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論文題目	INTERFACES OF INDIUM TIN OXIDE AND ORGANIC SEMICONDUCTOR THIN FILM STUDIED BY OPTICAL SECOND HARMONIC GENERATION. (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)		
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論文の内容の要旨

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

論文審査の結果の要旨

本論文では、近年電気メーカーが技術力を争っている有機エレクトロルミネッセント素子 (OLED) の分野において、有機分子層界面間の電子準位や分子の秩序などの情報を選択的に観測するために、光第二高調波発生(SHG)による分光の方法を発展させ、発生する SHG 光の位相を観測する手法を開発した。そして、いくつかの有機膜層について界面 SHG 光の位相の値を測定し、その物理的意味を検討した。

有機膜層試料については本学の村田英幸教授との共同研究で作成した。試料の構造はガラス基板/ITO/有機膜であり、試料は乾燥窒素で封じガラスキャップがかぶせた。有機膜としては、ペンタセン、 α -6T、銅フタロシアニン、m-MTDATA、2-TNATA、 α -NPD を選び、典型的な厚さは 100nm とした。

まず予備段階として、これらの試料からの SHG 光の強度を測定した。ITO 膜からは強い SHG 光が発生し、有機層はそれ単体では SHG 光を発生しないものの、それらが ITO 膜の上に乗ると SHG 光強度が変化し、ITO/有機膜の界面から SHG 光が発生していることが確認された。そして、その強度変化の理解のためには、界面から発生している SHG 光の強度とともに位相の情報も必要であることが強く示唆された。

そこで、界面からの SHG 光の位相の情報を検出するために、参照試料(α -SiO₂(001))からの SHG 光を重畳し、2つの試料の SHG の干渉効果により界面からの SHG 光の位相を決定する方法を採用した。この方法自体は先行研究中に存在するものであるが、埋もれた界面からの応答の解析例は存在しない。埋もれた界面からの応答を解析する場合には、界面上の有機層の色分散による SHG 光の位相への影響を考慮する必要があり、これを適切に解析したことが本論文のオリジナルな点である。

SHG 観測の光源はピコ秒の時間幅を持つ Nd:YAG レーザーの基本波出力(波長 1064nm)で、この光を試料に照射し、その反射光および、それに混じって発生する 532 nm の光との両方を参照試料に入射し、そこから透過してくる SHG 光を分光器に付けた光電子増倍管で観測

した。SHG 光の位相を観測するために参照試料を光軸にそって平行移動させ、空気の分散により振動する SHG 光強度を参照試料の位置の関数として求めた。この SHG 光強度は正弦関数を描くので、フィッティングにより SHG 光の位相を求め、2つの SHG 光の振幅の複素空間演算により界面 SHG 光の位相を抽出した。有機層としては、ペンタセン、銅フタロシアニン、 α -NPD について有意な情報が得られ、とくにペンタセンについては、特徴的な位相の値が観測され、その物理的起源について検討することができた。

以上、本論文におけるこれらの成果は、新規の非線形効果の位相の解析法として、学術的にもまた有機デバイス技術などへの将来の応用にも貢献するところが大きい。よって博士(マテリアルサイエンス)の学位論文として十分価値あるものと認めた。