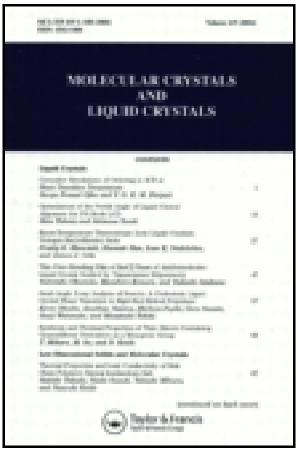

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# Conductivity Measurement of a $\pi$-Conjugated Polymer Based on Refractive Index Change

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Abstract
The evaluation of electrical conductivity for π-conjugated polymers is one of the most important areas for several electronic applications. To measure the electrical conductivity ($\sigma$) of a π-conjugated polymer thin-film, we attempted to use surface plasmon resonance (SPR). DC conductivity of the polymer thin-film was also measured by the traditional van der Pauw method and compared with the results derived from SPR method. These two conductivity values of the polymer thin-film obtained by different methods were very similar.

Keywords π-conjugated polymer; DC conductivity; surface plasmon resonance

## INTRODUCTION

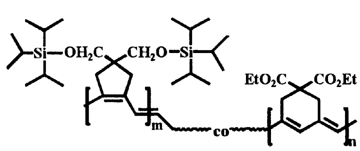
Recently, π-conjugated polymers have been widely investigated for their application in rechargeable batteries, electroluminescent displays, electronic, biosensors, and optical devices. Therefore, the evaluation of electrical conductivity for π-conjugated polymers is one of the most important areas of investigation for such applications. However, current methods to measure DC electrical conductivity of polymer thin-film has a number of problems such as high contact resistance, difficult construction of electrodes, and poor reproducibility of measurement results.[1]

To solve these problems in measuring the electrical conductivity of a polymer thin-film, we consider the relationship between the dielectric constant ($\varepsilon$) and conductivity ($\sigma$) with the Drude-Lorentz theory; a complex dielectric constant in conducting materials is related to electrical conductivity ($\sigma_0$).[2-3]

On the other hand, surface plasmon resonance (SPR) is a convenient well-known method to evaluate the thickness ($d$) and dielectric constant ($\varepsilon$) of polymeric thin-film.[4] Thus, it occurred to us that SPR could be used to measure the refractive index and extinction coefficient in a π-conjugated polymer thin-film; i.e., could be used as a convenient method of determining electrical conductivity.

## EXPERIMENTAL

The poly(1,6-heptadiyne) derivative (poly[4,4'-bis(triisopropylsiloxy) methyl-1,6-heptadiyne-*co*-(diethyldipropargylmalonate)]) (poly(IPSiOH -*co*-DEDPM)) (Scheme 1) was used as a π-conjugated polymer in this study.

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Scheme 1 A π-conjugated polymer used in this study.

To investigate the conductivity of the polymer thin-film, a sensor chip system like the schematic representation in Figure 1 was fabricated for the SPR experiment. The π-conjugated polymer thin-film was formed by spin coating. The casting solution of the π-conjugated polymer thin-film was composed of **1** in THF (Tetrahydrofuran, Aldrich chemical Co. Inc.) (1.0 wt%). The poly(IPSiOH-*co*-DEDPM) thin-film was doped by iodine using a gas-phase chemical doping method (doping ratio; 0.1 wt%).

A tailor-made SPR system based on the Kretschmann configuration was used to determine the optical constants of π-conjugated polymer thin-film (Figure 2). To determine thickness (*d*), ellipsometric measurement data were taken with AutoEL ellipsometer (Rudolph Tech. Inc.).

The refractive index and extinction coefficient of the poly(IPSiOH-*co*-DEDPM) thin-films were determined from SPR measurements and fitting by the Fresnel equation four-layer model.[5-6] DC conductivity of the thin-film was measured at room temperature by the traditional van der Pauw method and compared with conductivity as measured by the SPR method. SPR curves were taken in the air with a wavelength of 675 nm at 25℃.

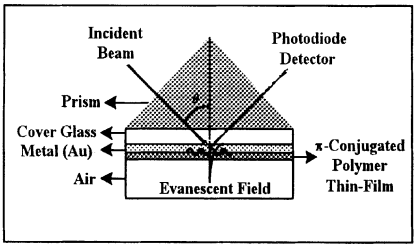


FIGURE 1 Structure of the sensor chip configuration.

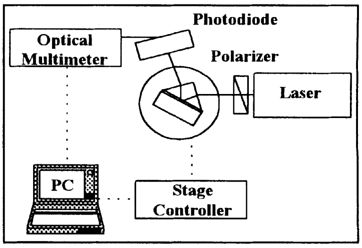


FIGURE 2 Experimental setup diagram of the SPR measurement.

## RESULTS AND DISCUSSION

As shown in Figure 3, different SPR curves were obtained; each curve showed a good coincidence with the theoretical fitting curve derived from the Fresnel equation. On the basis of the SPR curve we calculated optical constants of each film by the Fresnel equation (in case of $I_2$ doped thin-film, $n$ =1.62, $k$ = 0.58 and $d$ = 35 nm) and $\varepsilon_i$ = 1.88 and $\varepsilon_r$ = 2.29.[5] From these results, conductivity of $I_2$ doped polymeric thin-film is obtained as 600 S/cm by the Drude-Lorentz theory.[6] As a result of measurement by the van der Pauw method, the DC electrical conductivity of the iodine-doped thin-film is about 500 S/cm at room temperature. These two conductivity values for the π-conjugated polymer thin-film are quite similar.

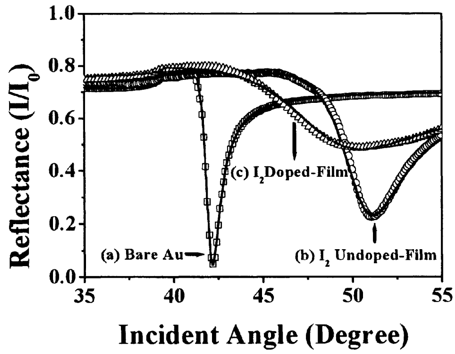


FIGURE 3 Experimental (symbols) and theoretical (lines) SPR curves for bare Au and poly(IPSiOH-*co*-DEDPM film of 35 nm thickness.

Therefore, we can very simply and correctly determinate electrical conductivity ($\sigma$) of the polymeric thin-film entirely by optical SPR methods without other treatments. It seems quite probable that SPR-conductivity measurement may be applied as a convenient method to several fields of studies related to $\pi$-conjugated conducting polymer thin-films.

Acknowledgements

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