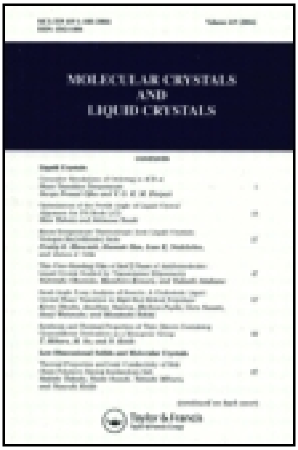

Molecular Crystals and Liquid Crystals

Transparent Conducting Coatings made by Chemical Nanotechnology Processes

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Version of record first published: 18 Oct 2010

To cite this article: M. A. Aegerter*, N. Al-Dahoudi, A. Solieman, H. Kavak & P. Oliveira (2004): Transparent Conducting Coatings made by Chemical Nanotechnology Processes, Molecular Crystals and Liquid Crystals, 417:1, 105-114

To link to this article: http://dx.doi.org/10.1080/15421400490478894

Mol. Cryst. Liq. Cryst., Vol. 417, pp. 105/[589]–114/[598], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478894

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TRANSPARENT CONDUCTING COATINGS MADE BY CHEMICAL NANOTECHNOLOGY PROCESSES

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Colloidal solutions containing fully redispersed crystalline In_2O_3*:Sn (ITO) nanoparticles with an average size up to 30 nm and adequate organic binders (e.g. hydrolysable silanes) offer new possibilities to coat substrates with a transparent or antiglare conducting layer by different wet chemical coating techniques. The layers can be fully processed by UV light irradiation at low temperature (<130°C). The process allows to coat any types of transparent substrates which cannot withstand high temperature such as plastics (tested with PC, PE, PMMA, PVC) and preformed glass substrates. The resistivity of these coatings is* $5 \times 10^{-2}\,\Omega$*cm and comparable to that of commercial organic conducting polymers. Sheet resistance as low as* $800\,\Omega_\square$ *and transparency in the visible range higher than 85% have been obtained for 600 nm thick single layers. The mechanical properties of these coatings is also reported. The coatings can be easily patterned at room temperature by soft photolithography technique.*

1. INTRODUCTION

Transparent conducting oxide (TCO) coatings are today essential components in numerous applications when a high transmission is required in combination with a high electrical conductivity. Such coatings are therefore used as electrodes in photoelectronic devices, as IR reflecting or heatable layers, for electromagnetic shielding, for dissipating static, etc. [1,2].

Wide band gap ($Eg \geq 3$ eV) n-type semiconductors such as tin doped indium oxide (ITO), antimony doped tin oxide (ATO) or aluminium doped zinc oxide (AZO) are among the most important and often used TCO materials. Such coatings are usually deposited by PVD (Physical Vapor Deposition) or CVD (Chemical Vapor Deposition) techniques [2,3]. These technologies

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*Corresponding author. Tel.: + 49-681-9300-317, Fax: + 49-681-9300-249, E-mail: aegerter@inm-gmbh.de are rather costly but produce the lowest sheet resistance, the ratio of the specific resistivity to the thickness of the coating, of typically $10\,\Omega_{\square}$ and adequate optical properties.

Wet-chemical processing of TCO films is a low cost alternative especially if a low sheet resistance is not of prime importance. The most frequently used is the sol-gel processing [4], which is based on the hydrolysis of soluble metal precursors in solution of organic solvents like alcohols. The gel film deposited has however to be converted to an oxide film by subsequent drying and heat treatment steps at relatively high temperature. A similar approach is followed by metal-organic deposition (MOD) where the oxide film is formed by thermolysis of the dried precursor film. These two processes require therefore heat treatment steps at a temperature ranging from 400°C up to 1000°C to obtain good electrical, optical and mechanical properties [4]. Moreover these techniques do not allow to deposit thick layers and a low sheet resistance can only be obtained with multilayers coatings, i.e. by repeating the whole coating procedure, a process not well adapted for industrial application. These techniques are therefore not adequate to coat heat sensible substrates like plastics and also preshaped glass devices.

A new route has recently been proposed by us and successfully worked out for many heat sensible substrates. It is based on the development of hybrid organic-inorganic sols containing the highest possible amount of already conducting crystalline oxide ITO nanoparticles [5,6]. The major advantages of this technique are the separation of the crystallization step of the TCO material from the process of film formation on the one hand and the redispersability of the obtained nanoparticles in a variety of lacquer composition on the other hand. This offers the possibility of curing layers either by a low temperature thermal treatment (<130°C) or by UV light irradiation by using polymerisable organic additives [7–11]. A high nanoparticles filling of the sol containing an adequate organic binder assures a reasonable conductivity and favors the obtention of thick single coatings ($\leq 1\,\mu$m). The use of nanoparticles with sizes smaller than 25 nm leads to a low light scattering and therefore to high transparency of the coatings.

The paper reports on the optical, electrical, mechanical and textural properties of such coatings polymerized by UV light irradiation at a temperature <130°C.

2. EXPERIMENTAL

The detailed preparation of In_2O_3:Sn crystalline conducting nanopowders with primary size adjustable up to about 25 nm prepared by a controlled growth technique is reported in [5,6,10,12,13].

Powders with size up to 25 nm mechanically redispersed in ethylene glycol with a carbon acid as dispersing agent form a blue paste, with solid content up to 60 vol% stable several months without evidence of agglomeration if a $pH < 6$ is maintained ($pH_{iep} = 8.5$). Ethanolic solutions containing lower amount of ITO particles and a small amount of a hydrolyzed binder such as 3-methacryloxypropylmethoxysilane (MPTS) and a photostarter (Irgacur 18U) added under ultrasonic agitation can be spin and dip coated to get conducting transparent layers or sprayed to get conducting antiglare layers.

Transparent coatings with thickness up to 1 μm have been obtained on substrates such as glass, PC, PMMA, PE, polyimide. The best properties are obtained by first submitting the wet coating to a UV irradiation (typical average intensity 105 mW/cm^2 for 110 s (Beltron)) with a further heat treatment at 130°C up to 20 h. A further annealing under forming gas or N_2 atmosphere performed at 130°C during 2 h improves further the electrical properties.

Antiglare conducting coatings have been obtained by spraying the substrates with the same sols for a period of 15 to 20 s with a SMTA mini-jet gun (0.5 mm nozzle, 3 bar). The coatings have been further processed as described above. Details on the experimental characterization technique can be found in [10,11].

3. RESULTS AND DISCUSSION

3.1. Transparent Conducting Coatings

The lowest specific resistivity $\rho = 9.5 \times 10^{-2}\,\Omega\,\mathrm{cm}$ was obtained using a hybrid sol containing 6 vol% MPTS and processing the coatings under UV light irradiation with a further post annealing in a reducing atmosphere (Fig. 1). The value is stable if the layers are kept in vacuum or in a protective atmosphere (e.g. N_2, Ar). Unfortunately, it slightly increases slowly with time to reach a stable value of about $9 \cdot 10^{-2}\,\Omega\,\mathrm{cm}$ in air (20°C, 40% RH) after about 7 days. The process is reversible: a new short time UV irradiation of same intensity (105 mW/cm^2, 120 s) allows to recover the previous resistivity. These changes depend on the thickness of the coating: the thicker the coating is, the smaller the variation is. The ratio $\rho_\square$ (7 days)/$\rho_\square$ ($t = 0$) is typically 10 for a 100 nm thick coating and diminishes to 2 for a 1 μm thick one.

The surface properties of the coatings are also reversibly altered during the UV treatment and the storage in air. Figure 2 shows the evolution of the electron work function ϕ measured using a Kelvin Probe (KP Technology) and the surface energy calculated from the measurements of the contact angle using different liquids (G2/DSA 10, G 40 program from Krüss. UV

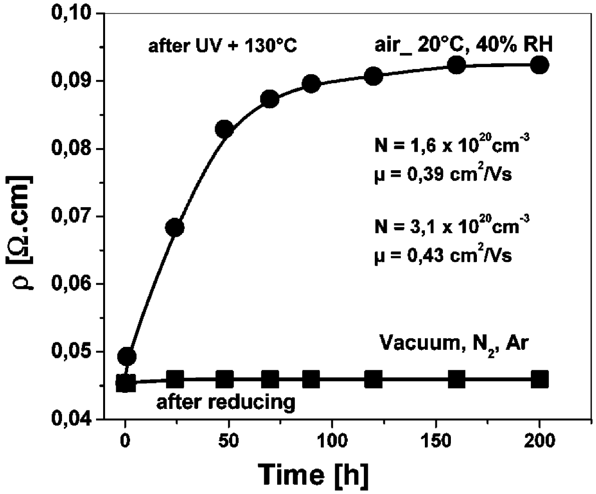


FIGURE 1 Time evolution of the resistivity of MPTS/ITO nanocomposite coatings (570 nm thick) kept in an inert atmosphere (vacuum, Ar, N_2) and in air respectively.

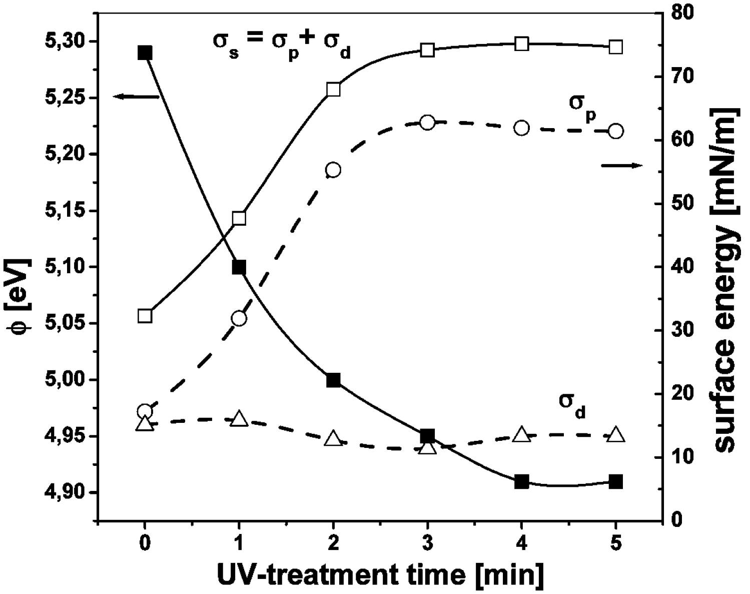


FIGURE 2 Variation of the electron work function ϕ and surface energy σ of a nanocomposite MPTS/ITO coating during UV irradiation (105 mw/cm^2). The indices p and d stay for the polar and dispersed components respectively.

irradiation decreases the work function from 5.3 eV down to 4.9 eV while the surface energy increases from 30 up to 75 mN/m. The variation of this last property is essentially due to its polar component (σ_p) as the dispersed ones remain unaffected. When the coatings are stored in a protective atmosphere, both properties remain constant but they return to their original values when the coatings are stored in air. As both properties reflect a surface effect, the values are fully correlated (Fig. 3).

The mechanisms responsible for these variations are not yet clear. The reversible change of the resistivity involves primarily a variation of the electron density N while the mobility of the electron μ remains practically constant. Besides the polymerization effect of the MPTS which bring and hold close together the ITO particles, the UV is thought to diminish the concentration of chemisorbed oxygen species adsorbed on the surface of the ITO particles which act as free electrons surface state traps, enhancing the carrier concentration and consequently decreasing the resistivity. The back reaction, i.e. the diffusion of O_2 species into the coating followed by a chemisorption at the surface of the ITO grains decreasing N and increasing ρ is possible as the coatings are porous. The creation of electron-hole by the UV light with a possible redox reaction at the surface of the particles is not discarded. The effect of the reducing treatment is however clearer. It increases the carrier concentration N by creating oxygen vacancies and electrons $(V_O)_x e'_{2x}$ in the particles.

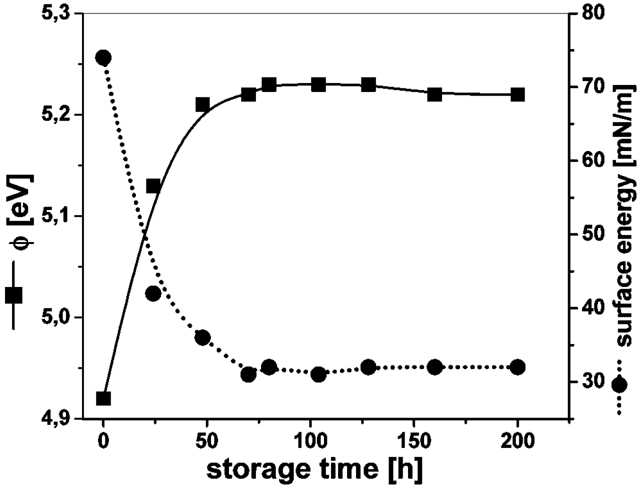
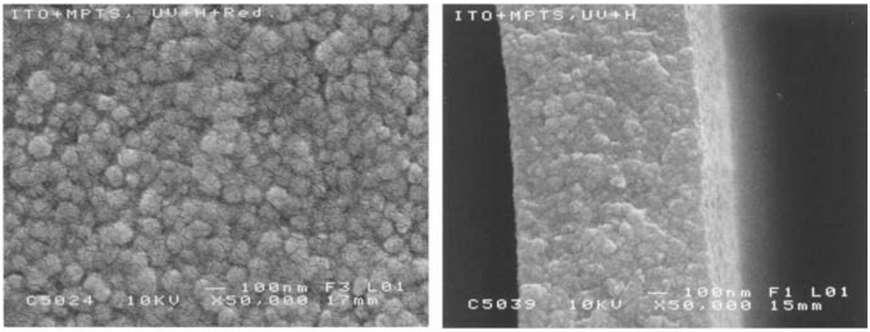


FIGURE 3 Variation of the electron work function ϕ and surface energy σ of a nanocomposite MPTS/ITO coating during storing in air.

The surface morphology of the coatings observed by SEM consists of loosely packed globular grains (raspberry like) about 100 nm in size formed by the aggregation of the ITO nanoparticles linked together by a small strip of polymerized MPTS (darker regions) (Fig. 4). The coating roughness measured by white light interferometry (WLI) on a $53 \times 70\,\mu\text{m}^2$ area with a lateral resolution of 600 nm is $R_a = 0.85\,\text{nm}$, with a peak-to-valley maximum value of $R_{PV} = 15\,\text{nm}$. When measured with a higher resolution on a $1 \times 1\,\mu\text{m}^2$ area (AFM), the values are $R_a = 6\,\text{nm}$.

The optical transmission and reflection of a coating deposited on a polycarbonate substrate is shown in Figure 5. A high transmission of about 87% is observed in the visible range. The influence of the carriers is clearly seen by the strong absorption (A = I-T-R) occurring in the near IR range ($900 < \lambda < 3\,\mu\text{m}$) and the increase of the reflection starting at $\lambda \approx 1.7\,\mu\text{m}$ extending to value $R \approx 45\%$ at $\lambda = 20\,\mu\text{m}$. Similar results have been obtained for coatings deposited on different plastic material (thick and foil substrates) such as PC, PMMA, PET. The strong decrease of the transmission in the UV range ($\lambda < 400\,\text{nm}$) due to ITO band-band transition makes these coatings interesting to protect the plastic substrates against UV radiation while the strong decrease of the transmission due to the carrier absorption observed at $\lambda > 900\,\text{nm}$ offers a sun and heat radiation protection.

The mechanical properties of the coatings deposited on PC substrate have been studied by various tests (Table 1). The adhesion is in agreement with the Tape test procedure (DIN 58196-K2) and the lattice cut test (ASTMD 3359, DIN 53151-Gt0 completely smooth cutting edges). No scratch (class 1) was observed after 10 rubbing cycles with an eraser under a load of 10 N (DIN 58196-G10) as well as with the milder test rubbing with



(a) (b)

FIGURE 4 Morphology of an MPTS/ITO nanocomposite coating. SEM images of a) coating surface, b) coating cross-section.

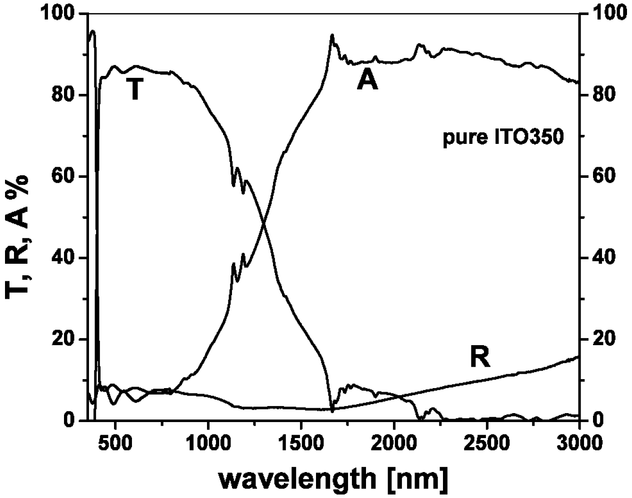


FIGURE 5 UV-near IR transmission (T) and reflection (R) measured against air of a 500 nm thick MPTS/ITO coating deposited on a 3 mm thick polycarbonate (PC) substrate and of an uncoated PC substrate.

a cotton cloth (DIN 58196-H25) (25 cycles). The results of the Taber test show that the coatings cannot be classed as really hard materials. The hardness measured using the Pencil test ASTM D 3363-92a is 1H. Higher values are obtained when the amount of MPTS is increased, but such coatings present also a higher value of the sheet resistance.

The coatings are also easily patterned by selective UV irradiation. The exposed parts strongly adhere to the substrate and the non-exposed parts

TABLE 1 Mechanical Properties of MPTS/ITO Nanocomposite Coatings on PC

Adhesion		Abrasion		Hardness
a	b	c, d	e	f
OK	Gt0	Class 1	Haze 15%@10 cycles Haze 42%@1000 cycles	1 H

a) Tape Test (DIN 58196-K2).
b) Lattice Cut Test (ASTM 3359, DIN 53151).
c) Abrasion with cotton cloth (DIN 58196-H25).
d) Abrasion with hard rubber (DIN 58196-G10).
e) Taber Test (DIN 52347/CS10F/5,4N).
f) Pencil Test (ASTM 3363-92a).

are easily washed under ultrasound in ethanol. Figure 6 shows typical line patterns obtained by UV irradiation through a metallic mask placed directly on top of the wet coating or by a 350 nm laser irradiation.

Antiglare-antistatic coatings obtained by a spraying process to get a final surface morphology with micrometer size roughness is shown in Figure 7. Glosses @ 60° ranging between 60 to 70 with a haze smaller than 10% have been obtained. The mechanical and electrical properties of these coatings are similar to those presented above.

4. CONCLUSIONS

Stable hybrid pastes and sols allowing the deposition of conducting, antistatic and antiglare-antistatic coatings fully processable at low temperature ($T < 130°C$) have been developed by modifying an ethanolic suspension of redispersed crystalline ITO nanoparticles with a hydrolyzed silane (MPTS)

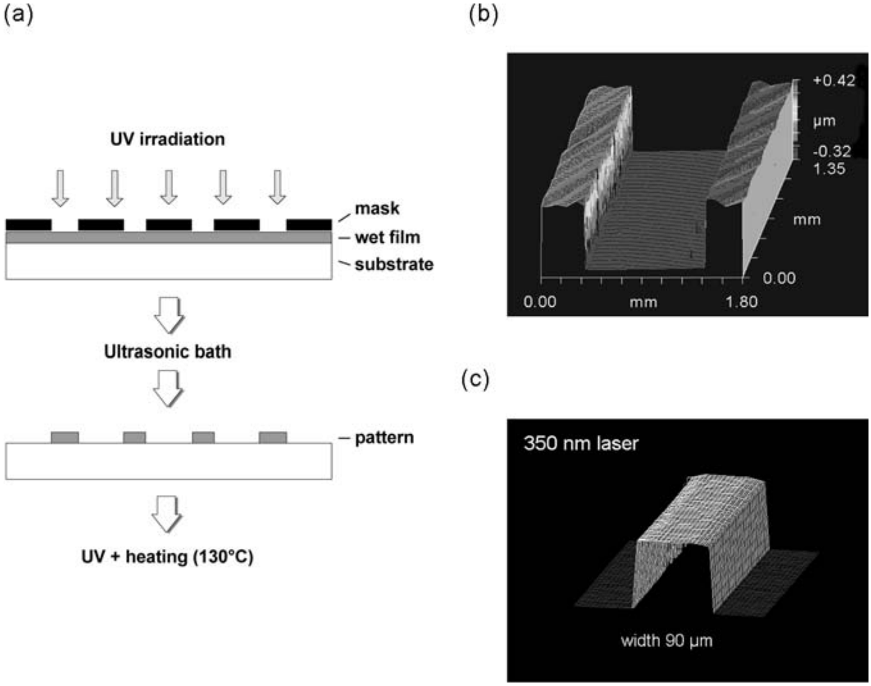


FIGURE 6 Line patterns obtained by selective irradiation through a mask (a, b) or by direct irradiation with a 350 nm laser (c) in combination with a removal of the non-exposed area by washing.

FIGURE 7 Glaze of a white object placed in front of a AS-AG coated plastic (left) and an uncoated one (right). The picture of the INM building placed 2 cm behind the substrates is clearly visible in both configurations.

acting as a binder. Single layers as thick as about 600 nm have been obtained by spin or dip coating processes on plastic (PMMA, PC, PE, polyimide) and glass substrates. The best curing process involves a UV irradiation ($105\,\mathrm{mW/cm^2}$, 110 s) followed by a heat treatment at $T = 130°C$ during 15 h and then a reducing treatment in forming gas. The coatings exhibit a high transparency ($T \approx 87\%$) and a stable resistivity $\rho = 9 \cdot 10^{-2}\,\Omega\,\mathrm{cm}$. The abrasion resistance is in agreement with DIN 58196-G10 class 1, the adhesion passes the tape test DIN 58196-K2 and the lattice cut test ASTMD 3359 or DIN 53151 and the pencil hardness according to ASTM D 3363-92c is 1 H. The surface roughness on a $53 \times 70\,\mu\mathrm{m}^2$ is low, $R_a \approx 1$ nm.

Antistatic coatings with similar sheet resistance presenting an antiglare effect (GU ~ 65) have been obtained on the same substrates by a spray process at room temperature followed by UV irradiation and N_2 annealing.

All these coatings are stable under UV or visible light irradiation and consequently their overall properties are better than those obtained with commercial conductive polymers.

The process can be applied to coat conducting coatings at low temperature ($T < 130°C$) on flat or slightly curved substrates such as CRT, LCD, PDP, touch screen panels, clean room discharge plates or bodies, plastic foils etc.

The concept of preparing crystalline ITO nanoparticles with a further redispersion into a polymerisable matrix is therefore quite adequate to obtain transparent or antiglare conducting coatings on plastic substrates and can be extended to other systems.

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