Characteristics of carrier injection on polarization-dependent photoexcitation in copper phthalocyanine thin films

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Abstract. The carrier concentration injected from a silicon substrate to a copper phthalocyanine thin film was found to depend on the incidence polarization of the photoexciting beam. The modulation efficiency of terahertz transmission due to transverse-magnetic (TM)-polarized excitation is distinctly higher than that due to transverse-electric (TE)-polarized excitation. Underlying this difference is the enhancement of carrier injection when the TM-polarized light is more transmitted through the surface of organic thin films than the TE-polarization light. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.JNP.7.073795]

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1 Introduction

Terahertz (THz) technologies for THz devices and THz imaging systems have developed considerably. Many researchers have extensively investigated for developing THz devices such as THz filters, switches, mirrors, and modulators. In particular, active THz modulation over a broad THz range became an important function for versatile THz devices. For active THz modulation, quantum-well or plasmonic structures were employed, and metamaterials based on hybrid structures of metals and semiconductors were also used to obtain a relatively high modulation efficiency. Very recently, a new method for active THz modulation has been reported by Yoo et al., who demonstrated highly efficient THz modulations over a wide spectral range by using organic copper phthalocyanine (CuPc) thin films deposited on a silicon (Si) substrate. The novelty of this paper is to understand the characteristics of THz modulation efficiency under the condition of different polarization of the photoexciting beam, which is important for wide applications of the new method for active THz wave modulation.

In this article, we present the characteristics of THz modulation on transmission through organic-inorganic hybrid structures which are composed of a 500-nm-thick CuPc thin film and a 500-μm-thick Si substrate. We report that the THz modulation efficiency is related to the carrier concentration injected from the Si substrate to the CuPc thin film, which depends on the incidence polarization of the photoexciting beam. The modulation efficiency of THz transmission is relatively high when the photocarriers are excited by a transverse-magnetic (TM)-polarized incident light, compared with the case of TE-polarized incident light. This phenomenon is explained by the enhancement of carrier injection which is expected since the TM-polarized light is more transmitted through the surface of organic thin films than the transverse-electric (TE)-polarization light.
2 Basic Properties and Fabrication of CuPc Thin Films

In this study, the CuPc powder β-form (Sigma-Aldrich) was used to fabricate CuPc films. Figure 1(a) shows the chemical structure of a CuPc molecule which consists of a core metal ion and a chelate organic ring with four nitrogen atoms. CuPc films of 500-nm thickness were deposited on a Si substrate with thickness of 500 μm, using thermal evaporation method. Three different types of samples were prepared at the annealing temperature, 27°C (room temperature), 150°C, and 250°C, respectively. The sample fabricated at 27°C shows randomly stacked CuPc molecules, as depicted in Fig. 1(b). As the annealing temperature increases, the column-like structures formed by stacking CuPc molecules together are increasingly crystallized, as shown in Figs. 1(c) and 1(d). The well-ordered α- and β-phases of CuPc films are fabricated under the conditions of temperatures of 150°C and 250°C, respectively. A main difference of two phases is the angle between b-axes and orthogonal axes to molecular planes, which of necessity causes the change of the direction of molecular stacking and its stacking density. Moreover, the structural change may be associated with the characteristics of carrier injection between the CuPc thin films and the Si substrate and charge transport in the CuPc films, thus altering the absorption properties of the incident electromagnetic waves.

3 THz Time-Domain Spectroscopy and Transmission Measurements

To measure the characteristics of THz transmission through the hybrid structures of the CuPc thin films and the Si substrate, we used a standard THz time-domain spectroscopy system. THz pulses are generated by using a p-type InAs wafer with (100) orientation and detected by using a photoconductive antenna method. The generated THz pulses are collimated by using two parabolic mirrors. The THz pulses are normally incident to the CuPc/Si hybrid structures, and a continuous optical beam is obliquely incident with the incidence angle of 75 deg at the same time. We used the laser beam with the wavelength of 785 nm at which the carriers are strongly excited on the Si substrate and the absorption on the CuPc thin film can be strongly suppressed.
The polarization of the incident optical beam is changed to be TM- and TE-polarized light, as shown in Fig. 2, by rotating a polarizer. In the case of the TM-polarized light, the electric fields are parallel to an incidence plane, whereas in the case of the TE-polarized light, the electric fields are normal to the incidence plane.

4 Polarization-Dependent Transmission Modulation of THz Waves in CuPc Thin Films

Figure 3 shows the peak values of normalized THz transmission of four different samples, a bare Si substrate and CuPc/Si hybrid structures prepared at different temperatures, 27°C (room temperature), 150°C, and 250°C, on the incident polarization and power of the optical beams for photoexcitation. The peak values of transmission amplitudes measured under the condition of

![Fig. 2 Schematic view of an experiment of the THz wave transmission through a CuPc film on Si under optical excitation. The optical beam for photoexcitation is obliquely incident with the incidence angle of 75 deg, and the THz pulses are normally incident to the surface of the samples.](image)

![Fig. 3 (a) Peak values of normalized THz transmission through the samples, a Si substrate (black squares) and hybrid CuPc/Si layers annealed at 27°C (red circles), 150°C (blue triangles), and 250°C (green inverted triangles), respectively, measured under the condition of TM-polarized excitation of incident optical beam. (b) Peak values of normalized THz transmission measured under the condition of TE-polarized excitation of incident optical beam. The laser power for photoexcitation is varied from zero to 80 mW.](image)
photoexcitation were normalized by ones measured without photoexcitation. As we easily expect, the transmission peaks may decrease with increasing the power of the optical beams as well as with improving the ordering properties of the crystallizing CuPc molecules. At the photoexciting power of 80 mW and the well-ordered structures of CuPc molecules, the peak value is <50%. Note that the peak values observed under the condition of TM-polarized excitation are relatively higher than those obtained under the condition of TE-polarized excitation.

To quantitatively compare the effects of differently polarized waves on THz modulation, we used the term modulation efficiency, $M = (P_{w/o} - P_w)/P_{w/o}$, where $P_{w/o}$ and $P_w$ are the peak values of transmission amplitudes measured without and with photoexcitation, respectively. Figure 4 shows the ratio between the modulation efficiencies, $M_{TM}$ and $M_{TE}$, in cases of TE- and TM-polarized optical beams. Only the values obtained at well-ordered $\alpha$- and $\beta$-phase CuPc films with relatively high modulation efficiencies are compared. At higher laser powers, the ratio can be reliably extracted since the values of modulation efficiency are relatively high. On the other hand, at lower laser powers, both the values of modulation efficiency in TM- and TE-polarized cases are too small. The ratio between two small numbers is therefore likely to be inaccurate. Nevertheless, the results at lower laser powers are quite consistent with those at higher laser powers. The modulation efficiencies for the TM polarization are >30% as large as those for the TE polarization. The reflectivity in the case when the electric field is perpendicular to the plane of incidence is larger than that in the case when the electric field is parallel to the plane of incidence on the surface of a CuPc thin film. This means that much more power of the incident optical beam for photoexcitation reaches the Si substrate and therefore the concentration of the photoexcited carriers will be increased. The enhancement of carrier injection from a Si substrate to a CuPc thin film and the amount of carrier transport within the CuPc film will be followed. The density of photoexcited carriers may increase and the incident THz waves are strongly modulated consequently. This may improve the modulation efficiency of THz transmission.

5 Conclusions

In conclusion, we have demonstrated that the carrier concentration injected from a silicon substrate to a CuPc thin film depends on the incidence polarization of the photoexciting beam. The modulation efficiency of THz transmission due to TM-polarized excitation is distinctly higher than that due to TE-polarized excitation. We have found that this phenomenon is due to the increase of the concentration of the photoexcited carriers, which is expected when the incident optical beams are more transmitted through the organic thin film.
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References

1. M. Tonouchi, “Cutting-edge terahertz technology,” Nat. Photonics 1(2), 97–105 (2007), http://dx.doi.org/10.1038/nphoton.2007.3.
2. J. N. Heyman, R. Kersting, and K. Unterrainer, “Time-domain measurement of intersubband oscillations in a quantum well,” Appl. Phys. Lett. 72(6), 644–646 (1998), http://dx.doi .org/10.1063/1.120832.
3. I. H. Libon et al., “An optically controllable terahertz filter,” Appl. Phys. Lett. 76(20), 2821–2823 (2000), http://dx.doi .org/10.1063/1.126484.
4. T. Kleine-Ostmann et al., “Room-temperature operation of an electrically driven terahertz modulator,” Appl. Phys. Lett. 84(18), 3555–3557 (2004), http://dx.doi.org/10.1063/1 .1723689.
5. H.-T. Chen et al., “Active terahertz metamaterial devices,” Nature 444, 597–600 (2006), http://dx.doi.org/10.1038/nature05343.
6. E. Hendry et al., “Ultrafast optical switching of the THz transmission through metallic subwavelength hole arrays,” Phys. Rev. B 75, 235305 (2007), http://dx.doi.org/10.1103/ PhysRevB.75.235305.
7. E. Hendry et al., “Optical control over surface-plasmon-polariton-assisted THz transmission through a slit aperture,” Phys. Rev. Lett. 100(12), 123901 (2008), http://dx.doi.org/10.1103/ PhysRevLett.100.123901.
8. H.-T. Chen et al., “A metamaterial solid-state terahertz phase modulator,” Nat. Photonics 3(3), 148–151 (2009), http://dx.doi.org/10.1038/nphoton.2009.3.
9. D. G. Cooke and P. Uhd Jepsen, “Optical modulation of terahertz pulses in a parallel plate waveguide,” Opt. Express 16(19), 15123–15129 (2008), http://dx.doi.org/10.1364/OE.16.015123.
10. T. Kleine-Ostmann et al., “Audio signal transmission over THz communication channel using semiconductor modulator,” Electron. Lett. 40(2), 124–126 (2004), http://dx.doi .org/10.1049/el:20040106.
11. W. L. Chan et al., “A spatial light modulator for terahertz beams,” Appl. Phys. Lett. 94(21), 213511 (2009), http://dx.doi.org/10.1063/1.3147221.
12. S. Zhang et al., “Photoinduced handness switching in terahertz chiral metamolecules,” Nat. Commun. 3, 942 (2012), http://dx.doi.org/10.1038/ncomms1908.
13. M. A. Seo et al., “Active terahertz nanoantennas based on VO2 phase transition,” Nano Lett. 10(6), 2064–2068 (2010), http://dx.doi.org/10.1021/nl1002153.
14. S. H. Lee et al., “Switching terahertz waves with gate-controlled active graphene metamaterials,” Nat. Mater. 11, 936–941 (2012), http://dx.doi.org/10.1038/nmat3433.
15. H. K. Yoo et al., “Organic conjugated material-based broadband terahertz wave modulators,” Appl. Phys. Lett. 99(6), 061108 (2011), http://dx.doi.org/10.1063/1.3626591.
16. H. K. Yoo et al., “Transmittances of terahertz pulses through organic copper phthalocyanine films on Si under optical carrier-excitation,” Appl. Phys. Express 5(7), 072402 (2012), http://dx.doi.org/10.1143/APEX.5.072402.
17. G. Guillaud, J. Simon, and J. P. Germain, “Metallophthalocyanines: gas sensors, resistors and field effect transistors,” Coord. Chem. Rev. 178(Part 2), 1433–1484 (1998), http://dx.doi.org/10.1016/S0010-8545(98)00177-5.
18. M. J. Cook and I. Chambrier, *The Porphyrin Handbook*, Elsevier Science, New York (2003).

19. F. Iwatsu, “Size effects on the alpha—beta transformation of phthalocyanine crystals,” *J. Phys. Chem.* 92(6), 1678–1681 (1988), [http://dx.doi.org/10.1021/j100317a057](http://dx.doi.org/10.1021/j100317a057).

20. R. Mason, G. A. Williams, and P. E. Fielding, “Structural chemistry of phthalocyaninato cobalt (II) and manganese (II),” *J. Chem. Soc. Dalton Trans.* 4, 676–683 (1979), [http://dx.doi.org/10.1039/dt9790000676](http://dx.doi.org/10.1039/dt9790000676).

21. S. Karan and B. Mallik, “Nanostructured organic-inorganic photodiodes with high rectification ratio,” *Nanotechnology* 19(49), 495202 (2008), [http://dx.doi.org/10.1088/0957-4484/19/49/495202](http://dx.doi.org/10.1088/0957-4484/19/49/495202).

22. R. D. Gould and A. K. Hassan, “AC electrical properties of thermally evaporated thin films of copper phthalocyanine,” *Thin Solid Films* 223(2), 334–340 (1993), [http://dx.doi.org/10.1016/0040-6090(93)90541-V](http://dx.doi.org/10.1016/0040-6090(93)90541-V).

23. P. Peumans, S. Uchida, and S. R. Forrest, “Efficient bulk heterojunction photovoltaic cells using small-molecular-weight organic thin films,” *Nature* 425(6954), 158–162 (2003), [http://dx.doi.org/10.1038/nature01949](http://dx.doi.org/10.1038/nature01949).

24. H. Fujikake et al., “Time-of-flight analysis of charge mobility in a Cu-phthalocyanine-based discotic liquid crystal semiconductor,” *Appl. Phys. Lett.* 85(16), 3474–3476 (2004), [http://dx.doi.org/10.1063/1.1805178](http://dx.doi.org/10.1063/1.1805178).

25. S. Ambily and C. S. Menon, “The effect of growth parameters on the electrical, optical and structural properties of copper phthalocyanine thin films,” *Thin Solid Films* 347(1), 284–288 (1999), [http://dx.doi.org/10.1016/S0040-6090(98)01744-1](http://dx.doi.org/10.1016/S0040-6090(98)01744-1).

26. M. D. Pirriera et al., “Optoelectronic properties of CuPc thin films deposited at different substrate temperatures,” *J. Phys. D: Appl. Phys.* 42(14), 145102 (2009), [http://dx.doi.org/10.1088/0022-3727/42/14/145102](http://dx.doi.org/10.1088/0022-3727/42/14/145102).

27. M. van Exter and D. Grischkowsky, “Optical and electronic properties of doped silicon from 0.1 to 2 THz,” *Appl. Phys. Lett.* 56(17), 1694–1696 (1990), [http://dx.doi.org/10.1063/1.103120](http://dx.doi.org/10.1063/1.103120).

28. Z. Jiang, M. Li, and X. C. Zhang, “Dielectric constant measurement of thin films by differential time-domain spectroscopy,” *Appl. Phys. Lett.* 76(22), 3221–3223 (2000), [http://dx.doi.org/10.1063/1.126587](http://dx.doi.org/10.1063/1.126587).

29. Y. Nakato, M. Shioji, and H. Tsubomura, “Photovoltage and stability of an n-type silicon semiconductor coated with metal or metal-free phthalocyanine thin films in aqueous redox solutions,” *J. Phys. Chem.* 85(12), 1670–1672 (1981), [http://dx.doi.org/10.1021/j150612a014](http://dx.doi.org/10.1021/j150612a014).

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