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Comparison of CPM, PDS and Optical Transmittance of Amorphous Carbon Nitride Films Made by a Nitrogen Radical Sputter Method

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ABSTRACT

Amorphous carbon nitride films a-CNx, deposited in our laboratory by a radical sputter method, show high photosensitivity $P_s$, where $P_s$ is the ratio of photoconductivity $\sigma_p$ and dark-electrical conductivity $\sigma_d$. A-CNx made a layer-by-layer method, LLa-CNx, has the highest photosensitivity in our various preparation conditions. The photoconductivity in a-CNx and LLa-CNx shows dependence on photon energy in the range 2 eV to 6.2 eV. The constant photocurrent method (CPM), photothermal deflection spectroscopy (PDS) and optical transmittance spectra are used to obtain the information in the optical energy gap and defect states. A-CNx and LLa-CNx are good photoconductors especially at energy higher than 3 eV. Therefore it is not difficult to obtain CPM spectra in the high photon energy region. CPM spectra are obtained by dc- and ac- measurements. The value of the absorption coefficient $\alpha$ spectra obtained by dc-CPM is larger than that of ac-CPM, which increases with increasing frequency of the measurement. In this paper, CPM data is used to discuss a model of density of states (DOS) of a-CNx by comparison with PDS and optical transmittance spectra.

INTRODUCTION

CPM is an effective method to study the near band gap energy region for photoconductive materials such as hydrogenated amorphous silicon a-Si:H and fullerene C$_{60}$ [1-3]. Amorphous carbon nitride films a-CNx shows good photoconductive properties and
very high dark resistivity [4-5]. A-CN$_x$ is interesting for applications to low dielectric constant materials and light emitting devices [5-7]. CPM is one of the method to study electronic properties near the optical band energy gap $E_0$. To the best of our knowledge, CPM has never investigated in carbon related materials except fullerene. CPM results are discussed in this paper with a model of density of states of a-CN$_x$, PDS and UV-VIS optical transmission data.

**EXPERIMENTAL**

We have prepared a-CN$_x$ using a graphite target of purity 99.999% by a nitrogen radical sputtering method. The layer-by-layer method, which is a cyclic process of a-CN$_x$ deposition by a nitrogen radical sputtering and surface treatment of thin a-CN$_x$ by atomic hydrogens, is used to get higher photoconductive LLa-CN$_x$ films [4-5]. In this process, sputter gas N$_2$ of purity 99.999% is used to create nitrogen radicals and molecular hydrogen H$_2$ of 99.99999% is used to produce atomic hydrogen for etching the surface. We have controlled the layer-by-layer system by a microcomputer to keep the process of sputtering and etching time at constant. Conditions for sputtering are rf 13.56 MHz with power of 85 W, N$_2$ sputtering gas of 0.12 Torr and the substrate temperature at 300 Celsius. For the etching of a-CN$_x$, atomic hydrogen is derived by the glow discharge of H$_2$ of 0.50 Torr at the same rf conditions to prepare nitrogen radicals. Table.1 shows gas-injection and -evacuation times and several physical properties of LLa-CN$_x$. The difference of preparation conditions between LLa-CN$_x$ #103 and #116 are the number of the layer-by-layer process. Samples with same properties and a different thickness are prepared to fit for each experimental conditions. LLa-CN$_x$ #103 is prepared for CPM and optical transmittance, and LLa-CN$_x$ #116 is for PDS. The reason to use the thin film LLa-CN$_x$ #116 is to get the wide range of absorption coefficient $\alpha$ by PDS, from infrared to visible range.

Electrodes of 60 $\mu$m gap with 6 mm in width are prepared for CPM measurement by the vacuum evaporation of Al on LLa-CN$_x$. A pyroelectric detector, Hamamatsu Photonics P2613, is used to obtain light intensity F. Monochromatic light from a Xe lamp and a Nikon G250 monochromator with grating of 600 mm$^{-1}$ are used as a light source. Keithley 6512 picoammeter is used to monitor the photocurrent until it becomes constant. The value of the photo intensity F is measured using a pyroelectric detector. For ac-CPM, constant
Table 1 Conditions to prepare LLa-CNx and their several physical properties.

<table>
<thead>
<tr>
<th>Preparation conditions &amp; properties</th>
<th>LLa-CNx#103</th>
<th>LLa-CNx#116</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[CPM, Optical T.]</td>
<td>[PDS]</td>
</tr>
<tr>
<td>rf power</td>
<td>85 W</td>
<td></td>
</tr>
<tr>
<td>substrate temperature T_s</td>
<td>300 Celsius</td>
<td></td>
</tr>
<tr>
<td>(a) N₂ gas pressure &amp; sputter time</td>
<td>0.12 Torr, 300 s</td>
<td>30 s</td>
</tr>
<tr>
<td>(b) 1st evacuating time</td>
<td>30 s</td>
<td></td>
</tr>
<tr>
<td>(c) H₂ gas pressure &amp; etching time</td>
<td>0.50 Torr, 40 s</td>
<td>30 s</td>
</tr>
<tr>
<td>(d) 2nd evacuating time</td>
<td>30 s</td>
<td></td>
</tr>
<tr>
<td>Number for the layer-by-layer process</td>
<td>81</td>
<td>8</td>
</tr>
<tr>
<td>refractive index</td>
<td>1.83</td>
<td>—</td>
</tr>
<tr>
<td>film thickness [nm]</td>
<td>1100</td>
<td>~100</td>
</tr>
<tr>
<td>Tauc gap [eV]</td>
<td>1.67</td>
<td>~1.61</td>
</tr>
<tr>
<td>N/C ratio</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>defect density [cm⁻³]</td>
<td>3.44×10¹⁸</td>
<td>—</td>
</tr>
</tbody>
</table>

photocurrent I_p is transformed to voltage signal using Hamamatsu photonics C2719 amplifier, and we read the value on a lock-in-amplifier.

RESULTS AND DISCUSSION

The measurements of PDS and UV-VIS optical transmittance are the same as before [4, 6]. The absorption coefficient α is obtained as the inverse of the incident photon number, 1/F, under a constant photocurrent, I_p, by using conventional CPM assumptions [1-3, 9]. Fig.1 shows dc-CPM spectra of LLa-CNₓ films measured at constant photocurrent 50 fA, 80 fA, 1 pA and 15 pA, with the applied voltage of 32 V DC. Characteristics of LLa-CNₓ films are high resistivity and high photoconductivity. In the case of 1 pA constant, it is possible to measure dc-CPM only from 4.2 eV to 4.7 eV. To sustain a constant photocurrent for wide range photon energy is not easy. It is also difficult to use a small photon number for CPM, which is limited by the sensitivity of a pyroelectric detector. Therefore it is needed to correct these spectra using correction factor ‘a’ as shown fig.2. In the correction, the data at 1 pA is took as a standard of photocurrent, and we multiply for each photocurrent; for example a=15 for I_p=15 pA. The obtained spectrum seems to be good under the assumption that the incident photon number is proportion to constant photocurrent I_p.
Ac-CPM measurements at different chopping frequency are also obtained by the same method. Fig.3 compares these measurements with dc-CPM of fig.2. The value of absorption coefficient $\alpha$ obtained from dc-CPM spectra is larger than that of ac-CPM, which increase with chopping frequency of the CPM measurement. In a-Si:H and $C_{60}$ solids, ac-CPM, measured at lower chopping frequency, are close to dc-CPM. But in LLa-CN$_x$ case, ac-CPM, at higher chopping frequency are close to dc-CPM. These difference may be dependent on the properties of localized electronic states. The origin of this difference has to be further investigated.
Figure 5
The value of absorption coefficient $\alpha$ from dc-CPM spectra are compared with that for PDS and optical transmittance spectra.

Fig.4 shows the dependence of CPM data, $a/F$, for LLa-CN$_x$ #103 at a fixed photon energy on chopping frequency. The largest $a/F$ value is that of dc-CPM. The minima of $a/F$ for every photon energy are close to 0.5 Hz.

The value of absorption coefficient $\alpha$ from dc-CPM are compared with PDS and optical transmittance spectra in fig.5. In this figure, the increase of absorption coefficient $\alpha$ at 3.7 eV is similar to photoconductivity spectra of LLa-CN$_x$ films [4].

The increase of excitation of electrons at about 3.7 eV in fig.5 can be attributed as shown fig.6 to a transition between a nitrogen lone pair band to a $\sigma^*$ anti-bonding conduction band ($E_{\text{LP-}$\sigma^*$}) or that from a $\pi$ bonding valance band to a $\pi^*$ anti-bonding conduction band ($E_{\pi^*}$) [4,10,11]. CPM data describes well the good photoconductive properties at photon energy $hv > 3.7$ eV.

CONCLUSION

Dc- and ac-CPM are obtained for LLa-CN$_x$ for first time. The frequency dependence of ac-CPM measurements needs to be further investigated. CPM spectra are showing the good photoconductive properties of LLa-CN$_x$. CPM data were discussed with a model of density states together with PDS and UV-VIS optical transmittance spectra.
ACKNOWLEDGEMENTS

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REFERENCES