Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

MULTIPLE SURFACE PLASMON EXCITATIONS AND NANOSTRUCTURED DEVICES OF ORGANIC ULTRATHIN FILMS

Futao Kaneko [a], Keizo Kato [a], Kazunari Shinbo [a] & Takashi Wakamatsu [b]

[a] Department of Electrical and Electronic Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan and Center for Transdisciplinary Research, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

[b] Dept.of Electrical Eng., Ibaraki National College of Technology, Nakane 866, Hitachinaka 312-8508 Japan

Version of record first published: 15 Jul 2010

To cite this article: Futao Kaneko, Keizo Kato, Kazunari Shinbo & Takashi Wakamatsu (2003): MULTIPLE SURFACE PLASMON EXCITATIONS AND NANOSTRUCTURED DEVICES OF ORGANIC ULTRATHIN FILMS, Molecular Crystals and Liquid Crystals, 407:1, 63-72

To link to this article: http://dx.doi.org/10.1080/744819014

Mol. Cryst. Liq. Cryst., Vol. 407, pp. 63/[459]–72/[468], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390263820

Taylor & Francis
Taylor & Francis Group

MULTIPLE SURFACE PLASMON EXCITATIONS AND NANOSTRUCTURED DEVICES OF ORGANIC ULTRATHIN FILMS

Futao Kaneko, Keizo Kato, and Kazunari Shinbo*
Department of Electrical and Electronic Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan and Center for Transdisciplinary Research, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

Takashi Wakamatsu
Dept.of Electrical Eng., Ibaraki National College of Technology, Nakane 866, Hitachinaka 312-8508 Japan

Surface plasmon (SP) excitations have been investigated in the attenuated total reflection (ATR) Kretschmann configuration of prism/metal/organic ultrathin films. Structure and optical properties of organic ultrathin films have been evaluated using the ATR measurement due to SP excitations. Recently, emission light through the prism was observed using direct irradiation of a laser beam from air to the organic films, that is, reverse irradiation. The emission spectra strongly depended upon the emission angles through the prism and were caused by multiple SP excitations. The emission properties also depend upon structure of metal and organic thin films, dye molecules, separation between metal and molecules, molecular interaction, and so on. It is thought that the phenomenon is useful for application to new devices utilizing multiple SP excitations, and nanostructured devices of organic films using multiple SP excitations are described.

Keywords: attenuated total reflection; emission; Kretschmann configuration; organic thin film; surface plasmon excitation

This work was partly supported by Grant-in-Aid for Scientific Research from the Japan Society of Promotion Science.

*Corresponding author. Tel.: +81-25-262-6741, Fax: +81-25-262-6741, E-mail: fkaneko@eng.niigata-u.ac.jp

1. INTRODUCTION

The attenuated total reflection (ATR) method using surface plasmon (SP) excitations, that is, the surface plasmon resonance (SPR) method is quite useful for evaluation of ultrathin films and sensing, since resonant SP excitations are strongly influenced by conditions of surfaces [1]. ATR measurements have been reported that evaluate structure and optical properties of organic ultrathin films on metal ultrathin films [2–5] and as one of sensing methods [6,7]. The ATR methods have been also investigated for device applications of organic ultrathin films, because of strong optical absorption and strong electric fields due to SP excitations [8,9].

Recently, emission light at a resonant angle region of SP excitations was observed through the prism in the ATR Kretschmann configuration, when metal ultrathin films on the prism or organic ultrathin films on metal films were directly irradiated from air by a laser beam [10–12]. Emission light through the prism was not monochromatic for organic dye films, but the spectra changed with emission angles where the emission light was measured through the prism [12–17]. The emission properties corresponded to the resonant conditions of SPs in the Kretschmann configuration, and it is considered that multiple SPs were induced by means of excitation of organic dye films by a laser beam, that is, reverse irradiation [12–17].

In this study, emission light properties due to multiple SP excitations have been investigated in details for various nanostructured organic films using the ATR method and the reverse irradiation in the Kretschmann configuration.

2. EXPERIMENTAL DETAILS

Various organic thin films, arachidic acid (C20) Langmuir-Blodgett (LB) films, merocyanine (MC) LB films, hetero LB films of MC and crystal violet (CV), and spin-coated polyvinylcarbazole (PVK) films with cyanine dye (CY) were deposited on microscopic cover glasses covered with vacuum evaporated metal thin films. Details of LB films have been reported elsewhere [17]. MC and CY are photosensitizing organic dyes showing photoluminescence (PL). CV (NKX-392), MC (NK2684) and CY (NK1533) were purchased from Hayashibara biochemical Lab., Inc. C20 has no optical absorption and is one of dielectric materials, and the thickness of the C20 monolayer was 2.76 nm [4]. CY at 10 wt% was dispersed in spin-coated PVK films and the thickness of the film used in this study was about 19 nm. Evaporated Ag and Al thin films of about 50 nm and 15 nm thick, respectively, were used as the SP active layers.

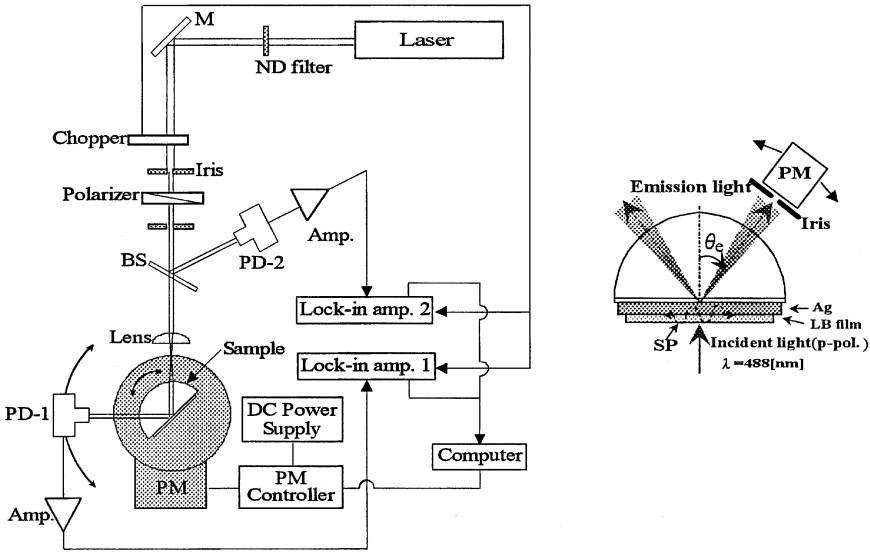

FIGURE 1 An ATR measuring system (a) and the reverse irradiation method (b) in the Kretschmann configuration.

Figures 1(a) and (b) show an ATR measuring system and the reverse irradiation method in the Kretschmann configuration, respectively. A complete description has been reported elsewhere [17]. In the ATR measurement, reflectance intensity to incident one, that is, the ATR signal was measured as a function of the incident angle, θ_i, of the laser beam. In this measurement, Ar^+ lasers ($\lambda = 488.0$ nm and 514.5 nm) and He-Ne lasers ($\lambda = 594.1$ nm and 632.8 nm) were used. In the reverse irradiation method as shown in Figure 1(b), samples were irradiated at the vertical incident angle by a p-polarized Ar^+ laser beam at 488 nm. Emission light through the prism was observed as a function of emission angle, θe, where the light was observed [12–17]. Spectra of the emission light were measured with and without a sharp cut filter below about 520 nm at various emission angles.

3. RESULTS AND DISCUSSION

3.1. ATR and Emission Properties in the Reverse Irradiation

Figure 2 shows ATR properties at 488 nm for Ag film, Ag/C20 (6 layers)/MC (2 layers) and Ag/C20 (6 layers)/MC (8 layers) films. Minima due to resonant excitations of SP were observed in the ATR properties. The

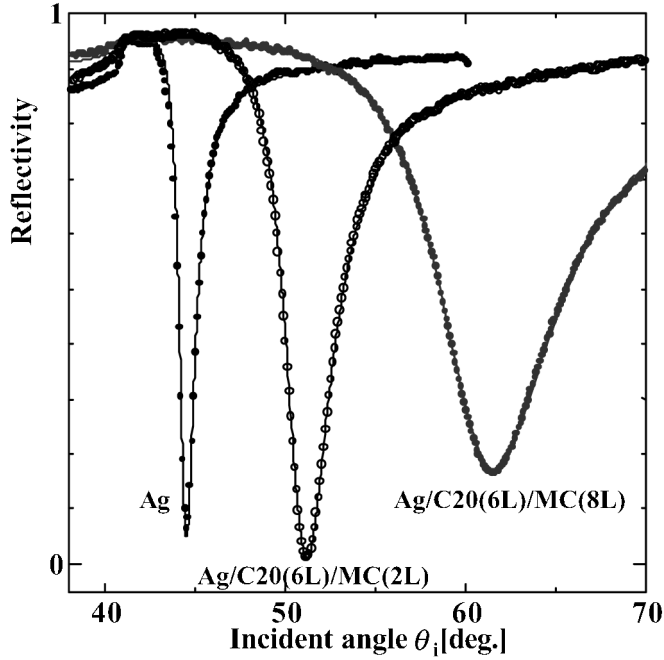

FIGURE 2 ATR properties at 488 nm for Ag film, Ag/C20 (6 layers)/MC (2 layers) and Ag/C20 (6 layers)/MC (8 layers) films.

resonant angles (θ_{SP}) of the SP at 488 nm were about 44°, 51° and 61° for Ag film, Ag/C20 (6 layers)/MC (2 layers) and Ag/C20 (6 layers)/MC (8 layers) films, respectively. Figure 3(a) and (b) show emission light in the reverse irradiation without and with a sharp cut filter below about 520 nm, respectively. The emission light without the filter in Figure 3(a) showed the peaks at about 44°, 50° and 60° that were the same angles as the resonant ones. The emission light contained mainly the wavelength of the laser. Emission light from the Ag films had only the laser wavelength of 488 nm and was not observed using the filter. However, emission peaks with the filter in Figure 3(b) were observed at about 44° and 47° for Ag/C20 (6 layers)/MC (2 layers) and Ag/C20 (6 layers)/MC (8 layers) films, respectively, and the spectra had the main peak at about 600 nm.

Figures 4(a) and (b) show ATR properties at various laser wavelengths and emission spectra at various emission angles using the reverse irradiation at 488 nm for the Ag/C20 (2 layers)/MC (16 layers) LB thin film [17]. The relation between the θ_{SP} and the wavelengths was caused by a dispersion property of SP in the Kretschmann configuration. The spectra in Figure 4(b) strongly depended on the emission angles and were related to

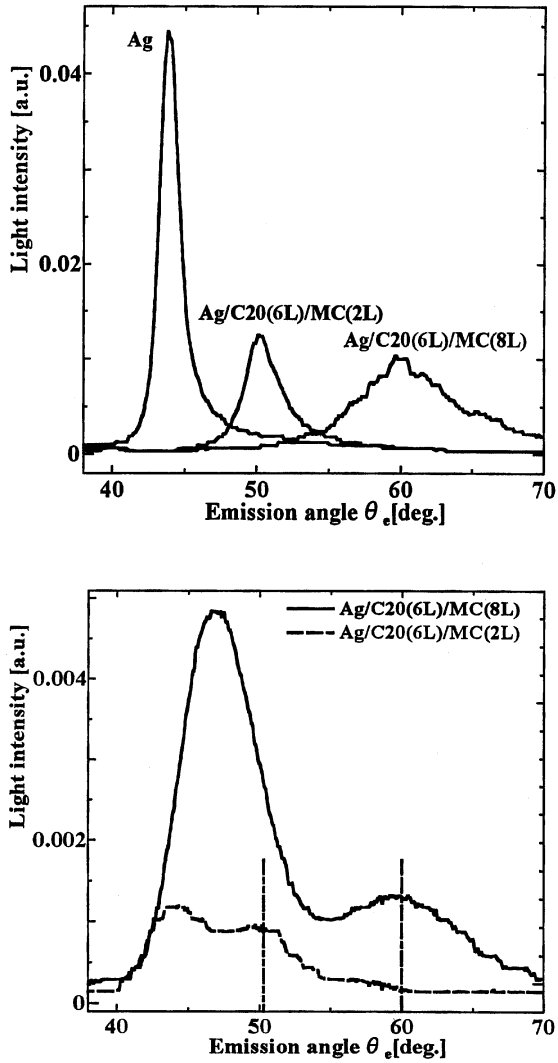

FIGURE 3 Emission light in the reverse irradiation without (a) and with a sharp cut filter below about 520 nm (b).

the PL property of the MC LB films [17]. Each spectrum almost corresponded to a part of the PL spectrum of the MC LB films showing a peak at about 600 nm [17].

The dispersion property of the SPs calculated from the emission peaks in Figure 4(b) was compared with the calculated one from the ATR

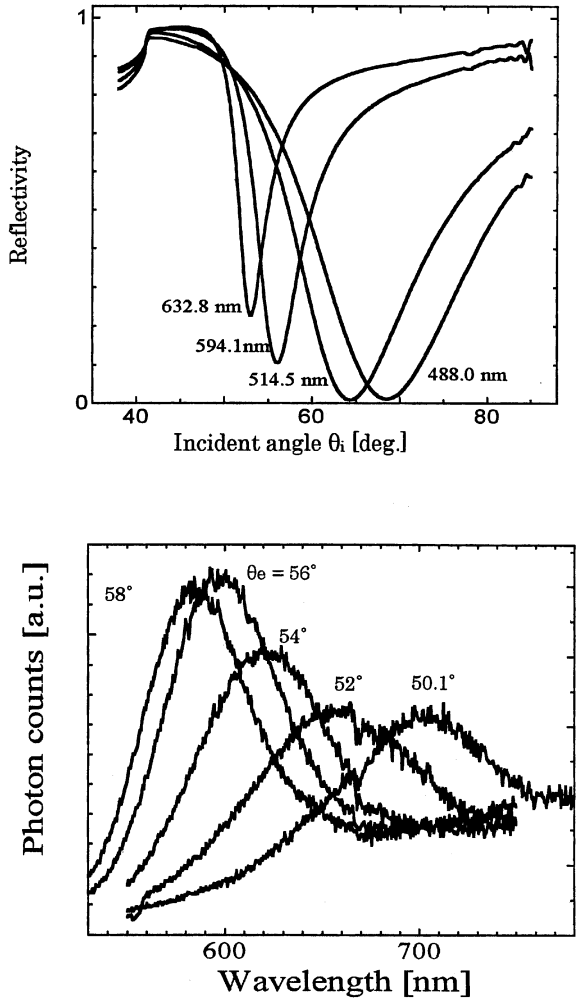

FIGURE 4 ATR properties at various laser wavelengths (a) and emission spectra at various emission angles using the reverse irradiation at 488 nm (b) for the Ag/C20 (2 layers)/MC (16 layers) LB thin film.

properties in Figure 4(a). Figure 5 shows the dispersion properties between the wavenumber, k_x, in the propagating direction of SPs and the angular frequency, ω. The dispersion property of the emission light agreed well to one of the ATR measurements [17]. It was thought that multiple SPs were simultaneously excited by the reverse irradiation and the emission light was generated due to the dispersion property of SP in the Kretschmann ATR configuration. Similar emission light through the

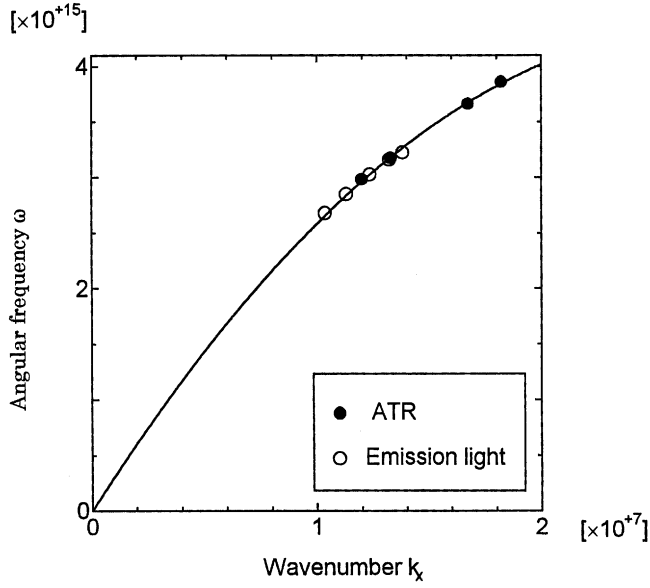

FIGURE 5 Dispersion properties ($k_x - \omega$ plot) of SPs calculated from the emission light and the ATR measurements.

prism has been reported for Ag/Rhodamine-B LB films [12–16]. These emission spectra also depended upon organic dye molecules and the structures in the configuration [12–17]. It is tentatively estimated that polarizations of excited organic dye molecules on the metal thin film induce vibrations of free electrons at the metal surface producing multiple SPs [17].

Figure 6 shows emission spectra for Ag/C20 (2 layers) /hetero LB film (16 layers) of MC and CV at various emission angles in the reverse irradiation. MC and CV LB films were alternately deposited and the total layers were 16 after two layers of C20 LB films were deposited on silver coated glass substrate. A complete description has been reported elsewhere [17]. There was no light emission below approximately 600 nm and the spectra were distributed around 700 nm as shown in Figure 5. Since the spectra in Figure 5 are different from the ones in Figure 4(b), the spectra were not due to MC molecules, but to CV molecules. No light emission from the prism/Ag/CV LB film without MC molecules was observed in the reverse irradiation. Therefore, it was thought that this phenomenon was caused by an energy transfer from MC to CV, such as a dipole-dipole interaction [17].

Emission properties in the reverse irradiation also depended upon structure of metal and organic thin films, dye molecules, separation

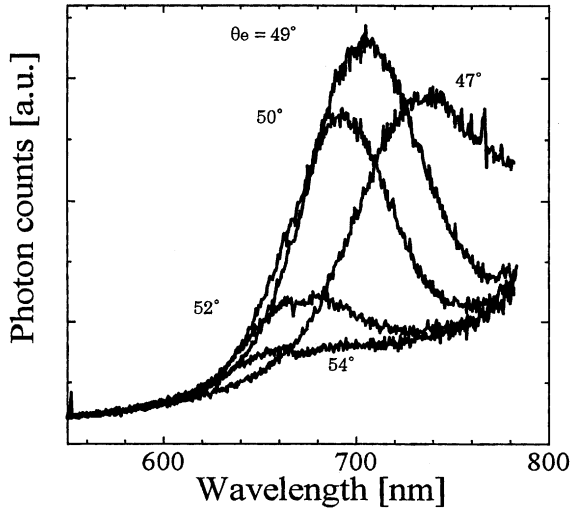

FIGURE 6 Emission spectra for Ag/C20 (2 layers) /hetero LB film (16 layers) of MC and CV.

between metal and molecules, molecular interaction, and so on. It is thought that the phenomenon is useful for application to new devices utilizing multiple SP excitations

3.2. Emission Light Due to Multiple SP Excitations and New Devices

Figure 7 shows a schematic diagram of the emission phenomenon due to multiple SP excitations. It is thought that the SP emission phenomenon involves the following processes: (1) multiple SP are induced by polarizations of excited organic dye molecules on metal thin films and/or by the surface roughness in the laser irradiation, (2) propagating on the metal surface, and (3) light that is converted from propagating multiple SPs is emitted at the resonant SP conditions in the Kretschmann configuration due to film properties and/or roughness of the films [17].

This phenomenon will be used as a new sensing technique and may be used as a device with light emission of selectable colors [17]. If we can control whichever of the three processes, emission light can be modulated in the spectra and/or in the emission angle and this phenomenon will be utilized for a signal processing device. Figure 8 shows an example that the emission light has been changed for the spin-coated PVK film with CY before and after heat treatment at 100°C for 20 min. The emission property in the emission angle varied after the heat treatment. Thus it is thought

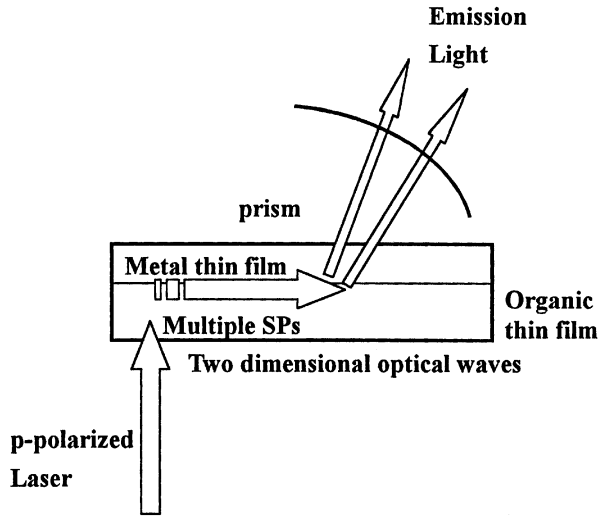

FIGURE 7 A schematic diagram of the emission phenomenon due to multiple SP excitations.

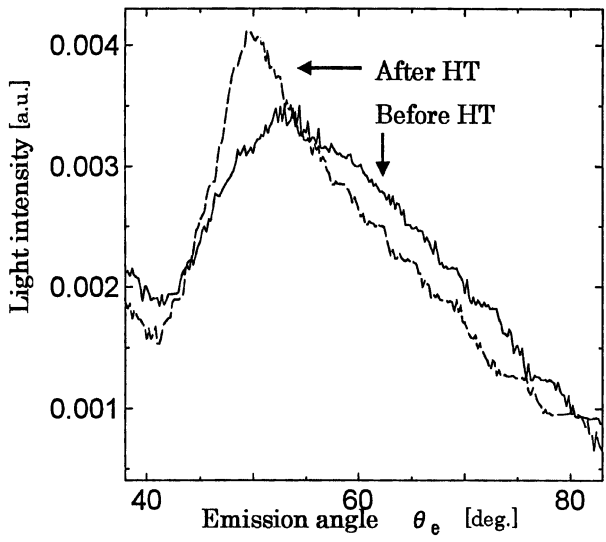

FIGURE 8 An example of the emission light before and after heat treatment at 100°C for 20 min for the spin-coated PVK film with CY.

that the phenomenon due to multiple SP excitations is very useful for device applications.

4. CONCLUSIONS

Emission light through the prism has been investigated using the reverse irradiation. The emission properties strongly depended upon the emission angles, dye molecules, molecular interaction and structure of thin films and were caused by multiple SP excitations. It is thought that the phenomenon is useful for application to new nanostructured devices utilizing multiple SP excitations.

REFERENCES

[1] Agranovich, V. M. & Mills, D. L. (eds.), (1982). *Surface Polaritons*, North-Holland, Amsterdam.
[2] Kaneko, F., Honda, S., Fukami, T., Kato, K., Wakamatsu, T., Shinbo, K., & Kobayashi, S. (1996). *Thin Solid Films*, *417*, 284–285.
[3] Kato, K., Saiki, H., Okuchi, H., Kaneko, F., Wakamatsu, T., Shinbo, K., & Kobayashi, S. (1996). *Thin Solid Films*, *420*, 284–285.
[4] Aoki, Y., Kato, K., Shinbo, K., Kaneko, F., & Wakamatsu, T. (1998). *IEICE Trans. Electron.*, E81-C 1098.
[5] Baba, A., Kaneko, F., Shinbo, K., Kato, K., Kobayashi, S., & Wakamatsu, T. (1998). *Jpn. J. Appl. Phys.*, *37*, 2581.
[6] Casalini, R., Wilde, J.N., Nagel, J., Oertel, U., & Petty, M.C. (1999). *Sensors and Actuators*, *B57*, 28.
[7] Kato, K., Dooling, C.M., Shinbo, K., Richardson, T.H., Kaneko, F., Tregonning, R., Vysotsky, M.O., & Hunter, C.A. (2002). *Colloids and Surfaces A, Physicohem. and Eng. Aspects*, *811*, 198–200.
[8] Wakamatsu, T., Saito, K., Sakakibara, Y., & Yokoyama, H. (1997). *Jpn. J. Appl. Phys.*, *36*, 155.
[9] Shinbo, K., Ebe, T., Kaneko, F. Kato, K., & Wakamatsu, T., (2000). *IEICE Trans. Electron.*, E83-C 1081.
[10] Pockrand, I., Brillante, A., & Möbius, D. (1980). *Chemical Physics Lett.*, *69*, 499.
[11] Kume, T., Hayashi, S., & Yamamoto, K. (1996). *Materials Science & Engineering*, *171*, A217/218.
[12] Nakano, T., Kobayashi, H., Shinbo, K., Kato, K., Kaneko, F., Kawakami, T., & Wakamatsu, T. (2001). *Mat. Res. Soc. Symp.*, *660*, JJ8.35.1.
[13] Nakano, T., Wakamatsu, T., Kobayashi, H., Kaneko, F., Shinbo, K., Kato, K., & Kawakami, T. (2001). *Mol. Cryst. Liq. Cryst.*, *370*, 265.
[14] Kato, K., Terakado, M., Shinbo, K., Kaneko, F., & Wakamatsu, T. (2001). *Thin Solid Films*, *393*, 97.
[15] Nakano, T., Kobayashi, H., Kaneko, F., Shinbo, K., Kawakami, K., & Wakamatsu, T. (2001). *IEE Japan Trans.*, *121-A*, 683.
[16] Kaneko, F., Nakano, T., Terakado, M., Shinbo, K., Kato, K., & Wakamatsu, T. (2002). *Mol. Cryst. Liq. Cryst.*, *377*, 53.
[17] Nakano,T., Terakado, M., Shinbo, K., Kato, K., Kaneko, F., Kawakami, T., & Wakamatsu, T. (2002). *Jpn. J. Appl. Phys.*, *41*, 4B 2774.