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Large-scale CO_2 laser-based sol-gel annealing of titanium dioxide on borosilicate glass

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Abstract

There are several ways to create optical filters on glass, such as the low-cost sol-gel coating. However, to make this process even more effective and flexible, a laser instead of a conventional furnace process was used to anneal the borosilicate glass samples. In previous studies, it was demonstrated that it is possible to generate similar refractive indices and film thicknesses with a CO_2 laser as with the furnace method. In this study, TiO_2-coated borosilicate glasses are annealed with a CO_2 laser. In particular, the main goal is to scan a large processing area (up to 475 x 468 mm²) and to achieve process speeds comparable to those in the furnace process. Microscopic images show a homogeneous layer and an ellipsometrically determined refractive index comparable to the reference sample from the furnace (laser sample: 2.32; furnace reference: 2.20). With a suitable process setup, it is therefore possible to process glass efficiently on an industrial scale.

Keywords: Laser Annealing, Sol-Gel Coating, Surface Functionalization, Borosilicate Glass, TiO_2

1. Introduction

In addition to vacuum-based processes such as chemical vapor deposition (CVD) or physical vapor deposition (PVD), the less expensive and more flexible sol-gel process is also used to coat glasses. Sol-gel coatings provide some of the same or similar properties (e. g. refractive index) as coatings produced by PVD/CVD [1,2,3]. In this process, the layer is dissolved in the sol-gel in nanometer size. The sol is then deposited on the substrate, where the solvent evaporates and a porous gel network is formed. The coating can be applied, for example, by spin-coating or dip-coating, which is also applied in this work. The resulting gel layer has a very porous, amorphous structure, because it still contains organic residues. These are removed only by pyrolysis at temperatures of 480 °C, which enables the layer network to become more compact. To bring the glass substrate to this necessary temperature, it must be heated slowly via temperature ramps to avoid thermal stresses in the material [4]. However, the furnace process for densification is time consuming and expensive because a furnace that is not fully loaded still requires the same amount of energy to achieve densification. Compared to furnace annealing, the use of a laser makes it possible to process a similarly high throughput of layers with lower energy requirements. Through innovative beam shaping, the throughput can be even higher. In addition, it enables selective and one-sided processing of sol-gel substrates, which is not possible in this way by means of a furnace process. For example, for one-sided coating, the non-coated side would have to be covered by another glass plate in the furnace process.

Depending on the application, different coating materials can be used on glass substrates. Titanium dioxide (TiO_2) is used

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for anti-reflective and photocatalytic coatings. Three different crystal phases exist for this material: Anatase, Rutile, and Brookite, whereby mainly the first two phases are used [5,6]. In this study, the refractive index of the anatase phase is interesting and is about 2.8 [7].

There are several scientific publications dealing with the thermal treatment of sol-gels by laser irradiation. Chung et al [8] and Lin et al [9] could show that it is possible to create the crystalline structure rutile on silicon wafers from amorphous TiO_2 layers using a CO_2 laser. However, these structures were inhomogeneously distributed over the laser processed area [10].

In previous work at the Laser Zentrum Hannover (LZH), it was shown that it is possible to create the same crystalline structure and simultaneously a homogeneous layer formation of TiO_2 sol gel layers with CO_2 lasers [11]. In this work, it will be demonstrated that, in addition to comparable refractive indices and coating thicknesses, laser treatment can also achieve process speeds that are industrially and economically viable compared to furnace treatment.

2. Experimental setup

Fundamentally, within the frame of the investigations presented in this paper, all glass samples are first sol-gel coated at PRINZ OPTICS GmbH and then laser processed at the Laser Zentrum Hannover e. V..

2.1. Sol-Gel application

The TiO_2 layers were prepared by dip-coating on borosilicate glass (Borofloat®, Schott, Germany) at the project partner Prinz Optics (PO) and annealed at 80 °C so that the samples could survive the transport to LZH. The coating speed was 3.5 mm/s, resulting in a reference layer thickness of about 62.5 nm after annealing at 480 °C in the furnace.

2.2. CO_2-Annealing

A CO_2 laser (Cx-10; Coherent, USA), with a wavelength of 10.6 µm and a max. output power of 120 W, is applied for the scanner-based thermal treatment. The power is regulated via the duty cycle (Table 1). In the focal position, the laser spot has a diameter of 330 µm. In order to achieve a more uniform power distribution and to avoid damaging the layer as well as the glass surface, the laser beam is defocused on the layer surface, which increases the diameter to about 830 µm. A galvanometer scanner (TS-30 [C] D1/AS; Raylase, Germany) and a linear translator module (Axialscan 30-C [100BO], Raylase, Germany) allow the laser beam to be scanned on a planar surface over a working field of 500 x 500 mm². However, the processed area was 475 x 468 mm² to reduce the heat generation at the edges of the glass plate and thus minimize the risk of breakage.

Preliminary tests were performed to determine the laser and scanning parameters that would result in a homogeneous layer without cracks or fracture (see Table 1.). The pretempered TiO_2 sol-gel layers were processed with a duty cycle (DC) of 40 % to 60 %.

Table 1. Laser and scanning parameters for selective sol-gel annealing.

Parameter	Symbol	Range
Wavelength	λ	10.6 µm
Frequency	*f*	50 kHz
Beam focus diameter	d	~830 µm
Duty Cycle	DC	40 %; 50 %; 60 %
Scanning speed	v	3500 mm/s
Line overlap	O	97 %
Hatch	H	0.025 mm

2.3. Material characterization

The surfaces of the layers are characterized by an optical microscope (Olympus BX60, MPlan 10x and 5x, Olympus, Japan). Additionally, selected samples are measured with a laser confocal microscope (VK-X1000; Keyence, Japan) to determine the surface topography and layer thickness.

The refractive index and layer thickness will be determined by ellipsometry. Here, linear polarized light is focused on the sample surface at a large angle of incidence. The reflected light experiences an elliptical polarization. This polarization state as well as the absolute value of the amplitude is measured and can be used to calculate the refractive index and the layer thickness via model analyses.

3. Results and discussion

3.1. Large-scale processing by means of a scanner system

The sol-gel layer in Fig. 1 has a homogeneous gold coloration. This gold coloration is typical for TiO_2 layers with a thickness of about 60 nm and indicates a nearly complete removal of the organic residues. Thus, a more uniform heat front could be generated even though the processed area was increased from 25 x 25 mm² to 475 x 468 mm².

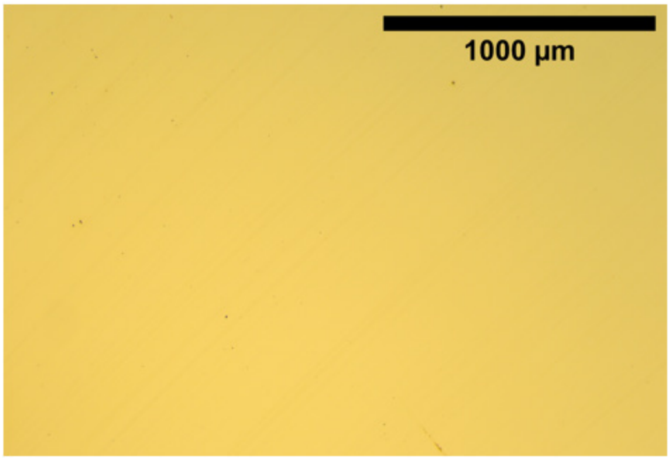

Fig. 1. Optical microscope image of laser annealed TiO_2 sol-gel layer generated with a DC of 40 % and 3500 mm/s scanning speed using a scanner system

The results of the ellipsometric measurements are shown in Fig. 2 and Fig. 3. The glass sample was divided into nine squares and each measured for thickness and refractive index. Fig. 2 shows the layer thickness obtained with the furnace reference sample and with the three laser powers.

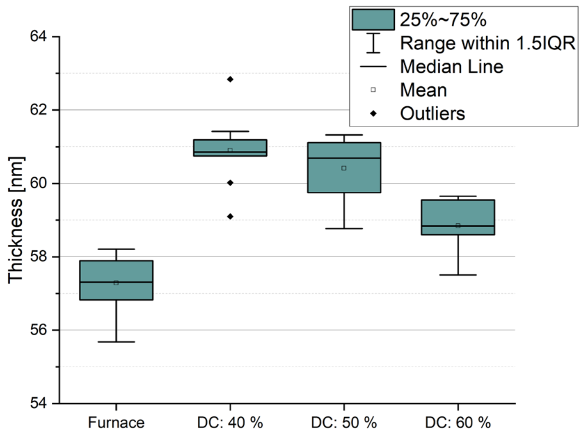

Fig. 2. Boxplot of the ellipsometric measurements of the layer thickness for the three laser powers and the furnace sample.

First, it can be seen that the film thickness is on average 3 nm (DC: 60 %) to 5 nm (DC: 40 %) thicker compared to the furnace annealed sample. The scatter of the values is approximately the same. It is easy to see that the layer thickness decreases with increasing laser power. This is because the higher the power, the higher the annealing temperature, which leads to more compaction of the sol-gel layer. It is important to ensure that the temperature does not exceed the glass transition temperature of approx. 525 °C in order to prevent glass damage.

For processing areas of 25 x 25 mm², layer thicknesses equal to or smaller than the furnace reference sample could already be achieved with laser powers of 40 % and scanning speeds of 3500 mm/s (see Table 2). The sol-gel layer in Table 2 was produced with a pulling speed of 6 mm/s, which resulted in a layer thickness of 66.3 nm after the furnace process.

Table 2. Results of the ellipsometric measurements for laser-tempered surfaces of the size 25 x 25 mm² and the furnace reference sample.

v	DC	Thickness	Refractive index
3500 mm/s	40 %	61.8 nm	2.344
3500 mm/s	50 %	64.4 nm	2.291
3500 mm/s	60 %	64.2 nm	2.328
Furnace		66.3 nm	2.277

Due to longer spatial distances of the individual scan lines for larger areas, the temperature of the heat front in front of the scan line is lower, which decreases the degree of densification. Thus, for large-scale processing a further increase of the laser power should reduce the layer thickness as well.

Fig. 3. shows the refractive index obtained with the furnace reference sample and with the three laser powers. The refractive index of the furnace reference sample is approx. 0.7 % - 2.62 % below the laser-tempered samples. With an increase in laser power, higher refractive indices can be achieved, which means an improvement in coating quality.

Actually, a higher refractive index should correlate with a thinner film thickness, as it can be seen in Table 2. for small areas. We assume that the refractive index varies within the layer, which indicates a gradient for densification. The processing time of the large areas using the scanner system was approx. 4032 s for the 475 x 468 mm² area.

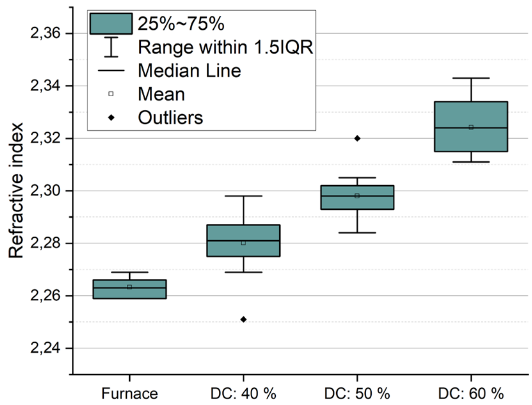

Fig. 3. Boxplot of the ellipsometric measurements of the refractive index for the three laser powers compared to the furnace sample.

3.2. Large-scale processing by means of an axis system

The processing time of the large areas with the scanner system is 4032 s, which is too long to be economical for industrial use. There are several ways to shorten the processing time of the laser based curing. In this work, the scanner system is replaced by a fixed lens and an axis system, on which the glass sample is placed. The inserted cylindrical lens creates a 6 mm long and 2 mm wide elliptical beam cross-section and is moved over the sample at a line spacing of 5 mm and a speed of approx. 62 mm/s. Instead of the Cx-10 laser, the more powerful E250 laser (Coherent, USA) with a DC of 18 % (approx. 130 W) was used. The glass sample was guided through the laser beam in a meandering pattern and a two-second pause was inserted at each turning point to reduce the heat accumulation at the end, which is caused by the deceleration and acceleration events. Due to the larger spot diameter, the processing time of the 475 x 468 mm² area could be reduced by the factor of four to 1000 s. Comparing the optical microscope images of Fig. 1 and Fig. 4, the same desired golden yellow discoloration can be seen.

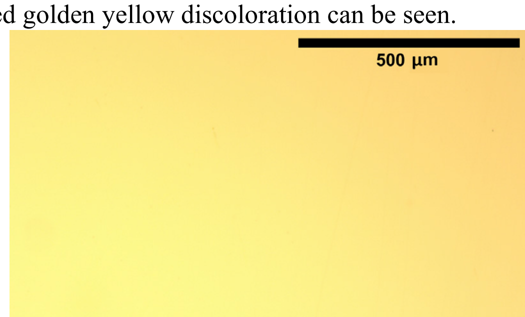

Fig. 4. Optical microscope image of laser annealed TiO_2-Sol-Gel layer generated with a DC of 18 % and 62 mm/s using an axis system

4. Conclusion

It could be demonstrated that laser annealing of TiO_2 sol-gel coatings produces the same or better coating properties with respect to the refractive index compared to furnace annealing. Thus, the laser annealed sample has a refractive index of 2.344 while the furnace annealed sample has a value of 2.277. The layer thickness was also reduced to 61.8 nm by laser annealing (furnace annealing 66.3 nm). A scaling of the laser processing parameters from 25 x 25 mm² to 475 x 468 mm² could be successfully implemented and thus allows the processing of large format glasses. The laser scanner based setup allows a flexible processing (selective and large area) but this is at the loss of the process speed. For an economical industrial implementation with large margins, the processing time could be reduced by the factor of four from 4032 s to 1000 s by using an axis system and adapted beam shaping (elliptical focus).

Acknowledgments

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