

NEXAFS observation of the in-plane anisotropic polymerization of a long-chain diacetylene derivative Langmuir-Blodgett film

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Introduction

It is well known that a thin film of a long-chain diacetylene derivative Langmuir-Blodgett (LB) film can be photopolymerized under the ultraviolet (UV) light irradiation, and it forms a polymer film with conjugated π -electron systems [1]. Although the network of the conjugated π -electron exists within each two-dimensional unit layer of the LB film, the in-plane polymerization direction is randomly distributed in it. If the in-plane polymerization direction can be controlled, a novel functionality will be expected to appear in the anisotropically polymerized LB film. In this study, we tried to control the in-plane polymerization direction by using a specially designed substrate whose surface had a periodic one-dimensional template structures.

Experimental Section

In order to fabricate the periodic template, we caused step-bunching on a 4° -off Si(111) substrate by direct current heating in ultrahigh vacuum [2]. Then this substrate was oxidized in a dry O_2 furnace to form an amorphous SiO_2 layer, on which the periodic structures still remained as shown in Fig. 1. Next a cadmium 10,12-pentacosadiolate (CdDA) monolayer was deposited by the LB method, and the film was photopolymerized by the UV irradiation. To determine the orientational distribution of the π -conjugated systems in the polymer film, polarized C K -edge near-edge X-ray absorption fine structure (NEXAFS) spectra were measured.

Results and Discussion

Fig. 2 shows the NEXAFS spectra of the poly-CdDA film on the step-bunched Si/SiO_2 surface before and after the azimuthal angle rotation by 90° , and enlarged ones around the C $1s$ - π^* transition. The incident angle of the p -polarized X-ray from the surface normal was 35° . These spectra revealed that the π -electron conjugation in the poly-CdDA film was more highly ordered along the one-dimensional periodic structures on the template surface than the direction across these structures. Especially, the C $1s$ - π^* ($C\equiv C$, nonconjugated) peak intensity was larger when E vector plane of incident X-ray was set in the direction along steps, indicating the in-plane anisotropy

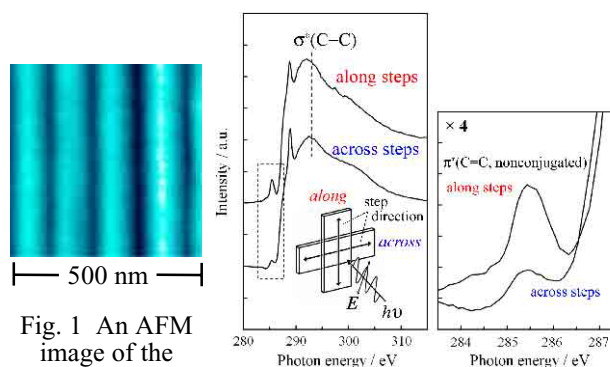


Fig. 1 An AFM image of the step-bunched and dry- O_2 oxidized ($1100^\circ C$, 1 h) 4° -off Si(111) surface.

Fig. 2 Azimuthal angle dependence of the NEXAFS spectra of the poly-CdDA film on the step-bunched Si/SiO_2 surface..

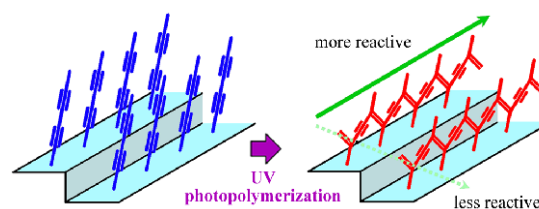


Fig. 3 Schematic illustrations of the anisotropic polymerization of the diacetylene derivatives on the step-bunched Si/SiO_2 surface.

of the π -conjugation. On the contrary, a polymer film fabricated on the flat Si/SiO_2 surface showed no in-plane anisotropy of the peak intensity, suggesting that the isotropic random photopolymerization occurred on the flat surface. We conclude from these results that the diacetylene groups in the LB film were preferentially photopolymerized in the direction not across, but along the periodic structures on the step-bunched Si/SiO_2 template surface, as shown in Fig. 3 [3].

References

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