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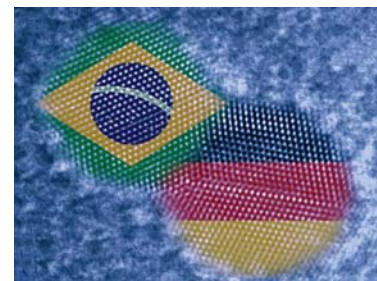
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Dr. Peter William de Oliveira is the leader of “Optical Materials” research group in the Leibniz-Institute of New Materials GmbH in Saarbruecken, Germany. Oliveira earned a M.S. degree in physics from the University of Sao Paulo and a Ph.D. degree from the University of Saarland (Germany). During the last 10 years he had evaluated and constructed a new technological platform for development of new materials for optical applications based on nanocomposites. His main research field at INM has been the design of GRIN (Graded Refractive INdex) nanocomposites for embossing, for lithography and holography as well as materials for interference coatings and for printed electronics. The developed know-how at “Optical Materials” group in the field of optical elements and coatings technology has attracted projects with German, European and overseas companies and institutions. He has authored over 45 publications and 30 patents.



## Large area production of optical coatings and devices by the sol-gel process

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### Coating Technology

Thin films technology occupies an important key position in the development of modern device technologies. For example the combination of high optical transmission in the visible range (between 380 nm to 780 nm) with high electronic conductivity, makes them an essential component for various types of displays (LCD, EL displays or touch screen panels), thin film solar cells and anti-reflective applications. Beyond the electrical conductivity, the closely related IR reflectivity and the photocatalytic effect opens a broad field of applications as heat insulating windows in architectural (low-emissivity glasses), security (electromagnetic shielding) or domestic areas (ovens, refrigerators) [1]. The thickness of such coatings is in the range of approx. 100 nm and thickness variations of only  $\leq \pm 2\%$  are demanded for high quality coatings. The most common coating techniques are PVD (Physical Vapor Deposition) [2] and CVD (Chemical Vapor Deposition) [3,4].

An advantage for the commercialization of the PVD or CVD process is that the process equipment including technology and material can be readily bought from suppliers. In the case of the wet coating area no standard equipment is available for large scale applications and the technological know-how has to be generated in the user's company. A similar situation is observed for the coating material, since coatings based on commercially available organic polymer materials are of interest only in a few application fields.

Wet coating materials are not standardized, not easily available and therefore have also to be developed by the users. Both factors, the non-availability of standard equipment and the non-availability of appropriate coating materials, seem to be the main draw back, and therefore wet coating techniques have not yet gained the same significance for large area/high volume applications as e.g. magnetron sputtering. This is in opposition to the large potential connected to chemical material synthesis, which allows generating highly functional coating materials with interesting properties for glass surfaces and, in addition to this, the equipment costs may be only a fraction of the costs of other techniques [5].

Nanostructured inorganic or mixed inorganic-organic materials became of interest for many areas in the last decade. Many coatings and devices have already been prepared with tuned properties between glasses and polymers, with improved optical properties, or with improved mechanical or resistance to chemicals. In addition to the molecular inorganic or inorganic-organic hybrid network, the magnetic, electric, optical or catalytic properties of nanoparticles resulting from the inorganic amorphous, crystalline, glassy or metallic state of matter also can be used for the material design [6].

Nanoparticles are usually fabricated by using chemical synthesis under specific conditions. During a precipitation process from liquid phases, surface modification agents have been added during or shortly after the formation of the precipitates. These interfere with the nucleating and growing particle to avoid agglomeration and to control size. Nanoparticles from many systems have been fabricated. It was shown that 6 nm SiO<sub>2</sub>-nanoparticles containing nanocomposite hybrid sols can be dried in form of crack-free films up to 14  $\mu\text{m}$  thickness after one step of dip-coating process and densification process at 450 °C. This is attributed to the increase of relaxation ability and flexibility. The nanoparticulate inorganic amorphous coating is insoluble in water and can be used as protective coating against acid attack. Boehmite nanoparticles were used to serve as condensation catalysts to prepare very

hard transparent coatings for polycarbonates and an overcoat with polymerizable nanoparticles was used to produce anti-reflective and ultra hard coatings. In systems with incorporated fluorosilanes, leading to low surface free energy coatings, nanoparticles were used to tailor the fluorine depth profile in self-aligning transparent easy-to-clean coatings by influencing the critical micelle concentration.

The commonly used TCO (transparent conducting oxide) materials are wide band gap ( $E_g \geq 3$  eV) n-type semiconductors, mostly employing pure or doped indium oxide ( $\text{In}_2\text{O}_3$ ), tin oxide ( $\text{SnO}_2$ ) or zinc oxide ( $\text{ZnO}$ ). The doping materials in the case of wet chemically deposited thin films, however, differ from those known from PVD and CVD, as for example an anionic fluorine doping is difficult to realize in wet chemical processing.

The most frequently used sol-gel TCO systems are reported in reference [7].

Due to the excellent electrical properties of the Indium Tin Oxide (ITO), the Sn-doped indium oxide ( $\text{In}_2\text{O}_3:\text{Sn}$ ), attracts the greatest attention, but the high costs limit its application. The carrier concentration in the ITO coating can be adjusted by the number of the oxygen vacancies induced using a post thermal treatment under inert or reducing conditions.

The principle properties of ATO, the Antimony-doped Tin Oxide ( $\text{SnO}_2:\text{Sb}$ ) are mainly its chemical and mechanical stability and its low number of processing steps. The smaller influence of oxygen vacancies makes it more thermally stable compared to ITO. On the other side, the resistivity of ATO coatings is typically at least one order of magnitude higher than that of ITO.

The AZO Aluminium-doped Zinc Oxide ( $\text{ZnO}:\text{Al}$ ) is the material of choice for most of the solar applications, as it exhibits a very high optical transmission and can easily be patterned by chemical etching. Highly conductive films, however, can only be obtained by a multiple deposition of thin layers leading to an orientation of the crystallites, and a subsequent post treatment under reducing atmosphere.

A representative of the group of ternary oxides is cadmium stannate (CTO -  $\text{Cd}_2\text{SnO}_4$ ), which is investigated for its high carrier mobility. In addition, some ternary oxides like zinc stannate (ZTO -  $\text{Zn}_2\text{SnO}_4$ ) have attracted attention as promising candidates for coatings with a higher work function, especially in view of future display developments.

Some sol-gel activities have been done in the area of TCO transparent conductors based on Nb-doped  $\text{TiO}_2$  (TNO) [8,9]. In 2006 the Furubayashi group published [10] a fabrication method of single crystal  $\text{Ti}_x\text{Nb}_x\text{O}_2$  films with  $x = 0.002 - 0.2$  deposited onto  $\text{SrTiO}_3$  substrates by pulsed laser deposition (PLD). The resistivities of films with  $x \geq 0.03$  are  $2$  to  $3 \times 10^{-4} \Omega \cdot \text{cm}$  at room temperature and the transmittances of films reach up to 97%. Sol-gel method has been used to produce  $\text{Ti}_{0.94}\text{Nb}_{0.06}\text{O}_2$  (TNO). The films have been formed by dip coating and a subsequent two step annealing treatment. They exhibit a minimum resistivity of  $19.3 \Omega \cdot \text{cm}$  and an average optical transmittance of about 75% in the visible range, indicating that the sol-gel method could be a feasible and promising method to fabricate TNO films.

The strategy to use opaque conducting nanowires like silver, gold or palladium to produce transparent and conductive coatings has been early used. But the aspect ratio of the fibers are not high enough to obtain a percolation of the fibers in a solid concentration below 10%. With the entrance of carbon nanotubes (CNT) in the field a new high conductive fiber with a high aspect ratio has been produced. Kaiser et al. [11] have used conductive CNTs as fillers in a polymer matrix to enhance conductivity, but the resulting nanocomposites exhibited little or no transparency in the visible range (400-800 nm). Coleman et al. [12] and Curran et al. [13] reported conjugated polymer-CNT composites using multi-walled CNTs, which showed percolation concentration of the CNTs exceeding 5 wt.%. The resulting nanocomposites were black with no transparency in the visible region. Shaffer and Windle [14] reported conductivities of a multi-walled CNT/poly(vinyl alcohol) composite, which also showed percolation above 5 wt.% nanotube loading and led to a black nanocomposite. The same group [15] reported another multi-walled CNT composite in an epoxy resin, which achieved percolation below 0.04 wt.%. An optical micrograph of the CNT/epoxy resin composite was reported, which revealed that the CNT phase was separated from the epoxy resin, showing several millimeters of resin-rich domains. The dispersion of CNTs in this material was very poor. This agglomeration of CNTs in selected areas of the composite could explain the high conductivity observed since this provides the "shortest path" for the current to travel.

Preliminary measurements of the conductivity of a CNT/poly(methyl methacrylate) (PMMA) composite were measured on a fiber [16]. The level of conductivity was relatively high ( $1.18 \times 10^{-3} \text{ Scm}^{-1}$ ) at 1.3 wt.% SWNT loading. However, the optical transparency in the visible range was not determined for the fiber sample. The mechanical properties of these fibers were much lower than the predicted value, which implies that the CNTs were not fully dispersed as Connel et al. [17] reported. New results concerning the applicability of the CNTs for conductive transparent coatings has been published by Pimenta showing a big potential of the CNTs to be used as electrodes for solar cell technology [18].

## Optical devices

The industrial fabrication of active and passive microoptical devices as gratings, micro lenses, micro lens arrays, Y-couplers lead to the development of new materials and technologies. This was limited in the last 10 years by high development costs and small market volumes for these elements. The market of micro optical elements has grown and requires new holographic techniques and new photosensitive coatings. The organic photopolymers have contributed significantly to the recent growth of holographic and lithographic applications, but the photoresists and photopolymers have shown limitations like non linear response in the deep UV, decrease of the diffraction efficiency (after wet development and subsequent UV-irradiation) and only very small modulation of the refractive index as well as the instability against weathering agents.

Micro optic elements are applied in a wide branch of optical products, like holograms, gratings, micro lens arrays, light guiding elements (waveguides, diffusers, reflectors), and optical data storage (CD-ROM). The structures of microoptical elements are based on the layers with surface relief patterns in the range of one  $\mu\text{m}$  to one hundred nm. The commonly used method to produce these microoptical elements are etching and photolithography, ion exchange, laser beam writing, or embossing.

The embossing process consists of a stamper (planar or roll) with a negative surface relief. The desired micro pattern can be produced by pressing the stamper into the material which is being fixed by curing or cooling and removing the stamper.

The embossing process, compared to the photolithography has at least two advantages: low production costs because of manifold replication of the master pattern. Also micro patterns with complicated cross sections can be obtained in a single step, whereas photolithography requires several cycles of coating, illumination and developing or etching.

One can distinguish between two different embossing techniques: hot embossing and reactive embossing. In the hot embossing process, a heated stamper is pressed onto a thermoplastic material and is removed after cooling. There is a time wasting at every cycle between 25 to 60 min for processing temperatures of 100 to 180 °C, which limits the speed of mass production of micro patterns. For the reactive embossing process a UV curable lacquer with a very low viscosity is used. To obtain a copy of the micro pattern the curing step has to be carried out underneath of the embossing stamper, which causes a low speed mass production. A disadvantage for organic monomers is their high shrinkage up to 16 vol. % during polymerisation process. Another problem for these organic nanomers is their poor thermal and mechanical stability.

The first generation of nano composite materials for the embossing process are synthesized by sol-gel route at INM. An inorganic component formed by the hydrolysis and condensation process included in the polymerization of organic component leading to an organic-inorganic network. This nano composite material with overall low shrinkage character (less than 5 vol. %) allows to accomplish the embossing with a near net shaping quality [19]. By adding a proper photo initiator to the nano composite material the curing by light irradiation (UV-VIS) is made possible. The inorganic component improves the thermal and mechanical stability in comparison to the pure organic polymers. The organic component allows the decrease of the densification temperature to less than 150 °C [19]. The nano composite material is based on methacryl oxypropyl trimethoxy silane and zirconium n-proxpoxide with methacrylic acid for starting the reaction. In Fig. 1 the thixotropic embossing process is shown.

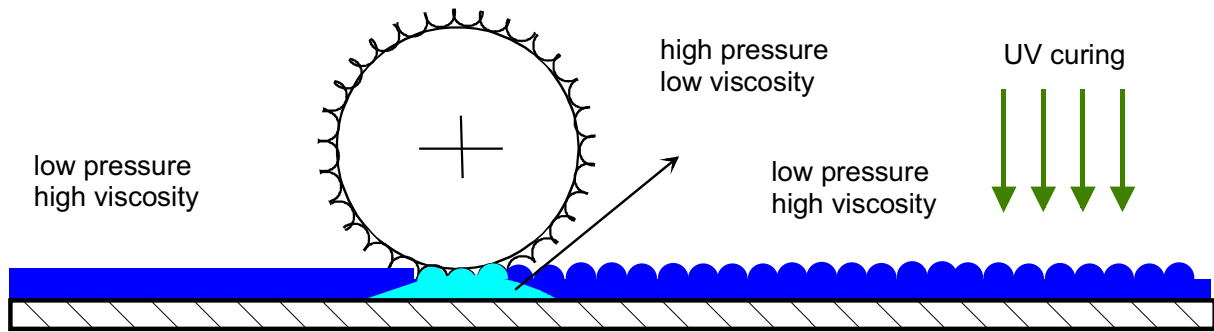


Fig. 1 Schematic diagram of thixotropic embossing.

The thixotropic embossing process has three different steps. First, a coated substrate foil with a high viscose thixotropic material is introduced in the embossing cylinder. Under high pressure the viscosity of the thixotropic coating will be drastically reduced. The last step (after the film has left the high pressure region) the gain in of the caused by the absence of the shear force. With this process the curing area can be extend to some meters, which will increase the production speed.

The relief hologram is a mass product with very low contrast and diffraction efficiency. Optical elements for display and security need to have volume and phase structures in order to fulfil the iniquity required for security labels.

For the production of passive optical elements conventional photoresists, sensitive to near UV light based on an aromatic polymer containing benzene rings, are largely used, but the mechanical properties and low aging agents stability have been limited for the application in displays or architecture. Chalcogenide films have high holographic energy sensitivity only in the visible region of the spectrum, which limits the periodicity of the gratings (min. periodicity about 300 nm) and the coating is therefore made by vacuum deposition or sputtering. Roxan (PMMA und cyanine dye films) can be used for three dimensional phase recording. The substrates can be coated by spin or dip coating techniques but the holographic energy sensitivity is only present in the visible range (min periodicity about 250 nm). Silver halide materials have a very high sensitivity (about  $10^{-7}$  j/cm<sup>2</sup>) and a high refractive index modulation ( $\Delta n=0.8$ ). However the maximum diffraction efficiency is controlled by the development step and contact with humidity produces a decrease of the amplitude of the refractive index modulation. The organic photopolymers show non-linear response in deep-UV and produce a very low signal/noise ratio (150:1) They also shown small variation in the intensity of the light resulting in a drastic overexposure of the resist (SNR 200 Deep-UV from Shipley). Some photopolymers show better irradiation response linearity at  $\lambda=257$  nm, but the absorption is more than 75% measured on a film of 400 nm of thickness (ex. SPR 505 from Shipley, or UV-resists from Du Pont). The holographic structure in organic photopolymers shows a decrease of the diffraction efficiencies by up to 50% in the case the holograms are read with deep ultraviolet. This is because the ultraviolet irradiation produces organic network formation and subsequent shrinkage of the unpolymers part of the hologram. None of the materials currently used for the recording of relief or phase holograms fulfill all of the requirements with respect to applications in integrated optics and to efficient processing. On the other hand a new class of holographic nanocomposites has shown great potential to produce holograms with a very high signal/noise value (450:1), a high refractive index modulation of  $1.5 \times 10^{-2}$  and the factor Gamma (linearity of the holographic sensitivity) can be adjusted by the type and concentration of the photoinitiator.

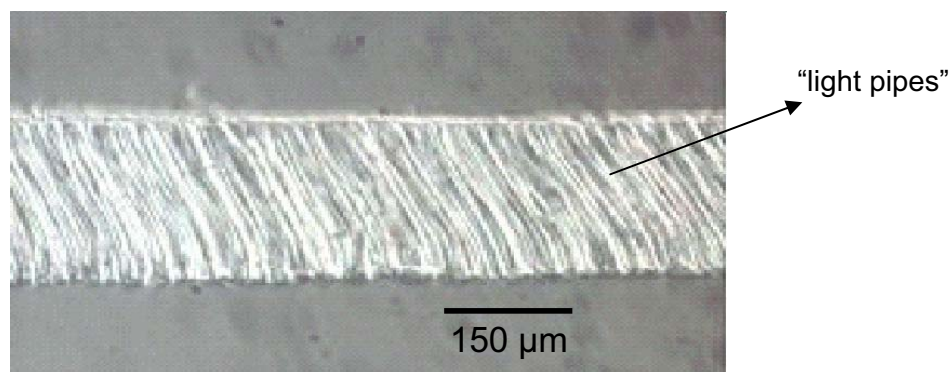
New photo polymerizable organic-inorganic hybrid materials based on methacryl silane and functionalized zirconium nano particles have shown advantages (like high refractive index modulation and a good signal/noise ratio) as holographic recording materials compared to photoresists or photopolymers. Thick films of this composite system were prepared and



volume diffractive gratings were fabricated by holographic copy technique developed at INM. The formation of the phase gratings by irradiation of a photosensitive material with a UV pattern is based 1) on the diffusion of high refractive index functionalized nanoparticles to areas with high irradiation intensity with 2) subsequent immobilization by full irradiation of the film. The relief grating can be formed by production of three-dimensional relief structures using a wet development step of the unpolymerized region or by a heat treatment to produce an inorganic network.

Holographic diffusers are key optical elements in liquid crystal displays (LCDs) used to manage incident light from sources over a defined angle to, keep the brightness uniform over the entire display area. Generally, the diffusers can be classified into three types: the particle-diffusing, the surface-relief type and the phase or volume diffuser. Particle diffusers rely on the transparent beads inside the plastic films of plates to scatter light [20]. The surface-relief diffusers scatter the light by the microstructures thereon, (e.g. micro lens, random phase [21], deterministic diffractive).[22] The surface relief diffuser is normally produced by embossing. Much research has been focused on volume phase diffusers owing to their unique properties, such as controllable diffusion angle, directional property, volume refractive index variation, and high transmittance or high efficiency. Hologram materials such as silver-halide sensitized gelatine, dichromated gelatine, photopolymers [23], and azobenzene polymers [24] have been used to fabricate the diffusers (see Fig. 2).

Ionic liquids are organic salts that are liquid at ambient temperature, preferably at room temperature. They often possess unusual properties such as non volatility, non flammability and may be considered as highly polar liquids. Ionic liquids may be seen as a tool with potential for use in sustainable processes such as solvent replacement, in catalytic reactions, in electrochemical devices and in synthesis of nano particles. Ionic liquids as “green solvents” have attracted increasing interests in polymerizations. Many types of polymerization have been studied using ionic liquids as media in common reactions including olefin polymerization, oxidative polymerization, condensation polymerization, enzymatic polymerization, conventional free radical polymerization, transition-metal-mediated radical polymerization and reverse atom transfer radical polymerization. In these radical polymerization processes, significantly enhanced polymerization rates and high molecular weights are usually observed due to the diffusion-controlled polymerization [25,26].

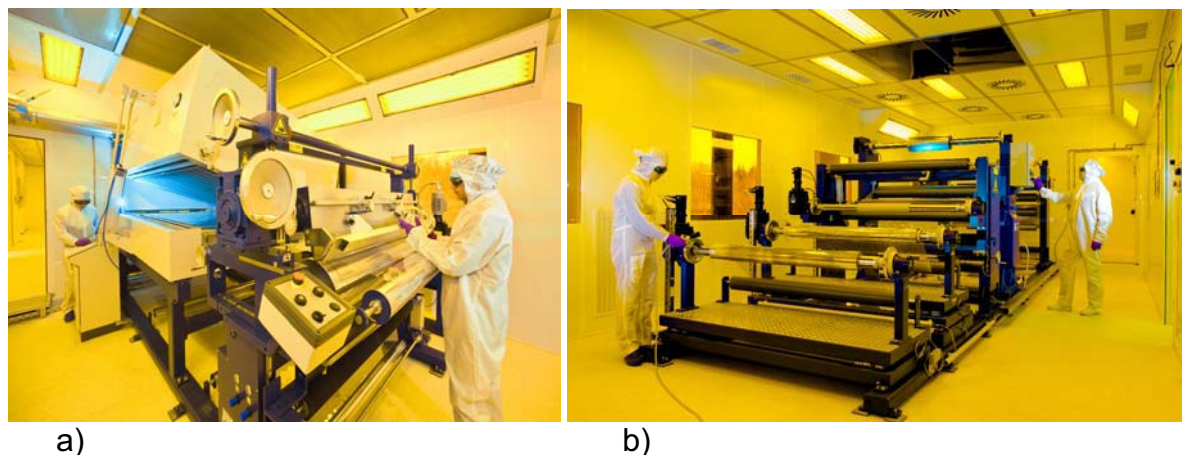


*Fig.2 Cross Section optical phase microscopy of an optical diffuser made by continuous roll-to-roll lithographic process.*

The formation of the light pipes (as in Figure 2) is attributed to the diffusion of the  $ZrO_2$  nanoparticles along the concentration gradient of their photopolymerizable bounds (Colburn-Haines effect) [27]. By local irradiation (holographic writing)  $ZrO_2$  nanoparticles are diffusing towards the irradiated region and their ligands are photopolymerized, leading to an up-concentration of high refractive index particles. Finally the structure is fixed by subsequent complete UV irradiation (350 nm to 450 nm) with  $250 \text{ mJ/cm}^2$  of intensity. The material provides thick phase gratings with the diffraction efficiency up to the theoretical maximum of 100%.

The next step to adjust the new diffuser to the commercialization will be the scaling up process, which will be done in the application centre of INM. The “up scaling” works will be divided in three phases: 1) the up scaling of the photosensitive material, 2) the coating of the photosensitive material in a roll-to-roll process and 3) the production of the volume phase diffuser using a continuous lithographic process.

In this paper we have shown only a few practical examples of the production of optical coatings and devices using wet chemical processes. One of the usually used coating techniques for the wet chemical processing of foils is the roll-to-roll process integrated with offset, doctor blade or reverse roll-coating setups. A typical machine developed for the wet coating process is shown in Figure 3.



*Fig.3 Roll-to-Roll coating machinery at INM application center. This machinery with 1.6 meters web is installed in a clean room with special illumination and explosion safety areas, which enable the work with high pressure vapor solvents types. a) coating setup and b) area for the optical and mechanical structuring of the films.*

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