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Description	

Optical second harmonic generation at heterojunction interfaces of a molybdenum trioxide layer and an organic layer

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We have observed optical second harmonic generation (SHG) from a space charge layer (SCL) in a stacked indium tin oxide (ITO)/molybdenum trioxide (MoO_3)/*N-N'*-diphenyl-*N-N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) system. When the MoO_3 thicknesses were increased, the SHG signals from this system decreased sharply at smaller MoO_3 thicknesses, and were saturated at MoO_3 thicknesses larger than 1 nm. These results prove the vital role of SCL in improvement of drive voltages of organic light-emitting diodes. © 2010 American Institute of Physics. [doi:10.1063/1.3513297]

Recently, the space charge layer (SCL) at interfaces in organic light-emitting diodes (OLEDs) has been studied to improve the performance of the devices.¹ Matsushima and Murata reported current density-voltage (J - V) characteristics of hole-only devices with various thicknesses of molybdenum trioxide (MoO_3) buffer layers and showed that a space-charge-limited current of *N-N'*-diphenyl-*N-N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) can be observed at a specific MoO_3 thickness of 0.75 nm due to a negligible hole injection barrier caused by efficient interfacial charge generation.¹ The interfacial charge generation mechanism consists of charge transfer from α -NPD to MoO_3 to form electron-hole pairs (SCL) and separation of the pairs under an external electric field. The charge transfer (SCL) was detected indirectly by fluorescence (FL) spectroscopy. Due to quenching of α -NPD excitons by SCL, FL peaks of α -NPD decrease in intensity in stacked films of α -NPD and MoO_3 .¹ However, by this method, if materials cannot exhibit FL, SCLs are impossible to be detected. In order to measure accurate amount of SCLs for a wide variety of materials, a direct method for observing SCLs has to be established.

In this study, we have observed optical second harmonic generation (SHG) from a stacked indium tin oxide (ITO)/ MoO_3 / α -NPD system in order to monitor the SCL formation at the MoO_3 / α -NPD interfaces directly. The SHG is a well established technique used to investigate electronic states at surfaces and interfaces.^{2,3}

The glass/ITO (150 nm)/ MoO_3 (X nm)/ α -NPD (60 nm) samples were fabricated as previously reported.^{4,5} The MoO_3 layer thickness was varied from 0 to 5 nm. We also prepared glass/ITO/ MoO_3 samples with different MoO_3 thicknesses from 0.25 to 5 nm using the same procedure in order to investigate SHG characteristics at the MoO_3 /ITO interface.

The experimental setup for the SH intensity measurements has been reported elsewhere.^{6,7} As the excitation light of SHG, we used the fundamental light of Nd³⁺:YAG laser (EKSPLA PL2143) with a photon energy of 1.17 eV, a pulse duration of 30 ps, and a repetition rate of 10 Hz. The pulse energy and the spot size on the sample and the incident angle were set at

$50 \pm 5 \mu\text{J}/\text{pulse}$, $\approx 1 \text{ mm}$, and 45° , respectively. In order to correct for the fluctuation of the incident light, the SH light intensities of the samples were normalized by that obtained from a GaAs(001) substrate. In order to take SH spectra, we used tunable IR light output from an optical parametric generator and amplifier system as the incident light. The pulse energy was $\approx 27 \mu\text{J}/\text{pulse}$. The incident angle was $\approx 67^\circ$. The band width of the IR light was $\approx 0.8 \text{ meV}$. All experiments were performed at room temperature. We used α - SiO_2 (0001) as a reference sample in order to correct for the wavelength dependence of the sensitivity of the optical system.⁸

Figure 1 shows the SH spectra of (a) glass/ITO (150 nm), (b) glass/ITO (150 nm)/ MoO_3 (0.75 nm)/ α -NPD (60 nm), and (c) glass/ITO (150 nm)/ MoO_3 (1 nm)/ α -NPD (60 nm) systems. In the spectrum (a) in Fig. 1, there are a strong peak at $\approx 2.17 \text{ eV}$ and some fine structures above 2.2 eV. The peaks originate from the electronic transition in the ITO bulk, since the SH intensity of an ITO substrate with the thickness 30 nm is significantly lower than that with 150 nm (see the dot (c) in Fig. 2). In density functional theory cal-

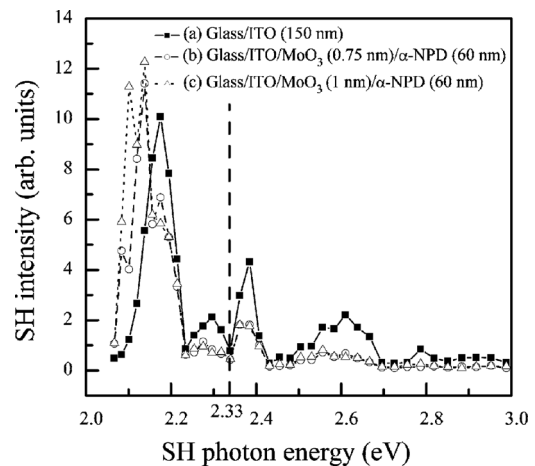


FIG. 1. SH spectra of (a) glass/ITO (150 nm), (b) glass/ITO (150 nm)/ MoO_3 (0.75 nm)/ α -NPD (60 nm), and (c) glass/ITO (150 nm)/ MoO_3 (1 nm)/ α -NPD (60 nm) systems. All spectra are normalized by the SH spectra of α - SiO_2 (0001). Dashed line represents SH photon energy used in studying SH intensity as a function of MoO_3 layer thickness.

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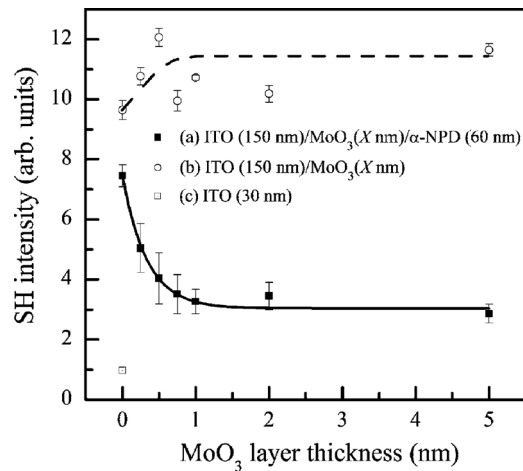


FIG. 2. SH intensities of (a) glass/ITO (150 nm)/MoO₃ (*X* nm)/ α -NPD (60 nm) system, (b) glass/ITO (150 nm)/MoO₃ (*X* nm) system, and (c) glass/ITO (30 nm) sample, as function of MoO₃ thicknesses [normalized by SH intensity from GaAs (001)]. Solid and dotted lines are guide to eyes.

ulation of an ITO substrate, the optical band gap was found to range from 1.7 to 2.6 eV as a function of the percentage of the tin content.^{9,10} Thus, we suggest that there are some domains with different percentage of the tin content in the ITO bulk, and these peaks correspond to the band gaps of the domains.

Spectra (b) and (c) in Fig. 1 have a strong peak at ≈ 2.14 eV with the width ≈ 0.05 eV, and this peak did not appear in spectrum (a) in Fig. 1. This is not due to electronic transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states in α -NPD since the energy difference between them should be larger than ≈ 2.6 eV.^{11,12} The electronic transition in the MoO₃ layer is not feasible, either, since the widths of the relevant bands of O 2*p*, Mo 4*d*, and gap states are far broader than 0.05 eV.¹² Thus, we suggest that it is contributed by electronic transition inter-hetero-materials.

There are several peaks above 2.2 eV in spectra (b) and (c) in Fig. 1, and their shapes are similar to those of the spectrum (a) but the intensities of (b) and (c) are reduced significantly when compared with that of (a). In order to understand the weaker SH intensities from the samples ITO/MoO₃/ α -NPD than that from ITO only in Fig. 1, we studied the dependency of the SH intensities on the thicknesses of the MoO₃ layer ranging from 0 to 5 nm in the ITO/MoO₃/ α -NPD system as shown in sample (a) in Fig. 2. In this measurement, we selected the fundamental photon energy as 1.17 eV due to the good stability of the light source. This is because the static electric field from SCLs modulates SH spectra uniformly, and thus one can select probe light with any photon energy.

In the line (a) in Fig. 2 we see the strongest SH signal at the MoO₃ thickness of 0 nm, which originates from the bulk ITO layer. With the increase in the MoO₃ thicknesses from 0.25 to 1 nm, the SH intensities decrease remarkably. The SH intensities are found to remain constant at the MoO₃ thicknesses greater than 1 nm. It is known that the topology of MoO₃ changes from island to film structures at the thickness of 0.75 nm on the interface of the ITO layer.⁵ The change in SH signal intensities of the samples (a) in Fig. 2 suggests a growth of SCL at the interfaces of MoO₃/ α -NPD

with the increase in the MoO₃ molecules till its topology has a uniform film structure.

We propose three candidate origins of the SH signal reduction. They are (1) a change in the Fresnel factor of the system due to the absorption of the incident or SH light in the MoO₃ layer, (2) a change in an electronic structure at the ITO/MoO₃ interface, and (3) a negative interference between the SH signals generated at the MoO₃/ α -NPD interface and at the bulk ITO layer.

In order to investigate the first candidate, we measured linear transmission and reflection spectra of the ITO/MoO₃/ α -NPD systems with different MoO₃ thicknesses ranging from 0 to 5 nm (the data not shown). The transmittance of light at the photon energy of 1.17 eV and the reflectivity of light at 2.33 eV are important because these photon energies correspond to those of the input and output light in our SHG measurement. The transmittance of the ITO/MoO₃/ α -NPD system at 1.17 eV is increased by $\approx 10\%$ with the increase in MoO₃ thicknesses from 0 to 5 nm. This result indicates that the absorption of the incident light under the SHG measurements is not effective. The reflection at 2.33 eV in the MoO₃ thickness range from 0 to 5 nm is increased by $\approx 10\%$ with fluctuation. This result shows that the absorption of the SH light in the MoO₃ layer is negligible. Thus, the first candidate origin is ruled out.

As the second candidate origin, the change in the electronic structure at the ITO/MoO₃ interface is discussed. At this interface, electrons transfer from ITO to MoO₃, so that the electron density is lowered in the surface of the ITO layer. Lee *et al.*¹¹ observed a remarkable SCL at this interface. Thus, the SHG from the ITO/MoO₃ interface or the ITO bulk might be modulated by the formation of the SCL in our samples. In order to check this possibility, we measured the SH intensities from the ITO/MoO₃ system as a function of the MoO₃ thicknesses as shown in Fig. 2(b). Comparing SH intensity of samples (b) with that of samples (a) in Fig. 2, the effect of the MoO₃ layer on the SHG from the ITO layer can be regarded as small. Thus this second candidate is also ruled out.

The remaining candidate origin is a negative interference between the SH signals generated at the MoO₃/ α -NPD interface and at the bulk ITO layer. The SH light generated at the interface is supposed to be induced by the broken symmetry by an electric field in the SCL. A coherently emitted light wave like optical SH light has a definite phase and the phase value depends on the source nonlinear polarization. When optical second harmonic waves from two different sources with a phase difference of π are superposed with each other, there should occur a negative interference in the output light intensity. Such is considered to be the case of the SH intensities in Fig. 2. Here the SHG from the MoO₃/ α -NPD interface and the bulk ITO layer has a negative interference and the total SH intensities decrease as a function of the MoO₃ thicknesses.

The SH signal's behavior seen in Fig. 2 is explained by the schematic diagram shown in Fig. 3. In Fig. 3(b), charge transfers from ITO to MoO₃ in the ITO/MoO₃ systems, so that the dipole moment at the interfaces points to the ITO layer. The SH signals generated at the ITO/MoO₃ interfaces constructively interferes with the signals from the ITO bulk. Thus, the SH intensities increased slightly after the MoO₃ deposition in the line (b) of Fig. 2. On the other hand, the dipole moment of the SCLs at the MoO₃/ α -NPD interfaces

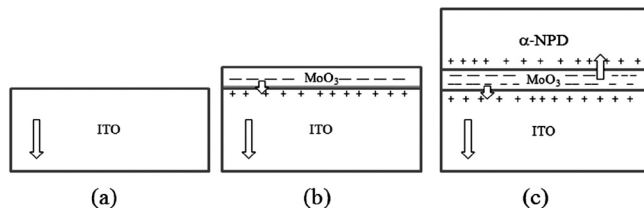


FIG. 3. Schematic diagram showing induced SH polarization in three cases, (a) ITO layer, (b) ITO/MoO₃ system, and (c) ITO/MoO₃/α-NPD system.

is oriented in the opposite direction as shown in Fig. 3(c). Thus, the SH signals generated from the MoO₃/α-NPD interfaces interfere destructively with the signals from underlayers, so that the intensities are dramatically reduced with the increase in MoO₃ thickness in the line (a) of Fig. 2.

The nonlinear susceptibility $\chi^{(2)}$ at the MoO₃/α-NPD interfaces is modulated by the electrostatic field in the SCLs, and thus it is proportional to the strength of the dipole moment. Since the modulated $\chi^{(2)}$ is proportional to the square root of the difference of the SH intensities,¹² we subtracted the SH intensities in the line (b) of Fig. 2 from that in the line (a), and then plotted the square root of the absolute values in Fig. 4. Thus, Fig. 4 represents the strengths of SCLs as a function of the MoO₃ layer thicknesses. In correlation with the result in the line (a) of Fig. 2, the $\chi^{(2)}$ increases remarkably with the increase in the MoO₃ thicknesses from 0.25 to 1 nm. The SH intensities are found to remain constant at the MoO₃ thicknesses greater than 1 nm. This is consistent with a result obtained using FL spectra in the previous study.¹ The results show that SHG measurement has a potential for quantitative analysis of the amount of the space charges.

We would like to notice that many necessary information for the quantitative determination of SCL, such as the dielectric functions of the materials, the band bending depth, and the third-order nonlinear susceptibility of MoO₃ and the resulting phases of the SH light fields, are still unknown. We could calibrate our data referring to the SCL parameters ob-

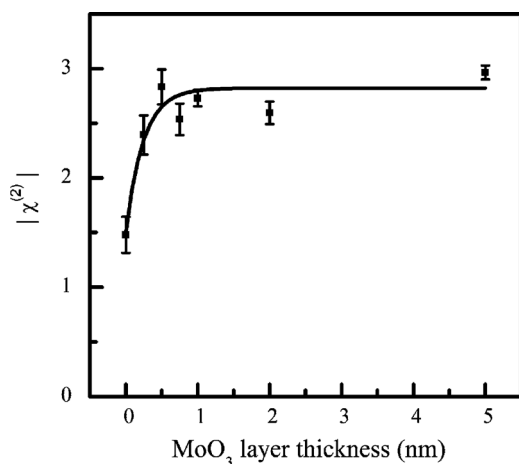


FIG. 4. Change in nonlinear susceptibility $\chi^{(2)}$ at MoO₃/α-NPD interfaces as function of MoO₃ layer thickness. Solid line is guide to eyes.

tained by other techniques. However, we can find no such other works so far. Thus, the quantitative investigation of SCLs is not realistic at the present stage.

It has been known that electron transfer occurs from lower-ionization-energy α-NPD to higher-work-function MoO₃ to induce formation of a SCL.¹³ Strength of the SCL is expected to depend on the coverage of the ITO layer with MoO₃ because incomplete coverage reduces a contact area between α-NPD and MoO₃. Thus, we assume that the initial increase in $\chi^{(2)}$ shown in Fig. 4 is attributable to the growth of the SCL because the coverage of the ITO layer with MoO₃ is increased.⁵ Moreover, since the ITO surface is completely covered by the MoO₃ layer in the larger MoO₃ thickness region,⁵ the growth of the SCL is stopped, resulting in the unchanged SH intensities. The growth of the SCL can be monitored by our SHG measurement, and the results are consistent with the exciton quenching characteristics previously reported.¹ Thus, we can conclude that SHG is a versatile technique to obtain information on the electronic states of stacked organic layers and to clarify operation mechanisms of organic electronic devices.

As further applications, SHG can be used for evaluating the doping effect in the organic layer. For instance, due to the MoO₃ doping in an α-NPD layer on a metal substrate, the Fermi level position with respect to the HOMO edge is modulated,¹⁴ and then the static electric field in the SCLs should change. Thus, SHG should be sensitive to the doping in the α-NPD interfaces. However, SH signals from a doped three-dimensional matrix (an amorphous bulk) are expected to be very weak, since dipoles are randomly oriented in the bulk and thus cancels each other. We also note that it is possible to perform similar measurements on the cathode side of the OLEDs, and to investigate the relevant metal-organic reaction or gap state formation.

¹T. Matsushima and H. Murata, *Appl. Phys. Lett.* **95**, 203306 (2009).

²Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).

³W. K. Zhang, H. F. Wang, and D. S. Zhengw, *Phys. Chem. Chem. Phys.* **8**, 4041 (2006).

⁴T. Matsushima, Y. Kinoshita, and H. Murata, *Appl. Phys. Lett.* **91**, 253504 (2007).

⁵T. Matsushima, G. He Jin, and H. Murata, *J. Appl. Phys.* **104**, 054501 (2008).

⁶M. Takebayashi, G. Mizutani, and S. Ushioda, *Opt. Commun.* **133**, 116 (1997).

⁷T. Kitahara, A. Sugwara, H. Sano, and G. Mizutani, *Appl. Surf. Sci.* **219**, 271 (2003).

⁸Y. Maeda, T. Iwai, Y. Sayake, K. Fujuu, S. Miyatake, D. Miyazaki, and G. Mizutani, *Phys. Rev. B* **78**, 075440 (2008).

⁹S. H. Brewer and S. Franzen, *Chem. Phys.* **300**, 285 (2004).

¹⁰S. H. Brewer and S. Franzen, *J. Phys. Chem. B* **106**, 12986 (2002).

¹¹H. Lee, S. W. Cho, K. Han, P. E. Jeon, C.-N. Whang, K. Jeong, K. Cho, and Y. Yi, *Appl. Phys. Lett.* **93**, 043308 (2008).

¹²O. A. Aktsipetrov, A. A. Fedyanin, E. D. Mishina, A. N. Rubtsov, C. W. van Hasselt, M. A. C. Devillers, and T. Rasing, *Phys. Rev. B* **54**, 1825 (1996).

¹³K. Kanai, K. Koizumi, S. Ouchi, Y. Tsukamoto, K. Sakanoue, Y. Ouchi, and K. Seki, *Org. Electron.* **11**, 188 (2010).

¹⁴M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, *Org. Electron.* **10**, 932 (2009).