

Production and characterization of RF-sputtered PbO-GeO₂ amorphous thin films containing silver and gold nanoparticles

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ABSTRACT

In the present work we report the characterization of PbO-GeO₂ films containing silver nanoparticles (NPs). Radio Frequency (RF) co-sputtering was used for deposition of amorphous films on glass substrates. Targets of 60PbO-40GeO₂ (in wt%) and bulk silver with purity of 99.99% were RF-sputtered using 3.5 m Torr of argon. The concentration of silver and gold NPs in the films was controlled varying the RF-power applied to the targets (40–50 W for the PbO-GeO₂ target; 6–8 W for the metallic target). The films obtained were annealed in air at different temperatures and various periods of time. Absorption measurements have shown strong NPs surface plasmon bands. Different widths and peak wavelengths were observed, indicating that size, shape and distribution of the silver NPs are dependent on the deposition process parameters and on the annealing of the samples. X-Ray Fluorescence and Transmission Electron Microscopy were also used to characterize the samples.

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1. Introduction

Bulk glasses and thin films containing metallic nanoparticles (NPs) present novel and interesting properties making these materials suitable for applications in optoelectronics, photonics and integrated optics, among others [1,2]. This is due to the local optical field enhancement due to the presence of the metallic NPs that may cause large enhancement of the nonlinear response of the material [3,4], and the increase of their luminescence properties [1,5–8]. In the last case, the intensification of the luminescence may also be caused by energy transfer from the metallic NPs to the fluorophores.

In this sense, lead-germanate oxide glasses with metallic NPs have proven to be interesting materials for photonic applications, since it presents low absorption in the visible and infrared regions, small cutoff phonon energy, and high linear and nonlinear refractive index [4,5,9]. Recently, we reported enhancement of the nonlinear optical response of PbO-GeO₂ films containing Cu and Cu₂O NPs [4]. One-order of magnitude improvement in the figure-of-merit for all-optical switching was observed in comparison with films without metallic NPs. We have also observed enhancement of rare-earth ions luminescence in germanate glasses containing silver or gold NPs [5,10–13].

2. Experimental procedure

The production of amorphous thin films containing silver and gold NPs was made by RF-sputtering. Two targets were sputtered simultaneously. One target was prepared with the composition 40GeO₂-60PbO (in wt%). The oxide powders were mixed and then submitted to 8 tons uniaxial press, followed by sinterization at 750 °C for 10 h. The other target was either metallic silver or gold, with a purity of 99.99%. Both targets had 2.0 in diameter.

The films were deposited on silica substrates, by using the RF-sputtering method (13.56 MHz). Silica substrates were placed at 15 cm from the targets. Before the film deposition, the base pressure was 1×10^{-5} Torr to minimize the presence of contaminants. During the process Argon plasma was used at 3.5 m Torr. The RF-power was not more than 50 W to prevent target damage. After the sputtering process, the obtained films were heat treated for different temperatures and periods of time in order to nucleate silver or gold NPs. Films with high adherence to the substrates and high mechanical strength were obtained.

The thicknesses of the fabricated films were measured with a profilometer and X-Ray Fluorescence (XRF) was used to investigate the chemical composition of the films. In order to observe the optical behavior of the thin films as a function of the heat treatment and to verify the absorption bands due to the surface plasmon resonance in the NPs, optical transmission and absorption measurements were performed. Transmission Electron Microscopy (TEM) analysis was employed for observation of the metallic NPs embedded in the films,

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Table 1

Parameters used in the deposition of lead-germanate thin films. In all processes, 3.5 mTorr of Argon was used, the deposition time was 120 min and the distance between the targets and the substrates was 15 cm.

Sample	Power (W) GeO ₂ -PbO target	Power (W)/shutter aperture (%) metallic target	Thickness (Å)	Deposition rate (Å/min)
GP	40	--	3920 ± 124	32
GPAg1	40	8/100	4869 ± 56	38
GPAg2	50	6/100	5051 ± 35	47
GPAg3	50	6/50	4766 ± 29	40
GPAu1	50	6/50	4350 ± 71	36
GPAu2	50	6/25	4405 ± 29	36

and determination of their size distribution. Electron Diffraction was also performed during TEM analysis in order to confirm the presence of gold and silver NPs.

3. Results

Table 1 describes the samples produced in this work. The thicknesses of the obtained films and their deposition rates are shown in Table 1, as well as the RF-power applied to the target. In order to control the concentration of metallic NPs in the films, the RF-power had to be reduced to 6 W but even for such powers we

Table 2

Composition of lead-germanate thin films obtained from X-Ray Fluorescence Analysis.

Sample	Ge (% wt)	Pb (% wt)	Metal (% wt)
GP	37.7	62.2	–
GPAg1	30.4	48.2	21.4
GPAg2	22.7	65.3	12.0
GPAg3	26.2	69.3	4.5
GPAu1	23.5	68.5	7.9
GPAu2	20.6	73.9	5.4

obtained more than 20% of metal content in the film. In these cases (samples GPAg1 and GPAg2), after heat treatment, the films presented micrometric clusters which were observable with the naked eyes. To prevent the formation of clusters and to reduce the metal content within the film, the shutter of the metal target was not completely opened during the deposition. This was made because

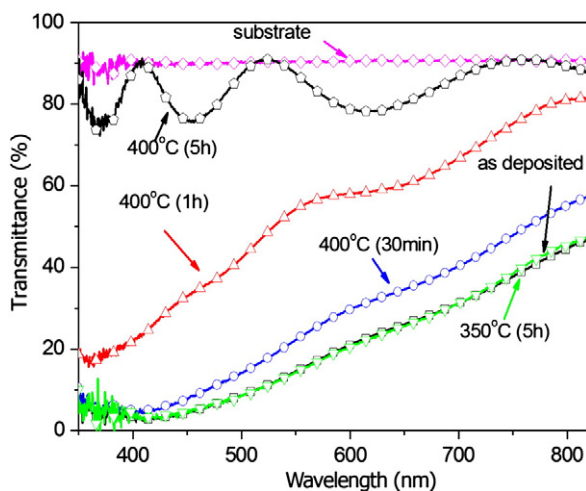


Fig. 1. Transmittance of sample GP heat treated for different temperatures and periods of time. The features are due to interference between the light beams reflected on the film and the substrate surfaces.

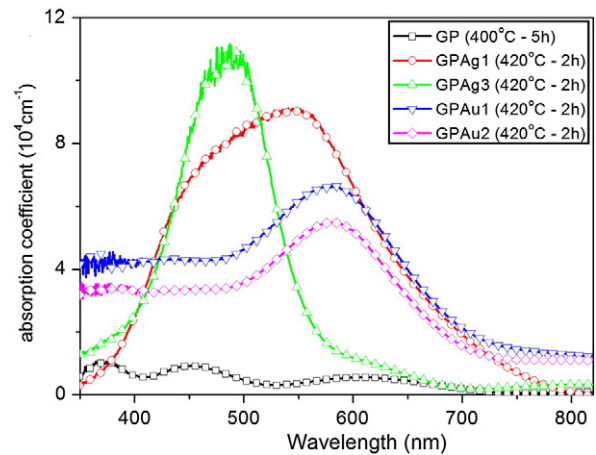


Fig. 2. Absorption spectra of the samples with/without metallic NPs.

further reduction of the power in the metal target was not possible due to poor Argon plasma stability. The shutter aperture used during the deposition process is also shown in Table 1.

XRF measurements (Table 2) showed that the film composition without metal content is very similar to the composition of the target. This indicates that the stoichiometry was maintained. Films containing up to 21.4 wt% of silver and 7.9 wt% of gold were obtained, depending on the RF-power and shutter aperture used in the metallic target.

Transmittance spectra of lead-germanate films without metallic NPs are shown in Fig. 1. We notice that the transmittance of the film after deposition is about 2% at 430 nm. The transmittance is largely enhanced after heat treatment; transparency is obtained after a treatment at 400 °C for 5 h. The fringe pattern is due to the interference between the light beams reflected on the film and substrate surfaces. This is not observed for the films without heat treatment due to the high optical absorption of the films.

The absorption measurements of the films containing metallic NPs are shown in Fig. 2. All the samples present strong absorption bands due to the surface plasmon resonance (SPR) of silver or gold NPs. For samples containing higher concentrations of silver (GPAg1 and GPAg2), we observe an intense and broad band centered at 500 nm related to the surface plasmon resonance (SPR) due to metallic NPs. For the films with smaller concentration of silver, the SPR absorption band is centered at 470 nm and presents smaller width. Samples containing gold NPs present the SPR absorption band centered at 590 nm.

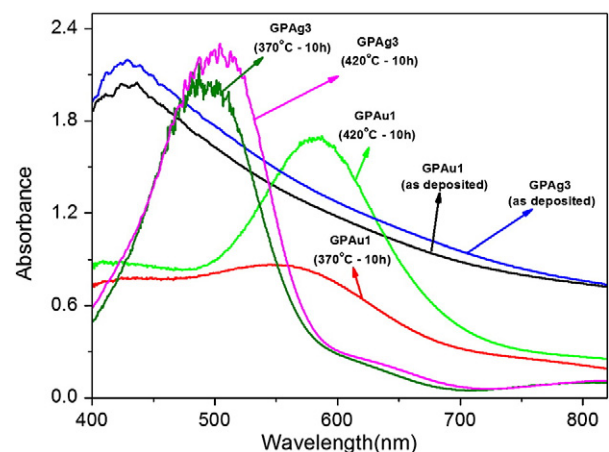


Fig. 3. Absorption spectra of the samples GPAu2 and GPAg3 as deposited and after heat treatment for different periods of time and temperatures.

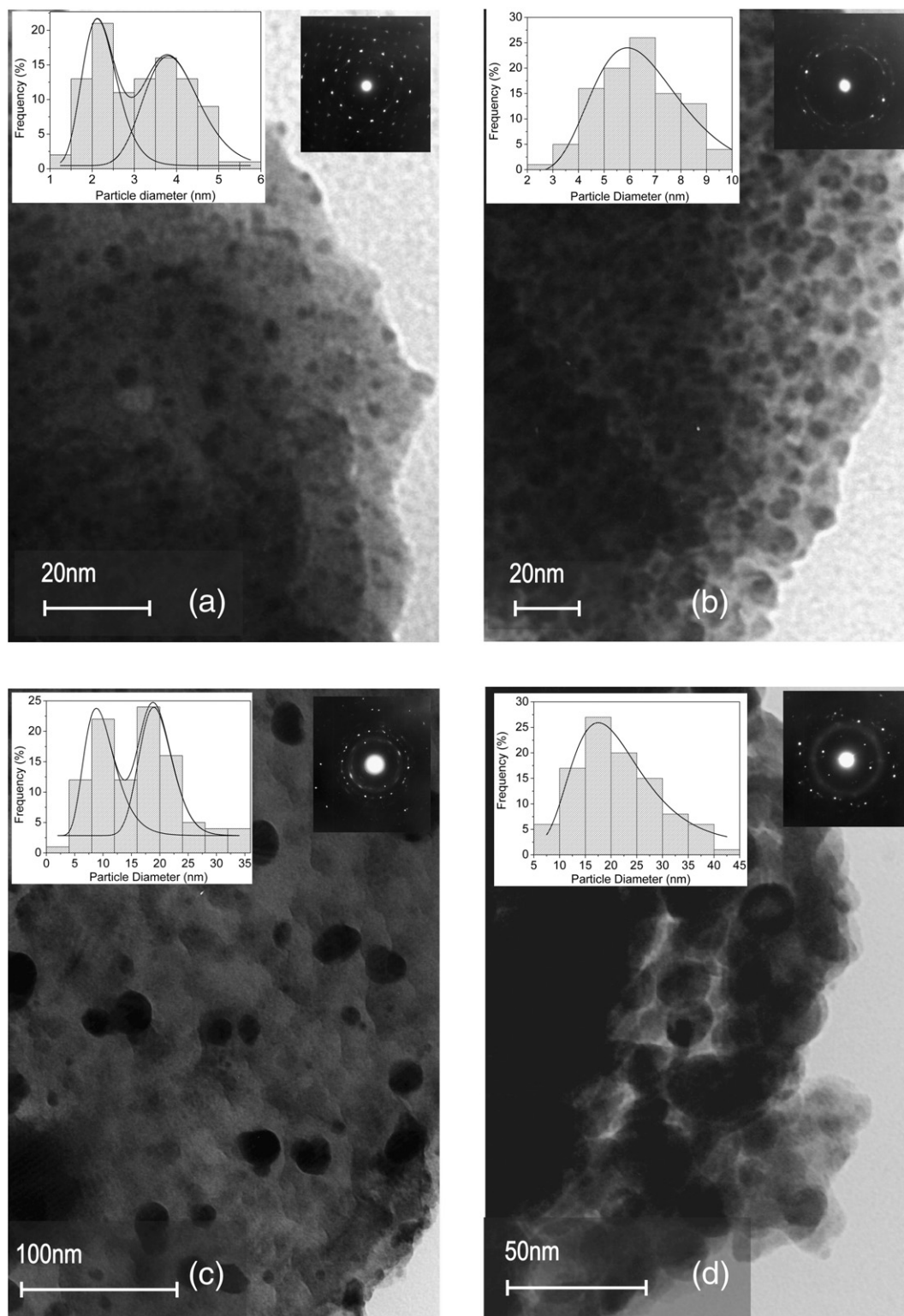


Fig. 4. TEM images for the sample GPAu1, heat treated for 10 h at 370 °C (a) and 420 °C (b) and for the sample GPAG3, heat treated for 10 h at 370 °C (c) and 420 °C (d). Electron Diffraction Patterns are shown for each sample (*right insets*). The histograms (*left insets*) show the size distribution of metallic NPs in the samples.

Fig. 3 illustrates the influence of the heat treatment on the optical absorption of samples GPAG3 and GPAu2. In both cases, we observe intensification and red shift of the resonance wavelength as the heat-treatment temperature and time are increased.

TEM analysis of samples GPAG3 and GPAu2 heat treated at 370 and 420 °C for 10 h is shown in Fig. 4. Electron Diffraction was used

to confirm the presence of gold and silver NPs. The histograms show the size distribution of the NPs inside the film. For the sample GPAG3 heat treated at 370 °C at 10 h, particles with average diameter around 8.8 and 18.8 nm were observed. In the same film, heat treated at 420 °C for 10 h, we noted a decrease in the concentration of the smaller particles (<10 nm) and an increase in the concentration of large

particles (>30 nm). Indeed, it was possible to observe the aggregation of silver NPs in the sample heat treated at 420 °C. In this case, the average diameter was around 17.5 nm.

The film GPAu2, heat treated at 370 °C for 10 h showed NPs with average size around 2.1 and 3.8 nm. When these results are compared to the analysis of the TEM images for the same sample, but heat treated at 420 °C for 10 h, we observe that the average diameter is around 5.9 nm.

4. Discussion

Sample GP, without metallic NPs presents a strong absorption in the blue region. This absorption may be caused by Pb^{2+} dimmers, which may be formed during the deposition process, due to the high concentration of lead in the film [14,15]. For heat treatment higher than 400 °C this absorption band vanishes, indicating that Pb^{2+} dimer concentration is decreased whereas Pb^{2+} monomers, which the absorption band is in the UV region (~355 nm), are formed. The mechanism which governs this process still lacks understanding.

For the other samples, heat treatment causes the reduction of metallic ions, nucleation and growth of the metallic nanostructures. These metallic structures usually present optical absorption in the visible region. The width of the absorption band is related to the metallic particles shape, size distribution and aggregation in the film [1,2]. Generally, bigger NPs and aggregates are responsible for the red shift on the resonance wavelength [1]. The center wavelength of the absorption band is also dependent on the shape of the NPs [1]. Thus, broad absorption bands, observed for the samples with higher metal concentration (GPAg1 and GPAg2) indicate the formation of metal aggregates, responsible for optical absorption in red and near infrared regions. In fact, micrometric clusters were observed in these films.

On the other hand, SPR absorption bands of samples with lower metal concentrations (GPAg3, GPAu1 and GPAu2) indicated that NPs in the films are smaller.

The analysis of the effect of heat treatment was made for the samples GPAg3 and GPAu2. The sample GPAg3 heat treated at 370 °C for 10 h showed the surface plasmon resonance band centered at about 490 nm. The resonance position is shifted to 500 nm, when the same sample is heat treated at a higher temperature (420 °C for 10 h). For the sample GPAu2 heat treated at 370 °C for 10 h, the center wavelength is about 560 nm. When the sample is heat treated at 420 °C during 10 h, the band intensity in the optical spectrum is enhanced and centered at ~580 nm. The enhancement of the absorption band and the red shift of the SPR wavelength is an indication that concentration of silver/gold NPs is increased within the sample and the average size of the particles is growing as a function of temperature and time, respectively. TEM analysis of the samples GPAg3 and GPAu2, annealed at different temperatures were used to verify the presence of the NPs and obtain size distribution of the nanostructures.

TEM images showed the growth of NPs at a higher temperature, therefore confirming the results obtained from the optical absorption measurements. Electron Diffraction was used to confirm that the NPs present in the films are metallic silver/gold, and also elucidated the amorphous nature of the host film, even after the successive heat treatments employed to nucleate and grow the metallic NPs.

5. Conclusions

In this work we could obtain good quality lead-germanate thin films, containing gold and silver NPs. The influences of the process parameters and heat treatment on the optical properties of the film were also studied. Large transmittance in the visible region was observed for lead-germanate films without metallic NPs after adequate heat treatment. The co-sputtering technique also has proven to be a powerful tool in the preparation of nanostructured thin films. Depending on the power used, it was possible to obtain films with up to 21% wt of silver. This would be hardly achievable for bulk glasses. Films containing metallic particles ranging from around 2.2 nm to micrometric clusters were obtained, depending on the parameters used during the deposition of the film and on the temperature and time of heat treatment. The optical absorption measurements of the films are also a good tool to estimate size distribution of the particles within the film. Thus, fabrication of nanostructured lead-germanate thin films was achieved and the results showed that the optical properties of the films can be modified by careful choice of the parameters used during the deposition process and by post-heat-treatment.

Further studies concerning the nonlinear optical properties of these films and their application in integrated optics are in progress.

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References

- [1] P.N. Prasad, Nanophotonics, Wiley, New York, 2004.
- [2] L. Novotny, B. Hecht, Principles of Nano-Optics, Cambridge University Press, Cambridge, 2007.
- [3] A.I. Rysnyanskiy, B. Palpant, S. Debrus, U. Pal, A.L. Stepanov, Opt. Commun. 273 (2007) 538.
- [4] L.A. Gómez, F.E.P. dos Santos, A.S.L. Gomes, Cid B. de Araújo, L.R.P. Kassab, Windson G. Hora, Appl. Phys. Lett. 92 (2008) 141916.
- [5] L.P. Naranjo, C.B. de Araújo, O.L. Malta, P.A. Santa Cruz, L.R.P. Kassab, Appl. Phys. Lett. 87 (2005) 241914.
- [6] C. Strohhofer, A. Polman, Appl. Phys. Lett. 81 (2002) 1414.
- [7] J. Kalkman, L. Kuipers, A. Polman, H. Gersen, Appl. Phys. Lett. 86 (2005) 041113.
- [8] T. Hayakawa, S.T. Selvan, M. Nogami, Appl. Phys. Lett. 74 (1999) 1513.
- [9] C.B. de Araújo, A. Humeau, G. Boudebs, V.D. Del Cacho, L.R.P. Kassab, J. Appl. Phys. 101 (2007) 066103.
- [10] D.M. da Silva, L.R.P. Kassab, S.R. Lüthi, C.B. de Araújo, A.S.L. Gomes, M.J.V. Bell, Appl. Phys. Lett. 90 (2007) 081913.
- [11] T.A.A. Assumpção, D.M. da Silva, L.R.P. Kassab, C.B. de Araújo, J. Appl. Phys. 106 (2009) 063522.
- [12] L.R.P. Kassab, F.A. Bonfim Junior, J.R. Martinelli, N.U. Wetter, J. Jakutis Neto, C.B. de Araújo, Appl. Phys. B 94 (2009) 239.
- [13] L.R.P. Kassab, D.S. da Silva, R.A. Pinto, C.B. de Araújo, Appl. Phys. Lett. 94 (2009) 101912.
- [14] Y.S. Kim, S.J. Yun, J. Phys. Condens. Matter 16 (2004) 569.
- [15] C.B. de Araújo, L.R.P. Kassab, R.A. Kobayashi, L.P. Naranjo, P.A. Santa Cruz, J. Appl. Phys. 99 (2006) 123522.