Materials Science, Vol. 20, No. 1, 2002

Redispersable nanopowders for wet chemical coating processes. Application to transparent conducting coatings[*]

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In_2O_3:Sn (ITO) sols made of crystalline nanoparticles fully redispersable in an ethanol solution containing hydrolyzed organosilanes have been developed to get thick conducting transparent and antiglare coatings on substrates which do not withstand high temperature such as plastics (PMMA, polycarbonate) and already processed glasses. The coatings were deposited by spin, dip and spray coating processes and cured by UV irradiation and/or by a low temperature heat treatment ($T = 130$ °C) in air and reducing atmosphere. Their electrical, optical, textural and mechanical properties are reported. Stable sheet resistance as low as 2 kΩ□ was obtained with a single 500 nm thick transparent layer. Antiglare-antistatic coatings exhibiting similar sheet resistance, a gloss of 60–70 GU, a clarity of 75–90% and an optical resolution > 8 lines/mm were obtained by a room temperature spraying process. The abrasion resistance of the transparent coatings is in agreement with DIN 58196 G10 – class 1, the adhesion with DIN 58196-K2 (tape test) and the pencil hardness (ASTM D 3363-92a) is 1H.

Key words: sol–gel, coatings, electronic conductivity, ITO nanoparticles, low temperature processing, plastic substrates

1. Introduction

Transparent conducting inorganic (TCO) coatings are today widely used as electrodes in optoelectronic devices (displays, smart windows and mirrors, etc.), as IR reflecting layers in low-emissivity glazings and oven windows, as heatable layers in defrosting windows, for electromagnetic shielding or dissipating static, etc. The most important materials bearing such properties are very thin metal layers (Ag, Au, etc.), conducting polymers and n-type oxide semiconductors such as indium tin oxide (ITO), fluorine or antimony doped tin dioxide (FTO, ATO), aluminium or gallium-doped zinc oxide (AZO, GZO).

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[*] The paper presented at the International Conference on Sol–Gel Materials, SGM 2001, Rokosowo, Poland.

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For the last group of materials practically all physical and chemical processes have been tested [1]. Wet chemical processes such as CVD, AACVD, spray pyrolysis and conventional sol–gel techniques require either a hot substrate ($T > 400$ °C) or a substrate which can be heated after the deposition to such a high temperature. These processes are therefore only adequate to coat glasses [2]. Moreover the conventional sol –gel process does not allow the deposition of thick layers and low sheet resistance can only be obtained with a multilayer coating. As it is necessary to repeat the whole coating procedure (deposition, drying, sintering) many times, the process is not well adapted for industrial application.

There is therefore a great interest to find a way to deposit by a sol–gel technique (spray, dip and spin coating) a single thick conducting layer, especially on substrates which do not withstand high temperature such as plastic materials and already processed glass devices. Till now, only physical deposition techniques are adequate [2].

One possible issue for the development of thick TCO coatings is the use of hybrid organic-inorganic sols containing a very large amount of already conducting crystalline oxide nanoparticles. Hybrid sols are known to allow the deposition of thick coatings which can be fully processed at low temperature, $T < 130$ °C (and also at high temperature). A high filling of the sol with crystalline n-type semiconducting nanoparticles which can be linked together with an adequate organic binder should assure a reasonable conductivity. Moreover, the use of nanoparticles assures a low light scattering and a high transparency of the coatings. In_2O_3:Sn (ITO) and SnO_2:Sb (ATO) conducting crystalline nanoparticles have been already developed in our institute. Their preparation, characterization and use for the development of conducting ATO membranes and ATO and ITO coatings sintered at high temperature have been reported [3–8].

The present paper summarizes the optical, electrical, mechanical and textural properties of thick transparent and antiglare conducting ITO coatings processed at temperature as low as 130 °C and deposited on plastics and glasses. Earlier reports can be also found in [9–11].

2. Experimental

The detailed preparation of redispersable crystalline ITO nanoparticles can be found in [9]. They exhibit the cubic In_2O_3 phase and no phase separation or orientation of the crystallites have been detected. The crystallite size determined by X-ray diffraction (222 peak) or transmission electron microscopy (TEM) is about 15 nm. The particles have a density of 6.45 g/cm^3 corresponding to 92% of the theoretical density of In_2O_3. The agglomerated particles can be fully redispersed in ethanol or water down to their primary size (ca. 15 nm) and a highly stable paste (> 1.5 year) have been obtained [9].

The sols developed to produce transparent conducting coatings were prepared as follows: an ethanolic solution containing 25 wt. % of redispersed ITO nanoparticles was modified by adding various amounts of hydrolyzed 3-glycidoxypropyltrimethoxysilane (GPTS) or 3-methacryloxypropyltrimethoxysilane (MPTS) under ultrasonic bath. PMMA, polycarbonate (PC) and glass substrates were coated by spin and dip coating process. The resulting films were cured in air or reducing atmosphere at 130 °C up to 20 hours, by UV irradiation with an average intensity of 105 mW/cm^3 during up 110 s (Beltron) or by a combination of both treatments.

The sols developed to produce antiglare conducting coatings were prepared as follows: an ITO nanoparticles solution (25 wt. %) was modified by adding GPTS. The sols were sprayed at room temperature for a period of 15 to 20 seconds using a SATA mini-jet spray gun (0.5 mm nozzle, 3 bar) on polycarbonate or glass substrates. The coatings, a few µm thick, were polymerized by UV irradiation (105 mW/cm^2, during 100 s).

The thickness of the coatings t was determined using a Tencor P10 stylus profilometer and the average roughness was measured with a Zygo New view 5000 white light interferometer. The morphology of the coatings (surface and cross section) was observed by scanning electron microscopy (SEM JEOL 6400) and HR-TEM (Philips, 200 keV), respectively. The abrasion resistance of the coatings was tested according to DIN 58196-G10 – rubbing with an eraser under a load of 9.8 N and DIN 58196-H25 – rubbing with a cloth under a load of 9.8 N, their hardness using the pencil test (ASTM D 3363-92a) and their adhesion using the tape test DIN 58196-K2.

Optical transmission and reflection were determined using a Variant Cary 5 E spectrophotometer in the wavelength range from 300 to 3000 nm while haze, clarity and gloss of the antiglare coatings were measured using a ByK Gardner Plus and a micro-TRI reflectometer.

The sheet resistance $R_{..}$ was measured by a 4-point technique and a contactless measurement device (Lehighton Electronics Inc.). The resistivity was calculated from $r = R_{..} t$.

3. Results and discussion

3.1. Transparent conducting coatings

The evolution of the sheet resistance of a 500 nm thick single layer MPTS/ITO coatings deposited on a 3 mm thick PC substrate is shown in Fig. 1 as a function of the sol composition for different annealing treatments, such as heat treatment in air, UV irradiation and annealing in nitrogen gas. Similar overall behaviour has been obtained with GPTS/ITO coatings. Whatever the treatment is, $R_{..}$ for pure ITO remains high (> 1 MΩ$_{..}$) and the coating adhesion is poor. Cured MPTS/ITO coatings present a minimum of the sheet resistance for a composition volume ratio of 6%. A heat treatment in air at 130 °C only slightly decreases the sheet resistance. In fact, IR spectroscopy shows that contrary to what can be observed with pure MPTS coatings, the heat treatment does not build a well defined Si-O-Si network (observed at 1050 cm^{-1}) and the presence of ITO particles seems to impede the polymerization and condensation processes [9]. On the opposite the UV treatment drastically reduces the sheet resistance. IR spectroscopy [9] shows that this treatment eliminates completely the C=C band (1036 cm^{-1}), strongly reduces the C=O band (1716 cm^{-1}) so that a well defined Si–O–Si network linking the conducting particles together is built allowing a much better conductivity. The lowest stable sheet resistance, $R_\square$ = 15 kΩ$_\square$ for GPTS/ITO and $R_\square$ = 2 kΩ$_\square$ for MPTS/ITO, have been obtained after a 110 s UV irradiation followed by a 15 h heat treatment in air at 130 °C. A further treatment in a reducing atmosphere (N_2) still lowers the value of the sheet resistance.

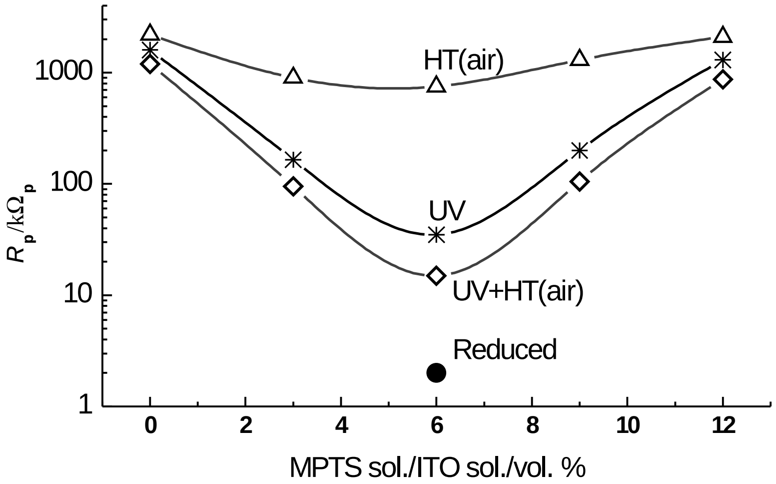


Fig. 1. Sheet resistance of 500 nm thick MPTS/ITO coatings vs. sol composition;
UV: irradiation by UV light 105 mW·cm^{-2}, 110 s, HT (air): heat treatment in air: 130 °C, 15 h

The values reported above have been measured in air at least one week after the coating's production and are stable. They however strongly depend on the type of atmosphere and the shelf live. Figure 2 shows the time evolution $R_p(t)$ measured for 500 nm thick MPTS/ITO coatings obtained without and with post-annealing in reducing atmosphere (N_2) and then left in vacuum and in air (about 50% RH). Immediately after the coating production the values of the sheet resistance are much smaller than those reported above, typically 800 Ω$_\square$ for N_2 annealed coatings. They remain constant in vacuum but steadily increase in air, to reach a maximum stable value (2 kΩ$_\square$) after about 7 days. Similar overall behaviour was observed with GPTS/ITO coatings.

The mechanisms leading to these variations are not yet clear, but are certainly related to the composition and the morphology of the coatings. Besides the polymerization process of MPTS an important effect of both the UV and the reducing treatment is probably to diminish the concentration of chemisorbed oxygen species on the surface of the ITO particles, which act as free electron traps surface states. This leads to an increase of the carrier concentration and consequently to a large reduction of the sheet resistance. As the coatings are still porous (see below) this behaviour is only stable if the coatings are kept in vacuum. When left in air, oxygen slowly diffuse into the coating and is chemisorbed again at the surface grains as charged species resulting in an electron transfer from the bulk to the adsorbed species. This induces a high band bending and increases the potential barrier height leading to an increase of the resistivity which reaches a stable value after about 5–7 days [12]. In this sense the coatings act practically as a (poor) oxygen sensor.

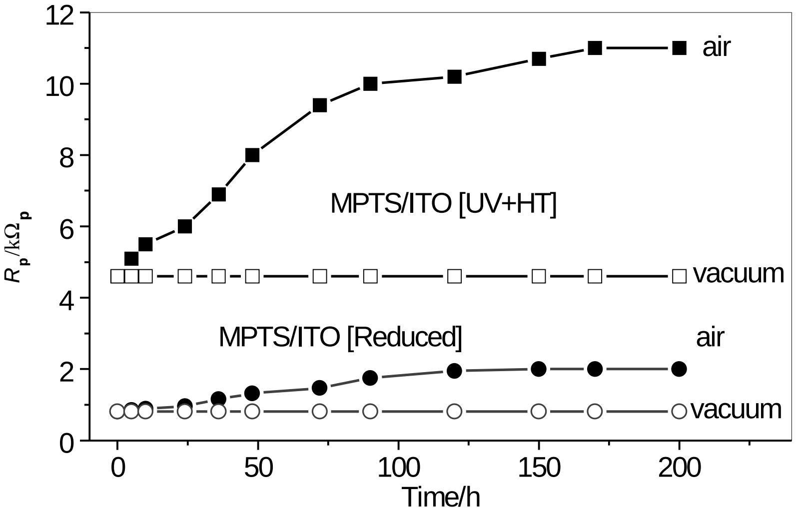


Fig. 2. Time evolution of the sheet resistance of 500 nm thick MPTS/ITO (6 vol. %) coatings left in vacuum and air. The coatings have been annealed in UV light (105 mW·cm^{-2}, 110 s) followed by a 15 h heat treatment in air at 130 °C with and without post annealing in a N_2 reducing atmosphere

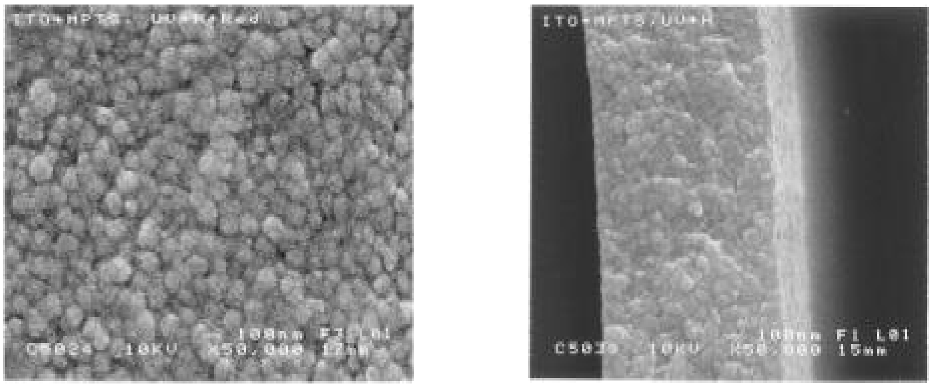


Fig. 3. SEM picture of the surface (left) and of a cross-section (right) of a MPTS/ITO coating UV cured (110 s) and heat treated at 130 °C, 15 h

The morphology of the coatings is shown in Fig. 3. The coating cured is built of loosely packed globular grains (raspberry like) about 100 nm in size. Each grain is made of an aggregation of 15 nm size ITO particles linked together by a small strip of polymerized MPTS (dark region on the figure).

The optical transmission and reflection spectra of a 3 mm thick PC substrate uncoated and one coated with a 500 nm GPTS/ITO layer are shown in Fig. 4. A high transmission of about 87% is observed in the visible range. The influence of the carrier is clearly seen by the strong absorption occurring in the near IR range (900 nm < *l* < 2000 nm) and the increase of the reflection for *l* > 2 µm.

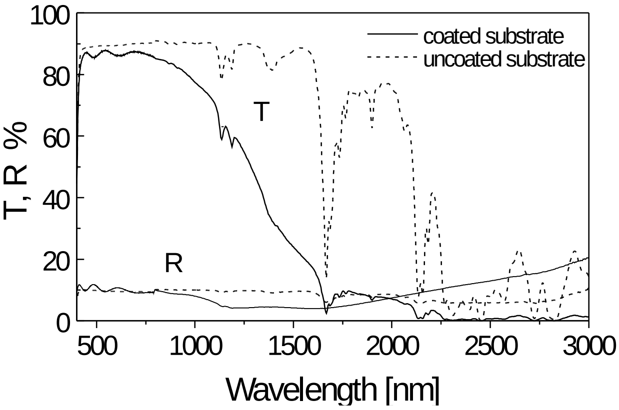
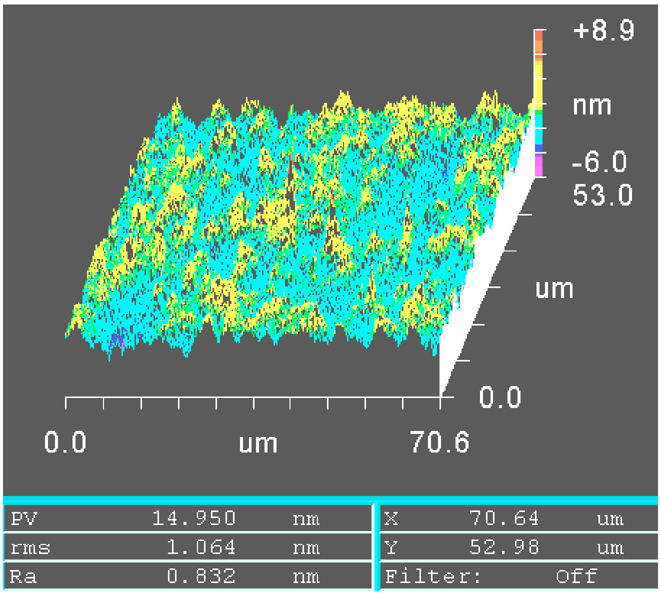


Fig. 4. UV-near IR transmission (*T*) and reflection (*R*) measured against air of a 500 nm thick GPTS/ITO coating deposited on a 3 mm thick polycarbonate (PC) substrate and of an uncoated PC substrate



PV	14.950	nm	X	70.64	um
rms	1.064	nm	Y	52.98	um
Ra	0.832	nm	Filter:	Off	

Fig. 5. Morphology of the surface of a 500 nm thick MPTS/ITO coating measured by white light interferometry with a lateral resolution of 600 nm

The morphology of the surface of the coating measured by white light interferometry with a lateral resolution of 600 nm is shown in Fig. 5. The coatings are extremely smooth and homogeneous with a roughness value $R_a = 0.85$ nm, with a peak-to-valley maximum value of PV = 14.9 nm (probably a dust particle).

The mechanical properties of the coatings deposited on PC substrate have been studied by various tests and are compared in Table 1 with two other commercial coatings, a Japanese product and a Baytron P conducting polymer coating [13].

Table 1. Mechanical properties of conductive coatings deposited on PC substrate

Test	INM (500 nm, *R*.. = 2 kΩ..)	Japanese Product (*R*.. = 50 kΩ..)	Baytron P® (500 nm, *R*.. = 8 kΩ..)
Tape test DIN 58196-K2	OK	OK	OK
Eraser test DIN 58196-G10	class 1	class 3	class 1
Pencil test ASTM D3363-92a	1 H	HB	1 H

The results show that the adhesion property tested using the Tape test procedure was good for all of them. No scratch (class 1) could be observed after 10 cycles with an eraser under a load of 10 N with our coatings and a 500 nm thick, 8 kΩ.. polymer coating made with the Baytron P product [13], but the Japanese product was highly scratched (class 3). The hardness measured using the Pencil test was 1H for our coating, HB for the Japanese product and 1 H for the Baytron P coating.

3.2. Antiglare conducting coatings

The spray gun delivers droplets with average size of 25 µm. When arriving on the cold substrate, they spread and form a rough surface which can be polymerized by UV irradiation or by heating at $T \approx 130$ °C. The thickness of the coatings is in the range of a few µm.

Table 2. Typical gloss, haze, clarity, resolution and abrasion of antiglare coatings deposited on plastic and glass substrates and cured by UV irradiation

Gloss @ 60°	Haze/%	Clarity/%	Resolution (USAF chart)	Abrasion (9.8 N)
60–70	≤ 10	75–90	≥ 8 lines/mm	DIN 58196-H 25

XRD measurements are in agreement with the random cubic In_2O_3 structure with crystallite size reflecting the size of the ITO particles (15 nm). Figure 6 shows the surface morphology of such coatings observed with an optical microscope. The size of the surface features varies from about 10 to 100 µm and the average roughness of the coatings measured by the profilometer along a 500 µm length is $R_a = 0.2$ µm with height variation of ± 0.4 µm. The sheet resistance is about 2.5 kΩ... Table 2 shows the results of the optical and abrasion properties of the coatings.

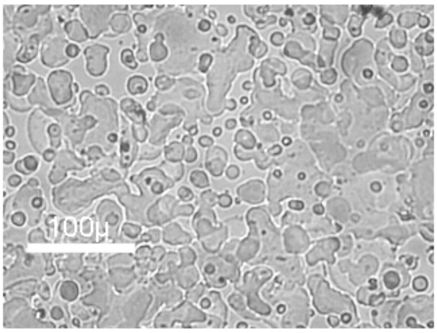


Fig. 6. Surface morphology of antiglare coatings sprayed at room temperature on a PC substrate and UV polymerized

Fig. 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 building placed 2 cm behind the substrates is clearly visible in both configurations

Figure 7 shows the optical effect of such coatings. The image (entrance of INM) placed 2 cm behind a coated and a non-coated substrate is clearly visible and the glare of the white object placed in front of the substrates is strongly reduced at the coated side.

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. They have been obtained by modifying an ethanolic suspension of dispersed crystalline ITO nanoparticles with hydrolyzed silanes (GPTS/MPTS) acting as a binder. Transparent ($T \sim 90$ °C) single layers as thick as 500 nm have been obtained by spin or dip coating processes on plastic (PMMA, PC and glass substrates). The curing process involves a UV irradiation (105 mW/cm², 110 s) followed by a heat treatment at $T = 130$ °C during 15 h and then a reducing treatment in nitrogen. The coating exhibits a stable sheet resistance as low as 2 kΩ.. (resistivity $r = 1.0 \cdot 10^{-1}$ Ω·cm). The abrasion resistance is in agreement with DIN 58196-G10 class 1, the pencil hardness is 1 H and the adhesion passes the tape test ASTM D 3363-92c. The roughness is low, $R_a = 1$ 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 a UV annealing. All these coatings are stable under UV or visible light irradiation. Their properties are presently better than those obtained with commercial conductive polymers.

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