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*COMMUNICATIONS*

# HYDROGENATED AMORPHOUS SILICON CARBON NITRIDE FILMS PREPARED BY PECVD TECHNOLOGY: PROPERTIES

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Hydrogenated amorphous silicon carbon nitride films were grown by plasma enhanced chemical vapor deposition (PE CVD) technique. The flow rates of $SiH_4$, $CH_4$ and $NH_3$ gases were 6 sccm, 30 sccm and 8 sccm, respectively. The deposition temperatures were 350, 400 and 450 °C. The RBS and ERD results showed that the concentrations of Si, C, N and H are practically the same in the films deposited at substrate temperatures in the range 350–450 °C. In photoluminescence spectra we identified two peaks and assigned them to radiative transitions typical for amorphous materials, *ie* band to band and defect-related ones. The electrical characterization consists of $I(V)$ measurement in sandwich configuration for voltages up to 100 V. From electrical characterization, it was found that with increased deposition temperature the resistivity of the amorphous SiCN film was reduced.

K e y w o r d s: hydrogenated amorphous silicon carbon nitride, PECVD

## 1 INTRODUCTION

The deposition of silicon carbon nitride has been widely studied due to their attractive properties, such as wear resistance, chemically inertness and wide band gap, which provide optical, electronic and other ambient applications [1–3]. Significant progress in this area has been made due to advancement of the film fabrication technologies, in particular physical vapor deposition (PVD) and chemical vapor deposition (CVD), as well as the characterization technique [4]. Most of the published works devoted to production of Si–C–N refer to high temperature deposition processes (CVD). High temperature deposition (typically between 600 and 1200 °C) is a strong limitation for industrial applications. Only few works has been published about the synthesis of Si–C–N at low growth temperatures. Pulsed laser deposition (PLD) was used by some authors [5], but there is some works published with ion sputtered deposition of carbon and silicon in a nitrogen atmosphere, with simultaneous nitrogen ion bombardment of substrates [6] and reactive magnetron sputtering [7]. SiCN was usually used as hard mask, which has good resistance to wet chemicals, aggressive etch and chemical polishing. The dielectric constant k value can be varied between 4.2 and 4.9 depending on the deposition temperature [8]. It was reported that SiCN can also show good barrier behavior for $Cu/SiO_2$ and Cu/black diamond low k material system [9].

The aim of this work was to investigate the properties of silicon carbon nitride thin films prepared by plasma enhanced chemical vapor deposition. For this one we used RBS, ERD, IR, PL and SE measurement. The current-voltage (I–V) characteristics of thin film structures made of silicon carbon nitride films grown on silicon substrates were studied.

## 2 EXPERIMENT

Hydrogenated amorphous silicon carbon nitride films were grown by plasma enhanced chemical vapor deposition. All films were prepared on lightly doped p-type Si substrates (100). The films were deposited in a high frequency parallel-plate plasma reactor in which the frequency and the RF power were maintained at 13.56 MHz and 0.05 $Wcm^{-2}$, respectively. The flow rates of $SiH_4$, $CH_4$ and $NH_3$ gases were 6 sccm, 30 sccm and 8 sccm, respectively. The deposition temperatures were 350, 400 and 450 °C. The concentrations of species in hydrogenated silicon carbon nitride films were analyzed using two RBS (Rutherford backscattering spectrometry) and ERD (elastic recoil detection) analytical method simultaneously, Fig. 1.

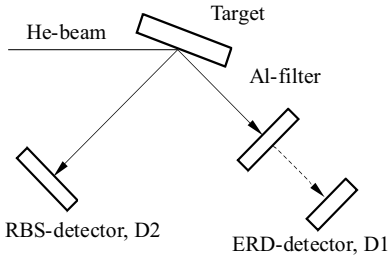



**Fig. 1.** The experimental ERD method arrangement. The sample orientation to the $^4He^+$ beam was at an angle $\alpha = 15°$. The detectors were fixed in the following geometry: detector D1 at an angle $\Theta_1 = 30°$, detector D2 at an angle $\Theta_2 = 135°$.

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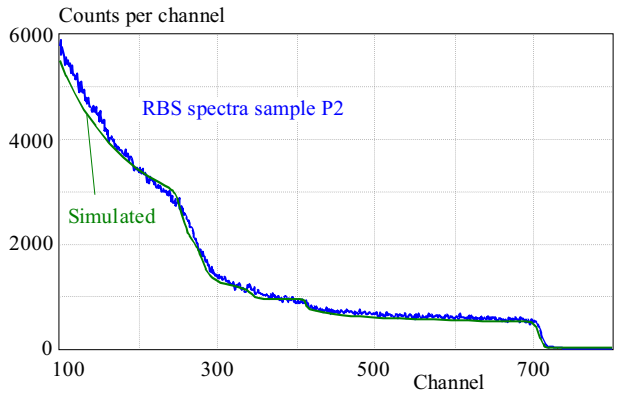



**Fig. 2.** RBS spectra of SiCN films deposited onto a silicon substrate for 2 MeV alpha particles detected at scattering angle of 135°. The spectra are for sample P2.

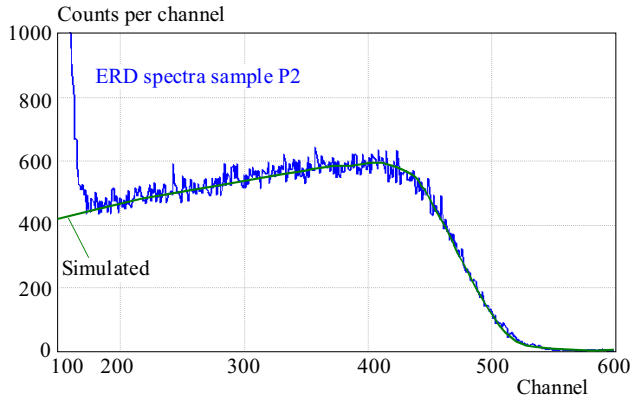



**Fig. 3.** The ERD spectra of recoiled hydrogen obtained with 2.3 MeV $^4He^+$. The spectra are for sample P2.

For this purpose the $^4He^+$ ion beam from a Van de Graaff accelerator at JINR Dubna was applied. The energy of 2.3 MeV was chosen. The target was tilted at an angle of 15° with respect to the beam direction and the recoiled protons were measured in forward direction at an angle of 30°. Another surface barrier detector for registering RBS spectra was located under an angle of 135°. For data processing the SIMNRA computer code was used [10]. Information about used model was presented in [11]. Chemical compositions were analyzed by infrared spectroscopy. The IR spectra were measured from 4000 to 400 $cm^{-1}$ by FT-IR Nicolet 8700 spectrometer. At photoluminescence measurements, the samples were placed in an optical cryostat with temperature set to 5 K . A diode laser with a 405 nm line was used as a pumping source. The PL signal was detected by a photomultiplier tube with GaAs photocathode and measured by a standard lock-in technique. For electrical characterization of the SiCN films vertical structures were formed on the prepared SiCN/Si samples. Circular Au dots with a diameter of 0.4 mm and a thickness of 70 nm were evaporated after the cleaning procedure of SiCN surface. Al served as large area back contact to Si substrate.

## 3 RESULTS AND DISCUSSION

The refractive index and thickness of SiCN films were measured by spectroscopic ellipsometry and for 40 minutes deposition data were for sample P1(350 °C) thickness 680 nm, refractive index 2.15, P2(400 °C) 695 nm and 2.17 and for P3(450 °C) 705 nm and 2.18, respectively. Figure 2 shows RBS spectra and Figure 3 ERD spectra of sample P2. In the case of samples P1, P2 and P3 the concentrations of silicon, carbon, nitrogen and hydrogen were P1(30, 25, 25, 24 at.%), P2(29, 23, 28, 22) and P3(30, 22, 30, 20), respectively. After modeling, we can show from calculated results the presence of small amounts of oxygen. There is no essential difference between the IR spectra of the samples. The FTIR spectra of deposited SiCN films show the most prominent widened peak between 600 $cm^{-1}$ and 1200 $cm^{-1}$ which can be deconvoluted into several peaks. From the IR spectrum of SiCN film sample P2 Figure 4 we could determine the following vibration frequencies: about 960: they can be roughly related to Si-N bonds; about 1050: they can be related to C-N bonds. The phonon or vibration frequency is related to Si-C and peaks have the center position about 750 $cm^{-1}$. We propose that absorption band at around 840 $cm^{-1}$ is caused by Si-C-N bond [12]. The side shoulder peaking at around 1000 $cm^{-1}$ is attributed to the wagging vibration of $CH_2$ bonded to silicon in Si-$(CH_2)_n$-Si groups and peak about 1250 $cm^{-1}$ is assigned to Si-$CH_3$ wagging modes [13]. Furthermore, there exists a small shoulder between 1000 $cm^{-1}$ and 1100 $cm^{-1}$ indicative of the existence of Si-O bond [14]. The bands around 2100 $cm^{-1}$ are assigned to Si-H stretching vibrations. The $CH_n$ band is situated around 2900 $cm^{-1}$. In this area, two sharp peaks are distinguished at 2950 $cm^{-1}$ and 2880 $cm^{-1}$ that could be attributed to the asymmetric and symmetric stretching vibration modes, respectively, of $CH_2$. Absorption band around 3350 $cm^{-1}$ could be attributed to N-H bond. All of the three samples show photoluminescence at 5 K temperature. In the PL spectra of all three samples a band between 550 nm and 750 nm can be unambiguously identified. The band peaks at around 610 nm. Higher-energy band peaking around 500 nm can be clearly resolved for sample P3, and it is much weaker for other two samples. It is well-known that in amorphous materials the luminescence originates in band to band transitions (more precisely, transitions between tails in energy bands) and band (band tail) to discrete level transitions, where discrete levels originate in structure defects. Hence, we assign luminescence bands in Fig. 5x to these two fundamental transitions. In the figure, other narrow peaks in the range 420 nm – 470 nm can be observed. Their origin is still unclear. We also cannot exclude mix with some insufficiently filtered laser modes of pumping diode laser. From I-V characteristics (Fig. 6) of structure Au/SiCN/SiAl for all samples are observed dispersions in characteristics that are due to the inhomogenity of SiCN film parameters. At higher voltages, the current is limited by the series resistance due to ohmic contact and

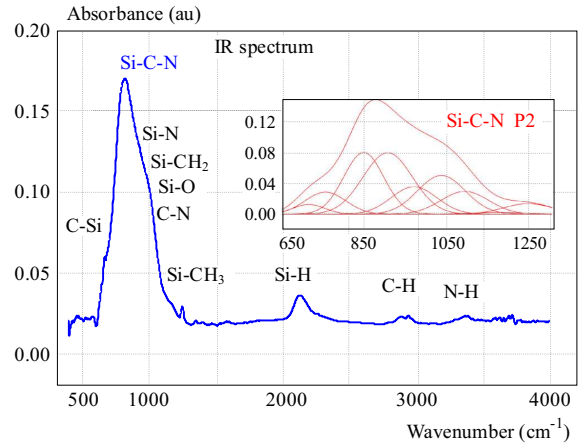



**Fig. 4.** Typical FTIR spectrum of SiCN film-sample P2 with inserting picture of main peak deconvolution

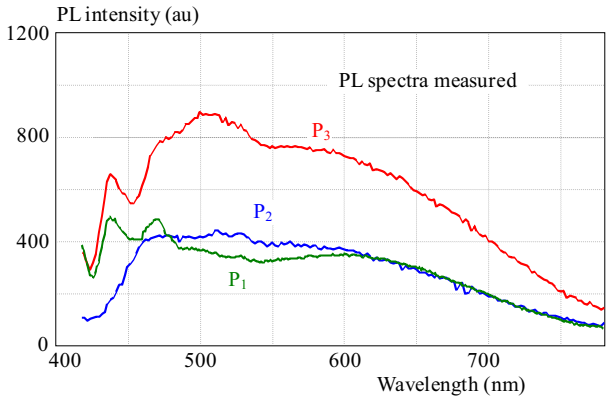



**Fig. 5.** Photoluminescence spectra of samples deposited at different temperature of substrates: P1(350 °C); P2(400 °C); P3(450 °C).

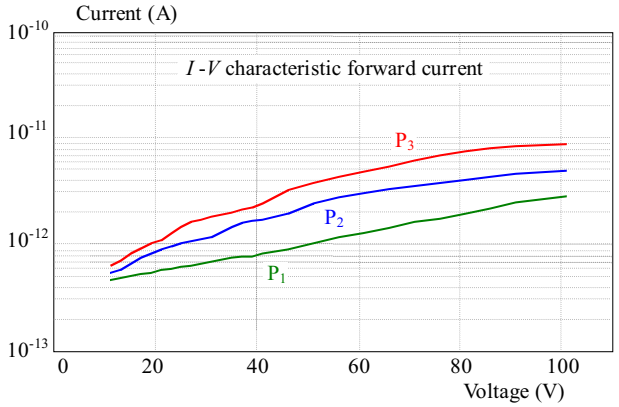



**Fig. 6.** I-V characteristics of structures Au/SiCN/Si/Al with silicon carbon nitride films prepared at different temperatures of substrate: P1(350 °C); P2(400 °C); P3(450 °C).

the bulk resistance of SiCN layer. It was found that with increased deposition temperature the conductivity of the amorphous SiCN films was increased a little.

## 4 CONCLUSION

We have investigated the properties of hydrogenated amorphous silicon carbon nitride films prepared by plasma enhanced chemical vapor deposition. The RBS results showed that the concentrations of Si, C and N are practically the same in the films deposited at substrate temperatures in the range 350–450 °C. 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. IR results showed the presence of Si-C, Si-C-N, Si-N, Si-H, C-H, C-N, N-H and Si-O bonds. From the photoluminescence spectra we proposed two recombination processes, band to band and defect recombination concerning PL. The electrical conductivity was evaluated by means of I-V measurements of structures prepared from SiCN films. It was found that with increased deposition temperature the resistivity of the amorphous SiCN films was reduced.

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