Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Organic/Inorganic Heterostructures of Phthalocyanine and Cadmium Selenide by Molecular Beam Deposition

Yasuo Imanishi [a] , Shingo Ishihara [a] & Tomoyuki Hamada [a]

[a] Hitachi Research Laboratory, Hitachi Ltd., 7-1-1, Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12, JAPAN

Version of record first published: 04 Oct 2006

To cite this article: Yasuo Imanishi, Shingo Ishihara & Tomoyuki Hamada (1998): Organic/Inorganic Heterostructures of Phthalocyanine and Cadmium Selenide by Molecular Beam Deposition, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 315:1, 111-116

To link to this article: http://dx.doi.org/10.1080/10587259808044318

Mol. Cryst. Liq. Cryst., 1998, Vol. 315, pp. 111–116
Reprints available directly from the publisher
Photocopying permitted by license only

Organic/Inorganic Heterostructures of Phthalocyanine and Cadmium Selenide by Molecular Beam Deposition

YASUO IMANISHI, SHINGO ISHIHARA, and TOMOYUKI HAMADA
Hitachi Research Laboratory, Hitachi Ltd., 7-1-1, Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12, JAPAN

Novel organic/inorganic heterostructures composed of phthalocyanato tin(IV) dichloride ($SnCl_2Pc$) and cadmium selenide (CdSe) were fabricated by using of molecular beam deposition (MBD). By means of some structural analyses (XRD, TEM), the crystalline and multilayered structure of the deposited film was verified. Linear and nonlinear optical properties of the heterostructure were also measured, by which the third-order nonlinear optical susceptibility and two components of response time for the multilayers was estimated as 1.8×10^{-8} esu, less than 80 fsec, and 5 psec, respectively. The processability and its good optical performance of this organic/inorganic heterostructure is exploring toward a new kind of optoelectronic switching material.

Keywords: organic/inorganic heterostructures; phthalocyanato tin(IV) dichloride ($SnCl_2Pc$); cadmium selenide (CdSe); molecular beam deposition (MBD); multilayered structure; optical Kerr effect

INTRODUCTION

Recently much attention have been paid on the development of new third-order nonlinear optical materials for their potential capabilities to all-optical devices (optical switch, clock, *etc.*) for optical terabits telecommunications. Among the many nonlinear optical materials π-electron conjugated organic compounds, like polydiacetylene, phthalocyanine, and J-aggregates of cyanine dye molecules, are greatly promising[1]. However, more drastic improvement of optical nonlinearity is needed to achieve compact all-optical switch of semiconductors such as InGaAs MQW with slow switching speed. For this purpose we have

been studying on optical nonlinearities in organic molecules[2, 3]. Tin dicholophthalocyanine ($SnCl_2Pc$) indicated unique optical spectrum and high performance of nonlinearity[3]. In this paper, we will introduce our further results on $SnCl_2Pc$ and inorganic semiconductor cadmium selenide (CdSe) heterostructures by molecular beam deposition (MBD) method.

EXPERIMENTALS

A special MBD equipment[4] was adopted to fabricate $SnCl_2Pc$ and CdSe heterostructure. A glass substrate was adopted and its temperature was kept at 23 °C during deposition. The structures of the multilayer were investigated by several techniques such as X-ray diffraction (XRD) and transmission electron microscopy (TEM), and its effects on optical properties such as absorption spectra and optical Kerr effect were also estimated. As for an optical Kerr measurement a mode locked titan sapphire laser with a regenerative amplifier system (wavelength 790 nm, repetition 1 kHz, pulse energy 0.8 mJ, pulse width 130 fsec) was used as a light source[4].

RESULTS AND DISCUSSIONS

At first different vapor pressure and thermal stability of the two materials should be considered. Figure 1 shows the cross-sectional TEM view of the multilayers, $(CdSe/SnCl2Pc)_{20}$/glass. Twenty numbers of periodic layers with dark (CdSe) and bright ($SnCl_2Pc$) contrast can be observed. The unit layer thickness (CdSe+$SnCl_2Pc$) is ca.10 to 15 nm, and the total thickness 225 nm. Lattice images of CdSe microcrystals can be seen in the expanded view of the TEM[5]. Figure 2 indicates the small angle XRD of the film, in which sharp diffraction for 9.3 nm corresponding to the unit layer thickness of the thin film and the side peaks toward smaller angle region can be recognized. These facts indicates the MBD film of $SnCl_2Pc$ and CdSe can be regularly multilayered crystalline structure, despite of their different crucible temperature (325 °C for $SnCl_2Pc$ and 625 °C for CdSe). Such layer-by-layer formations of phthalocyanine/naphthalene derivative[6] , phthalocyanine/phthalocyanine[7], or phthalocyanine/SiO_x[8] via vapor deposition technique were verified by several

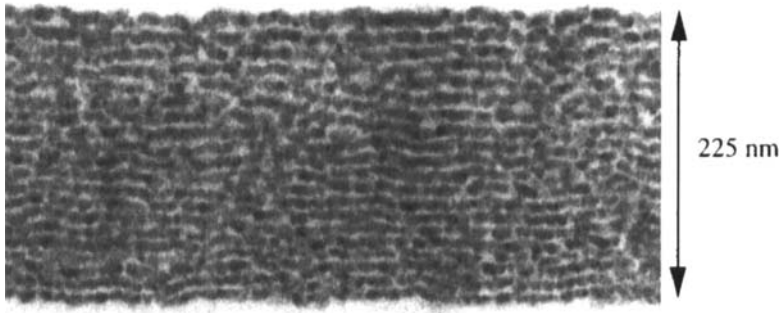

Figure 1 The cross-sectional TEM image of the organic/inorganic multilayers $(CdSe/SnCl_2Pc)_{20}$/glass

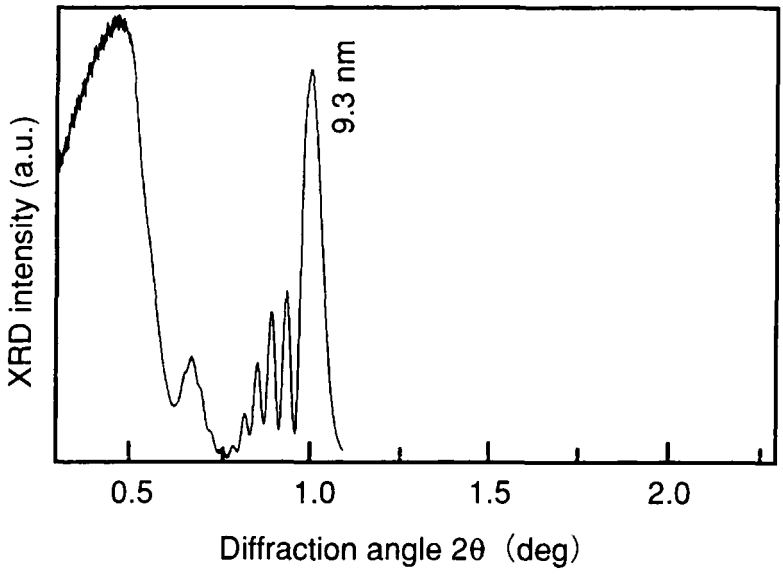

Figure 2 The small angle XRD pattern of the organic/inorganic multilayers $(CdSe/SnCl_2Pc)_{20}$/glass

authors. For this combination, we also succeeded the layered structure fabrication of crystalline molecular and inorganic semiconductor.

In this composite system at least two mesoscopic effects could be expected for the enhancement of nonlinear optical performance, *i. e.*, exciton confinements in inorganic semiconductors and local field effect around organic molecules. Figure 3 shows (a) the absorption spectra of the multilayers and (b) the simple summation of the two spectra for each single layers of the components at 23°C. The phthalocyanine have large absorption (700 to 800 nm) and its peaks at 730 and 760 nm corresponded to molecular π-π^* excitation of phthalocyanine (Q-band). Meanwhile CdSe shows broad interband absorption (shorter than 700 nm). The spectrum for the multilayers seems to be similar band shape to the summed one.

The nonlinear optical susceptibilities of the multilayers were measured by optical Kerr gate method[9]. Figure 4 shows the decay curves of optical Kerr signal for the multilayers and the reference glass (HOYA FD59) at 23°C. For the thin film there are two components of Kerr signal decay. The change of refractive index $\delta n\ (t)$ at time t induced by a pump light pulse with the intensity $I_{\text{pump}}(t)$ is expressed by the following equation.

$$\delta n\ (t) = n_{\text{fast}} I_{\text{pump}}(t) + \frac{n_{\text{slow}}}{\tau} \int_{-\infty}^{\infty} I_{\text{pump}}(t - t')\exp(-t'/\tau)\,dt'$$

Here we assumed the two component of nonlinear refractive index: n_{fast} relaxing within the pulse duration (τ_{pulse}), and n_{slow} with the relaxation time τ longer than τ_{pulse}. As for the reference glass sample, we omitted the slow component. The third-order nonlinear susceptibility $\chi^{(3)}$ of the fast component for the film was estimated by the following equation.

$$\frac{\chi_s^{(3)}}{\chi_r^{(3)}} = \left(\frac{n_{0,s}}{n_{0,r}}\right)^{-1} \left(\frac{T_{0,s}}{T_{0,r}}\right)^{-2} \left(\frac{I_{\text{pump},s}}{I_{\text{pump},r}}\right) \left(\frac{n_{\text{fast},s}}{n_{\text{fast},r}}\right) \frac{\alpha L_r}{\exp(-\frac{1}{2}\alpha L_s)[1 - \exp(-\alpha L_s)]}$$

Here n_0 is linear refractive index, α is absorption coefficient of the film, L is thickness of the film or reference, T_0 is transmittance of the light, and suffix s and r is sample and reference, respectively. The estimated $\chi^{(3)}$ and α is 1.8×10^{-8} esu and 1.0×10^{5} cm^{-1}, almost half of the single layer of $SnCl_2Pc$ (2.7×10^{-8} esu and 2.0×10^{5} cm^{-1}). The value of for CdSe was less than 1×10^{-9}

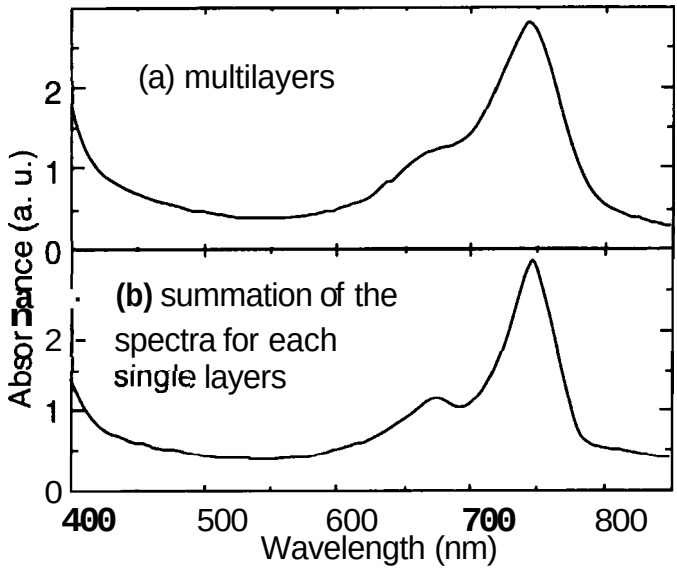

Figure 3 The absorption spectra of (a) the multilayers and (b) summation of the spectra for each single layers

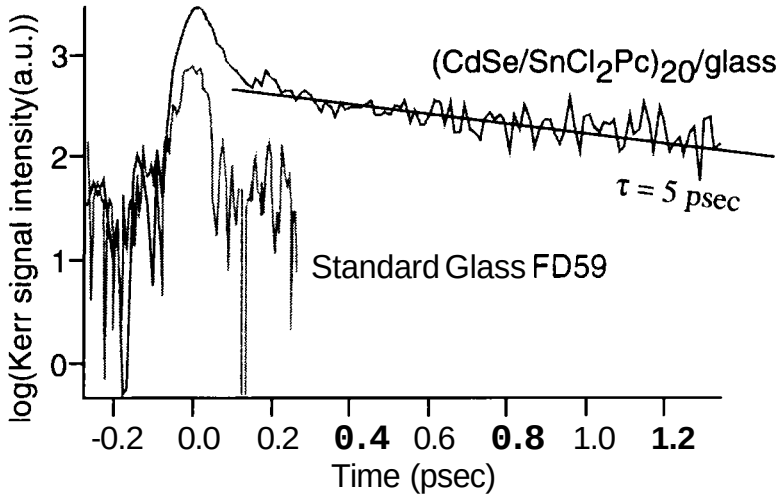

Figure 4 The decay of optical Kerr signal for the multilayers and standard glass FD59

esu. In the light of local field effect, $\chi^{(3)}$ enhancement of organic molecules in high refractive index media was observed[10]. Since in our experiment linear refractive index n_0 of $SnCl_2Pc$ and CdSe is 1.5 and 2.2, respectively, the ratio of dielectric constant $(n_{0,CdSe} / n_{0,SnCl2Pc})^2$ is 2.15 and twice of $\chi^{(3)}$ should be expected. To investigate such local field enhancement of $\chi^{(3)}$ we will need the incident angle dependence of Kerr signal. Or exciton confinement effect of inorganic semiconductor in organics should be detected by the wavelength dependence of $\chi^{(3)}$.

In conclusions, we succeeded the fabrication of organic/inorganic multi-layered structure $(CdSe/SnCl_2Pc)_{20}$/glass by means of MBD. We observed the layer-by-layer structure and also estimated optical Kerr response of the film. The processability and its good optical performance of this organic/inorganic heterostructure is exploring toward a new kind of optoelectronic switching material.

This work was performed by Hitachi Ltd. under the management of Japan High Polymer Center (JHPC) supported by New Energy and Industrial Technology Development Organization (NEDO).

References

[1] Nalwa, H. S. and Miyata, S. (eds.), Nonlinear Optics of Organic Molecules and Polymers, CRC Press (1997).
[2] Imanishi, Y., The Fifth Symposium on Nonlinear Photonics Materials, Extended Abstracts, Japan High Polymer Center, p. 257 (1996).
[3] Ishihara, S., Imanishi, Y., Engel, M. K., and Isogai, M., Extended Abstracts of the 56th Autumn Meeting of the Japan Society of Applied Physics, 28p-R-8, p. 1019 (1995).
[4] Japan High Polymer Center (ed.), Annual R&D Report on Nonlinear Photonic Materials **7**, 292 (1996).
[5] Imanishi, Y., Jpn. J. Appl. Phys., to be published.
[6] Imanishi, Y., Hattori, S., Kakuta, and A., Numata, S., Phys. Rev. Lett. **72**, 2098 (1993).
[7] Nonaka, T., Mori, Y., Nagi, N., Matsunobe, T., Nakagawa, Y., Saeba, M., Takahagi, T., and Ishitani, A., J. Appl. Phys. **73**, 2826 (1993).
[8] Tanaka, J., Awaji, H., Koshioka, M, Nakajima, A., and Nevin, W. A., Appl. Phys. Lett. **61**, 2184 (1992).
[9] Ho, P. P., Picosecond Kerr Gate (Alfano, R. R., ed., Semiconductors Probed by Ultrafast Laser Spectroscopy), Academic Press, p.409 (1984).
[10] Fischer, G. L., Boyd, R. W., Gehr, R. J., Jenekhe, S. A., Osaheni, J. A., and Sipe, J. E., Phys. Rev. Lett. **74**, 1871 (1994).