These values were measured by spectroscopic ellipsometry. An example of plasma optical emission spectrum generated by a SiH_{4} and CH_{4} glow discharge is shown in Fig. 1. When fabricating nc-SiC:H film from SiH_{4} and CH_{4}, it is known that the \(I(CH^{+})/I(SiH^{+})\) ratio, \(I(CH^{+})/I(SiH^{+})\), is in a proportional relationship to the ratio of the numbers of carbon and silicon atoms inside the film. The measured IR spectrum revealed the main absorption region between 400 and 2000 cm\(^{-1}\). From the measured IR spectrum were determined the following vibration frequencies: 520 to 530 and 1090 to 1093 can be related to \(SiO_{2}\) the higher wavenumber can be also related to Si-N bonds close to Si_{3}N_{4} bonds; 944 to 950 and 1000 to 1005: they can be roughly related to Si-N bonds from Si_{3}N_{4}; 1260 to 1265: they can be related to C-N bonds; 606 to 610: it can be related to Si-C localised vibration normally found in Si due to C in single crystalline Si. The main phonon or vibration frequency is related to SiC and have the following characteristics determined from the reflection spectra: center position 795 cm\(^{-1}\), width 178 cm\(^{-1}\); center position 795 cm\(^{-1}\), width 45 cm\(^{-1}\); center position 804 cm\(^{-1}\), width 42 cm\(^{-1}\). The non stressed phonon position of cubic SiC is 796 cm\(^{-1}\). In amorphous material a shift to higher values indicate on recrystallisation or nucleation of small crystallites. Fig. 2 shows RBS spectra of the deposited amorphous silicon carbide film. After modelling, we
can show from calculated results the presence of small amounts of oxygen and nitrogen while the concentrations of hydrogen in the SiC film are approximately 20 at.%. Both of the elements nitrogen and oxygen represent 2-4 at.% in the film. The SiC film contained also other species which were under the detection limit of RBS method. The concentrations of Si and C in the SiC film are 32 and 35 at.% respectively. The ERD spectra are shown in figure 3. The AFM micrographs of the SiC films prepared by PECVD reveal that the film surface is rather smooth and
compact. From the XRD measurement was determined only one type of SiC hexagonal polytype. Figure 4 shows
PL intensities measured at two different temperatures. It can be seen that PL intensity is higher at 6 K measurement
temperature and PL peak emission wavelength decrease. From I-V characteristics of prepared diode structures

![PL spectra measured:](image)

**Fig. 4.** Photoluminescence spectra measured at different temperatures.

Au/SiC/Si/Al before irradiation by neutrons, figure 5, we can show, that the conductivity of the SiC layer prepared
at 450 °C for sample is very small about $10^{-12}$ S for reverse current. From I-V characteristics of structure
Au/SiC/Si/Al for all Schottky contacts we observed dispersion in characteristics that is due to the inhomogeneity of
SiC film parameters. At higher voltages, the current is limited by the series resistance due to ohmic contact and the
bulk resistance of SiC layer. In figure 6 we can see I-V characteristics for diode structure Au/SiC/Si/Al after
irradiation by neutrons with fluence of $5 \times 10^{11}$ cm$^{-2}$. From measured I-V characteristics we can see difference before
and after irradiation. It can be explained by the degradation of interface between top contact and film surface -
increasing density of interface state. Change of forward current can be explained by change of bulk film properties
after neutron irradiation.

![I-V sample irradiated](image)

**Fig. 5.** I-V characteristics for diode structures Au/SiC/Si/Al with Au top contacts (d=1.2 mm) on SiC
film a) and I-V characteristics for diode structure Au/SiC/Si/Al with Au top contacts (d=1.2 mm) on
SiC film after irradiation by neutrons with fluence of $5 \times 10^{11}$ cm$^{-2}$ b).
4. Conclusion

We have investigated the structural and electrical properties of nc-SiC films prepared by plasma enhanced chemical vapor deposition at 450 °C. The RBS results showed that the concentrations of Si and C in the films are practically the same. The concentration of hydrogen was determined by the ERD method and the value is approximately 20 at. %. The films contain a small amount of oxygen and nitrogen. IR results showed the presence of Si-C, Si-N, C-H and Si-O bonds. PL intensity is higher at 6 K measurement temperature and PL peak emission wavelength decrease. From measured I-V characteristics we can see difference before and after irradiation at forward and reverse currents for diode structure.

5. Acknowledgements

This research has been supported by the Slovak Research and Development Agency under the contracts APVV-0713-07 and SK-UA-0011-09 and by the Scientific Grant Agency of the Ministry of Education of the Slovakia and Slovak Academy of Sciences, No. 2/0192/10.

References

[1] H. Morkoc, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, M. Burns: Large-band gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies. J. Appl. Phys., 76 (1994), 1363-1394.
[2] H. Zhang, Z. Xu: Structural and optical properties of four- hexagonal polytype nanocrystalline silicon carbide films deposited by plasma enhanced chemical vapour deposition technique. Thin Solid Films, 446 (2004), 99-105.
[3] E.G. Wang: A model for buffer layer formed on silicon during HFCVD diamond growth: Physica B, 185 (1993), 85-89.
[4] H. Colder, P. Marie, L. Pichon, R. Rizk: Hydrogenated nanocrystalline silicon carbide: fabrication, properties and heterostructure device application. Phys. Stat. Sol. (c), 1 (2004), 269-273.
[5] M. Vetter, C. Voz, R. Ferre, I. Martin, A. Orpella, J. Puigdollers, J. Andreu, R. Alcubila: Electronic properties of intrinsic and doped amorphous silicon carbide films. Thin Solid Films, 511-512 (2006), 290-294.
[6] J. Huran, I. Hotovy, J. Pezoltd, N.I. Balalykin, A.P. Kobzev: Effect of deposition temperature on the properties of silicon carbide thin films. Thin Solid Films, 515 (2006), 651-653.
[7] S.K. O'Leary, S.R. Johnson, P.K. Lim: The relationship between the distribution of electronic states and the optical absorption spectrum of an amorphous semiconductor: An empirical analysis. J. Appl. Phys., 82 (1997), 3334-3340.