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## ADDITIVE INKJET PATTERNING OF SEMICONDUCTING AND UV-ABSORBING LAYER STACKS

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Material printing has been successfully employed for the deposition of a great variety of functional materials forming thin layers, various patterns 2D (arrays, gaps, sandwich) and even 3D structures. Authors affiliated to Brno University of Technology have previously reported [1] the deposition of conventional titania sol-gel formulations based on tetraisopropoxy titanate and acetylacetone by a modified office inkjet printer equipped with piezoelectric print head (Epson R220). In this way they were able to prepare thin layers of TiO<sub>2</sub> with excellent optical properties and photocatalytic performance. Thick multilayer coatings were printed with the help of poly(ethylene glycol) acting as viscosity modifying, templating and anticracking agent [2]. These papers inspired further cooperation of Brno and Prague teams resulting into a new project focusing onto the development of inkjet direct patternable titania coatings based on the Prague team's original sol-gel reverse micelles dip-coated composition [3]. Separate original research articles giving detailed information on the sol development, optimization the photoexcitation properties of the TiO<sub>2</sub> printed layers [4] as well as on its photocatalytic activity [5] have been published recently.

During this experimental work, the direct patterning method performed by piezoelectric inkjet printing proved to be an attractive method for depositing liquid formulations onto solid supports. It provides clean, efficient and highly repeatable way of coating. Moreover, it is easy to up-scale to coat large substrates by means of industrial large-format printers and at the same time it brings the possibility to produce 2D patterns with micrometer accuracy. These features make direct inkjet patterning one of the prominent deposition techniques for the quickly expanding field of printed electronics.

Moreover, the micellarly templated titania layer consistently delivered highly predictable and repeatable performance, making it well suited for employment in sensing applications. The general concept of one such application is presented in Petr Klusoň's paper included in this proceedings as well. Since this concept relies the control of titania layers photoelectric conversion efficiency, a technical solution for this control needed to be developed. In this paper and corresponding lecture, we present a general technological outline of several possible solutions to this task.

The discussed photochemical devices were fabricated in an innovative way utilizing a specialized experimental printer FUJIFILM Dimatix (Dimatix Materials Printer DMP-2831). Commercial ITO coated glass plates (5–15 ohm, 50 ×12.7 ×1.1 mm, Delta-Technologies Ltd., USA.) were used as substrates. Prior to printing, the plates were washed in deionized water, then in isopropanol and quickly dried in nitrogen blow.

An in-house developed reverse micelle sol formulation (see [4] for details) was used for titania patterning. Prepared sol was sonicated for 5 minutes and then loaded into a syringe. A 0.2 um membrane filter (Pall Corporation, USA) and a blunt needle were attached to the syringe luer port and the sol was filtered and filled into the Dimatix ink tank in once. A Dimatix 10 pL printing head was attached to the tank and mounted into the Dimatix printer. A simple rectangular pattern 8x12 mm was printed onto the ITO glass plates. Printed substrates were gelled and dried at 110 °C for 30 minutes and calcined in air for 4 hours at 450 °C. The

resulting layers are smooth, glossy, clear and transparent, with a slight color tint originating from light interference. SEM imaging revealed the characteristic even porous structure free of defects. SEM cross-sectional images were also used to determine the layer thickness which is appr. 110 nm per single layer. AFM imaging revealed the globular structure originating from the micellar nature of sol. It is evident that the printed and calcined layer maintained the imprints of individual micelles very well. On the other hand, the globular surface topology is extremely regular with minimal vertical deviations and therefore contributes to the very high smoothness of the printed layer. Raman spectroscopy and XRD was used to study the phase structure and pure anatase phase was found in all printed samples, details are discussed in [5].

In order to control the IPCE of the resulting TiO<sub>2</sub> layer, it is necessary to overprint it by a top attenuating layer acting as UV-cut filter. This relatively easy and straightforward task can be accomplished by employing various materials and pattern designs. Nevertheless, several key aspects influence or even restrict the choice and needed to be respected in order to deliver optimum functionality:

- Numerous conventional UV screens and filters compositions are readily available. However, in order to pattern them directly, they must comply with quite narrow viscosity limits of the used printhead.
- While some of these commercial UV absorbers come as true analytical solutions, many of them are in the colloidal form. If solid particles are present in the printing formulation, their diameter must be well below (preferably by two orders of magnitude) the print head nozzle diameter (50–20 μm typically) and their aggregation must be prevented.
- Surface tension plays a key role in the drop-formation process. Moreover, the polar and disperse components need to match the properties of printed substrate. Poor wetting will result into banding artifacts formation while too enhanced wetting will limit the printing resolution due to significant dot-gain.
- Solvent mixture needs to be carefully designed to prevent premature drying in the printhead resulting into nozzle clogging. However, reasonably rapid evaporation off the substrate is necessary to avoid prolonged drying.
- Patterned UV-cut filter is in an intimate contact with the bottom titania layer and is therefore the subject of its inherent photoinduced catalytical activity. Therefore there is a very strict demand for the filter layer stability and degradation resistance.
- Visual transparency is preferred with respect to the suggested application of this device.

These to much extend contradicting requirements prohibitively limited the material choice for the top UV attenuating layer. Therefore a third party became involved in our project. Centre for Organic Chemistry Ltd. supplied some of their specialty products, namely the COSOL E (polymeric UV absorber, [6]) and S6492 (acrylate film forming agent). These materials proved highly potent and useful for the formulation of printable UV-cut filter enabling the fabrication of first prototype series and yielding a solid proof of concept functionality.

## References

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