Enhancement in the Photoluminescence Properties of SiO$_2$:Ge Embedded in a Polymeric Matrix

G. Lesly Jiménez$^1$, C. Falcony$^2$, C. Vázquez-López$^2$, J. I. Golzarri$^3$, and G. Espinosa$^1$

$^1$Doctoral Program in Nanoscience’s and Nanotechnology, Center for Research and Advanced Studies of the National Polytechnic Institute, 2508 IPN Avenue, 07360 Mexico City, Mexico
$^2$Department of Physics, Center for Research and Advanced Studies of the National Polytechnic Institute, 2508 IPN Avenue, 07360 Mexico City, Mexico
$^3$Institute of Physics, National Autonomous University of Mexico (UNAM), 04520 Mexico City, Mexico

*Email: gljimenez@cinvestav.mx

ARTICLE INFORMATION

Received: June 16, 2018
Revised: July 04, 2018
Accepted: July 18, 2018
Published online: August 6, 2018

Keywords: Photoluminescence, Polymer films; SBC; PTFE

DOI: 10.15415/jnp.2018.61022

ABSTRACT

Polymer films of styrene butadiene copolymer (SBC) mixed with SiO$_2$:Ge powder were successfully obtained by the drop casting method. The SBC concentration (in chloroform solution) was 10% w/v and the SiO$_2$:Ge powder was mixed (mass ratio 80:20 respectively). The thicknesses of the films obtained were 50, 100, and 200 µm. In addition, polymer films of polytetrafluoroethylene (PTFE) preparation (60% dispersion in water), were obtained mixing 2 ml of PTFE and 0.05 g of SiO$_2$:Ge powder with a mass relation of 98% polymer and 2% SiO$_2$:Ge. The photoluminescence emission spectra (PL) of SBC doped with SiO$_2$:Ge resulted in similar characteristics to those for SiO$_2$:Ge powders, although their intensity shows an increase 3.5 times approximately, compared with the pure powder. On the other hand, the PTFE films with SiO$_2$:Ge present just one peak in the PL emission at 439 nm but their intensity increases 18 times respect to the powder. The photoluminescence excitation (PLE) spectra of the SiO$_2$:Ge powders show the characteristic peaks at 248 nm (most intense) and at 366 nm. However, when the powder is embedded either in SBC or PTFE the peak at 366 nm shows an important increase which seems to indicate an energy transfer from the polymer to the SiO$_2$:Ge.

1. Introduction

In the last decade the research in films of SiO$_2$ doped with germanium has increased, due to their potential applications in optoelectronics and solar cells [1,2]. However, it is necessary to improve the photoluminescence (PL) properties to make them more attractive for these applications. For that reason, some research groups have implemented strategies as thermal treatments [3], the confinement of Ge in a sandwiched structure [4] or use a polymer as a matrix to improve their PL properties. In this work, SiO$_2$:Ge powders were embedded in two different polymers, the first was styrene butadiene copolymer (SBC) whose transmittance characteristics are very interesting for optoelectronic applications, obtaining an improvement in the PL intensity. On the other hand, the polymer films with PTFE shows an enhancement in the PL intensity of around 18 times.

2. Experimental Overview

2.1 Materials

SiO$_2$: Ge commercial optical fiber manufactured by Nokia Cable, with 150 µm diameter was used. Ge concentration in the fiber was determined by EDS, resulting 0.3 %. Styrene butadiene copolymer (SBC) was provided by Ineos Styrolution Co. identified as Styrolux 3G46, and polytetrafluoroethylene preparation (60 wt% dispersion in H$_2$O) (PTFE dispersion) was purchased from Sigma Aldrich.

2.2 Preparation of SiO$_2$:Ge Powders

The optical fiber was cut in stretches of 30 cm and the plastic material that protects it was removed. Then the fiber was cleaned with ethanol. Finally, the optical fiber was cut in little pieces and pulverized until obtaining uniform powders.
2.3 Polymer - SiO$_2$:Ge Films

2.3.1 SBC - SiO$_2$:Ge films

The polymer films were prepared by the drop casting method using SiO$_2$:Ge powders. The powders were dispersed in 5 ml of chloroform with a concentration of 2\% w/v\%. The dispersion was sonicated for 1 h and then was mechanically stirred during 30 min. Then, SBC was added in the previous dispersion at a concentration of 10\% w/v in chloroform. From the final mix some aliquots (0.5, 1 and 2 ml) were dropped into different small beakers. The films with different thicknesses were obtained after the solvent was evaporated.

2.3.2 PTFE dispersion - SiO$_2$:Ge films

The polymer composites were obtained by a rot molding process, using PTFE dispersion and SiO$_2$:Ge powders. First, 3 ml of PTFE dispersion (whose density is 1.5 g/ml at 25°C) was added in a 10 ml beaker, then 40\% w/v of SiO$_2$:Ge powders were added and were mechanically stirred during 30 min. Then this solution was heated at 90°C until water has evaporated. Finally, the material obtained was processed by a rot molding process until obtaining three different thickness polymer films.

2.4 Characterization

SiO$_2$:Ge and the polymer films were characterized by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR spectrophotometer in the 400 - 4000 cm$^{-1}$ range. In the case of SiO$_2$:Ge powders, they were embedded in KBr pellets to perform the FTIR measurements. The mass spectroscopy was obtained with a Discovery TGA 5500 with a Discovery mass spec of TA Instruments. Photoluminescence emission (PL) and excitation (PLE) spectra were measured at room temperature with an Edinburgh Instruments fluorescence equipment, Mod. FLS980.

3. Results and Discussion

3.1 FTIR Analysis

Figure 1 shows the FTIR transmission spectra for a) SiO$_2$:Ge powders, b) SiO$_2$:Ge embedded in SBC, and c) pure SBC. The IR spectrum of SiO$_2$:Ge powders (Figure 1a) exhibits the stoichiometric vibrations from SiO$_2$ at 450 cm$^{-1}$, 800 cm$^{-1}$, and 1080 cm$^{-1}$, which correspond to Si - O - O rocking, bending and stretching, respectively [4, 2]. Additionally, a shoulder at 1020 cm$^{-1}$ is shown, that is related to nonstoichiometric SiO$_x$ (x < 2) [4]. However, the vibrations attributed to Ge - O - Ge (580 - 870 cm$^{-1}$ [5]) are not present. In the case of Figure 1c, the characteristic vibrations of SBC at 543 cm$^{-1}$, 701 cm$^{-1}$, 755 cm$^{-1}$, and 1451 cm$^{-1}$ are observed, corresponding to C - C, C - H, out of plane bend, the ring mode of styrene an scissors mode of CH$_2$ vibration modes, respectively [6]. Finally, the polymer films doped with SiO$_2$:Ge show an important contribution from SBC. These spectra show all the characteristic vibrations from SBC and only one vibration of SiO$_2$:Ge that is observed at 460 cm$^{-1}$ and corresponds to a Si - O - Si rocking mode.

Figure 1. FTIR transmission spectra for a) SiO$_2$:Ge powders, b) SiO$_2$:Ge embedded in SBC and c) pure SBC.

Figure 2. FTIR spectra for a) SiO$_2$:Ge , b) SiO$_2$:Ge embedded in PTFE and c) PTFE.

Figure 2 exhibits the FTIR spectra for a) SiO$_2$:Ge , b) SiO$_2$:Ge embedded in PTFE and c) PTFE. Figure 2c, shows the characteristic vibrations of PTFE that are located at 505 cm$^{-1}$, 552 cm$^{-1}$, 637 cm$^{-1}$, 1153 cm$^{-1}$, 1252 cm$^{-1}$ and 1304 cm$^{-1}$ that correspond to F - C - F bending, rocking, wagging, very strong asymmetric stretching, shoulder asymmetric stretching and stretching of C - C, respectively [1,2,7,8]. If SBC vibrations at 543 cm$^{-1}$, 701 cm$^{-1}$, 755 cm$^{-1}$, and 1451 cm$^{-1}$ are observed, corresponding to C - C, C - H, out of plane bend, the ring mode of styrene an scissors mode of CH$_2$ vibration modes, respectively [6]. Finally, the polymer films doped with SiO$_2$:Ge show an important contribution from SBC. These spectra show all the characteristic vibrations from SBC and only one vibration of SiO$_2$:Ge that is observed at 460 cm$^{-1}$ and corresponds to a Si - O - Si rocking mode.

In the case of SiO$_2$:Ge embedded in PTFE (Figure 2b) is observed the characteristic vibration from PTFE, however neither vibration from SiO$_2$:Ge powders was observed, maybe due to the SiO$_2$:Ge powders are completely embedded. If
these materials are embedded completely, the PL spectra could be changed compared with the pure powders.

3.2 Thermal behavior

Thermal behavior of SBC, PTFE and SiO$_2$:Ge powders embedded in these polymers were studied by TG-MS in the temperature range 20 - 640°C. In Figure 3 the thermograms are shown, with a heating rate of 10°C/min under Helium environment. In Figure 3 the curves 1 and 2 show that the SBC and SiO$_2$:Ge powders embedded in this polymer have similar thermal behavior. These materials present a fast loss weight at ~370°C and the complete degradation around 500°C. Also, the main decomposition comes from the SBC monomer (C$_8$H$_8$) (curve a in Figure 3) and is bigger in the polymer composites (curve b in Figure 3). The last one may be due to SiO$_2$:Ge powders, which are very stable at high temperatures because this material is uniformly embedded, which improves their thermal resistance.

In the case of PTFE and the composites of PTFE with SiO$_2$:Ge powders, the thermal stability observed is observed until ~550°C. In this case, the monomer decomposition (C$_4$F$_4$) on the PTFE composites (curve d in Figure 3) is bigger than PTFE polymer films (curve c in Figure 3), maybe, because of the concentration of SiO$_2$:Ge powders is lower. For this reason, it is believed that if the concentration of SiO$_2$:Ge powders in PTFE solution increases, the decomposition of the monomer will be reduced.

3.3 UV-vis transmittance of composites

Figure 4 shows the transmittance in the UV region of the SBC composites obtained by the drop casting method. Clearly, the optical transmission decreases as the thickness increases. The optical transmission corresponding to the PTFE is too small to be measured.

3.4 Photoluminescence Properties

3.4.1 SBC doped with SiO$_2$:Ge powders

The photoluminescence emission (PL) and excitation (PLE) spectra of SiO$_2$:Ge powder, SBC, and the composites of different thicknesses are shown in Figures 5a and 5b. In Figure 5a the samples of pure SiO$_2$:Ge powders have an emission band in the blue region (400 – 500 nm) where two peaks at 417 and 440 and a shoulder at 469 nm are observed. The peak at 417 nm corresponds to transition T$_\Sigma^T$ (T $\pi$) $\rightarrow$ S$_0$, which is attributed to the GeO color centers in SiO$_2$:Ge [4,5]. In the case of the band at 469 nm it can be associated to a radiative recombination between electrons and holes in GeO that may be present in the SiO$_2$:Ge powder [9]. However, the reported peak is very broad (400 – 600 nm). For that reason, it is believed that the peak at 440 nm is part of that recombination.

The enhancement in the PL spectra was 3.5 times, approximately, in the composites with 50 µm compared with those of the pure powders. Also, the peaks of the spectra are narrower, the peak at 440 is higher and the slight shoulder at 469 is more noticeable. This improvement is due to an energy transfer from SBC polymer to the SiO$_2$:Ge that facilitates the transition of T$_\Sigma^T$ (T $\pi$) $\rightarrow$ S$_0$ associated with the absorption at 329 nm of GeO. The enhancement in this transition is important because it is not frequently observed. The common transition in SiO$_2$:Ge is S$_1$ $\rightarrow$ S$_0$ associated with the absorption of GeO at 242 nm, which is appreciated in the pure powders [10], and the PL reduced as the thickness increases, due to the transmittance reduction that does not allow a good recombination [11].

The PLE spectra of SiO$_2$:Ge powders show their main peak at 248 nm which is attributed to S$_1$ $\rightarrow$ S$_0$ transition of
the GeO color centers [12,4], however, an efficient energy transfer from the SBC polymer to the powders exhibited an increase in the peak associated with $T_2(T\pi)\rightarrow S_0$ transition, present at 365 nm that decreases as the thickness increases. Also, as the thickness increases, a band at 317 nm is observed, maybe as a contribution of the polymer [13]. The origin of the decrease of the PL spectra as the thickness increases is in accordance with the transmittance spectra shown in Figure 4.

Figure 5. Photoluminescence and photoluminescence excitation spectra of the samples indicated. For PL spectra the excitation wavelength was 246 nm for the pure SBC polymer, the other samples were excited with 368 nm. For PLE the detection energy corresponds to $\lambda_{em} = 438$ nm in all cases.

### 3.4.1 PTFE doped with SiO₂:Ge powders

PL and PLE of SiO₂:Ge powders, PTFE and composites of PTFE are exhibited in Figures 6a and 6b. PL spectra of the PTFE composites at different thickness exhibits a similar behavior, however, it is different from the spectra of SiO₂:Ge pure powders. In this case is observed a broadband from 400 to 550 nm with its main peak at 439 nm, with an enhancement in its intensity of around 20 times. As mentioned before, this polymer films have a poor transmittance. PLE spectra of PTFE exhibit two peaks and a shoulder at 249, 288 and 341 nm. This PL intensity is bigger than SiO₂:Ge powders and can be overlap all its spectrum. PTFE composite films shows similar behavior as SBC composites, however, it is observed an additional peak at 288 nm attributed to a PTFE emission. The main peak at 341 nm is attributed to $T_2(T\pi)\rightarrow S_0$ transition from GeO color centers. In this case the enhancement in the intensity is due to an efficient energy transfer from the PTFE polymer to the SiO₂:Ge powders due to a better overlapping. It is important to note that this intensity increases as the thickness increases, however, when the thickness was around 1 mm its PL intensity did not exhibited a big chance between this thickness and 200 mm, due to the poor optical transmittance of the polymer [14].

Figure 6. Photoluminescence and photoluminescence excitation spectra of the samples indicated. For PL spectra the excitation wavelength was 287 nm for the pure PTFE polymer. The other samples were excited with 368 nm. For PLE the detection energy corresponds to $\lambda_{em} = 438$ nm.

### 4. Conclusions

Thin films of SiO₂:Ge powders embedded in two polymeric matrices were successively obtained. The polymers are (a) styrene butadiene copolymer (SBC) and (b) polytetrafluoroethylene
(PTFE). The obtained films have thermal stability up to 370°C for the first one and up 550°C for the other, respectively. The photoluminescence properties of both polymeric structures were enhanced by an efficient energy transfer between the SBC and PTFE polymers to SiO$_2$:Ge powders. This is validated by the overlap of the PL excitation spectra of SiO$_2$:Ge powders with the polymer PL emission spectra. The PL spectra are associated with the color centers of germanium that are present as it can be observed in the FTIR spectra by the vibrations at 460, 796, 1020, and 1080 cm$^{-1}$.

Acknowledgements

The authors acknowledge the financial support from Conacyt (grant 5147). The authors also thank the technical assistance of Marcela Guerrero, Ana Bertha Soto, Blanca Estela Zendejas and Julián Alarcón from Departamento de Física, and Ulises Galindo from Departamento de Química del CINVESTAV. This work was partially supported by Dirección General del Personal Académico de la UNAM, Project UNAM-DGAPA-PAPIIT- IN103316.

References

[1] B. Pivac, P. Dubček, J. Popović, J. Dasović, S. Bernstorff et al., Journal of Applied Crystallography. 49, 1957–1966 (2016). https://doi.org/10.1107/S1600576716014175

[2] C. N. Ye, X. M. Wu, N. Y. Tang, L. J. Zhuge, W. G. Yao et al., Science and Technology of Advanced Materials. 3, 257–260 (2002). https://doi.org/10.1016/S1468-6996(02)00024-4

[3] M. Martini, F. Meinardi, A. Paleari, G. Spinolo, and A. Vedda, Physical Review B. 57(7), 3718–3721 (1998). https://doi.org/10.1103/PhysRevB.57.3718

[4] J. K. Shen, X. L. Wu, R. K. Yuan, N. Tang, J. P. Zou et al., Applied Physics Letters. 77(20), 3134–3136 (2000). https://doi.org/10.1063/1.1325399

[5] S. K. Shen, X. L. Wu, X. M. Bao, R. K. Yuan, J. P. Zou, Physics Letters A. 273, 208–211 (2000). https://doi.org/10.1016/S0375-9601(00)00492-8

[6] N. S. Allen, A. Barcelon, M. Edge, A. Wilkinson, and Galan-Merchan et al., Polymer Degradation and Stability. 86, 11–23 (2004). https://doi.org/10.1016/j.polymdegradstab.2003.10.010

[7] A. Gruger, A. Régis, T. Schomatk, and P. Colomban, Vibrational Spectroscopy 26, 215–225 (2001). https://doi.org/10.1016/S0924-2031(01)00116-3

[8] C. Y. Liang, and S. Krimm, Journal of Chemical Physics. 25(3), 563–571 (1956). https://doi.org/10.1063/1.1742964

[9] X. C. Wu, W. H. Song, B. Zhao, Y. P. Sun, J. J. Du, Chemical Physics Letters. 349, 210–214 (2001). https://doi.org/10.1016/S0009-2614(01)01213-1

[10] M. Josephine, Applied Optics. 21, 136–140 (1982). https://doi.org/10.1364/AO.21.000136

[11] N. J. Johnson, S. H. Shuo-Diao, E. M. Chan, H. Dai, A. Almutairi, Journal of the American Chemical Society. 139, 3275–3282 (2017). https://doi.org/10.1021/jacs.7b00223

[12] S. Mirabella, S. Cosentino, A. Gentile, G. Nicotra, N. Piluso et al., Applied Physics Letters. 101(011911), 1–4 (2012).

[13] J. Nishii, N. Kitamura, and H. Yamanaka., Optics Letters. 20, 1184–186 (1995). https://doi.org/10.1364/OL.20.001184

[14] T. Gao, X. M. Bao, F. Yan, and S. Tong, Physics Letters. A. 232(3-4), 321–325 (1997). https://doi.org/10.1016/S0375-9601(97)00387-3