Available online at www.sciencedirect.com

ScienceDirect

Procedia CIRP 74 (2018) 386–389

www.elsevier.com/locate/procedia

10th CIRP Conference on Photonic Technologies [LANE 2018]

Functional coatings of sol-gel on glass substrate using CO_2 laser irradiation

K. Wesang[a,]*, P. von Witzendorff[a], A. Hohnholz[a], O. Suttmann[a], S. Kaierle[a], L. Overmeyer[a]

[a]*Laser Zentrum Hannover e.V., Hollerithallee 8, 30419 Hannover, Germany*

* Corresponding author. Tel.: +49 511 2788-284 ; fax: +49 511 2788-0. *E-mail address:* k.wesang@lzh.de

Abstract

Often Glass products achieve their component functionality only by a specific surface finishing, such as coating or patterning. Compared to vacuum based CVD and PVD coating techniques, the equipment for wet-chemical deposition of sol-gels is less expensive. Heat is needed for a chemical reaction to cure gels and form solid functional layers. In this study, sols with titanium and zirconium were applied on glass substrates by dip coating. The investigated layer thicknesses were in the range between 320 nm and 650 nm. The gel layers were annealed with CO_2 laser radiation. Different scanning speeds and laser powers were investigated. Microscope images were used to compare the laser-annealed layers with oven-annealed layers. To conclude, the oven-process can be substituted by laser annealing and additionally enables local patterning. This allows gradient coating solutions for architecture applications.

Keywords: glass; laser annealing sol gel coating; TiO_2 coating; ZrO_2 coating

1. Introduction

Compared to vacuum based CVD and PVD coating techniques, the equipment for wet-chemical deposition of sol-gels is less expensive. A sol is a colloidal dispersed solution which initially forms a liquid wet film, and the particles aggregate as a result of the evaporation of this solvent. After the formation of a network between the particles, the residual solvent dries out of the pore space within a few seconds. Afterwards a thermal treatment or firing process is necessary to enhance the mechanical properties and achieve structural stable coating on the substrate.

There are several formulations for sol-gels which use is depended from their application. Generally, ZrO_2 sol-gel coatings are used as wear-resistant and anti-corrosive layers, while TiO_2 sol-gel coatings are used for photocatalytic, easy-to-clean, and antimicrobial applications. For example, the sol-gel layer has optical interference layers that allow defined reflection and transmission properties. These coatings are in consumer electronics, for example, as additional discs, for televisions, as data display devices, for projection screens and in the field of architecture, or for design objects. In the lighting industry, coatings can apply to cover lamps. Titanium dioxide in crystal structure exists in three phases: rutile, anatase and brookite. In optoelectronic applications the rutile phase and anatase phase of titanium dioxide are necessary.

Often the patented sol-gel laser tempering is preceded by thermal furnace processes. Normally ZrO_2 and TiO_2 have higher melting temperatures, which are above the glass transition temperature of borosilicate glass. But in sol-gel solutions, ZrO_2 and TiO_2 are present as finely divided nanoparticles. Therefore, a lower burn-in temperature is needed than with pure ZrO_2 and TiO_2. This makes sol-gel solutions interesting for the coating of glass. In the conventional furnace annealing, temperatures up to 600°C are required. Depending on the heating rate and the temperature, the different phases of ZrO_2 and TiO_2 are generated.

Laser-based sol-gel curing has also been reported in scientific publications. Typical laser sources are CO_2 lasers, solid-state lasers and excimer lasers.

In the references, Chung at al. [1] and Lin at al. [2] performed studies on TiO_2 sol-gel layers on silicon wafers

10.1016/j.procir.2018.08.153

using a CO_2 laser. In their experiments they used a laser power in the range of 0.5 to 3 W and a defocused mode. They observed that this process lead to the transformation from the amorphous to crystalline phase rutile of TiO_2.

Also excimer lasers have proven to be a tool for laser annealing [3, 4]. In the following study, CO_2 laser annealing with higher average laser power is investigated with the aim to find parameters which are suitable for in-situ sol-gel coating and laser tempering of borosilicate glass without using any furnace.

2. Experimental setup

2.1. Sol-gel

On the on hand sol solutions with the target composition ZrO_2 were applied to borosilicate glass by dip coating. The main factors which influence the thickness of the sol-gel coating are the viscosity and the velocity during the dip coating process. The monolayer thickness of ZrO_2 is about 370 nm. Monolayer system means that the substrate was once dipped in the coating solution and this layer was cured. Monolayers are not meant on the molecular level of atoms.

On the other hand the TiO_2 sol-gel coating which should reduce the fingerprints on glass panes has a monolayer thickness of 320 nm and a triple layer thickness of 650 nm. During firing, the residual organics can escape from the coating, the porosity of the layer decreases, and the layers becomes denser and thus are smaller than compared to the starting coating.

2.2. CO_2 laser

For the laser annealing experiments of the sol-gel coatings a CO_2 laser is used. This CO_2 laser has a wavelength of 10.6 µm and the maximum laser power is 35 W. The laser beam with a focus diameter of approximately 250 µm is focused onto the surface of the glass by a galvanometer scanner. The scanning field is about 300 x 300 mm². By using the graphical user interface, the laser annealed area had a size of 25 x 25 mm². The relation between duty cycle and the laser power is linear. So the duty cycle of a pulse width modulation waveform is the percentage of the high signal period. If the amplitude of the 5 kHz signal is high for 100 µs and low for 100 µs, it has a 50 % duty cycle. If the signal's amplitude is high for 190 µs and low for 10 µs it has a 95 % duty cycle.

Table 1 shows an overview of the experimental laser parameters.

Table 1. Overview of laser parameter

Laser parameter	
Wavelength	10.6 µm
Beam focus diameter	250 µm
Scanning speed	250 - 4000 mm/s
Duty cycle	10 % - 60 %

3. Results and discussion

3.1. Laser annealing of ZrO_2 sol-gel coating

For the sol-gel coatings of ZrO_2 different scanning speeds from 250 mm/s to 4000 mm/s were used. From 2000 mm/s to 4000 mm/s is the process window with a constant frequency of 10 kHz, shown in Table 2. In the range of a duty cycle from 40 % to 60 % no cracks in the coating were visible. So the ZrO_2 coating can be annealed at a high scanning speed of about 4000 mm/s.

Table 2. Duty cycle for annealing ZrO_2 sol-gel

	Scanning speed v	Duty cycle DC		
		1	2	3
A	2000 mm/s	40 %	50 %	60 %
B	3000 mm/s	40 %	50 %	60 %
C	4000 mm/s	40 %	50 %	60 %

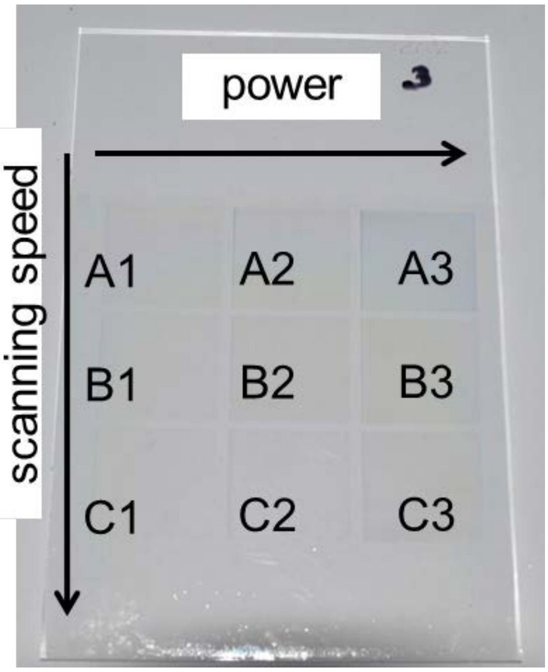

Fig. 1. ZrO_2; Macroscopic image after laser annealing

The microscope images in Fig. 2 show the test areas A2 to C3 for the ZrO_2 coating with a layer thickness of 370 nm. From the column (2) to the column (3), the duty cycle DC was increased stepwise and from the row (A) to the row (C) the scanning speed was increased from 2000 mm/s to 4000 mm/s. After the laser tempering no cracks or damages in the layer or in the glass substrate for the selected range of the duty cycle are visible.

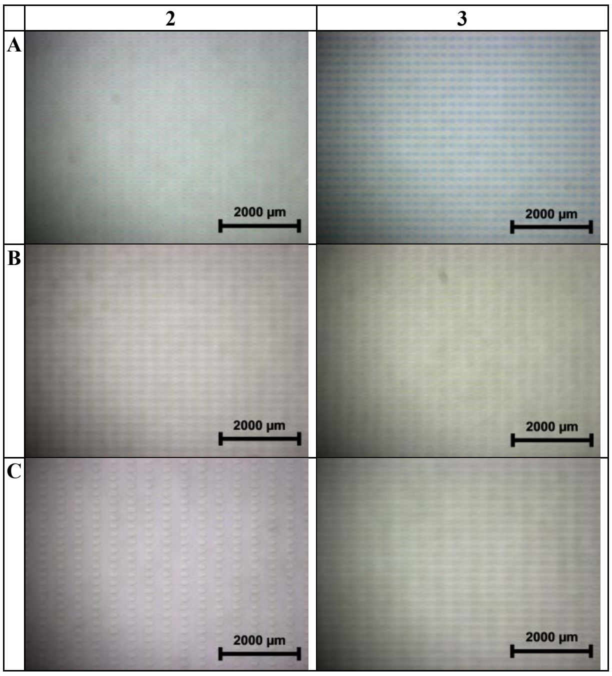

Fig. 2. ZrO_2: Stereomicroscope images after laser annealing

In Fig. 3 the black dots in the diagram are the annealed ZrO_2 sol-gel areas without cracks and the red dots show the undesired cracks of the sol-gel coating.

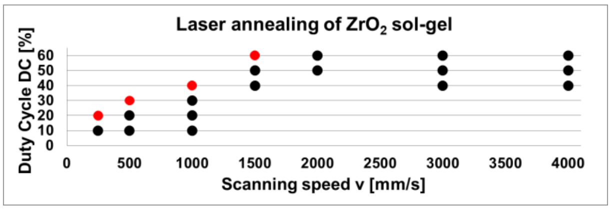

Fig. 3. ZrO_2: Laser annealing process threshold

After laser annealing, no oven annealing is necessary. Observations show that with suitable burn-in parameters, the samples show no changes such as tensions even after a long time. In general, these produced ZrO_2 sol-gel coatings improve the scratch resistance and have a thermocatalytic effect on glass substrates.

3.2. Laser annealing of TiO_2-sol-gel coating

Table 3 gives an overview of the scanning speeds from 250 mm/s to 1000 mm/s which were used to anneal the TiO_2 sol-gel coatings. The laser frequency was constant at a value of 10 kHz. With the duty cycle DC of 10 % to 30 % no cracks in the TiO_2 coating can be observed.

It is observed that the tempering behavior of the ZrO_2 and the TiO_2 sol-gel materials is completely different.

Table 3. Duty cycle for annealing TiO_2 sol-gel

	Scanning speed v	Duty cycle DC		
		1	2	3
A	250 mm/s	10 %	20 %	30 %
B	500 mm/s	10 %	20 %	30 %
C	1000 mm/s	10 %	20 %	30 %

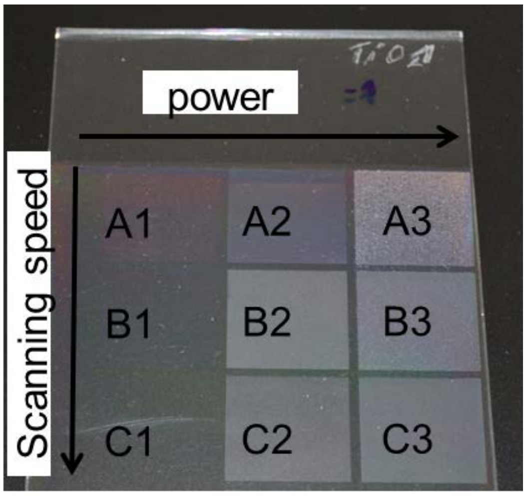

Fig. 4. TiO_2: Macroscopic image after laser annealing

The microscope images in Fig. 5 show the investigated areas A2 to C3 after the thermal treatment with the CO_2 laser of the TiO_2 coating with a layer thickness of 320 nm. From column (2) to the column (3), the duty cycle was increased stepwise and from row (A) the scanning speed to row (C) was increased from 250 mm/s to 1000 mm/s. With a scanning speed of 500 mm/s and a duty cycle of 30 % cracks are clearly visible. While the laser annealed process lead to the rutile phase of TiO_2, the oven tempering process leads to the anatase phase which is measured by X-ray diffraction. It depends on the application which phase is suitable. The rutile phase absorbs UV irradiation and leads to an increase of the scratch resistance of the coating.

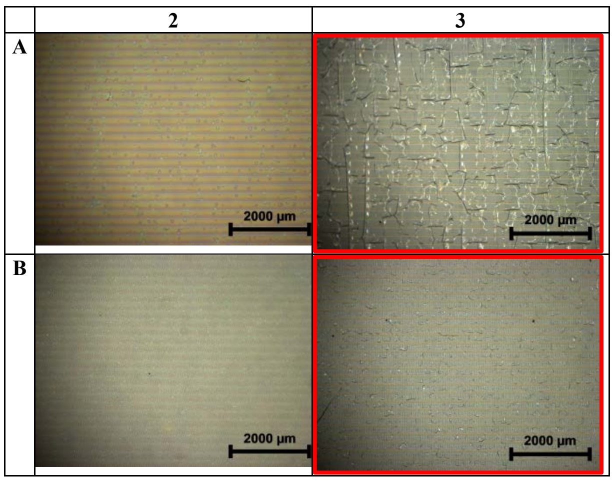

Fig. 5. TiO_2: Stereomicroscope images after laser annealing

However the anatase phase has the effect of photocatalytic activity. So these generated coatings are antibacterial and easy to clean.

In Fig. 6 the blue dots in the diagram are the annealed sol-gel areas of TiO_2 without cracks and in the red dots show the damages of the sol-gel coating.

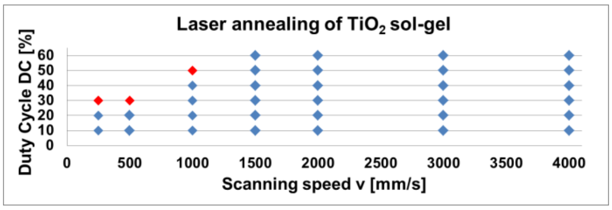

Fig. 6. TiO_2: Laser annealing process threshold

3.3. Selective laser annealing

In Fig. 7, the logo and the rectangle of the TiO_2 sol-gel triple layer with a thickness of 650 nm were cured by the laser to demonstrate the spatial selectivity. This is an advantage in comparison to the oven tempering. A desired discoloration of the layer, which is macroscopically comparable to the oven-annealed sample, was achieved.

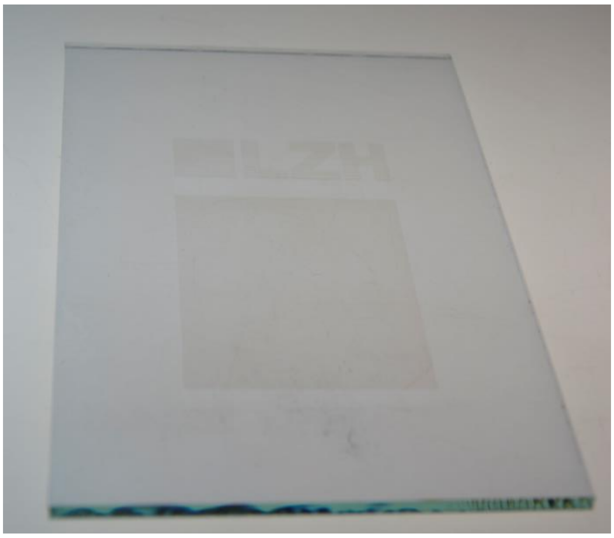

Fig. 7. Selective laser annealed sol-gel coating of TiO_2

Conclusion

With the CO_2 laser, both single-layer and triple-layer sol-gel material systems can be cured on glass substrate. For two different sol-gels TiO_2 and ZrO_2, the laser annealing process was investigated and the laser parameters were determined. The laser parameters have to be adapted on the sol-gel material. Although for both sol-gel coating solutions the same parameters have been set, different process windows were determined. Due to the different chemical compositions, also the observed burn-in behaviors were not equal. No additional post processing such as a heat treatment is necessary to avoid stresses in the glass.

The TiO_2 sol-gel which was annealed in the conventional oven process has the anatase phase and the laser annealed process lead to the rutile phases.

The laser annealing process of TiO_2 sol-gel coatings can be used for photocatalytic, easy-to-clean, and antimicrobial applications.

In further investigations, a temperature-controlled burn-in of sol-gel coatings will take place. There will be detailed investigations about the baking temperatures and also crystallographic measurements. Furthermore, it is pursued to simulate the laser burn-in process thermally.

Acknowledgements

The project “Laser annealing of coatings for the industrial production” with the acronym “LaSiP” has been funded by AIF-IGF 19454 N together with the project partner Fraunhofer ISC.

Author

Kristin Wesang studied Material Science at the Martin-Luther-University Halle-Wittenberg and graduated with diploma in Engineering 2008. Then she worked as a research and development engineer for laser marking of glass for almost 4 years. Since 2013 she has been a member of the glass group at the Production and Systems Department at the Laser Zentrum Hannover e.V. (LZH). Her current research and development focuses on laser processes for glass materials, particularly drilling, cutting, ablation, and laser annealing.

References

[1] Chung, C. K., Chuang, K. P., Cheng, S. Y., Lin, S. L., Hsie, K. Y. “Effect of solution contents on the evolution of microstructure and photoluminescence of laser-annealed rutile TiO_2 thin films”, J. of Alloys and Compounds 574, (2013) p. 83-87

[2] Lin, S. L., Wang, H. Y., Chung, C. K., Chuang S. F. ”The effect of sol-gel composition ratio on phase transformation of titanium dioxide under CO_2 laser annealing”, Proceedings 6th IEEE International, Conference on Nano/Micro (2011)

[3] Berkani, O., Latrous, K., Hamzaoui, H. El, Bouazaoui, M., Capoen, B. “UV laser irradiation –induces crystallization in titania thick film prepared using sol-gel method”, J. of New Technology and Materials Vol. 20, No 02, (2012) p. 13-17

[4] Starbova, K., Yordanova, V., Nihtianova, D., Hintz, W., Tomas, J., Starbov, N. “Excimer laser processing as a tool for photocatalytic design of sol-gel TiO_2 thin films”, Applied Surface Science 254, (2008) p. 4044-4051