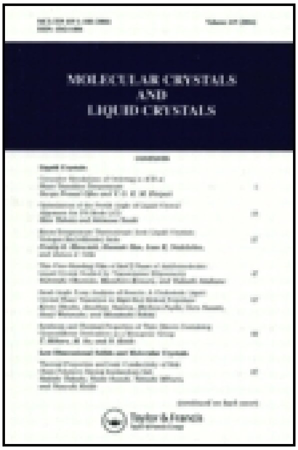

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Studies on UV-Photoinduced Surface Anisotropy of Polyimide Films by NEXAFS Spectroscopy

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Polyimide films irradiated with linearly polarized deep UV (LPDUV) light can align liquid crystals perpendicularly to its polarization direction. We report an experiment using near edge X-ray absorption fine structure (NEXAFS) spectroscopy with high surface sensitivity to elucidate the LC alignment mechanisms by total electron yield (TEY) and partial electron yield (PEY) methods. The dichroic ratio of O K-edge π* peak intensity, originated from C=O bond, shows different UV exposure dependence for TEY and PEY cases. We can conclude that the LPDUV irradiated film possesses the depth dependence of anisotropy.

Keywords: NEXAFS; polyimide; photoinduced alignment; surface anisotropy; linearly polarized UV

INTRODUCTION

Rubbing of polyimide surface is a widely accepted technique to align liquid crystal (LC) molecules. However this method has several problems for display applications, for example, pollution with dust particles and generation of electrostatic charge. Instead of the rubbing method, photoalignment methods [1-3] have attracted much attention to overcome these problems. Among these, Photo-induced decomposition [4-6] has been actively studied, because this method utilizes widely accepted polyimide material to be a potential alternative to the rubbing method. Poly [4, 4'-oxydiphenylene-1, 2, 3, 4-cyclobutanetetracarboxiimide](CBDA-ODA) films (Figure 1) exposed by linearly polarized deep ultra violet (LPDUV) light may align LC molecules perpendicularly to the polarization of UV [7, 8]. CBDA-ODA films provide the best LC alignment by a LPDUV exposure of 1J/cm^2. Sakamoto et al [9] successfully showed by transmission IR spectroscopy that the surface anisotropy of LPDUV-irradiated CBDA-ODA film arises from the preferential cleavage of cyclobutane ring. Macroscopic evaluation of its alignment capability and anchoring strength have also been conducted, but the surface specific information and hence the detailed understanding of the mechanism of photodecomposition is still lacking. In this paper, we have investigated surface anisotropy of LPDUV-exposed polyimide by near edge X-ray absorption fine structure (NEXAFS) spectroscopy with use of total electron yield (TEY) and partial electron yield (PEY) tech-

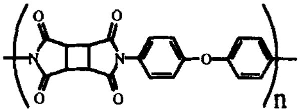

FIGURE 1 Molecular structure of CBDA-ODA

niques. By use of linear polarized synchrotron radiation, electrons in inner shell orbitals like 1s or 2p are excited to vacant discrete or continuum states. The photon energy required for this transition is characteristic of an element. Hence, we can investigate the molecule by element and bond selective observation. The penetration depth of soft X-rays is about 500 Å, but the only electrons near at the surface (about 50 Å) can escape from the sample because the electrons are almost scattered in the bulk. The surface sensitive observation can be achieved to detect the electrons from the surface. TEY method detecting all electrons from the surface is the simplest technique. PEY method sets a retarding voltage at the front of the detector and cut lower kinetic energy electrons. PEY is useful because it has a shallower escape depth than that of TEY and hence reduces background.

EXPERIMENT

A precursor, polyamic acid dissolved in butyl cellosolve was spin-coated on ITO and imidized at 250°C for one hour to make CBDA-ODA films. Thickness of the films were 200nm. The film was exposed by 257 nm (15mW/cm^2) linearly polarized deep UV (LPDUV) light which was the second harmonic of 514nm, Ar$^+$ laser.

The NEXAFS measurement was carried out at beam line 7A and 11A of Photon Factory(KEK PF BL7A, 11A). The synchrotron radiation light was incident normal to the substrate. TEY and PEY were used to detect the electrons from the sample surface. The base pressure during the measurements was 10^{-8}Torr.

RESULT & DISCUSSION

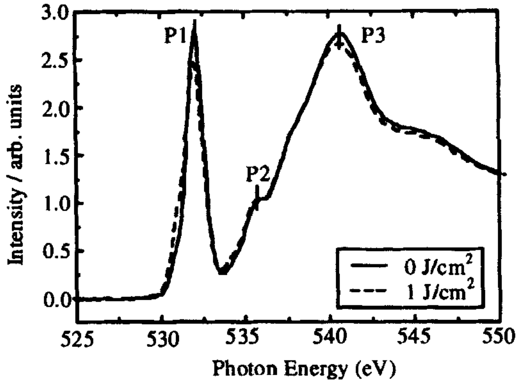

FIGURE 2 O K-edge NEXAFS spectra of CBDA-ODA. The solid line and dashed line represent 0 J/cm^2, 1 J/cm^2 UV exposure($E^{SX}//E^{UV}$)respectively.

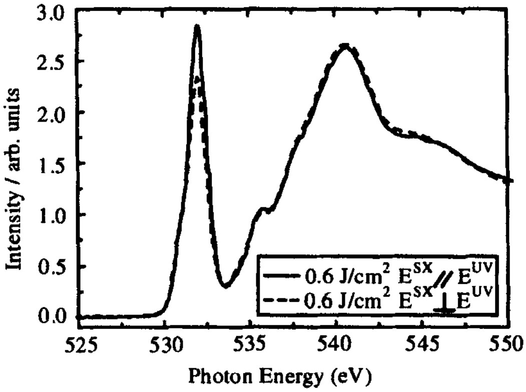

FIGURE 3 O K-edge NEXAFS spectra for 0.6J/cm^2 irradiated sample. The intensity difference at the O 1s → π * transition , 532.3eV, is clearly observed for $E^{SX}//E^{UV}$, $E^{SX}\perp E^{UV}$cases.

O K-edge Spectra of CBDA-ODA are shown in Figure 2. Spectral changes by LPDUV exposure can be observed. Particularly, the intensity of the first peak(P1) at 532.3 eV attributed to O 1s → π * transition is reduced and small shoulder peak appears at 532eV. Figure 3 summarizes how spectra are different between $E^{SX}//E^{UV}$ and $E^{SX} \perp E^{UV}$, for 0.6J/cm^2 irradiated sample. Here, $E^{SX}//E^{UV}$ represents the electric field vectors of soft X-ray (E^{SX}) and LPDUV (E^{UV}) being parallel with each other and $E^{SX} \perp E^{UV}$ represents those being perpendicular. The intensity of P1 for $E^{SX}//E^{UV}$ is lager than that of $E^{SX} \perp E^{UV}$. It should be noted that this difference corresponds to the photo-induced surface anisotropy of polyimide. Since the direction of O 1s →π* transition moment is perpendicular to the polyimide chain, the intensity differences can be interpreted in such a way that the polyimide chains are decomposed along LPDUV polarization as has been reported [4].

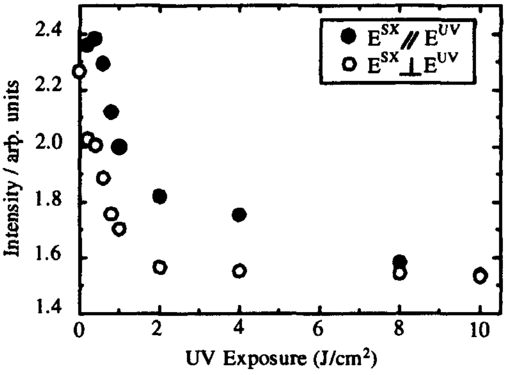

FIGURE 4 UV exposure dependence of O K-edge π * peak(P1) intensity.

Figure 4 shows the radiation energy dependence of the peak P1 intensity. The peak intensity for $E^{SX}//E^{UV}$ increases up to 0.6J/cm^2 and then gradually decreases, while that for $E^{SX} \perp E^{UV}$ is monotonically decrease. This difference suggests that the randomization of the decomposed polyimide chain parallel to E^{UV} occurs at the first stage of decomposition [9]. UV irradiation more than 0.6J/cm^2 may cause carbonyl group decomposition or desorption of a polyimide surface.

To evaluate photoinduced anisotropy more quantitatively, we use the following phenomenological dichroic ratio:

$$\text{Dichroic Ratio}\,(\text{O 1s} \rightarrow \pi^*) = \frac{I(E^{SX} // E^{UV}) - I(E^{SX} \perp E^{UV})}{I(E^{SX} // E^{UV}) - I(E^{SX} \perp E^{UV})} \times 100 \quad (\%)$$

In Figure 5, we show the radiation energy dependence of dichroic ratio. The dichroic ratio obtained from PEY shows the maximum value at 0.6J/cm^2 UV irradiation, and then decreases to zero at 10J/cm^2. This result shows good correlation with LC alignment capability [4]. On the other hand, the dichroic ratio from TEY shows maximum at 2J/cm^2 UV exposure. Since TEY technique observes deeper region than PEY, and also due to the results from Figure 5, the alignment capability of LPDUV polyimide is determined at a shallower region from the surface. Ohara reported that the TEY escape depth for alkanes is 35 Å. We can estimate the alignment controlling region of LPDUV polyimide is approximately 20 Å. Figure 6, shows the UV irradiation energy dependence of C 1s →

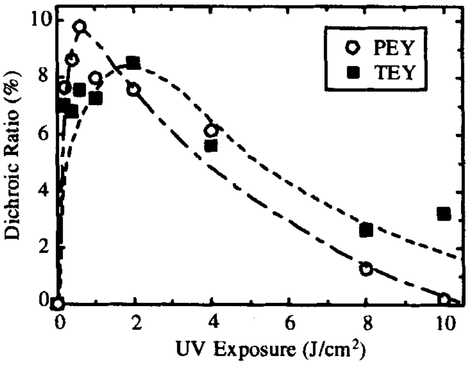

FIGURE 5 Dichroic ratio of O1 intensity. The dashed and dashed-dotted line is a guide to the eye.

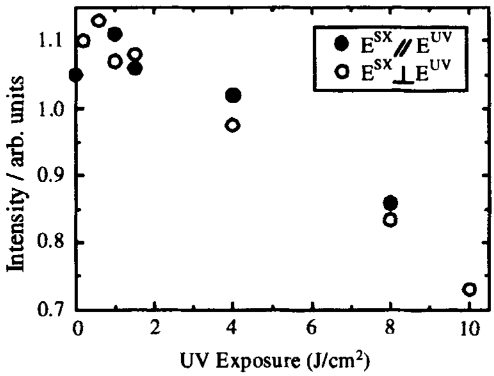

FIGURE 6 UV exposure dependence of C K-edge π * peak (C 1s → π * transition) intensity.

π^* transition peak intensity. Though we don't observe large anisotropy for C K-edge spectra [11], an intensity maximum is observed at 0.6J/cm^2 UV exposure, indicating formation of extra C=C double bonds from cyclobutane imide to maleimide ring at the first stage of decomposition [9]. The intensity is reduced in the exposure range over than 0.6J/cm^2. This is because the cleavage of cyclobutane ring has almost finished at 0.6J/cm^2 and the phenyl ring may start to decompose or desorb from the surface.

CONCLUSION

We investigated LPDUV irradiated CBDA-ODA films by NEXAFS spectroscopy. The dichroic ratio of O K-edge π^* peak with PEY method has a maximum value at 0.6J/cm^2, and its UV exposure dependence exhibits good correlation with LC alignment capability. The alignment control region for LPDUV polyimide was roughly estimated to be 20 Å. At the first stage of decomposition, we could confirm the cleavage of cyclobutane imide ring to maleimide ring.

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