

Title	インジウムスズ酸化物と有機半導体界面の光学的第二高調波の研究
Author(s)	Ngah Demon, Siti Zulaikha Binti
Citation	
Issue Date	2014-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/12300
Rights	
Description	Supervisor:水谷 五郎, マテリアルサイエンス研究科, 博士

Dissertation Abstract

The energetic structure at the interface that governs charge carrier dynamics in organic device has attracted abundance of interface related researches. Here, the scope of study is the interface between the indium tin oxide (ITO) and the organic semiconductor layer. The electronic properties at the interface of hole injection contact, the ITO with the organic semiconductor layer are the key factor to understand the injection barrier of the charge carriers during device operation. The nonlinear optical second harmonic generation (SHG) is employed as selective probe for surface and interface studies. The application of SHG has been demonstrated for wide range of organic and inorganic materials ever since the advancement of laser technology. Currently, the SHG investigation on organic semiconductor thin film is in favor of the contemporary interest in organic light emitting diodes and organic solar cells. The main idea of my research is to analyze the character of charge transfer dipole at the interface between the ITO and the organic semiconductor layer using the nonlinear effects of SHG. And, the second objective is to interpret the information of SHG phase obtained from the double layer structure.

In present study, the strength of the charge transfer complex at the interface of ITO is elucidated using the ionization energy of the organic semiconductor thin film. Sample of bare ITO substrate and organic thin film of m-MTDATA, 2-TNATA, CuPc, pentacene, α -6T and α -NPD are prepared for this purpose. In the first stage of experiment, the strength of electric field at the interface is analyzed from SHG intensity measurement of ITO and ITO/organic structures in the reflection geometry. The fundamental (1064 nm) and SHG (532 nm) lights are *p*-polarized. The Fresnel factor analysis is applied to treat the macroscopic local field effect (the *L* factors) at both fundamental and SHG light in the samples. In this first analysis, SHG interference from the interface has manifested in the result of ITO/2-TNATA, ITO/pentacene and ITO/ α -6T structures. At this stage of experiment, I have recognized that the insufficiency of relying on the data of SHG intensity only, since the sign of SHG is also significant information. Thus, in order to process the SHG that emerged from the interface, the experiment of SHG phase has become an obligatory to this study.

Mainly featured as a sensitive probe for orientation of molecules, the SHG phase measurement is also known for many nonlinear effect applications. One of the prominent works in extracting SHG phase shift was demonstrated by K. Kemnitz and his co-workers in 1986 [4]. The technique is to use the phase difference given by the fundamental light at two SHG sources, the target sample and the reference. The same experiment is established in this study with α -quartz (0001) as the second source of SHG. The experimental steps and necessary groundwork to obtain the phase shift from the interface of ITO/organic have been properly addressed. The total phase shift of the ITO/organic samples is directly calculated using the phase of oscillation

pattern of bare ITO as reference. The next step of analyzing the phase, however, does not come in a straight forward fashion. I showed the method to apply the phase correction due to dielectric dispersion in organic thin films in order to extract the absolute phase of the charge transfer dipole. As a result, the SHG from the interface of ITO/CuPc and ITO/pentacene is presented using the solution of the complex plane. In another experiment, the phase of SHG from ITO/ α -NPD indicated that the SHG from the interface is relatively weak when compared to the phase of bare interface of ITO.

The absolute phase from the interface, $\phi_{interface}$ has solved the ambiguity from the previous measurement of SHG intensity. For this particular experiment, the phase of SHG from the interface of ITO/organic semiconductor is found to yield not only from the effect of static dipole but also from the imaginary part of the susceptibility, χ . This finding is not in fine agreement with the static dipole model previously proposed by our group. Nevertheless this experiment is a direct observation of the phase thus, gives more accurate interpretation of the SHG at interface of organic semiconductor. The imaginary part of susceptibility implied that there may be electronic resonance in the origin of phase shift. The discussion is produced using the data of SHG spectroscopy and the spectra of absorption coefficient of organic molecules. But more importantly, I propose that the phase shift can be due to spatial fluctuation of dipole density at the interface of charge transfer.

The study of charge transfer at the interface of ITO/organic semiconductor is performed using the characteristics of SHG intensities and the SHG phases obtained from the ITO and the ITO/organic double layer structures. The nonlinear phase interferometry is demonstrated as the effective technique to avoid the misinterpretation of SHG measurement in general, other than being a potential probe of molecular orientation. Further application of this interferometry technique in the investigation of organic semiconductor system is currently being pursued by our group. My contribution to this field is by showing the extensive analysis of the phase shift from buried interface of ITO/organic thin film, this report is important for the study of SHG at the interface of organic device.

Keyword: second harmonic generation, interface, thin film, organic semiconductor, phase measurement