Solid-state Ag$^+$ Ion Migration for the Controlled Precipitation of PbS Quantum Dots in Glasses

Kai Xu and Jong Heo

Department of Materials Science and Engineering, and Division of Advanced Nuclear Engineering, Pohang, University of Science and Technology (POSTECH), Nam-Gu, Pohang, South Korea

Abstract: Precipitation of PbS quantum dots (QDs) controlled by solid-state Ag$^+$ ion migration and subsequent thermal treatment was investigated. Ag$^+$ ions migrated from Ag paste applied on the surface into glass at 320°C. After following heat treatment, PbS QDs formed in the near surface area where Ag paste was coated. Sizes of the PbS QDs were larger in Ag$^+$-migrated surface regions than those in Ag$^+$-free glasses, and PbS QDs can grow at temperatures as low as 420 and 430°C. Ag nanoparticles (NPs) also formed during the thermal treatment. These results suggest that Ag NPs supplied the nucleating sites and promote the formation of PbS QDs in glasses. The spatial distribution of PbS QDs in glasses can also be controlled through solid-state Ag$^+$ ion migration.

1 INTRODUCTION

Lead sulfide (PbS) has a narrow-gap energy (E_g = 0.41 eV at 298 K) and a large exciton Bohr radius (a_B = 18 nm), which allows PbS quantum dots (QDs) to have size-tunable optical properties in near-infrared spectra (Wise, 2000). Glasses are suitable matrices to host semiconductor QDs, because they can prevent the aggregation of QDs and have the high chemical stability (Woggon, 1997). Therefore, glasses containing PbS QDs have the potential applications as saturable absorbers for near-infrared lasers (Malyarevich et al., 2008) and in amplifiers for fiber-optic telecommunication (Heo and Liu, 2007).

Thermal treatment of the precursor glass is the most common method of precipitating QDs in glasses (Borrelli and Smith, 1994). Ion implantation and femtosecond laser irradiation have been attempted to control the spatial distribution of QDs in glasses. For example, ion implantation can induce the formation of PbS QDs within hundreds of nanometers from the surface of glasses (Lamaestre et al., 2005). Femtosecond laser irradiation can also control the spatial precipitation of PbS QDs inside glasses (Liu et al., 2010). However, these external fields always cause the serious damages on the parent glasses.

Noble metallic nanoparticles (NPs), such as Ag and Au NPs, are well-known as nucleating agents for controlled crystallization of glasses (Stookey, 1959) or controlled shape and size of PbS nanocrystals in liquid solutions (Yong et al., 2006). Recently, precipitation of Ag NPs as nucleating agents to control the formation of PbS QDs in glasses has been reported (Xu et al., 2011). A few tens of parts per million (ppm) of Ag$^+$ ions were added in molten glass batches, and precursor glasses were prepared by the melt-quenching method. After heat treatment, intensities of the absorption and photoluminescence (PL) from PbS QDs increased with the addition of Ag. This was attributed to the increased number density of PbS QDs with increasing Ag. However, the maximum solubility of Ag$^+$ ions in molten glasses was only ~40 ppm, and this limited concentration of Ag$^+$ ions made the control of PbS QDs precipitation in glasses difficult.

Ion-exchange method has been extensively used to fabricate optical waveguides in Na-glasses (Najafi, 1992). This method can incorporate the large amount of Ag$^+$ ions in the glass surface compared to melt-quenching method. Therefore, Ag$^+$ ions were incorporated into glasses by dipping the glasses into AgNO$_3$ solution (Xu and Heo, 2012a) or melt (Xu and Heo, 2012b). After thermal treatment, the size of PbS QDs precipitated in the Ag$^+$ ion-exchanged surface regions was larger than that in Ag$^+$-free regions. However, the long ion-

exchange duration in $AgNO_3$ solution causes the contamination of the glass surface. The migration of Ag^+ ions was very fast inside the $AgNO_3$ melt, and it makes the control of amount of Ag^+ ions difficult. The solid-state Ag^+ diffusion is proposed as an alternative approach to incorporate the Ag^+ ions into glasses (Najafi, 1992).

This paper reports the solid-state Ag^+ migration into glass for the controlled formation PbS QDs in glasses. Ag paste was used as the source of Ag^+ ions and heat was applied to induce Ag^+ ion diffusion. Ag NPs and PbS QDs were precipitated after subsequent thermal treatment. PL spectra show that PbS QDs can form into larger sizes and preferentially precipitate in the Ag^+-migrated regions.

2 EXPERIMENTS

A glass with a nominal composition (mol %) of $50SiO_2$ - $35Na_2O$ - $5Al_2O_3$ - $8ZnO$ - $2ZnS$ - 0.8 PbO was prepared using melt-quenching. Starting powders of ~25 g were ground in ethanol using ZrO_2 balls. The mixtures were kept in an oven at 110°C for 24 h to remove ethanol and moisture, then melted in an alumina crucible at ~1350°C for 45 min. The melts were poured into a pre-heated brass mold and pressed to a thickness of ~1.5 mm using an iron plate. The glass was annealed at 350°C for 3 h to release the thermal stress, then cut into pieces of ~1.0×1.0 cm. Finally, the pieces were optically polished to the thickness of ~1.0 mm.

One side of glass was coated with 0.1-mm-thick Ag paste, then heat-treated at 320°C for 2 h to allow Ag^+ ion migration. Afterwards, remaining Ag paste on glass surface was removed using acetone, and specimens were further heat-treated for 10 h at 420, 430, 440 or 450°C, respectively, to induce precipitation of Ag NPs and PbS QDs.

Formation of QDs was confirmed using a transmission electron microscope (TEM) under an accelerating voltage of 200 kV. Oxidation states of silver in glasses were identified by X-ray photoelectron spectroscopy (XPS) using Mg-Kα ($h\nu$ = 1253.6 eV) radiation. The depth of Ag penetration was analyzed using energy dispersive X-ray spectroscopy (EDX) after polishing a cross-section of the glass. PL spectra were recorded using an 800-nm excitation beam from a continuous-wave Ti-sapphire laser. Signals were collected and amplified using a combination of a mechanical chopper of 50-Hz frequency, a 1/4 m monochromator, an InGaAs detector and a lock-in amplifier system. All measurements were performed at room temperature.

3 RESULTS & DISCUSSION

3.1 Appearance of Glasses

After Ag^+ ion migration at 320°C and heat treatment at temperatures ≤ 430°C, the color of the glass surface that was coated with Ag paste turned into dark brown. The region without Ag paste did not show any color change and remained yellowish (Figure 1).
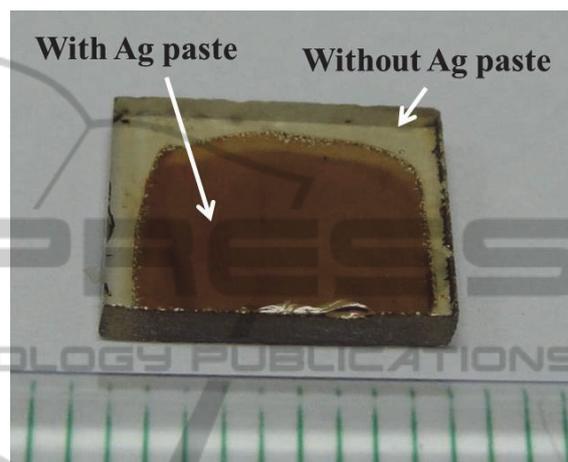
Figure 1: Photograph of the glass after Ag^+ ion migration at 320°C for 2 h and heat treatment at 430°C for 10 h.

3.2 Formation of PbS QDs

To identify the crystal structure precipitated in the glass, a TEM specimen was prepared from the dark brown surface using the focused ion beam milling. A TEM micrograph of a single crystal in Figure 2 shows the fringe spacing of ~0.17 nm. This is similar to the (222) plane spacing of bulk PbS, and therefore, we believe PbS QDs formed in the glass surface that was coated with Ag paste. Unfortunately, the crystals relative with Ag could not be identified from the TEM images.

3.3 PL Spectra of PbS QDs in Glasses

PL spectra were recorded to demonstrate the effect of Ag^+ ion migration on the formation of PbS QDs. The incident laser excited only the glass surface where Ag^+ ions migrated. Clear PL bands from PbS QDs were observed (Figure 3a). The center wavelengths of PL shifted from ~1160, ~1260, ~1390 to ~1530 nm when heat-treatment temperatures increased from 420, 430, 440 to 450°C. PL spectra from glasses without Ag^+ ion migration were also recorded as shown in Figure 3b (Xu and

Heo, 2012b). The center wavelengths of PL were ~1000 and ~1100 nm at heat-treatment temperatures of 440 and 450°C, respectively. It is obvious that PbS QDs in glass surface coated with Ag paste photoluminesced the longer wavelengths than did those in unaffected regions. These results indicated that the sizes of PbS QDs in Ag^+ migration regions were larger than those in Ag^+-free regions, which is similar with the results from Ag^+ ion-exchange in $AgNO_3$ solution or melt (Xu and Heo, 2012a, b).
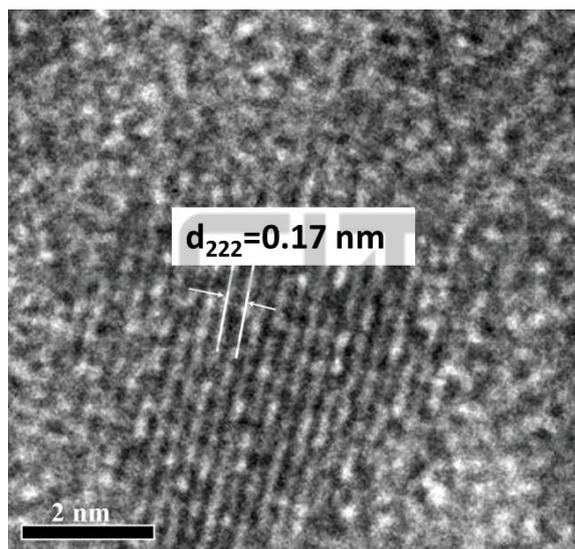
Figure 2: TEM micrograph of a single PbS crystal. Glass was subjected to Ag^+ ion migration at 320°C for 2 h and heat treatment at 430°C for 10 h.

Another effect is that PbS QDs precipitated at lower temperatures (420 and 430°C) after Ag^+ ion migration. We did not observe any emission from PbS QDs in Ag^+-free glasses when heat-treatment temperatures are less than 430°C (Figure 3b). But, after Ag^+ ion migration, emissions from PbS QDs were observed at heat-treatment temperatures of 420 and 430°C. This indicated that precipitation of PbS QDs in glasses can be facilitated through Ag^+ ion migration.

3.4 Ag NPs Promote the Formation of PbS QDs in Glasses

At temperature of ~320°C, the neutral Ag^0 in paste is oxidized to Ag^+ ions, which then diffuse into glass (Najafi, 1992). During the heat treatment, Ag^+ ions inside glasses are reduced to Ag^0 by capturing electrons from impurities or non-bridging oxygens, then aggregate to form Ag NPs (Wang, 1997). The chemical states of silver in the glasses were identified by XPS spectra. Figure 4 showed XPS spectra of $Ag_{3d5/2}$ from the glass containing Ag^+ ions after heat treatment (Xu and Heo, 2012b). The XPS $Ag_{3d5/2}$ spectrum was separated into two peaks using Gaussian curve fitting procedures. Results clearly showed that the neutral Ag (Ag^0) formed in glasses after heat treatment, indicating the formation of Ag NPs, but many Ag^+ ions still remained, probably forming Ag_2S or Ag_2O crystals.
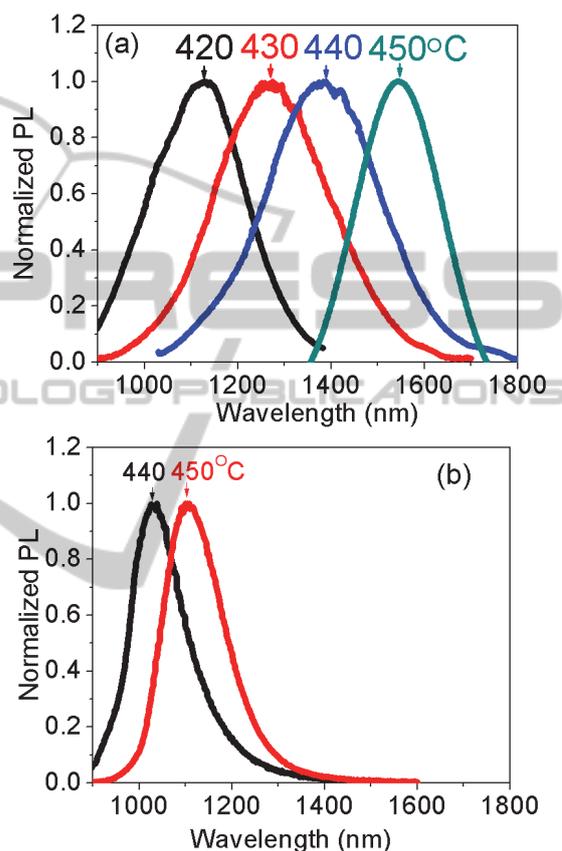
Figure 3: (a) Normalized PL spectra from glass surfaces when glasses were subjected to Ag^+ ion migration at 320°C for 2 h and then heat treatment at 420, 430, 440 and 450°C for 10 h. (b) Normalized PL spectra from Ag^+-free glasses at heat-treatment temperatures of 440 and 450°C for 10 h.

Ag NPs thus formed in glasses normally have an absorption peak at wavelength of ~400 nm, but this absorption peak was buried by PbS QDs in our glasses. To confirm Ag NPs formed in our glasses during the thermal treatment, we prepared a PbS QDs-free glass with a nominal composition (mol %) of $50SiO_2 - 35Na_2O - 5Al_2O_3 - 8ZnO - 2ZnS$. The glass was subjected to the same procedures as before: Ag^+ ion migration at 320°C for 2 h by coating Ag paste, then heat treatment at 400°C for

10 h to nucleate nanocrystals. A weak absorption shoulder was observed at wavelength of ~405 nm (Figure 5), which indicated that Ag NPs precipitated in the glass. Thus, we assumed that Ag NPs were also formed in glasses containing PbS QDs at this low temperature of 400°C. During the initial stage of heat treatment, Ag NPs quickly formed and provided the nucleating sites for PbS QDs. Therefore, PbS QDs precipitated at lower temperature, and grew into the larger size after Ag^+ ion migration as we observed in Figure 3a.
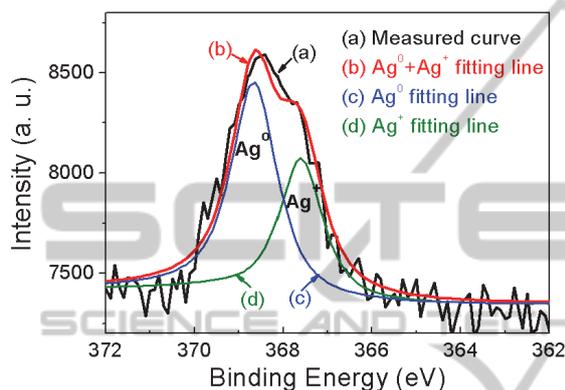
Figure 4: XPS spectra of $Ag_{3d5/2}$ from the glass containing Ag^+ ions after heat treatment. Line (a) is measured curve, and lines (b), (c) and (d) are results of the curve fitting by assuming that the high binding energy component is due to the neutral Ag (Ag^0) while the low binding energy component is from oxidized Ag^+ ions (Xu and Heo, 2012b).

EDX analysis showed that Ag^+ ions migrated ~30 μm into glass containing PbS QDs when it was subjected to Ag^+ ion migration at 320°C for 2 h and heat treatment at 430°C for 10 h (Figure 6). Therefore, we believe that PbS QDs precipitated within this ~30 μm layer in this glass.

3.5 Controlled Spatial Distribution of Pbs QDs in Glasses

Ag paste with "PbS" word was coated on the glass surface to evaluate the feasibility of controlling the spatial distribution of PbS QDs in glasses. Afterwards, sample was heat-treated at 320°C for 2 h for Ag^+ ion migration. After removing the Ag paste, glass was heat-treated again at 420°C for 10 h to nucleate PbS QDs. Photograph shows that the word of "PbS" with dark brown appeared on the glass surface where Ag paste was coated (Figure7). PL spectrum from "PbS" word was also recorded as shown in Figure 8. The center wavelength of PL was ~1150 nm, which is similar with the spectrum in

Figure 3a, and is from PbS QDs. Therefore, the pattern of PbS QDs in glasses can be controlled by simply control of Ag^+ ion inside glasses. Solid-state Ag^+ migration could provide the more effective way to control the spatial distribution of PbS QDs in glasses, compared to ion implantation and femtosecond laser irradiation techniques.
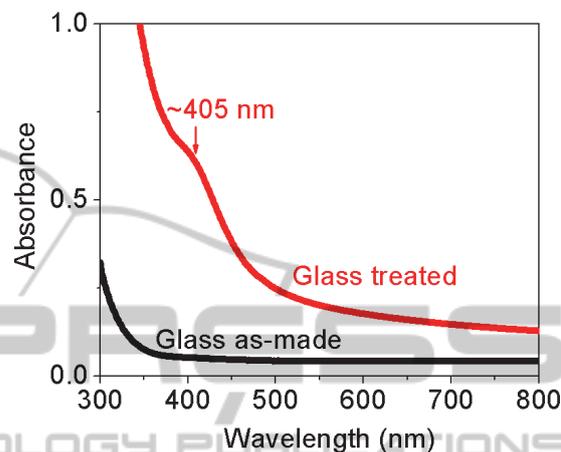
Figure 5: Absorption spectra of PbS QDs-free glass as-made and the glass after Ag^+ migration at 320°C for 2 h and then heat treatment at 400°C for 10 h.
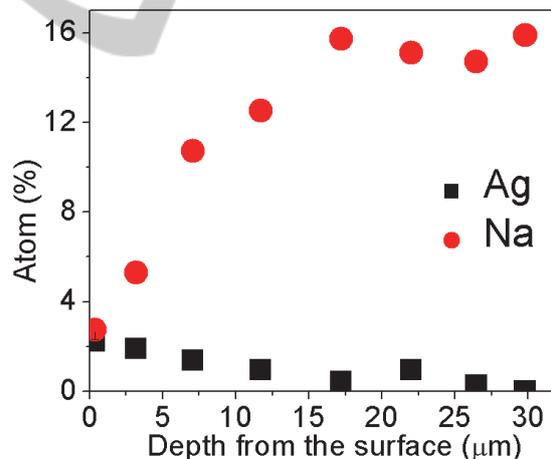
Figure 6: Ag concentration along the cross-section of glass by EDX analysis. Glass was subjected to Ag^+ ion migration at 320°C for 2 h and heat treatment at 430°C for 10 h.

4 CONCLUSIONS

Solid-state Ag^+ ion migration and subsequent thermal treatment were used to control the precipitation of PbS QDs in glasses. After Ag^+ ion migration and following heat treatment, PbS QDs

formed and were confirmed by TEM image. PbS QDs in Ag^+-migrated glass surface photoluminesced the longer wavelengths than those in Ag^+-free glass when heat-treatment temperatures were 440 and 450°C. PbS QDs can also precipitate at temperatures as low as 420 or 430°C after Ag^+ ion migration. Ag concentration analyzed by EDX indicated that PbS QDs could precipitate within ~30 μm layer from the glass surface. XPS and optical absorption spectra confirmed that Ag NPs formed at the initial stage of heat treatment. Ag NPs thus formed provided the nucleating sites and promote the formation of PbS QDs in glasses. Solid-state Ag^+ ion migration method can effectively control the spatial distribution of PbS QDs in glasses, and it has the potentials on space-selective formation of PbS QDs in glasses for micro- or nano-photonic devices.
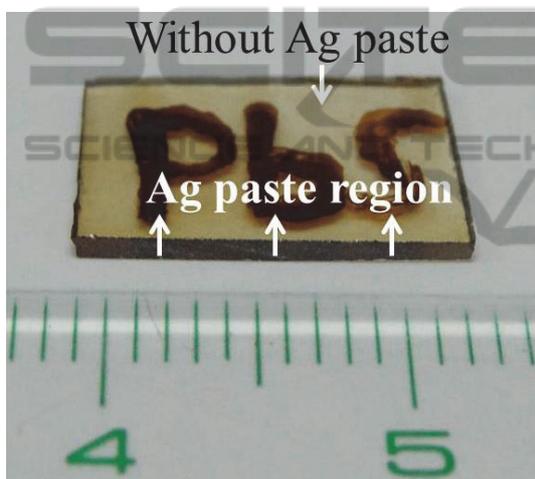
Figure 7: Photograph of PbS QDs with "PbS" word in glass. Glass was subjected to Ag^+ ion migration at 320°C for 2 h and then heat treatment at 420°C for 10 h.
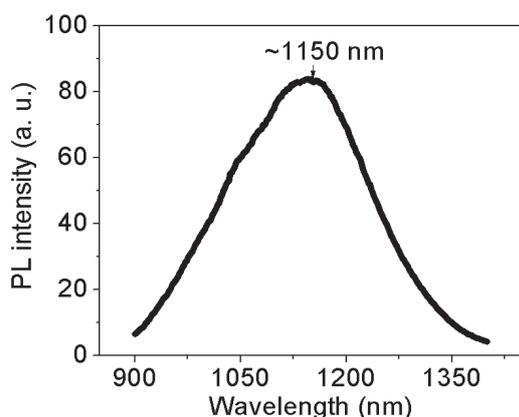
Figure 8: PL spectrum from "PbS" word in Figure 7. Glass was subjected to Ag^+ ion migration at 320°C for 2 h and then heat treatment at 420°C for 10 h.

ACKNOWLEDGEMENTS

REFERENCES

Borrelli, N. F. and Smith, D. W. (1994). Quantum Confinement of PbS Microcrystals in Glass. *J. Non-Cryst. Solids,* 180, 25-31.

Heo, J. and Liu, C. (2007). PbS Quantum-Dots in Glass Matrix for Universal Fiber-Optic Amplifier. *J. Mater. Sci: Mater Electron.,* 18, S135-39.

Lamaestre, R. E., Majimel, J., Jomard, F. and Bernas, H. (2005). Synthesis of Lead Chalcogenide Nanocrystals by Sequential Ion Implantation in Silica. *J. Phys. Chem. B,* 109, 19148-55.

Liu, C., Kwon, Y. K., Heo, J., Kim, B. H. and Sohn, I. (2010). Controlled Precipitation of Lead Sulfide Quantum Dots in Glasses Using the Femtosecond Laser Pulses. *J. Am. Ceram. Soc.,* 93, 1221-24.

Malyarevich, A. M., Yumashev, K. V. and Lipovskii, A. A. (2008). Semiconductor-Doped Glass Saturable Absorbers for Near-Infrared Solid-State Lasers. *J. Appl. Phys.,* 103, 081301- 25.

Najafi, S. I. (1992). *Introduction to Glass Integrated Optics*. Artech House, Boston.

Stookey, S. D. (1959). Catalyzed Crystallization of Glass in Theory and Practice. *Ind. Eng. Chem.*, 51, 805-08.

Wang, P. W. (1997). Formation of Silver Colloids in Silver Ion-exchanged Soda-lime Glasses during Annealing. *Appl. Surf. Sci.*, 120, 291-98.

Wise, F. W. (2000). Lead Salt Quantum Dots: the Limit of Strong Quantum Confinement. *Acc. Chem. Res.*, 33, 773-80.

Woggon, U., (1997). *Optical Properties of Semiconductor Quantum Dots*. Springer, Berlin.

Xu, K., Liu, C., Dai, S., Shen, X., Wang, X. and Heo, J. (2011). Influence of Silver Nanoclusters on Formation of PbS Quantum Dots in Glasses. *J. Non-Cryst. Solids*, 357, 2428-30.

Xu, K. and Heo, J. (2012a). Lead Sulfide Quantum Dots in Glasses Controlled by Silver Diffusion. *J. Non-Cryst. Solids*, 358, 921-24.

Xu, K. and Heo, J. (2012b). Effect of Silver Ion-Exchange on the Precipitation of Lead Sulfide Quantum Dots in Glasses. *J. Am. Ceram. Soc.,* 95, 2880-84.

Yong, K. T., Sahoo, Y., Choudhury, K. R., Swihart, M. T., Minter, J. R. and Prasad, P. N. (2006). Control of the Morphology and Size of PbS Nanowires Using Gold Nanoparticles. *Chem. Mater.*, 18, 5965-72.