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Characterization of Liquid Crystal Alignment on Rubbed Polyimide Film by Grazing-Incidence X-Ray Diffraction

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SUMMARY We developed a new method for characterizing molecular distribution in very thin liquid crystal layer (5–40 nm) evaporated onto rubbed polyimide film used by grazing-incidence X-ray diffraction (GIXD). The diffraction peaks corresponding to intermolecular correlation perpendicular to longitudinal axis of liquid crystal molecule and the clear anisotropic distribution of liquid crystal molecules in a thin layer were successfully observed. We found that in the vicinity of the alignment film, the intermolecular spacing correlation perpendicular to longitudinal axis of the 5CB molecule was expanded by the alignment film, and that the ordering of the 5CB was not so high. As the distance from the alignment film the spacing came close to the intrinsic intermolecular spacing.

key words: *LC, thin film, alignment, rubbed polyimide film, grazing-incidence X-ray diffraction*

1. Introduction

The understanding of the alignment mechanism of liquid crystal (LC) on alignment film is of fundamental interest and of industrial importance for the manufacturing of LC devices. Rubbed polyimide films have been used as liquid crystal alignment films in LC displays. It is widely considered that molecules of liquid crystals are aligned by intermolecular interactions with polyimide molecules of rubbed films, and characterization of polyimide molecular orientation is an essential item to develop and fabricate liquid crystal displays (LCDs). Until now, using by Grazing Incidence X-ray Diffraction (GIXD), which is very powerful technique to characterize molecular alignments of thin films, we have studied effects of rubbing, washing and annealing on the surface structure of polyimide film [1]–[3].

We are now challenging to characterize molecular alignment of very thin liquid crystal layer (4–40 nm) formed on polyimide (PI) film to Investigate dependence of molecular orientation of LC film surface on LC thickness to discuss interaction between LC and PI. The result of our recent approaches to characterize molecular alignments of thin liquid crystal film with using GIXD is reported in this paper.

2. Experiments

2.1 Sample Preparation

4-pentyl-4-4biphenylcalbonitrile, denoted 5CB and poly (pyromellitic dianhydride oxydianiline), denoted PMDA-ODA were selected as liquid crystal and an alignment film in this experiment. Samples were prepared in the following procedure. Polyamic acid solution of PMDA-ODA was coated on Si substrates using a spinning coater. After prebaking at 80°C for 5 min to dry solvent, curing for imidization was performed at 250°C for 30 min. Then, all films were rubbed in the condition that insert depth of fiber was set 0.4 mm. Rotation and translation speed of a rubbing roller were set at 300 rpm and 20 mm/s.

5CB is a rod-shaped polar molecule and has nematic liquid crystal phase in the temperature range from 24°C to 35°C. As shown in Fig. 1, the evaporation was executed under air atmosphere using evaporation chamber. By heating 5CBs at 100°C, 5CBs are gradually evaporated onto the rubbed PMDA-ODA coated substrate. The evaporation time was 5 min, 10 min, 20 min, 40 min and 100 min.

2.2 X-Ray Reflectivity (XRR)

X-Ray reflectivity (XRR) is a well established technique for noncontact thin film metrology. Information such as film thickness, mass density and interfacial roughness can be obtained by fitting a theoretical curve based on Parratt's formalism [4] to a measurement. Monolayer structure and roughness on a liquid [5] and layer-by-layer growth [6] can be measured with high accuracy. The reflectivity technique

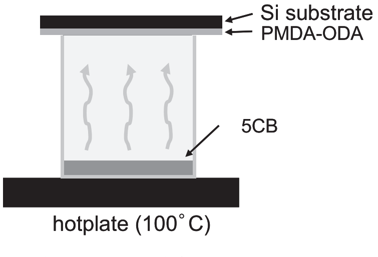

Fig. 1 The setup for the form of 5CB thin film onto the rubbed PMDA-ODA coated Si substrate. The 5CB in a petri dish was heated by a hot plate at 100°C. 5CBs are gradually evaporated onto the rubbed PMDA-ODA coated substrate. The evaporation time was 5–100 min.

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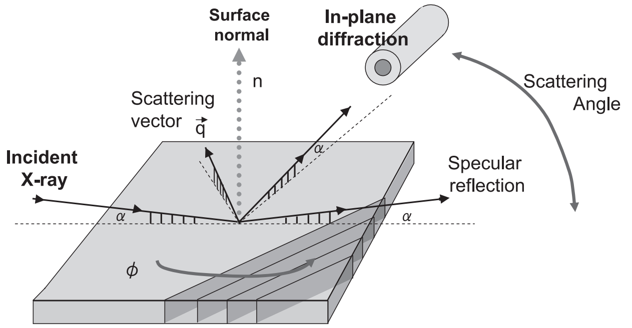


Fig. 2 Schematic diagram of the Grazing incidence X-ray diffraction (GIXD) geometry of the incident and scattered X-ray beams at the sample. Scattering measurements were performed with the sample nearby horizontal using a multi-axis diffractmater such as the angles of the incident and diffraction beams with respect to the substrate surface are very small (less than 0.2°). Therefore, the direction of the scattering vector was essentially parallel to the film surface. The incident X-rays are diffracted by lattice planes perpendicular to the surface or thin films and the diffracted X-rays has information about structure parallel to the surface.

has been used to prove layer fluctuations in thin smectic-A films [7] and interfacial roughness [8].

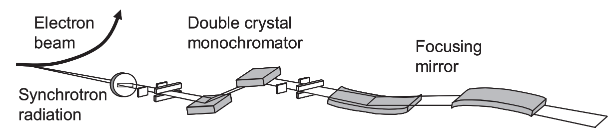
2.3 Grazing Incidence X-Ray Diffraction (GIXD)

Grazing incidence X-ray diffraction (GIXD) is suitable technique to characterize polymer alignments of thin films [1]–[3], [9]–[11], since it can provide a depth profile of the molecular orientation by controlling the incident angle of X-rays to the sample surface. In GIXD, incident X-rays are impinged on the sample surface with a very small incident angle, and X-rays are diffracted by in-plane periodicities of surface or thin films, as shown in Fig. 2. When the incident angle is smaller than the critical angle for the total reflection, penetration of the X-rays is limited to several nanometers from the surface. Generally, the critical angles of polymers are less than 0.2°, and controllability of the incident angle must be 0.01°. Thus, high intensity and low emittance of synchrotron radiation X-rays are necessary for surface-sensitive characterization by GIXD.

2.4 Instruments

XRR and GIXD measurements were performed at SPring-8, since X-rays from synchrotron radiation light source were essential for the experiments. GIXD profiles of the films were observed using the multi-axis diffractometer installed in the X-ray beamline BL19B2 at SPring-8. The optical component is shown in Fig. 3(a). The incident X-ray energy was set at 10 KeV by a Si(111) double crystal monochromator, and contamination of higher harmonics in the incident beam was reduced using two Rh-coated mirrors set at 4.4 mrad of the incident angles. The height and width of the incident beam were 0.1 mm and 8.0 mm, respectively. The intensity of the incident X-ray beam was monitored by an ionization chamber. Scattered X-rays from samples were detected by a NaI scintillation counter through a Soller slit with a 0.089° divergent angle ("KeV" Co. Ltd.). Samples were set their surface normal to be perfectly parallel to the φ axis of the diffractometer, in order that the scattering plane was set horizontal (parallel to X-ray polarization) and parallel to the sample surfaces. Schematic diagram of the experiment is shown in Fig. 3(b). X-ray reflectivity measurements were also performed in the same setting to characterize the mass density and film thickness.

(a) Optical component of BL19B2



(b) Experimental setup of XRR and GIXD mesurement

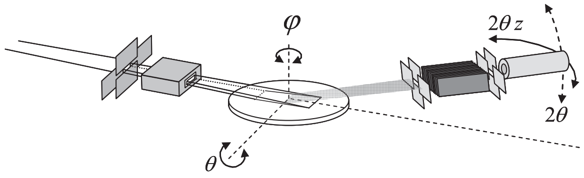


Fig. 3 Schematic view of BL19B2 beamline (Engineering Science Research I). The white light emitted from a standard SPring-8 bending magnet is introduced into a double crystal monochromator with Si(111) crystal cooled down with a water chiller. The two Rh-coated mirrors (in a vertical scattering geometry) are for rejecting higher harmonics of incident photons. The slit1 is located upstream of the ionization chamber to restrict the beam size of the incident beam and confine the beam to the sample surface at small angles of incidence. The incident beam intensity is monitored using the ionization chamber and diffracted X-rays from samples are detected by a NaI scintillation counter through a Soller slit with a 0,089° divergent angle. Two sets of the slits (slit2 and slit3) were used to eliminate stray radiation. The sample was blanketed in a helium atmosphere to reduce air scattering and to minimize sample degradation in the high flux of incident beam.

3. Results and Discussion

3.1 X-Ray Reflectivity

Figure 4 shows observed X-ray reflectivities of (a) bare Si substrate, (b) the rubbed PMDA-ODA film coated on Si substrate, (c)(d) the 5CB evaporated film onto the rubbed PMDA-ODA coated substrate. The evaporation times were (c) 10 min and (d) 40 min. Because there was no thin film, the reflectivity shown in Fig. 4(a) was smooth curve called the Fresnal reflectivity. It should drop as $\propto 1/|q|^4$ beyond the critical angle. The root-mean-square (rms) value of the surface roughness from fitting was determined to be 0.45 nm. In the case of a film on a substrate shown in Figs. 4(b), (c) and (d), Kiessig fringes are generated by the interference between the X-rays partially reflected from the air-film and from film-substrate interfaces. In Fig. 4(b), the reflectivity showed the Kiessig fringes with single periodicities (about 0.062°) caused by the PMDA-ODA film. The estimated

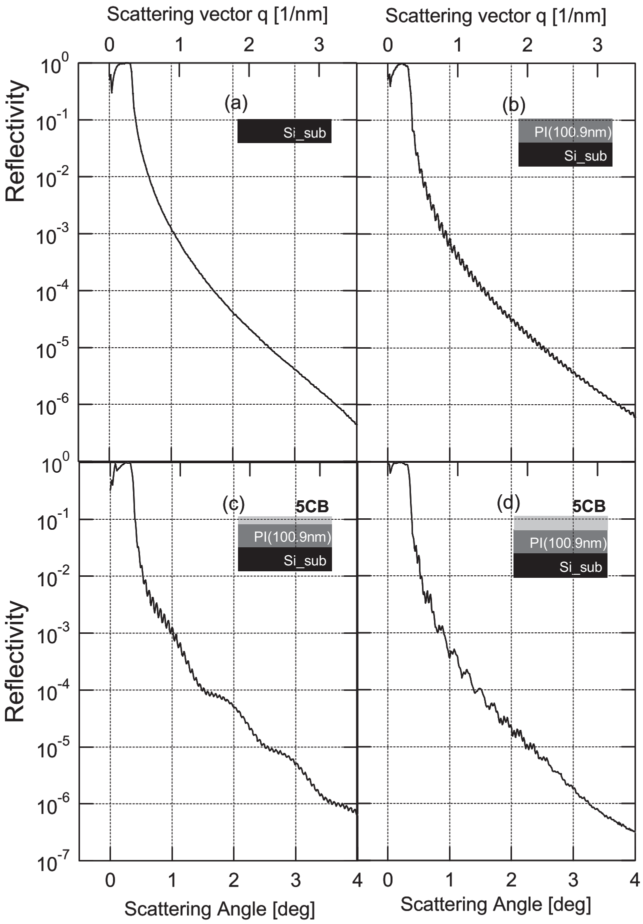


Fig. 4 Observed X-ray reflectivities of (a) the Si substrate, (b) the PMDA-ODA film, (c) the 5CB film evaporated for 10 min onto the PMDA-ODA film, and (d) the 5CB film evaporated for 40 min onto the PMDA-ODA film. From profile fitting, the mass density of the 5CB layer was 1.10 g/cm^3 and the critical angles for the X-ray total reflection of the 5CB was calculated to be 0.122°.

mass density and film thickness of the PMDA-ODA were 1.42 g/cm^3 and 100.9 nm. The X-ray reflectivity curves of the 5CB evaporated film showed two superimposed periodicities with different amplitude, indicating the presence of two layers of different thickness and electron densities. In Fig. 4(c), shorter periodic fringes with about 0.053° caused by total thickness of the PMDA-ODA film (100.9 nm) and the 5CB layer evaporated for 10 min and longer periodic fringes with about 0.86° caused by the 5CB layer. The estimated mass density and film thickness of the 5CB layer were 1.10 g/cm^3 and 8.9 nm. Similarly, from Fig. 4(d), the thickness of the 5CB layer evaporated for 40 min was 38.4 nm. Liner relation between the layer thickness of the 5CB and evaporation time was observed as shown in Fig. 5.

3.2 φ-2θz in GIXD Geometry

Surface sensitive profiles of in-plane φ-2θz scans shown in Figures 6(a)–(d) were obtained in the condition that incident angle was set at 0.10°. In this condition, we could obtain surface sensitive information of the 5CB thin film, since the penetration depth of the incident X-ray was about 10 nm. Figure 6(a) shows the in-plane φ-2θz scans of the rubbed PMDA-OAD film and Figs. 6(b), (c), (d) shows these of the 5CB evaporated film onto the rubbed PMDA-OAD film. The thicknesses of the 5CB were 3.9 nm, 18.9 nm and 38.5 nm. In Fig. 6, open circles and solid circles indicated observed in-plane φ-2θz profiles in parallel and normal to rubbing direction. The in-plane diffraction patterns of the rubbed PMDA-OAD film in normal and parallel directions show broad scattering peaks around 14.0°. These peaks correspond to the PI interchain spacing. The peak in normal direction was observed at higher scattering angle than that in parallel direction. This means that the interchain spacing in parallel direction should be longer than that in normal direction. In Figs. 6(b), (c), strong and somewhat broad diffraction peaks were clearly observed around 16.0° in in-plane φ-2θz profiles. These diffraction peaks comes from intermolecular correlation perpendicular to longitudinal axis of 5CB. Surface sensitive peak of the 5CB layer was more intense in normal to rubbing direction

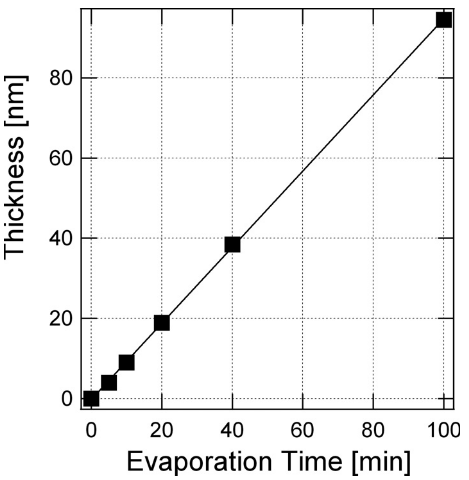


Fig. 5 The thickness of 5CB layer evaluated from the XRR measurements. Liner relation between the layer thickness of the 5CB and evaporation time was observed.

3.3 In-Plane Rocking Scan in GIXD Geometry

In-plane distributions of 5CB molecules were characterized by in-plane rocking scans, as follows: Detector was set at 16.0° of scattering angle, and a sample was rotated along its surface normal to observe dependence of peak intensity on in-plane orientation of the 5CB layer. Figure 6(e) shows in-plane rocking scan profiles of the rubbed PMDA-OAD film and Figs. 6(f), (g), (h) show the 5CB layer evaporated on the rubbed PMDA-ODA film. Sample orientation was defined to be 0°, when the rubbing direction was normal to the scattering vector. In the profile of the 5CB layer on the rubbed PMDA-ODA film, the 16.0 peak was most intense in normal (0°, 360°) and anti-normal (180°) direction. The clear anisotropic distribution of the 5CB molecules was observed. In our previous study about the rubbed PMDA-ODA films

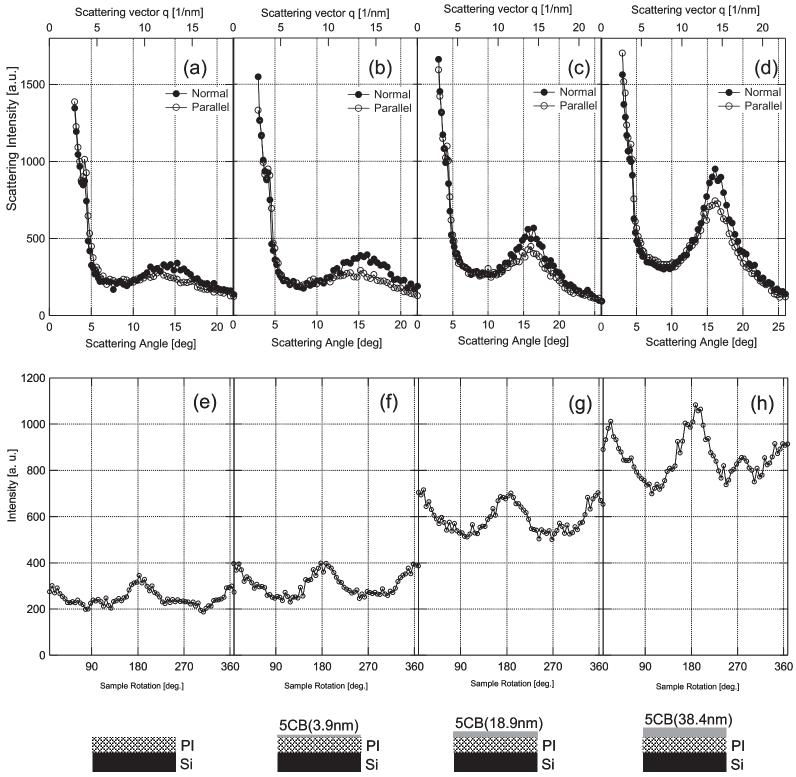


Fig. 6 In-plane φ-$2\theta z$ profiles of (a) the rubbed PMDA-ODA film, (b)–(d) the 5CB evaporated film onto the rubbed PMDA-ODA film and in-plane rocking profiles of (e) the rubbed PMDA-ODA film, (f)–(h) the 5CB evaporated film onto the rubbed PMDA-ODA film.

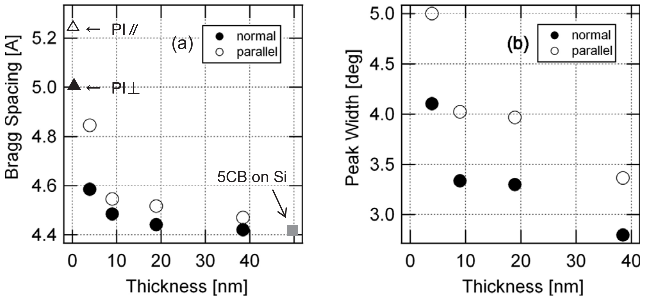


Fig. 7 Estimated Bragg spacing (a) and peak width (b) of the 5CB's broad diffraction peaks around 16.0°.

[1], it was found that polymer chain of the PMDA-ODA near the surface was aligned in the rubbing direction. Then, these results indicate that the 5CB molecules preferentially aligned in aligned direction of polymer chain. However, remarkable intensities coming from LC were observed even in parallel direction, and LCs are not perfectly aligned.

3.4 Dependence of Thickness of the 5CB Layer

Figures 7(a), (b) show Bragg d-spacings and width of the 5CB's broad diffraction peaks around 16.0° estimated by profile fitting. In addition, Bragg spacings in the normal (solid triangle) and parallel (open triangle) direction corresponded to the PI chain, and that of 5CB directly deposited on Si substrate without the rubbed PMDA-ODA film (gray square) are indicated in Fig. 6(a). It is considered that the Bragg spacings estimated from the scattering angle of broad peaks around 16° correspond the average intermolecular distances. The estimated Bragg spacings from the observed profiles in both normal and parallel directions should mainly correspond the average intermolecular distances in perpendicular directions to molecular axis of 5CB. The larger Bragg spacing of LC in parallel direction can be explained by the consideration that LC molecules were strongly bounded by PI chains in parallel direction with longer interchain spacings. Estimated Bragg spacings in both directions decreased as increasing film thickness. Decreasing of difference of Bragg spacing between parallel and normal direction was also observed, and Bragg spacings seems to approach that of the LC film directly deposited on Si substrate. Estimated Bragg spacing in parallel and normal direction seem extrapolate to those of rubbed polymide film. The behaviors of LC described above suggest that LC molecules should be strongly bounded by rubbed polyimide film, and that LC molecules should be in the similar periodicity of rubbed PI. As the distance from the alignment film, the effect of the alignment film become weaker and the intermolecular spacing of the 5CB come close to the intrinsic intermolecular spacing. Decreasing width of the peaks around 16° with thickness increasing is considered to indicate that lower LC ordering at interface.

4. Conclusion

We developed new method for characterizing molecular distribution in very thin liquid crystal layer (5 nm–) evaporated onto rubbed polyimide film. The diffraction peaks corresponded to intermolecular correlation perpendicular to longitudinal axis of 5CB and the clear anisotropic distribution of a liquid crystal molecular in thin layer was successfully observed used by grazing-incidence X-ray diffraction (GIXD). The liquid crystal layer was formed by heat evaporation onto the rubbed alignment film. X-Ray reflectivity measurements showed that thicknesses of the rubbed alignment film was 100.9 nm and those of the liquid crystal layer were 8.9 nm for 10 min and 38.5 nm for 40 min and liner relation between the layer thickness of the 5CB and evaporation time was observed. In the surface sensitive in-plane diffraction, we found that the Bragg spacing and ordering estimated from the diffraction peak position and width depend on the film thickness of the 5CB film. In the vicinity of the alignment film, the intermolecular spacing correlation perpendicular to longitudinal axis of the 5CB molecule is expanded by the alignment film and the ordering of the 5CB are not so high. As the distance from the alignment film the spacing come close to the intrinsic intermolecular spacing.

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References

[1] I. Hirosawa, T. Koganezawa, and T. Sakai, “Effect of rubbing on polymers for liquid crystal alignment film studied by grazing-incidence X-ray diffraction and reflection ellipsometry,” IEICE Trans. Electron., vol.E90-C, no.11, pp.2070–2075, Nov. 2007.

[2] I. Hirosawa, T. Koganezawa, and T. Sakai, “Effects of rubbing condition and soaking time on surface crystallization of rubbed polyimide film by soaking into acetone,” IEICE Trans. Electron., vol.E91-C, no.10, pp.1593–1598, Oct. 2008.

[3] T. Koganezawa, I. Hirosawa, and T. Sakai, “Dependence of kind of solvents for washing on surface of rubbed polyimide film,” IEICE Trans. Electron., vol.E91-C, no.10, pp.1587–1592, Oct. 2008.

[4] L.G. Parratt, “Surface studies of solids by total reflection of X-rays,” Phys. Rev., vol.95, no.3, pp.359–369, July 1954.

[5] R.M. Richardson and S.J. Roser, “X-ray reflectivity from insoluble monolayers spread on aqueous subphases,” Liq. Cryst., vol.2, no.6, pp.797–814, Nov. 1987.

[6] P.S. Pershan, A. Braslau, A.H. Weiss, and J. Als-Nielsen, “Smectic layering at the free surface of liquid crystals in the nematic phase: X-ray reflectivity,” Phys. Rev. A, vol.35, no.11, pp.4800–4813, June 1987.

[7] R. Holyst, D.J. Tweet, and L.B. Sorensen, “Fluctuations in thin smectic-*A* films,” Phys. Rev. Lett., vol.65, no.17, pp.2153–2156, Oct. 1990.

[8] D.E. Savage, J. Kleiner, N. Schimke, Y.-H. Phang, T. Jankowski, J. Jacobs, R. Kariotis, and M.G. Lagally, “Determination of roughness correlations in multilayer films for x-ray mirrors,” J. Appl. Phys., vol.69, no.3, pp.1411–1424, Feb. 1991.

[9] B.J. Factor, T.P. Russell, and M.F. Toney, “Surface-induced ordering of an aromatic polyimide,” Phys. Rev. Lett., vol.66, no.9, pp.1181–1184, March 1991.

[10] B.J. Factor, T.P. Russell, and M.F. Tony, “Grazing incidence X-ray scattering studies of thin films of an aromatic polyimide,” Macromolecules, vol.26, pp.2847–2859, 1993.

[11] M.F. Toney, T.P. Russell, J.A. Logan, H. Kikuchi, J.M. Sands, and S.K. Kumar, “Near-surface alignment of polymers in rubbed films,” Nature, vol.374, no.6524, pp.709–710, April 1995.

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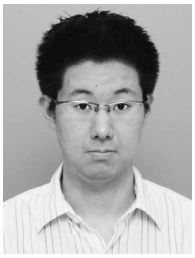

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