

Anisotropic propagation of surface plasmon polaritons caused by oriented molecular overlayer

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We performed reverse attenuated total reflection measurements on 50-nm-thick Ag thin films coated with oriented sexithiophene molecular layers. The dispersion curves obtained clearly demonstrate that the wavevectors of surface plasmon polaritons propagating parallel to the molecular orientation have larger magnitudes than those propagating perpendicular to the molecular orientation. The results provide us with an approach to generate anisotropic propagation of surface plasmon polaritons simply controlled by the molecular orientation of an overlayer. © 2009 American Institute of Physics. [DOI: 10.1063/1.3184586]

Surface plasmon polaritons (SPPs) that propagate along a metal-dielectric interface have been explored extensively in the past decades due to their potential in a variety of applications, including surface-enhanced Raman scattering,¹ surface-plasmon-resonance sensors,² and subwavelength optics.³ SPPs can be excited by excited fluorophores placed very close to a metallic surface.⁴ When an appropriate decoupling device such as a prism and grating is used, the excited SPPs can be converted into light,⁵ resulting in a phenomenon called surface-plasmon-coupled emission (SPCE).^{6–8} The SPCE displays unique properties, strongly directional emission and unique polarization, for instance, that can be useful in sensing applications.^{7,8}

In general, SPPs propagate uniformly in all directions at an interface between a metal and an isotropic dielectric medium. Gryczynski *et al.*⁷ reported a circular pattern of SPCE from a fluorescent polyvinyl alcohol (PVA) film evaporated on a 50-nm-thick Ag film decoupled by a hemisphere prism and projected onto a screen. The circular pattern implies that the wavevectors of SPPs propagating in all directions have the same magnitude. Hiep *et al.*⁹ recently studied the effects of fluorophore orientation on the SPCE pattern by using sexithiophene (6T) molecules deposited on 50-nm-thick Ag films. For a randomly oriented 6T overlayer, they observed a circular SPCE pattern with a uniform intensity distribution, which demonstrates uniform excitation of SPPs. In contrast, the SPCE pattern observed for the oriented 6T layer exhibited a nonuniform intensity distribution with much stronger intensities along the direction of the 6T molecular orientation. This result indicates that SPPs are excited most efficiently along the 6T molecular orientation. If we look more closely at the observed SPCE pattern for the oriented 6T layer [Figs. 3(b) and 3(c) in Ref. 9], we find that the pattern is an ellipsoid elongated along the molecular orientation. The ellipsoidal SPCE pattern suggests that the propagation of the SPPs is anisotropic. Namely, the magnitude of the SPP wavevector depends on the direction of propagation and is larger along the molecular orientation. Although several efforts have been devoted to develop a theoretical analysis of the anisotropic propagation of SPPs at an interface between a

metal and an anisotropic dielectric medium,^{10,11} experimental studies on such propagation are still lacking.

As an extension of the previous work by Hiep *et al.*,⁹ in this study we perform reverse attenuated total reflection (RATR) measurements for Ag films coated with oriented 6T molecular overlayers. The RATR measurements allow us to determine the dispersion curves for SPPs propagating parallel and perpendicular to the molecular orientation. From the dispersion curves, we obtain quantitative information about the anisotropic SPP propagation.

Samples were prepared by a method similar to that described in our previous paper.⁹ Thin Ag films 50 nm in thickness were first vacuum-deposited (10^{-6} Torr) on glass substrates. Then, 6T thin films with a thickness of 10 nm were vacuum-deposited on the Ag surface with a deposition rate of 0.5–1.0 nm/min. According to previous studies on thiophene oligomers,^{12–14} vapor deposited films are polycrystalline and show varying degrees of order, depending on preparation conditions such as the deposition rate and substrate temperature. When deposited at a low rate, 6T molecules grow almost upright on the substrate (within $\sim 25^\circ$ of the surface normal) with no preferential in-plane orientation.¹³ In order to align the molecules in a preferential direction, the 6T films were rubbed several times in one direction using a wiping paper. This rubbing method was previously used to align octithiophene¹⁴ and *p*-sexiphenyl^{15,16} molecules. Finally, an additional 6T film 10 nm in thickness was vacuum deposited at a rate of 10 nm/min to achieve a total thickness of 20 nm. As a reference, a 20-nm-thick nonrubbed 6T film deposited on a 50-nm-thick Ag film was also prepared. The reference sample was produced in exactly the same manner as the rubbed sample, apart from skipping the rubbing process.

Polarized photoluminescence (PL) spectra were measured to confirm the orientation of the 6T molecules. The sample was set in such a way that the normal to its surface lay in the horizontal plane and the rubbing direction was vertical. The plane of incidence was taken as the horizontal plane and excitation light with a wavelength of 408 nm from a laser diode was directed on the sample surface with an incident angle of 45° . The polarization of the incident light was set to be vertical. Emitted light was detected from the normal to the sample surface and passed through a camera lens and a polarizer. The polarized light was then focused on

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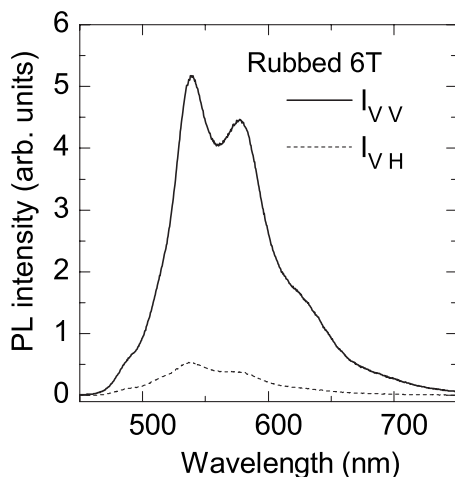


FIG. 1. Polarized PL spectra for rubbed 6T sample. I_{VV} (I_{VH}) is the intensity of vertically (horizontally) polarized emission produced by vertically polarized excitation light. The rubbing direction is set vertical.

the entrance slit of a 25 cm single monochromator equipped with a Si charge-coupled device. A polarization scrambler was inserted in front of the entrance slit. The intensity of the horizontal (I_{VH}) and vertical (I_{VV}) components of the emitted light was analyzed.

Polarized PL spectra of the rubbed 6T film on Ag are shown in Fig. 1. Both I_{VV} and I_{VH} exhibit two peaks at ~ 540 nm (2.30 eV) and ~ 580 nm (2.14 eV), and a shoulder at 635 nm (1.95 eV). These PL band positions are in good agreement with the literature,^{17,18} in which each band corresponds to 0–0, 0–1, and 0–2 vibronic progressions. The PL intensity showed a strong dependence on the polarization direction. While the polarization of the excitation light and the rubbing direction were fixed to vertical, the PL intensity was found to have a maximum (minimum) value when the direction of the polarization was vertical (horizontal). The dichroic ratio (defined as I_{VV}/I_{VH}) calculated directly from the peak heights was about 10. This confirms that the transition dipole moment of the rubbed 6T sample was oriented predominantly parallel to the rubbing direction. In contrast, the nonrubbed 6T sample did not exhibit dichroism, which confirms that the molecules in the nonrubbed sample were randomly oriented. The prepared 6T films were also examined by an atomic-force microscope (AFM). The AFM images obtained are very similar to those reported by Vidélot *et al.*,¹⁴ which is further evidence for the preferential orientation of 6T molecules along the rubbing direction.

To gain an insight into the anisotropic SPP propagation, RATR measurements were carried out. The configuration used for RATR measurements is shown in Fig. 2. The sample was attached to a hemicylindrical prism made of BK7 glass with index matching fluid. Light from a tungsten lamp was incident on the sample surface after passing through an aperture and a lens. In such a configuration, SPPs are excited with the aid of surface roughness in the wide spectral range of the lamp.¹⁹ Decoupled light was collected by an optical fiber cable with a solid angle of $\sim 10^4$ Sr⁻¹ and sent to the same monochromator as used for the PL measurements. The observation angle θ was varied from 45° to 59° with a step size of 1°. It should be noted that in conventional ATR measurements, SPP excitation is detected as a dip in the reflectance spectrum, while in the present RATR measurements,

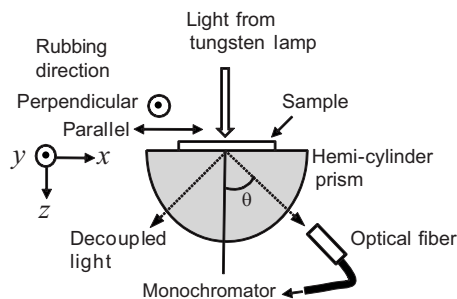


FIG. 2. RATR measurement scheme. Decoupled light is collected by an optical fiber and guided to a monochromator.

SPP excitation is detected as a pronounced peak in a spectrum of the decoupled light. In the configuration shown in Fig. 2, SPPs propagating along the x -axis can be detected. In order to investigate the anisotropic SPP propagation for the rubbed sample, we measured the spectra of the decoupled light by setting the rubbing direction parallel and perpendicular to the x -axis, as depicted in Fig. 2. This allowed us to determine the SPP wavevectors parallel ($k_{\text{SPP}}^{\parallel}$) and perpendicular (k_{SPP}^{\perp}) to the rubbing direction.

RATR spectra obtained for the two configurations from several observation angles are shown in Figs. 3(a) and 3(b), after being corrected by the raw spectrum of the tungsten lamp. Pronounced peaks are seen which shift to shorter wavelengths as the observation angle increases. For a given observation angle, the peak for the parallel configuration

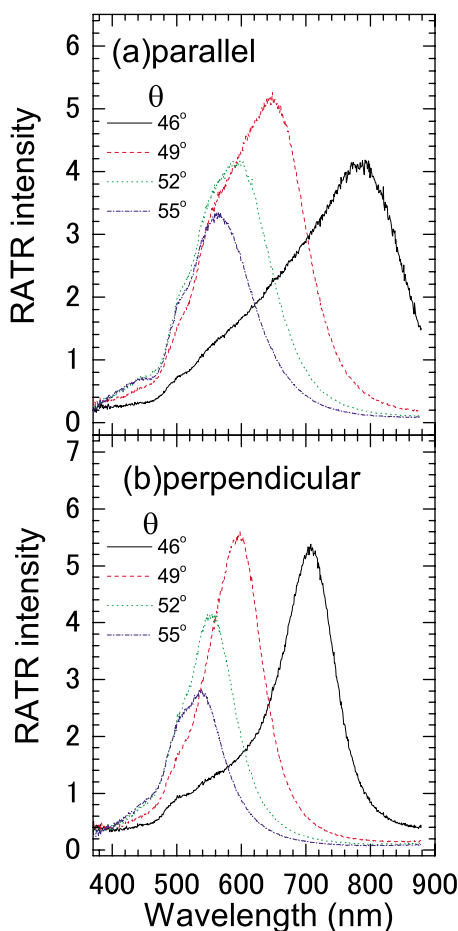


FIG. 3. (Color online) RATR spectra for (a) parallel and (b) perpendicular configuration observed at different observation angles.

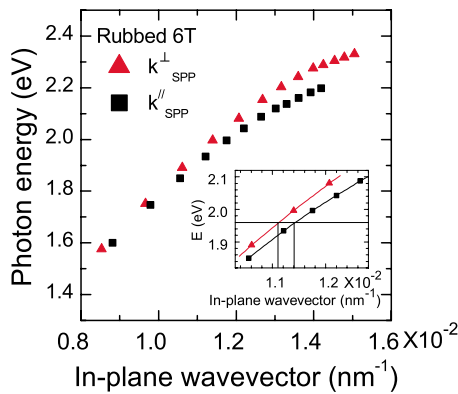


FIG. 4. (Color online) Dispersion curves for k_{SPP}^{\perp} and $k_{\text{SPP}}^{\parallel}$ in the rubbed 6T sample. Inset is an enlarged figure for a specific wavevector region.

[Fig. 3(a)] is located at a longer wavelength than that for the perpendicular configuration [Fig. 3(b)]. In contrast to the rubbed sample, the RATR peak for the nonrubbed sample was found to be located at the same wavelength for a given observation angle even when the sample was rotated around the normal axis. When a RATR peak is located at a wavelength λ for an observation angle θ , the magnitude of the SPP wavevector is given by $k_{\text{SPP}} = (2\pi/\lambda)n_p \sin \theta$, where n_p is the refractive index of the prism. Using this expression, we can obtain the dispersion relations for $k_{\text{SPP}}^{\parallel}$ and k_{SPP}^{\perp} in the rubbed 6T sample. The results are plotted in Fig. 4. The inset shows the dispersion curves enlarged in a region of wavevector from 1.03×10^{-2} to $1.28 \times 10^{-2} \text{ nm}^{-1}$. The interpolated curves for each configuration are also shown. Figure 4 demonstrates that in the whole measured wavelength region, $k_{\text{SPP}}^{\parallel}$ is larger than k_{SPP}^{\perp} , which clearly demonstrates that the thin oriented molecular overlayer induces anisotropy in the SPP wavevector.

It is of interest to compare the dispersion relations obtained by the RATR spectra with those obtained by conventional ATR spectra. For the rubbed 6T sample, we performed angle-scan ATR measurements for configurations perpendicular (k_{SPP}^{\perp}) and parallel ($k_{\text{SPP}}^{\parallel}$) to the rubbing direction using the 632.8-nm-line of a He-Ne laser. The ATR spectra exhibited reflectivity dips at $47.0^\circ \pm 0.1^\circ$ and $49.1^\circ \pm 0.1^\circ$ for perpendicular and parallel configurations, respectively. These dip positions yield $k_{\text{SPP}}^{\perp} = 1.10 \times 10^{-2} \pm 0.01 \text{ nm}^{-1}$ and $k_{\text{SPP}}^{\parallel} = 1.14 \times 10^{-2} \pm 0.01 \text{ nm}^{-1}$ at $E = 1.96 \text{ eV}$ (632.8 nm). These values are in good agreement with $k_{\text{SPP}}^{\perp} = 1.11 \times 10^{-2} \text{ nm}^{-1}$ and $k_{\text{SPP}}^{\parallel} = 1.14 \times 10^{-2} \text{ nm}^{-1}$ deduced from the dispersion curve shown in the inset of Fig. 4 by interpolating the data to $E = 1.96 \text{ eV}$.

The displacement of the dispersion curve seen in Fig. 4 can be attributed to the anisotropic optical properties of the rubbed 6T film. In an anisotropic material, the dielectric constant is strongly dependent on the direction. The present rubbed 6T film is thought to have three principle values of a dielectric tensor ϵ_{\parallel} , ϵ_{\perp} , and ϵ_z , corresponding to the directions parallel and perpendicular to the rubbing direction, and

normal to the film surface, respectively. The relationship $k_{\text{SPP}}^{\parallel} > k_{\text{SPP}}^{\perp}$ suggests that $\epsilon_{\parallel} > \epsilon_{\perp}$. Recent theoretical analyses of SPP propagation at an interface between a metal and an anisotropic dielectric medium^{10,11} predict a displacement of the dispersion curves that depends on the SPP propagation direction. Although these analyses have been carried out for a uniaxial medium and differ from our biaxial 6T thin film, the predicted displacement agrees qualitatively with the present observation. Further experimental and theoretical studies are required to fully account for the displacement of the dispersion curve caused by the anisotropic overlayer.

In conclusion, we prepared oriented 6T layers on Ag thin films and observed anisotropic SPP propagation generated by the oriented molecular overlayer. From RATR measurements, it was found that the SPP wavevector parallel to the molecular orientation takes a larger value than that perpendicular to the molecular orientation. The results presented here may provide useful information for the development of plasmonic devices based on the anisotropic SPP propagation as suggested in recent theoretical papers.^{10,11}

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- ¹K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, and M. S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).
- ²Z. Salamon, H. A. Macleod, and G. Tollin, *Biochim. Biophys. Acta* **1331**, 117 (1997).
- ³W. L. Barnes, A. Dereux, and T. W. Ebbesen, *Nature (London)* **424**, 824 (2003).
- ⁴G. W. Ford and W. H. Weber, *Phys. Rep.* **113**, 195 (1984).
- ⁵H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, *Springer Tracts in Modern Physics* (Springer, Berlin, 1988), Vol. 111.
- ⁶G. Winter and W. L. Barnes, *Appl. Phys. Lett.* **88**, 051109 (2006).
- ⁷I. Gryczynski, J. Malicka, Z. Gryczynski, and J. R. Lakowicz, *Anal. Biochem.* **324**, 170 (2004).
- ⁸K. Ray, H. Szmajcinski, J. Enderlein, and J. R. Lakowicz, *Appl. Phys. Lett.* **90**, 251116 (2007).
- ⁹H. M. Hiep, M. Fujii, and S. Hayashi, *Appl. Phys. Lett.* **91**, 183110 (2007).
- ¹⁰A. A. Krokhin, A. Neogi, and D. McNeil, *Phys. Rev. B* **75**, 235420 (2007).
- ¹¹R. Li, C. Cheng, F. F. Ren, J. Chen, Y. X. Fan, J. Ding, and H. Wang, *Appl. Phys. Lett.* **92**, 141115 (2008).
- ¹²P. Lang, R. Hajlaoui, F. Garnier, B. Desbat, T. Buffeteau, G. Horowitz, and A. Yassar, *J. Chem. Phys.* **99**, 5492 (1995).
- ¹³W. Gebauer, M. Skolowski, and E. Umbach, *Chem. Phys.* **227**, 33 (1998).
- ¹⁴C. Vidélot, V. Grayer, J. Ackermann, A. E. Kassmi, D. Fichou, and G. Hadziioannou, *Synth. Met.* **139**, 115 (2003).
- ¹⁵N. Aoki, Y. Koshiba, and Y. Ueda, *Jpn. J. Appl. Phys., Part 1* **44**, 4088 (2005).
- ¹⁶M. Era, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.* **67**, 2436 (1995).
- ¹⁷A. Mani, J. Schoonman, and A. Goosseens, *J. Phys. Chem. B* **109**, 4829 (2005).
- ¹⁸E. Da Como, M. A. Loi, F. Dinelli, M. Murgia, F. Biscarini, R. Zamboni, and M. Muccini, *Synth. Met.* **155**, 287 (2005).
- ¹⁹S. Hayashi, *Surf. Sci.* **158**, 229 (1985).