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doi: 10.1016/j.radmeas.2011.01.004

Formation and assignment of silver defect centres in phosphate glass induced by femtosecond laser pulses

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ABSTRACT

We have investigated the formation and assignment of silver defect centres such as Ag^0, Ag^{2+} and other molecular silver species induced by femtosecond (fs) laser pulse irradiation. In particular, direct precipitation of silver nanoparticles without heat treatment was demonstrated to clarify the formation kinetics of silver defect centres in a radiophotoluminescent phosphate glass by 250 kHz high repetition rate fs laser pulses. Comparison using X-ray- and fs laser-irradiation methods is also presented.

PACS: 78.60.-b; 81.05.Kf; 78.40. Pg; 78.70.En; 78.70.Dm

Keywords: Radiophotoluminescence (RPL), Glass dosimeter, Silver defect species, Femtosecond laser

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1. Introduction

Recent advances in high-intensity femtosecond (fs) laser pulses have made it possible to fabricate small noble metal particles such as gold and silver atoms embedded in glasses (Watanabe et al., 2001; Zhao et al., 2004; Shimotsuma et al., 2005) as well as encode various functional microstructures inside transparent materials (Kawamura et al., 2004; Kurobori et al., 2005; Kurobori et al., 2007). As far as silver-doped phosphate glass, Watanabe et al. (2001) demonstrated a photosensitivity in soda-alumina-phosphate glass doped with Ag^{+} upon exposure to ultraviolet (UV) fs laser pulses and found the formation of colour centres such as Ag^{0} and Ag^{2+} in the glass. Zhao et al. (2004) investigated the precipitation and dissolution of nanoparticles in Ag^{+}-doped phosphate glass by irradiation with a near-infrared (IR) 800 nm fs laser pulses and further annealing at various temperatures. Recently, intense fs laser pulses with high-peak power densities (~100 TW/cm^2) and high repetition rates (>200 kHz) have enabled direct precipitation of silver nanoparticles in silver-activated silicate glass without heat treatment (Ma et al., 2009).

As one of other practical applications of silver-doped phosphate glass (the sample denoted with “PG:Ag”), after PG:Ag is exposed to ionising radiation such as beta-, gamma- and X-rays, it emits an intense radiation-induced orange luminescence by UV excitation, which is called radiophotoluminescence (RPL). Such a dose-dependent RPL phenomenon in PG:Ag

has been widely applied to a ideal personal and environmental monitoring dosimeter (Hsu et al., 2006; Ranogajec-Komor et al., 2008; Chiyoda Technol Corporation, 2007).

Recently, we have systematically investigated the assignments and optical properties of X-ray-induced silver-related species of PG:Ag by means of various optical measurements such as RPL decay curve analysis, peak fitting analysis and heat treatments (Kurobori et al., 2010; Zheng and Kurobori, 2011). It was established from these results that the decomposed six Gaussian bands induced by X-ray irradiation in PG:Ag were, in turn, attributed to Ag^{+}, Ag_3^{+} or Ag_3^{2+}, Ag_2^{+}, Ag^{2+}, Ag^{0} and hole-trap centres, respectively. In addition, some similar spectral studies of the silver-related species created after different irradiation have also been reported to clearly attribute these Ag_m^{x+} centres in various glasses (Maurel et al., 2009; Jiménez et al., 2009; Miyamoto et al., 2010).

This paper examines the formation and assignment of silver defect centres such as Ag^{0}, Ag^{2+} and other molecular silver species induced by fs laser pulse irradiation. In particular, direct precipitation of silver nanoparticles in PG:Ag without heat treatment was demonstrated for the first time to clarify the formation kinetics and give an additional evidence of silver-related colour centres in a RPL glass by 250 kHz high repetition rate fs laser pulses. Comparison using X-ray- and fs laser-irradiation methods is also presented.

2. Experimental details

A commercially available GD-450 dosimeter (AGC Techno Glass Co. Ltd.) was used as the radiophotoluminescent PG:Ag. Samples were cut from the original glass dosimeter plate to a size of approximately 10 × 7 × 1 mm^3. The weight composition of the GD-450 dosimeter was 31.55% P, 51.16% O, 6.12% Al, 11.00% Na and 0.17% Ag. An additional sample without Ag (the sample denoted with "undoped PG") was used as a reference sample.

All samples were coloured by irradiation from an X-ray unit with a copper target operated at 30 kV and 20 mA. In this work, the samples were irradiated by doses of 4.90 Gy and 24.5 Gy. Absorption, excitation and emission measurements were performed at room temperature using a Hitachi U-2010 UV-vis and an F-2500 fluorescence spectrophotometer.

For the direct photo-induced reduction from Ag^+ ions to Ag^0 centres in PG:Ag, this work used a regeneratively amplified 800-nm Ti:sapphire laser (Coherent, Mira and RegA) that emitted 80-fs, 250-kHz mode-locked pulses. The fs laser pulses were focused using a 20 × objective lens (NA=0.45) to a depth of 250 μm beneath the sample surface with the help of a computer-controlled 3D *X*-*Y*-*Z* stage at a speed of 1 mm/s and 100 μm/s. The pulse energy ranged from 2 to 3 μJ/pulse and the spot diameter was approximately 2 μm.

The numbers of successive pulses at the focal points were 2.5 × 10^5 shots in 1 s. A square 5 × 5 mm^2 area was written inside the sample line by line using the intense and high

repetition rate fs laser pulses to measure the absorption, excitation and emission spectra of the irradiation region inside the glass sample.

3. Results and discussion

3.1 Optical characteristics and peak fitting analysis

Figs. 1 show the optical absorption spectra of (a) 1.0-mm-thick undoped PG and (b) 1.0-mm-thick PG:Ag, respectively, before and after X-ray irradiation. Prior to X-ray irradiation, both samples were colourless with an absorption edge at about 300 nm and then both samples were irradiated by X-rays to an absorbed dose of 24.5 Gy at room temperature. Fig. 1(a) shows the absorption spectrum before (dashed-and-dotted line) and after (solid line) X-ray irradiation. Moreover, the absorption spectrum was decomposed into a sum of separate Gaussian bands to characterise radiation-induced defect centres, as shown in the inset. Concerning to the radiation-induced effects in phosphate glass, Ebeling et al. (2002) investigated the assignment of X-ray-induced defects in ultra- and meta-phosphate glasses of high purity by means of band separation of the optical spectra. In our undoped PG, the absorption spectrum (Curve 1) could be decomposed into 4 separate Gaussian bands (dashed line, Curves 2-5） peaking at 206 nm (6.03 eV), 224 nm (5.53 eV), 273 nm (4.54 eV) and 440 nm (2.82 eV), respectively. According to Ebeling et al. (2002), the absorption bands located

at 206 (Curve 2) and 224 nm (Curve 3) are ascribed to electron trapped PO_3 and PO_4 defect centres, respectively. Moreover, the absorption band at 273 nm (Curve 4) corresponds to absorption of oxygen-related hole centres of unknown structure (OHC). Broad absorption band at 440 nm (Curve 5), termed the phosphorus-oxygen-hole-center (POHC), is due to one or two non-bridging oxygen of a PO_4 unit trapping a hole (Griscom et al., 1983).

Fig. 1(b) shows the absorption (solid line) and excitation (dashed-and-dotted line, Curves 1 and 2) and RPL spectra (solid line, Curves 3-5) of the X-ray irradiated PG:Ag under an absorbed dose of 24.5 Gy. The absorption spectrum is obviously due to the superposition of a number of individual absorption bands corresponding to the different colour centres. Therefore, the peak fitting analysis was carried out on the basis of the strong analogy with X-ray-irradiated silver-doped sodium chloride (NaCl:Ag) (Kurobori et al., 2010). The absorption spectrum could be decomposed into the sum of separate Gaussian bands (indicated by a dashed line) from “A” to “F”, peaking at 225, 252, 270, 307, 354 and 424 nm, respectively. The excitation spectra consist of two different spectra. One spectrum peaks at 308 nm (Curve 1) for an emission at 560 nm (orange), and the other peaks at 270 and 345 nm (Curve 2) for an emission at 450 nm (blue). The former corresponds to the decomposed 307 nm Gaussian band, while the latter corresponds to the decomposed 270 and 354 nm bands, respectively. The blue emission with some portion of the orange emission are strongly related

to the 270 and 345 nm excitation bands, which is completely analogous to the blue emission of NaCl:Ag associated with bands “B” and “C” (Kurobori et al., 2010), respectively.

3.2 Femtosecond laser exposure

According to our report (Kurobori et al., 2010), it was established through RPL decay curve analysis, peak fitting analysis and heat treatments that the decomposed six Gaussian bands in X-ray irradiated PG:Ag as shown in Fig. 1(b), marked as “A” to “F”, were attributed to Ag^{+}, Ag_3^{+} or Ag_3^{2+}, Ag_2^{+}, Ag^{2+}, Ag^{0} and POHC bands, respectively.

In this work, an additional evidence to attribute the 345 nm band (“E” band) in X-ray irradiated PG:Ag to Ag^{0} centres was demonstrated by directly fs laser pulse irradiation. It is well-known that irradiation with fs laser pulses as well as X-rays and subsequent annealing at high temperature (~770 K) for 10 min in silver-doped glasses bring about the reduction of Ag^{+} ions to Ag^{0} atoms and result in the formation of plasmonic nanoparticles, as observed by means of luminescence, electron spin resonance (ESR) and transmission electron microscopy (TEM) (Zhao et al., 2004; Shimotsuma et al., 2005).

Fig. 2 shows the absorption spectra before (Curve 1) and after irradiation of X-ray (Curve 2) and fs laser pulses (Curves 3 and 4). Note that these irradiated absorption spectra show the difference in absorbance between the X-ray and fs laser irradiated- and nonirradiated-glasses. For Curves 3 and 4, the average power was 500 and 700 mW at scanning rates of 1 mm/s

and 100 μm/s, respectively. The spot diameter was approximately 2 μm. The peak power density of the laser beam irradiated on the sample was estimated to be 8.0×10^{14} W/cm^2 for Curve 3 and 1.1×10^{15} W/cm^2 for Curve 4, respectively. For Curve 3, a peak position at 315 nm of the absorption band was in good agreement with that of the X-ray irradiated absorption band (Curve 2), while for Curve 4 the spectrum was dominated by an absorption band at 407 nm that could be ascribed to the surface plasmon resonance (SPR) of the formed silver nanoparticles (Zhao et al., 2004; Shimotsuma et al., 2005).

Note that irradiation with X-ray and high peak power density (1.1×10^{15} W/cm^2) fs laser pulses yields different absorption peak wavelengths of the Ag^0 centres as described above: the former is 345 nm and the latter is 407 nm. One of the reasons for this difference is that when fs laser pulses are focused inside the sample at a high repetition rate over 250 kHz, the temperature at the focal point increases to as high as several thousand Kelvin (Sakakura et al., 2008), a much higher temperature than that reached in normal heat treatment. As a result, highly successive fs laser pulses and a slow scanning rate caused cumulative heating around the focal point. Increasing the temperature greatly increased the average size of nanoparticles formed by fs laser irradiation, resulting in a red-shift of the peak wavelength. Moreover, Ma et al. (2009) reported that the light intensity in the focus of the beam on the order of 10^{15} W/cm^2 was high enough to generate multi-photon ionisation in the glass matrix, and the heat

accumulated by the 250-kHz fs laser resulted in the subsequent Ag nanoparticles growth process.

It was found from the above results that the 345 nm band corresponding to the decomposed "E" band was identifiable as the tapped electron Ag^0 centres (reaction: $Ag^+ + e^- \rightarrow Ag^0$) due to almost overlap between the "E" and SPR band. In addition, the 270 nm band corresponding to the decomposed "C" band also increases in intensity after high intensity (1.1×10^{15} W/cm^2) fs laser pulses, therefore the "C" band was identifiable as the Ag_2^+ centres (reaction: $Ag^+ + Ag^0 \rightarrow Ag_2^+$). As increasing the Ag^0 centres, then the Ag_2^+ band with coupling to Ag^0 centres also increases.

On the other hand, the 310 nm band corresponding to the decomposed "D" band was attributed to the trapped hole Ag^{2+} centres (reaction: $Ag^+ + h^+ \rightarrow Ag^{2+}$). In the case of PG:Ag, the holes are captured by PO_4 tetrahedron at the beginning of the migration and then the holes come to produce the Ag^{2+} centres due to interaction with Ag^+ ion by the time passing. As a result, metallic nanoparticles (Ag^0 centres) can form and grow quickly under elevated temperatures at the beginning stage after fs laser irradiation, while the Ag^{2+} centres need long elapsed time to form. A prominent decrease in intensity around "D" band may be considered to reflect the above explanation.

Fig. 3 shows the excitation and emission spectra of high intensity (1.1×10^{15} W/cm^2) fs laser irradiated PG:Ag. Excitation spectra were detected at 450 (blue RPL) and 570 nm

(orange RPL) and emission spectra were excited at 310 (Ag^{2+} band), 360 (Ag^{0} band) and 407 nm (SPR, Ag nanoparticles), respectively. Note that orange or blue emission for an excitation at 407 nm could not be observed, which give an additional evidence for the band assignment to silver nanoparticles. Moreover, for the excitation spectra detected at 450 nm, photoluminescence (PL) peaking at 302 nm (Kurobori et al., 2010) excited by the Ag^{+} band at 240 nm becoms predominant and thus a shoulder part of the PL completely overlaps a blue RPL at 450 nm. In addition, shorter wavelength regions of the excitation spectrum detected at 570 nm are not stable as shown in Fig. 3, which may reflect the characteristics of the induced Ag_2^{+} ($Ag^{+} + Ag^{0} \rightarrow Ag_2^{+}$) centres. On the other hand, in the case of low intensity fs laser irradiated PG:Ag, both emission and excitation spectra were very similar to those of X-ray irradiation.

4. Conclusions

In summary, we have investigated the formation and assignment of silver defect centres, in particular, Ag^{0}, Ag^{2+} and Ag_2^{+} species induced by high- and low-intensity fs laser pulse irradiation. Direct precipitation of silver nanoparticles in a silver-activated phosphate glass without heat treatment was demonstrated to clarify the origin of silver defect centres by 250 kHz high repetition rate fs laser pulses. The intensity threshold of fs irradiated region for direct formation of surface plasmonic Ag nanoparticles was the order of 10^{15} W/cm^2.

However, more detailed information is needed for a satisfactory explanation of the different glass matrix structure between the Ag^0 centres at 450 nm induced by X-ray irradiation and SPR at 407 nm induced by high intensity fs laser irradiation.

Acknowledgements

We would like to thank Dr. M. Sakakura, Dr. Y. Shimotsuma, Prof. K. Miura and Prof. K. Hirao at Kyoto University for their contributions to the femtosecond laser experiments.

Figure captions

Fig. 1 (a) Absorption spectrum before (dashed-and-dotted line) and after (solid line) X-ray irradiation with a dose of 24.5 Gy. Irradiation induced band was decomposed into a sum of separate Gaussian bands (Curves 2-5) as shown in the inset. (b) Absorption, excitation and RPL spectra of PG:Ag after X-ray irradiation with a dose of 24.5 Gy. Irradiation induced band was decomposed into six Gaussian bands (marked as A to F, dashed lines). Excitation spectra were detected at 560 nm (Curve 1) and 450 nm (Curve 2). RPL spectra were excited at 310 nm (Curve 3), 270 nm (Curve 4) and 340 nm (Curve 5).

Fig. 2 Absorption spectra before (Curve 1) and after X-ray (Curve 2) and fs laser (Curves 3 and 4) irradiation. Curve 2 was irradiated at a dose of 4.90 Gy. Laser intensity for Curves 3 and 4 was 8.0×10^{14} and 1.1×10^{15} W/cm^2, respectively. Decomposed "C", "D", and "E" bands were shown for comparison.

Fig. 3 Excitation and RPL spectra of PG:Ag after high intensity (1.1×10^{15} W/cm^2) fs laser irradiation. Excitation spectra were detected at 450 and 570 nm and RPL spectra were excited at 310, 360 and 407 nm, respectively.

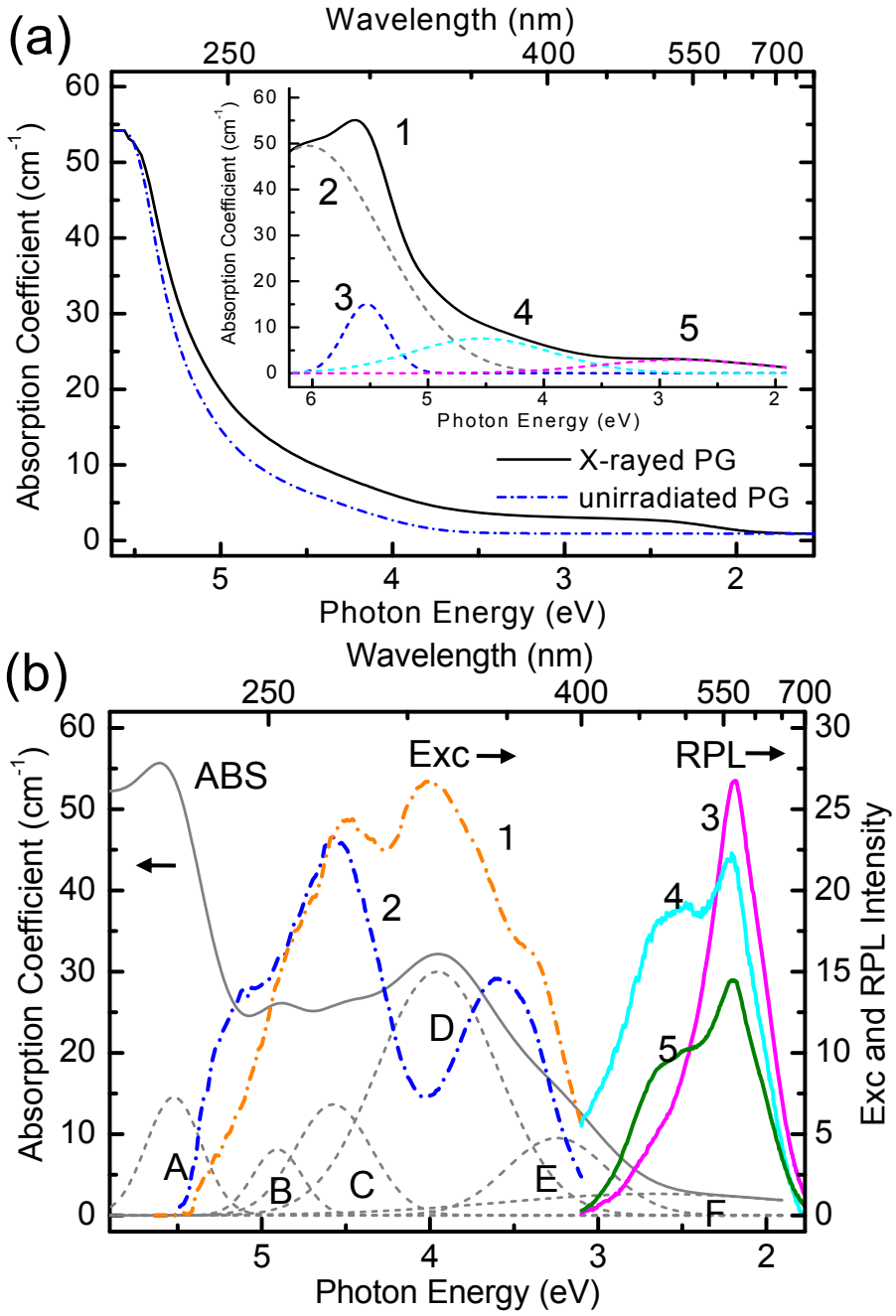

Fig.1a,b W. Zheng et al.

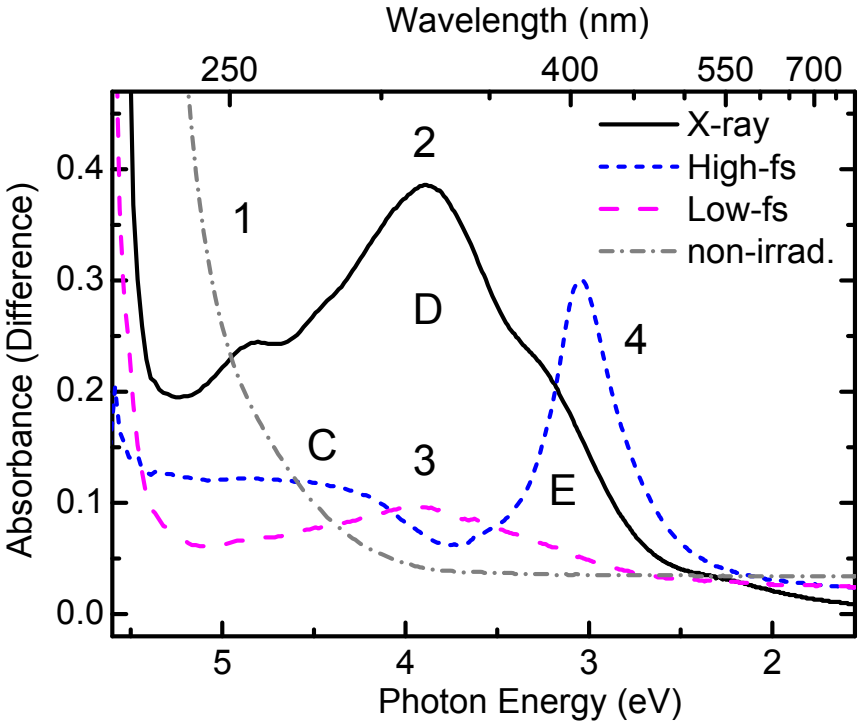

Fig.2 W. Zheng et al.

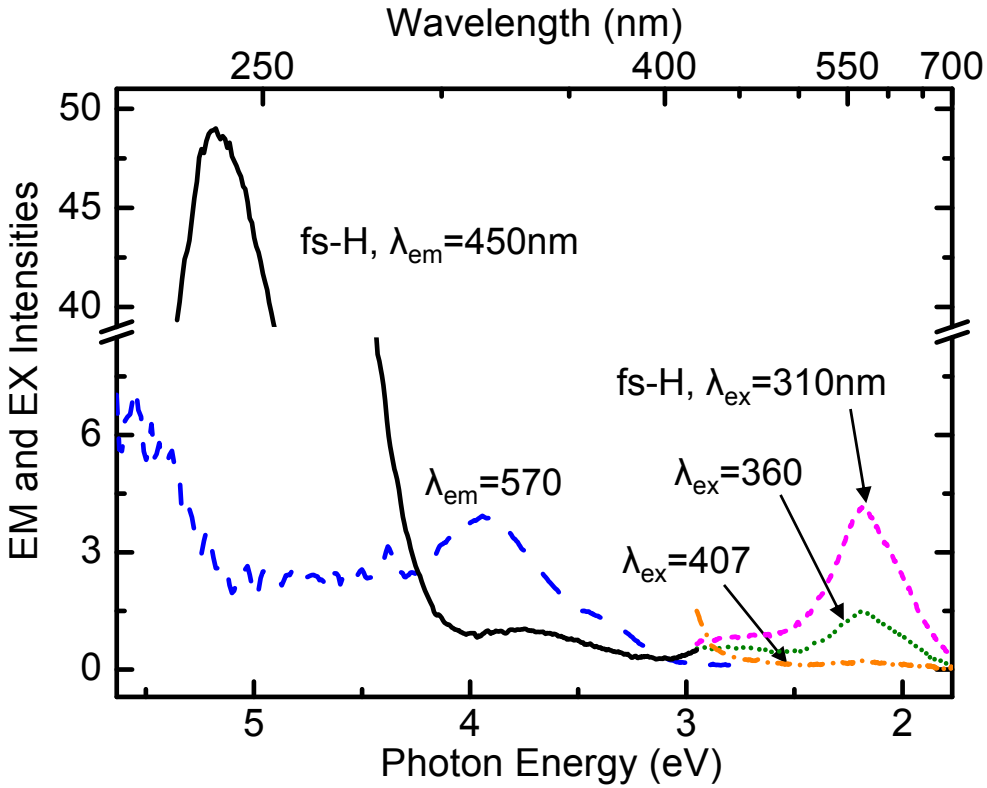

Fig.3 W. Zheng et al.

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