JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 10, October 2011, p. 1235 - 1239

Glasses containing silver nano particles irradiated by ultrashort multi wavelength femtosecond laser

O. VERON [a], J.-P. BLONDEAU [a*], B. CAPOEN [b], D. JEGOUSO [b]
[a] *Institut PRISME - UPRES 4229, Orleans University, 21 rue de Loigny La Bataille, 28000 Chartres, France*
[b] *PhLAM -UMR8523, Université de Lille 1-CNRS, Bat. P5 USTL, F-59655 Villeneuve d'Ascq cedex, France*

The ultrashort femtosecond irradiation of silicate glasses containing silver nano particles was investigated at two wavelengths after ionic exchange. Glass samples were prepared by immersion in a molten salt bath (T = 320°C) composed of 10 % $AgNO_3$-$NaNO_3$ in molar concentration and for a part of them further annealed. This method is well known for silver substitution from the molten salt to the alkaline initially embedded in the glass as sodium [1-2-3]. The aim of our study is either to induce defects in the glass matrix for silver ionic exchanged samples with an exposure to a pulsed laser at λ=800nm in a non thermal regime, or to modify the particles shape and size by an irradiation at λ=410nm in a thermal regime by resonant absorption of silver nano particles [4-5-6-7]. In order to modify the glass structure it is necessary to excite simultaneously six electrons at λ=800nm (Energy of 1.55eV) which is possible with the 42fs ultrashort pulse time [8].

(Received March 3, 2011; accepted October 20, 2011)

Keywords: Silver, Glass, Multiwavelength, Femtosecond laser

1. Introduction

Metallic nano-particles embedded in glasses as silver, copper or gold have interesting optical properties from a color or a non linearity point of view by the possibility to adjust the typical surface plasmon resonance (SPR) [9-10-11]. Indeed glass color change can be obtained by acting on size, shape and volumic fraction of particles embedded in these glasses [12-13]. These local parameter changes are allowed using a femtosecond pulsed laser source in order to control the deposited energy and the deposited fluence inside the glass. Ultrashort pulse ionization leads to induction of local defects in the glass volume. In our experiments, the purpose is either to irradiate in a thermal regime with a free electron generation to create structural defects at λ=800nm or to irradiate at λ=410nm.

2. Experimental details

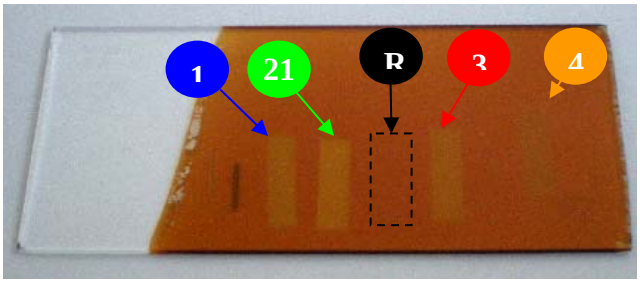
Soda lime glass slides (76 × 26 × 1 mm^3) with a molar concentration of 72.2 % SiO_2, 14.3 % Na_2O, 1.2 % K_2O, 6.40 % CaO, 4.3% MgO, 1.2% Al_2O_3 were prepared by a silver-sodium exchange process and immersed for τ = 10 and 240 minutes in a molten salt bath of 10 % $AgNO_3$ in $NaNO_3$ at T = 320°C. In these conditions the sodium ions at the glass surface are replaced by silver ions contained in the bath according to the exchange time.

The two samples for various exchange times were measured by UV/Visible Absorption with a JASCO V-530 Spectrophotometer in the in-line transmission configuration with a resolution of 0.5nm for a 200 to 1000nm range. A part of the exchanged sample was annealed one hour in an oven at 450°C to promote the silver nano particles growth. The ionic exchanged samples were irradiated at λ=800nm with a femtosesecond Titane-Saphir pulsed laser (Frequency 1kHz,) and the further annealed one was irradiated at λ=410nm. The Laser source is a Spectra-Physics Tsunami (Ti :Sapphire Regenerative Amplifier Systems) amplified with a Spitfire Pro. The pulse duration is about 42fs after the amplifier. The wavelength is defined by the Optical Parametric Adaptater. The intensity is measured by a powermeter just before the working area. The deposited energy vary from 88.1 kJ/m² to 705.2 kJ/m² for the 410nm irradiation and from 101.8 to 814.9 kJ/m² for the 800nm irradiation.

3. Results and discussion

3.1 410nm irradiation

In this case, the irradiation occurs in agreement with the silver surface plasmon resonance and leads to a thermal regime. The aim is to promote the particle shape change by resonant absorption. Absorption spectra versus the increasing deposited energy from 88.1 to 705.2 kJ/m^2 is plotted in Fig.1 and compared to the exchanged sample.



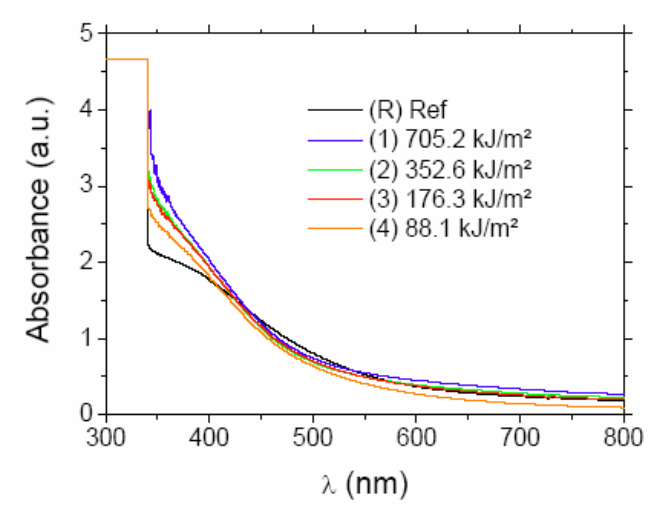


Fig.1. Colors change (Decreasing deposited energy from 1 to 4) and absorption spectra for one exchanged sample (10%AgNO3 in NaNO3 at T=320°C during 4h and annealed 1h at 450°C). The sample was irradiated at λ=410nm for various deposited energy.

These spectra exhibit particular change in the UV/Visible region increasing with the deposited energy and below 500nm which is associated to color variation. Each spectrum is fitted in Fig.2 with two gaussian laws G1 and G2 in order to plot the FWHM and intensity of the surface plasmon resonance versus the deposited energy. The laser wavelength at λ=410nm is resonant with the typical SPR absorption in the case of spherical particles population. The Peak position of the SPR (or Absorption) is located at λ_p=350nm (G1) for the reference glass, after irradiation this major contribution makes a light blue-shift and a new contribution appears near λ_p=550nm (G2). This new contribution is correlated to the lengthening of the particles and a depolarization factor [14-15-16-17].

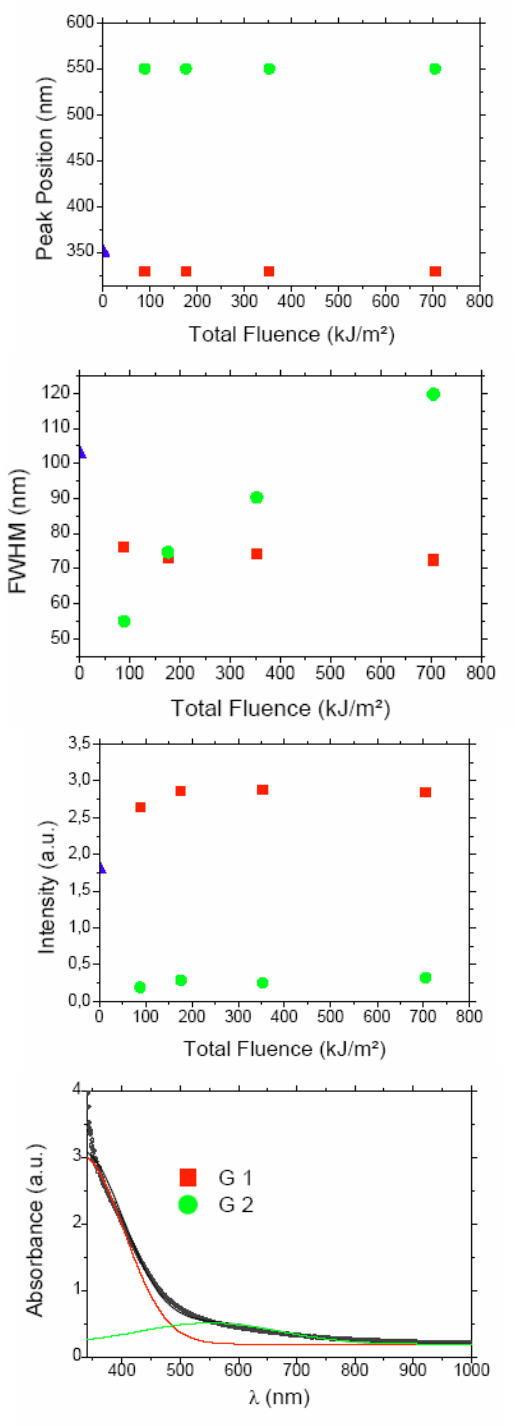


Fig. 2. Spectra fitting for one sample exchanged in 10%$AgNO_3$ in $NaNO_3$ at T=320°C. Deposited energy of 705.2kJ/m^2.

3.2 800nm irradiation

The main objective of the irradiation at λ=800nm is to generate numerous defects in the glass matrix which is transparent at this wavelength. Non bridging oxygen hole centers and trapped electrons can be generated and therefore lead to local precipitation of silver inside the glass. After irradiation at λ=800nm, a grey zone appears correlated to a radical change of the absorption spectra and to the defects formation (Fig.3).

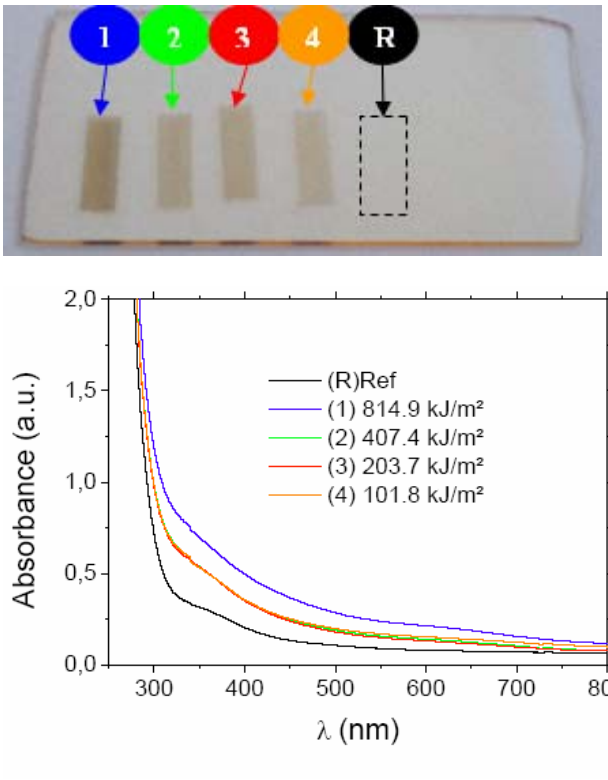


Fig.3 Color changes (Decreasing deposited energy from 1 to 4) and absorption spectra for one sample exchanged in 10%$AgNO_3$ in $NaNO_3$ at T=320°C during 10min (Ref). The sample was after irradiated at λ=800nm for various deposited energy from 101.8 to 814.9 kJ/m².

To obtain an efficient explanation of this contrast phenomenon, the most significant affected spectrum (the highest deposited fluence *814.9 kJ/m²*) was subtracted to the reference exchanged glass sample. An evaluation of the gaussian contributions of the resulting spectrum is given on Fig.4. These three populations are attributed to known defects respectively E'(≡Si•) at 305nm and NBOHC (≡ Si –O) ″Non-Bridging Oxygen Hole Center″ at 430nm and 623nm.

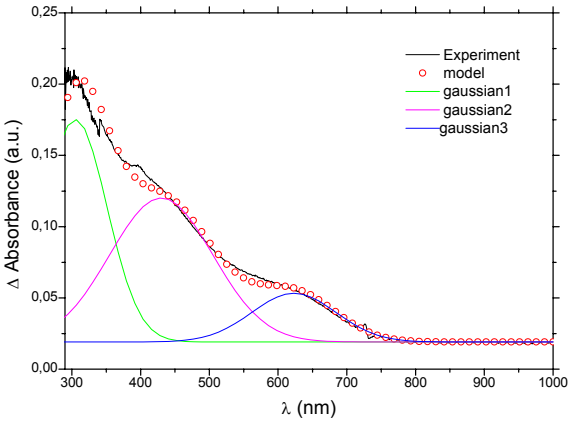


Fig.4. Identification of the defects by subtraction between the spectra for 814.9 kJ/m² as deposited energy and ref glasses. E' center : 305nm (G1) ; NBOHC1 : 430nm (G2) ; NBOHC2 : 623nm (G3).

This sample was then annealed in an oven according to the represented sequence in Fig.5. Annealing was stopped when a significant contrast appeared and the corresponding absorption spectra were plotted in Fig.6. The intensity of the typical silver plasmon resonance located around 400nm increases according to the total deposited energy and is correlated to the particle growth. The fit of these spectra in Fig.7 according to the three parameters evolution : peak position, FWHM and intensity have a good correlation with the growth of silver spherical particles due to the increase of the total deposited fluence [18-19-20].

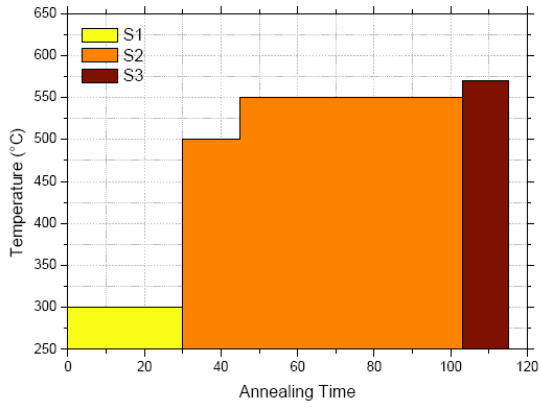


Fig.5.: Evolution of the temperature for the annealed sample after irradiation at λ=800nm. S1: the irradiated zone disappears, S2: all the glass colors, S3: a contrast for the irradiated zone appears.

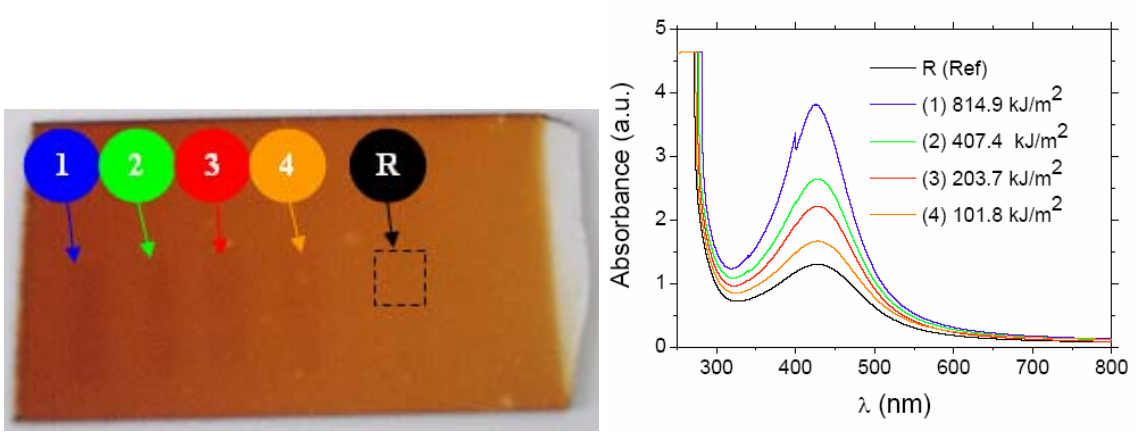


Fig.6: Absorption spectra for one exchanged sample in 10%$AgNO_3$ in $NaNO_3$ at T=320°C during 10min (Ref). The sample was irradiated at 800nm for various deposited energy from 101.8 to 814.9 kJ/m^2 then annealed.

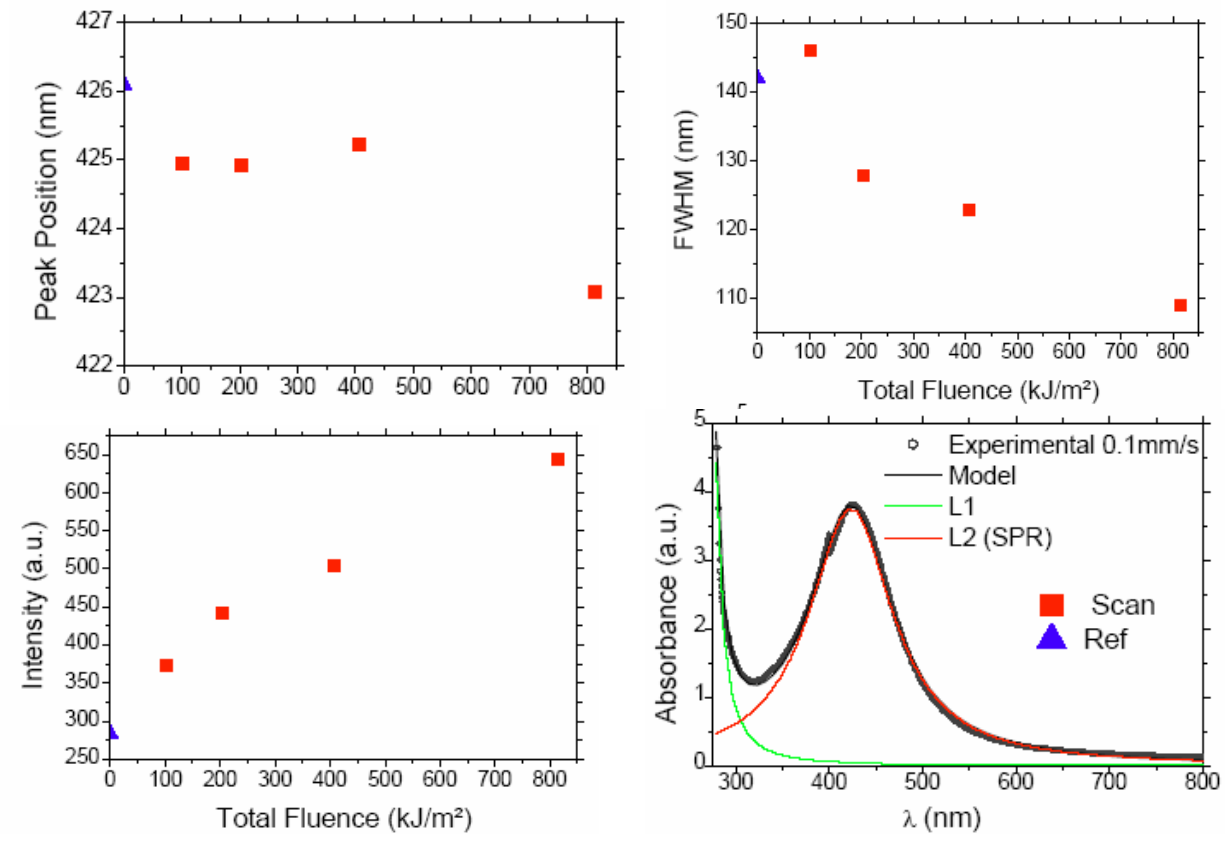


Fig.7. Absorption spectra fitting for one sample exchanged in 10%$AgNO_3$ in $NaNO_3$ at T=320°C during 10min (Ref). The sample was irradiated at 800nm for various deposited energies then annealed.

4. Conclusions and trend

The ultrashort femtosecond irradiation experiment for both wavelength λ=410nm and λ=800nm presents a lot of new interesting interaction effects on silver ions or small silver nano particles embedded in glasses. For the femtosecond irradiation experiment at λ=410nm near the surface plasmon resonance of silver, the sample was ion exchanged and further annealed [21-22] The irradiation leads to a shape change of the silver particles by thermal effects and the appearance to a new absorption contribution around 550nm due to depolarization effect. For the irradiation experiment λ=800nm, the sample used was only ion exchanged and doesn't contain silver nano particles. After irradiation, the laser generates structural defects into the silicon dioxide by multi ionization [23-24-25] and in particular : E' center (≡Si•) which corresponds to a hole trapped by a site of vacant oxygen, defects NBOHC ″non-bridging oxygen hole center″ (≡ Si –O) which is attributed to a hole trapped by a non-bridging

oxygen, where ″–″ indicates a link and ″ • ″ a not mated electron. The further annealing of the sample leads to a local precipitation of silver and recombination of the defects. These effects are particularly interesting for three dimensional development in photonics.

Acknowledgements

We want to thank particularly Pr. Mohammed Bouazaoui for his warm welcome in Laboratory Phlam from Lille.

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*Corresponding author: jean-philippe.blondeau@univ-orleans.fr