Ultrafast all-optical light modulation in the near infrared region by phase sensitive polymer guided wave mode geometry containing porphyrin tapes

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A phase sensitive detection was introduced into reflection type all-optical light modulation based on guided wave mode (GWM) geometry. A polymer film containing a copper porphyrin tape and a low refractive polymer film formed GWM at specific incident angle and wavelength. Sensitive changes of output intensity were observed upon femtosecond laser excitation depending on azimuthal angles of the analyzer, which was caused by phase changes at the GWM by Δk alone. The present system has a great advantage as compared with the conventional GWM or simple transmission methods for all-optical light modulation especially for materials showing the ground state absorption. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3159620]

All-optical control of near infrared (NIR) light is very important for ultrafast optical data processing or telecommunication technologies. A Fabry–Pérot modulator has been used as tunable wavelength switches and wavelength filters.[1,2] Some semiconductors and organic compounds were studied for all-optical processing in such modulators.[1–6] A large area all-optical modulator based on transient bleaching of organic *J*-aggregate films have been demonstrated as a serial-parallel converter called as femtosecond large area parallel processor (FESLAP).[3] We have also investigated a reflectance type guided wave mode (GWM) geometry for ultrafast all-optical modulation by the use of two different polymer thin films or a thin polymer film on a metal film.[4–6] These GWM films demonstrated much higher modulation sensitivity and wavelength tunability as compared with simple transmittance type device such as FESLAP.

A spectroscopic ellipsometric method has been used for absorption measurements in a wide wavelength region by attenuated total reflection.[7,8] Using metal and dielectric films with surface plasmon resonance geometry or two different dielectric films with GWM, detection of very small refractive index changes and highly sensitive two-dimensional imaging were achieved by applying ellipsometric phase detection.[9,10] Significantly large phase shift was observed in these systems near the specific incident angle corresponding to GWM.[10,11] Schreier *et al.*[11] reported that extremely large phase change together with lateral beam displacement occurred in some different dielectric films formed a waveguide. Liu *et al.*[12] have reported from calculation that an imaginary part of the complex dielectric constant is important to large positive and negative optical beam shift in the GWM composed of a prism, air, a dielectric layer, and a glass. They compared the lateral beam shift of the order of millimeters with theoretical calculation.

Materials in the waveguide layer showing absorption, the imaginary part of complex refractive index, are essential to form GWM in two polymer layers efficiently.[5,6] Porphyrin tapes in which porphyrin rings are directly connected at three positions and arranged in a manner of tapes have been synthesized systematically up to 12-mer to show specific optical properties.[13–17] Porphyrin tapes with large expanded π-electron systems are expected as advanced materials for photonics or electronics. They have three absorption peaks corresponding to Soret-like transitions along the long and short axis transitions, and *Q*-band-like low-energy transition. The *Q*-band-like absorption bands are shifted to longer wavelength approaching near to midinfrared region dependent on the number of porphyrin units.[14] Furthermore, the relaxation process of porphyrin tapes was found to be accelerated with increasing the number of arrays due to nonradiative process.[17] Copper porphyrins usually show extremely fast intersystem crossing from excited singlet state and have relatively long lifetime of the excited triplet state. However, copper porphyrin tapes with more than four arrays show very short lifetime of the excited triplet state due to a very small energy gap.[17]

This letter reports a technique for ultrafast all-optical light processing by the phase sensitive GWM containing porphyrin tapes. Most light modulators reported so far are based on the real part change (Δn) of complex refractive index driven by electric field, heating or photochromism. We now propose a method for all-optical phase modulation, which can be achieved only by photoinduced imaginary part change (Δk). We developed a GWM geometry in order to fully utilize ultrafast photoresponses of copper porphyrin tape tetramer (CuT4) as a prominent candidate for all-optical switching in the NIR region.

A schematic representation of the present GWM system is shown in Fig. 1 together with the structure of CuT4, in which we added a polarizer, a quarter-wave plate, and an analyzer to the composite polymer GWM system we reported previously.[4–6] Absorption and transient absorption spectra are shown in Fig. 2(a) for an ARTON® (JSR, Co. Ltd.) film containing CuT4. The relaxation time for excited CuT4 in the film was estimated to be less than 1.3 ps (95%)

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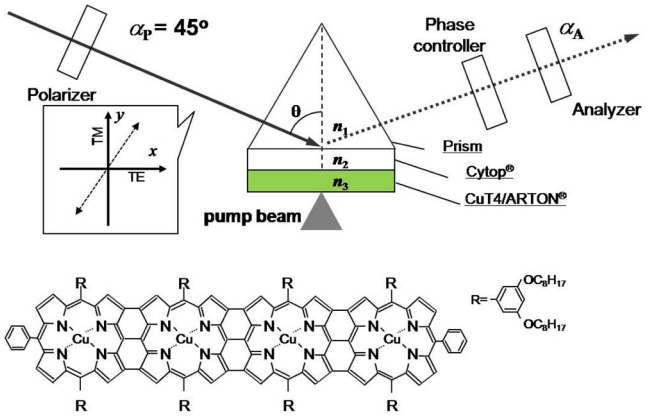

FIG. 1. (Color online) Schematic representation of a phase sensitive GWM geometry and the structure of copper porphyrin tape tetramer, CuT4.

with a very small contribution (5%) of slow component (*ca.* 30 ps). The fast component is most probably due to the internal conversion ($S_1 -> S_0$) and/or the intersystem crossing ($S_1 -> T_1$), while the slow component can be assigned to the accelerated relaxation of excited triplet state.[17] Figure 2(b) shows the difference extinction coefficient spectrum of Δk estimated from the observed transient absorption spectra in the NIR region, and that of Δn calculated by the Kramers–Kronig transformation based on Δk. It is indicated that Δn is almost zero and Δk is +0.0006 at about 1100 nm, where the k-value at the ground state was estimated to be 0.0014 from the absorption spectrum in Fig. 2(a) and its thickness.

ARTON® film containing CuT4 (2.0 wt %) was spin-coated on Cytop® film which was also prepared by spin-coating on a BK7 substrate. It was coupled with a prism by using a matching oil. The thickness value of CuT4/ARTON® and Cytop® films are 400 and 600 nm, respectively. The GWM is formed at specific incident angle in the CuT4/ARTON® film which is located between lower refractive index Cytop® and the air.

Output intensities dependent on an azimuthal angle of an analyzer (α_A) were calculated by the Jones matrix.[18] Parameters used are as follows; $n_1=1.503$, $n_2=1.335$ ($d_2=400$ nm), $n_3=1.52+ki$ ($d_3=600$ nm), the incident angle $\theta=71.1$ °, and the azimuthal angle of a polarizer $\alpha_p=45$ °, respectively. When $k=0$, the linearly polarized incident light having azimuthal angle of 45° from x-axis (TE mode) should pass through the analyzer in the arrangement of $\alpha_A=\alpha_P=45$ °. It can be seen as the bright area around 1300–1400 nm in contour graph in Fig. 3(a). However, the output intensity through the polarizer ($\alpha_P=45$ °) and the analyzer becomes very small near 1100 nm at $\alpha_A=45$ ° as shown in Fig. 3(a), which indicates that large phase change occurred near the GWM. Significant change of the intensity and the phase are also expected for both TM and TE modes at the GWM conditions due to continuous phase conditions for propagating wave in the waveguide layer, which is called as the Goos–Hänchen shift.[10,11] The output intensity becomes almost zero at $\alpha_A=45$ ° because linearly polarized incident light at 45° from x axis changes to that at 135° when the phase difference between TM and TE modes is $\pi/2$ near the GWM conditions. On the other hand, the perpendicular combination of an analyzer and a polarizer ($\alpha_A=135$ °, $\alpha_P=45$ °) gave the reversed intensity changes, showing the maximum output intensity at about 1100 nm, as shown in Fig. 3(a).

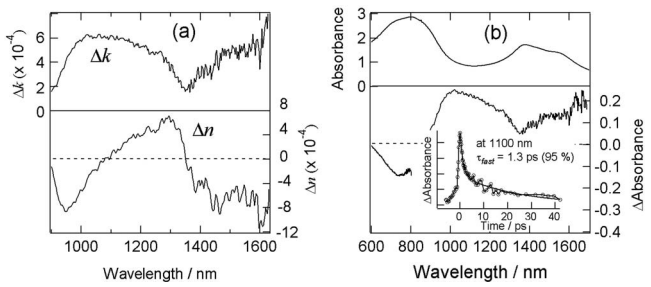

FIG. 2. (a) Absorption and transient absorption spectra upon excitation femtosecond laser at 800 nm for CuT4/ARTON® film (2.0 wt %). (b) Spectra of observed extinction coefficient change (Δk), and of Δn by Kramers–Kronig transformation from Δk.

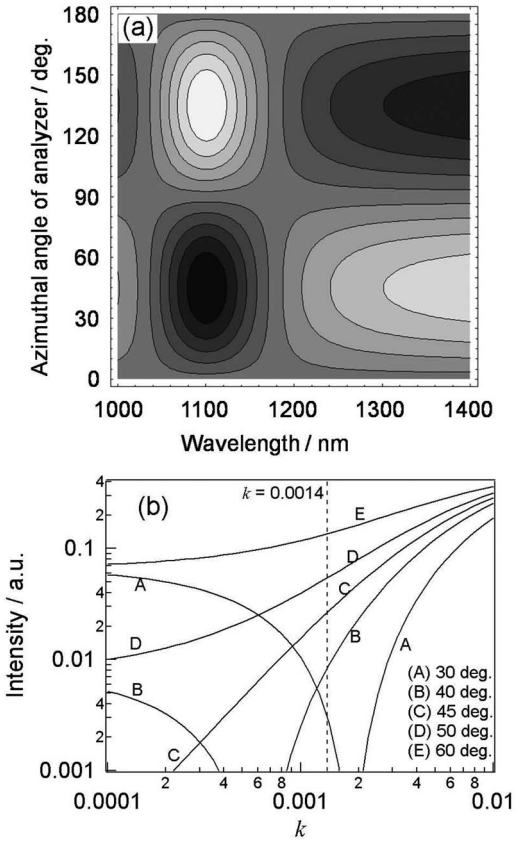

FIG. 3. (a) The calculated output intensity plotted against α_A and wavelength for the model consisted of Cytop® film (400 nm) and the waveguide layer (600 nm) with $\alpha_P=45$ °. The refractive indices of BK7, Cytop®, and the waveguide layer are as follows; $n_1=1.503$, $n_2=1.335$ and $n_3=1.50+0i$, respectively. The output intensity increases from 0 (dark) to 1 (white). (b) Calculated output intensity as a function of $\log(k)$ at various α_A from (a) 30° to (e) 60°.

The extinction coefficient dependence of output intensity is shown in Fig. 3(b) at the α_A values from 30° to 60°. If we use $k=0.0014$ of the ground state and its increment of +0.0006 at 1100 nm upon excitation as mentioned above, the output intensity is expected to decrease at $\alpha_A=30$ °, and to increase at 40°–60°, as shown in Fig. 3(b). It is thus strongly suggested that optical modulation of output intensity can be expected for both directions between dark and bright states by appropriate combination of the polarizer and the analyzer due to small change Δk alone, which is most easily achieved by transient absorption or bleaching upon photoexcitation.

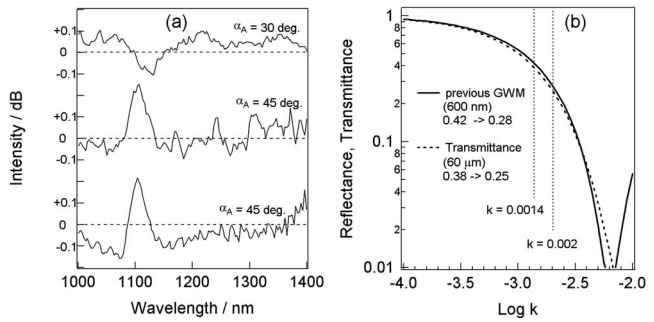

FIG. 4. (a) Output intensity changes just after femtosecond laser excitation for phase sensitive GWM geometry consisted of an ARTON® film (600 nm) containing CuT4 (2 wt %) on a Cytop® film (400 nm) at three azimuthal angles of the analyzer; 30°, 45°, and 60° from the top. (b) The solid and broken lines show reflectance for the previous GWM method without phase detection and transmittance for the 100 times thicker film (60 μm) as a function of log(k), respectively.

Figure 4(a) shows the observed reflection spectra just after 800 nm femtosecond laser excitation for the CuT4/ARTON® film at $\alpha_A = 30\,°$, 45° and 60°. In the case of $\alpha_A = 30°$, the intensity decreased, whereas at $\alpha_A = 45\,°$ and 60°, the intensity increased near 1100 nm after femtosecond laser excitation. The photoinduced change was approximately 5% due to the increase in k of the film by the transient absorption. These results well correspond to the calculated results shown in Fig. 3(b). It should be noted that the output intensity of the present system is, in principle, easily adjusted to zero by simply selecting appropriate angles of the polarizer and the analyzer before excitation, whereas it is very difficult to get zero reflectance in the previously reported GWM geometry except at the special value denoted as k_c.[5,6] In order to achieve zero reflectance for a system having finite k-value such as CuT4, it was necessary to precisely design the thickness of low refractive index layer to satisfy the k_c condition. It was easy to attain zero intensity in the absence of a sample but was difficult with for the CuT4/ARTON® film. This explains why the output change upon excitation shown in Fig. 4(a) was much smaller than expected. The distribution of incident angles was found to considerably affect the minimum intensity, about 0.1°. By using a laser diode emitting at 1063 nm, the minimum intensity with $\alpha_A = 45\,°$ observed at the GWM was less than 4% of that with $\alpha_A = 135\,°$, which was much smaller than that observed by femtosecond white light at the GWM. Therefore, relatively large minimum intensity with $\alpha_A = 45\,°$ was assigned to the distribution in both wavelength and incident angle of incompletely collimated and spectrally broadened femtosecond white light. According to calculation, more than 50% change is expected if the initial minimum reflectance is less than 0.03. The present system is more appropriate to optically switch collimated laser with single wavelength, for example, gigahertz to terahertz optical telecommunication signals in the NIR region. Calculated results for the previously reported GWM with Cytop® (400 nm) and CuT4/ARTON® (600 nm) layers and the simple transmission with the 100 times thicker film (60 μm) are given in Fig. 4(b) by solid and broken lines, respectively. The reflectance of the GWM is expected to decrease by 33% from 0.42 to 0.28 if there is no surface roughness, while the transmittance of 100 times thicker film (60 μm) will decrease by 34% from 0.38 to 0.25 if k changes from 0.0014 to 0.002, as shown in Fig. 4(b).

In conclusion, we have demonstrated an all-optical processing by the phase sensitive GWM geometry. Photoinduced complex refractive index change occurs due to transient absorption (Δk) of CuT4 and its Kramers–Kronig transformation (Δn). The response was less than 1.3 ps in the transient absorption measurement at 1100 nm. The output signal through a polarizer and an analyzer set at the input and output of GWM was demonstrated to show sensitive positive or negative changes depending on the azimuthal angle of the analyzer at 1100 nm where only Δk increased upon femto second laser excitation. The present system is concluded to have a great advantage as compared with the previously reported GWM or simple transmission methods for all-optical modulation especially with materials showing the ground state absorption.

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