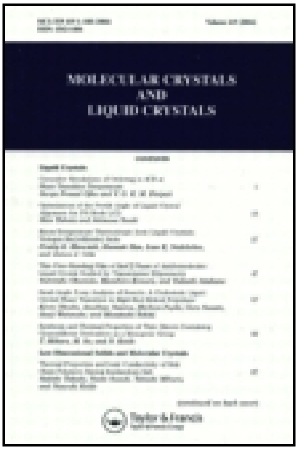

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

SURFACE PLASMON RESONANCE AND EMITTED LIGHT PROPERTIES OF POLYSTYRENE SPHERE FILMS

Kazunari Shinbo [a], Syunsuke Miyabayashi [a], Kazushi Yoshizawa [a], Hidehiko Shimizu [a], Keizo Kato [a], Futao Kaneko [a], Masato Tanaka [b], Takashi Wakamatsu [c] & Rigoberto C. Advincula [d]

[a] Niigata University, Department of Electrical and Electronic Eng., Ikarashi 2-8050, Niigata 950-2181, Japan

[b] Niigata University, Department of Chemistry and Chemical Eng., Ikarashi 2-8050, Niigata 950-2181, Japan

[c] Dept. of Electrical Eng., Ibaraki National College of Tech., Hitachinaka, Japan

[d] Dep. of Chem., Univ. of Houston, 136 Fleming Building, Houston, TX 77204-5003, USA

Version of record first published: 15 Jul 2010

Mol. Cryst. Liq. Cryst., Vol. 407, pp. 73/[469]–80/[476], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390263848

SURFACE PLASMON RESONANCE AND EMITTED LIGHT PROPERTIES OF POLYSTYRENE SPHERE FILMS

Kazunari Shinbo, Syunsuke Miyabayashi, Kazushi Yoshizawa, Hidehiko Shimizu, Keizo Kato, and Futao Kaneko
Niigata University, Department of Electrical and Electronic Eng., Ikarashi 2-8050, Niigata 950-2181, Japan

Masato Tanaka
Niigata University, Department of Chemistry and Chemical Eng., Ikarashi 2-8050, Niigata 950-2181, Japan

Takashi Wakamatsu
Dept. of Electrical Eng., Ibaraki National College of Tech., Hitachinaka Japan

Rigoberto C. Advincula
Dep. of Chem., Univ. of Houston, 136 Fleming Building, Houston, TX 77204-5003, USA

Polystyrene sphere films were fabricated and the optical properties were investigated using surface plasmon spectroscopy (SPS) and emitted light due to reverse irradiation utilizing SPS Kretschmann configuration. The films were fabricated using sphere dispersed solution with various diameters from about 100 to 300 nm. The morphologies of the fabricated films were observed using atomic force microscopy and the sphere films had almost three layer structure. In SPS curve, large dip and shallow broad dip were observed at around 75° and 50°, respectively. The dips were considered to be due to the three layer structure and some defects in the film. Furthermore, emitted lights due to reverse irradiation were also observed as a function of the emitted angle in the Kretschmann configuration of the SPS measurement. Emitted lights due to surface plasmon excitation were also observed and the peak angle of the emitted light almost corresponded to the dip angle of the SPS curves.

The authors are grateful to Dr. Akira Baba of Max-Plank-Institute for Polymer Research for helpful discussions.
*Corresponding author. Tel.: +81-25-262-6741, Fax: +81-25-262-6741, E-mail: kshinbo@eng.niigata-u.ac.jp

Keywords: emitted light; Maxwell-Garnett theory; polystyrene micro-sphere; reverse irradiation; surface plasmon spectroscopy.

1. INTRODUCTION

Dielectric spheres attract much interest for new characteristics that cannot be observed in bulk states, such as optical localization, photonic band and so on [1–3]. Polystyrene (PS) spheres also show some unique optical modes and studies using near-field optics have been reported recently [4]. For developing devices using such micro-spheres, it is very important to fabricate 2-dimensional sphere films and to evaluate structure and optical properties of the films. The attenuated total reflection (ATR) method utilizing surface plasmon resonance, that is, the surface plasmon spectroscopy (SPS) is one of quite useful techniques to evaluate thickness and/or dielectric constants of ultrathin films [5–9]. Furthermore, emitted light through the prism can be observed due to reverse irradiation in the SPS Kretschmann configuration [7–9]. It is considered that the part of the energy of the surface plasmon is emitted through the prism as far-field light. The emitted lights are quite promising for developing new type of sensors, optical devices and so on [9].

In this study, films of PS sphere with submicron size were fabricated, and surface morphologies of the films were observed using an atomic force microscopy (AFM). The SPS and emitted light properties due to the reverse irradiation were also investigated in the prism/silver/PS sphere film Kretschmann configurations. The method is potentially relevant for investigating packing and crystallization of particles and their application to photonics.

2. EXPERIMENTAL DETAILS

The PS spheres were obtained as literature [11]. Fabrications of the PS films were carried out as follows [4]. Distilled water containing spheres with various diameters from about 100 to 300 nm was prepared. The concentration of the sphere was 10.0 wt% for the solution and the solution was dropped on substrates coated with Ag films. The substrates were maintained for certain period, t_e, for solvent (water in this case) evaporation inducing assembly of the spheres. After that, the substrates were spun in 4000 rpm for 20 s and sphere films were obtained.

The sample surface was observed using AFM (Digital Instrument, Nanoscope III-a). The SPS and emitted light measurements were carried out for the fabricated films. Figures 1(a) and 1(b) show the sample configurations of the measurements. The SPS curves were observed using He-Ne laser with wavelength at 632.8 nm. BK-7 prism was used in this study. Emitted lights through the prism were observed around dip angles of SPS curves when the laser beam was irradiated normal to the film from the air, as shown in Figure 1(b). The irradiation method in Figure 1(b) is described reverse irradiation below. Such emitted lights are due to surface plasmon (SP) excitations that were induced by the modulation of excitation condition due to surface roughness and so on [7]. Moreover, if the samples have photoluminescent dye, polarizations of excited organic dye molecules induce vibrations of free electron at metal surface producing SPs and emitted lights through the prism can be observed [8,9]. The experimental setup for the SPS and emitted light measurements is shown in Figure 2.

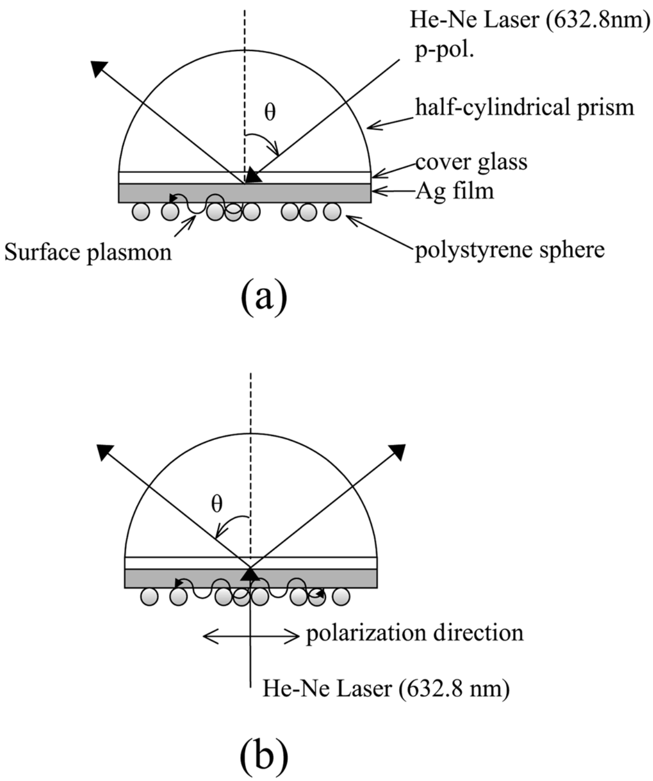

FIGURE 1 Sample configurations of SPS (a) and emitted light (b) measurements.

3. RESULTS AND DISCUSSION

3.1. AFM Image of the PS Micro-Sphere Film

The AFM image of the PS sphere film on Ag films is shown in Figure 3. Spheres of 100 nm are mainly observed in the film. Some large spheres up to 300 nm were also observed because the original solution used for fabrication contained such spheres. The cross-sectional image showed the film had mainly three layers of 100 nm spheres. The period of solvent evaporation in the fabrication process, t_e, was 3 hours for the film. Sphere films were fabricated with various periods of solvent evaporation t_e and it was found that 3 or 4 hours were needed for the film fabrication. The film fabricated with t_e of 4 hours had a little denser packing than Figure 3.

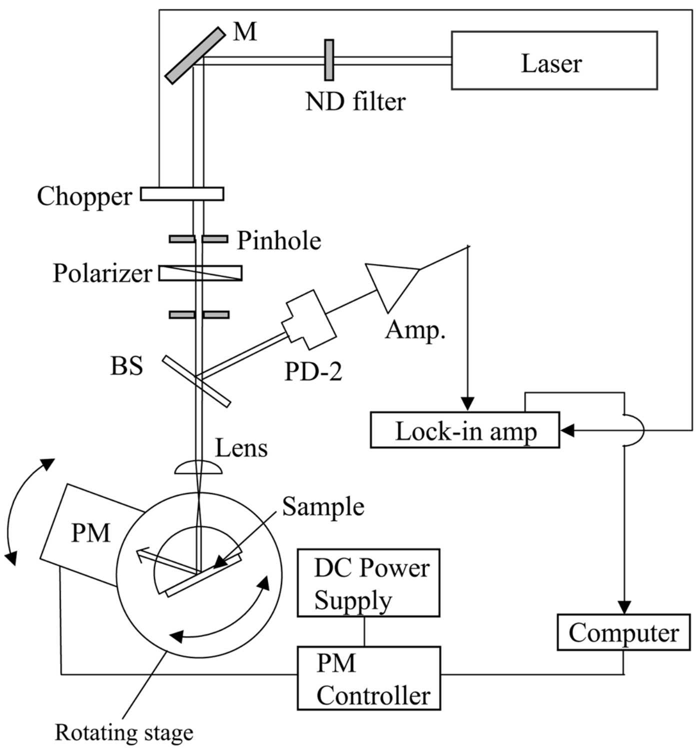

FIGURE 2 Measuring system of the SPS and emitted light properties.

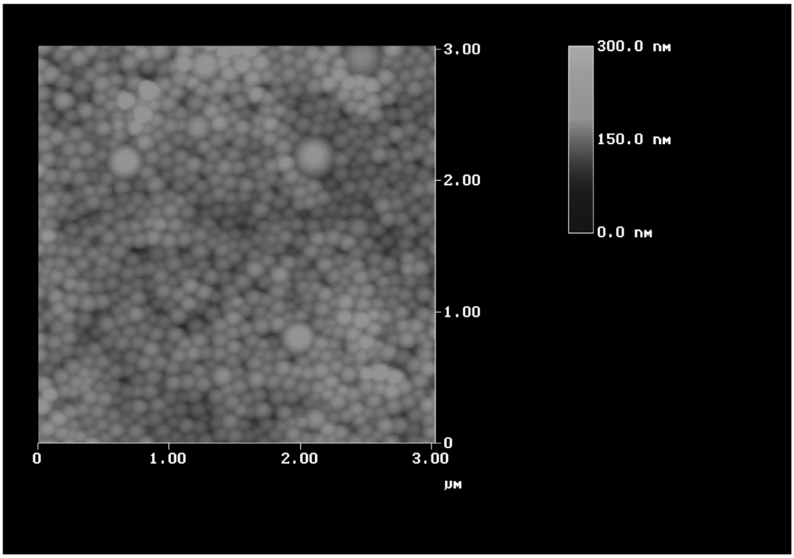

FIGURE 3 Top-view AFM image of the sphere film.

3.2. SPS and Emitted Light Properties of the PS Micro-Sphere Film

Figure 4 shows the SPS curve for the same film with Figure 3). SPS curve of bare Ag film is also shown in the figure. Large dip at around 75° is observed and is tentatively estimated to be due to the three sphere layers mainly formed in the film. Geometrically, the thickness of the film is about 245 nm if we assume the film has an ideal hexagonal closest packed structure with three sphere layers. Using this thickness, the dielectric constant inducing SPS dip at 75° is calculated to be 1.93. Although the dielectric constant of bulk polystyrene, ε_p, is $2.5281 + i \cdot 0$ [3], the SPS curves are considered to depend on the average dielectric constants of the films. The average dielectric constants of the films were calculated using the following equation of the Maxwell-Garnett theory [12],

$$\varepsilon_{AV} = \varepsilon_m \frac{\varepsilon_p(1+2\varphi) + 2\varepsilon_m(1-\varphi)}{\varepsilon_p(1-\varphi) + \varepsilon_m(2+\varphi)} \tag{1}$$

where ε_{AV} is average dielectric constants, ε_p is dielectric constant of the particle, $2.5281 + i \cdot 0$, ε_m is dielectric constant of the matrix media (air, $1.0 + i \cdot 0$), and φ is the volume ratio of the polystyrene. If we again assume the fabricated films have an ideal hexagonal closest packed structure, volume ratio of polystyrene in the film is 0.74 and then the

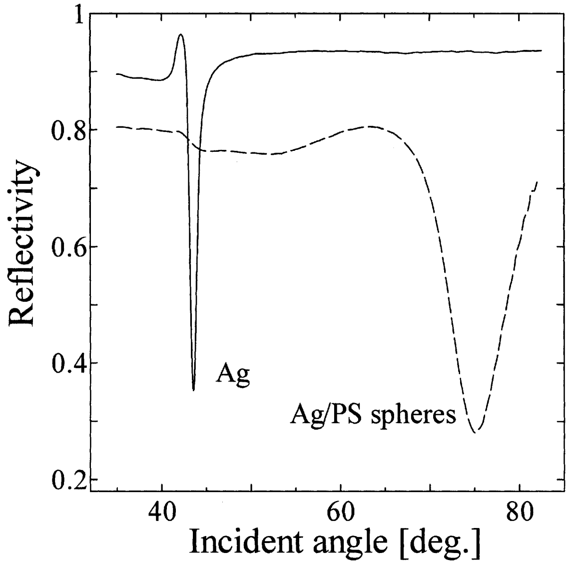

FIGURE 4 SPS curve of the fabricate sphere film.

average dielectric constant is calculated to be about 2.00. It is a little larger than the dielectric constant calculated from the experimental SPS curve above, 1.93. It was considered to be due to the small polystyrene volume ratio of the films at interface layers between air and sphere film and between Ag and sphere film, and loose packed areas in the film.

The experimental SPS curve in Figure 4 has also a small and broad dip from around 50° and is considered to be due to some defects in the film.

Furthermore, as clearly seen at around the critical angle of the SPS curves in Figure 4, the whole reflectivity of sphere film was smaller than that of the Ag film. It is considered to be due to the light scattering induced by the adsorbed spheres.

Figure 5 shows the emitted light property through the prism/Ag/100 nm PS sphere film due to the reverse irradiation. Two peaks were observed and the peak angles of emitted light almost corresponded to the dip angles of the SPS curves in Figure 4. The results showed that the emitted lights were caused by the SP excitations [7–9]. The intensities were larger than that of bare Ag film. It is considered that the large emitted lights are induced by strong excitations of SP due to large roughness introduced to the sample by the sphere adsorption [7].

These SPS and emitted light properties are considered to be useful for investigating optical properties and fabricating new kinds of optical devices [8,9].

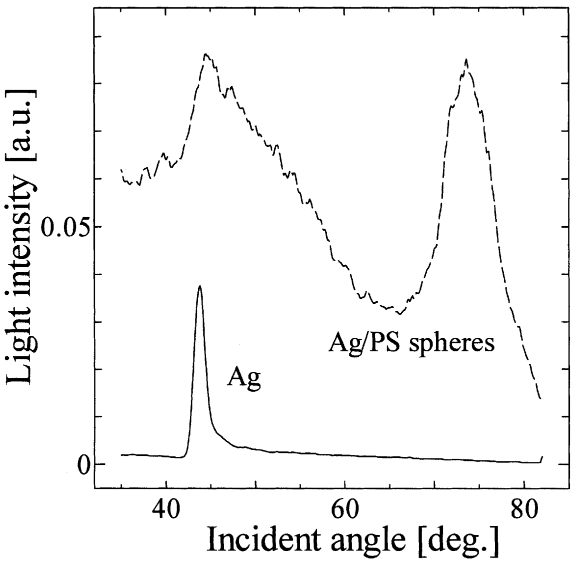

FIGURE 5 Emitted light curve of the sphere film.

4. CONCLUSION

Polystyrene sphere films were fabricated and the structure and the SPS properties were investigated. The films had almost three layer structure of the spheres. The SPS curve had two peaks at around 75° and 50° and the peaks were considered to be due to three layer structure and some defects in the film, respectively. The emitted light through the prism due to reverse irradiations in the SPS Kretschmann configuration were also observed and the peak angle of the emitted light properties almost corresponded with the dip angle of the SPS curves. The emitted lights were considered to be caused by the SP excitations. These results are useful for investigating optical properties of dielectric spheres and developing new kinds of optical devices.

REFERENCES

[1] Fujimura, T., Itoh, T., Imada, A., Shimada, Koda, T., Chiba, N., Muramatsu, H., Miyazaki, H., & Ohtaka, K. (2000). Near-field optical images of ordered polystyrene particle layers and their photonic band effect. *Journal of Luminescence*, 87–89, 954–956.

[2] Ashkin, A. & Dziedric, A. (1977). Observation of resonances in the radiation pressure on dielectric spheres. *Phys. Rev. Lett.*, *38*, 1351–1354.

[3] Haraguchi, M., Nakai, T., Shinya, A., Fukui, M., Koda, T., Shimada, R., Ohtaka, K., & Takeda, K. (2000). Optical modes in two-dimensionally ordered dielectric spheres. *Jpn. J. Appl. Phys.*, *39*, 1747–1751.

[4] Fujimura, T., Itoh, T., Hayashibe, K., Edamatsu, K., Shimoyama, K., Shimada, R., Imada, A., Koda, T., Segawa, Y., Chiba, N., Muramatsu, H., & Ataka, T. (1997). Observation of local light propagation in ordered LATEX layers by scanning near-field optical microscope. *Mater. Sci. & Eng.*, *B48*, 94.

[5] Agranovich, V. M. & Mills, D. L. (Eds.) (1982). *Surface Polaritons*, North-Holland Pub.: Amsterdam.

[6] Baba, A., Kaneko, F., Shinbo, K., Kato, K., Kobayashi, S., & Wakamatsu, T. (1998). Evaluation of tilt angles of nematic liquid crystal molecules on polyimide Langmuir-Blodgett films using the attenuated total reflection measurement method. *Jpn. J. Appl. Phys.*, *37*, 2581– 2586.

[7] Shinbo, K., Miyabayashi, S., Kobayashi, H., Shimizu, H., Kato, K., Kaneko, F., Kawakami, T., Tanaka, M., Wakamatsu, T., & Advincula, R. C. (2003). Fabrication and surface plasmon excitation properties of polystyrene submicron and micron sphere thin films. *Jpn. J. Appl. Phys.*, *42*, 2506–2510.

[8] Nakano, T., Terakado, M., Shinbo, K., Kato, K., Kaneko, F., Kawakami, T., & Wakamatsu, T. (2002). Light emission property from organic dye thin films due to excitation of multiple surface plasmons. *Jpn. J. Appl. Phys.*, *41*, 2774–2778.

[9] Kaneko, F., Sato, T., Terakado, M., Nakano, T., Shinbo, K., Kato, K., Tsuboi, N., Wakamatsu, T., & Advincula, R. C. (2003). Emission light and multiple surface plasmon excitations at prism/Ag/merocyanine Langmuir-Blodgett films. *Jpn. J. Appl. Phys.*, *42*, 2511–2515.

[10] Wakamatsu, T., Nakano, T., Shinbo, K., Kato, K., & Kaneko, F. (1999). Detection of surface-plasmon evanescent fields using a metallic probe tip covered with fluorescence. *Rev. Sci. Instr.*, *70*, 3962–3966.

[11] Natsukaze, S., Taguchi, Y., & Tanaka, M. (1998). *Journal of Japan Society of Colour Material*, *71*, 232.

[12] Ung, T., Liz-Marzán, L. M., & Mulvaney, P. (2002). Gold nanoparticle thin films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *202*, 119–126.