Wet chemical deposition of multifunctional conducting coatings made with a nanocomposite suspension

N Al-Dahoudi[1] and M A Aegerter[2]

1 Physics Department, Al Azhar University, PO Box 1277-Gaza, Palestine

2 Leibniz-Institut fuer Neue Materialien, Im Stadtwald, Geb 43, 66123 Saarbruecken, Germany

Keywords

Nanoparticles, sol-gel, transparent conducting oxide (TCO), infrared shielding, indium tin oxide

Summaries

Wet chemical deposition of multifunctional conducting coatings made with a nanocomposite suspension

A nanocomposite suspension made of redispersable crystalline In_2O_3:Sn (ITO) nanoparticles and a hybrid organic-inorganic additive was prepared to obtain single 600nm-thick, transparent, electrically-conducting layers. The rheology of the suspension was adjusted so that the formulations could be used to coat different glass and polymer substrates and foils using wet chemical deposition techniques such as spin coating, dip coating, spray coating and web coating. The optical properties (transmission, reflection, absorption) showed that the layers transmitted more than 87% in the visible range, acted as infrared (IR)-shielding coatings for ($\lambda > 1.5\mu m$, and effectively reduced the intensity of solar light (Air Mass (AM) 1.5 Global solar spectrum). At the same time, the layers acted as UV blockers for wavelengths less than 400nm, protecting the polymer substrates and foils from degradation when exposed to UV irradiation. The layers exhibited a high conductivity ($\sigma \sim 1100 Sm^{-1}$) which made them useful for electrostatic and antistatic purposes as well as for devices that require a transparent conducting coating with sheet resistance higher than a few $k\Omega_\square$. Furthermore, the layers showed excellent adhesion on all substrates and high resistance against abrasion and weathering degradation, results that are quite promising with respect to their outdoor use.

La déposition chimique humide de revêtements conducteurs à fonctions multiples et préparés à partir d'une suspension nanocomposite

On a préparé une suspension nanocomposite à partir des nanoparticules redispersables cristallines de In_2O_3:Sn (ITO) et d'un additif hybride organique-inorganique afin d'obtenir des couches simples, conductrices d'électricité, transparentes et d'une épaisseur de 600nm. La rhéologie de la suspension a été réglée afin de rendre les formulations capables d'être utilisées pour revêtir des substrats et des feuilles (foils) variées en verre et en polymère, grâce à des techniques qui dépendent de la déposition chimique humide telles que le dépôt à la tournette, le revêtement par immersion, la pulvérisation et le « web coating ». Les propriétés optiques (transmission, réflexion, absorption) ont montré que les couches transmettaient plus de 87% dans le domaine de la gamme visible, agissaient en tant que revêtements protecteurs contre l'infrarouge (IR) pour ($\lambda > 1.5\mu m$) et réduisaient, d'une manière efficace, l'intensité de la lumière solaire (masse d'air (AM) 1.5 spectre solaire global). En même temps les couches agissaient en tant que bloqueurs d'UV pour les longueurs d'onde de moins de 400nm, en protégeant les feuilles et substrats de polymère contre la dégradation pendant leur exposition à l'irradiation UV. Les couches ont fait preuve d'un haut degré de conductivité ($\sigma \sim 1100 Sm^{-1}$) ce qui les a rendus utiles dans les domaines de l'électrostatique et de l'antistatique aussi bien que dans le domaine des appareils qui demandent un revêtement conducteur transparent ayant une résistance par carré plus élevée que quelques $k\Omega_\square$. En plus les couches ont fait preuve d'une adhésion excellente sur tous les substrats et D'un haut niveau de résistance contre l'abrasion et les dégradations dues aux intempéries. Ces résultats sont plutôt prometteurs pour ce qui concerne l'utilisation des couches à l'extérieur.

Naßchemische Deposition von multifunktionellen leitenden Beschichtungen, die mittels einer Nanokompositsuspension hergestellt wurden

600nm dicke transparente leitfähige Beschichtunglagen wurden mittels einer Nanokompositsuspension aus redispergierbaren kristallinen In_2O_3:Sn (ITO) Nanopartikeln und einem organisch/anorganischem Hybridadditiv hergestellt. Die Rheologie der Suspension wurde angepaßt, damit die Formulierung für die Beschichtung verschiedener Glas- und Polymersubstrate und -folien mittels naßchemischer Depositionsmethoden wie Spin Coating, Dip Coating, Spray Coating und Web Coating verwendet warden kann. Die optischen Eigenschaften (Transmission, Reflektion, Absorption) zeigten, daß die Lagen zu 87% im visuellen Spektrum leiten, aber gleichzeitig als Schutzlage für Infrarot von $\lambda > 1.5\mu m$ dienen und damit die Intensität von Sonnenlicht effektiv vermindern (Air Mass (AM) 1.5 im globalen Solarspektrum). Zur gleichen Zeit dienten die Schichten als UV-Blocker für Wellenlängen von 400nm oder weniger, was die Polymersubstrate und -Folien vor UV-Degradation schützte. Die Schichten waren stark leitend ($\sigma \sim 1100 Sm^{-1}$), was sie für elektrostatische und antistatische Anwendungen geeignet macht. Sie sind ebenfalls für Anwendungen, die eine transparented leitende Beschichtung mit einem Flächenwiderstand von mehr als ein paar $k\Omega_\square$ verlangen, geeignet. Darüberhinaus zeigten die Schichten hervorragende Adhäsion zu allen Substraten und eine starke Abrasionsresistenz und Witterungsbeständigkeit, was sie vielversprechend für den Außeneinsatz macht.

Introduction

Because of simultaneous combinations of high electrical conductivity, high transparency in the visible region and high reflectivity in the infrared (IR) region, transparent conductive layers are very interesting systems and are important in several industrial applications such as low-emittance coatings and heat mirror coatings, radiation shielding, transparent electrodes, electrostatic coatings, antistatic coatings and as gas sensors.[1] Among the various known transparent conducting oxides, indium tin oxide (ITO) is one of the more interesting materials for obtaining coatings that have these physical properties and can be used industrially for several applications.[2,3]

Such materials have been deposited on many substrates using versatile physical and chemical deposition methods, each having advantages and disadvantages. The chemical processing requires a relatively high substrate temperature (>300°C) in order to create layers that possess good optical and electrical properties, because a high deposition or sintering temperature is usually necessary for crystalline films to be produced. This requirement does not allow the coating of polymeric substrates, pre-formed glasses or devices based on amorphous silicon that may be seriously degraded during the deposition process or after post-annealing. Moreover, the low temperature, chemical deposition of inorganic coatings onto these kinds of substrates, using sols that are adequate for high-temperature processing, results in non-adhesive layers or in soft, easily scratched layers. Thus, new concepts and approaches are required.

The concept used in this work was to separate the crystallisation step of ITO materials from the process of film formation. For this purpose, crystalline nanoparticles had been prepared and then redispersed in different lacquers. This offered the possibility of curing the layers either by a low-temperature thermal treatment (< 150°C) or by UV light irradiation when polymerisable organic additives are used.4 Moreover, nanoparticles lead to low light scattering and to high transparency of the coatings. Also, overall, when a hybrid sol is used, the acquisition of single thick coatings is favoured.

Experimental set-up

The coating sols were obtained by dispersing a blue coloured ITO powder having an average crystallite size of 25nm (cubic In_2O_3 structure) obtained by a wet chemical precipitation process.[5] The dispersion of the powder was carried out in a viscous matrix of ethylene glycol and a dispersing agent using a milling process. A highly viscous paste was obtained with a solid nanoparticles content ranging between 70 and 75wt%. The ITO paste was then dispersed under stirring for 30 minutes at room temperature in an organic solvent such as ethanol to obtain a pure ITO suspension at different respective concentrations. The blue suspension was centrifuged at 4500rpm for ten minutes to remove the larger agglomerates, and then filtered using a 0.45μm filter. The ITO suspension was then modified by adding different amounts of pre-hydrolysed 3-methacryloxypropyltrimethoxysilane (MPTS) and mixed in an ultrasonic bath for five minutes. The suspensions were stable against aggregation for several months.

The deposition of the modified suspensions was achieved using, respectively, spin-coating, dip-coating or web-coating processes on glass substrates, plastic substrates and foil substrates. After drying, all the coatings were UV-treated under identical conditions (Beltron, 105mWcm^{-2} for five minutes) and by annealing them at $T < 150$°C under N_2 or forming gas (a mixture of 92% N_2 and 8% H_2) atmosphere for two hours.

Sol characterisation: The zeta potential of the coating solution was measured using an Acoustosizer II equipment (Colloidal Dynamics). Relevant values were determined by titrating the pH, starting from a value of 2 up to 12. The dynamic viscosity of the sols was measured according to DIN 53018 using a physical rotational Viscometer ME2 using a ninepin disc accessory.

Coatings characterisation

Optical properties

The optical transmission properties were determined using a Varian Cary 5E spectrophotometer in the wavelength range of 300 to 3000nm. Haze and clarity were measured using a ByK Gardner Plus instrument (ASTM D 1003). A 300W Xenon arc lamp, with an optical filter providing a close match to the air mass 1.5 Global solar spectrum (Oriel Instrument, model SP81160–1452), was used to measure the shielding of solar radiation by measuring the intensity of the irradiance through air, of the uncoated substrates, commercial conducting glasses (a fluorine-doped tin oxide (FTO) deposited on float glass plates called K-glass) and ITO-coated substrates. The detector was a calibrated Ophir Nova 2A-SH thermopile having a flat broadband response between 0.19 and 20μm.

Mechanical properties

The thickness (t) of the coating was determined using a Tencor P10 profilometer. The abrasion resistance of the coatings was tested according to DIN 58196 - by rubbing the coatings with a cloth (H25) or a hard eraser (G10) under a load of 9.8N, the adhesion according to DIN 58196-K2 (tape test) and ASTMD 3359 or DIN 53151 (lattice cut test) and their hardness according to ASTM D3363-92a (pencil test).

Electrical properties

The sheet resistance ($R_\square$) was measured by the four points technique using a Keithley picoammeter/voltage source model 487. The conductivity was calculated from $\sigma = 1/(R_\square t)$.

Results and Discussion

Sol characterisation

Figure 1 shows the measurements of zeta potential over a pH range $2 < \text{pH} < 12$ for a pure ITO suspension. The isoelectric point of the suspension, pH_{iep}, lies at 7.5. It was therefore necessary to use a $\text{pH} < 6$ in order to obtain stable suspensions. The dispersed particles with a positive potential higher than + 30mV formed a stable suspension and no agglomeration was observed during their storage at room temperature for more than one year. The modified suspensions used for the deposition of the coatings had a pH of about 3 to 4.

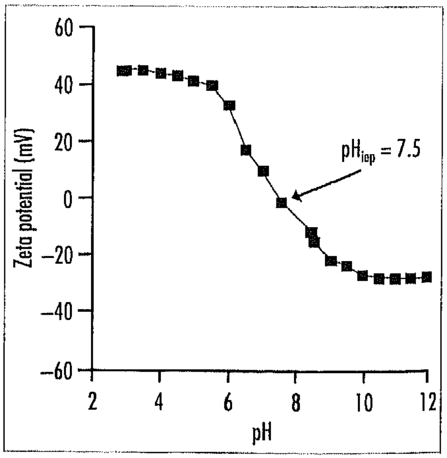

Figure 1: Zeta potentiol of ITO suspension as a function of pH

Figure 2 shows the viscosity and shear stress of the ITO paste, the pure ITO suspension, and MPTS-modified ITO suspension as a function of the shear rate. The diluted pure ITO suspensions (25wt% nanoparticles) and the modified ITO suspensions (22wt% nanoparticles) behaved practically as Newtonian fluids in the evaluated main shear rate range, a condition that is preferred for spin or dip coating processes. The viscosity of the paste (72wt% of ITO nanoparticles) was much higher and clear shear thinning behaviour was observed. This behaviour was more appropriate for web-coating processes.

Coating characterisation

Optical properties

Figure 3 shows the UV-VIS-NIR transmission spectrum of a spin-coated MPTS/ITO layer deposited on a 6mm float glass, on a 6mm float glass substrate, and on a commercial conducting glass (K glass). All of the spectra exhibited high transmission (T) in the visible range. The substrate and K-glass showed a large transmission window, extending from the UV region up to $\lambda = 2.7\mu m$ and $\lambda = 1.8\mu m$ (half value of T) respectively. The transmission spectrum of the nanocomposite MPTS/ITO layer sharply decreased in the NIR (near infrared) region and for $\lambda > 1.7\mu m$, the value was almost $T = 0$. This effect came from a high absorption peaking at $\lambda > 1.5\mu m$, related to the high number of free carriers and the low mobility of the carriers.[4] A similar result is shown in Figure 4 for the MPTS/ITO layer deposited on a $100\mu m$-thick PET foil.

Figure 5 shows the relative intensity of the solar radiation (AM 1.5 Global) measured through air, a 6mm float glass substrate, a K-glass and the MPTS/ITO layer deposited on float glass. The intensity of the irradiance through air was normalised to 100. The uncoated glass substrate reduced the value down to 86%, the K-glass down to 71% and the MPTS/ITO deposited layer on float glass down to 60%. The MPTS/ITO layer was therefore a good shielding coating against the solar radiation.

Also, the coatings had a strong absorption in the UV region for $\lambda < 0.4\mu m$. They can therefore act as a protective layer against the degradation of the polymer substrates when exposed to UV irradiation. For example, clear colourless polycarbonate (PC) substrates change to a yellow-brown colour, mass opaque when exposed to UV irradiation but retain their clarity and transparency in the visible region when coated with the nanocomposite layer. The layers exhibited a clarity and haze of 99.4% and 1.7% respectively.

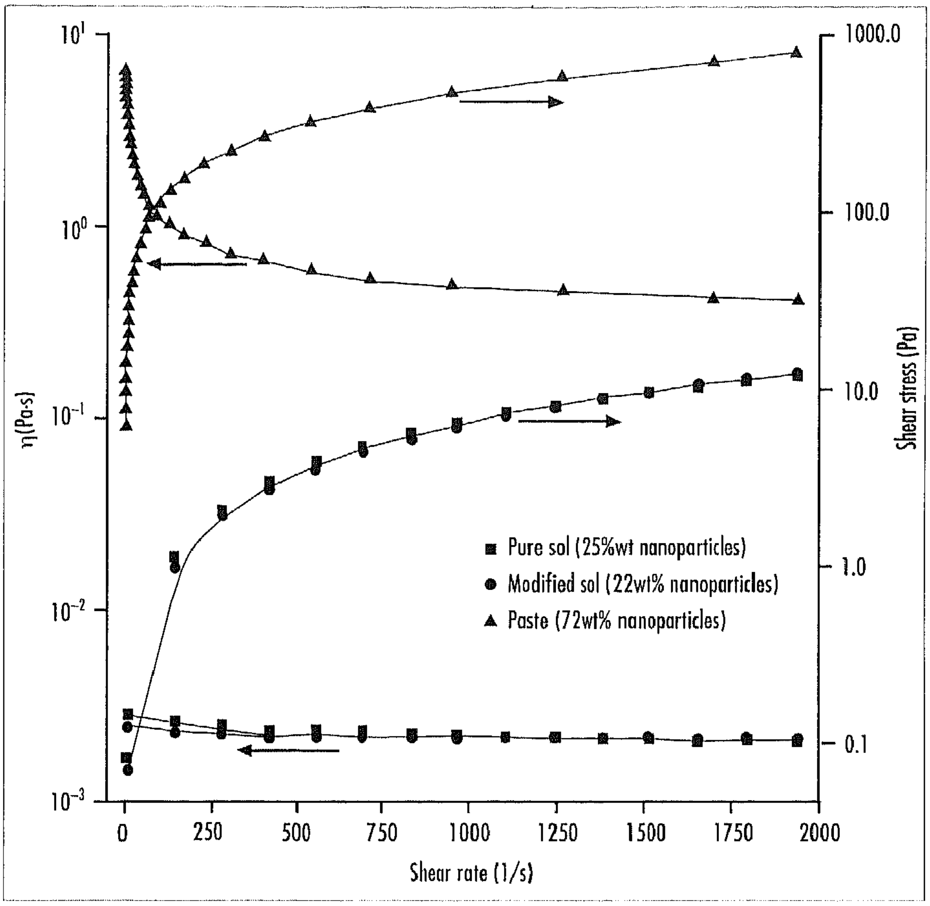

Figure 2: Dynamic viscosity and shear stress of the ITO paste, a pure ITO and MPTS-modified ITO sols as a function of the shear rate

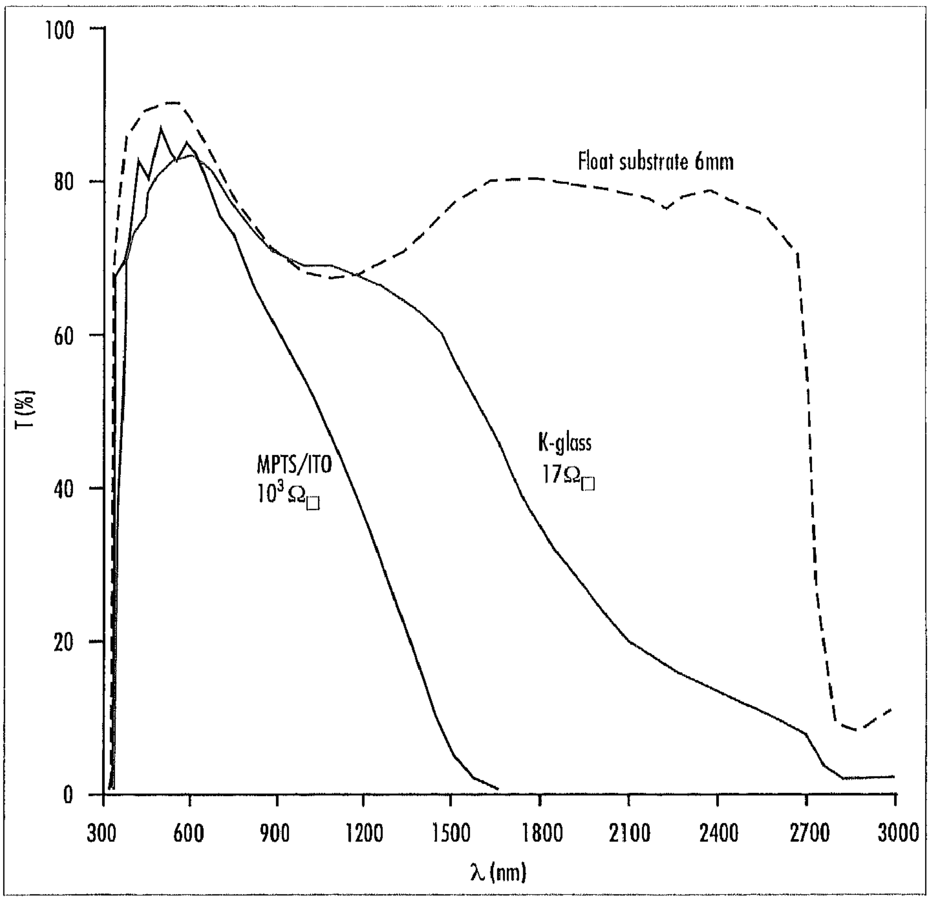

Figure 3: Transmission specttra in the UV-VIS-NIR region for a 6mm float glass substrate, a K-glass and a MPTS/ITO laer deposited on a 6mm float glass substrate

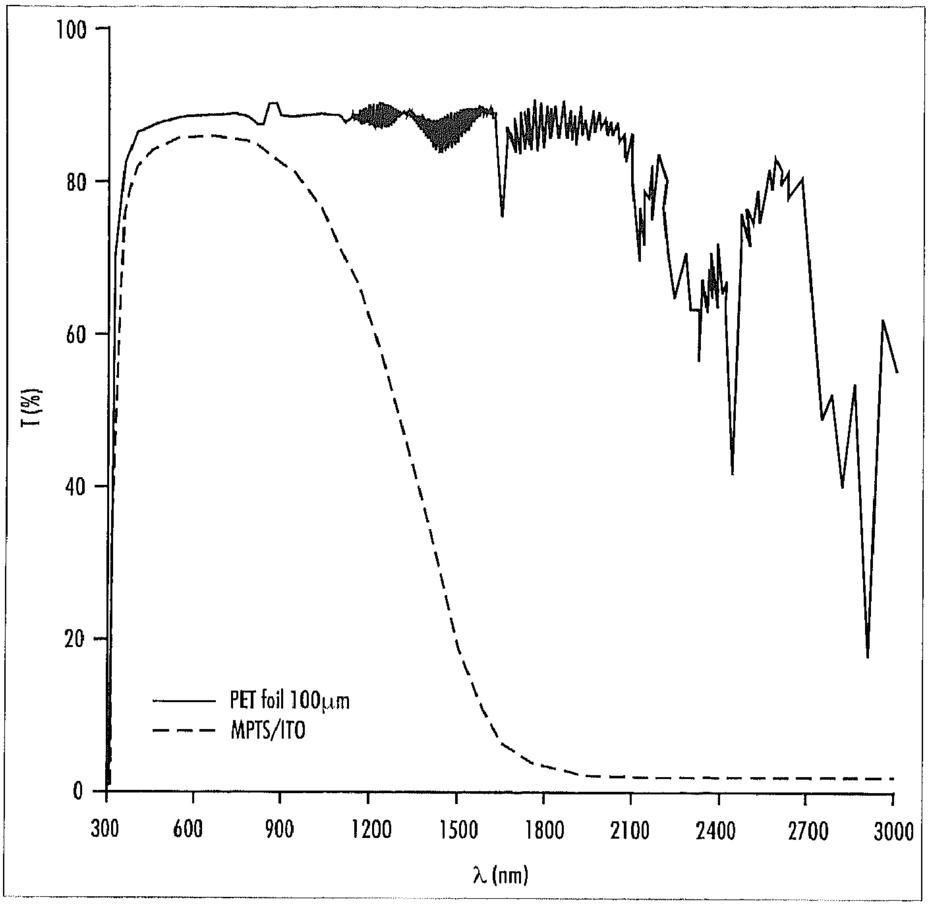

Figure 4: Transmission spectrum in the UV-VIS-NIR region for a spin-coated MPTS/ITO layer deposited on a 100μm-thick PET foil and the uncoated PET foil

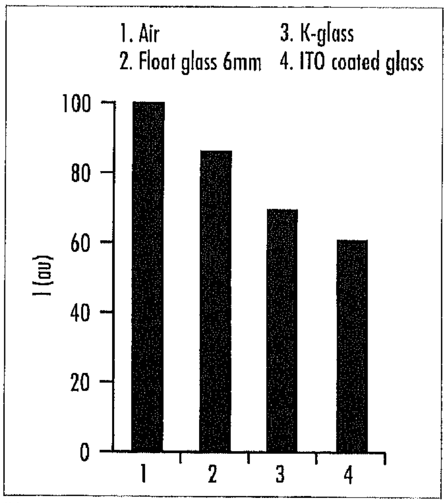

Figure 5: Intensity of a simulated solar irradiation through air (normalised to 100), a 6mm float glass, a K-glass and a MPTS/ITO coated float glass

Electrical properties

A wide range in electrical conductivity of the ITO layers was obtained, depending on the volume fraction of the conducting ITO nanoparticles in the composite suspension. Figure 6 shows the variation of the electrical conductivity of UV-treated layers as a function of the volume fraction of the conducting nanoparticles in the nanocomposite suspension. The values increased continuously from 10^{-4} (Sm^{-1}) to 3×10^{2} (Sm^{-1}). At low concentrations, the conducting particles were distributed without effective contact between them. On raising the concentration, the conducting particles started to aggregate and form better contacts with each other. Jing *et al*[6] explained the electrical conductivity percolation threshold for a polymer/conducting particle composite on the basis of the interparticle distance which decreases when the particle size decreases and the particle volume fraction increases. A stable electrical conductivity as high as $1100 Sm^{-1}$ was achieved for a single 570nm-thick MPTS/ITO layer UV irradiated and then further heat-treated in a reducing forming gas (non oxidising atmosphere) at 130°C for two hours, where oxygen vacancies were produced, resulting in more free electrons.

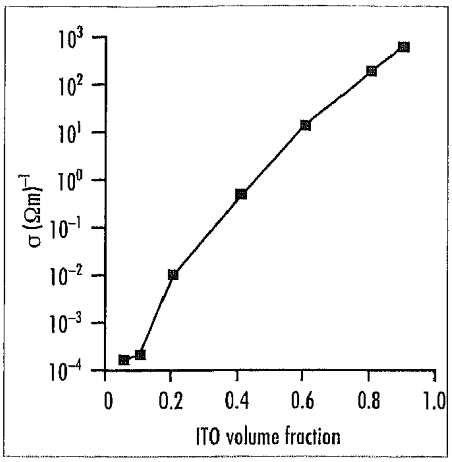

Figure 6: Conductivity of a MPTS/ITO layer deposited on PC substrates as a function of the ITO volume fraction

This range of electrical conductivity can therefore be easily adapted either to remove the electric charges from a surface for which a sheet resistance < 10 $k\Omega_\square$ is usually required[7] or to prevent the accumulation of dust where a sheet resistance in the range of $M\Omega_\square$ is sufficient.

Mechanical properties

The mechanical stability of the coatings is also an important factor to be taken into consideration. The coatings gave excellent adhesion on many glass substrates, polymer substrates and foils when tested with the tape test procedure (DIN 58196-K2) and by the lattice cut test (ASTMD 3359, DIN53151). The resistance against abrasion was excellent, according to the rubber test (DIN58196-G10). The hardness measured using the pencil test (ASTM D 3363-92a) ranged between 1H and 6H as the concentration of MPTS of the composite was increased.

The changes in electrical conductivity and the optical transmission at 550nm of

Table 1: Changes of the electrical sheet resistance and transmission at 550nm of MPTS/ITO coatings deposited on various polymer substrates after abrasion, adhesion and humidity tests

	Abrasion resistance DIN 58196-G10 (rubber test)				*Adhesion resistance DIN 58196-K2 (tape test)*				*Humidity resistance 95% RH, 60°C, 100 hours*			
Substrate	*PC*	*PMMA*	*PVC*	*PET*	*PC*	*PMMA*	*PVC*	*PET*	*PC*	*PMMA*	*PVC*	*PET*
Increase in sheet resistance (%)	6	7	10	10	< 1	< 1	< 1	< 1	20	26	29	30
Decrease in transmission (%)	< 1	2	2	3	< 1	< 1	< 1	< 1	3	5	5	7

PC = polycarbonate; PMMA = poly(methyl methacrylate); PVC = poly(vinyl chloride); PET = poly(ethylene terephthalate)

MPTS/ITO coatings, deposited on different polymer substrates, was measured after applying different mechanical and weathering tests. The results are listed in Table 1. The values remain practically identical except for those determined after storing the layer at 95% relative humidity during 100 hours. Here, the electrical conductivity decreased by about 20 to 30% and the transmission by 3 to 7%.

Nevertheless, the coatings showed very good optical stability, mechanical stability and electrical stability after weathering (ISO 4892-2) DIN 53 387, consisting of two cycles of irradiance (340nm, $0.05 W/m^2/nm$, $T = 65°C$) and 50% relative humidity for 100 hours. These layers appear, therefore, to be good candidates for outdoor applications.

Conclusions

A hybrid suspension containing ITO nanoparticles and MPTS in ethanol has been developed into transparent conductive nanocomposite ITO layers via wet chemical deposition methods on several glass substrates and polymeric substrates and foils. The coatings can be fully processed at low temperatures ($T < 150°C$). The layers show high transparency and clarity in the visible region and reduce the optical transmission effectively in the near infrared range. The wide range of their electrical conductivity values ($\sigma = 10^{-4} - 10^{3} Sm^{-1}$) allows for the creation of antistatic and electrostatic properties for the polymer surfaces. The stability of the layers against abrasion, scratch or weathering degradation is good.

References

1. Gordon R, 'Criteria for choosing transparent conductors', *MRS Bulletin*, **1**, 52-7, 2002
2. Chopra K, S Major and D Pandya, 'Transparent conductors - A status review', *Thin Solid Films*, **102**, 1-46, 1983
3. Hartnagel H, A Dawar, A Jain and C Jagadish, *Semi-conducting Transparent Thin Films*, Institute of Physics Publishing, 1995
4. Al Dahoudi N, 'Wet chemical deposition of transparent conducting coatings made of redispersable crystalline ITO nanoparticles on glass and polymeric substrates', PhD Thesis, University of Saarland and INM, 2003
5. Nonniger R, C Goebbert, H Schmidt, R Drumm and S Sepeur, 'Method for preparing suspensions and powders based on indium tin oxide and the use thereof', German Patent 19849048, 2000
6. Jing X, W Zhao and L Lan, 'The effect of particle size on electric conduction percolation threshold in polymer/conducting particle composites', *Journal of Material Science Letters*, **19**, 377-9, 2000
7. Gläser H, *Large Area Glass Coating*, (1st English edition), Von Ardenne Anlagentechnik GmbH, Dresden, 2000