

Photovoltaic Characteristics of Nitrogen-doped Camphoric Carbon Films Deposited by XeCl Excimer Laser

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Nitrogen-doped amorphous carbon films (a-C:N) were deposited on quartz and single-crystal silicon substrates by pulsed laser deposition technique (PLD) at room temperature with different nitrogen partial pressures in the range of 0.1 to 800 mTorr. The soot for the target was obtained from burning camphor, a natural source. The effect of nitrogen incorporation in camphoric carbon (CC) films on the optical, electrical, and photovoltaic properties was investigated. The optical gap for the undoped film is about 0.95 eV. The optical gap remains unchanged for low N content and decreases to about 0.7 eV. With higher N content the optical gap increases. The room temperature conductivity (σ_{RT}) is found to increase with N incorporation, which may be due to lattice vibrations leading to the scattering of charge carriers by the N atoms and the more amorphous nature of the carbon films. A study of activation energy revealed that the Fermi level of the n-C:N film moves from the valence band to near the conduction band edge through the midgap. The results indicate successful doping for the film deposited at low nitrogen content. The short circuit current density and open circuit voltage (J-V) characteristics of a-C:N/silicon photovoltaic cell under illumination were observed to improve upon N-incorporation in the carbon layer.

Key words: pulsed laser deposition, camphoric carbon, photovoltaic cell, nitrogen doping, a-C:N

1. INTRODUCTION

The ability to dope using nitrogen gas is a new direction for the application of carbonaceous material in electronic devices. At present, there are numerous reports of attempts to use nitrogen gas and ion as a doping source. However, reports from various research groups are contradictory [1-5]. Cohen *et al.* [2] reported on the properties of the crystalline phase of carbon nitride (CN_x). They proposed β -C₃N₄, a form of CN alloy analogous to β -Si₃N₄, should have a hardness closer to a diamond [3]. Considerable interest in carbon nitride has already been shown in the field of protective coating for magnetic and optical materials [4,5]. Recently Nitta *et al.* [5] reported on photoconductivity from amorphous-CN_x films, which is encouraging for future application in optoelectronic devices. We analyzed carbon film obtained from camphoric carbon (CC) soot target [6-12], which reveals better properties compared to carbon film obtained from the conventional graphite target [8].

In this study, carbon films were deposited on quartz and single-crystal silicon substrates by pulsed laser deposition technique at room temperature using CC soot target. The effect of N incorporation in carbon film is investigated using X-ray photoelectron spectroscopy (XPS), optical absorption in the UV|VIS|IR region, and electrical resistivity measurements. The doping

modification of temperature dependence that occurs in N doped n-type amorphous carbon (a-C:N) films when they are deposited at different ambient N partial pressures (NP) and photovoltaic properties of a-C:N films on p-type Si (a-C:N/p-Si) were also investigated and discussed. The objective of this study is to dope slightly p-type a-C to electrically semiconducting a-C:N for their possible application as semiconductors and optoelectronic devices.

2. EXPERIMENT

Camphor (C₁₀H₁₆O), a source of available in nature, was used as a starting precursor for carbonaceous thin film. Camphor was burnt in a 1-metre-long and 11-cm-diameter quartz tube. Details of the camphor molecule, burning system, and the target preparation method and deposition chamber are described elsewhere [8]. In brief, the soot deposited along the walls of the tube was collected, dried in the oven for an hour, and pressed into pellets. These pellets were used as targets for carbonaceous thin films. Films were deposited on silicon and quartz substrates by XeCl excimer laser. The laser pulse energy was 150mJ on the window. To incorporate nitrogen in the film, we introduced N₂ gas in the PLD chamber via leak valve. The pressure of the N₂ was varied between 0.1 to 800 mTorr. Prior to of N₂ insertation, the chamber was evacuated until

about 10^{-6} Torr. The films were deposited on Si and quartz substrates.

The Tektronix VX1410 Intelli Frame from Sony was used for current-voltage (I-V) measurement of films deposited on quartz substrates, and the Cryomini Compressor from Iwatani Plantech was used to maintain the temperature of the chamber (2-probe method). Electron-beam-evaporated gold electrodes (thickness = 100 nm) were used in a gap cell configuration and silver paste was used as a point contact on gold electrodes for conductivity measurements.

Undoped carbon film is reported to show p-type characteristics [13-15]. Therefore, we deposited carbon films obtained from CC targets on n-Si substrates (Sample A/n-Si). N incorporated carbon films were deposited on p-Si substrates (a-C:N/p-Si). The resistivity of the substrates about 5-10 $\Omega\text{-cm}$. Gold (Au) electrodes of about 15 nm were deposited on carbon film for the top contact and for the back contact, about 100 nm antimony-gold electrode on n-Si, and Au electrode on p-Si was deposited by conventional electron beam evaporation method. The contacts are shown to be ohmic. Junction current-voltage (I-V) characteristics of dark and under illumination were measured by Hewlett-Packard HP4145B. A solar simulator was used to study photovoltaic properties and a Xenon lamp was used as the light source to illuminate the junction at 1.5 sun AM1 condition.

3. RESULTS AND DISCUSSION

XPS was measured by a SSX-100 XPS system of Surface Science Instruments utilizing using an $\text{AlK}\alpha$ ($h\nu = 1486.6$ eV) radiation as an X-ray source, under high vacuum conditions of about 10^{-10} Torr. The chemical bonding state in the films was analyzed after the 0.5 keV Ar^+ ion etching of film surface for 3 min. The atomic % of N in the film was determined from XPS spectral analyses. The N content was about 0.6% for the film deposited at 0.3 mTorr and increased to about 1.5% for the film deposited at 10 mTorr. With a further increase of NP, the N content increased to about 3.41 at% at 200 mTorr, and saturated thereupon to reach about 3.49 at% at 800 mTorr. From the measurement results, the electrical conductivity (σ) is plotted against inverse temperature (T) on a logarithmic scale. As shown in Fig. 1, the σ of the films was measured as a function of T between 50 and 400 K. The T dependence of σ shows two regions, in the 50 to 300 K (variable range hopping) and above 300 K range (simple activation region), which indicate domination of the hopping conductivity of the films.

The activation energy (E_a) was determined from the slope of $\ln \sigma$ versus $1/T$ for the above room temperature (RT) region [16]. The variation of the E_a and RT conductivity (σ_{RT}) as a function of NP is shown in Fig. 2 (left axis) and Fig. 2 (right axis), respectively. At 0.1 mTorr, the

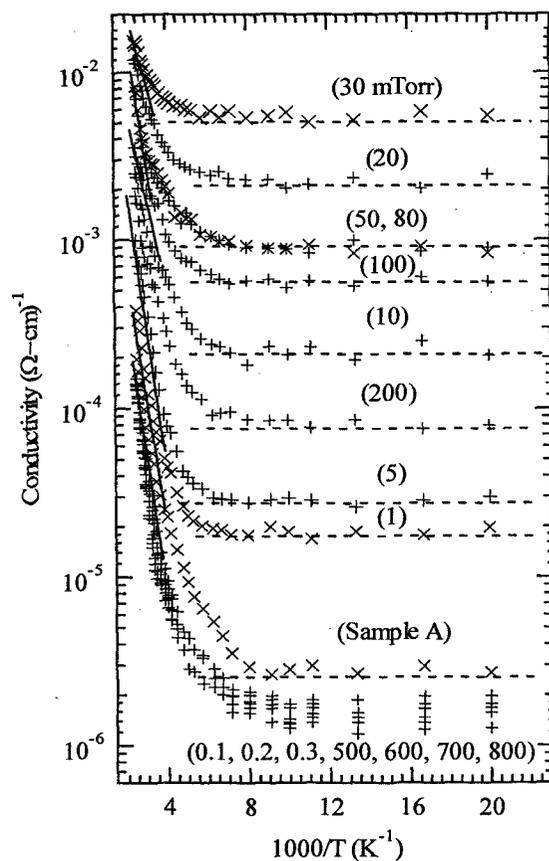


Fig. 1. Temperature-dependent conductivity of Sample A and a-C:N films deposited in various ambient nitrogen partial pressures.

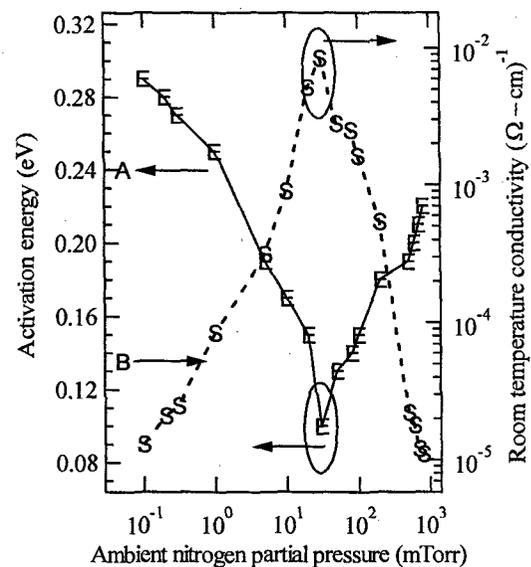


Fig. 2. Activation energy (E_a) and room temperature conductivity (σ_{RT}) of Sample A, and a-C:N films deposited in various ambient nitrogen partial pressures. (Left axis: E_a of Sample A (A) and n-C:N films (E). Right axis: σ_{RT} of Sample A (B) and n-C:N films measured by 2-probe method (S).)

E_a is increased to 0.29 eV (Sample A: 0.24 eV), whereas σ_{RT} is decreased to $1.3 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$ (Sample A: $5.2 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$). With a further increase of NP up to 30 mTorr, the E_a decreases, increases gradually and sharply thereafter. Above 30 mTorr the E_a and σ_{RT} increase with NP.

For comparison, σ_{RT} also was measured by using 4-point probe resistance measurement (hereafter, also referred to as 4-probe method). The σ_{RT} measured by 4-point probe method (Fig. 3 right axis) also showed almost the same conductivity characteristics as σ_{RT} measured by 2-probe method (Fig. 2 right axis), with maximum conductivity for the n-C:N films deposited at 30 mTorr, which decrease in lower and higher NP.

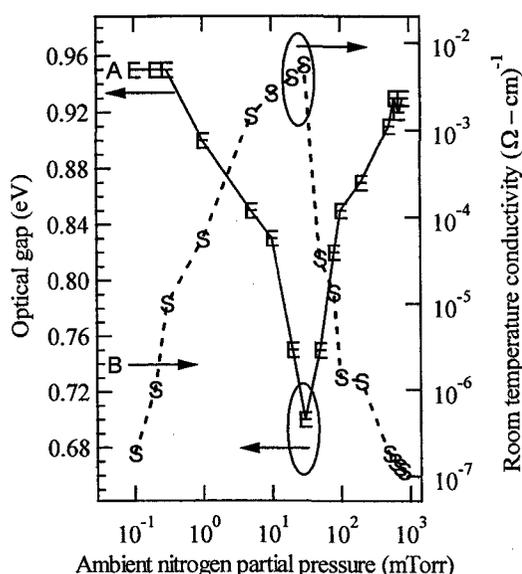


Fig. 3. Optical gap (E_g) of Sample A and n-C:N films deposited in various ambient nitrogen partial pressures. (Left axis: E_g of Sample A (A) and n-C:N films (E). Right axis: σ_{RT} of Sample A (B) and n-C:N films measured by 4-point probe method (S).)

Optical gap (Fig. 3 left axis) for the undoped film is about 0.95 eV. The optical gap remains unchanged for low nitrogen content and decreases to about 0.7 eV for film deposited at 30 mTorr NP. With higher nitrogen content the optical gap increases. The σ_{RT} of the carbon film is observed to decrease with N content initially and increase with higher N content until the films deposited at 30 mTorr. However, the decrease of σ_{RT} is observed for films deposited above 30 mTorr NP. We can relate this variation of resistivity to the doping of nitrogen in our films for low content of nitrogen, as the optical gap remains almost unchanged until for the films deposited at 10 mTorr. Since both the optical gap and resistivity decrease with higher N content, this phenomenon can be related to graphitization.

However, the increase of optical gap and decrease of σ_{RT} with more N content (above 30 mTorr) can be related to a structural change in

carbon film that might be due to the formation of CN_x and is expected to be a promising material for electronic, specifically, optical applications.

The J-V characteristic of the n-C/p-Si photovoltaic cell under illumination at 1.5 sun AM1 condition was measured (Fig. 4). The photovoltaic parameters are calculated from the J-V curve. The short circuit current density (J_{SC}) plotted in the left axis and open circuit voltage (V_{OC}) plotted in the right axis as a function of NP of a-C:N/p-Si photovoltaic cell is shown in Fig. 5.

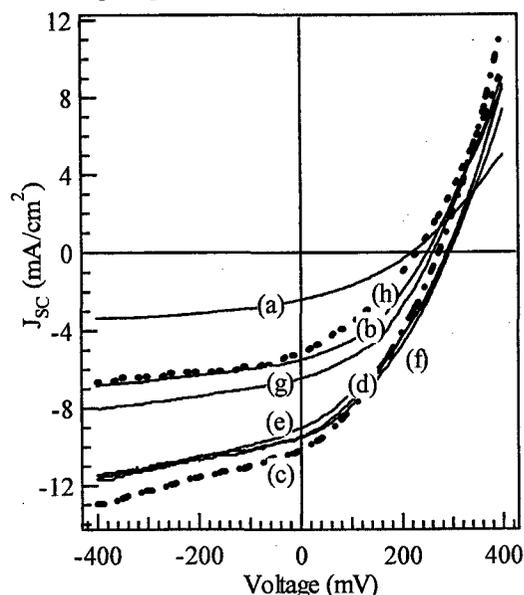


Fig. 4. Current-voltage characteristics of n-C:N/p-Si cell under illumination deposited in various ambient nitrogen partial pressures of (a) 0.3, (b) 1, (c) 10, 20, 30, 50, 80, and 100 mTorr.

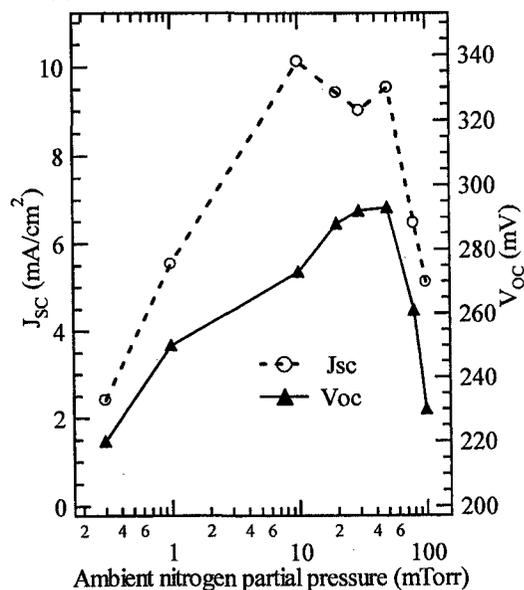


Fig. 5. Short circuit current density plotted in the left axis and open circuit plotted in the right axis as a function of nitrogen partial pressures of a-C:N/p-Si photovoltaic cell.

The J_{SC} and V_{OC} vary from 2.4 to 10.2 mA/cm^2

and 0.22 to 0.29 V, respectively. For both parameters a gradual increase is observed initially (for low N content) and a decrease thereafter (for high N content). The cell with a carbon layer deposited at 30 mTorr yields the electrical conversion efficiency, η is observed to be approximately 1.47% ($\eta = 1.47\%$). With further increase of NPP, the conversion efficiency degrades. The fill factor (FF) increases up to 56% for the cell with a carbon layer deposited at 30 mTorr and decreases thereupon. The variation of η and FF as a function of NP of a-C:N/p-Si photovoltaic cell is shown in Fig. 6, where efficiency is plotted in the left axis and fill factor plotted in the right axis. Photovoltaic properties (η , FF, etc.) results are better for nitrogen-incorporated CC compared to the phosphorus-doped camphoric carbon reported earlier [17]. The change of J-V characteristics with NPP, which controls the photovoltaic properties, is related to the change in optoelectronic properties, such as optical gap, conductivity, and defect states of the carbon layer due to doping/incorporation of nitrogen in carbon. The photovoltaic characteristics with nitrogen content are improved and agree well with the film properties.

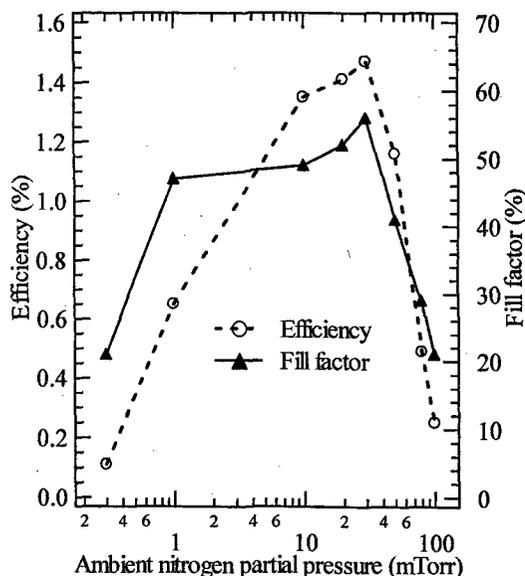


Fig. 6. Efficiency plotted in the left axis and fill factor plotted in the right-axis as a function of nitrogen partial pressures of a-C:N/p-Si photovoltaic cell.

4. CONCLUSIONS

The effect of N incorporation in CC thin film by PLD system was investigated. As N is incorporated, the optical gap remains unchanged while resistivity decreases indicate doping of N in CC films. With an increase of N content in the CC film, the reduction in resistivity and optical gap is due to the graphitization of CC film. With further N addition in CC films, this results in an increase of the optical gap and resistivity and is

attributed to structural modifications through formation of some form of C-N alloy (CN_x). The results indicate successful doping for the film deposited at low N content. The photovoltaic characteristics of the a-C:N/p-Si photovoltaic cell with N content are improved and agree well with the film properties.

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