Optical Bistability of Poly(3-octylthiophene)/ Polymethylmethacrylate Composite Waveguides Processed by Organic Gas

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Abstract The optical bistable characteristics are very stable for P3OT/PMMA composite film after exposure to organic gas. This suggests that composite film exposed to organic gas has larger grain size, better molecular orientation, homogeneous bulk and smooth surface compared to that before organic gas treatment. The effect of PMMA molecular weight on the optical bistability of P3OT/PMMA composite waveguides was investigated and the on-off shift was found to decrease with the increasing of PMMA molecular weight. The bistable characteristics of P3OT/PMMA are good and the on-off position shift is less compared with P3HT/PMMA.

1 Introduction

The π -conjugated organic materials especially polymers have been investigated extensively for electronic and optoelectronic devices due to their large nonlinearity and ultrafast response time, low cost, and simple device fabrication process. Optical bistable characteristics in nonlinear composite materials have attracted much interest because of their potential applications for integrated optical devices. The optical bistability in InSb and GaAs has been studied extensively, both theoretically and experimentally, and advances in the understanding of the underlying process that give rise to the large third-order nonlinearity in the semiconductors have been reported¹⁾. Optical bistability can be established in all-optical signal processing in large-capacity optical transmission devices. However, the switching speed of an optical switch fabricated with an inorganic semiconductor is on the order of nanosecond. On the other hand, highly functionally organic materials have a π -electron conjugated systems like polymers, thus the optical device fabricated from these materials are expected to have a switching speed on the order of femtoseconds. Therefore, organic and polymer systems are expected to be appropriate materials in the fabrication of optical bistable devices. The optical bistabilities

[†] Department of Electrical Engineering, Aichi Institute of Technology, 1247 Yakusa, Toyota, Aichi 470-0392, Japan of optical devices (quasi-waveguide) composed of a prism and a dye/PMMA composite thin film were investigated. The optical bistable characteristics in a quasi-waveguide interferometer with third-order optical nonlinearity in the guiding film composed of soluble poly(diacetylene) (poly-4BCMU) were demonstrated²⁾. This device shows input-output characteristics analogous to those of a nonlinear Fabry-Perot resonator. In addition, the ultra-fast optical bistable characteristics of quasi-waveguides and waveguides prepared with vanadyl-phthalocyanine doped polymer films was observed. After organic gas treatment for 25 hrs in 1, 2-dichloroethane vapor, the third-order nonlinear susceptibility of a tertiary butyl vanadyl phthalocyanine [(t-Bu) 1.45 VOPc]/PMMA composite thin film was increased 3). The optical bistability displayed excellent stability, high sensitivity, and effective reproducibility. Previously we have systematically investigated the optical bistability of a poly(3-hexylthiophene)/ polymethylmethacrylate (P3HT/PMMA) composite waveguide. Moreover the effects of organic gas treatment and PMMA molecular weight on the optical bistability of a P3HT/PMMA waveguide have been analyzed and the results reported ⁴⁾. Here we report the optical bistability of P3OT/ PMMA composite waveguide for different input laser power intensities and the effect of organic gas treatment for 25 hrs on the optical bistability of composite waveguides. We evaluated the effect of PMMA molecular weight on the optical bistable characteristics of the P3OT/PMMA composite films and the on-off shift was found to decrease with the increase of PMMA molecular weight. The P3OT/PMMA waveguide shows good optical bistable characteristics and less on-off position shift compared with the P3HT/PMMA waveguide.

2 Experimental Procedure

Regioregular poly(3-octylthiophene) (RR-P3OT) (electronic grade, regioregularity>99% and polymethylmethacrylate (PMMA) with two different molecular weights (Mw~5050 and 9980) from Aldrich and 1, 1, 2, 2-tetrachloroethane from WAKO Chemicals were purchased. The P3OT/PMMA composite solutions were prepared by dissolving of P3OT (0.38 wt %) and PMMA (6.95 wt %) in 1, 1, 2, 2-tetrachloroethane at room temperature (20°C). Two different P3OT/PMMA composite solutions were prepared with respect to PMMA molecular weights (PMMA, Mw~5050, 9980) respectively. Then, the composite solutions were warmed at 80°C using an ultrasonic vibrator for uniform concentration in the entire volume of the solution. A triangular prism was cleaned in the sequence of acetone, ethanol and deionised water using an ultrasonic cleaner before spin coating the composite solution. To fabricate the P3OT/PMMA (PMMA, Mw~5050) composite thin film waveguide, the composite solution was dropped using a micro-syringe on the top of the triangular prism arranged in a spin coater. Then, the thin film was coated at a speed of 1,200 rpm and the spin coating time is 120 s. Under the same other P3OT/PMMA conditions, (PMMA, Mw~9980) waveguides were prepared. A total of four waveguides were prepared and the thickness of the spin coated composite thin films was measured to be approximately 3 µm using a surface profile measuring system (Dektak IIA, Sloan Tech. Corp.). The two prepared P3OT/PMMA composite waveguides were treated with organic gas for 25 hrs to evaluate the effect of organic gas treatment on the optical bistability. A glass container was arranged with special modifications suitable for organic gas treatment of the P3OT/PMMA waveguide. A glass container was filled with 1, 1, 2, 2-tetrachloroethane. Then, the quasi-waveguide constructed with a triangular prism and P3OT/PMMA composite film was inserted with a hanger into a saturated organic gas-filled glass container for 25 hrs. The organic gas treatment was performed at room temperature (20°C)^{3, 4)}. A Nd:YAG laser beam having a wavelength of 1,064 nm, a pulse width of 5 ns, and a repetition rate of 10 Hz was used as a source in the experiment to determine the optical bistable characteristics of the P3OT/PMMA waveguide. The laser beam was turned (90°) by a mirror and then split into two beams using a beam splitter. In the split beams, one beam was used as a reference light and the other beam was irradiated to

the waveguide through a convex lens with a focal length of 150 mm, exciting the transverse magnetic (TM) modes. Photo diodes (S5971-Hamamatsu Photonics) with pinhole (100 μ m) were used to detect the reference and output optical beams. The input and output photo diodes were connected with a digital oscilloscope (2.5 GS/s) to observe the bistable characteristics of the waveguide. The incident angle (30°) of the composite film coupled with a prism was adjusted by turning the rotation stage, which has a measurement accuracy of 1 min. The optical bistable characteristics of the P3OT/PMMA composite thin film waveguide were measured for different (0.16, 0.20, 0.24, and 0.26 GW/m²) input laser power intensities.

3. Results and Discussions



Fig.1 Input power dependence of optical bistability of P3OT/PMMA composite thin film (PMMA, Mw~5050).



Fig. 2 Optical bistability measured for the quasi-waveguide constructed with a triangular prism and P3OT/PMMA composite thin film treated with organic gas for 25 hrs.

Figure 1 shows the optical bistability of a quasi-waveguide

composed of a triangular prism and a P3OT/PMMA (PMMA Mw~5050) composite thin film. The optical bistability of the P3OT/PMMA composite thin film was measured for different input laser power intensities $(0.16, 0.20, 0.24 \text{ and } 0.26 \text{ GW/m}^2)$. As shown in Fig. 2, the input intensity dependence of optical bistability was observed and the on-off position is shifted according to the input intensity. Concerning the input power intensity dependence of optical bistability, the switching on-off position of the optical bistability measured with different input power intensities, shifts according to the increase in input power intensity. This indicates that when P3OT/PMMA composite film is irradiated with laser light, thermal expansion occurs in the film. It is supposed that the change in the on-off position with the input laser power intensity dependence of optical bistable characteristics is very likely to be thermal expansion due to laser irradiation. Therefore, the refractive index of the composite film irradiated with laser light changes according to the increase in input laser intensity. The shift of the on-off position of the optical bistability measured with different input laser power intensities is attributed to the change in the refractive index of P3OT/PMMA composite film irradiated with laser light. The measured optical bistability shows good hysteresis characteristics. The on-shift width between the input laser power intensity 0.24 GW/m² and 0.26 GW/m² is 0.06 GW/m^2 . The off-shift width between the laser power intensity 0.24 GW/m² and 0.26 GW/m² is 0.03 GW/m². Figure 2 shows the input power intensity dependence of the optical bistable for P3OT/PMMA characteristics measured (PMMA, Mw~5050) composite film treated with organic gas for 25 hrs. The optical bistability was observed for different input laser power intensities and the on-off position was shifted as shown



Fig. 3 Input laser power dependence of optical bistability characteristics of P3OT/PMMA (PMMA, Mw~9980) waveguide.

in Fig. 2. On the input power dependences of optical bistability, the switching on-off position of the optical bistability shifts according to the increase in input power intensity. In the input laser power dependence of optical bistability, the switching on-off position shifted with the increase in input laser power intensity. The shift of the on-off position according to the input laser power is decreased compared to that before being treated with organic gas. The bistable characteristics are very stable for P3OT/PMMA composite film exposed to organic gas. This indicates that the P3OT/PMMA composite film after being exposed to organic gas is improved with a larger grain size, and better molecular orientation, homogeneity, and surface smoothness than before organic gas treatment. Figure 3 shows the optical bistability measured with the quasi-waveguide composed of a triangular prism and P3OT/PMMA (PMMA Mw~9980) composite thin film for different input laser power intensities. The input power intensity dependence of optical bistability, the switching on-off position of the optical bistability measured with different input power intensities, and the shift increases according to the input power intensity. The on-shift width between input laser power intensities of 0.24 GW/m^2 and 0.26 GW/m^2 is 0.04 GW/m^2 and the off-shift width between the same input power intensities is 0.02 GW/m². Figure 4 shows the input laser intensity dependence of the optical bistable characteristics measured for P3OT/PMMA composite thin film (PMMA Mw~9980) treated with organic gas for the same input laser power intensities. The optical bistabilities shift towards the high-input laser power intensity of the switching on-off position with the increase in input laser power intensity, and increase the width of the bistable loop according to the increase in input laser power intensity. The on-shift width between input laser power intensities of 0.24 GW/m² and 0.26 GW/m² is 0.02 GW/m². The off-shift width between the same-input laser power intensities does not change much with input power intensities and the shift is negligible. The optical bistability shows good stability and hysteresis characteristics after organic gas treatment due to better film property. The on-off shift of the P3OT/PMMA composite waveguide is decreased according to the increase in PMMA molecular weight with the waveguide treated with organic gas. The high molecular weight PMMA has enhanced polymer stacking and electronic delocalization and it influence in the device performance. It is considered that optical bistability of P3OT/PMMA composite thin film has better performance with high molecular weight PMMA. The on-off position shift is less compared with P3HT/PMMA⁴⁾.



Fig. 4 Input laser power dependence of optical bistability characteristics of P3OT/PMMA (PMMA, Mw~9980) waveguide treated with organic gas for 25 hrs.

4. Conclusion

P3OT/PMMA composite solutions were prepared with two different PMMA molecular weights. The optical bistable characteristics of P3OT/PMMA composite thin films were measured for different input laser power intensities. The measured optical bistability displayed excellent stability and hysteresis characteristics. In the input laser power dependence of optical bistability, the switching on-off position shifted with the increase of input laser power intensity. The optical bistable characteristics are very stable for P3OT/PMMA composite film after exposure to organic gas. This suggests that composite film exposed to organic gas has larger grain size, better molecular orientation, homogeneous bulk, and smooth surface compared to that before organic gas treatment. The effect of PMMA molecular weight on the optical bistability of P3OT/PMMA composite waveguides was investigated and the on-off shift was found to decrease with the increasing of PMMA molecular weight. The bistable characteristics of P3OT/PMMA are good and the on-off position shift is less compared with P3HT/PMMA. This article is a part of manuscript of The Institute of Electrical Engineers of Japan (IEEJ).

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