Materials Science in Semiconductor Processing 88 (2018) 65–72

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Structural, optoelectronic and mechanical properties of PECVD Si-C-N films: An effect of substrate bias

A.O. Kozak[a,*], V.I. Ivashchenko[a], O.K. Porada[a], L.A. Ivashchenko[a], T.V. Tomila[a], V.S. Manjara[b], G.V. Klishevych[b]

[a] Institute for Problems of Materials Sciences NAS of Ukraine, 3, Krzhyzhanovsky Str., 03142 Kyiv, Ukraine
[b] Institute of Physics NAS of Ukraine, 46, Nauki ave., 03028 Kyiv, Ukraine

ARTICLE INFO

Keywords:
Amorphous Si-C-N films
Plasma-enhanced chemical vapor deposition
Photoluminescence
Photoluminescence excitation
Chemical bonding
Nanoindentaion

ABSTRACT

Structural, optoelectronic and mechanical properties of amorphous silicon carbon nitride (Si-C-N) thin films produced by plasma enhanced chemical vapor deposition (PECVD) at different negative substrate biases (U_d) are studied. The films are characterized by X-ray diffraction, atomic force microscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, optical transmittance spectroscopy, nanoindentation as well using the results of the measurements of photoluminescence (PL) and PL excitation (PLE) spectra. All deposited films are found to be X-ray amorphous. An increase in U_d leads to: a smoothing of the film surface; a decrease of the transparency; an increase of refractive index from 1.69 to 1.92; a decrease of the energy gap from 4.15 to 2.38 eV; an increase in nanohardness and elastic modulus from 14 GPa to 24 GPa and from 147 GPa to 190 GPa, respectively. These results were explained in terms of the bonding configuration from XPS and FTIR measurements. The PL spectra of the films deposited at lower negative substrate bias have one PL band in the region between 530 and 540 nm, whereas the PL spectra of the films deposited at higher negative substrate bias show two PL bands at 530–570 nm and 640–650 nm. On the basis of the PLE data, it was shown that these PL bands are related to the electronic recombination between the conduction band and the valence bands and their tails within the amorphous N-rich and C-rich Si-C-N-O-H networks.

1. Introduction

Up to date, thin silicon carbon nitride (Si-C-N) films are of interest due to the unique optoelectronic properties as a variable band gap in the range from 0.96 to 5.6 eV and refractive index between 1.44 and 2.2, high transparency in the visible range of spectra, on the one hand, and the excellent mechanical properties, namely, high hardness (up to 38 GPa), high structural and thermal stability until 1350 °C, low roughness, strong adhesion to a substrate, and good abrasive wear resistance [1–7]. The combination of these properties has enabled the efficient application of Si-C-N films in semiconductor devices and as wear-resistant coatings. In particular, they can be used as thin films with variable optical characteristics in ultraviolet light sensors, and as sensitive layers in gas sensors, as well as protective and wear-resistant coatings on optoelectronic devices and metal surfaces [7–10].

Different chemical vapor deposition (CVD) or physical vapor deposition (PVD) methods, such as plasma enhanced CVD (PECVD) [2,5,8,11,12], thermo-CVD (high temperature heating) [3], hot-wire CVD [9,10], magnetron sputtering [5], pulsed laser deposition [13] are often used for the preparation of Si-C-N films. It is well established that film properties are sensitive to deposition parameters and precursors used. The main PECVD parameters are substrate temperature, discharge power and negative substrate bias (U_d). During deposition, two processes take place: i) film deposition due to the chemical reactions between adsorbed species on the growing film surface, and ii) the sputtering of the deposited film. The sputtering occurs due to the breaking of the weak bonds on the film surface, which promotes the densification of the films, and an increase of their quality [2,6]. These two processes are controlled by deposition conditions. The recent review of the properties of Si-C-N films deposited by using different methods was done in Ref. [14]. We note that, despite a huge experimental material accumulated on Si-C-N films, so far, the comprehensive studies of the Si-C-N films that could combine good optoelectronic and mechanical properties are in an infant stage. Such films might be used for the production of semiconductor devices for the exploitation under extreme conditions.

In this work, Si-C-N films were produced by PECVD at different substrate biases using the liquid precursor hexamethyldisilazane

---

[*] Corresponding author.
E-mail address: andri.kozak@ipms.kiev.ua (A.O. Kozak).

https://doi.org/10.1016/j.mssp.2018.07.023
Received 5 April 2018; Received in revised form 13 June 2018; Accepted 15 July 2018
1369-8001/ © 2018 Elsevier Ltd. All rights reserved.

Table 1
Deposition parameters.

U_d (V)	− 5, − 50, − 100, − 150, − 250
F_{N2} (sccm)	0.5
F_{H+HMDS} (sccm)	12
P_C (Torr)	0.2
T_S (°C)	450
P_W (W/cm^2)	0.2

U_d – substrate bias voltage, F_{N2} – nitrogen flow rate, F_{H+HMDS} – hydrogen flow rate through a bubbler with the HMDS vapor, P_C – working pressure, T_S – substrate temperature, P_W – discharge power density.

(HMDS) [5]. The optoelectronic, mechanical and structural properties of the deposited Si-C-N films were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, optical transmittance spectroscopy, nanoindentation, as well the results of the measurements of photoluminescence (PL) and PL excitation (PLE) spectra. Below, for simplicity, the expression “increase (decrease) of substrate bias” will mean the change of its absolute value.

2. Experimental details

Si-C-N films were produced using the HMDS vapor and nitrogen by means of PECVD. The negative bias was applied to a substrate by an additional radio-frequency (5.27 MHz) generator. The HMDS vapor was delivered into the reactor chamber by hydrogen from the thermostat-controlled bubbler heated up to 40 °C. All deposition parameters are listed in Table 1.

The films were deposited on both the (100) oriented silicon wafers and transparent quartz substrates. The surface oxide on the silicon wafer surfaces were cleaned by dipping into the 10% hydrofluoric acid for 3 min and the final etching of the substrates was carried out by treating with the hydrogen plasma into the reaction chamber. The film thickness was estimated by an optical interference profilometer. The film surface was analysed by AFM microscope “NanoScope IIIa Dimension 3000TM”. The structure of the film was investigated by X-ray diffraction using a diffractometer “DRON-3M” in Cu Kα- radiation. FTIR measurements were carried out by using a spectrometer “FSM 1202” LLC “Infraspek” in the range of the wave numbers of 400–4000 cm^{-1}. XPS core-level spectra were measured by a UHV-Analysis-System, SPECS, under the Mg Kα radiation (E = 1253.6 eV). XPS spectra were measured after argon etching during 3 min. The Raman spectra were measured in the range of 100–3200 cm^{-1} with the help of the Via Renishaw Raman microscope equipped with the He-Ne laser excitation at 632.8 nm. Measurements of the UV–VIS transmission spectra were carried out by using a two-beam optical spectrometer SPECORD-M40 in the range of wavelengths of 200–900 nm. Photoluminescence spectra (PL) were investigated at room temperature by using an experimental installation for the recording of PL spectra. The main unit of this installation is the automated monochromator SPM-2 (Carl Zeiss, Jena). The installation enables one to measure the intensity of PL spectra at a certain wavelength in the visible range. Photoluminescence is excited by a low powerful LED laser (~ 25 μW/cm^2, λ = 405 nm). Our analysis shows that this power is enough to excite PL from bulk states [15]. This laser does not heat films during optical measurements, which, in contrast to Hg lamps, does not lead to lowering the accuracy of measurements. The photoluminescence excitation (PLE) spectra of the deposited Si-C-N films were recorded using the HITACHI MPF-4 spectrofluorometer equipped with a xenon lamp. The conversion of its analogue output signals into a digital form was carried out using a digital converter. The excitation wavelengths were in the range of 320–525 nm (3.88–2.36 eV, respectively). Nanoindentaion of the films was carried out by the NanoIndenter G200 device (Agilent Technologies) using continuous stiffness measurement (CSM) mode. The indentations were produced with a Berkovich triangular pyramid diamond tip. Nanohardness (H) and elastic modulus (E) were determined according to the Oliver and Pharr method [16].

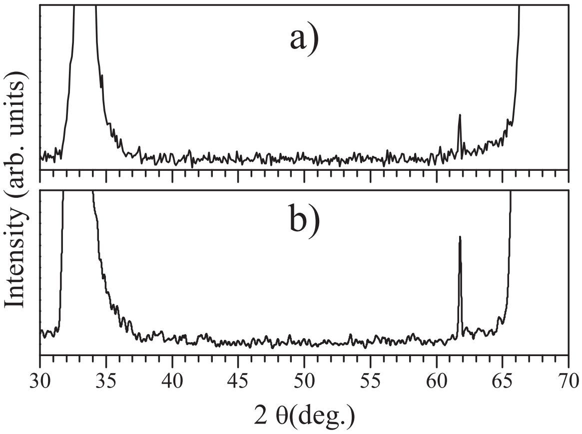

Fig. 1. X-ray patterns of Si-C-N films deposited at U_d = − 5 V (a) and U_d = − 250 V (b). The peaks at 2Θ ~ 33°, 62° and 69° correspond to the silicon substrate.

3. Results and discussion

3.1. Film structure

We carried out XRD measurements of the deposited films to analyze their microstructure. X-ray patterns of the Si-C-N films deposited on silicon substrates are shown in Fig. 1. There are no any features that could be assigned to any crystallites in the films. It follows that the deposited films are X-ray amorphous.

3.2. Film surface morphology and thickness

Fig. 2(a) and (b) show the AFM images of the surface of the films deposited at U_d = − 5 V and U_d = − 250 V, respectively. The scanning area was 1 μm × 1 μm. From Fig. 2 one can observe that the films are very smooth and the film surfaces exhibit an excellent morphological homogeneity with low roughness. The values of the RMS roughness (R_q) and average roughness (R_a) of the films deposited at various substrate biases were R_q = 0.33 nm and R_a = 0.27 nm (U_d = − 5 V), R_q = 0.27 nm and R_a = 0.22 nm (U_d = − 250 V). We see that an increase in negative substrate bias leads to the insignificant smoothing of the film surface: substrate bias accelerates ions and charged particles, thereby promoting the etching of weak bonds and possibly the densification of the films. As a result, the roughness of the film surface slightly decreases and the film thickness increases from 200 nm to 700 nm with increasing U_d from − 5 V to − 250 V, respectively.

3.3. Film composition

The chemical composition of the films was estimated using the XPS data. The Si, C, N, O contents in these films are approximately 36, 36, 14 and 14 at% and 37, 41, 13 and 9 at% for the films deposited at U_d = − 5 V and − 250 V, respectively. An increase of the concentration of carbon in the film is accompanied by decreasing the oxygen content, whereas the concentration of silicon and nitrogen remains unchanged. The oxygen in the films can be due to the residual oxygen absorbed on the reactor chamber walls. Since the reduction of the film roughness is accompanied with lowering the oxygen content some oxygen may come from the ambient air after deposition [17]. We could not estimate the hydrogen content in the films because the XPS analysis did not give such a possibility. However, in the FTIR spectra the hydrogen bonds are clearly seen. Also, it was found that hydrogen bands decrease with increasing substrate bias which indicates that the hydrogen content

Download English Version:

https://daneshyari.com/en/article/7117310

Download Persian Version:

https://daneshyari.com/article/7117310

Daneshyari.com