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In situ optical study of the phase transformation kinetics of plasmonic Ag in laser-irradiated nanocomposite glass

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ABSTRACT

A real-time spectroscopic study of the optical response of plasmonic Ag produced during thermal processing of laser-irradiated silver nanocomposite glass has been carried out. Specifically, this work addresses the early stage of in situ heat treatment prior to the plasmonic coupling which has been reported for relatively high temperatures and long holding times [13]. The data supports the plasmonic Ag phase transformation in the confined "super nucleation" regimes created as a result of the photofragmentation of Ag nanoparticles by the laser pulses. Consistent application of the Kolmogorov–Johnson–Mehl–Avrami theory in the 623–653 K relatively low temperature range to optical data collected in the 1–15 min time window allows for determining an activation energy for the phase transformation in the non-interacting regime at 0.55 (±0.04) eV.

1. Introduction

Optical interactions between energetic laser beams and nanoscale metal particles embedded in amorphous inorganic hosts have been a topic of interest from both fundamental and applied perspectives. From the more fundamental side, the ultrafast relaxation dynamics of the matrix-suspended nanoparticles (NPs) have been extensively studied by laser spectroscopy techniques [1–4]. On the other hand, laser irradiation has been employed in a variety of treatments aimed for the tailoring of material properties, where the following modifications have been reported for metal–dielectric composites: particle size reduction [5]; particle dissolution and bleaching [6,7]; formation of luminescent metal clusters [8]; particle shape modification [9,10]; NP growth [11]; and three-dimensional patterning [12]. Certainly intricate due to the many variables involved, the end result appears dependent on the optical and physicochemical properties of the material and the irradiation conditions employed.

Recently, a novel finding of fundamental and applied significance has been revealed for laser-irradiated Ag nanocomposites [13]. Namely, the phenomenon of plasmonic coupling has been effectively achieved and studied for Ag NPs embedded in phosphate-based glass, attained by a two-step modification: (*i*) an initial step of nanosecond laser irradiation at photon energy of 2.33 eV (532 nm); and (*ii*) a subsequent stage of thermal treatments. In the first step (*i*), confined "super-nucleation" domains are induced by the high-fluence nanosecond laser irradiation promoting photofragmentation of Ag NPs in the matrix. In the second step (*ii*), a particle re-growth process leading to the development of strongly interacting NPs is activated during an in situ isothermal processing carried out for relatively high temperatures and long holding times. A significant outcome in this latter step is that considerable narrowing of the Ag NP size distribution was achieved as revealed by transmission electron microscopy (TEM) [13]. Nevertheless, thus far the early stage of the post-laser thermal treatment, i.e., the regime of nanoparticulate Ag phase transformation prior to plasmonic coupling, has not been studied in detail. Such is the purpose of this work, in which the kinetics of the process is quantitatively studied by the in situ heat treatment (HT) and real-time monitoring of the optical response of the plasmonic metal clusters after the laser irradiation.

The selected material system consists of a melt-quenched heat-treated Ag nanocomposite glass which has been previously described [14] and possesses the characteristic of lacking a reducing agent. In this particular case, a post-laser HT then relates to the plasmonic particle precipitation caused exclusively by silver atoms/clusters 'dissolved' by the laser pulses. Thus, the kinetics of Ag NP precipitation solely connected to the effects of the photofragmentation can be assessed apart from additional particle growth assisted by chemical reduction within the glass matrix. The data produced in this work certainly indicates that the laser treatment generates the non-plasmonic silver fragments which respond dramatically to glass HT. Particularly, a rapid growth of the surface plasmon resonance (SPR) of the clusters is triggered at relatively low HT temperatures. The optical response is followed in real time during HT in the 623–653 K range in an early stage from 1 to 15 min precluding the plasmonic coupling effects. A low energy barrier for the

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non-interacting plasmonic NP precipitation is determined, supporting the use of combined laser and thermal processing as important tools for fabrication of plasmonic nanocomposites for photonic applications.

2. Experimental

The material which is the object of study consists of an aluminophosphate glass of the P_2O_5:Al_2O_3:CaO:SrO:BaO type with an additional 4 mol% of Ag_2O prepared by melting and HT processes as described in Ref. [14]. Samples of the Ag nanocomposite glass attained (polished to about 0.4 mm thick) were subjected to the photofragmentation/bleaching by laser irradiation with linearly polarized laser pulses from a 5 ns Nd:YAG laser, operating at 2.33 eV (532 nm), 10 Hz, at a laser fluence of 150 mJ/cm^2 for 30 min [13]. The irradiated samples were stored at room temperature, namely for a period of three years before the subsequent HT stage was initiated. Remarkably, the samples showed no deterioration throughout the storing period, testifying in favor of the stabilizing effect of the glass on the silver clusters [15].

A CRAIC Technologies FLEX microspectrophotometer (MSP) operating with a xenon lamp was used to collect optical absorption spectra. The MSP was further equipped with a Linkam THMS600 temperature control stage in order to conduct in situ optical measurements of the laser-irradiated glasses during HT. The measurements were performed with a 10× objective on 97.4 μm × 97.4 μm sample areas with particular attention given to keep sample position and conditions constant during the fixed-temperature experiments. Samples were heated to the desired temperatures at a rate of 100 °C/min. This heating rate represents a twofold increase relative to the previously employed in our group [13] as to reduce the time necessary to achieve the desired temperatures for the isothermal time-dependent measurements. HT temperatures were selected as 623, 633, 643 and 653 K. The use of such relatively low temperatures as compared to those employed in Ref. [13] allows confidence in eluding the manifestation of the plasmonic coupling shown to be favored at high temperatures. Further, the optical absorption data was collected in a short time window during the early phase of HT, namely, at 1 min intervals with a total holding time of 15 min.

3. Results and discussion

As the material under study lacks a reducing agent, the formation of Ag NPs in the glass has been observed due to the reduction of silver ions to the neutral state during the melting where the release of gaseous oxygen can take place [14]. A subsequent HT further incorporates 'dissolved' silver atoms/clusters into existing plasmonic nuclei thereby resulting in an amplified SPR band around 410 nm [14]. A spectrum of the nanocomposite glass as obtained by melting and HT processes (i.e. before irradiation) is shown in Fig. 1, clearly exhibiting the SPR peak characteristic of the spherical Ag NPs in the matrix. Such silver particles have been observed by TEM to be in the 3–8 nm diameter range [14]. The subsequent laser treatment produces the photobleaching effect as observed in the corresponding spectrum in Fig. 1 (collected after the three-year storing period). Clearly, the SPR band vanishes upon laser irradiation consistent with the previously reported Ag NP dissolution via laser-induced photofragmentation of the silver particles [13]. Further, the 'dissolved' silver was effectively stabilized in the glass stored at room temperature.

Upon the subsequent post-laser HT, the plasmonic properties of the glass recover promptly during the temperature ramp-up time [13]. Inspection by TEM revealed in our previous work on the laser- and heat-treated aluminophosphate glass that the developed NPs are quite small and considerably uniform in diameter ranging from 1.5 to 4.9 nm with an average of 2.9 (±0.6) nm [13]. Herein, as illustrated in Fig. 2 for the relatively low temperature of 623 K, the SPR band of the plasmonic Ag clusters certainly develops rapidly during the temperature rise and up to 1 min. The absorption band further narrows and

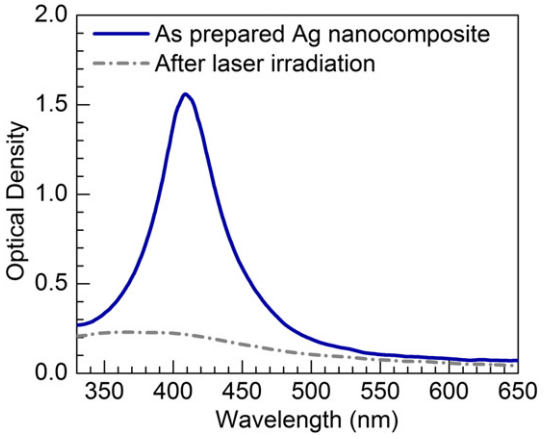

Fig. 1. Optical absorption spectra of samples of Ag nanocomposite glass as prepared by melting and thermal treatment, and after the subsequent step of laser irradiation (collected after the three-year storing period).

grows in intensity during the isothermal treatment up to the 15 min of holding time prescribed. Consistent results were observed in the time-evolution of optical spectra for glass samples heat-treated at 633, 643 and 653 K (not shown). Indeed, the SPR remained Lorentzian-shaped as characteristic of non-interacting NPs, i.e. silver atom aggregation produces NPs remaining far apart from each other as to respond to incoming light as a collection of plasmonic particles merely 'isolated' by the dielectric medium. A particle-to-particle separation for strongly-interacting Ag NPs measured as nearest-neighbor distance (center-to-center) was found within ~2 − 7 nm range, where statistical analysis yielded a mean distance of 3.9 (±0.8) nm [13]. If the electrodynamic coupling due to particle–particle interactions within short NP distances was manifested, a shoulder to the low energy side of the plasmonic absorption would rise [13], which evidently is not the present case.

The increase in optical density is considered a reflect of the precipitation of the NPs in the confined "super-nucleation" domains, where the kinetics of the process have been observed to follow the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory of phase transformations with an Avrami index of 1 [13]. The peak optical densities (*OD*) registered for the glass samples heat-treated at 623, 633, 643, and 653 K are plotted in Fig. 3 (normalized) as a function of holding time. Appropriately, the volume fraction of the plasmonic metal phase can be herein

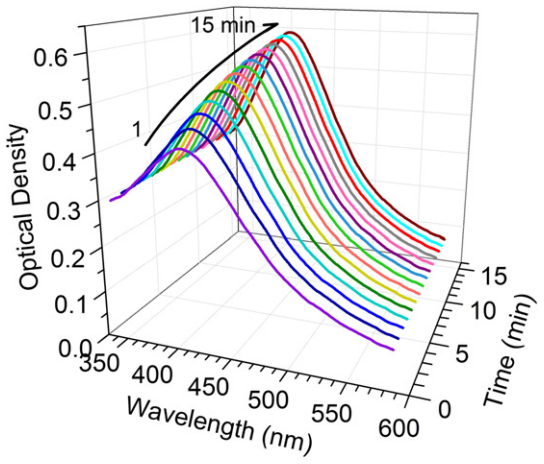

Fig. 2. Optical absorption spectra of irradiated Ag nanocomposite recorded in real time during thermal treatment at 623 K from 1 to 15 min at intervals of 1 min.