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Electrical and optical properties of pulsed laser ablated diamond-like carbon films

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Amorphous diamond-like carbon (DLC) thin films were deposited on fused silica and single crystal silicon substrates by pulsed laser ablation using a focused beam from an XeCl excimer laser and a pyrolytic graphite target. The structure and properties of the films were studied by scanning electron microscopy (SEM), X-ray diffraction, micro-Raman and Fourier transform infrared (FTIR) spectroscopy, electrical conductivity and optical measurements.

By varying the peak power density of the laser beam between 10^9 and 10^{10} W/c m^2 and the deposition temperature between room temperature and 200 °C it was found to be possible to tailor the properties of the deposited films between the extremes of diamond-like and graphite-like carbon. The optical band gap of the films varied from zero (graphite-like films) to a maximum value of 1.35 eV (DLC). By introducing hydrogen into the chamber during deposition, the DLC band gap could be increased to 2.2 eV. The real part (n) of the visible wavelength refractive index ranged from 2.4 to 2.5 for good quality DLC films. The imaginary part (k) of the refractive index was highest at short wavelengths, and reduced when approaching the near-infrared region. It was possible to vary the electrical conductivity of the unhydrogenated films by eight orders of magnitude between DLC and graphite-like material. The conductivity of the DLC films exhibited an $\exp(-T^{-1/4})$ dependence on temperature which is characteristic for amorphous semiconductors.

1. INTRODUCTION

Diamond-like carbon (DLC) is amorphous carbon with some properties similar to those of diamond. DLC-films are hard, chemical resistant and wear resistant, electrically insulating and partly transparent (optical gap typically 0.5-2 eV) [1]. DLC contains both trigonally (sp^2-bonded) and tetrahedrally (sp^3-bonded) coordinated carbon in the microstructure [2].

DLC-films are produced using chemical vapor deposition (CVD) techniques at elevated temperatures or other deposition methods such as sputtering, ion beam deposition and pulsed laser deposition (PLD) [3-6]. In the PLD process the properties of the films can be controlled by the laser fluence, the substrate temperature and the ablation atmosphere. In this study, effects of these parameters on the electrical and optical properties of DLC films have been investigated.

2. DEPOSITION PROCESS

The PLD process was carried out using an XeCl excimer laser (λ = 308 nm) and a pyrolytic graphite target. The peak power densitiy was varied between 10^9 and 10^{10} W/c m^2. The pulse repetition rate was 25 Hz. and the target-to-substrate distance 30 mm. The power density was calculated from the measured pulse energy of the laser and the spot size on the target; the laser fluence was varied by defocusing the beam. The spot size was measured by optical microscopy and

scanning electron microscopy (SEM) from the trace created by a laser pulse. The films were deposited on fused silica and silicon (100) or (111) substrates at temperatures between room temperature and 300 °C. The base pressure of the vacuum chamber was about 10^{-5} mbar and an atmosphere of 0.25 - 1 mbar H_2 was used when the effect of hydrogen was studied. The thickness of the films was between 100 nm and 200 nm depending on the power density and the number of pulses. Typical deposition times were 10 - 20 min.

3. MEASUREMENTS AND RESULTS

The structural properties of the films were characterized by scanning electron microscopy (SEM), X-ray diffraction, Fourier transformation infrared (FTIR) and micro-Raman spectroscopy. The optical properties of the films were studied by transmittance and reflectance measurements in the visible region from 400 nm to 800 nm. Electrical conductivity was measured from 77 K to room temperature.

The films ablated at room temperature using the excimer laser were hard and electrically insulating. The surface of the films was smooth and flat without major features. The effect of the substrate was insignificant. X-ray diffraction did not show any crystalline structure in either case. FTIR spectroscopy was used to detect chemically bonded hydrogen in the films, and a broad absorption band was detected between 2700 cm^{-1} and 3200 cm^{-1} in films ablated in 0.25-1 mbar H_2. No hydrogen absorption was detected in the films prepared under vacuum conditions (detection limit about 3 at.-%).

Raman spectra were measured on a Jobin-Yvon T 64000 triple Raman spectrometer equipped with a CCD-detector and both micro and macrosampling accessories. Excitation was by means of the 514 nm and 488 nm lines of an argon ion laser in the backscattering configuration. The spectra for the substrate temperatures up to 100 °C consisted of a broad band in the intermediate range between the bands of disordered graphite. The evolution towards a clear observation of these graphite-like bands with increasing substrate temperature was apparent [6].

3.1. Optical measurements

The optical band gap and the complex index of refraction were derived from the transmittance and reflectance measured in the visible region from 400 nm to 800 nm by a single-grating monochromator. The optical band gap was extrapolated from a plot of $(aE)^{1/2}$ as a function of photon energy E (Figure 1). a is the absorption coefficient of the film.

The optical band gap for films prepared at room temperature and in vacuum was 0.45 eV - 1.35 eV depending on the power density. The optical band gap reduced to zero at deposition temperatures between 100 and 200°C. The largest band gap under vacuum

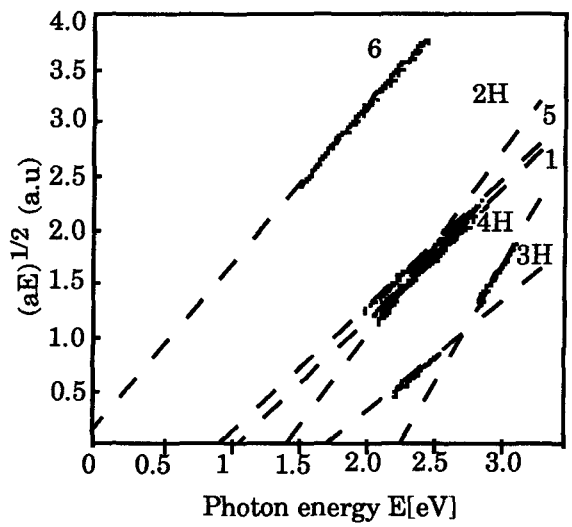


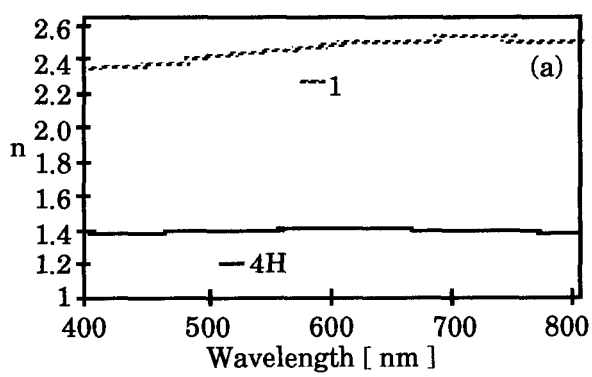
Figure 1. $(aE)^{1/2}$ as a function of photon energy E (Tauc plot) for some DLC-films deposited on fused silica (Table 1). Optical band gaps are extrapolated from the curves.

Table 1
Ablation parameters for DLC-films

Sample	Power density 10^9 W / cm^2	Ablation temperature °C	H_2 (mbar)
1	6	20	0
2H	10	20	0.25
3H	9	20	0.50
4H	9	20	1
5	6	100	0
6	6	200	0

conditions was achieved at the highest power density of $8 \cdot 10^9$ W/cm^2 , but a hydrogen atmosphere of 1 mbar increased the gap to 2.2 eV

Figure 2a shows the real part (n) and Figure 2b the imaginary part (k) of the complex index of refraction as a function of wavelength for a hydrogen-free and a hydrogenated film. The curve have been determined from transmittance and reflectance measurements. n varied only slightly, between 2.4 and 2.5, in the visible region. k was highest at low wavelengths, and reduces when approaching the near-infrared region. The absorption coefficients at 400 nm and 800 nm were $1.04 \cdot 10^5$ cm^{-1} and $8 \cdot 10^3$ cm^{-1}, respectively.



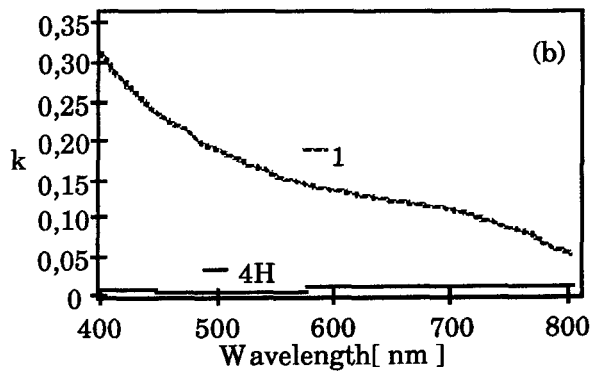


Figure 2. Variation of (a) the real part (n) and (b) the imaginary part (k) of the complex index of refraction as a function of wavelength in the visible region for a hydrogen-free and a hydrogenated film deposited at room temperature. The thickness of the films was 105 nm.

3.2. Electrical conductivity

Electrical conductivity was measured by the four point probe method using evaporated gold contacts. Gold contacts were evaporated on the surface of the films. Figure 3 shows the electrical conductivity at room temperature as a function of substrate temperature and the power density of the laser for films ablated on fused silica. A large increase in

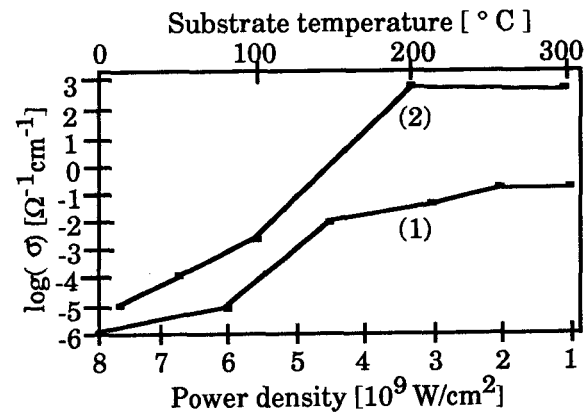


Figure 3. Electrical conductivity at room temperature as a function of the power density (curve 1) and substrate temperature (curve 2) for films deposited on fused silica.

deposited at T_s = 200 °C and a less drastic increase was observed when the laser fluence was reduced. The electrical conductivity as a function of temperature (Figure 4) showed an $\exp(-T^{-1/4})$ dependence characteristic for amorphous semiconductors [7]. Hydrogenated films showed electrical conductivity below the measuring limit, i.e. less than $10^{-6}\,\Omega^{-1}\,cm^{-1}$.

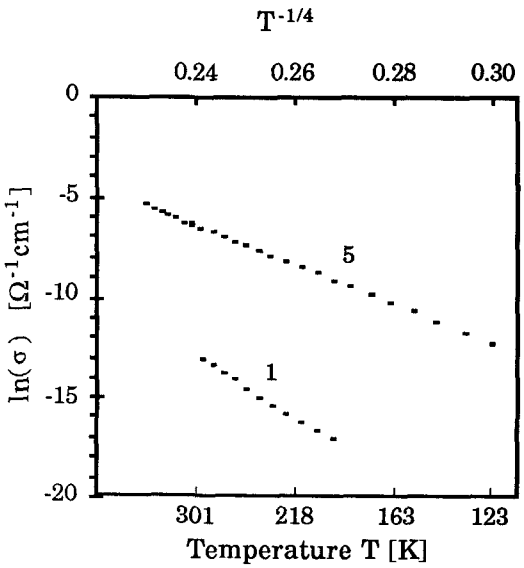


Figure 4. Electrical conductivity as a function of temperature for a DLC film deposited at 20°C (curve 1, Table 1.) and at 100°C (curve 5, Table 1.).

4. CONCLUSION

In the PLD method, it was found to be possible to tailor the optical and electrical properties of the deposited films between the extremes of diamond-like and graphite-like carbon by varying the peak power density of the laser beam and the deposition temperature. The optical band gap of the films varied from zero (graphite-like films) to a maximum value of 1.35 eV (DLC). By ablation in a low-pressure hydrogen atmosphere at room temperature, it was possible to widen the optical gap and to achieve high resistivity. The electrical conductivity of the unhydrogenated films coould be varied by eight orders of magnitude between DLC and graphite-like material. Properties of films deposited at substrate temperatures lower than 150 °C were diamond-like. Deposition above 150 °C yielded more graphite-like films with clearly different optical and electrical properties.

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