Ag nanocrystal-incorporated germano-silicate optical fiber with high resonant nonlinearity

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Silver nanocrystal-incorporated germano-silicate optical fiber was fabricated by modified chemical vapor deposition and solution doping techniques. By measuring the wavelength shift of the fringes obtained from the long-period fiber grating pair, upon pumping with an argon-ion laser at 499 nm, the resonant nonlinear refractive index around 1550 nm was estimated to be $5.4 \times 10^{-16}$ m$^2$/W. The observed high resonant optical nonlinearity of the silver nanocrystal-incorporated fiber is attributed to the contribution from the surface plasmon resonance of silver nanocrystals embedded in the fiber core. © 2008 American Institute of Physics. [DOI: 10.1063/1.2957029]

Future optical switching systems are expected to process net data rates approaching a terabit per second (Tbit/s).1 These advantageous time-division-multiplexed systems require ultrafast optical switches possessing a high Kerr effect and an extremely fast response time. Metal nanoparticles are of special interest as nonlinear materials for ultrafast all-optical switching and computing because of their relatively large third-order nonlinearity and ultrafast response time of picosecond level.2,3 The third-order nonlinear susceptibility of metal nanoparticles dispersed in glass can be enhanced by seven orders ($10^7$ times) of magnitude near the surface plasmon resonance (SPR) frequency.4

In a metal nanocrystal system—such as gold, silver, and copper dispersed in a transparent matrix—an absorption peak due to the SPR is usually observed in the visible spectral region.2,4 In Au and Cu nanocrystals, the interband transitions of the $d$ band to the $sp$ bands lie in the same spectral region as the SPR. Consequently, both the SPR and the interband transitions contribute to the nonlinear processes, making it difficult to separate out the sole SPR contribution to the nonlinear optical properties. However, in the case of Ag nanocrystals, the contribution to nonlinear optical properties can be easily distinguished because the SPR energy ($\approx 2.9$ eV) is far from the interband transitions energy ($\approx 3.9$ eV).5 Based on our previous research related to glass optical fibers doped with Au and Si nanocrystals,6 we fabricated Ag nanocrystal-incorporated germano-silicate optical fiber Ag_Fiber by modified chemical vapor deposition (MCVD) and solution doping techniques. We investigated the linear and nonlinear optical properties of these nanocrystals.

Due to high-temperature-induced self-reduction reactions during the MCVD processes, the doped Ag$^+$ ions were easily transformed into Ag$^0$ atoms and subsequently clustered into nanocrystals inside the silica glass.7 Since cerium ions are considered an effective trap center by providing and capturing charge carriers in host materials,8 we introduced Ce$^{3+}$ ions in the core of the fiber preform during the solution doping process to prevent the Ag nanocrystals from being oxidized into Ag$^+$ ions again during the formation of fiber preform. The related sensitizing reaction inside the fiber core is as follows:8,9

$$\text{Ag}^+ + \text{Ce}^{3+} \rightarrow \text{Ag}^0 + \text{Ce}^{4+}.$$  (1)

Compared with a reference fiber without a dopant (Ref. Fiber), Fig. 1 shows the absorption spectrum of the Ag_Fiber with the absorption peak centered at 501 nm (2.47 eV), which is due to the SPR absorption of the Ag nanocrystals. This is indirect evidence of the existence of Ag nanocrystals inside the fiber core.2,6 The average radius of the doped Ag nanocrystals was estimated to be 3.29 nm by Eq. (2):11

$$R = \frac{n_0 V_F \lambda^2_{\text{SPR}}}{2 \pi c \Delta \lambda_{\text{SPR}}},$$  (2)

where $V_F$ is the Fermi velocity of the electrons in bulk metal ($V_F=1.39 \times 10^6$ m/s for silver), $c$ is the light velocity in vacuum ($c=3.0 \times 10^8$ m/s), $n_0$ is the refractive index of the

![FIG. 1. Absorption spectra of the fibers doped with (Ag_Fiber) and without Ag nanocrystals (Ref. Fiber).](image-url)
host material ($n_0=1.4552$ for the germano-silicate fiber core in this experiment), $\lambda_{P,SPR}$ is the characteristic peak wavelength at which SPR occurs, and $\Delta\lambda_{SPR}$ is the full width at half maximum of the absorption band. Both $\lambda_{P,SPR}$ and $\Delta\lambda_{SPR}$ depend on the surrounding composition and size of the metal nanoclusters forming the composite.

The long-period fiber grating (LPG) pair method upon pumping was adopted to estimate the resonant optical nonlinearity of the Ag_Fiber. The resonant nonlinear refractive index $n_2$, $[(P,SPR)$, the effective length $L_{eff}$, and the effective area $A_{eff}$ of the made fibers are estimated as shown in Ref.12 and the data are summarized in Table I. The latter further includes the peak wavelength of the LPG fringe $\lambda_{P,LPG}$, the wavelength shift $\Delta\lambda_{LPG}$ of the LPG fringe, the fringe spacing $S$, the pumping power $P_{pump}$ from the 499 nm continuous-wave argon-ion laser (launched into the tested fiber), and the slope coefficient $\kappa_w$ determined from the linear region of the function $\Delta\lambda_{LPG}/P_{pump}$. As shown in Fig. 2, the total fringe shift $\Delta\lambda_{LPG}$ of the Ag_Fiber LPG pair was 0.5323 nm at the optical communication window of 1550 nm upon pumping with the 499 nm argon-ion laser at the launched power of 90 mW. The resonant nonlinear refractive index $n_{2,R}$ of the Ag_Fiber in the vicinity of 1550 nm was estimated to be $5.4 \times 10^{-16}$ m$^2$ W$^{-1}$, which is more than 13 times of that of the Ref. Fiber and also four orders of magnitude larger than the nonresonant nonlinear refractive index $n_{2,NR}$ of the commercial single mode silica fiber.13

In total, three possible electronic contributions can be considered to explain the photo-induced absorption and nonlinear response observed in the Ag_Fiber: Interband transitions, intraband transitions, and hot electrons, as illustrated in Fig.3.2,14 When the excitation frequency is close to the SPR frequency ($501$ nm or $2.47$ eV, in our experiment)—as is the case for Ag nanocrystals excited at 499 nm ($2.48$ eV), which is far from the interband transition energy ($\geq 3.9$ eV or $\leq 316$ nm) mentioned above—no energy is absorbed to promote the interband transitions between the spatially localized $d$ valence bands and the free-electron-like $sp$ conduction band, thus excluding the contribution from the interband transitions to the nonlinear processes. Part of the excitation energy promotes the intraband transitions between the filled and empty states in the $sp$ conduction band. However, its contribution is as small as that with the order of $10^{-17}$ m$^2$ W$^{-1}$ and therefore cannot be the main origin of the observed nonlinear response of the Ag_Fiber.4 Hot electrons, which are conduction electrons but are easily raised to high temperature when excited near the SPR frequency, are not in thermal equilibrium with the lattice. Their Fermi–Dirac distribution is therefore changed; part of the one-electron levels below the Fermi level is emptied whereas part of the levels above the Fermi level is occupied (see Fig. 3). This modifies the absorption coefficient and dielectric function of the composite, leading to the distinct nonlinear refractive index change according to the Kramers–Kronig relation.15,16 Consequently, we can conclude that the SPR contribution from the hot elec-

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{eff}$</th>
<th>$L_{eff}$</th>
<th>$\lambda_{P,LPG}$</th>
<th>$S$</th>
<th>$\kappa_w$</th>
<th>$n_{2,R}$</th>
</tr>
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<tbody>
<tr>
<td>Unit</td>
<td>$\mu m^2$</td>
<td>cm</td>
<td>nm</td>
<td>nm</td>
<td>nm/mW</td>
<td>$10^{-16}$ m$^2$/W</td>
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<tr>
<td>Ag_Fiber</td>
<td>57.6</td>
<td>14.69</td>
<td>1549</td>
<td>5.02</td>
<td>0.00575</td>
<td>5.4</td>
</tr>
<tr>
<td>Ref. Fiber</td>
<td>68.2</td>
<td>14.96</td>
<td>1548</td>
<td>3.07</td>
<td>0.00267</td>
<td>0.4</td>
</tr>
</tbody>
</table>

FIG. 2. (a) Fringes in transmission spectrum of the Ag_Fiber with the LPG pair upon argon-ion laser pumping at 499 nm, (b) enlarged chosen point in (a), and (c) pumping power dependence of the fringe shifts.
nanocrystals, i.e., the generation and relaxation of the hot electrons originating from the $sp$ conduction band when excited at 499 nm, is the mechanism mainly responsible for the observed high $n_{2, R}$ of the Ag_Fiber. It is important to note that the $n_{2, R}$ of the Ref. Fiber, i.e., intrinsic $n_{2, R}$ solely from the host glass materials, is also three orders of magnitude larger than its $n_{2, NR}$, which is attributed mainly to the near-UV linear absorption-induced nonlinearity from the germano-silicate glass fiber itself.\textsuperscript{2,16} Even though the thermo-optic effects from the intense pumping signal at 499 nm will definitely contribute to the whole $n_{2, R}$ of both the Ag_Fiber and the Ref. Fiber, it is omitted from our current discussion due to its extremely small value compared with the electronic contribution (the hot electron contribution as to the Ag_Fiber and the near-UV linear absorption contribution as to the Ref. Fiber in this letter).\textsuperscript{17,18}

In summary, we successfully fabricated germano-silicate optical fiber containing Ag nanocrystals by MCVD and solution doping techniques. The SPR absorption band of the Ag nanocrystals was found to appear centering at 501 nm (2.47 eV). The resonant nonlinear refractive index $n_{2, R}$ at 1550 nm was estimated to be $5.4 \times 10^{-16}$ m$^2$/W by using the LPG pair method upon pumping with the 499 nm argon-ion laser. This high $n_{2, R}$ was mainly attributed to the generation and relaxation processes of the hot electrons arising from the $sp$ conduction band when excited near SPR frequency of silver nanocrystals.

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