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SCIENCE DIRECT
Diamond & Related Materials 14 (2005) 1839 – 1842
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Nitrogen incorporated diamond-like carbon films by microwave surface wave plasma CVD

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Available online 15 August 2005

Abstract

Nitrogen incorporated diamond like carbon films have been deposited by microwave surface wave plasma chemical vapor deposition (MW-SWP-CVD), using methane (CH_4) as the source of carbon and with different nitrogen flow rates (N_2/CH_4 flow ratios between 0 and 3). The influence of the nitrogen incorporation on the optical, structural properties and surface morphology of the carbon films were investigated using different spectroscopic techniques. The nitrogen has been incorporated into DLC:N films which was confirmed by the X-ray photoelectron spectroscopy (XPS) measurement. Moreover, the nitrogen incorporation was accompanied by a variation in the optical gap, which was attributed to the removal or creation of band tail states.

Keywords: Nitrogen incorporation; Optical gap; DLC:N films; MW-SWP-CVD

1. Introduction

Nitrogen incorporated diamond like carbon (DLC:N) films are of great technological importance as many of their properties can be tailored by varying the amount of nitrogen incorporation for divers industrial application [1,2]. Although DLC:N film have been prepared using a variety of methods [3,4], the properties of DLC:N films deposited by the microwave surface wave plasma chemical vapor deposition (SWP-CVD in short) technique have rarely been reported.

SWP-CVD is a novel mass-production technology for producing diamond and diamond-like carbon (DLC) films. Microwave discharges have an advantage over dc and rf due to their inherent superiority in terms of quality of discharge [5]. By this technique, a large-diameter (~30 cm), high electron density ($\sim 10^{11}$ cm^{-3}) and low electron temperature (~3 eV) can be formed without using a magnetic field for plasma processing, especially, this method has potential to deposit relatively large area thin films and useful to avoid plasma induced damages on substrate surface.

The aim of our research is to fabricate the DLC:N film using the novel SWP-CVD technique. To study the characteristics of the DLC:N films, we carried out measurements of X-ray photoelectron spectroscopy (XPS), ultraviolet–visible (UV–VIS) spectroscopy, Raman spectroscopy, and atomic force microscope (AFM). In this paper, the preliminary results are presented in details.

2. Experimental setup

In this study, we employed the SWP-CVD system for the deposition of DLC:N thin film at low temperature. CH_4 and N_2 are used as source gas, whereas Ar is used as carrier gas. A schematic diagram of the SWP-CVD apparatus is shown in Fig. 1. The SWP was produced in a 30 cm diameter cylindrical vacuum chamber by introducing a 2.45 GHz microwave through a quartz window via slot antennae. The details about the apparatus have been described elsewhere [5,6].

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doi:10.1016/j.diamond.2005.07.014

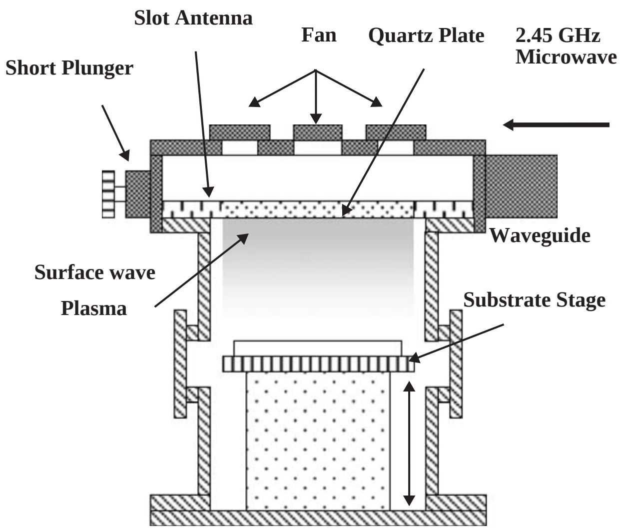

Fig. 1. Schematic diagram of the SWP-CVD apparatus.

Film deposition was carried out on n-type silicon (100) and quartz substrates. Prior to transferring it into the chamber, the substrates were thoroughly cleaned in ultrasonic organic solvents and finally etched in H_2O : HF (10 : 1) solution to remove the native oxide layer on the surface.

The vacuum chamber was evacuated to a base pressure of $\sim 2 \times 10^{-4}$ Pa, prior to the deposition of the DLC:N films. The launched microwave power was set at 500 W. The flow rates of CH_4 and Ar were kept at 10 and 280 sccm, respectively. Simultaneously nitrogen (flow rates from 0 to 30 sccm) was added into the chamber, and a constant working pressure is maintained at 60 Pa during the deposition.

3. Results and discussion

3.1. Film composition

Compositional chemical analysis of the DLC:N film was performed by XPS measurement (SSX-100) utilizing Al Kα ($h\nu$ = 1486.6 eV) radiation. Fig. 2 shows the XPS spectrum for one of the DLC:N films (N_2/CH_4 flow ratio: 10 : 10). In Fig. 2, the nitrogen peak is found, indicating that the nitrogen has been incorporated into the DLC:N film [7]. In addition, the oxygen peak is also observed in the spectrum due to surface chemisorbed oxygen species [8]. Fig. 3 shows the nitrogen (N) content (in atomic percentage) of the DLC:N films as a function of N_2 flow rate into the chamber. There is an initial rapid incorporation of N into the DLC:N films when the N_2 flow is increased from 0 to 10 sccm, and reached to the maximum value of 7.2 at.%. And thereafter, with further increasing the N_2 flow rate, the N content decreases gradually, suggesting that N cannot be incorporated into the DLC:N films efficiently under the excess N_2 condition. The variation of N content in the films shows a correlation with the variation of the optical gap (will be discussed below); higher N content corresponds to lower optical gap.

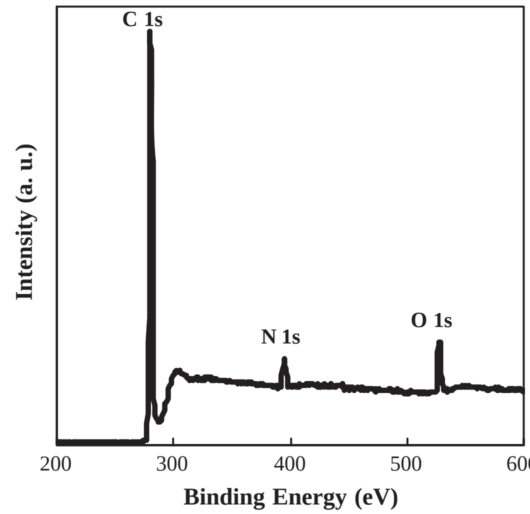

Fig. 2. XPS spectra for the DLC:N sample (N_2/CH_4 flow ratio: 10 : 10).

3.2. Optical properties

UV–Visible measurements were carried out on films deposited on the quartz substrate. The optical gap (E_g) was extracted from the absorption coefficient (α) using the Tauc relationship [9].

$$(\alpha E)^{1/2} = B(E - E_g), \tag{1}$$

where E is the photon energy, B is the Tauc constant.

Fig. 4 shows the variation of optical gap for the films obtained at different nitrogen flow rates. It is found that the optical gap rapidly decreases from 2.9 to 2.5 eV, when the nitrogen flow rates increase from 0 to 10 sccm. Similar behavior has been reported by Hayashi et al., the trend of decreasing optical gaps with increasing nitrogen flow rates was interpreted as an increase in the disorder, as determined

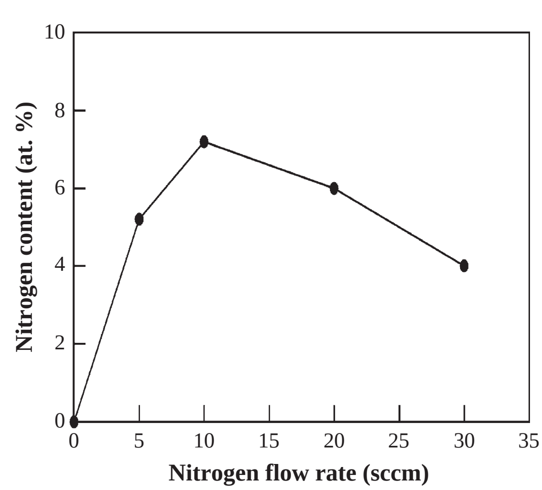

Fig. 3. Nitrogen atomic percentage in the DLC:N films as a function of N_2 flow rate into the chamber.