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## Liquid Crystals

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# Effects of plasma treatments on correlation between chemical structures of DLC films and liquid crystal alignment

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In an effort to obtain an improved liquid crystal (LC) alignment layer for liquid crystal display device applications, amorphous diamond-like carbon thin films were deposited on ITO-coated glass substrates by an rf magnetron sputtering technique at room temperature and then treated with plasma in various atmospheres. The polarized images and pretilt angles of the LC cells showed that LC alignment was enhanced by post-plasma treatments of the films. In Raman and X-ray photoelectron spectroscopy spectra of the films, an increase in the fraction of  $sp^2$ -bonding was observed after post-plasma treatments of the films. In particular,  $H_2$  plasma-treated film had the largest fraction of  $sp^2$ -bonding at the film surface and showed much improved alignment capabilities. These results suggest that  $\pi$ -bondings of the  $sp^2$ -structure at the surface rather than the bulk play an important role in LC alignment.

## 1. Introduction

Aligned liquid crystals (LCs) are widely used in display device applications. The uniform alignment of a LC is an essential issue for flat panel display applications. As an alignment layer, rubbed polyimide has usually been used because of the uniform alignment and high pretilt angle of LCs. However, the rubbing process has some drawbacks such as the generation of contaminated particles and electrostatic charges [1–3]. As an alternative, the uniform alignment of a LC has been attempted recently by non-contact alignment methods using ultraviolet (UV) or ion-beam (IB) exposure to inorganic substrates [4]. Since LC alignment by IB exposure of diamond like carbon (DLC) thin films was first reported [5], comprehensive studies have been focused on DLC thin films as inorganic layers for LC alignment [6, 7]. Stohr *et al.* reported that LC molecules could be aligned on IB-irradiated DLC films due to carbon cluster rings or benzene rings [5]. More recently, several groups have studied LC alignment capabilities by irradiating DLC thin films with UV light [8], because the use of UV light for LC alignment has advantages over the IB method in that it is a non-vacuum process and improves the homogeneity of the pretilt angle [9].

In this study, we report on the correlation between (a) the change in chemical structure of the DLC films due to plasma treatments in different ambients and (b) LC alignment. Post-plasma treatments of the DLC thin films were carried out in different ambients in order to modify the chemical states at the film surface before UV irradiation. These treatments were found to increase  $sp^2$ -bonding in the DLC films, resulting in the enhancement of LC alignment.

## 2. Experimental procedure

The DLC thin films were deposited on indium tin oxide (ITO)-coated glass substrates by rf magnetron sputtering using a 5N purity carbon target. While the sputtering chamber was initially evacuated to a base pressure of about  $1.4 \times 10^{-5}$  Pa, the working pressure for film deposition was maintained at 0.67 Pa with Ar ambient gas. The DLC films were deposited at room temperature with a carbon rf power of 150 W. The thickness of the films was approximately 20 nm. As-deposited DLC films were subsequently plasma-treated in  $N_2$  or  $H_2$  ambients for 5 min at room temperature using an inductive coupled plasma (ICP) coil around the substrate holder. The films were then exposed to UV light for 1 min to control the orientational order at the film surface. A 1 kW mercury lamp was used as an

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oblique non-polarized UV source. Oblique exposure could give an effect like an S-wave in the non-polarized UV light irradiation. The energy and incident angle of the UV light were 26 mW and  $45^\circ$ , respectively.

The LC cells were assembled into an antiparallel structure by filling them with a nematic liquid crystal (NLC) ( $T_c=76^\circ\text{C}$ ,  $\Delta\epsilon=8.2$ , MJ001929 from Merck Co.) to measure LC alignment capabilities and pretilt angles. In order to investigate the structural characteristics of the DLC films due to the plasma treatments in different ambients, Raman spectroscopy was performed at room temperature in backscattering geometry using an  $\text{Ar}^+$  ion laser at 514.5 nm as an excitation source. The chemical states at the surface of the DLC films were analysed by X-ray photoelectron spectroscopy (XPS) using a 1486.6 eV Al  $K_{\alpha}$  source.

### 3. Results and discussion

The alignment capabilities of as-deposited,  $\text{N}_2$  plasma-treated, and  $\text{H}_2$  plasma-treated DLC films were first evaluated by observing LC cells prepared with these DLC films using a polarizing microscope. Figure 1 shows polarized images of the aligned LCs with UV irradiation on various DLC films. As shown in figure 1(a), in the case of the cell fabricated with the as-deposited films, alignment defects of the LCs are observed due to the presence of randomly oriented and non-aligned LCs. After the plasma treatments of the films, the LC alignment capabilities are enhanced. In case of the cell fabricated with  $\text{N}_2$  plasma-treated films, defects decrease as compared with the case of the as-deposited films, and there are almost no defects in the cell fabricated with  $\text{H}_2$  plasma-treated films.

The LC pretilt angles of the cells prepared using as-deposited and plasma-treated DLC films are shown in figure 2. While the LC pretilt angle of the cell with as-deposited films is  $0.05^\circ$ , this abruptly increase after plasma treatments of the films. In particular, for the cell with  $\text{H}_2$  plasma-treated films, the LC pretilt angle reached  $1.2^\circ$ .

In order to investigate the chemical structures and bonding types of as-deposited and plasma-treated films, Raman spectroscopy was carried out with the results shown in figure 3. This method is useful in obtaining information on  $\text{sp}^2$ -sites in amorphous carbon thin films which are related to the LC alignment and pretilt angle [7]. In Raman spectra, two peaks near  $1580$  and  $1350\text{ cm}^{-1}$  are observed, which are assigned to a single graphite peak (G-peak) and a disordered graphite peak (D-peak), respectively [10–12]. The positions and the intensity ratio ( $I_D/I_G$ ) of the D-peak and G-peak for as-deposited DLC films remain almost unchanged before and after UV irradiation. On the other hand, for both

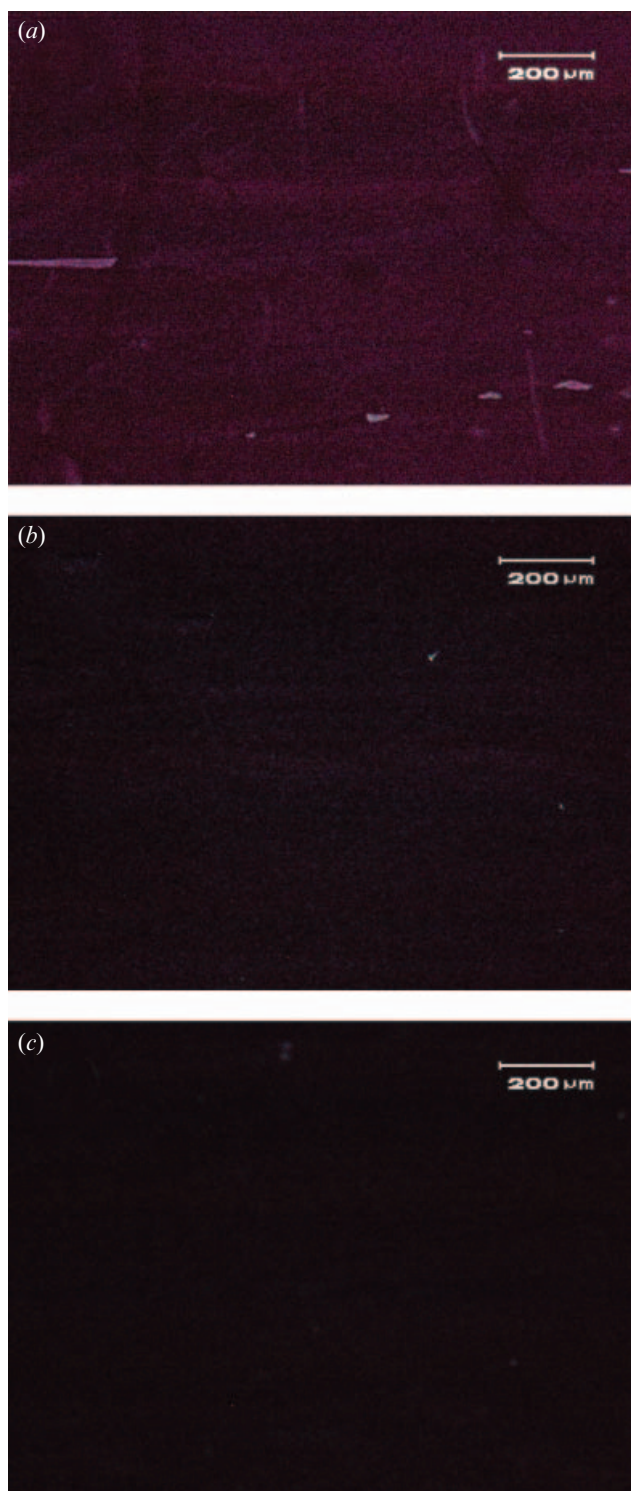


Figure 1. Micrographs of UV-aligned LC cells fabricated using (a) as-deposited, (b)  $\text{N}_2$  plasma-treated, and (c)  $\text{H}_2$  plasma-treated DLC thin films.

plasma-treated films, G-peaks and D-peaks shift to slightly higher wave number positions, and  $I_D/I_G$  ratios increase before and after the UV irradiation, indicating

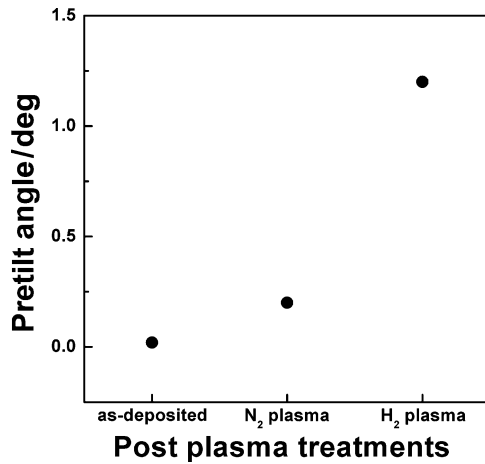


Figure 2. Comparison of the pretilt angles of UV-aligned LC cells fabricated using as-deposited, N<sub>2</sub> plasma-treated, and H<sub>2</sub> plasma-treated DLC films.

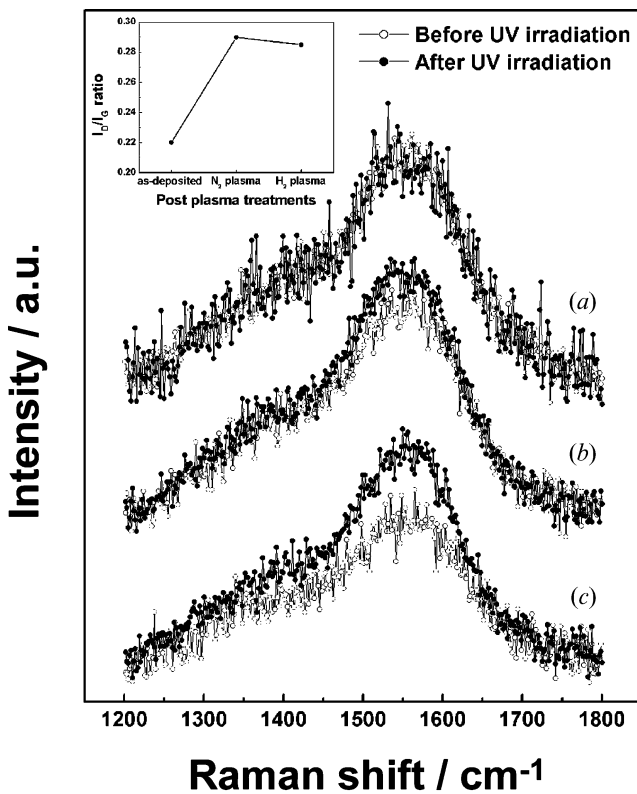


Figure 3. Raman spectra of (a) as-deposited, (b) N<sub>2</sub> plasma-treated, and (c) H<sub>2</sub> plasma-treated DLC films before and after UV irradiation. The inset shows the change in the intensity ratio of D-peak and G-peak ( $I_D/I_G$ ) due to the plasma treatments after UV irradiation of the films.

that the size or number of sp<sup>2</sup>-domains in the DLC films increases by post-plasma treatments and UV irradiation [13]. This again implies that there is a strong correlation between sp<sup>2</sup>-bondings and LC alignment. The inset of

figure 3 shows clearly the change in  $I_D/I_G$  ratios due to the plasma treatments after UV irradiation of the films. In both plasma-treated films,  $I_D/I_G$  ratios increase more than 30% but there is almost no difference in  $I_D/I_G$  ratios between N<sub>2</sub> plasma-treated and H<sub>2</sub> plasma-treated films.

The chemical states at the surface of the DLC films were investigated in detail by XPS, focusing on the

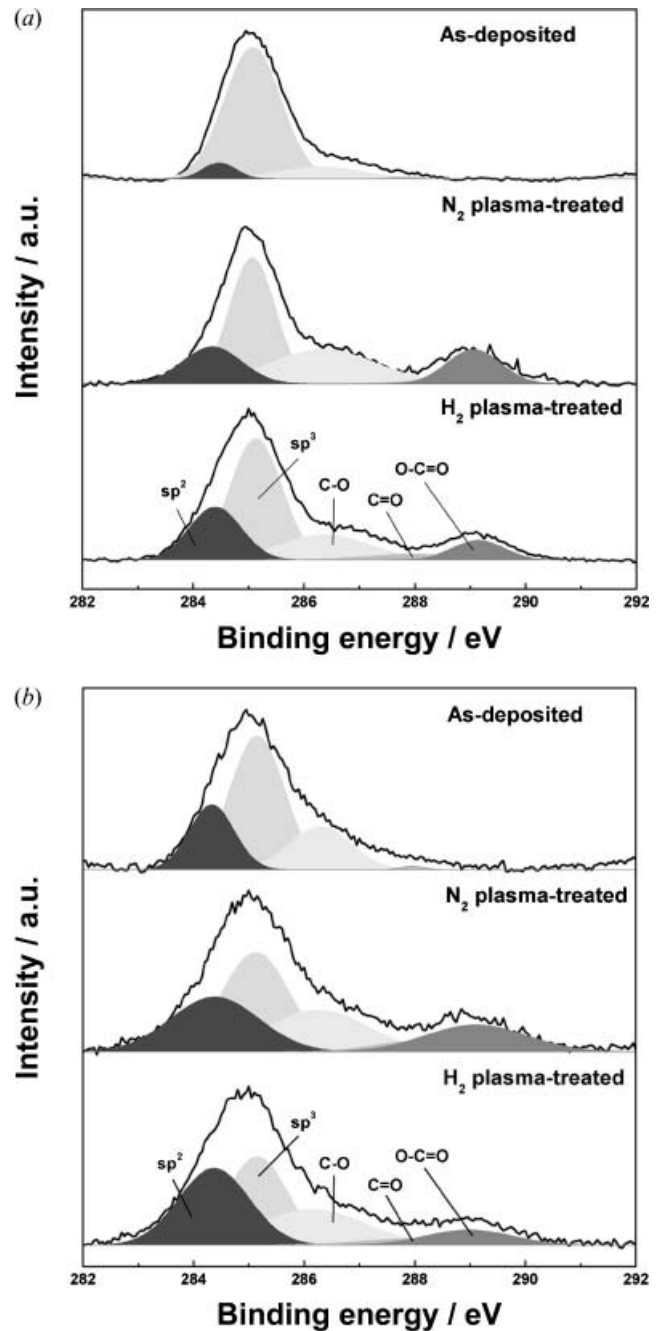


Figure 4. C 1s XPS spectra for as-deposited, N<sub>2</sub> plasma-treated, and H<sub>2</sub> plasma-treated DLC films (a) before and (b) after UV irradiation.

Table 1. Atomic % areas of each chemical state in the deconvoluted C 1s XPS spectra.

Post-plasma treatment	Before UV irradiation			After UV irradiation		
	As-deposited	N <sub>2</sub> plasma	H <sub>2</sub> plasma	As-deposited	N <sub>2</sub> plasma	H <sub>2</sub> plasma
sp <sup>2</sup> (C=C)	5.97	16.04	21.40	22.60	25.13	32.70
sp <sup>3</sup> (C-C)	81.68	42.42	48.63	43.32	34.69	32.10
Bondings between C and O	12.36	41.54	29.96	32.93	40.19	35.19

relative fraction of C=C sp<sup>2</sup>- and C-C sp<sup>3</sup>-bondings at the film surface, since the chemical bonding at the surface has a close relationship to LC orientation. Figure 4 shows C 1s XPS spectra of as-deposited, N<sub>2</sub> plasma-treated and H<sub>2</sub> plasma-treated DLC films before and after UV irradiation. The C 1s spectra of the DLC films were deconvoluted into two main peaks at 284.4 and 285.2 eV, which are assigned to sp<sup>2</sup>- and sp<sup>3</sup>-bondings, respectively [14]. The other peaks at 286.3, 288.0 and 298.0 eV are attributed to the bondings between carbon and oxygen [15, 16]. The portion of each bonding can be obtained from the atomic % areas of the deconvoluted sub-peaks of C 1s XPS spectra. These atomic % areas for various bonding states are summarized in table 1. For as-deposited films without any plasma treatment, UV irradiation increases the proportion of sp<sup>2</sup>-bonding from 5.97% to 22.60%. This shows that UV irradiation selectively destroys carbon network and induces sp<sup>2</sup>-bondings [4, 5].

It is expected that induced sp<sup>2</sup>-bondings lead to unidirectional alignment of LC molecules parallel to the UV-irradiated direction. Such a phenomenon has been found in IB-irradiated DLC films [5]. After the plasma treatments, the proportions of sp<sup>2</sup>-bonding are much higher than in as-deposited film even without UV irradiation. From this, it is inferred that the chemical states at the film surface are affected by the bombardment by activated hydrogen and nitrogen ions during the plasma treatments, leading to the generation of sp<sup>2</sup>-bonding [17–19]. In particular, in H<sub>2</sub> plasma-treated film, atomic % area of sp<sup>2</sup>-bonding before UV irradiation is 21.4%, which is comparable to that of UV-irradiated as-deposited films. It is therefore believed that the influence of the plasma treatment in H<sub>2</sub> rather than N<sub>2</sub> ambient is more effective for the change in the chemical structures at the film surface. The portion of sp<sup>2</sup>-bonding in N<sub>2</sub> plasma-treated and H<sub>2</sub> plasma-treated samples further increased after UV irradiation, reaching 25.13% and 32.70%, respectively. These results suggest that the plasma treatment of the DLC films, especially in H<sub>2</sub> ambient, can enhance LC alignment capability such as LC alignment and pretilt by modifying the DLC film surface to increase the portion of π-bondings of sp<sup>2</sup>-states.

#### 4. Conclusions

In summary, amorphous DLC films were deposited on ITO-coated glass substrates by an rf magnetron sputtering method at room temperature, and the change in their chemical structures due to post-plasma treatments was investigated in terms of the relationship between sp<sup>2</sup>-fraction in the films and LC alignment. The polarized images and pretilt angles showed that LC cells prepared using plasma-treated films had much enhanced LC alignment capabilities over that of the cell prepared directly from as-deposited films. The Raman and XPS analyses indicated that enhanced LC alignment resulted from the sp<sup>2</sup>-bonding at the surface generated by the plasma treatments of the films. These results suggest that π-bondings of sp<sup>2</sup>-structure at the surface of the DLC films are an important factor in LC alignment, and that post-treatments of the DLC films by plasma can substantially improve LC alignment capabilities through the conversion of surface structure to sp<sup>2</sup>-states.

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