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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 $a\text{-CN}_x$, deposited in our laboratory by a radical sputter method, show high photosensitivity P_s , where P_s is the ratio of photoconductivity σ_p and dark-electrical conductivity σ_d . $A\text{-CN}_x$ made a layer-by-layer method, $LLa\text{-CN}_x$, has the highest photosensitivity in our various preparation conditions. The photoconductivity in $a\text{-CN}_x$ and $LLa\text{-CN}_x$ 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 band gap and defect states. $A\text{-CN}_x$ and $LLa\text{-CN}_x$ 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 α 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 $a\text{-CN}_x$ 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 $a\text{-Si:H}$ and fullerene C_{60} [1-3]. Amorphous carbon nitride films $a\text{-CN}_x$ 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 E₀. 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 N₂ of purity 99.999% is used to create nitrogen radicals and molecular hydrogen H₂ 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, N₂ 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 H₂ 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 α by PDS, from infrared to visible range.

Electrodes of 60 μm 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-CN_x and their several physical properties.

Preparation conditions & properties	LLa-CN _x #103 [CPM, Optical T.]	LLa-CN _x #116 [PDS]
rf power	85 W	
substrate temperature T _s	300 Celsius	
(a) N ₂ gas pressure & sputter time	0.12 Torr, 300 s	
(b) 1st evacuating time	30 s	
(c) H ₂ gas pressure & etching time	0.50 Torr, 40 s	
(d) 2nd evacuating time	30 s	
Number for the layer-by-layer process	81	8
refractive index	1.83	—
film thickness [nm]	1100	~ 100
Tauc gap [eV]	1.67	~ 1.61
N/C ratio	0.64	0.64
defect density [cm ⁻³]	3.44 × 10 ¹⁸	—

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-CN_x 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-CN_x films are high resistivity and high photoconductivity. In the case of 1pA 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 .

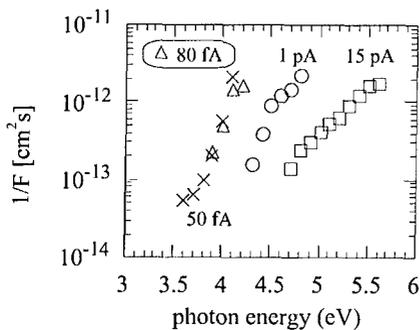


Figure.1 dc-CPM spectra
[LLa-CN_x#103]
(F [cm²s]: photon number)

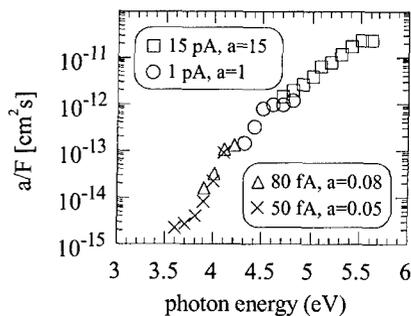


Figure.2 The correction of
dc-CPM spectra [LLa-CN_x#103]
(F [cm²s]: photon number)

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 α 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 C₆₀ 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.

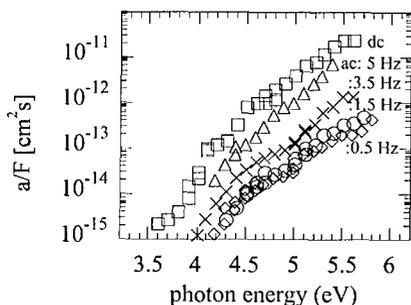


Figure.3
Comparison with ac- and
dc-CPM spectra.
(F [cm²s]: photon number)

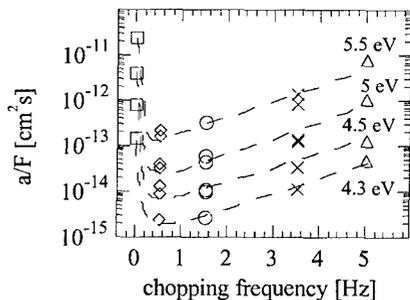


Figure.4
The dependence of CPM data, a/F, in LLa-CN_x
#103 at a fixed photon energy on chopping
frequency.(F [cm²s]: photon number)

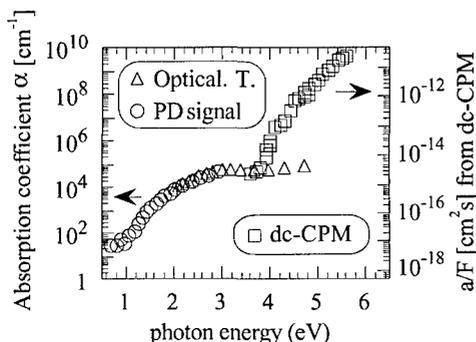


Figure.5

The value of absorption coefficient α 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 α from dc-CPM are compared with PDS and optical transmittance spectra in fig.5. In this figure, the increase of absorption coefficient α 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 σ^* anti-bonding conduction band ($E_{LP-\sigma^*}$) or that from a π bonding valance band to a π^* anti-bonding conduction band ($E_{\pi-\pi^*}$) [4,10,11]. CPM data describes well the good photoconductive properties at photon energy $h\nu > 3.7$ 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.

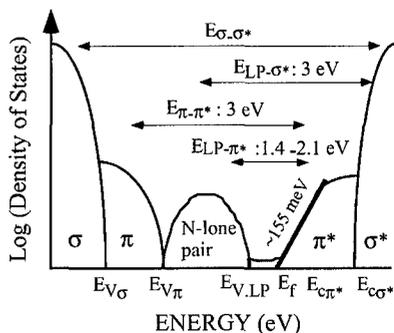


Figure.6

A model of the electronic state density of a-CN_x [4].

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