Inkjet printing of tungsten sol-gel ink

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Abstract: *Tungsten (VI) oxide – WO_3 is one of the widely studied inorganic semiconductors with outstanding chromogenic properties. Its unique optical and electrical properties enable application in energy efficient systems (e.g. smart windows), sensors, displays, storage units, electric and photo catalysts and solar cells. The WO_3 layers are mostly made by expensive vacuum sputtering (PVD), chemical vapour deposition (CVD) and electro-deposition, but it is also possible to deposit layers from sol-gel solutions using dip-coating or spin-coating. On the other hand printing of the WO_3 layers is unexplored area, although enabling flexibility of the substrates, patterning, multi-layer deposition and R2R mass production favouring low cost of the final devices. According to our knowledge this is the first report showing the feasibility of inkjet printing of tungsten sols.*

Keywords: *inkjet printing, peroxopolytungstic sol, WO_3, chromism*

1 Introduction

Tungsten (VI) oxide – WO_3 is identified as one of the most efficient inorganic electrochromic material. It has excellent electrochromic properties in the visible and infrared part of the spectrum and enables high optical modulation at relatively low price. It can be used as a buffer layer or p-/n-type semiconductor, therefore applicable in a range of different applications like sensors, displays, storage units, electric and photo catalysts and solar cells etc [1]–[5].

WO_3 layers are mostly made by RF vacuum sputtering, chemical vapor deposition (CVD), electrodeposition or coating of suspensions or solutions made by sol-gel processing (e. g. dip-coating and spin-coating) [1]. Coating techniques are limited in control of deposition, multi-layered structures and patterning. Today electronic systems production dictates cheaper and adoptable mass production. Due to increasing market demands of consumer electronics at low cost conventional and digital printing techniques are gaining importance. Nowadays inkjet printing is one of the most promising technique as it enables precise and contact-less transfer, the use of many materials, sampling and selective multi-layer construction [6]. Nevertheless the inkjet printing requires precise development of the solutions/inks for the particular substrate as well as precise adaptation of printing settings to avoid defects in printouts such as inhomogeneous film formation, formation of cracks, irregular deformed lines and other defects (e.g. coffee ring, fishbone effect etc.) [7]–[8]. Regarding the solution/ink properties the viscosity, surface tension, and evaporation rate of the ink should be carefully adjusted taking into account also printing settings such as voltage, the shape of pulse, substrate and ink temperature, size and speed of ink drops, etc. [9]. The viscosity, surface tension and evaporation rate of the ink can be controlled by combining solvents, as recently reported by Chouiki and Schoeftner [10]. Optimal ink for Drop on Demand – DOD inkjet system should have the viscosity around 0.01 Pas (0.002–0.03 Pas) and the surface tension around 30 mN/m [11]. Furthermore, the viscosity needs to be high enough to allow the smooth delivery of the ink between the printer head and the cartridge, while the surface tension of the ink plays an important role on the interaction between the printer nozzle and ink, as well as on the spreading of drops over the substrate surface. Ideally, the surface tension must be high enough to be held in the nozzle without dripping and low enough to allow the droplet spreading over the substrate surface to form a continuous film [12]. It is important to mention that homogeneity of printouts depends also on drop formation mechanism which is influenced by fluid and surface properties.

Drop dynamics and the interaction between droplet and substrate surface are of great importance when deposition techniques such as spraying or inkjet printing are used. Various dynamic phenomena are observed during drop formation such as splashing, spreading, receding, bouncing and crown formation [13]. Printability of the inks, drop dynamics and film formation can be predicted with various computational simulations using different theoretical models [14]–[17]. The printability of the ink could be assessed with the Z number $(Z = \sqrt{d \cdot \sigma \cdot \delta}/\eta)$, where d is the diameter of nozzle, σ is the surface tension, δ is the density and η is the viscosity of printable liquid. Some theories predict a stable drop formation when $Z > 2$ [18] while others determined that a printable fluid should have a Z value between 1 and 10 [19]. The lower limit is governed by the viscosity of fluid and its printing ability, while upper limit is determined by the point at which multiple drops are formed instead of single droplet [17].

Printing of functional sol-gel materials is a new and underexplored area of research. Inkjet printing of sol-gel functional materials is very complex and in addition to fine tuning of rheological properties of the solutions, there is a necessity to control the gelation of sols and interactions between different materials. There are some reports describing inkjet printing of inorganic layers (e.g. SiO_2, ZnO, TiO_2, V_2O_5 etc.) which were used as transparent electrically conductive and dielectric substrates, components for photoactive layers, layers for chromogenic systems and sensors [6], [10][12][18]. According to our knowledge the only relevant publication [20] referring printing of WO_3 material describes inkjet printing of suspensions based on TiO_2 and WO_3 nanopowders with different solvents and additives.

In this contribution we focus on inkjet printing of sol-gel derived tungsten solution on glass substrate. Our major challenge in applying inkjet printing technique for the deposition of functional tungsten solution material was the formulation of ink with suitable viscosity and surface tension. The peroxo sol-gel synthesis [21] was used to prepare the peroxo polytungstic acidic sols which were then further modified with different solvents in order to obtain suitable jetting solution. Furthermore, we characterize the rheological and physicochemical properties of WO_3 sols and the morphology and the quality of the transparent WO_3 printouts.

2 Experimental

2.1 Preparation of WO_3 sol

Firstly, we synthesized peroxo-tungsten acid (PTA) by reacting 5 g of tungsten monocrystalline powder (99.9 %, Aldrich) and 20 ml of hydrogen peroxide (30 %, Belinka). The sol was prepared by heating the PTA solution to 120 °C and during stirring a solvent was added. We prepared two WO_3 sols based on two different solvents, namely isopropanol (puriss, Sigma-Aldrich) and mixture of isopropanol and 2-propoxy ethanol (puriss, Sigma-Aldrich). Sols are named as WO_3-1 for WO_3 sol based on isopropanol and as WO_3-2 for WO_3 sol based on a mixture of isopropanol and 2-propoxy ethanol. Prepared sols were orange and contained 5 g of tungsten powder in 30 ml of WO_3 sol.

2.2 Inkjet printing of WO_3 layers

Glass substrates were cleaned with 2 vol. % Mucasol (Sigma Aldrich) aqueous solution, distilled water and isopropanol or with a mixture of isopropanol and 2-propoxy ethanol. Inkjet printing was performed using a piezoelectric Dimatix Materials Printer Series 2800 (Fujifilm Dimatix Inc.) equipped with silicon print head cartridges having 16 nozzles, each with a nominal drop volume of 10 pL. We varied different printing settings, such as substrate and solution temperature, jetting voltage, printing frequency, drop spacing and cartridge angle.

2.3 Characterization

The viscosity of the WO_3 sols was measured at 20 °C using Vibro Viscosimeter model SV-1A. Contact angles, surface tension and surface energy measurements of substrates were carried out using a Krüss DSA 100 goniometer measured by static sessile drop method. The surface free energy was calculated from the measured contact angles of distilled water, diiodomethane and formamide using the Owens-Wendt model. Surface tension of the WO_3 sols was determined with stalagmometric method. Quality and morphology of WO_3 layers was monitored with digital optical camera (Digi 2.0 Micro Scale) and scanning electron microscope (JSM 6060-LV, JEOL). Moreover, image analysis (ImageJ tools) was applied to follow the shape and size of droplets printed at voltages from 10−40 V using different formulations of WO_3 sols on glass substrate.

3 Results and discussion

Standard WO_3 sols prepared via peroxo route are based on highly volatile ethanol [21] which has the viscosity of 6.1 mPas and surface tension of 27.2 mN/m at 20 °C. A high evaporation rate of ethanol results in clogged nozzles causing defects on layers like inhomogeneity, coffee ring, fishbone effect etc [7]. Therefore we modified the synthesis of the WO3 sol by replacing ethanol with isopropanol (sol WO_3-1) and mixture of isopropanol and 2-propoxy ethanol (sol WO_3-2). The result was higher viscosity of the sols and more suitable surface tension, while the addition of 2-propoxy ethanol, as a solvent with higher boiling point (b. p. 150−150 °C; [23]) slows down the evaporation, for details see Table 1.

Table 1: Density, viscosity, surface tension and Z number of WO_3 sols at 20 °C

WO_3 sols	Density (g/cm^3)	Viscosity (mPas)	Surface tension (mN/m)	Z number (/)
WO_3-1	1.054	8.41	22.1	2.566
WO_3-2	1.124	11.1	25.5	2.157

The surface tension of the substrate has to be 10 mN/m higher than the surface tension of the printable liquid to achieve good wetting. Diodomethane, distilled water and formamide were used as test liquids to determine the surface tension of glass substrate. The results of surface tension measurement reveal that the surface free energy of glass substrate is 63.1 mN/m, which is still 30 mN/m higher when compared to the surface tension of the sols. Results disclose that the surface tension of substrates and solution are not perfectly matched. Further improvements like surface cleaning and treatment of substrates or modifications of solution are needed to further optimize the printing process.

Dynamics of droplets and formation of printed film can be predicted by theoretical models as described in the introduction part. To determine the printability of WO3 sols, the calculations of Z number $(Z = \sqrt{d \cdot \sigma \cdot \delta}/\eta)$ was made. Firstly, we determined the velocity of sols (v) droplets at different voltages using Dimatix Drop Watcher set-up. The results are shown in Figure 1. As expected, printing velocity increases with increasing the voltage.

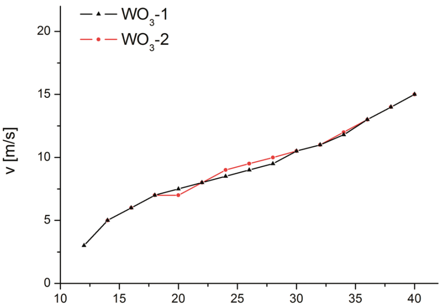


Figure 1: The velocity of WO_3 sols vs. applied voltage

The printability of the ink was assessed with the Z number. In our study the Z values were around 2 for WO_3 sols, respectively (Table 1). Therefore, regardless of the differences in the theories we presume good printability of the WO_3 sols.

We have analysed printed WO_3 droplets deposited on glass substrate at different voltages with digital optical camera, SEM and image analysis. Image analysis of printed WO_3 droplets using two different WO_3 sols on glass substrates while applying different voltage was made. The results are presented in Figure 2 and 3 showing that WO_3-2 sol illustrates better droplet interaction with glass substrate and minor defects. Results also show the impact of increasing printing voltages to the shape and size of droplets. The droplets area is 0.11 mm^2 and goes up to 0.23 mm^2 applying 19 V and 40 V, respectively.

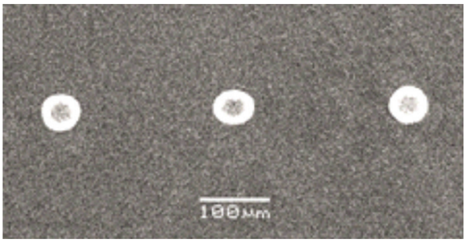
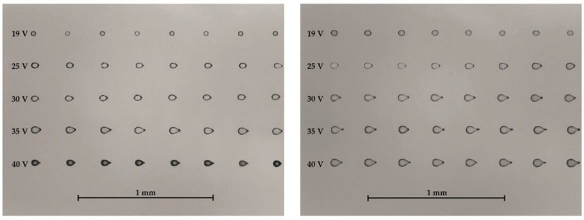


Figure 2: SEM image of WO_3 droplets (sol WO_3-2) on glass substrate printed at 19 V

Figure 3 shows SEM image of WO_3 droplets using sol WO_3-2 sol on glass substrate printed at 19 V. The image indicates a minor deformation of droplets in shape and size. The estimated diameters of droplets printed using WO_3-2 sol are around 0.08 mm.



WO$_3$-1 WO$_3$-2

Figure 3: Optical images of dried WO3 droplets printed on glass at voltages of 19–40 V using WO_3-1 and WO_3-2 inks

Nevertheless while printing WO_3 sols we were faced with various problems (e.g. misdirected nozzles, non-jetting nozzles, non-matched velocities etc), which were related to improper rheological and physicochemical properties of the WO_3 sols. The improper printing settings (e.g. voltage, frequency, drop spacing and temperature) and inappropriate properties of the WO_3 sol (e.g. viscosity and surface tension) resulted in different defects of printouts such as fishbone defect and inhomogeneous layer formation (Figure 4). An example of transparent WO_3 printout that does not show optical defects is shown in Figure 5.

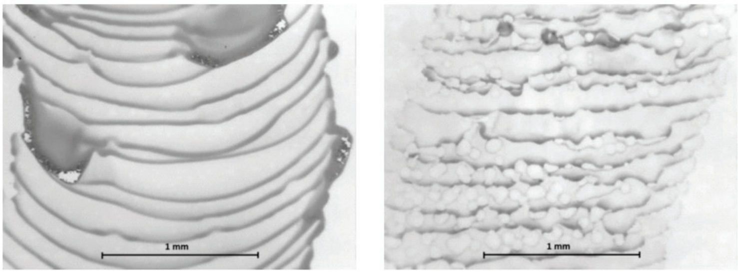


Figure 4: Defects in inkjet printing of WO_3 sol; fishbone (left) and inhomogenous layer (right

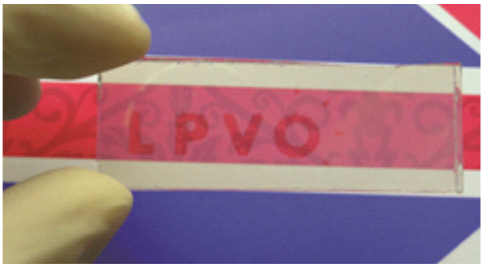


Figure 5: Inkjet transparent WO_3 printout

4 Conclusions

The results show that it is possible to realize transparent WO_3 layers free of optical defects with ink-jet printing using sol-gel derived WO_3 solution. The rheological and physicochemical properties of WO_3 sols can be adjusted for inkjet printing. In general, the results of this study open a new way for WO_3 layer manufacturing and could significantly utilize future development of chromogenic as well as other optoelectronic device.

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