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Direct micro-carbonization inside polymer using focused femtosecond laser pulses

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Localized modification of electric conductive properties inside polyfluorene derivative by using focused femtosecond laser was demonstrated. Photoinduced structures are composed of amorphous carbon transferred from three-dimensional configuration of cardo structure. Such space-selective photoinduced microstructures exhibit high electrical conductivity of about 30 S/m. © *2014 AIP Publishing LLC*.
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Coherent photon pulses with duration in femtosecond regime have opened new frontiers in material research of light-matter interactions.[1,2] The ultrafast feature of femtosecond laser pulses has been widely used for direct imaging of chemical reactions in gases[3] and terahertz spectroscopy based on photoconductive emitters[4] excited by femtosecond lasers. As a source of localized energy deposition, intense ultrashort light pulses have become key technologies for direct modification inside transparent materials due to new applications and phenomena ranging from 3D optical waveguides,[5] 5D optical storage,[6,7] polarization imaging sensor,[8,9] to 3D self-organized subwavelength nanostructures.[10] The process, initiating by a multiphoton ionization, exhibits a highly nonlinear dependence on the intensity of the light beam. The light is absorbed by photoelectrons, and the optical excitation ends before the surrounding lattice is perturbed, which results in highly localized breakdown without collateral damage of material.[11] In recent years, the existence of non-thermal ultrafast phase transitions has been observed on the surface of several materials such as silicon,[12] gallium arsenide,[13] and carbon.[14,15] In many cases, these transient phases are metal-like disordered or glassy phases resulting from laser-induced electron-hole plasma. More recently, a variety of permanent and metastable phase transformations, which are based on the structural rearrangement due to thermal accumulation[16] and the shock wave generation,[17] have been observed.[18–20] Polymer materials such as polymethylmetacrylate (PMMA), polycarbonate (PC), and polydimethylsiloxane (PDMS) are widely used in many applications due to high adjustable properties, high chemical resistance and advantageous optical properties. In the last decade, many researchers extensively have studied on the interaction between polymer materials and femtosecond laser pulses, ranging from multi-photon photo-polymerization,[21] polarization-dependent surface ablation,[22] to refractive index change.[23] However, few investigations relating spatial modification of electron properties based on the phase transformation were performed.[15,24] Here, we report the observation of a localized photoconversion to graphite-like structure inside polyfluorene derivatives composed of 3D cardo structures induced by intense ultrashort light pulses. The spiral microstructures composed of an amorphous carbon are continuously formed inside polyfluorene along with the laser spot moving by using a spatial light modulator (SLM). Depending on the writing conditions, such photoinduced amorphous structures have electrical conducting properties of a maximum of 30 S/m.

In the experiments, a regeneratively amplified mode-locked Ti:Sapphire laser pulse (Coherent Inc.; central wavelength: 800 nm, pulse width: 70 fs, pulse repetition rate: 1 kHz) was focused via an objective lens (Nikon; LU Plan Fluor, 60×0.55 N.A.) into a polyfluorene sample (Osaka Gas Chemical Co.; bland of OKP4) of $10 \times 10 \times 3$ mm size. This polyester has a high refractive index of 1.607, extremely low birefringence, and high transparency (optical band gap of ~4 eV). The pulse energy was tuned by a neutral density filter. A series of cylindrical structures with certain spacing were directly written by scanning with the typical speed of 2 μm/s along the laser irradiation direction from the bottom to the top surface. A typical diameter of the cylindrical modified region for the pulse energy of 100 nJ was estimated to be ~2 μm. The spiral microstructures were written by moving the sample in the direction of light propagation from the bottom to the top surface during the irradiation of femtosecond laser pulses. During moving sample, the lateral position of the laser focal spot was moved by changing spatial phase on SLM (Hamamatsu Photonics; LCOS-SLM). After writing, the sample surface was polished along the modified region, and then the cross-sectional surface was inspected by using an optical microscope, a scanning electron microscope (JEOL; JSM-6700F), and a confocal Raman spectrometer (Tokyo Instruments; Nanofinder 30). The local electrical properties of the photoinduced structures were evaluated by a nano-probing system (Hitachi High-Tech; N-6000).

A black cylindrical structure was induced inside the sample without any surface damages for the laser fluence larger than 1.6 J/cm^2 (Fig. 1(b)). Therefore, the threshold of the photoinduced structural change inside polyfluorene was estimated to 1.6 J/cm^2. The scanning electron images (SEIs) reveal that the morphology within a laser-irradiated region obviously remain densified, namely, a void does not exist (Figs. 1(c) and 1(d)). Incidentally, the dark spot in the middle

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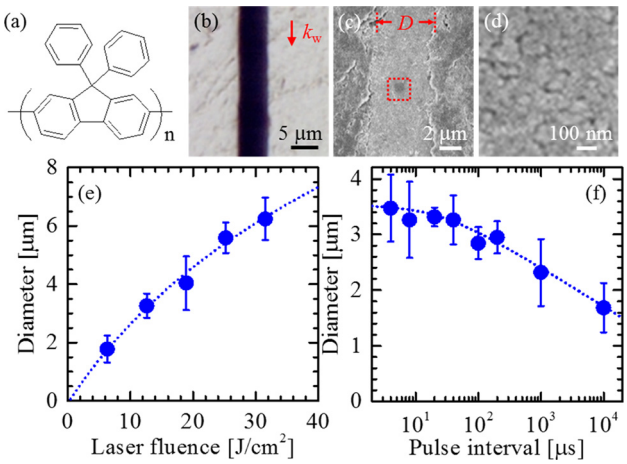

FIG. 1. Schematic of cardo structure of polyfluorene (a), optical micrograph (b), and SEI (c) on the cross-sectional surface of the photoinduced structures. The high magnification SEI in the dotted area in (c) is also shown in (d). Arrow of k_w indicates the laser propagation direction. D indicates the diameter of the photoinduced structure. Diameter of the photoinduced structure as a function of the laser fluence (e) and the pulse interval (f).

of written structure (Fig. 1(b)) is the artifact caused by a contamination during the observation at higher magnification (Fig. 1(c)). The diameter of the cylindrical photoinduced structures logarithmically increased with increasing the laser fluence (Fig. 1(e)). While, the diameter logarithmically decreased with increasing the laser pulse interval (Fig. 1(f)). In the case of the pulse interval shorter than 200 μs, unbroken cylindrical structures were formed by moving a tightly focused laser spot with the laser fluence of 1.8 J/cm^2.

The current-voltage characteristics of the photoinduced structures were measured by using two-terminal method (Fig. 2(a)). The distance between the two probes were measured to be 80 μm under SEI. It should be noted that, in our experiments, the impedance contribution of the wiring and contact resistances was very small enough to be ignored. We have also observed the SEIs of around the nanoprobe tips

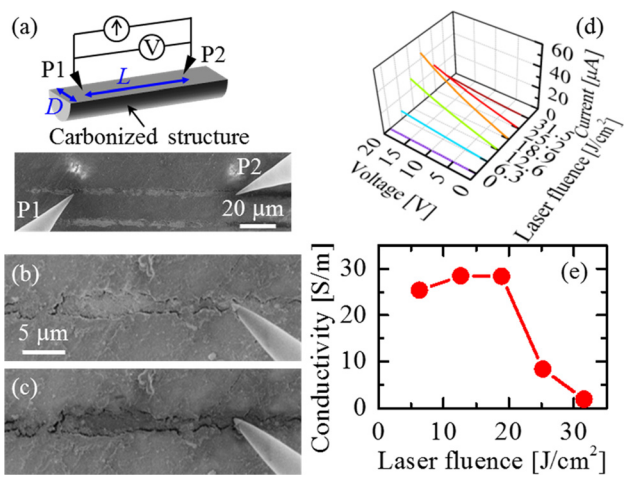

FIG. 2. (a) Schematic illustrations of the two-terminal method and the semicircular column-shaped test sample, where P1 and P2 are the nanoprobes. SEI during the conductivity measurements using two-nanoprobes is also shown. SEIs of around the nanoprobe tips before (b) and after (c) the contact with the objects are also shown. (d) I-V characteristics as a function of the laser fluence. (e) Specific electrical conductivity of the modified regions as a function of the laser fluence.

before and after the contact with the modified region (Figs. 2(b) and 2(c)). Although no apparent change of the brightness of the surrounding region was observed, the brightness of SEIs in the modified region became dark during the probe contacts with the object. This phenomenon can be interpreted that since the polyfluorene does not have high electric conductivities, the irradiated electrons during SEI observation were diffused away through nanoprobe tips. This result evidently indicates that the photoinduced structures have electric conductive properties. We have also confirmed that the electrical resistivities of the modified regions were proportional to the distance between nanoprobes. Fig. 2(d) shows the current-voltage characteristics as a function of the laser fluence. Although the initial polyfluorene shows no electrical conductivity, the photoinduced structures in polyfluorene exhibit electrical conductive properties depending on the laser fluence; especially, the maximum conductivity was obtained at about 20 J/cm^2. Assuming that a measured region is a semicircular column-shaped structure (Fig. 2(a)), the electrical conductivities of the photoinduced structures can be obtained from the following equation: $\sigma = 8L/\pi RD^2$, where σ and R is the electrical conductivity and the measured resistance for the photoinduced structure with the length of L and the diameter of D (Fig. 2(a)). Despite the increase of the diameter of the induced structure with increasing the laser fluence, the electrical conductivities increase slightly with increase of the laser fluence, and then reached the maximum of about 30 S/m at the laser fluence of about 20 J/cm^2. Because this result is contrary to the equation, we speculated that there are other dominant factors affecting the conductivities. Considering the fact that the Raman intensity of the I_D/I_G is inversely proportional to the graphite crystallize size,[25] the relatively ordered carbon structures are thought to be formed in the relatively low fluence (Fig. 4(b)). While, in the case of the higher laser fluence than 20 J/cm^2, unfortunately, the electrical conductivities decreased dramatically.

To investigate the decrease of electrical conductivity for higher laser fluence, we performed the time sequential observation of the photoinduced structure corresponding to the number of pulses (Fig. 3). The modifications induced by three different laser fluence were observed from the direction perpendicular to the laser propagation (k_w). In the initial stage below 10 pulses, the structural modification occurs via multiphoton ionization process, regardless of the laser fluence. In this process, a filamentous fine structure was formed around the beam focus. After the several tens of pulses, the structural change was elongated to the laser incident direction, which can be interpreted in terms of the thermal process through the one-photon absorption by the existing modified structure, because the π electrons in graphite show a broad absorption from UV to IR. In the case of the low laser fluence of 6.3 J/cm^2, a black teardrop-shaped structure was formed. Such shape is considered to be attributed to the spherical aberration due to the refractive index mismatch between the air and the polyfluorene. In particular, in the case of the higher laser energy, it is well known that the filamentation caused by the balance between the self-focusing and the plasma generation also extend the modification along the laser propagation direction.[26] This phenomenon causes severe localization of the laser energy, leading to the

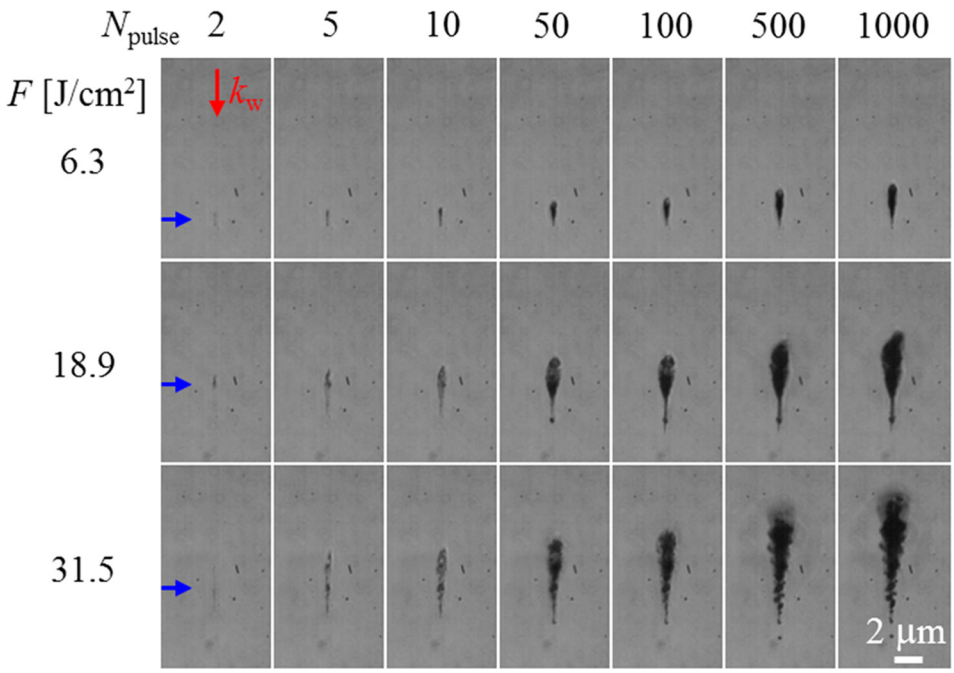

FIG. 3. Time sequential photos of the photoinduced structures corresponding to the number of shots (N_{pulse}) taken by high speed camera. The laser pulse repetition rate is 1 kHz. F is the laser fluence. Arrow of k_w indicates the laser propagation direction. The blue arrows with lateral direction indicate the focal location.

formation of the thick and discontinuous structures. Indeed, the thicker teardrop-shaped structures caused by the multiple filamentation were induced for the higher laser fluence than 18.9 J/cm^2.

In order to reveal the microscopic structural change induced by laser irradiation, we carried out micro-Raman spectroscopy on the cross-sectional surface with 1 μm spatial resolution (Fig. 4). The several narrow peaks corresponding to the ring stretch mode of fluorene and the C-C stretching mode between phenylene rings were observed in the Raman spectrum of the initial polymer. On the other hand, in the photoinduced structures, two broad Raman peaks were observed at around 1580 cm^{-1} and 1345 cm^{-1}. These two peaks are attributed to the G-peak (~1580 cm^{-1}) and the D-peak (~1345 cm^{-1}), which are derived from disordered carbon structure (Fig. 4(a)). These peaks are normally assigned to optical zone center phonon of E_{2g} symmetry involving the in-plane bond-stretching motion of all pairs of sp^2 sites and K-point phonons of A_{1g} breathing mode of C sp^2 atoms in rings, respectively.[27] The broad D-peak is indicative of the existence of disordered carbon in a carbon network, showing that the photoinduced structures are composed of graphite transformed from conformation of a polyfluorene derivative. Furthermore, the shape of Raman spectrum is considered to depend on a number of factors: clustering of the sp^2 phase, structural disorder, or the sp^2/sp^3 ratio.[27] Results of the curve-fitting indicate a large overlap between G- and D-peaks, implying that a crystallite size of sp^2 carbon structure is quite small (Fig. 4(a)). It is well known that the intensity ratio of I_D/I_G, called as R-value, increases with increasing disorder.[23] The R-value for the photoinduced structures slightly decreased from 6 to 4 with increase in the laser fluence and reached a minimum at about 20 J/cm^2 (Fig. 4(b)). These results indicate that the degree of disorder is high and amorphous carbon is induced, suggesting that the percentage of the photoinduced sp^2 carbon is small. To improve the electric conductivities, a polymer structure in which aromatic rings are oriented three-dimensionally is required. Another possibility of the low electrical conductivities of the photoinduced structures compared to the graphite is density of the modified region. Fluorene derivative polymer has lower density of about 1.22 g/cm^3 compared to that of graphite of 2.26 g/cm^3. Although the photoinduced regions were relatively dense, very fine nanovoids with several nanometers size were observed (Fig. 1(e)). These nanovoids cause to decrease the conductivity of photoinduced structure. Besides, in the case of the higher laser fluence, although the R-value changes little, the formation of the discontinuous structures owing to the multi filaments implies the low electric conductive properties. When the structural densification

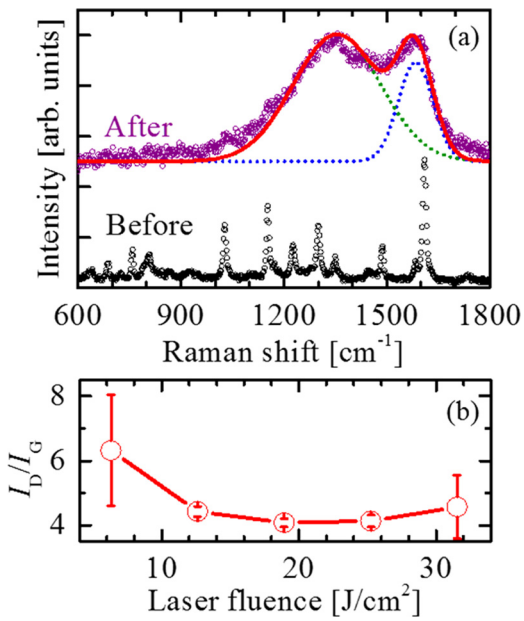

FIG. 4. (a) Raman spectra of fluorene polymer before and after laser irradiation. The components of the G-peak (blue dashed line) and D-peak (green dashed line) deduced from the peak fittings (red solid line) are also shown. (b) Profile of Raman peak intensity ratio of I_D/I_G for the photoinduced structures as a function of laser fluence.

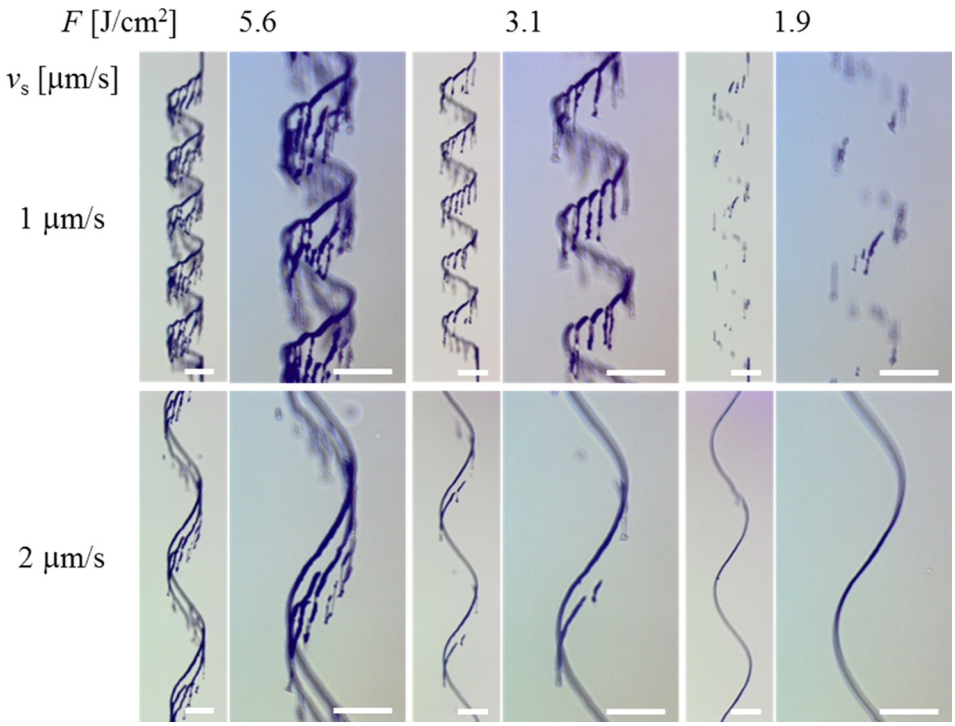

FIG. 5. Optical microscope images of the photoinduced spiral microstructures by the femtosecond laser pulses with the various fluence ranging from 5.6 to 1.9 J/cm^2 and the different writing speed of (upper row) 1 μm/s and (lower row) 2 μm/s. There are two different magnification photos, respectively.

as large as the density of graphite can be induced inside a focal volume, it is possible to enhance the electrical conductivities. Recently, an atomistic simulation of graphitization of the diamond surface by laser irradiation was reported.[24] This permanent phase transformation can be interpreted in terms of the structural rearrangement from the 3D carbon network to the 2D graphite layer due to thermal accumulation and the shock wave generation. Consequently, in the case of the polymer structure including a lot of aromatic rings, graphite is considered to be induced by the femtosecond laser irradiation.

Apart from the basic understanding, we have also demonstrated the formation of the spiral microstructures with an electric conductivity (Fig. 5). Such spiral structure with electric conductivities has a potential to serve as a solenoidal magnet, and is reminiscent of a terahertz metamaterial.[28]

By switching the computer generated holograms (CGH) on the SLM in synchronization with the Z axis motorized stage, the focal spot was connected spirally. The switching speed of the CGH patterns was 60 Hz. The spiral microstructures with the helical period of 40 μm and 80 μm were formed at the stage speed of 1 μm/s and 2 μm/s, respectively. In the case of the helical period of 40 μm, no apparent continuous microstructures were induced. While, for the faster writing speed of 2 μm/s and the lower laser fluence of 1.9 J/cm^2, the smooth and continuous spiral microstructures were formed. By optimizing the writing conditions, more complicated microstructures with electric conductive properties can be directly formed inside polyfluorene derivative.[15]

In summary, we have shown that the photoinduced structures in polyfluorene derivative by the femtosecond laser irradiation exhibit the electric conductive properties of about 30 S/m. Such photoinduced structures are identified as an amorphous carbon with sp^2 carbon structure. We believe with confidence that such microstructures act as a metallo-dielectric photonic crystals and an electronic devices on flexible platforms.

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[1]S. K. Sundaram and E. Mazur, Nat. Mater. **1**, 217 (2002).
[2]W. Yang, P. G. Kazansky, and Y. P. Svirko, Nat. Photonics **2**, 99 (2008).
[3]H. Ihee, V. A. Lobastov, U. M. Gomez, B. M. Goodson, R. Srinivasan, C.-Y. Ruan, and A. H. Zewail, Science **291**,458 (2001).
[4]G. Klatt, F. Hilser, W. Qiao, M. Beck, R. Gebs, A. Bartels, K. Huska, U. Lemmer, G. Bastian, M. B. Johnston, M. Fischer, J. Faist, and T. Dekorsy, Opt. Express **18**, 4939 (2010).
[5]M. Sakakura, T. Sawano, Y. Shimotsuma, K. Miura, and K. Hirao, Opt. Express **18**, 12136 (2010).
[6]Y. Shimotsuma, M. Sakakura, P. G. Kazansky, M. Beresna, J. Qiu, K. Miura, and K. Hirao, Adv. Mater. **22**, 4039 (2010).
[7]J. Zhang, M. Gecevičius, M. Beresna, and P. G. Kazansky, Phys. Rev. Lett. **112**, 033901 (2014).
[8]Y. Shimotsuma, K. Miura, and K. Hirao, Int. J. Appl. Glass Sci. **4**, 182 (2013).
[9]M. Gecevičius, M. Beresna, and P. G. Kazansky, Opt. Lett. **38**, 4096 (2013).
[10]Y. Shimotsuma, P. G. Kazansky, J. Qiu, and K. Hirao, Phys. Rev. Lett. **91**, 247405 (2003).
[11]D. Du, X. Liu, G. Korn, J. Squier, and G. Mourou, Appl. Phys. Lett. **64**, 3071 (1994).
[12]C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983).
[13]P. Saeta, J.-K. Wang, Y. Siegal, N. Bloembergen, and E. Mazur, Phys. Rev. Lett. **67**, 1023 (1991).
[14]H. O. Jeschke, M. E. Garcia, and K. H. Bennemann, Appl. Phys. A **69**, S49 (1999).
[15]M. Shimizu, Y. Shimotsuma, M. Sakakura, T. Yuasa, H. Homma, Y. Minowa, K. Tanaka, K. Miura, and K. Hirao, Opt. Express **17**, 46 (2009).
[16]M. Sakakura, M. Shimizu, Y. Shimotsuma, K. Miura, and K. Hirao, Appl. Phys. Lett. **93**, 231112 (2008).
[17]M. Sakakura, M. Terazima, Y. Shimotsuma, K. Miura, and K. Hirao, Opt. Express **15**, 5674 (2007).

[18]K. Miura, J. Qiu, T. Mitsuyu, and K. Hirao, Opt. Lett. **25**, 408 (2000).
[19]H. Adachi, K. Takano, Y. Hosokawa, T. Inoue, Y. Mori, H. Matsumura, M. Yoshimura, Y. Tsunaka, M. Morikawa, S. Kanaya, H. Masuhara, Y. Kai, and T. Sasaki, Jpn. J. Appl. Phys., Part 2 **42**, L798 (2003).
[20]D. Tan, Y. Yamada, S. Zhou, Y. Shimotsuma, K. Miura, and J. Qiu, Nanoscale **5**, 12092 (2013).
[21]S. Maruo, O. Nakamura, and S. Kawata, Opt. Lett. **22**, 132 (1997).
[22]J.-M. Guay, A. Villafranca, F. Baset, K. Popov, L. Ramunno, and V. R. Bhardwaj, New J. Phys. **14**, 085010 (2012).
[23]P. J. Scully, D. Jones, and D. A. Jaroszynski, J. Opt. A: Pure Appl. Opt. **5**, S92 (2003).
[24]C. Z. Wang, K. M. Ho, M. D. Shirk, and P. A. Molian, Phys. Rev. Lett. **85**, 4092 (2000).
[25]F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126 (1970).
[26]A. Couairon, L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, Phys. Rev. B **71**, 125435 (2005).
[27]A. C. Ferrari and J. Robertson, Phys. Rev. B **61**, 14095 (2000).
[28]H.-T. Chen, J. F. O'Hara, A. K. Azad, A. J. Taylor, R. D. Averitt, D. B. Shrekenhamer, and W. J. Padilla, Nat. Photonics **2**, 295 (2008).