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SPR microscopy with ATR Otto configuration for observing thin boundary lubrication films

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ABSTRACT – This study proposed a novel method for in-situ observation of thin boundary lubrication films based on the attenuated total reflection (ATR) in Otto configuration. The developed system was composed of the point contact between a high refractive index prism and a copper hemisphere, and other optical components. As sample oils, base oil (Hexadecane) and base oil with additives (1% Oleic acid) were used. The measurement of SPR spectrum allows making a quantitative analysis for identifying the value of thickness and coverage of adsorbed films.

1. INTRODUCTION

The use of Surface plasmon resonance (SPR) is a powerful method for measuring the properties of thin films adsorbed on solid/solid interfaces. The advantages in using SPR method are its high sensitivity, simple construction, and high time performance. The small changes of refractive index of an observing adsorbed film can be detected in order of 10^{-5} with a high time resolution of few second [1].

In the field of tribology, in-situ observations of lubricant films during sliding motion have been strongly required to understand the mechanism of lubrication. For the request, the use of the Otto SPR configuration is the best choice to apply SPR measurement techniques for tribology situations. By using the Otto configuration, the SPR signals involving information of adsorbed films can be easily detected.

In this study, we firstly developed a tribotester with an in-situ SPR microscopy based on Otto ATR configuration. This system employs the point contact between a high refractive index prism and a copper hemisphere. By comparison between the obtained SPR signals and theoretical calculation results, the coverage of adsorbed films was quantitatively estimated.

2. EXPERIMENTAL DETAILS

2.1 Theory of Multi Optical Layer Model

The response SPR signals were theoretically calculated based on the multi optical layer model [1]. In the Otto configuration, a three-layer structure with prism/lubricants and lubricants/copper interfaces was assumed as a calculation model. These three layers have different dielectric constant ε_i; thus, the wave number in the perpendicular direction to the contacting surface k_{iz} for light of frequency ω is given by

$$k_{iz} = \frac{\omega}{c}\left[\varepsilon_i - \varepsilon_1 \sin^2\theta_1\right]^{\frac{1}{2}} \tag{1}$$

where subscripts i means the number of layers; i = 1: prism layer, i = 2: lubricant layer, and i = 3: metal layer. Therefore, reflectivity is defined as

$$R = \left|\frac{r_{12} + r_{23}\exp(i2k_{2z}d)}{1 + r_{12}r_{23}\exp(i2k_{2z}d)}\right| \tag{2}$$

where

$$r_{ij} = \frac{\varepsilon_i k_{jz} - \varepsilon_j k_{iz}}{\varepsilon_i k_{jz} + \varepsilon_j k_{iz}}. \tag{3}$$

The observed SPR signals include the wavelength dependence of reflectivity. Therefore, the comparison between measured reflectivity curves and Eq. (3), we can find the dielectric constant, i.e., refractive index, of the adsorbed layers.

It should be noted that when adsorbed films are formed on the metal surfaces, four-layer models should be used. In this case, the theoretical equation for the reflectivity can be similarly solved.

2.2 Experimental Setup

Figure 1 illustrates a schematic of the developed optical system with the ATR Otto configuration. As shown in the figure, the point contact between a high refractive index prism and a copper hemisphere with a diameter of 25.4 mm was used. The normal load of 1.2 N was applied by loading the copper hemisphere, which is connected to the y-directional motorized stage via a soft double cantilever (spring constant k = 594N/m). The value of normal load was calculated from the

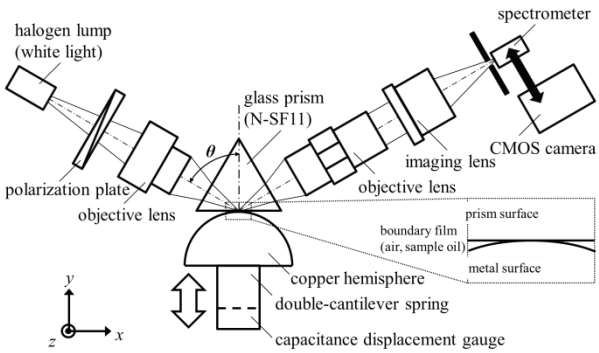

Figure 1 Schematic diagram of the optical system.

measurement of the deflection of the double-cantilever. The surface roughness of the copper hemisphere was set to be R_a = 0.032μm by polishing processes.

As a light source, a white light (halogen lamp, PICL-NEX, NPI) was used. The light goes through a polarization plate and an objective lens (5X, f = 200 mm), and then, it was totally reflected at the lower face of the regular triangle high refractive index prism made of refractive index 1.785. The direction of polarization of the light can be changed by rotating a polarizer. The reflected light at the contact interface was imaged by using a second objective lens (10X, f = 200 mm) and an imaging lens (1X, f = 200 mm). The contact images were captured by a CMOS camera (2048×2048 pixels with a pixel size 5.5μm×5.5μm, Point Grey).

Furthermore, the spectrum of the refractive light was measured by using a spectrometer. To fix the spectrometer, the CCD camera was replaced by a spectrometer without the change of these positions. It should be noted that in order to increase the resolution of the spectrum measurement, the reflective light was spatially filtered with a pinhole (φ=100μm).

2.3 *Lubricants*

As lubricants, two types of oils were prepared: (1) Hexadecane, (2) Hexadecane with 1.0% Oleic acid. These oils were dropped on the outside of the contact after the normal load was applied. After the scheduled period, the contact images and SPR spectrum were measured.

3. RESULTS AND DISCUSSION

3.1 *Reflected Light Images at Contact Points*

Figure 2 shows SPR images around the contact regions. Left and right figures are the results in p and s -polarized light, respectively.

As shown in the images, it was found that the blue outer circle surrounds the central contact region, and it was observed only p -polarized light. From the Hertz contact theory, these regions are located at the outside of direct contact regions, as illustrated in the upper figures. Considering these above results, it was found the blue circles indicate the SPR signals.

3.2 *SPR Spectrum*

Figure 3 shows the wavelength dependence of reactance (SPR spectrum) at the point depicted at the white circle in Figure 2(a). Red and blue curves are the SPR spectrum in Hexadecane and Hexadecane with 1.0% Oleic acid lubricants, respectively. In addition, dotted lines of each color show theoretical values, which was fitted by changing the coverage of adsorbed films of oleic acid based on least square method.

We can clearly see a down-bel-shape curve, which corresponds to the well-known shape of SPR spectrum. By applying a small amount of oleic acid, the curve slightly shifts to the right hand. It means that the effective refractive index of lubricants near the contact interface increases by the formation of adsorbed films.

Furthermore, it was found that the theoretical curves are well fitted; here, the coverage of the adsorbed

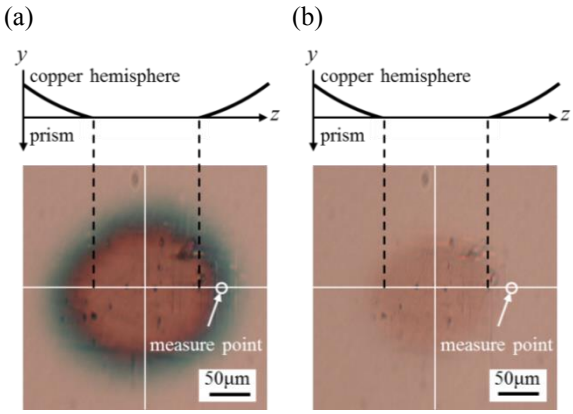

Figure 2 Schematic illustration of the contact geometries and SPR images around the contact regions; (a) p -polarized light, (b) s -polarized light.

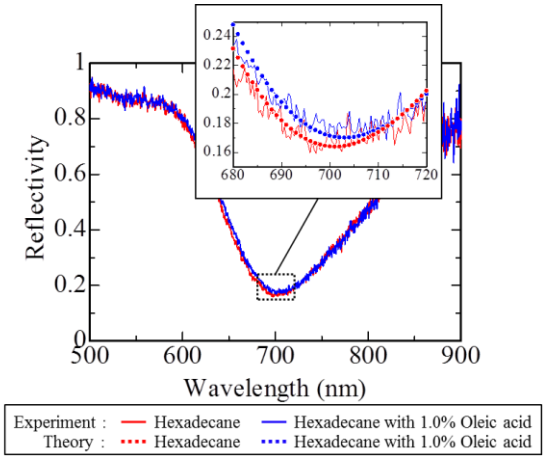

Figure 3 SPR spectrum at the white circle depicted as the white circle in Figure 2(a): (1) Hexadecane, (2) Hexadecane with 1.0% Oleic acid.

film is formed by oleic acid. By fitting processes, the coverage of the adsorbed film was quantified as 46%.

As described above, a quantitative estimation of the coverage of adsorbed films was realized. This estimation was performed at the outside of the contact region. For in-situ observation in the contact regions, more improvement of the optical system was required. In addition, in the theoretical model, it was assumed that a flat monolayer was formed as the adsorbed film. More accurate discussion, the improvement of theoretical models was also needed. However, finding of this study provides the high possibility of ATR Otto configuration for in-situ observations of thin lubricant films.

4. CONCLUSION

Through experiments, the high possibility of the in-situ SPR microscopy for the observation of thin lubrication films was obtained. In addition, required improvements to realize a high accuracy analysis were also discussed.

5. REFERENCE

[1] T. Okamoto, and K. Kajikawa, “Plasmonics - basics and application-”, pp.16-46, 2010.