

Luminescence enhancement by Au nanoparticles in Er³⁺-doped germano-silicate optical fiber

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Abstract: We report on the fabrication of the Au nanoparticles/Er³⁺ codoped germano-silicate fibers by modified chemical vapor deposition and solution doping processes. Absorption and luminescence characteristics of the Er³⁺-doped germano-silicate fibers incorporated with Au nanoparticles in the core of the fibers were investigated. The Au nanoparticles were found to be effective absorbents for hydroxyl groups to enhance the luminescence of Er³⁺ ions upon pumping with the 980nm laser diode.

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References and links

1. Y. Sun, J. W. Sulhoff, A. K. Srivastava, J. L. Zyskind, T. A. Strasser, J. R. Pedrazzani, C. Wolf, J. Zhou, J. B. Judkins, R. P. Espindola, and A. M. Vengsarkar, "80nm ultra-wideband erbium-doped silica fiber amplifier," *Electron. Lett.* **33**, 1965-1966 (1997).
2. K. Song and M. Premaratne, "Effects of SPM, XPM, and Four-Wave-Mixing in L-band EDFAs on fiber-optic signal transmission," *IEEE Photon. Tech. Lett.* **12**, 1630-1632 (2000).
3. Y. Liu, S. Burtsev, S. Hegarty, R. S. Mozdy, M. Hempstead, G. G. Luther and R. G. Smart, "Four wave mixing in EDFAs," *Electron. Lett.* **35**, 2130-2131 (1999).
4. S. Tammela, M. Hotoleanu, P. Kiiveri, H. Valkonen, S. Sarkilahti, and K. Janaka, "Very short Er-doped silica glass fiber for L-band amplifiers," in *Optical Fiber Communications Conference*, OSA Technical Digest Series (Optical Society of America, 2003), Vol. 1, pp. 376-377.
5. P. L. Chu, "Nonlinear effects in rare-earth-doped fibers and waveguides," in *Proceedings of Lasers and Electro-Optics Society Annual Meeting (LEOS'97 10th Annual Meeting, Academic, San Francisco, CA Technical meeting, 1997)*, pp. 371-372.
6. R. A. Betts, T. Tjugiato, Y. L. Xue, and P. L. Chu, "Nonlinear refractive index in Erbium doped optical fiber: theory and experiment," *IEEE J. Quantum. Elect.* **27**, 908-913 (1991).
7. J. W. Arkwright, P. Elango, and G. R. Atkins, "Experimental and theoretical analysis of the resonant nonlinearity in ytterbium-doped fiber," *J. Lightwave Technol.* **16**, 798-806 (1998).
8. H. Dislich, "Sol-gel 1984→2004," *J. Non-Cryst. Solids* **73**, 599-612 (1985).
9. H. Kozuka and S. Sakka, "Preparation of gold colloid-dispersed silica-coating films by the sol-gel method," *Chem. Mater.* **5**, 222-228 (1993).
10. C. Coutier, W. Meffer, P. Jenouvrier, J. Fick, M. Audier, R. Rimet, B. Jacquier, and M. Langlet, "The effects of phosphorus on the crystallisation and photoluminescence behavior of aerosol-gel deposited SiO₂-TiO₂-Er₂O₃-P₂O₅ thin films," *Thin Solid Films* **392**, 40-49 (2001).
11. C. Strohhofer and A. Polman, "Silver as a sensitizer for erbium," *Appl. Phys. Lett.* **81**, 1414-1419 (2002).
12. M. Fukushima, N. Managaki, M. Fujii, H. Yanagi, and S. Hayashi, "Enhancement of 1.54-μm emission from Er-doped sol-gel SiO₂ films by Au nanoparticles doping," *J. Appl. Phys.* **98**, 024316-1~4 (2005).
13. S. Ju, V. L. Nguyen, P. R. Watekar, B. H. Kim, C. Jeong, S. Boo, C. J. Kim, and W. -T. Han, "Fabrication and optical characteristics of novel optical fiber doped with the Au nanoparticles," *J. Nanosci. Nanotechnol.* **6**, 3555-3558 (2006).
14. A. Lin, D. H. Son, I. H. Ahn, G. H. Song, and W. -T. Han, "Visible to infrared photoluminescence from gold nanoparticles embedded in germano-silicate glass fiber," *Opt. Express* **15**, 6374-6379 (2007).
15. A. Lin, B. H. Kim, S. Ju and W. -T. Han, "Fabrication and third-order optical nonlinearity of germano-silicate glass optical fiber incorporated with Au nanoparticles," *Proc. SPIE* **6481**, 64810M1-7 (2007).

16. G. Baysinger, T. F. Koetzle, L. I. Berger, K. Kuchitsu, N. C. Craig, C. C. Lin, R. N. Goldberg, A. L. Smith, "Section 4: Physical constants of inorganic compounds," in *Handbook of Chemistry and Physics*, D. R. Lide ed., (CRC Press LLC, Boca Raton, 2000), paper 4-61.
17. W. Yan, B. Chen, S. M. Mahurin, E. W. Hagaman, S. Dai and S. H. Overbury, "Surface sol-gel modification of mesoporous silica materials with TiO₂ for the assembly of ultrasmall gold nanoparticles," *J. Phys. Chem. B* **108**, 2793-2796 (2004).
18. F. Hache, D. Ricard, C. Flytzanis, and U. Kreibig, "The optical Kerr effect in small metal particles and metal colloids: the case of gold," *Appl. Phys. A* **47**, 347-357 (1988).
19. K. Puech and W. J. Blau, "Ultrafast relaxation dynamics of the optical nonlinearity in nanometric gold particles," *J. Nanopart. Res.* **3**, 13-21 (2001).

1. Introduction

The Er³⁺-doped fiber amplifiers (EDFAs) have been extensively studied as key devices for wavelength division multiplexing (WDM) optical communication systems with the development of high-power semiconductor laser diodes (LD). Especially, the L-band EDFAs are known to have high gain, low noise, and wide-gain band over 80nm [1]. However, there has been a need to reduce the length of the erbium doped fiber (EDF) for cost down maintaining the high performance. The long EDF has several drawbacks. First, the long EDF increases the nonlinear optical phenomena, especially four wave mixing (FWM), which is proportional to the square of the length of the EDF [2, 3]. This nonlinear interaction between the optical signals creates inter-channel cross talk and thus degrades transmission capacity. Secondly, polarization mode dispersion (PMD) becomes a limiting factor in the 40Gbit/s and beyond transmission systems designed to operate over long distances [4]. Therefore, the EDF contribution to the total PMD has to be minimized. Finally, long fiber length creates challenges for the fiber management in the large-scale amplifier assembly.

The increase of Er³⁺ ions concentration in the fiber core is an effective method to get higher amplification, whereas high concentration of Er³⁺ ions may lead to high resonant nonlinearity when the EDF is pumped at 980nm [5-7]. Therefore, use of the modified chemical vapor deposition (MCVD) and solution doping processes to make EDF with low Er³⁺ concentration of ppm level but keep high efficient emission at the same time is more attractive than the traditional melting and sol-gel methods [8, 9]. The hydroxyl groups usually inevitably exist in silica-based or germano-silicate glass fibers. Since two vibrations of hydroxyl groups are enough to bridge the gap of about 6500cm⁻¹ between the ground ⁴I_{15/2} state and the first excited ⁴I_{13/2} state of Er³⁺, the excited Er³⁺ efficiently transfers energy to the vibration of hydroxyl groups and relaxes nonradiatively [10]. The enhancement of luminescence of Er³⁺ from the Er-SiO₂ films was achieved by doping silver ions, which used Ag/Ag⁺ groups as photosensitizers to transfer the energy from the pumping source to Er³⁺ ions [11]. As high as 500 times enhancement was also reported in the Au nanoparticles (NPs) doped sol-gel SiO₂ films, in which Au NPs played as a chemical absorbent for hydroxyl groups and thus increased the number of hydroxyl-group free Er³⁺ [12].

We made great efforts to conduct research on noble metal NPs incorporated silicate-based fibers in the field of nanophotonics [13-15], aiming to combine the amazing nanoscience and nanotechnology with the traditional geometric optics together. In this study, we attempted to realize the enhancement of Er³⁺ luminescence by the incorporation of Au nanoparticles in the germano-silicate fiber by use of the conventional MCVD and solution doping processes. Based on the previous work on the fabrication of Au nanoparticles incorporated fibers [13] and through a series of experiments using Er³⁺ singly-doped fiber (EDF), Au NPs/Er³⁺ co-doped fibers (Au_EDF), Au NPs singly-doped fiber (Au_Fiber) and the reference fiber without any dopant (Ref. Fiber), we show that Au NPs are effective to enhance the luminescence of Er³⁺ ions upon pumping with 980nm LD.

2. Experiments

All the four designed fibers were fabricated in house using the MCVD and solution doping processes, which was detailedly described in Ref.13 reported by our group. The characteristics of the fibers are shown in Table I. The concentrations listed in the table are nominal concentration and the solution doping time was fixed at 2 hours.

Table I. Characteristics of the germano-silicate fibers doped with Er^{3+} and/or Au particles

Sample	Doping Solution (Concentration)	Cut-Off Wavelength	Core Diameter
Unit	mol%	nm	μm
EDF	Er^{3+} (0.1)	1110	8.04
Au_EDF	Au^{3+} (1.0) Er^{3+} (0.1)	1150	8.04
Au_Fiber	Au^{3+} (2.5)	1159	8.94
Ref. Fiber	---	1180	9.04

Due to the boiling temperature as high as 2856 [16], Au atoms and their clusters could survive from the MCVD process with the temperature up to 2350. Since the structure of the fiber (8-10 μm diameter core surrounded by 125 μm diameter outside cladding) and the extremely low dopant concentration of ppm level make the Au NPs difficult to detect by direct measurement methods, such as Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD), the cut-back method was used to measure the absorption spectrum of the optical fiber to confirm the formation and existence of the Au NPs in the core of fiber [14]. The core diameter and the cut-off wavelength of the fibers listed in Table I allow for single transverse mode operation at the communication window of 1550nm. Figure 1 illustrates the experiment setup for absorption and emission measurements. Absorption was measured with the 30m-length fibers and the fibers were twisted with 8cm radius to remove the possible bending loss. As for the emission measurement, a 980nm LD or a 488nm Argon-ion laser was used.

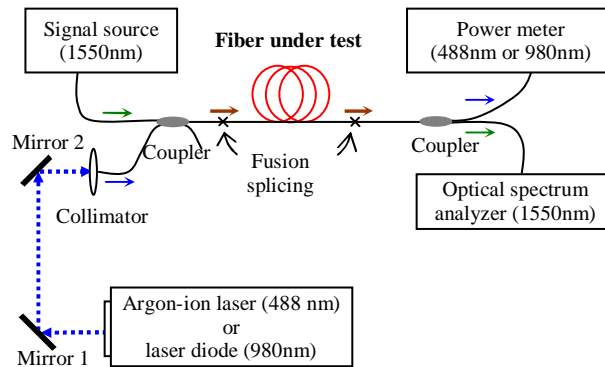


Fig.1. Schematic diagram of the experiment setup for absorption and emission measurements.

3. Results and discussion

3.1 Linear absorptive optical properties of EDF and Au_EDF

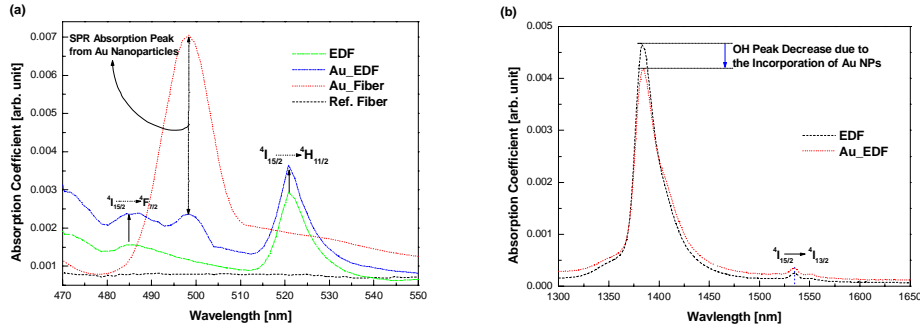


Fig. 2. Absorption spectra of the EDF, the Au_EDF, the Au_Fiber and the Ref. Fiber: (a) at 460nm ~ 560nm (b) at 1300nm ~ 1650nm.

Figure 2(a) compares the absorption spectra of the four made fibers, showing the surface plasmon resonance (SPR) absorption peak around 498.4nm found in Au_Fiber compared with Ref. Fiber reported by our group before [14,15]. As shown in Fig. 2, in Au_EDF and EDF the absorption peaks were found to appear from 460nm to 560nm and at 1385 nm, respectively. Two absorption peaks at 488nm ($^4I_{15/2} \rightarrow ^4F_{7/2}$) and 520nm ($^4I_{15/2} \rightarrow ^4H_{11/2}$) were due to Er^{3+} ions and the peak at 1385 nm was from the OH impurities. The absorption intensity of these two typical peaks from Er^{3+} ions increased after the incorporation of Au, and this kind of increase was thought to be due to the side-band effect of the SPR absorption peak of Au NPs around 498.4nm. On the contrary, as shown in Fig. 2(b) the peak intensity at 1385 nm from OH impurities decreased, which was believed to be ascribed to the more passive performance of hydroxyl groups when exposed to Au NPs besides them, rather than Au NPs reducing the actual amount of hydroxyl groups in a germano-silicate fiber [12].

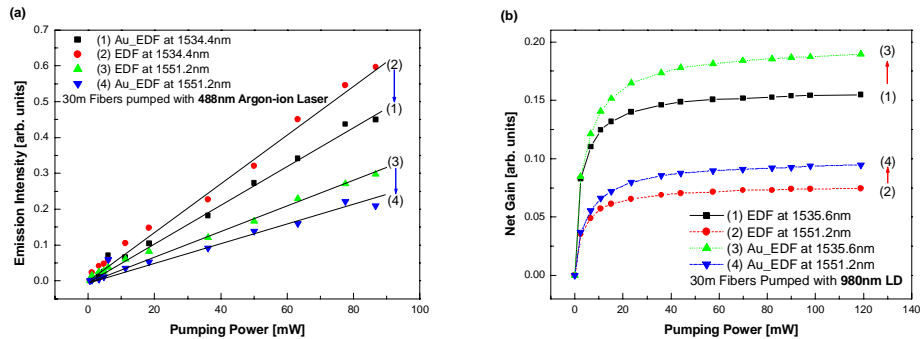


Fig. 3. Comparison of the luminescence of the EDF and the Au_EDF pumped (a) with the 488nm Argon-ion laser and (b) with the 980nm laser diode

3.2 Luminescence of EDF and Au_EDF pumped with different sources

The emission of the fibers was obtained by pumping with different light sources such as 488nm Argon-ion laser and 980nm LD and shown in Fig. 3. The luminescence intensity of the fibers increased with the increase of the pump power regardless of the dopants. As shown in Fig. 3(a), the luminescence intensity of the Au_EDF decreased compared to that of the EDF when it was pumped with the 488nm Argon-ion laser. On the other hand, the luminescence of the Au_EDF increased when pumped with the 980nm LD and moreover the net gain at the communication window became saturated with the increase of the pump power due to the low level concentration of Er^{3+} ions in this experiment as shown in Fig. 3(b). Since the hydroxyl groups in a glass are known to preferentially coordinate around Au NPs due to their large surface area [17], the Au_EDF has more hydroxyl-free Er^{3+} ions than the EDF. Thus the net gain of the Au_EDF was obviously higher than that of the EDF when pumped at 980nm, the wavelength far from the SPR absorption peak of Au NPs.

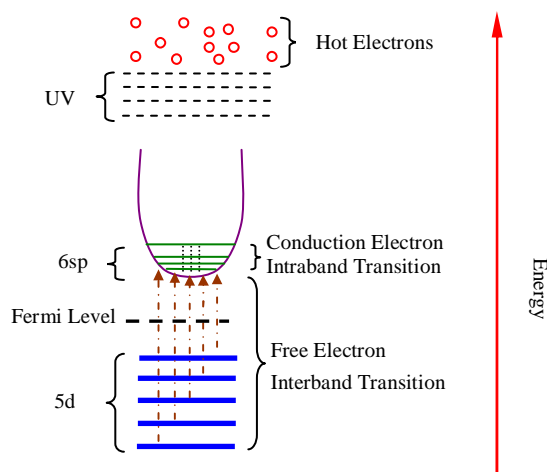


Fig. 4. Schematic energy level diagram of Au atoms¹⁵

It is interesting to note that the emission of the Au_EDF was smaller than that of the EDF when the pumping source was the 488nm Argon-ion laser as shown in Fig. 3(a). The optical properties of gold are known to be due to 5*d* (valence) and 6*sp* (conduction) electrons [18]. The outermost *d* and *s* electrons are treated together leading to 6 bands: 5 of them are fairly flat and lie a few *eV* below the Fermi level, they are usually denoted *d* bands, the 6th one being almost free-electron-like, i.e. roughly parabolic with an effective mass very close to that of a free electron as shown in Fig. 4 [15]. This last band is known as the conduction band or *sp* band. When the Au NPs are confronted with a laser beam of the frequency ω close to the SPR frequency ω_s of Au NPs, there are three kinds of transitions: the conduction electron intraband transition due to the Drude dielectric constant, the free electron interband transition between the *d* and *sp* bands, and the photoexcited hot electrons pumped at the wavelength around the SPR absorption peak of Au NPs. Among them, the free electron interband transition and the photoexcited hot electrons will absorb most of the energy of the incident 488nm laser beam, and then transfer the energy to the surrounding dielectric glass lattice rather than to the Er^{3+} ions within a few picoseconds [19]. Because of this energy loss, Er^{3+} ions in the Au_EDF did not absorb the pumping energy as high as in the EDF, which is in turn responsible for the decrease of the emission found in the Au_EDF when pumped with the 488nm Argon-ion laser.

4. Summary

In summary, we successfully made EDF codoped with Au NPs by MCVD and solution doping processes. Au NPs were found to be effective chemical absorbent for hydroxyl groups by increasing the number of hydroxyl-free Er^{3+} ions and consequently enhancing the luminescence of Er^{3+} ions upon pumping with the 980nm LD. Due to the SPR absorption originating from the free electron interband transition and the photoexcited hot electrons of Au NPs, the opposite and negative effects also turned up when pumped with the 488nm Argon-ion laser.

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