Research Paper

Terahertz Wave Modulation in PCBM-Deposited Metallic Slit Arrays

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Abstract

The properties of terahertz (THz) wave modulation were investigated in organic-deposited metallic slit arrays fabricated on a Si substrate. The organic thin layer (fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester, also known as PCBM) acts as an active layer controlled by the incident light; thus, modulating the transmission of the incident THz waves. This is due to the photoexcited electron transfer from the silicon substrate to the PCBM layer, which results in the organic layer becoming metallic. The metallic slit arrays show plasmonic properties, such as wavelength-dependent transmission, which depends on the structural arrangements of the slits. When the polarization of the incident THz waves is parallel with the direction of the metallic slits, a cut-off frequency clearly appears, while for perpendicular polarization, the transmission is considerably enhanced by the plasmonic property. The hybrid structures of organic-metallic slits deposited on a silicon substrate enable the active control of the spoof surface plasmon-mediated transmission of THz waves. This finding can help realize multi-functional THz devices and design spectrally controllable THz wave modulators for THz sensing or imaging systems.

Keywords: Terahertz wave, Organic, Modulation

I. Introduction

The development of terahertz (THz) devices has attracted significant research interest owing to their broad application in various fields, including THz spectroscopy, imaging, and communications [1-3]. In particular, active THz modulators have been extensively investigated for their use as active optical filters, active beam splitters, active mirrors, switches, and transistors. Various technologies have been applied to achieve active modulation of THz wave transmission. Different materials and structures, such as metamaterials, vanadium dioxide (VO₂), graphene, and semiconductor nanostructures, have been investigated by several research groups [4-9].

Recently, organic-based hybrid structures were suggested for the active control of the transmission of THz waves [10]. These structures have shown excellent properties and remarkable performance in terms of modulation efficiency, dynamic range, and functionality. Since our group reported organic-based active THz modulators with a modulation efficiency of 55 % in 2011 for the first time, the modulation efficiency had been steadily improved. In 2017, Yoo *et al.* demonstrated the optimal conditions for higher modulation efficiency in trilayer hybrid structures based on fullerene derivative [6,6]-phenyl-C61-butyric

acid methyl ester (PCBM) [11]. In the present study, the modulation efficiency reached nearly 100 %, achieved by optimizing the conditions of the annealing temperature, the intensity and wavelength of the excitation laser, the thickness of the organic layers, and the arrangement of the organic thin films. Several other research groups have reported that the active modulation of THz waves can be achieved by using different organic materials, polymers, or even perovskites [12-16]. Although these studies provide useful methods for improving the modulation efficiency, spectral broadness, and structural simplicity for convenient fabrication, specific functionalities, such as a selective active modulation, need to be further investigated for various applications of active THz modulators.

In this paper, we present organic-deposited metallic slit arrays fabricated on a Si substrate used for active THz modulators. The organic thin layer, which acts as an electron acceptor, is made of PCBM. The photoexcited electrons on the Si substrate are injected into the PCBM thin layer due to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy level relationship between the Si and the PCBM. The transmission rate of THz waves is decreased by the contribution of the long-lived carriers due to the separation of electrons and holes. This indicates that the PCBM thin layer becomes more metallic under photoexcitation. A plasmonic structure, consisting of periodic arrays of slits sandwiched between the Si substrate and PCBM thin layer,

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is applied to systematically realize wavelength- and polarization-dependent modulation of THz waves. The organic-metal-Si hybrid structures can be useful for designing actively controllable multi-functional THz devices and THz systems, such as spectroscopy, sensing, and imaging, requiring a complex composition of several different devices with various functions.

II. Experimental details

The plasmonic structure, consisting of periodic arrays of metallic slits, was fabricated on a Si substrate with the thickness of 500 μm and high resistivity of up to $1.0 \times 10^5 \Omega \cdot \text{cm}$, by conventional photolithography techniques. Figure 1(a) shows a microscopic image of the sample and an enlarged image with the details of the period and the width of the metallic slits. The PCBM molecules with purity higher than 99.5 %, purchased from Sigma-Aldrich (product number: 684449), were deposited on the plasmonic-Si hybrid structure, using a spin coating method. Figure 1(b) shows the molecular structure of the PCBM molecule. The thickness of the PCBM thin layer was $\sim 150 \text{ nm}$, achieved by varying the rotation speed of the spin coater and the organic concentration. Figure 1(c) shows a schematic diagram of the THz wave modulation experiment. The THz waves are incident on the side of the PCBM thin layer, and the active sample area where the THz waves and optical beams overlap with each other is fixed by a pinhole with the diameter of 3 mm. The dynamics of the photoexcited carriers at the interface between the PCBM and Si depends on the HOMO-LUMO energy level diagram shown in Fig. 1(d).

The modulated THz transmission was measured using a

Figure 1. (a) Microscopic images of the metallic slit arrays deposited on the Si substrate. The period and the width of slits are 140 and 50 μm , respectively. (b) Structure of a PCBM molecule. (c) Schematic diagram of the THz wave modulation experiment. The optical beam for photoexcitation is incident on the PCBM/metallic slit arrays/Si hybrid structure. (d) HOMO-LUMO energy level diagram of the PCBM/Si bilayer structure.

THz time-domain spectroscopy system. The THz waves were generated by a (100) p-type InAs wafer and the transmissions were measured by a photoconductive antenna method [17]. Using a cw laser diode with the wavelength of 785 nm and laser power up to 220 mW, the electrons and holes were generated on the active sample area with a diameter of $\sim 3 \text{ mm}$, formed by focusing the optical beam. The transmission time-domain signals measured with and without photoexcitation were compared and the spectral amplitudes were obtained by Fourier-transform method.

III. Results and discussion

Figure 2 shows the transmission spectra of 0° transverse magnetic (TM) and 90° transverse electric (TE) polarized THz waves, measured on the plasmonic-Si hybrid structure (without the PCBM thin layer), with and without photoexcitation, respectively. In the geometric regime, the wave-guided modes originated from the boundary conditions due to the width of metallic slits can be observed for the TE polarization. In this case, the effect of surface plasmons does not appear, while for the TM polarization, the transmission spectra measured at 0° polarization indicate the enhancement of the transmitted THz waves in the subwavelength limit [18]. For the Si substrate, the first waveguide mode appearing at 90° polarization is determined by the equation $\lambda_r = 2n(p - a)$, where n is the refractive index of Si, a is the width of metallic slits, and p is the period of metallic slit arrays. Therefore, the cut-off frequency, specifically the first waveguide mode, appears near 0.6 THz, as shown by the red curve in Fig. 2. On the contrary, for the TM polarization, the transmitted THz waves are enhanced due to the plasmonic effect of surface charges as well black curve, Fig. 2. Under the condition of photoexcitation, the transmissions of THz waves are reduced with consistent

Figure 2. Measured amplitude transmission spectra of the plasmonic-Si hybrid structure for 0° (TM) and 90° (TE) polarizations, with or without photoexcitation for each polarization.

differences throughout all frequency ranges. This is solely due to the effect of the photoexcited carriers on the Si substrate.

The dependence of laser power of the optical beam for photoexcitation on the modulation efficiency was investigated. Figure 3 shows the measured transmission amplitude spectra of the PCBM-plasmonic slits-Si trilayer hybrid structure, for 0° [Fig. 3(a)] and 90° [Fig. 3(b)] polarizations. As the laser power increases, the transmission rapidly decreases; in other words, the modulation efficiency dramatically increases, compared with those of the plasmonic slits-Si bilayer structure. The experimental results reveal that the remarkable change in the transmission of THz waves strongly depends on the presence of the PCBM layer. This implies that the increase in the modulation efficiency is associated with the carrier diffusion and injection at the interface between the PCBM thin film and the Si substrate.

When the optical beam with a center wavelength of 785 nm is incident on the Si substrate, photoexcited electrons and holes are generated. Based on the HOMO-LUMO energy level shown in Fig. 1(d), the photoexcited electrons are injected from the Si substrate into the PCBM thin layer. The PCBM thin layer becomes more metallic

due to the long-lived carriers due to the separation of the free electrons and holes; consequently the transmission of the incident THz waves is greatly reduced.

To quantitatively analyze the modulation efficiency, the spectral intensity modulation efficiency is defined as [12]

$$M = \frac{\int |E_{un}(\omega)|^2 d\omega - \int |E_{ex}(\omega)|^2 d\omega}{\int |E_{un}(\omega)|^2 d\omega}, \quad (1)$$

where E_{un} and E_{ex} represent the electric field amplitude spectra measured with and without photoexcitation, respectively [20]. To analyze the characteristics of the frequency-dependent modulation of THz waves, the value of the peak modulation efficiency obtained at a specific frequency is given by

$$M_p = \frac{|E_{un}(\omega_0)|^2 - |E_{ex}(\omega_0)|^2}{|E_{un}(\omega_0)|^2}. \quad (2)$$

Figure 4(a) shows the spectral intensity modulation efficiency, M , of the THz wave transmission, plotted as a function of the laser power of the optical beam for photoexcitation. The black and red curves indicate the M values for 0° (TM) and 90° (TE) polarizations, respectively. For both cases, the modulation efficiencies

Figure 3. Measured amplitude transmission spectra of the PCBM-plasmonic-Si hybrid structure by varying the laser power of the optical beams, for (a) 0° (TM) and (b) 90° (TE) polarizations.

Figure 4. (a) Modulation efficiency of THz wave transmission for the PCBM-plasmonic slits-Si trilayer hybrid structure plotted as a function of the laser power of the optical beams for photoexcitation, for 0° (black squares) and 90° (red circles) polarizations. (b) Peak modulation efficiencies at different laser power values as a function of frequency.

increase with the increase in the laser power of the optical beam. The modulation efficiency reaches nearly 60 % at only 20 mW (0.28 W/cm^2) and approximately 90 % at only 100 mW (1.4 W/cm^2). This implies that regardless of the rather complex structure of the PCBM-plasmonic slits-Si hybrid, compared to that of organic-Si bilayers, the modulation efficiency is highly sensitive to the density of photoexcited carriers accumulated in the PCBM thin layer.

To quantitatively analyze the frequency-dependent properties of the modulation efficiency, we calculated the M_p values at frequencies of 0.3, 0.6, 0.9 and 1.2 THz, as shown in Fig. 4(b). As expected, the modulation efficiencies increase with the increase in the laser power of the optical beam over all frequencies. However, the rate of increase of the modulation efficiency is different at different frequencies, but still depending on the laser power. At a fixed laser power of 20 mW, the modulation efficiency at longer wavelengths (lower frequencies) is higher than those at shorter wavelengths. Apparently, the behavior of the PCBM thin layer becomes similar to that of metal more easily at longer wavelengths when the carrier concentration is relatively low. This is similar to that of the plasma frequency, determining the spectral boundary exhibiting metallic properties, which shifts to higher frequencies with the increase of carrier concentration. Understanding the wavelength-dependent modulation efficiency can be useful for the design of active THz modulators with frequency-selective function.

IV. Conclusions

In this study, optically controllable THz wave modulators based on a PCBM-plasmonic metamaterial-Si trilayer hybrid structure were investigated. The decrease in the transmission of THz waves was due to the PCBM thin film, which acts as an active layer, and the characteristics of the wavelength-dependent modulation was explained by the contribution of the plasmonic metamaterial structure based on the periodic arrays of metallic slits. The cut-off frequency was clearly observed at 0° (TE) polarization, while the enhancement of the transmission of THz waves occurred at 90° (TM) polarization. In all cases, the modulation of the transmission of the THz waves was realized throughout the THz frequency range, despite that the modulation efficiency slightly depends on the wavelength of the incident THz waves. The understanding

of these phenomena can provide practical benefits in the design of spectrally controllable THz modulators for advanced THz sensing or imaging systems and in realizing multi-functional THz devices.

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