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The effect of laser sintering on the microstructure, relative density, and cracking of sol-gel-derived silica thin films

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Abstract

Combining sol-gel processing and laser sintering is a promising way for fabricating functional ceramic deposition with high dimensional resolution. In this work, crack-free silica tracks on a silica substrate with a thickness from ~360 nm to ~950 nm, have been obtained by direct exposure to a CO₂ laser beam. At a fixed scanning speed, the density and microstructures of the silica deposition can be precisely controlled by varying the laser output power. The porosity of the laser-sintered silica tracks ranged from close to 0% to ~60%. When the thickness of the silica deposition exceeded the critical thickness (eg, ~2.2 μm before firing), cracks occurred in both laser-sintered and furnace-sintered samples. Cracks propagated along the edge of the laser-sintered track, resulting in the crack-free track. However, for the furnace heat-treated counterpart, the cracks spread randomly. To understand the laser sintering effect, we established a finite element model (FEM) to calculate the temperature profile of the substrate during laser scanning, which agreed well with the one-dimensional analytical model. The FEM model confirmed that laser sintering was the main thermal effect and the calculated temperature profile can be used to predict the microstructure of the laser-sintered tracks. Combining these results, we were able to fabricate, predesigned patterned (Clemson tiger paw) silica films with high density using a galvo scanner.

Keywords

cracks/cracking; films; silica; sol-gel

1 | INTRODUCTION

Ceramic thin films have been widely used for a variety of applications including environmental barrier,¹⁻³ biomedical implants,⁴⁻⁶ and optoelectronic devices^{7,8} as they are in general chemically inert, stable at high temperature, and typically are dielectric materials. With superior optical, electrical, or magnetic functionalities and mechanical properties, ceramic films such as silica YSZ, mullite, and alumina have received enormous attention in many applications.⁹⁻¹² Many methods have been applied to fabricate these ceramic films, including sol-gel dip or spin coating, thermal spray, plasma spray, electrophoretic deposition, chemical, and physical vapor depositions.¹³⁻¹⁸ Among them, the sol-gel deposition has become one of the most popular methods for decades, because it requires simple instruments and delivers excellent composition controls.^{19,20} However, the sol-gel film deposition faces its own limitations. One of them is due to the difficulty of precisely patterning these films over a small local area. This limitation hinders the fabrication of precise devices using the sol-gel method. Another limitation in sol-gel thin film deposition is that the cracking is uncontrollable when the thickness of the film exceeds a “critical thickness,” defined as the thickness at which cracks start to occur during sintering, as the strain energy stored in the film exceeds the required energy for creating new cracks.

Laser processing of sol-gel films has been investigated to address this challenge of conventional sol-gel film process.^{21,22} In addition, as a promising technology for additive manufacturing of advanced ceramic materials, laser sintering has stimulated significant interest in fundamental research to understand the mechanism of sintering under such extreme processing conditions.²³⁻²⁵ One of the advantages of laser sintering is that it is capable of localized sintering within an ultra-short duration leading to precisely controlled geometries. This makes it an attractive technology to be practically employed in manufacturing industries. Laser sintering also demonstrates great promises in flexibly controlling the microstructure of materials, such as the porosity, by simply tuning the laser-operating parameters.^{26,27} However, there are still limitations in laser sintering of the sol-gel thin films. One of the limitations is small critical thickness. Usually, the critical thickness of the sol-gel-derived thin films is about a few hundred nanometers.²⁸ In most of the previous works, the thickness of the laser densified sol-gel thin films was less than 500 nm.²⁹⁻³² This thin layer limits its application. For example, the common optical devices such as waveguides need to have a thickness larger than the wavelength. Moreover, during the laser processing of sol-gel films, the temperature distribution is essential for understanding the microstructural evolution of materials, as it triggers multiple thermally induced processes such as chemical reactions, sintering, and phase transformations. To better tune the physical and chemical properties of the resultant materials, it is therefore desirable to understand the temperature profile induced by preset laser-operating parameters and relate the microstructures of processed films with calculated temperature profiles.

Silica is a versatile structural and functional material. It is an important optical material which allows doping of a great variety of foreign elements that are optically active. Therefore, laser sintering of silica has been widely applied in applications such as the manufacturing of silica waveguides.²⁹⁻³²

In this study, a CO₂ laser was used to process a sol-gel-derived silica films which were dip-coated on glass substrates. To demonstrate the versatility of this approach to control the microstructure and properties, the laser output power was varied at a fixed scanning speed. The microstructure and shrinkage of the laser-sintered films were measured and compared with the films sintered in a furnace to evaluate the quality of the laser-sintered films. In this paper, we demonstrate that the cracking of the sol-gel films, when the thickness exceeds the critical thickness, can be controlled using laser sintering. Using a finite element model (FEM), the temperature profile of the substrate during laser scanning was calculated and correlated with the dimensions of the laser-sintered tracks. This calculation was also used to fabricate, pre-designed patterned silica films of high density using a galvo scanner.

2 | EXPERIMENTAL PROCEDURES

2.1 | Preparation of silica sols and dip-film

Tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄, 98%, Acros Organics, NJ, USA) and hexamethyldisiloxane (HMDS, O[Si(CH₃)₃]₂, 98.5%, Sigma-Aldrich, MO, USA) were used to prepare the precursor for silica. The composition of the precursor is listed in Table 1. TEOS and HMDS were mixed in ethanol at room temperature inside a glove box under flowing argon. Then, deionized water (DI-water) was added to this solution dropwise by a syringe pump. Nitric acid (HNO₃, 70%, Sigma-Aldrich, MO, USA) was added to adjust the pH of the solution to about 2.0. Subsequently, the solution was hydrolyzed at 70°C for 5 hours under vigorous stirring. The obtained solution was then kept in an oven at 80°C for condensation until viscous sols were obtained. To adjust the viscosity of the sols for dip-coating and prevent crack formation, polyvinylpyrrolidone (PVP, Mw: 1 300 000, Sigma-Aldrich, MO, USA) was dissolved in ethanol with a weight ratio of PVP: ethanol = 1:10, and then mixed with the sols using a high-intensity ultrasonic probe. The amount of added PVP was 50 wt% of the weight of SiO₂ in the sols.

The obtained silica sols were deposited on fused silica substrates (500 µm in thickness) using the dip-coating method. The withdrawal velocity of the substrate in dip-coating was set at 40 mm/min. After dip-coating, the obtained samples were dried at room temperature for laser processing.

2.2 | Laser processing

The schematics of the laser processing systems are shown in Figure 1A. A CO₂ laser (Firestar v20, SYNRAD, WA, USA) with a free space wavelength of 10.6 µm was used to process the sol-gel deposited films. As shown in Figure 1A, ZnSe lens with a focal length of 50 mm was used to focus the CO₂ laser beam into a small spot with a diameter (D) of ~220 µm ($1/e^2$ diameter). A three-axial motorized translation stage was used to position the substrate. The top surface of the substrate was placed at the focal point of the laser beam. During processing, the CO₂ laser was illuminated on the substrate while the translation stage was controlled by the computer to move the substrate at a controlled speed. This setup was used to fabricate the silica tracks due to its relatively low scanning speed. For scanning the complicated pattern, a two-axial galvo scanner (intelliSCAN 14, SCANLAB, Germany) was used to control the scanning beam.

As shown in Figure 1B, the CO₂ laser beam was focused on the top surface of a coated fused silica substrate and scanned along the path from A to B. Starting from 0.1 W, the lowest output power of the laser, samples were sintered at different laser power (P) with a fixed scanning speed (V) of 0.1 mm/s. The laser power density (W), defined as $W = 4P/(\pi D^2)$, was used as the criteria to evaluate the sintering results. After scanning a 10 mm-track on the surface of the silica deposition, the substrate was washed by ethanol in an ultrasonic bath for 5 minutes. Since the silica precursor was ethanol based, the regions without laser processing can be readily removed by ethanol. For reference and comparison, identical films were also sintered in a furnace. Films, obtained using the same dip-coating conditions, were heated to 1100°C at a heating rate of 5°C/min in a furnace and held at 1100°C for 1 hour followed by furnace cooling to the room temperature.

2.3 | Characterization

The microstructures of the samples were characterized using an optical microscope (Olympus BX60, Olympus Corp.) and a scanning electron microscope (SEM, Hitachi S-4800, Hitachi Ltd.). To evaluate the shrinkage, density, and porosity of the silica thin film before and after laser processing, the thickness of the sintered thin films was measured using an atomic force microscope (AFM, Alpha300, Witec Instruments Corp.). Since the densification of the thin film was constrained by the substrate and the thickness of the film is much smaller than its in-plane dimension, it can be assumed that the silica thin film only shrank in the normal direction.³³ Therefore, measuring the thickness before and after sintering is the common method to study the constrained sintering of the thin film. The shrinkage, density, and porosity can be obtained using the thickness data. The shrinkage of the thin film after laser scanning is calculated from the change in the thickness using the following equation (Equation [1]):

$$\text{Shrinkage} = \frac{\text{Thickness (before)} - \text{Thickness (after)}}{\text{Thickness (before)}} \times 100 \% \quad (1)$$

A fully dense thin film is defined as where there is no microstructure difference between the film and substrate under SEM observation. Assuming that the thin films all have the same density before heat treatment, the relative density is calculated based on the percent shrinkage difference between the observed film and fully dense film using the following equation:

$$\text{Relative density} = \frac{1 - \text{Shrinkage of fully dense film}}{1 - \text{Shrinkage of observed film}} \times 100 \% \quad (2)$$

The porosity of the thin film is calculated by the following equation:

$$\text{Porosity} = (1 - \text{relative density}) \times 100 \% \quad (3)$$

2.4 | Numerical modeling

To understand the temperature profile induced by the CO₂ laser on materials, an FEM model was developed for the experimental parameters used. COMSOL Multiphysics Software (COMSOL, Inc., MA, USA) was used for the simulation in this study. Based on the schematic diagram of the laser heating protocol in Figure 1B, a CO₂ laser beam was simulated on the top surface of a fused silica substrate and moved from A to B. Since the thickness of the silica sol-gel deposition is much smaller than the thickness of the substrates, the laser spot size, and the laser wavelength, it was neglected in the simulation. The thermal properties of the fused silica substrate are shown in Table 2. The following conditions are assumed for the modeling of the temperature profile of the substrate:

1. The thermal conductivity (k) of the fused silica, which has a significant effect on the values of the induced temperature, is temperature dependent. For better estimate of the temperature profile, upper and lower bounds of the values of k at different temperatures were used to calculate the temperature profiles. The lower bound is $k_l = 1.38 \text{ W/(m}\cdot\text{K)}$ which is the thermal conductivity at 20°C, and the upper bound is $k_h = 2.1 \text{ W/(m}\cdot\text{K)}$ which is the thermal conductivity at 1100°C³⁴
2. Since the energy distribution of a laser beam is assumed as a Gaussian function, the following function was used to simulate a moving laser beam:

$$H(x, y) = \text{Power} \times g(x - w(t)) \times g(y) \quad (4)$$

where g is the standard Gaussian function with a standard deviation of 55 μm and w is denoted as the position of the laser beam at a certain time. For a Gaussian beam, the Gaussian beam radius (ω_0) is the radius at which the intensity decreases to $1/e^2$ of the peak value. At $2\omega_0$, the intensity is 0.0003 of the peak value, which indicates that at this point, most of the area under the Gaussian curve can be covered. Therefore, in this way, $2\omega_0$ can be assumed as 4σ (99.994% area). In our paper, $\omega_0 = 110 \mu\text{m}$, thus $\sigma = 55 \mu\text{m}$.

1. The laser beam scans for one time from A to B. The length of AB is 10 mm.
2. A point probe was placed on point C, the center of AB, to obtain the temperature values at this point during laser scanning
3. The input power was set at 0.7 W and the scanning speed was fixed at 0.1 mm/s. Therefore, the duration of laser scanning was 100 seconds.
4. The ambient temperature (T_{amb}) is the room temperature (293.15 K)

The heat-transfer equations that were used for the calculation, in this case, are also listed below:

1. Time-dependent heat transfer equation:

$$k \cdot \nabla^2 T = \rho C_p \cdot \frac{\partial T}{\partial t} \quad (5)$$

1. Thermal radiation equation:

$$R = \varepsilon \sigma \cdot (T_{\text{amb}}^4 - T^4) \quad (6)$$

1. Thermal convection equation:

$$q = h_{\text{air}} \cdot (T_{\text{ext}} - T) \quad (7)$$

where T_{ext} represents the external temperature, which is equal to T_{amb} in this case.

3 | RESULTS AND DISCUSSION

3.1 | Effect of laser power on the processing of the sol-gel silica

To quickly confirm whether the deposition was damaged after laser scanning, artificial scratches were made on the deposition using a blade before laser sintering and the laser beam was scanned perpendicularly to the scratches (Figure 2E). If the scratch disappeared after laser scanning, it indicates that the deposition was removed or damaged by the laser at this power level. Table 3 summarizes the features of the laser-sintered samples. When the laser output power was less than 0.4 W, no obvious change was observed on both the substrate and the silica sol-gel film. The tracks, after laser sintering, could be totally dissolved using ethanol washing. As the laser output power increased in the range of 0.5-0.7 W, the silica under the laser tracks was not removed by the laser and the laser-sintered tracks were intact after ethanol washing. When the scanning laser power reached 0.8 W, the edge of the scratch mark faded out at the center of the scanning path (Figure 2F), although no obvious damage to the substrate was observed from the SEM image (Figure 2D). The processed track was not dissolved after ethanol washing. When the power was equal or above 0.9 W, the substrates were deformed by the laser beam, which was observed in the SEM images and the cross-section view of these samples (Figure 2A-C).

The power density of each sample is shown in Table 3. These results suggest that 21 W/mm² can be considered as the damage threshold for the sol-gel-derived fused silica thin film. At this power density, the laser beam can cause the flow of the silica to instantaneously heal the scratches, but not damage the silica substrate. This indicates that the temperature induced by this power density is probably between the sintering temperature of the silica film and the softening point of the substrate. In the range of 0.5-0.7 W, the films were sintered by the laser beam, which should be considered as the effective range of the laser output power for processing this sol-gel silica films used in this study.

3.2 | Microstructure and porosity of the silica tracks after laser scanning

After being processed by the laser power of 0.5, 0.6, and 0.7 W, silica thin films with different microstructures and thicknesses were obtained. Figure 3A-D shows the cross-section SEM images of the silica thin films before (Figure 3A) and after laser scanning. Before sintering, round-shape particles with an average size of about 20 nm were observed. Slit-like boundaries with size of about 1-2 nm were observed between the particles. After scanning the film at the laser power of 0.5 W, the size of the particles decreased to about 10 nm and the gaps between the particles became smaller. When the film was processed at 0.6

W, the microstructure appears sintered. Grains were observed and the boundaries between the grains were blurry. When the power increased to 0.7 W, the interface between the thin film and the substrate vanished.

At the laser power of 0.5 W, the decrease in particle size can be attributed to the elimination of polymer additives in the sol-gel film. But the temperature induced at this power was not enough to densify the film. As power increased, the porosity of the film decreased as the materials started to sinter. At 0.7 W, the disappearance of the interface between the film and the substrate was attributed to full densification of the silica film, which showed the same microstructure as the dense silica substrate.

To measure the thickness after laser processing, the edges of the scratches were scanned using AFM to obtain the difference in height between the center of the surface of silica track and the substrate. Figure 4 shows that the film had a thickness of ~944, ~733, and ~361 nm after being processed at 0.5, 0.6, and 0.7 W, respectively. The shrinkages calculated using Equation (1) for these three samples are shown in Table 4. The shrinkage increased from ~19% to ~68% as the power increased from 0.5 to 0.7 W at a fixed scanning speed. As shown in the microstructure (Figure 3), the films scanned at 0.7 W power sintered to full density. Using this and the film shrinkage, the porosity for films sintered at different laser powers can be estimated. Table 4 shows that as the power increased from 0.5 to 0.7 W at a fixed scanning speed, the porosity could be controlled from ~60% to ~0%. Furthermore, the sample scanned using 0.7 W laser power showed almost the same percent shrinkage as the furnace-treated film (sintered at 1100°C for 1 hour). These results reveal that the porosity of the laser-sintered materials film can be locally controlled by varying the operating parameters (eg, laser power) during laser sintering. With this ability, many properties of materials, such as the dielectric constant, and mechanical performance, can be flexibly controlled.³⁵⁻³⁷ To evaluate the consistency of laser sintering process, the same laser parameters were used to process the samples with different as-deposited thicknesses. As shown in Table 5, when using the same set of laser parameters, similar percent shrinkage at ~68% and porosity at ~0% can be obtained for all the laser-sintered samples. Therefore, the laser sintering process, in this case, showed great repeatability.

3.3 | Control the cracking of the thick silica film by laser sintering

In our previous report, laser sintering technology has shown its advantage in controlling the cracking of the sol-gel-derived thin film even when its thickness is over the critical thickness.³⁸ Figure 5 shows the optical images of the thick silica film (thickness: ~2.2 μm) treated by laser and furnace, respectively. While significant random cracking occurred when the silica film was treated in furnace at 1100°C for 1 hour (Figure 5B), the laser-sintered silica track remained crack-free and smooth (Figure 5A). As the laser can locally treat the materials, the heating area can be well controlled by the laser. When a track was scanned by the laser on the thin film, the cracks was guided to only propagate along the edges of the laser-treated zone. These results indicated that the cracking can be controlled to be a non-damaging factor with laser sintering, even when the thickness of the sol-gel-derived thin film is above its critical crack-free thickness. After laser sintering, the thickness of the track was reduced to ~704 nm when the laser power was 0.7 W, as shown in Figure 6.

3.4 | The temperature profile of laser scanning—the modeling of laser heating

To verify the accuracy of the numerical FEM model, which is a numerical solution technique, a one-dimensional (1-D) heat conduction model was first conducted using the FEM model and compared with the analytical solution. For a time-dependent 1-D heat conduction model with constant surface heat flux as shown in Figure 1A, the analytical equation is solved using Equation (5) as follows³⁹:

$$T(x, t) = \frac{2q_0'' \left(\frac{\alpha t}{\pi}\right)^{1/2}}{k} \exp\left(\frac{-x^2}{4\alpha t}\right) - \frac{q_0'' x}{k} \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha t}}\right) + T_i \quad (8)$$

where q_0'' is the constant surface heat flux, which is the intensity of the laser beam in this case, $\alpha = \frac{k}{\rho C_p}$ is the thermal diffusivity of the materials, and T_i is the initial temperature which equals to 298.15 K (assuming room temperature).

Using the thermal properties of the fused silica for Equation (8), the temperature values along the x axis at different times can be plotted as shown in Figure 7B. When the input constant heat flux was set at 10 W/mm², the calculated results of the FEM model well matched the analytical solution. The results indicate that the FEM model is accurate to predict the temperature profile induced by the laser beam.

This 10 W/mm² heat flux was chosen to mimic the real situation. The real power density in the experiment was 13–18 W/mm², as shown in Table 3. The purpose of the analytical solution was to make sure that FEM modeling gave the correct temperature distribution so that we can trust the FEM modeling.

Figure 8 shows the calculated temperature profiles on the surface of the silica substrate at 50 seconds during laser scanning with a laser power of 0.7 W. Since the scanning speed was slow, the temperature profile at certain moment can maintain a Gaussian distribution. The calculated temperature at the center position (T_c) along the sintered silica track was ~1754°C for $k = 1.38$ W/(m·K), while it was ~1131°C for $k = 2.1$ W/(m·K). Based on the width of the silica track sintered at 0.7 W (Figure 8A), which was ~140 μm, the calculated temperature on the two sides of the sintered track (T_s) can be also evaluated from the model. The calculated T_s was ~1211°C for $k = 1.38$ W/(m·K), while it was ~779°C when k was set at 2.1 W/(m·K).

When the thermal conductivity of the fused silica at the room temperature was used in the simulation, the calculated T_c was more than 600°C higher than the temperature that was used to obtain the fully dense silica thin film in the furnace (1100°C). This temperature of 1754°C is even larger than the typical softening point of the fused silica. However, from the experiment, the silica substrate was not damaged by the laser beam until the laser power reached 0.9 W (Figure 2). So, this calculated temperature at the power of 0.7 W with $k = 1.38$ W/(m·K) should be much higher than the actual temperature on the silica substrate. This apparent anomaly is resolved by noting that the thermal conductivity of the fused silica increases as the temperature increases. With higher thermal conductivity, more energy is needed to further raise the temperature, which will slow down the rise of the temperature

during heating. To obtain a more realistic value of temperature, the thermal conductivity was modified to 2.1 W/(m·K) which is the thermal conductivity of the fused silica at 1100°C. The reason for using this value is because the fully dense silica thin films with similar microstructure and shrinkage ratio can be obtained both at 0.7 W with laser and 1100°C with furnace. Indeed, the calculated T_c was close to 1100°C after this modification. Since the heating rate during laser processing is so high that less than ~1 second was needed to heat certain spot on the substrate from room temperature to the sintering temperature, the thermal conductivity of the silica substrate can be assumed to be constant. To compare the temperature profile induced by the laser with the experimental results as well as to further evaluate the scanning spacing effect of laser beam, the thickness profile across the laser-sintered track was measured by the AFM. As shown in Figure 8B, the thickness variation at the cross section of the track has been obtained after scanning the AFM tip across the track on the surface. Apparently, the thickness profile showed similar Gaussian distribution as the calculated temperature distribution as well as the laser beam profile. This indicated that the sintering of the thin film did depend on the temperature profile induced by the laser beam. In this way, a more realistic temperature profile has been obtained from this FEM model, which matched to the experimental observation of the resultant microstructure.

The thermal conductivity of silica kept changing during laser sintering for two reasons: (a) the intrinsic thermal conductivity of silica is temperature dependent and (b) the porosity of silica also evolved during laser sintering. In our modeling, we found that only when the highest thermal conductivity was assumed (the k of fully dense silica at 1100°C), we can have a good match between modeling and experimental observation. This led to our conclusion that the laser sintering can instantaneously heat the film and caused the sintering. Thus, the effects of thermal conductivity at low temperature and porosity were insignificant. Also, this thermal conductivity modification in the modeling suggested that using the same laser parameters, the induced temperature profile highly depended on the thermal conductivity of the materials. With smaller thermal conductivity, the heat generated by the laser energy will conduct slower within the bulk material so that higher temperature can be locally induced.

3.5 | Patterned silica films fabricated by laser sintering

With the help of the galvo scanner, silica thin films with desired patterns can be obtained. The scanning of the laser beam was designed to follow the pattern line-by-line with a scanning speed between 0.1 mm/s and 2.0 m/s. By controlling the spacing between two scanning lines, the scanning speed and the laser power, the sol-gel deposition can be sintered in a two-dimensional continuous area instead of a single track. Figure 9A shows the silica thin films sintered in the pattern of a “tiger paw.” The power and the scanning speed was set at 0.7 W and 0.1 mm/s, respectively, which were the same parameters under which dense silica track was obtained. The spacing between two scanning lines was set at less than 50 μm according to the FEM model as well as the experimental results to ensure the uniformity of the sintered surface. As seen from the results in Figure 8B,C, a nonuniform surface was obtained by the single scanning. Especially within the width of ~50 μm at the center of the track, the film thickness varied about 80 nm. Therefore, to obtain a uniform surface, the spacing between two scanning lines should kept smaller than 50 μm to overcome the

nonuniformity of the single track. In this way, crack-free dense silica thin films with designed patterns can be realized.

After laser scanning, the samples were also washed by ethanol in an ultrasonic bath for 5 minutes. The film scanned by laser bonds firmly to the substrate, while the rest of areas without laser processing were removed. Under an optical microscope (Figure 9B), no cracks or gaps of adjacent scanning lines were observed on the surface of the sintered films.

To confirm that the thin film was fully sintered, the thickness of this sample was also measured by AFM to evaluate the shrinkage ratio. As shown in Table 6, the films sintered by this 2-D method exhibited similar shrinkage ratio as both the furnace-sintered films and the laser-sintered silica tracks.

4 | CONCLUSION

In this paper, we have demonstrated that at a fixed scanning speed, the porosity of the silica thin films can be flexibly controlled from almost 0% to ~50% by changing the laser output power. Compared with the conventional sintering method, laser sintering technique can not only obtain the fully dense thin film with similar microstructures, but also flexibly manipulate the porosity and microstructures of the sintered bodies locally. In addition, sintering can be accomplished in a very short time. When the thickness of the film exceeded the critical thickness, laser sintering has the advantage of controlling the crack propagation direction to be along the edge of sintered track. This advantage of laser sintering ensured the crack-free tracks. To understand the thermal effect of laser sintering, an FEM was developed and confirmed by the analytical solution to calculate the temperature profile induced by the CO₂ laser. The FEM model shows that laser operating parameters can be mapped to correspond to the temperature profile of the substrates, which provides a good reference for the process control. Moreover, 2-D laser sintering has been realized using the galvo scanner. In this way, sintered silica thin films with designed patterns can be obtained.

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FIGURE 1.

A. Schematic diagram of the laser processing system. B. Schematic diagram of the laser heating process (unit: mm); a coated fused silica substrate is heated by a laser beam which moves from A to B

FIGURE 2.

(A)-(D): SEM images of the cross section of the samples scanned by laser at different power.

A: 1.1 W, B: 1.0 W, C: 0.9 W, D: 0.8 W. (E): Optical image of the surface of the deposition at the scratch before laser scanning. (F) Optical image of the surface of the deposition at the scratch after laser scanning at 0.8 W. All samples are scanned at the speed of 0.1 mm/s.

SEM, scanning electron microscope

FIGURE 3.

(A) SEM image of the sample before laser sintering. (B)-(D) SEM images of the samples scanned by laser at B: 0.5 W, C: 0.6 W, D: 0.7 W. All samples are scanned at the speed of 0.1 mm/s. (E): SEM image of the sample sintered in a furnace at 1100°C for 1 h. SEM, scanning electron microscope

FIGURE 4.

Thickness of the laser-sintered tracks measured by AFM after laser scanning at 0.5, 0.6, and 0.7 W. The thickness of the thin films before sintering is also measured as reference. AFM, atomic force microscope

FIGURE 5.

Optical images of A: the laser-sintered track and B: the furnace treated of the thick film (laser output power: 10 W, scanning speed: 0.1 mm/s, film thickness: $\sim 2.2 \mu\text{m}$)

FIGURE 6.

Thickness of the laser-sintered thick tracks measured by AFM after laser scanning at 0.5 and 0.7 W. The thickness of the films before sintering ($\sim 2.2 \mu\text{m}$) is also measured as reference. AFM, atomic force microscope

FIGURE 7.

A. Schematic diagram of the 1-D heat conduction model. B. The plots of the temperature values along the x axis from 0 to 1 s of the 1-D heat conduction model, calculated by the analytical equation and the FEM model. These two results match excellently.

FIGURE 8.

A. Optical image of the top view of the laser-sintered silica track (laser power: 0.7 W, scanning speed: 0.1 mm/s). B. The thickness profile of the cross section of the laser-sintered silica track obtained by AFM. The temperature profiles of the silica substrate at 50 s during laser scanning calculated with different thermal conductivities (k) C: $k = 2.1$ W/(m·K), D: $k = 1.38$ W/(m·K) (laser power: 0.7 W, scanning speed: 0.1 mm/s). AFM, atomic force microscope

FIGURE 9.

A. Picture of the silica thin films in the pattern of a tiger paw sintered by 2-D laser scanning. A tweezer was used to hold a fragment of silica substrate at the top and light was shone from the side. B. Optical image of the sintered silica films pattern at the scratch

TABLE 1

Silica sol-gel precursor composition

TEOS	HMDS	H ₂ O	Ethanol	HNO ₃ (70%)
0.075 mol	0.0125 mol	0.1 mol	21.0 g	~4 drops

Abbreviations: HMDS, hexamethyldisiloxane; TEOS, tetraethyl orthosilicate

TABLE 2

Thermal properties of fused silica

Name	Symbol	Unit	Value
Heat capacity	C_p	J/(kg·K)	703
Density	ρ	kg/m ³	2203
Emissivity	ϵ	—	0.75
Absorptivity	a	—	96%
Thermal conductivity at 20°C	k_r	W/(m·K)	1.38
Thermal conductivity at 1100°C	k_h	W/(m·K)	2.1

TABLE 3
The characteristics of samples sintered at different laser output power ($v = 0.1 \text{ mm/s}$)

Power (W)	Power density (W/mm ²)	Substrate	The scratch mark on the deposition	Laser-scanned tracks after ethanol washing
0.4	10.5	No damage	Intact	Dissolved
0.5	13.2	No damage	Intact	Intact
0.6	15.7	No damage	Intact	Intact
0.7	18.4	No damage	Intact	Intact
0.8	21.0	No damage	Partially disappeared	Intact
0.9	23.7	Damaged	Partially disappeared	Intact

Shrinkage, relative density, and porosity of the laser-sintered thin films under different laser parameters as well as the furnace-sintered sample

TABLE 4

Laser processing parameters	Before (nm)	After (nm)	Percent shrinkage	Relative density	Porosity
As-deposited	1170	—	0%	≈31%	≈69%
0.5 W, 0.1 mm/s	1170	944	19.3%	≈38%	≈62%
0.6 W, 0.1 mm/s	1170	733	36.7%	≈50%	≈50%
0.7 W, 0.1 mm/s	1160	361	68.8%	≈100%	≈0%
1100°C, 1 h	1160	368	68.2%	≈98%	≈2%

TABLE 5

Microstructure consistency of the silica film using the same laser processing parameters

Laser processing parameters	Before (nm)	After (nm)	Percent shrinkage	Relative density	Porosity
0.7 W, 0.1 mm/s	556	175	68.5%	≈99%	≈1%
0.7 W, 0.1 mm/s	1170	733	68.9%	≈100%	≈0%
0.7 W, 0.1 mm/s	2231	361	68.4%	≈98%	≈2%

TABLE 6

Comparison of the shrinkage ratio of silica thin films sintered in different dimensions

Condition	Before (nm)	After (nm)	Shrinkage ratio	Porosity
Furnace sintered	1160	368	68.2%	~0%
Silica tracks	1160	361	68.8%	~0%
Silica thin film pattern	1160	367	68.3%	~0%