

# Vacuum ultraviolet, ultraviolet and visible absorption spectra study of hydrogenated amorphous carbon films prepared by RF plasma chemical vapour deposition

M. NAKAYAMA, M. SHIBAHARA

R&D Center, TDK Corporation, 2-15-7 Higashi-Ohwada, Ichikawa City, Chiba 272, Japan

K. MARUYAMA, K. KAMATA

Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

The properties of amorphous carbon films deposited by RF plasma chemical vapour deposition (CVD) vary with its deposition conditions and synthetic systems [1–8]. The present authors have already reported that the properties of the hydrogenated amorphous carbon films deposited can be improved significantly by the additional negative d.c. bias, independently of the RF power used to stimulate reactions, in the RF plasma CVD method [9, 10]. The effect of the d.c. bias in the RF plasma CVD system can easily be confirmed by a comparison between the properties of the amorphous carbon films with and without the additional d.c. bias: both the refractive index and micro-Vickers hardness of the hydrogenated amorphous carbon films have increased [9], and the threshold energy for photoelectron emission has decreased [10] with increasing additional negative d.c. bias.

As for the studies on the ultraviolet (UV) and visible absorption spectra of hydrogenated amorphous carbon films, there are several papers [1, 2, 5, 6, 11–17] on Tauc's optical gaps of these films. Most of them discuss the relationship between the structure and the optical band gap of the films synthesized by RF plasma CVD under various plasma conditions with changing self-bias. Dischler *et al.* [5, 6] concluded that the optical gap varied linearly with the content of bonded hydrogen in the films. On the other hand, it was revealed using extended X-ray absorption fine structure (EXAFS) [14], nuclear magnetic resonance (NMR) [15, 16] and infrared spectra [1, 2, 5, 6, 10] studies that a considerable number of double bonds existed in the films. Moreover, Robertson and O'Reilly [17] discussed the electronic structure of amorphous carbon films, and theoretically showed that double bonds in the films decreased the energy of the optical band gap.

The main purpose of this letter is to study the absorption spectra from visible to vacuum ultraviolet (VUV) of the films under various additional d.c. bias conditions. The energy of the absorption edge, which is the same energy reported as the optical band gap [1, 2, 5, 6, 11–17], is determined by the Tauc plot of the films. The present authors will discuss the d.c. bias effect, resulting to the wide-range absorption spectra including VUV, on the

energy of the absorption edge and the other properties of the films.

Hydrogenated amorphous carbon films were synthesized by the RF plasma CVD system with parallel electrodes, reported in the previous work [9, 10]. The thickness of the films deposited was 45–1200 nm. Synthetic quartz plates (Shin-etsu Quartz, Suprasil, 30 mm diameter  $\times$  0.5 mm thick) and Si(100) substrates were placed on the electrode which was electrically isolated from the chamber and RF source of the apparatus. Negative d.c. bias of up to  $-500$  V was additionally applied between the chamber and substrate in this experiment (the quartz plate and Si substrate were negative to the chamber). Experimental conditions are summarized in Table I.

The UV and visible spectra of the films were measured with a double beam spectrometer (Hitachi U-3400) from 240 nm to 700 nm. The VUV spectra of the films were measured with a VUV spectrometer (Jasco VUV200) from 160 nm to 240 nm. The film thickness, micro-Vickers hardness, amount of functional groups and photoelectron emission of the films were measured by the same methods as in the previous work [9, 10].

The Tauc plot for the hydrogenated amorphous carbon films synthesized with and without additional d.c. negative bias are shown in Fig. 1. The energies of the absorption edge of the films, which were determined by the extrapolation of the plots, decreased from 2.7 to 1.2 eV with increasing negative bias as summarized in Table II. These Tauc plots of the films synthesized under  $-250$  V and  $-500$  V bias conditions show slightly convex curves, which suggest that existence of broad absorption peaks, over 4.5 eV photon energy range. This will be discussed in a later part of this study.

The amounts of hydrogen incorporated in the

TABLE I Experimental conditions

Substrate temperature ( $^{\circ}\text{C}$ )	200
$\text{CH}_4$ gas flow rate ( $\text{cm}^3 \text{min}^{-1}$ )	7.5
$\text{H}_2$ gas flow rate ( $\text{cm}^3 \text{min}^{-1}$ )	5.0
Total pressure (Pa)	4.0
RF power (W)	500
Bias voltage (V)	0 $\sim$ $-500$
Substrates	Si (100), synthetic quartz

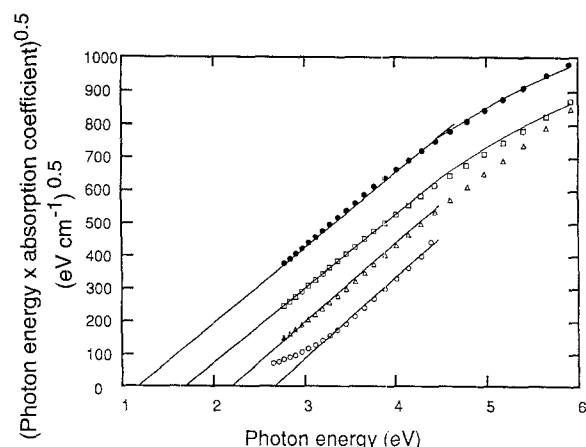


Figure 1 Tauc plots in UV and visible regions for the amorphous carbon films synthesized with and without additional d.c. negative bias on synthetic quartz plate heated at 200 °C. (○) 0 V; (△), -120 V; (□), -250 V; (●), -500 V.

TABLE II Absorption edge

Bias voltage (V)	Absorption edge (eV)
0	2.5
0	2.7
-120	2.2
-150	2.1
-250	1.9
-250	1.7
-500	1.2

films and double bonds (C=C) were calculated from the integral absorption coefficients of FT-IR peaks near  $2900\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$ , respectively [10]. Fig. 2 shows the relationships between the energy of the absorption edge and the integral absorption coefficients of IR peaks near  $2900\text{ cm}^{-1}$  (absorption of  $\text{CH}_2$ ,  $\text{CH}_3$  groups) and the peak around  $1620\text{ cm}^{-1}$  (absorption of C=C bonds). The energy of the absorption edge increases with increasing amount of  $\text{CH}_2$ ,  $\text{CH}_3$  groups, and with a decreasing number of C=C bonds in the films.

When amorphous carbon films are deposited under the conditions of additional d.c. negative bias,

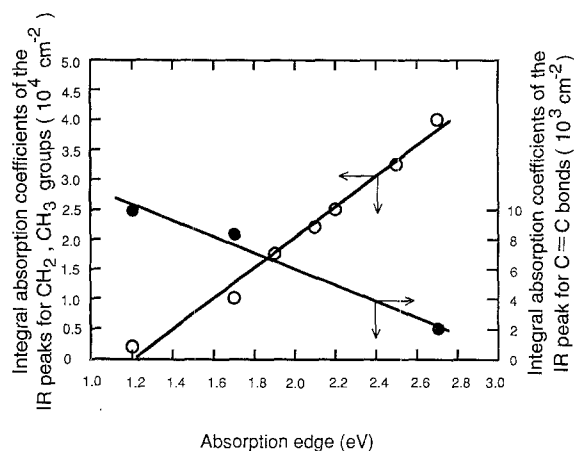


Figure 2 Relationships between the absorption edge and the integral absorption coefficients of the IR peaks near  $2900\text{ cm}^{-1}$  (absorption of  $\text{CH}_2$  and  $\text{CH}_3$  groups), or the peak around  $1620\text{ cm}^{-1}$  (absorption of C=C bonds).

various positive ions generated in the RF plasma are accelerated to the substrate by the additional d.c. electrical field. The collision of the positive ions with the films might result in the elimination of hydrogen and also increase the number of double bonds (C=C) in the films. Jansen *et al.* [15,16] also showed that the decrease of incorporated hydrogen in hydrogenated amorphous carbon films led to an increase of double bonds in the films.

The relationship between the energy of the absorption edge and UV threshold energy of the films [10] is shown in Fig. 3. This figure shows that the energy of the absorption edge increases with increasing UV threshold energy. It was revealed in the previous paper [10] that the additional d.c. negative bias decreases the UV threshold energy and the number of  $\text{CH}_2$ ,  $\text{CH}_3$  groups of the films, and that the increase of the UV threshold energy may be caused by the lowering of the top level of the valence band [18], similarly to the behaviour of hydrogen bonds in hydrogenated amorphous silicon.

In order to clarify the effect of double bonds (C=C) on the energy of the absorption edge, VUV absorption spectra of the films were measured. It is well known that organic compounds with double bonds (C=C) or conjugated double bonds (C=C-C=C) have absorption in the VUV, UV and visible regions [9-22]. For example, the absorption maxima of  $\text{CH}_2=\text{CH}_2$ ,  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ ,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  and  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$  are 173 nm, 190 nm, 219 nm and 228 nm, respectively [20-22]. In contrast, carbon compounds without double bonds, such as polyethylene films, synthetic diamond film [23] and natural diamond [24], have no absorption in the UV and visible regions.

The absorption spectra (from 160 nm to 700 nm) of the films synthesized with and without d.c. negative bias are shown in Fig. 4a. The specific absorption bands of the organic compounds with double bonds [20-22] are also shown schematically in Fig. 4b. Two peaks at around 195 nm and 230 nm, indicated by the arrows in the wide-range absorption spectra of Fig. 4a, become more outstanding with

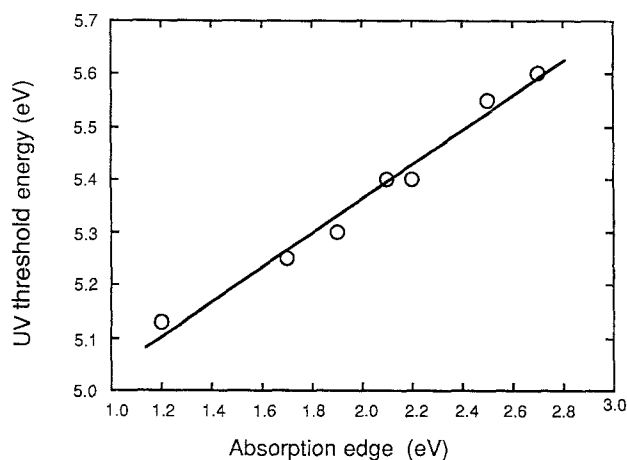


Figure 3 Relationship between UV threshold energy for photoelectron emission and absorption edge of the carbon films on synthetic quartz plate heated at 200 °C.

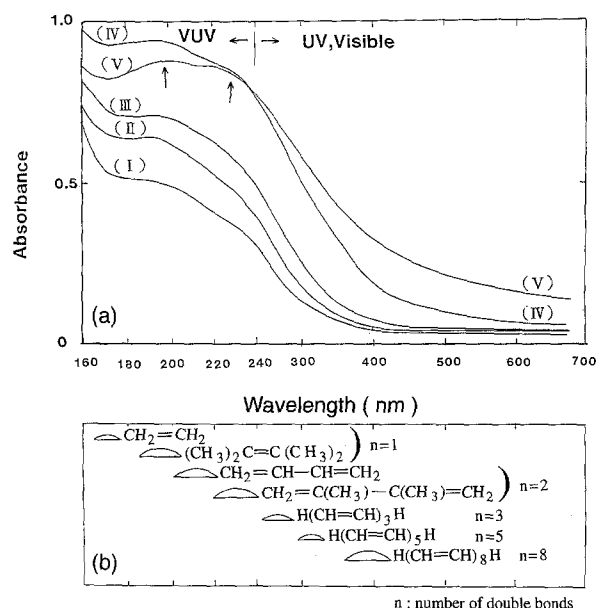


Figure 4 (a) Absorption spectra in VUV, UV and visible regions (from 160 nm to 700 nm) for the amorphous carbon films synthesized with and without bias on synthetic quartz plate heated at 200 °C: (I) bias 0 V; (II) bias -150 V; (III) bias -250 V; (IV) bias -350 V; and (V) bias -500 V. (b) Specific absorption of organic polyenes with conjugated double bonds.

increasing additional d.c. negative bias voltage. These two absorption peaks might be assigned to substituted ethylene and diene derivatives [20–22]. Additionally, it was reported that the absorption peaks of organic compounds shift to longer wavelengths and absorption bands become broader with an increasing number of double bonds in the compounds [19–22]. As shown in Figs 4a and 1, the absorbance at long wavelengths increases, and the line of Tauc's plots shifts to lower energies with increasing additional d.c. negative bias. Judging from the above results, the energy of the absorption edge of the films might be governed substantially by the growing of the broad absorption bands of polyenes at long wavelengths. This speculation agrees well with the theoretical calculation by Robertson and O'Reilly [17] that polyene chains exist in the films.

In conclusion, the energy of the absorption edge of the hydrogenated amorphous films, synthesized by RF plasma CVD, decreased from 2.7 eV to 1.2 eV with increasing additional negative d.c. bias. This energy decrease corresponds to the decrease of UV threshold energy, the decrease of hydrogen content, and the increase of double bonds in the films. From the analysis of wide-range absorption spectra, various broad absorption bands by poly-

enes, including absorption peaks at 195 nm and 230 nm, were considered to exist. Therefore, the decrease of the energy of the absorption edge might be attributed to the development of broad absorption bands of the longer polyenes formed by the applied additional negative bias.

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