Laser-induced dendritic microstructures on the surface of Ag+-doped glass

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Fractal dendritic silver microstructures are observed on the surface of the Ag+-doped glasses as a result of a photothermal interaction with a focused multiline cw high-power ($P_{\text{max}}=8$ W) Ag+ laser beam. It is found that evolution of the structures depends on the exposure time and also on the concentration of the silver ions in the sample. The fractal dimension of the generated dendritic microstructures increases with the exposure time. Instability of the contact line of the molten silver flow toward the periphery of the interaction area is discussed as a result of the temperature gradient, due to the Gaussian intensity distribution across the laser beam. © 2006 American Institute of Physics.

I. INTRODUCTION

Composites, formed by embedding semiconductor or metal nanoclusters in a glass matrix, have important applications in optoelectronics (e.g., all optical switching technology, planar waveguides, etc.). They also show remarkable nonlinear optical properties. Therefore, the interaction of high-power laser beams with these optical materials has been studied by several research groups.

Silver-ion-doped glass is one of the most investigated cases, because it has interesting optical properties and can be fabricated rather easily. Depending on the conditions of the experiments and characteristics of the sample, different effects may result from the interaction. Here we name a few of the effects: reduction of silver ions to neutral nanoparticles, manipulation of size and size distribution of the silver particles in the glass matrix, diffusion of the silver particles toward the surface of the matrix, fabrication of microlenses as a controlled result of the interaction, high-power laser-induced dichroism in the Ag+-doped glasses, and formation of microsilver particles.

In this article, we report the effects of irradiating a concentrated silver ion-doped glass with a focused cw high-power Ar+ laser beam ($P_{\text{max}}=8$ W), working in a multiline regime. We have observed dendritic microstructures of neutral silver particles, around the incident point of the laser beam, that are formed as a result of the irradiation (Fig. 1). The fractal character of such structures is an interesting finding in that they are generated optically via the interaction with a laser beam.

It is observed that the extent of the dendritic structures, which forms on the periphery of the interaction area as a result of the interaction, grows with exposure time. As will be shown later, the fractal dimension of these structures also increases with exposure time. The formation of these structures is discussed as a result of photothermal effects, induced by the laser beam on the sample. The focused laser beam strongly heats the sample at the incident point. This leads to the annealing of the silver ions, and the production of the silver monomers. The neutral silver clusters are consequently formed. The produced silver particles diffuse toward the surface and at the same time melt. Due to the transverse Gaussian intensity distribution of the laser beam, a temperature gradient is established from the center toward the periphery, which generates a Marangoni force at the surface of the melt.

Similar silver fractal-like structures are grown on glass, using silver electrodes, with possible applications to luminescence probes and labels.

The organization of this report is as follows. In Sec. II we present the details of experimental setup and procedures. In Sec. III we present the results. Section IV is devoted to our discussions. Conclusions are given in Sec. V.

FIG. 1. Laser-induced dendritic microstructure on the surface of a Ag+-doped glass. The sample was ion-exchanged at 460 °C for 6 h with mixed molten salt: NaNO3/AgNO3 (90 wt %/10 wt %). The laser beam was focused by a microscope objective (40×). The exposure time was 10 s and the fractal dimension was found to be 1.8. Such large structures were rarely obtained in our experiments.
II. EXPERIMENT

The samples (Ag⁺-doped glass) of our experiments are prepared using the well-known ion-exchange method. The concentration of the diffused Ag⁺ ions and their diffusion depth in the glass matrix depend on the temperature and duration of the ion-exchange process, and also on the concentration of the silver ions in the molten salt. It is known that the concentration of the diffused Ag⁺ ions depends on the type of glass material used. Our samples were made from a commercial soda-lime glass slide (20 × 30 × 0.8 mm) of the following composition (wt %): 80% SiO₂, 9.41% CaO, 4% Na₂O, 3.3% MgO, 2.2% Al₂O₃, 0.41% K₂O, 0.2% S, 0.11% Fe₂O₃, 0.11% P₂O₅; the samples were then immersed into a molten NaNO₃/AgNO₃ mixed salt (90%/10%) at 400 °C for 4 h. We found that the induced dritic structures could not be generated for dilute samples.

The setup we used to record and view the induced dritic structures is shown in Fig. 2. A cw high-power (P_max = 8 W) Ar⁺ laser, working in multiline regime (λ₁ = 457.9 nm, λ₂ = 476.5 nm, λ₃ = 488 nm, λ₄ = 496.5 nm, λ₅ = 514.5 nm) was used as a source (i.e., pump beam). The laser beam is focused by a microscope objective (40×) on the sample. A shutter controls the exposure time. The microscope is equipped with a charge-coupled device (CCD) camera. For filtering the laser beam and the induced fluorescence radiation, a red filter and a blue filter were used in the microscope, respectively. The dark-field method was used to obtain better contrast for the photos of the laser-induced structures.

In order to study the changes in the induced structures as the exposure time is increased, two methods may be used: (1) long exposure with different exposure times on different spots on the sample, and (2) short repeated shots on the same spot. Figure 3 shows the laser-induced structures obtained by method (1), using the exposure time of 5 s.

III. RESULTS

The temperature at the laser incident spot is high enough to melt the glass locally. Upon the exposure to the laser shot, the temperature at the point of incidence rises rapidly, leading to the reduction of silver ions to the neutral atoms, and formation of micrometer sized silver particles (Fig. 3 and Ref. 7). The micrometer sized silver particles come rapidly to the surface, and spread around the incident point of the laser beam. This account is based on the movies taken during the experiment using the setup shown in Fig. 2. At the same time, a system of co-centered rings of the silver particles is produced (Figs. 3 and 4). An increase of the exposure time reduces the width of the silver rings. A further increase in the exposure time leads to an instability on the outer side of the last ring and the onset of the formation of the dendritic structures (Fig. 3). During the interaction, the newly born dendritic structures grow, but after a few shots their radial growth slows down and finally stops. This should be related to the limited amount of the silver in the sample. Further irradiation leads to the destruction of the generated structures. Based on the pictures taken during the experiment, it seems that the movement of the neutral micrometer sized silver particles toward the periphery of the incident spot happens in almost fixed channels on the surface of the sample (Fig. 5). The average speed of the branch tips during the interaction is about 5−6 μm/s. The branches have a size distribution between 15 and 100 μm (mostly between 15 and 30 μm), depending on the sample used.
During the interaction, the sample is placed vertically in the experimental setup, and the circular symmetry of the grown dendritic structures around the interaction area implies that gravity has no important role in the formation of the structures.

The scanning electron microscopy (SEM) studies (Figs. 6 and 7; exposure time: 3 s) confirm that the neutral silver particles produced in the vicinity of laser beam incident point (block 25.3 in Fig. 6) are in the form of molten silver droplets [Figs. 7(a) and 7(b)], which then join together and form the dendritic microstructures. Turning off the laser beam freezes the molten silver stream [Fig. 7(c)].

The generation of silver dendritic nanostructures, produced by different methods, results in the broadening into the long wavelength part of the spectrum and the appearance of a related maximum. In our case, the fractal structures are micrometer sized, and as the exposure time increases, the absorption spectrum is shifted up more or less uniformly. We attribute this to the increase of the silver coverage, and the drop in transmittance.

IV. DISCUSSION

A. Formation of the neutral silver

As mentioned earlier, the interaction of the high-power cw Ar+ laser leads to the reduction of the silver ions to neu-
tral atoms. The proposed mechanisms for this process are discussed in Refs. 3 and 7. The rise of the temperature of the interaction area due to the absorption of the laser beam by the sample increases the mobility of the Ag\(^{+}\) ions and the electrons of nonbinding oxygen in the matrix. Thus, by detaching the electrons from their surrounding medium, i.e., the glass matrix, the silver ions change into neutral silver atoms. The silver atoms could then aggregate and form neutral silver clusters. This process of aggregation is exothermic.\(^{15}\) It is well known that the interaction of a high-power laser beam with Ag\(^{+}\)-doped glasses leads to the appearance of an absorption band with a peak around 410 nm.\(^{7,16}\) This peak is related to the surface plasmon resonance of the generated nanometer sized colloidal neutral silver clusters.\(^{7,15}\)

Using a highly Ag\(^{+}\)-doped glass sample, one may establish a supersaturated condition by rapidly increasing the laser beam power.\(^{7}\) This leads to the formation of micrometer sized neutral silver clusters. At the same time, the produced silver particles diffuse toward the surface of the sample. Similar phenomena are reported also by other researchers,\(^{3,5}\) with no emphasis on an explanation. We suggest that degassing of the sample in the interaction area may assist the diffusion of the produced silver toward the surface of the samples. Movies taken during the experiment support this scenario.

B. Formation of co-centered silver rings

It can be seen from Figs. 3 and 4 that a few co-centered rings are formed by the silver particles. The rings are centered about the incident point of the laser beam. These co-centered rings are formed because of the Airy rings of the focused laser beam. Focusing the laser beam by a microscope objective lens results in the appearance of Airy rings. Then, the produced neutral silver on the surface of the sample moves to the minima of the intensity distribution,\(^{17,18}\) and forms the above-mentioned rings. To confirm this suggestion, we made a comparison between the Airy rings on the sample and the produced silver rings. The result is shown in Fig. 4. It is clearly seen that most of the silver particles are placed in the minima of the intensity distribution of the Airy rings on the surface of the sample.

C. The fractal dimension of the dendritic microstructures (DMS)

To study the temporal evolution of DMS formation on Ag\(^{+}\)-doped glass, we irradiated three points on the same Ag\(^{+}\)-doped glass with the same laser beam, but with different exposure times of 1, 3, and 5 s. The setup is shown in Fig. 2. For this part of the experiment, we used the bright-field method of microscopy and photography. Figure 8 shows the DMS shapes formed after 1, 3, and 5 s exposure times. To evaluate the changes in the DMS shape versus exposure time, we calculate the fractal dimension \(D\) of the DMS from the photos shown in Fig. 8. To extract the DMS from the regions devoid of them, we converted the monochromic intensity color version (GIF format) of the original RGB photos to black-and-white photos using a threshold color intensity of 120, i.e., 0 stands for black and 255 stands for white. We have evaluated the correctness of the extraction by a visual comparison of the extracted shapes with those of the original gray intensity photos. The boundary of the 5 s exposure DMS is, however, extracted manually due to the low contrast across the boundary. To calculate the fractal dimension of the extracted DMS, we use the box-counting method. In this case, the DMS is assumed to be a fractal structure.

![FIG. 7. Some magnified areas of Fig. 6: (a) the block indicated by 25–3; (b) the block indicated by 25–4; (c) the block indicated by 25–5. The droplets of the silver can be seen on the surface and near the surface of the sample (a), (b). The concentration of the droplets near the roots of the treelike structures is more than that of those near the center of the interaction area [compare (a) and (b)]. In (c) the dendritic microstructure can be seen.]

![FIG. 8. The original RGB photo of the DMS at 1, 3, and 5 s of exposure time, from left to right, respectively. The photos are used to calculate the fractal dimension \(D\). The bright-field method was used to take these microphotographs.]

silver particles diffuse toward the surface of the sample. Similar phenomena are reported also by other researchers,\(^{3,5}\) with no emphasis on an explanation. We suggest that degassing of the sample in the interaction area may assist the diffusion of the produced silver toward the surface of the samples. Movies taken during the experiment support this scenario.
method a given black-and-white DMS photo is subdivided into squares with dimension \( r \), and for each \( r \) the number of squares with at least one black pixel \( (N) \) is counted. Then a log-log plot of \( N \) vs \( r \) is drawn and the best fitting line is obtained. The slope of the best-fitted line gives us the fractal dimension. To avoid any bias toward smaller values of \( r \), we establish that such a forced spreading may undergo a finger instability. Such instabilities have been observed to be prone to the formation of fractal-type branching structures.\(^{26,27}\) If we take the surface tension of the flow as a function of temperature, \( \gamma = \gamma (T) \), then the produced tension is equal to the gradient of \( \gamma \) (Ref. 10):

\[
\nabla \gamma = - b \frac{\gamma (T, T)}{\nabla T(x)},
\]

where \( b \) is a positive coefficient. The minus sign means that the produced force acts in the direction of decreasing temperature. This is called the Marangoni effect. Spreading of viscous fluid sheets on a solid surface is a two-dimensional Stokes flow. Neglecting the gravitational force, in first order of approximation, the flow in the \( x \) direction has the following simple form in the quasi-static regime:

\[
\eta \frac{\partial^2 u}{\partial x^2} = \frac{\partial p}{\partial x},
\]

where \( \eta \) is the viscosity, \( u = u(x, y) \) is the fluid velocity, and \( z \) is the coordinate perpendicular to the solid surface. For simplicity, we have assumed a rectangular geometry instead of a circular one. The pressure \( p \) in the liquid is related to the curvature of the film surface by

\[
\frac{\partial p}{\partial x} = - \frac{\gamma}{d^3} \frac{d h}{dx^3},
\]

where \( h = h(x, y) \) describes the surface of the film and \( \gamma \) is the surface tension. In many systems, including liquid silver, surface tension has a marked dependence on temperature. Any temperature variation, then, may generate a surface tension gradient \( \sigma = d \gamma / dx \), which is called the Marangoni surface stress. Integration of Eq. (3), subject to Eq. (4) and a no-slip boundary condition on the solid surface, gives the following height averaged velocity for the liquid film\(^{10}\):

\[
u_o(x) = \frac{h}{2 \eta} \frac{\tau}{3} + \frac{3}{3} \frac{h^2}{3} \frac{d^3 h}{dx^3}.
\]

There are two terms in Eq. (5): one gives the flow induced by the Marangoni force and the second term is due to the Laplace pressure. The onset of instability is obtained when these two terms are comparable. The characteristic length, \( l \), thus obtained,

\[
l = h_o \left( \frac{3 h_o \tau}{\gamma} \right)^{-1/3},
\]

gives the scale of the wavelength of the fingering instability. Here, \( h_o \) is the thickness of the flat film. From the experiment, \( h_o \) and \( \tau \) are approximated to be about 1–2 \( \mu \)m and 70 N/m\(^2\), respectively. Surface tension \( \gamma \) is taken to be 0.9 N/m\(^2\).\(^{18}\) Thus, using Eq. (6) the characteristic length \( l \) becomes about \( 20 \mu \)m, which is in good agreement with our experimental results for the average size of the fingerings (Fig. 6).

V. CONCLUSIONS

In summary, we have reported the observation of a dendritic silver microstructure, generated by applying a focused cw multilines Ar\(^+\) laser beam on the surface of a silver-ion-exchanged glass matrix. Evolution of the induced structures
is studied. The formation of such microstructures is attributed to a temperature gradient produced by the Gaussian laser beam, and the appearance of an instability of the contact line. The instability comes as a result of the balance of the driving force (Marangoni effect) and the Laplace pressure, which leads to a fingering process of molten silver on the surface of the glass matrix. We show that these dendritic microstructures are fractal. It is found that the fractal dimension of the structures depends on the exposure time. Metal-enhanced fluorescence and certain types of luminescence probes and labels have been reported as possible applications for such fractal structures.\(^{11}\)

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