

MULTIPRO - 3rd Year Highlights Part 1 (Months 24-30)

This document outlines the main highlights and achievements in the third year (1.11.08-31.3.09) of the MULTIPRO project. It is recommended that the accompanying 1st and 2nd Year Highlights document be read before this report.

The work in months 24-30 involved:

1. Molecular Modelling - to use the model developed in the project to investigate selected nano-particle composites and conductive Ag inks.
2. Developing New Materials – draws on the modelling work to design, develop and manufacture the novel composite-composite materials. Furthermore, conductive Ag inks have been further developed for use in LED circuits.
3. Use the reactive deposition technology based on M³D to build project demonstrators in the newly developed materials.
4. Device design for the Multifunctional materials.

1. Molecular Modelling – the Fundamental Science.

Hala Laboratory of Thermodynamics and Università degli Studi di Trieste

The materials which are being developed in the MULTIPRO project consist of Hybrid Inorganic-Organic Matrices with embedded Nano-particles. A multiscale approach which combines both molecular and mesoscale modeling was developed¹ to efficiently represent and model these systems. This was a challenging process due to the complexity of the composite materials structures and their interactions on processing.

The systems investigated have been selected because of their industrial importance in two different manufacturing processes: LED encapsulation and conductive circuit inks. Relevant results have been obtained in the description of the systems without using any experimental data, thus providing an interesting tool for the nano-engineering of new complex nano-structured materials.

Fig. 1 shows an inorganic / organic hybrid system in which the Matrix of GPTMS is reticulated at atomistic level at a given degree of reticulation. The model is consistent with experimental results.

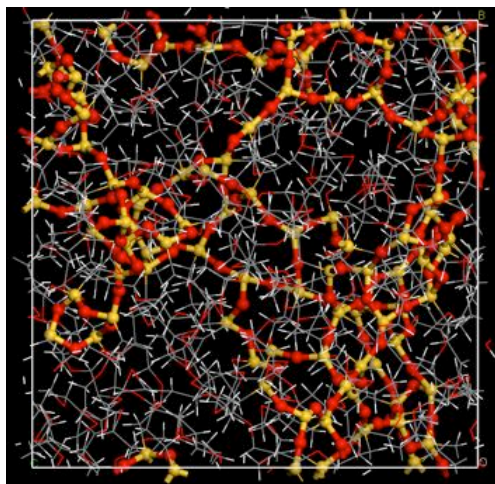


Figure 1: Atomistic structure of the system GPTMS at a reticulation degree of 0.93.

This matrix is then put in contact with the inorganic nano-particles (ZnS, TiO₂,...) and a reaction occurs, forming the final nanostructure, for which multiscale modelling is used to estimate macroscopic properties, such as Young Modulus. **Fig. 2** shows the results of the micro FEM simulations for a ZnS nano-particle loading of 15% and **Fig. 3** for a TiO₂ nano-particle loading of 15%.

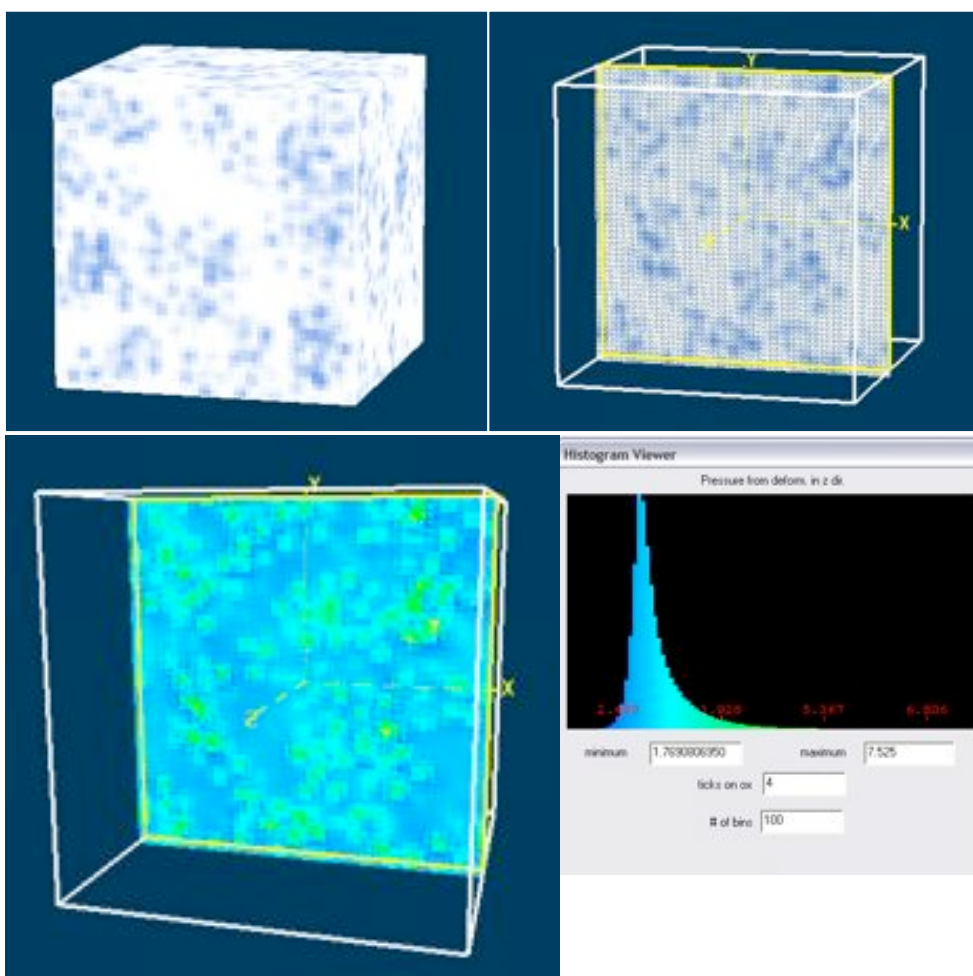


Figure 2: Mechanical properties distribution output from microFEM at 15% loading of ZnS.

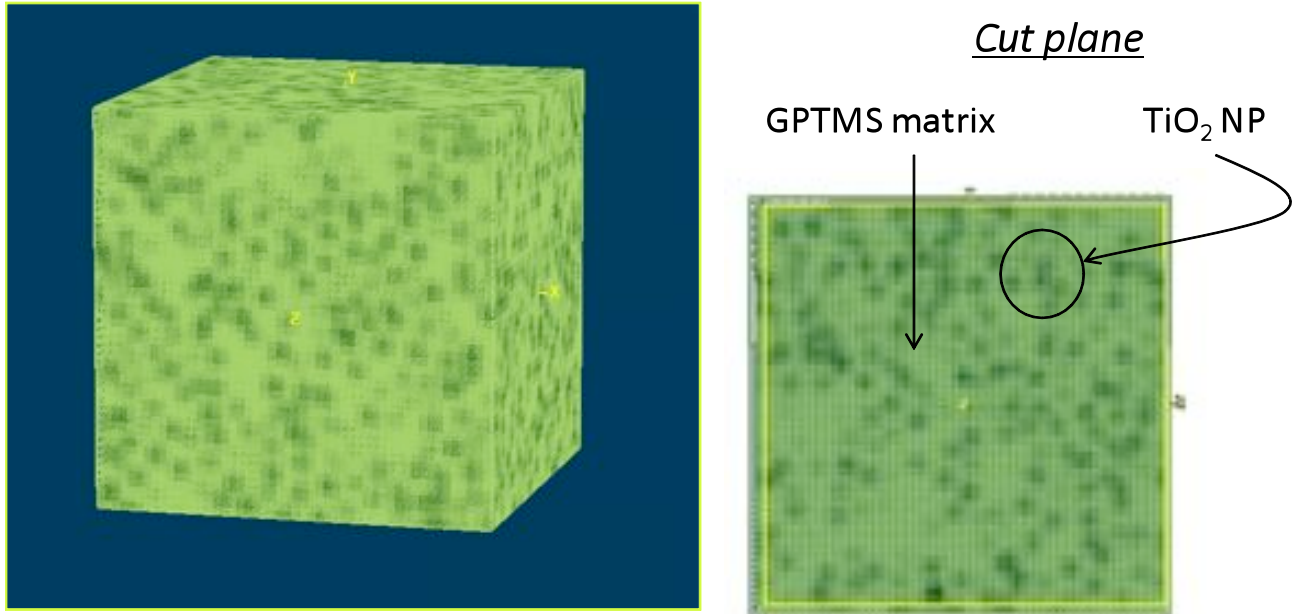


Figure 3: Mechanical properties distribution output from microFEM at 15% loading of TiO₂.

Fig. 4 reports the calculated values of mechanical properties (Young Modulus) enhancements as a function of TiO₂ loading for the final reticulated inorganic / organic hybrid.

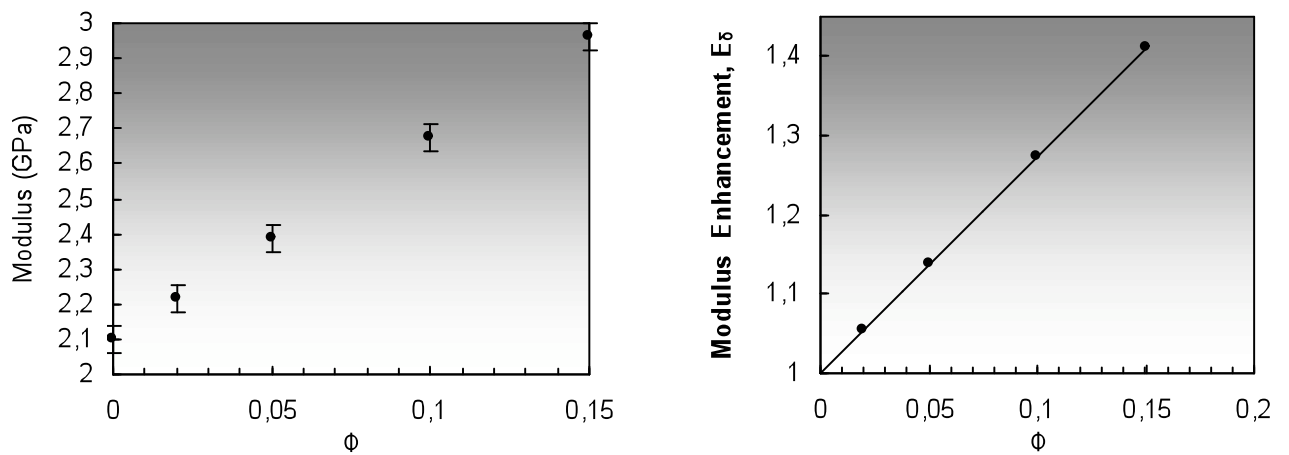


Figure 4: Mechanical properties enhancement as a function of TiO₂ loading.

Another type of system investigated in MULTIPRO is the printing ink. The dispersion of conductive nano-particles in the printing ink gives to the ink interesting electrical properties, thus allowing the manufacturing of electrical circuits using a printer rather than other technologies. One of the problems encountered in the final products is to avoid the formation of clusters that will reduce the percolation effect at constant loading of conductive nano-particles. **Fig. 5** shows how multiscale molecular modeling can predict the agglomeration and de agglomeration of silver nano-particles as a function of the solvent used.

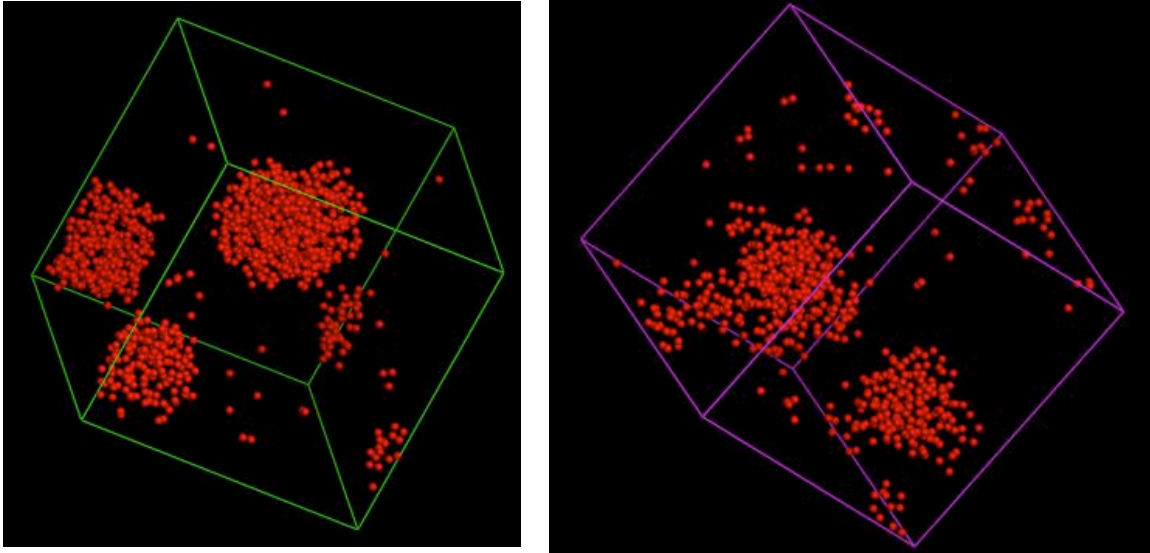


Figure 5: Agglomeration of nanoparticles.

¹ A full description of the modelling process, theory and the time evolution particle-particle composite system is shown on the MULTIPRO website [Modelling web page](#).

2a. Developing New Materials (Encapsulisation Materials).

Università degli Studi di Padova (University of Padova)

The high refractive index materials developed in the first two years, based on hybrid organic-inorganic matrices and titania nano-particles, were found to be particularly interesting for the fabrication of thick planar coatings, but not for the fabrication of hemispherical LED glob top, mainly due to the material cracking when deposited using the dispense system at CRP. The interest has been therefore shifted to a purely hybrid material containing phenyl groups and without inorganic fillers. This system (DPhTiA) has been synthesised starting from Titanium Isopropoxide, a Diphenylsilane precursor and a specifically synthesized plasticizer.

The refractive index of films obtained with this material is approximately 1,62 at 620nm, **Fig. 6**.

The precursor solution for this matrix material was also design to host the core-shell nano-particles necessary to produce white light from standard LEDs.

These particles have been already synthesised during the previous period, but their preparation had to be refined in order to get the right colour emission. Yellow emitting Quantum Dots (QD) with fluorescent quantum yield around 45% have been now obtained, **Fig. 7-8**. Such nano-particles can be treated with the usual procedures to make them compatible with the hybrid materials used in this project. The different emission effects can be seen in **Fig. 8** where the materials containing the new QDs are compared with the previous ones.

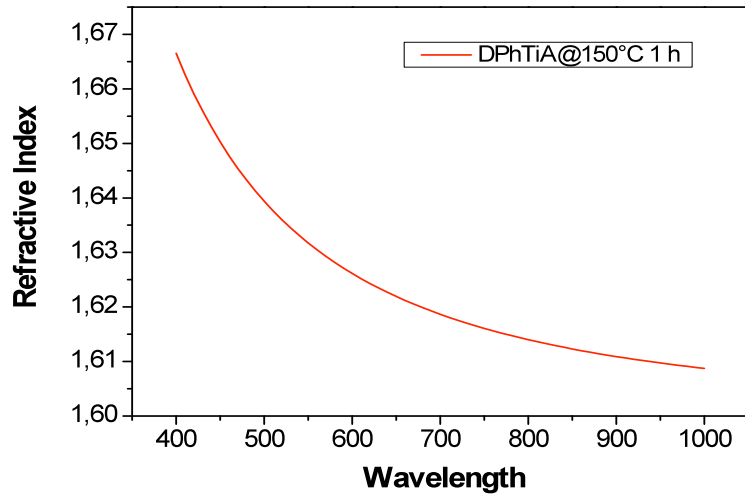


Figure 6. Refractive index vs. Wavelength for a film of DPhTiA cured at 150 °C.

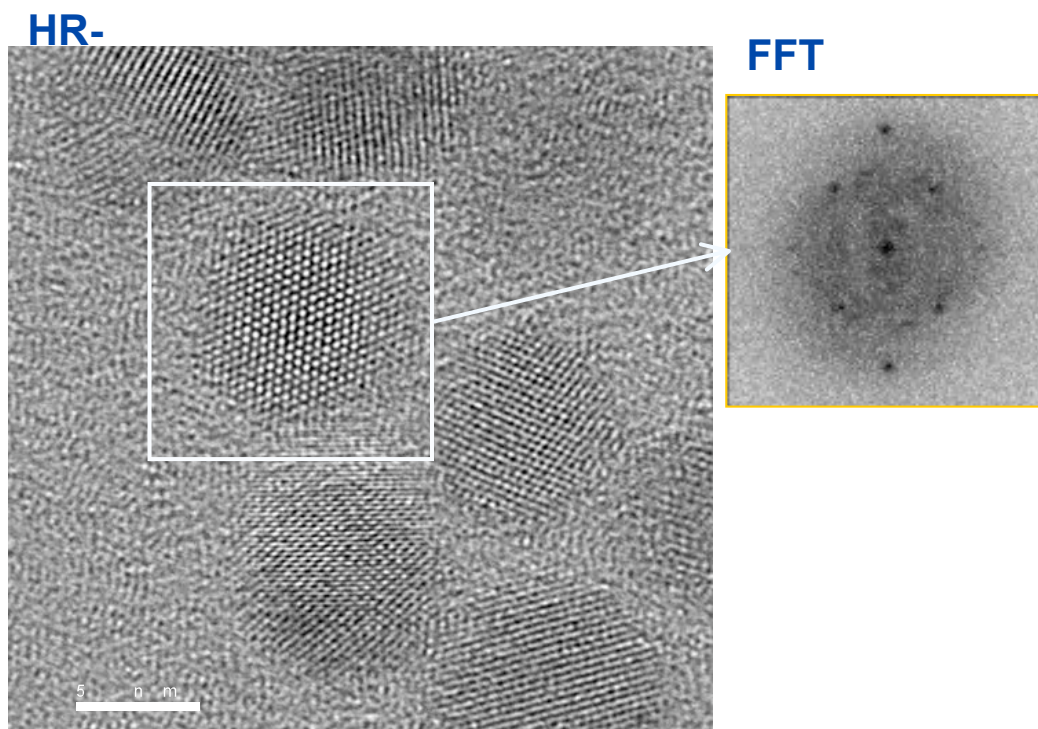


Figure 7. TEM and FFT images of multishell NPs

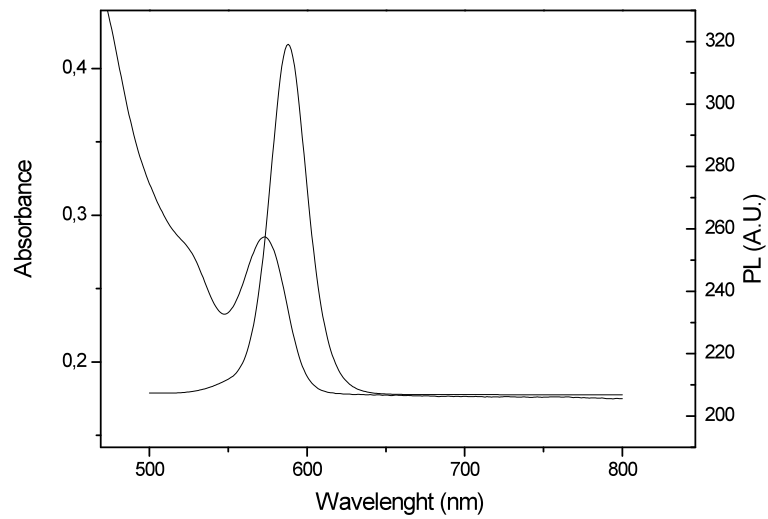


Figure 8. Absorbance and photoluminescence of yellow emitting QDs.



Figure 9. Red and yellow emitting particles in solution under standard UV lamp irradiation

The sol containing these nano-particles were tested for deposition both at IFAM and at CRP. Current work is focussed on addressing the ability to deposit hemispherical shapes of these materials and, more critically, the formation of bubbles at the edges of the LED upon curing.

2a. Developing New Materials (Conductive Silver Inks).

Cima NanaoTech.

The main goal of this work was to produce conductive ink with low resistivity which would be suitable for printing the LED circuits and interconnects. In order to achieve this goal, different formulae and different powders of Ag/Cu and Ag were used in the ink production.

P104

The resistivity of the conductive ink made from P104 (Ag/Cu) powder is usually too high when using low temperature sintering. The assumption is that Cu oxides, present as residue in the ink, are the cause for high resistivity. The material was modified by washing the nano-particle powder with ammonia after leaching step to dissolve surface Cu_2O contamination.

Inks were then prepared and tested from the washed powders. Two samples were sent to Fraunhofer IFAM for testing.

P2XX and P200 series

Assuming that Cu oxides are the cause for relatively high resistivity, P200 series inks, which do not contain Cu, may offer improved resistivity. A concern associated with the use of pure Ag in the ink is the some-what larger average particle size of the powder, which may disturb certain printing processes, such as ink-jet. Pure Ag nano-powders are routinely prepared in Cima for other purpose. Some of these powders were used to prepare inks according to current practice, and the ink was tested (one sample was sent to Fraunhofer IFAM for trial).

3. Reactive Deposition Technology.

Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung.

Work performed during month 24 - 30

IFAM optimized the M³D (now re-branded Aerosol Jet[®]) process parameters for deposition of sol-gel materials from UNIPD to achieve hemisphere shaped encapsulation of led chips. In **Fig. 10** a 45° side view of an encapsulated led chip is shown using a DphTiA with QD suspension.

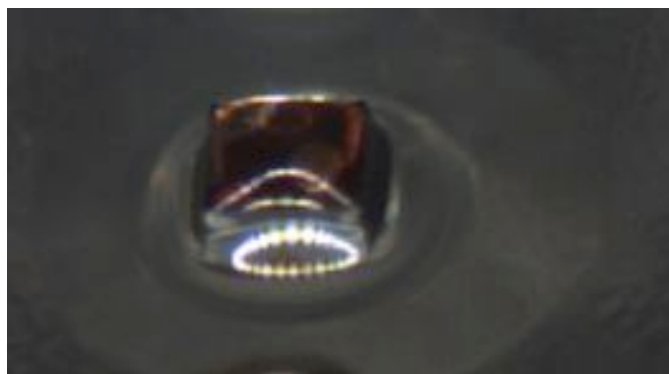


Figure 10. Encapsulation of an LED chip with a DphTiA with Quantum Dot suspension using the Aerosol Jet[®] process .

Besides IFAM evaluated the process parameters for Aerosol printed silver structures to achieve highest conductivity and best adhesion on the substrate. Now up to 70 % conductivity compared to bulk silver is possible. This optimized process parameters are used to print a 7 segment display demonstrator for led flip chip bonding, **Fig. 11**.

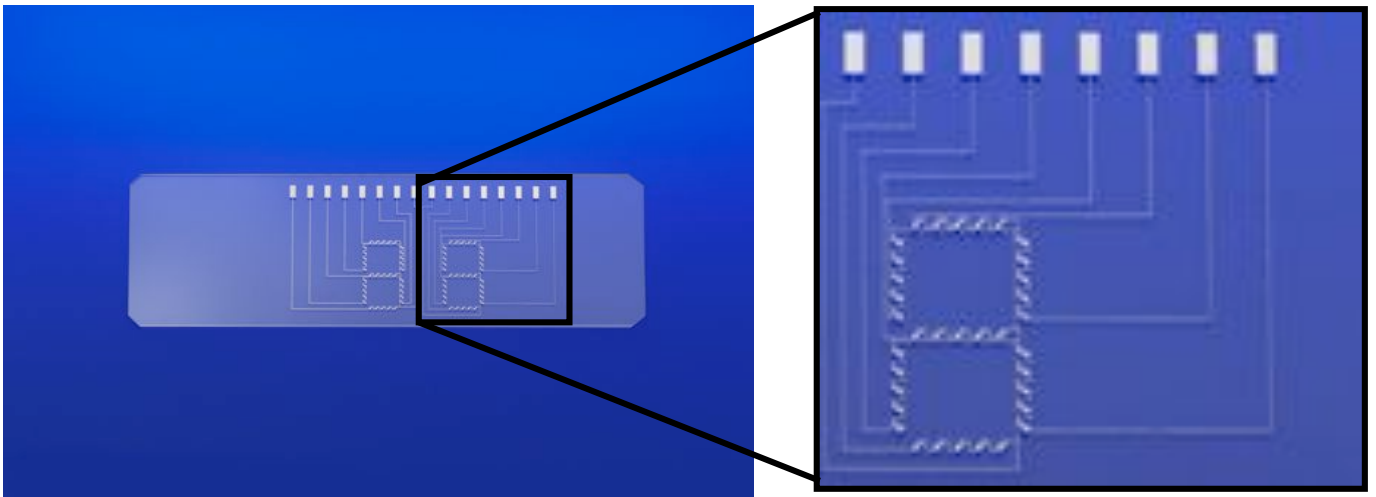


Figure 11: Aerosol Jet® printed 7 segment display demonstrator for led flip chip bonding.

4. Device Design.

Centro Ricerche Plast-Optica

The study proposed in MULTIPRO is strongly related to the needs of real life applications. The properties of the multi-functional materials under development will directly respond to the necessities of the industrial application.

For this reason, technology exploitation and validation is made by the realisation of three demonstrators in the field of LED-based lighting and display technology.

During the last year of the project CRP is going to design and develop three demonstrators:

- Head-up display (low content information) for automotive application;
- DRL (daylight running light) for automotive front lamp;
- Lighting device for general illumination.

Each demonstrator exploits the material and the technology developed in the framework of MULTIPRO project.

The first demonstrator designed by CRP is a LED-based spot light device. The demonstrator includes three chip-LED white sources coupled with optics in order to produce the light output according desiderata. In order to correctly design a priori the geometry of each demonstrator optical simulation has been performed. Ray tracing simulation tools allows the light to be designed by simulating the luminous output of the LED array, **Fig. 12**.

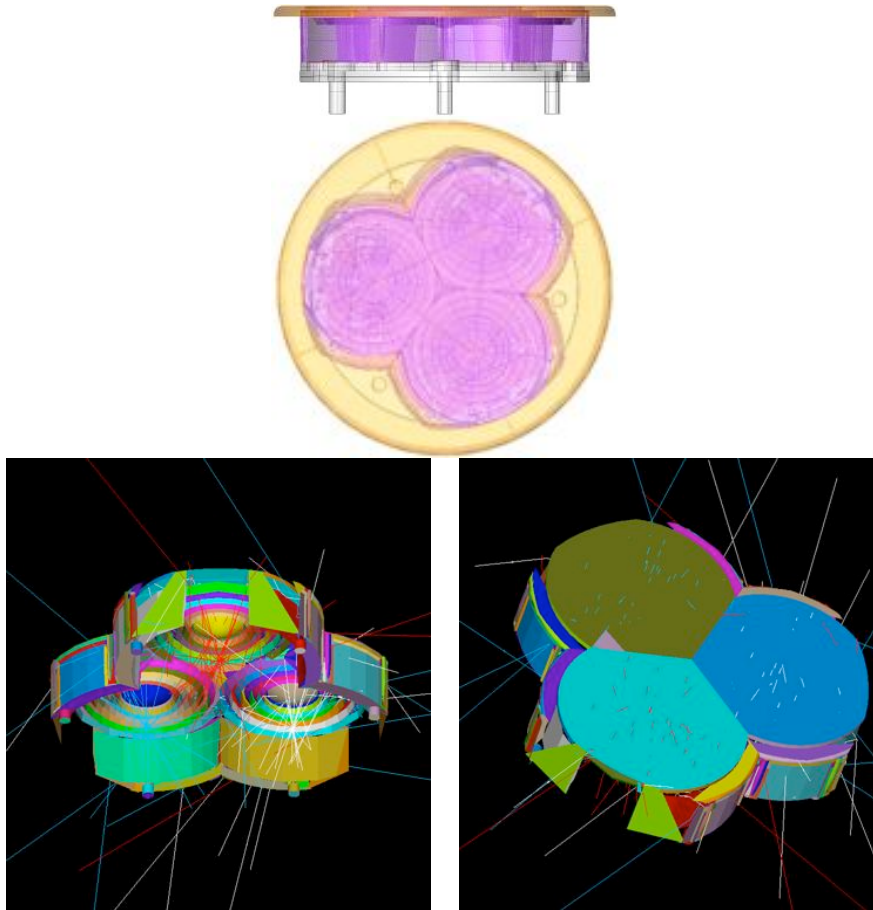


Figure 12. Optical design and simulation for 3 Watt spot lamp.

The white chip-LED sources will be assembled with COB technology at CRP labs. In particular the coating of blue chip-LED will be realized with UNIPD hybrid material that includes quantum dots for wavelength conversion for blue to yellow radiation. The packaging of the sources will be realized by M³D deposition technology, implemented by IFAM.