Flame coatings by CCVD (Pyrosil) for R2R applications

Flame CVD technology and applications for R2R processes

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Introduction

Modifying and functionalizing surfaces using deposited thin films largely happens in vacuum like physical vapor deposition (PVD) processes, thermal or electron beam evaporation, major chemical vapor deposition (CVD) processes are thermal, low pressure or plasma assisted CVD. Vacuum processes are connected to high costs for the system engineering and operation, especially for continuous large area coatings.

This is why several atmospheric pressure coating techniques are developed and experienced. The deposition under atmospheric pressure conditions is an excellent method for producing cost-effective and large-scale thin films.

An example for such an atmospheric pressure process is the combustion CVD (CCVD) process. A starting material is chemically converted in the flame for a coating. Initial developments were carried out in the 1980's to promote adhesion of metal-polymer composites in the dental technology [1]. Further development at INNOVENT e.V. led to functional layers. Initially, to improve adhesion and to inhibit corrosion, silicon oxide layers (SiO_x) of a few 10 nm's thickness were deposited. The present state of the art allows the deposition of large-area coatings [2, 3] of several meters in width by means of flaming and with it the adjustment of thickness and quality. In addition, the deposition of almost all metal oxides [4, 5], phosphates [5] or even precious metals like gold and silver are possible. An overview of various CCVD processes and resultant displayable thin solid films (typically <500 nm) are shown in [4].

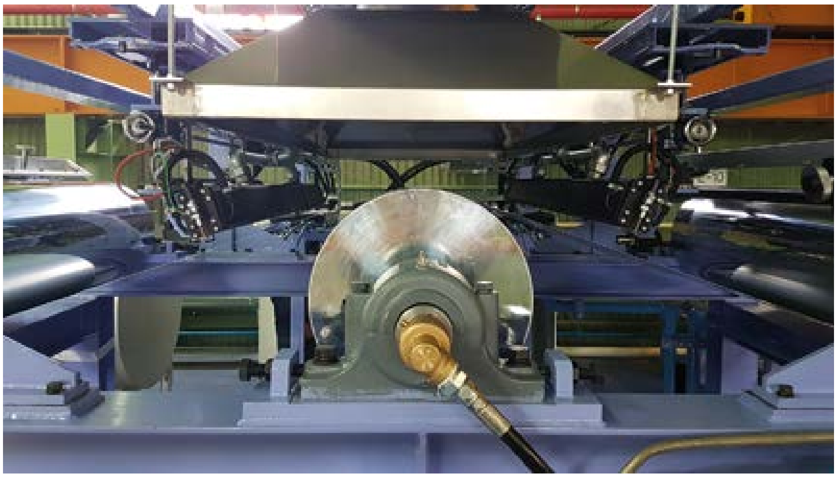

FIGURE 1: **CCVD coating line for steel coils.**

CCVD technology

At the conventional CVD, the film forming gaseous components are introduced into a reaction chamber. These substances are present as a liquid or solid and must be held under low pressure at a high temperature to produce sufficient vapor pressure and the film formation process from the gas phase takes place at high temperatures (400 - 1300 °C) by chemical reactions at or in the immediate vicinity of the hot substrate surface [6].

Using CCVD (**Fig. 1**) these reactions are transferred into the hot area of the flame, which provides the necessary energy. The temperature of flames using propane and air as fuel ranges between 800 °C and 1800 °C [7].

The advantage of flame-based coating methods is the significantly lower facility costs compared to vacuum coating equipment with an equivalent coating performance [8]. The advantages compared to classical CVD [9, 10] are mainly:

- A wide selection and availability of cheap precursor chemicals
- Simple supply or evaporation of the

SUMMARY

Most optical, electrical, mechanical or biological active thin films are deposited using the well known and established vacuum based physical vapor deposition and chemical vapor deposition methods. The deposition of thin functional layers under atmospheric pressure conditions is an attractive alternative for especially large-area coatings like roll to roll applications (R2R). In recent years many different methods have been established for various applications. Particularly the flame-based techniques offer a cost-effective solution.

The basic principles of the flame-based deposition techniques are shown and the technical realization is given by means of selected examples of the current research and developments. The formation of silicone oxide layers with a wide range of properties is investigated in detail. Applications like adhesion promotion, optical effective and barrier layers are reviewed.

 DOI:10.1002/vipr.202200786

precursors by aerosol droplets or vapor
- High deposition rates (in a large range varied by precursor concentration and –mass flow)

Since the development of the CCVD process is based on the deposition of SiO_x (Pyrosil) the conversion of organic siloxanes are used industrial as precursor for the deposition of SiO_2 for decades. The gas-air mixture is premixed using a gas supply unit, where the gas-air ratio is adjusted. Depending on the state of the precursor, different supply is used and fed directly into the burner mixture (**Fig. 2**).

In contrast to other non-vacuum-based methods, the main advantages are: high dynamic deposition rates depending on the precursor and the parameters up to 30 nm/s, large area coatings (up to 2,0 m width), low substrate temperature and a line speed of more than 100 m/min is achievable. This can be realized by varying the process parameters. Cost-effective precursors, readily available and manageable gases as well as economical facility technology allow this method to be used for the large-scale deposition of thin layers under atmospheric pressure conditions with little effort.

Possible substrates are glass, ceramics, metals, synthetics and even textiles.

Application of Pyrosil layers for R2R applications

Adhesion promotion

The first application of the CCVD and the reason for its originally development was the improvement of adhesion on metals and ceramics. The flame pyrolytic deposition of thin SiO_x films (PYROSIL) enriches the surfaces with reactive silanol (Si-OH) groups. The silanol groups are the docking target of adhesion promoter substances (so-called primer) which are sprayed onto the SiO_x film before applying the adhesive or which are already contained in the adhesive. In this way a continuously covalent bonding chain is built up from the substrate to the adhesive polymer (**Fig. 3**).

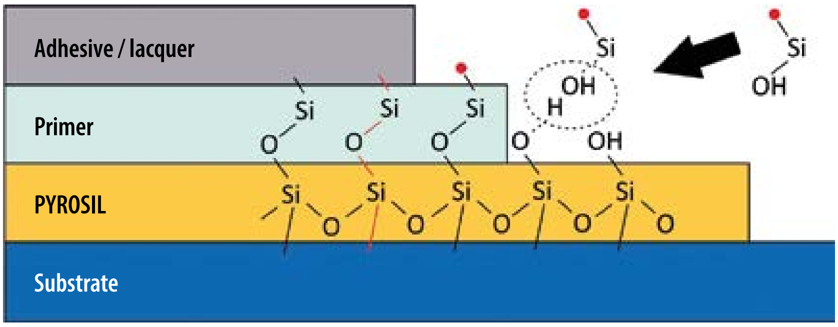

FIGURE 3: **Concept of adhesion for SiO_x films.**

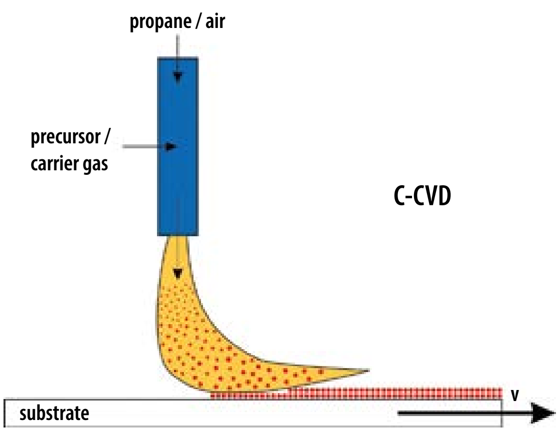

FIGURE 2: **Schematic view of the Pyrosil technology.**

Starting from these originally applications used in dental technology, the range of use has been extended to a wide field. Most of plastics and polymers, but also glass or textiles can be activated with this technique. In many cases the effect of the Pyrosil coating is obvious after performance tests in contrast to other surface activation methods. This is due to the strong chemical bonding formed by this process whereas other activations only build physically acting groups.

Barrier layers

Formation of barrier layers is one of the possible applications of the CCVD process. By using balanced parameters like working distance, precursor concentration, substrate velocity and substrate temperature, it is possible to form a dense and smooth SiO_x film acting as a barrier layer on polymers or glass.

Increasing barrier properties of polymer foils

Polymers like PET or PP are distinguished by a broad spectrum of properties, but the applicability as packaging is reduced by the low barrier effect against gas and flavoring substances due to the macromolecular structure. To reduce this disadvantage, special barrier materials are applied. The reduced oxygen- (OTR) and water vapor transmission rate (WVTR) directly increases the minimum durability of the packed product.

By adjusting the CCVD process, it was possible to deposit SiO_x thin films for barrier applications. Different processing parameters had to be varied in

ZUSAMMENFASSUNG

Flammenbeschichtungen durch CCVD (Pyrosil) für R2R Anwendungen

Die meisten optisch, elektrisch, mechanisch oder biologisch aktiven Schichten werden unter Verwendung der bekannten und etablierten vakuumbasierten physikalischen und chemischen Gasphasenabscheidungsverfahren abgeschieden. Die Abscheidung dünner Funktionsschichten unter Atmosphärendruckbedingungen ist eine attraktive Alternative besonders für großflächige Beschichtungen wie Rolle zu Rolle-Anwendungen (R2R). In den letzten Jahren haben sich viele verschiedene Verfahren für verschiedene Anwendungen etabliert. Besonders die flammenbasierten Techniken bieten eine kostengünstige Lösung.
Anhand ausgewählter Beispiele aus aktueller Forschung und Entwicklung werden die Grundprinzipien der flammenbasierten Abscheidetechniken aufgezeigt und die technische Umsetzung gegeben. Die Bildung von Siliziumoxidschichten mit unterschiedlichsten Eigenschaften wird detailliert dargestellt. Anwendungen wie die Haftvermittlung, Antireflex- und Barriereschichten werden vorgestellt.

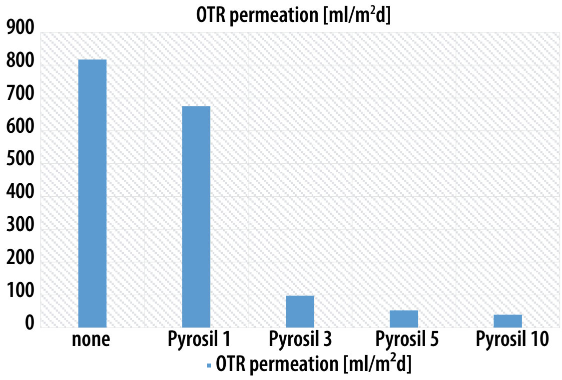

FIGURE 4: OTR values for CCVD barrier coatings on BOPP.

order to not damage the thin (12 µm) foils. The purpose was a significant improved barrier effect against oxygen (OTR) and water vapor (WVTR). The values of OTR for BOPP by using different coating parameters are provided in **Fig. 4.**

Another example is the barrier coating of PET foils. The initial OTR value of the untreated PET foil is around 110 $cm^3/(m^2 \cdot day \cdot bar)$. Even a 10 nm thin SiO_x film improves the OTR value to < 2 $cm^3(m^2 \cdot day \cdot bar)$. Increasing the film thickness to around 20 nm further reduces the OTR to 0.3 $cm^3(m^2 \cdot day \cdot bar)$. The water vapor barrier properties are increased by adjusting the process parameters. The WVTR values of samples with a thickness of up to 15 nm are around the untreated PET foil. For film thicknesses of 20 nm the WVTR is reduced to 1.5 $g/(m^2 \cdot day)$.

Corrosion protection

An additional application of the thin SiO_x coatings is the corrosion protection. Here the combination of the adhesion promotion of the SiO_x layers and barrier properties of the layer forms an excellent corrosion protection for semifinished products like painted steel coils. An example for such an application is shown in **Fig. 1**. The thickness of the applied SiO_x thin film is in the order of 30 nm and thus not visible.

Antireflective coatings

The CCVD process provides a simple but economical alternative coating for enhancing the light transmission of transparent substrates by a broad-band reducing of the surface reflection.

By controlling the above mentioned process parameters, it is possible to adjust the effective refractive index of the SiO_x film matching to the substrate index, e.g. for float glass, acrylic glass (PMMA) or polycarbonate.

On standard float glass the light reflection can be reduced from 8% to 3%. Applied on both sides this yields a transmission increase from 91% up to 95%. The long term stability of these pyrolytic coatings on float glass was verified according to DIN EN 1096-2, Class A. Because of the hydrophilic effect of the SiO_x coating, the flamed panes also exhibit a lower tendency to pollute. These two effects together demonstrate the potential of the CCVD for photovoltaic applications. (**Fig. 5**).

Outlook

Antibacterial coatings and transparent conducting oxides are focus of future developments. The selection of possible chemicals is enormous and ranges from liquid chemicals to solids and even nanoparticles can be used. Liquid chemicals with sufficient vapor pressure can be introduced as gas, solid chemicals have to be dissolved in appropriate solvents and can be introduced as aerosol mist and solid nanoparticle suspensions also can be used as an aerosol. As a versatile method, flame pyrolysis allows the deposition of thin layers under atmospheric pressure conditions for several applications.

Acknowledgements

The authors thank the colleagues at INNOVENT and SURA Instruments who were incorporated in the different projects for their work and support.

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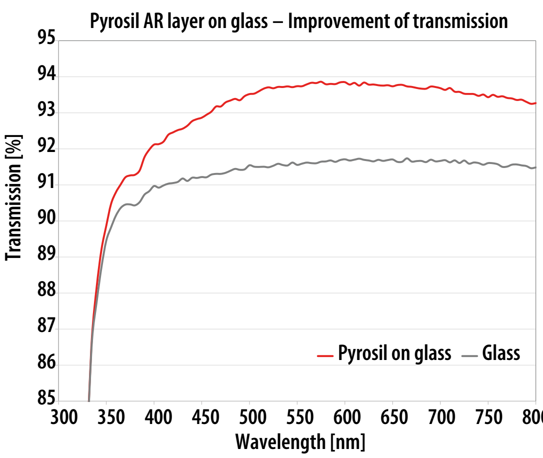

FIGURE 5: Antireflective properties of SiO_x CCVD layers on white float glass.

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