Multi-Purpose Nonlinear Optical Microscope. Principle and its Applications to Polar Thin Film Observation

© Y. Uesu, N. Kato

Department of Physics, Waseda University
3–4–1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
E-mail: uesu93@mn.waseda.ac.jp

Multi-purpose nonlinear optical microscope is an optical microscope which images 2*D* distribution of the optical second harmonic (SH) waves from a specimen. Image contrast can be obtained either by inhomogeneous distribution of nonlinear optical tensor components or by the interference between SH waves from a specimen and a standard plate. This microscope also functions as a fluorescence (FL) microscope, and SH and FL images can be obtained from same part of a specimen. Absorption and FL spectra from a specific part of a specimen are measured through an optical fiber, which connects an ocular with a polychromator. These functions are especially useful to investigate the *J*-aggregate state of polar dye molecules. Several photographs taken by the microscope revealed the structure of merocyanine dye / arachidic acid mixed monolayer and the role of bridge ions in subphase.

Experiments started in the 1970s for visualizing inhomogeneous distributions in a specimen using the second harmonic (SH) waves which the specimen produces [1,2]. Recent developments of the spatial resolution and sensitivity of Charge Coupled Device (CCD) camera and image processing techniques enable us to obtain more easily high quality images of various kinds of bulk materials and surfaces. We made good use of development of the technology and constructed a multi–purpose nonlinear optical microscope called SHCM and successfully applied it to observations of ferroelectric domain structures [3–5] and periodically inverted domain structures in quasi–phase match devices for frequency–converter [6]. Recently we have installed a Langmuir trough to the SHGM and performed in–situ observations of monolayer molecules at air–water interface, in particular, those of the *J*-aggregate state of polar dye molecules. In this paper, we discuss the principle of the SHGM, describe its structure and show several photographs taken by the SHGM, emphasizing useful application to polar thin film studies.

1. Principle of measurement

The SHGM has some distinctive features: First, it can distinguish areas not only with different magnitude but also different sign of the second–order nonlinear optical tensor component (*d*-tensor). This is especially important to observe anti–parallel ferroelectric domain structures, which have not been observed by usual optical microscopes. Second, SH images of monolayer molecules at air–water interface or on substrate can be obtained with relatively short exposure time. Third, 2*D* fluorescence images can be obtained from the same part of the specimen as in SH image. As the forth feature, quantitative measurements of absorption and fluorescence spectra can be performed in a specific part of a specimen. These are quite useful to study the *J*-aggregate state of polar dye molecules.

When a specimen contains domains with different crystallographic orientations, the anisotropy of *d*-tensor can image the domain structure. The *d*-tensor d_{ijk}, the third-rank polar tensor, connects the nonlinear dielectric polarization component $P_i^{(2\omega)}$ and product of electric fields $E_j^{\omega}E_k^{(\omega)}$ of the incident light wave as follows:

$$P_i^{2\omega} = \varepsilon_0 d_{ijk} E_j^{(\omega)} E_k^{(\omega)}. \quad (1)$$

Therefore, if the crystallographic orientation differs, the intensity contrast Γ is produced by the effective magnitude of *d*-tensor and coherence length l_c of the specimen. An example is the case where d_{311} and d_{333} are concerned as is shown in the case of ferroelectric 90° domain structures in $BaTiO_3$

$$\Gamma = \left(d_{311} l_c(d_{311}) / d_{333} l_c(d_{333})\right)^2, \quad (2)$$

where l_c is defined as $l_c = \lambda/4(n^{(2\omega)} - n^{(\omega)})$ using refractive indeces $n^{(2\omega)}$ and $n^{(\omega)}$ of fundamental and SH waves, respectively.

In the case of ferroelectric anti–parallel domain structures, the magnitude of *d*-tensor is the same but the sign is different for + and − domains and the phase difference of the SH waves produced in these domains are π. Therefore if a standard SHG plate is placed in front of the specimen,

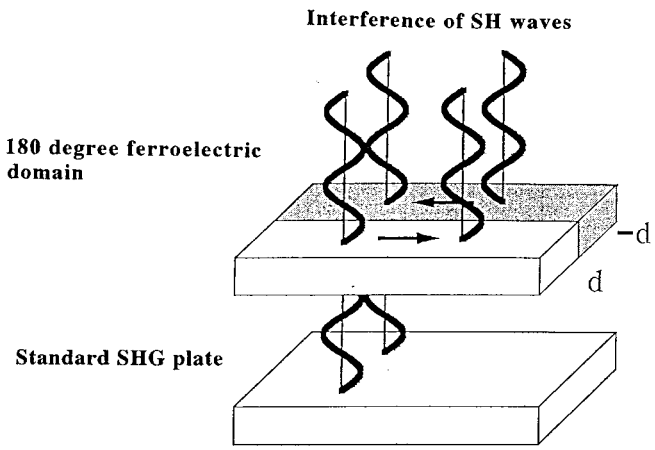

Figure 1. Principle of the SHG microscope for observing anti-parallel ferroelectric domain structures.

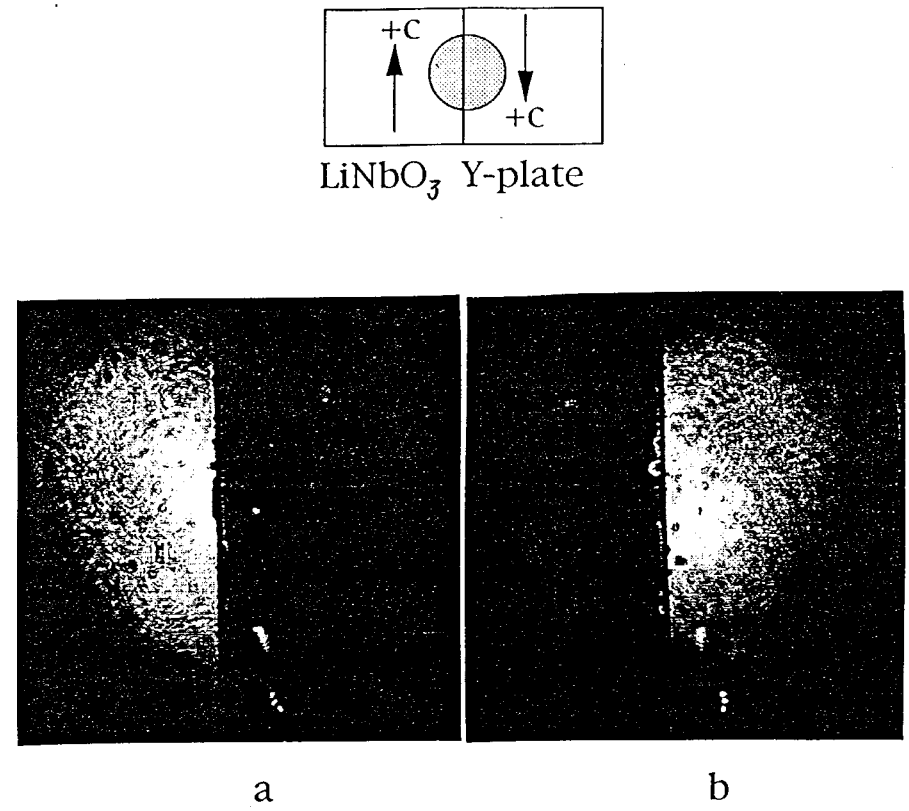

Figure 2. SH images of two *Y*-cut plates of $MgO:LiNbO_3$ with opposite *z* axes. The intensity contrast is reversed by rotating a glass phase plate.

the interference between SH waves from the plate and the specimen can produce the intensity contrast as shown in Fig. 1. In order to get the maximum contrast, the amplitude and phase of SH waves from the SHG plate and one domain of the specimen should be identical. This condition can be realized by inserting a plate generating uniform SH wave and a glass plate and by rotating them to vary the amplitude and phase. Fig 2 shows two *Y*-cut plates of $MgO:LiNbO_3$ with opposite *z* axes. By rotating the glass plate, the contrast of two plates is reversed, which shows clearly the visualization of anti-parallel ferroelectric domain structure by the SHGM.

2. Details of Multi-Purpose Nonlinear Optical Microscope

Schematic illustration of the SHGM is shown in Fig. 3. As a light source, Nd^{3+} : YAG laser (wavelength of 1.06 μm, repetition frequency of 10 Hz, pulse width 20 ns, maximum energy per pulse 200 mJ in front of specimen) is used. The wavelength of the incident laser beam can be varied from 1.2 to 1.3 μm using Forsterite ($Cr^{4+} : Mg_2SiO_2$) laser. Through a half-wave plate, a polarizer, an SHG plate and a glass plate, the incident and frequency-doubled beams enter the specimen. Then the resultant SH wave is selected by filters and its 2*D* distribution is registered by the Integrated CCD camera. When a monolayer of dye molecules is observed, a specially designed Langmuir trough is set up below an objective lens mounted with an IR cut filter.

Fluorescence (FL) images are obtained when the frequency-doubled beam directly impinges a specimen. Thus SHG and FL images from the same part of specimen are compared. An optical fiber connecting an ocular and a polychromator facilitates the measurement of absorption or FL spectra.

3. Observations of Polar Thin Films

3.1. Ferroelectric thin films. Recent development of ferroelectric thin films for the application to non-volatile memory devices is remarkable. FeRAM will replace DRAM in some application fields in very near future. Ferroelectric thin films are fabricated on a substrate by various techniques and its alignment should be properly evaluated. We applied the SHGM to examine the homogeneous alignment of the c-axis of $Ba_2NaNb_5O_{15}$ (BNN) thin film on MgO substrate. Fig. 4 shows the result. When the c axis of BNN is perpendicular to the substrate, vertical incidence of laser beam should produce no SH wave. Fig. 4, *a* shows the existance of SHG region, and further inclination of the specimen generates more homogeneous and more intense SH waves as shown in Fig. 4, *b*. These facts clearly show that the c-axis is inclined in this bright region in Fig. 4, *a*.

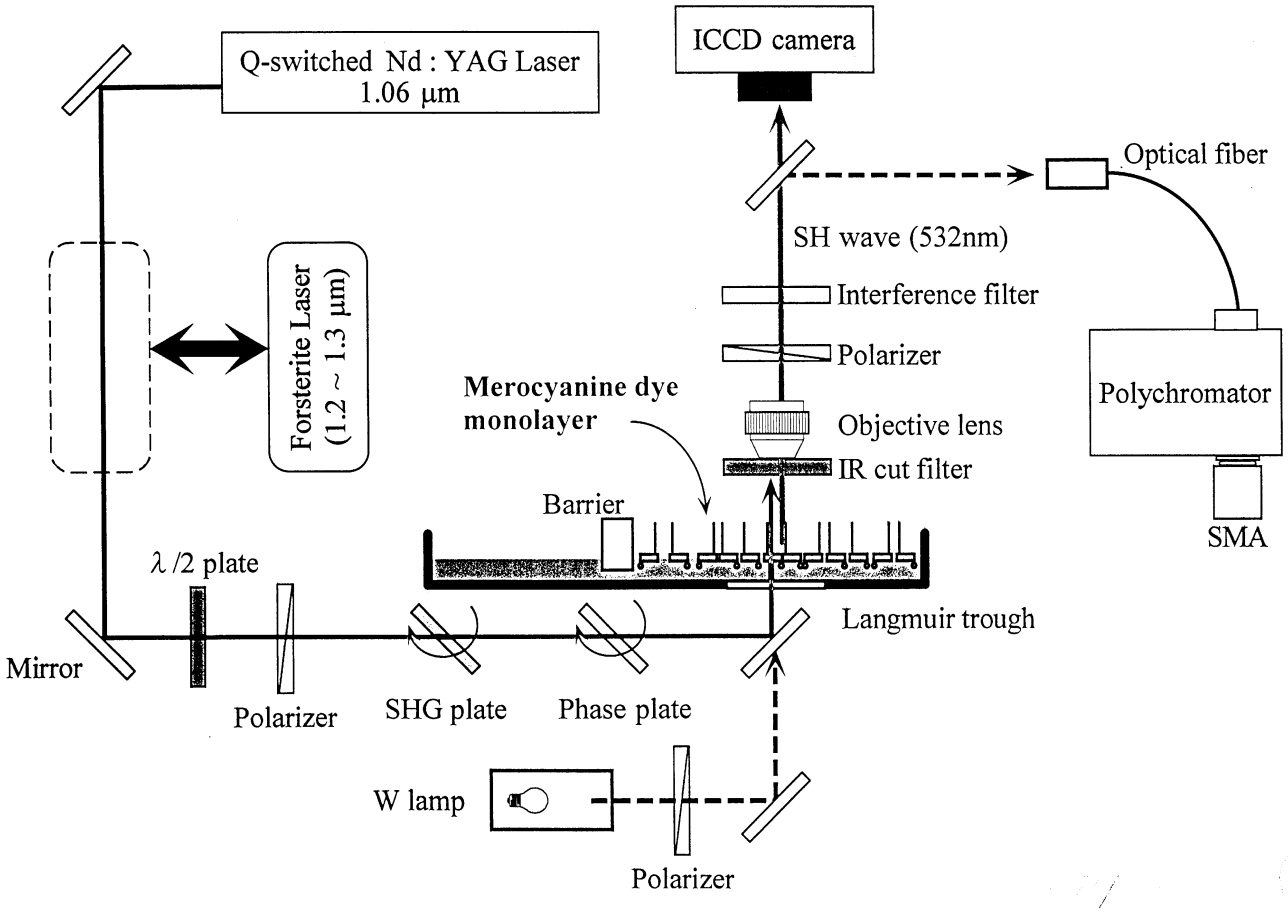

Figure 3. Schematic illustration of the SHGM.

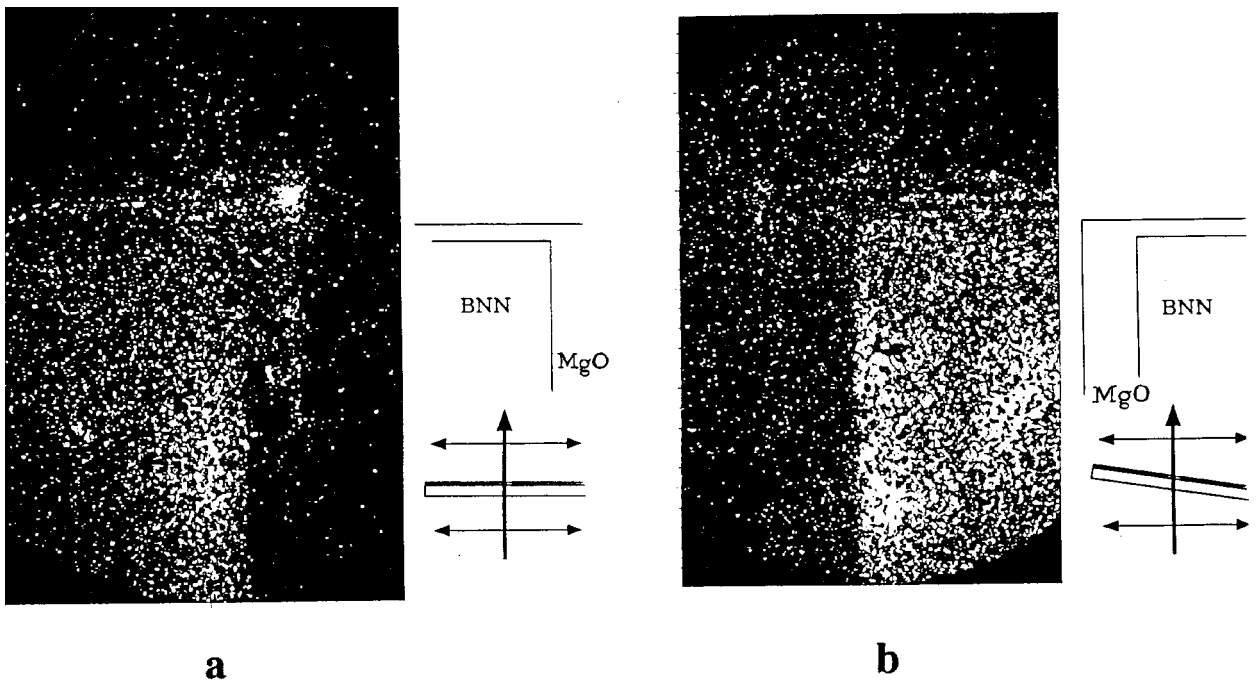

Figure 4. SH images of ferroelectric thin film BNN / MgO. *a* — shows the image with perpendicular incidence of the fundamental laser beam, *b* — image with small inclination of the specimen with respect to the incident direction.

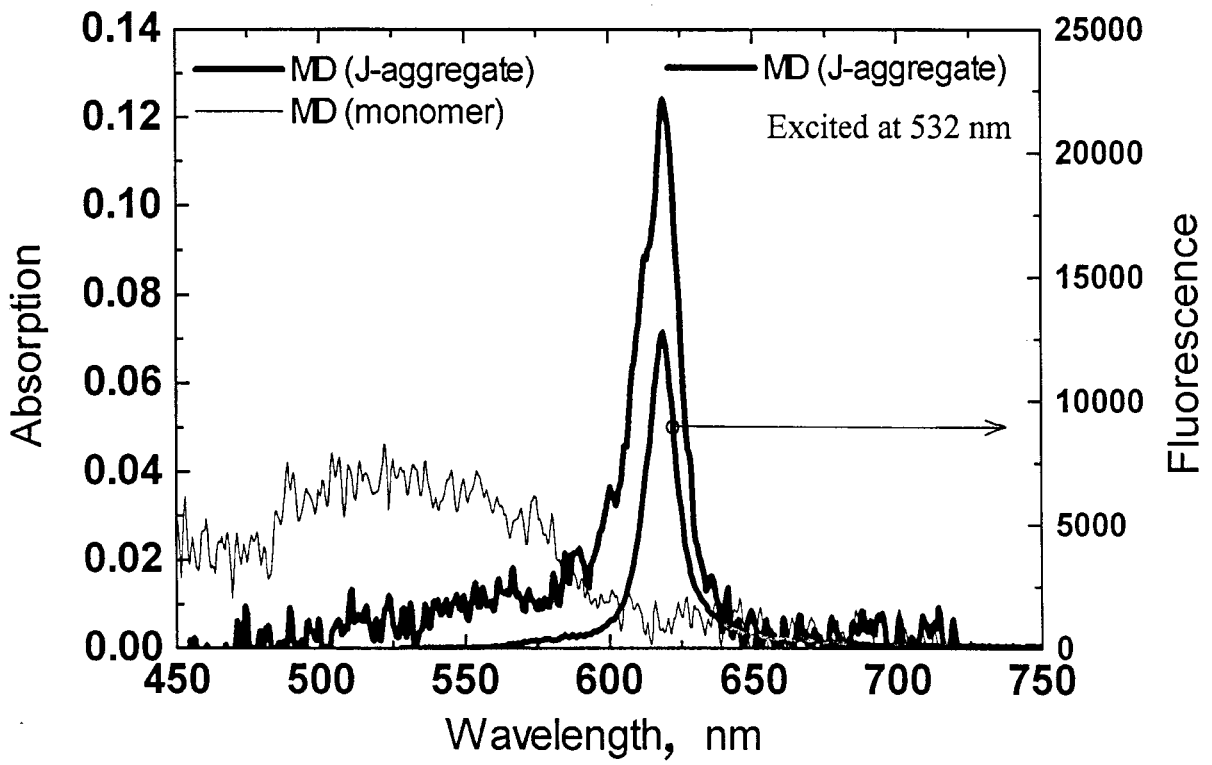

Figure 5. Absorption and fluorescence spectra of *J*-aggregate MD and monomer MD.

3.2. *J*-aggregate of merocyanine dye molecules. A kind of dye molecules is known to make 2*D* assemblage in a regular form. When it is exited by light illumination, the exited part consisting of several molecules forms an exiton, which propagates like a soliton on the molecular assemblage. The exited aggregate is termed the *J*-aggregate [7]. The *J*-aggregate lowers the interaction energy of molecules and manifests characteristic absorption and fluorescence spectra. This state of molecules is considered to be supermolecule and some applications to nonlinear optics and opto-electric transform devices are expected [8].

Using the Langmuir trough we prepared the *J*-aggregate of merocyanine dye (MD) molecules which are used as spectral sensitizators in the photographic process. To stabilize the structure, arachidic acid (AA) molecules were mixed with MD. The *J*-aggregate was formed with special kinds of ion species, NH_4^+, Mg^{2+} or Cd^{2+} in subphase. The formation was verified by absorption and fluorescence spectra as shown in Fig. 5 measured by the SHGM. Fig. 6 shows the SH and FL images of the same part of MD/AA mixed monolayer at air-water interface. Mostly one to one correspondences were obtained in both images, which shows that the *J*-aggregate of MD is SHG active and molecules align along the same direction. The SHG active region (bright in the figure) has a rectangular form and shows anisotropy. The long axis of the rectangle is nearly parallel to a barrier plate which compresses the molecules on water (see Fig. 6). More precise analysis of the polarization dependence shows that the long axis of MD molecules inclined to the long axis of the rectangle region.

Finally, comparing these images with AFM image [9], we obtain a conceptual image of MD/AA mixed monolayer as shown in Fig. 7. It consists of three domains, i.e. the *J*-aggregate of MD, monomer state or collapsed aggregation state of MD and AA regions. These three parts have different heights, which AFM easily distinguishes, but AFM cannot determine polar regions. On the other hand, the SHG image discriminates the polar region where dipole moment of molecule aligns along particular direction, while FL image shows the *J*-aggregate state without knowledge of polar state. Thus complementary observations of the SHGM and AFM is quite useful to study the structure of MD/AA mixed monolayer. It should be also stressed that SHGM revealed the role of ion in subphase. Among the ions used in the present experiment, NH^{4+} produces largest domain size of the *J*-aggregate which is as large as 50 μm long.

Acknowledgements

The authors are grateful to H. Aida, H. Mohri and K. Saito, Waseda University, for their participations to experiments.

The work was supported by the Special Contraction Fund for Promoting Science and Technology, Agency of Science and Technology, Japan.

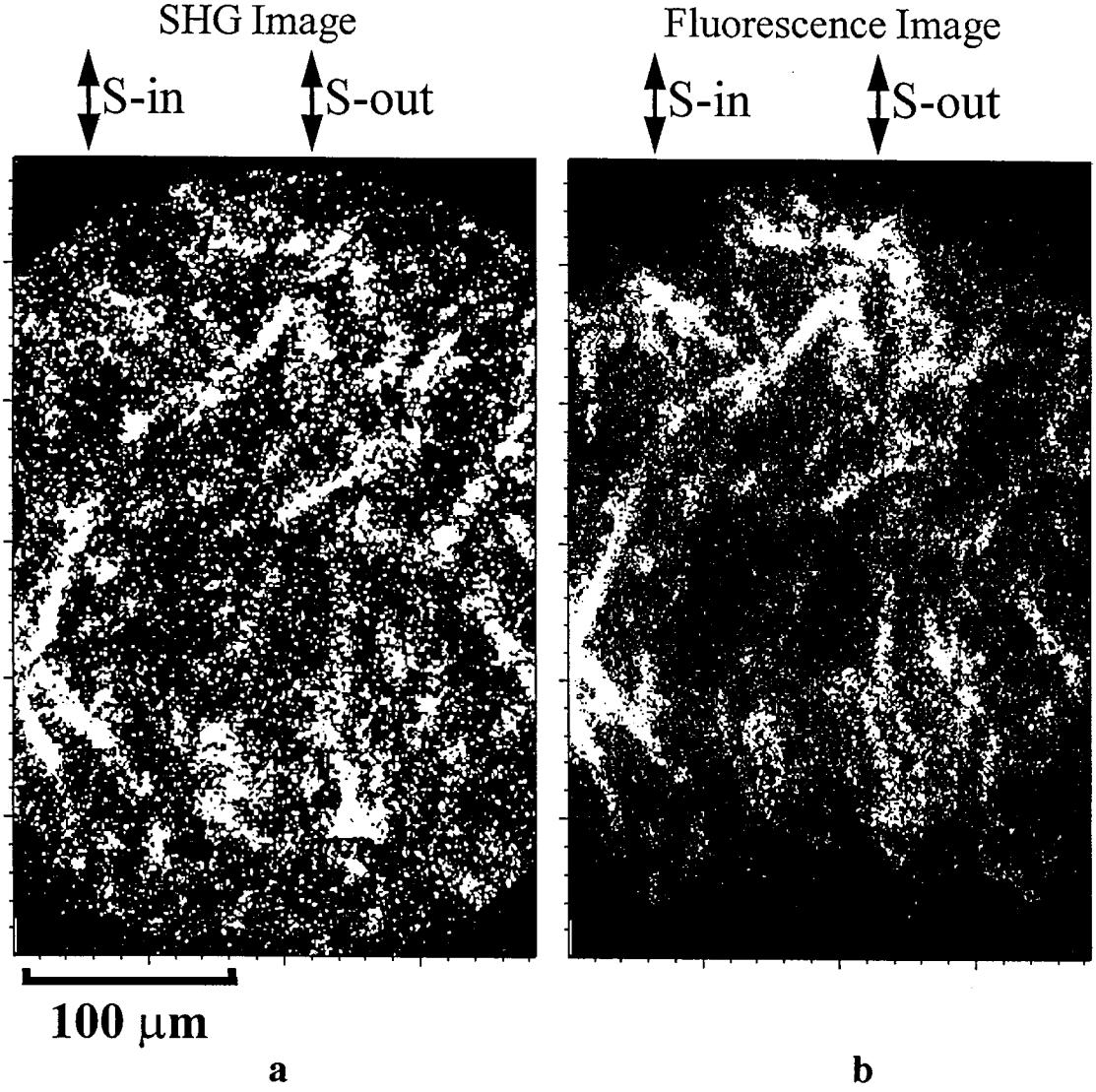

Figure 6. SH and FL images of the same part of MD / AA mixed monolayer at air-water interface.

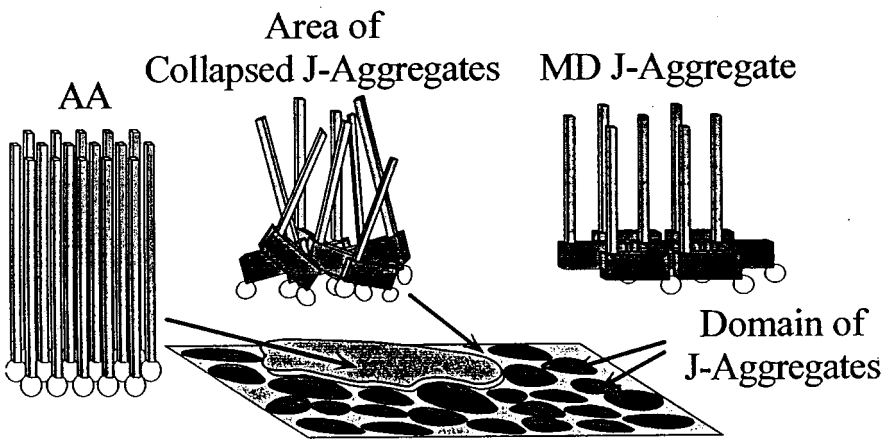

Figure 7. Conceptual image of Md / AA mixed monolayer.

References

[1] R. Hellwarth, P. Christensen. Optics Commun. **12**, 318 (1974).
[2] J.N. Gannaway, C.J.R. Sheppard. Optical and Quantum Electronics **10**, 435 (1978).
[3] Y. Uesu, S. Kurimura, Y. Yamamoto. Applied Physics Lett. **66**, 2165 (1995).
[4] Y. Uesu, S. Kurimura, Y. Yamamoto. Ferroelectrics, **169**, 249 (1995).
[5] Y. Yamamoto, S. Kurimura, Y. Uesu. Applied Optics, **36**, 602 (1997).
[6] S. Kurimua, Y. Uesu. J. Appl. Phys. **81**, 369 (1997).
[7] H. Kuhn, C. Kuhn. J-aggregation / Ed. by T. Kobayashi. World Scientific (1996). P. 1.
[8] A.K. Ghosh, T. Feng. J. Appl. Phys. **49**, 5982 (1978).
[9] N. Kato, H. Aida, K. Saito, Y. Uesu, J. Korean. Phys. Soc. **32**, S1076 (1998).