Periodic Report on Simulation and Experimental Results # 2

Plasmon Enhanced Photonics (PLEAS)

1st September 2006 – 30th August 2008

24 Month Report
Autumn 2008
www.eu-pleas.org

OBJECTIVES OF THIS REPORT

This report represents some of the work carried out within EU funded framework 6 project PLEAS on Plasmon Enhanced Photonics (ISA-FP6-034506). This report will be made available on the PLEAS website www.eu-pleas.org. This report is technical in nature and is a selection of work on the 'Simulation and Design of Plasmonic Enhancing Structures'. For non-technical reports please visit the Press Release page of our website.

The main object of the PLEAS project is to investigate specific plasmon enhancing structures for the photonics industry, along with an investigation of the technologies to implement them. In order to do this over the last 24 months we have concentrated on advancing our understanding of plasmon structures which can improve light emitting diodes (LEDs) and photodetectors. Due to the sensitive nature of this work, we only publish here initial work done on simulation and experiments for LEDs and photodetectors. For further details on this work and other work done within the project we refer you to the list of publication on the PLEAS website www.eu-pleas.org.

PLASMONS IN PHOTONICS INDUSTRY

Plasmonic phenomena have been investigated on light-emitting devices previously, focussing on the modification of the spontaneous emission by placing the metallic structure very close (< 50nm) to the emitter. The light can then be directly generated in a surface plasmon, which is then coupled to radiation by the appropriate structuring. In this way, non-radiative recombination processes can be suppressed. However, this technique is only beneficial for very low internal quantum efficiencies, initially most of the interest was for organic-LEDs and hence not applicable to high-efficiency state-of-the-art LEDs. Here we investigate plasmon phenomena to improve inorganic LEDs.

Many claims in the literature of extremely high transmission through sub wavelength apertures, have been misleading. This perhaps explains why there has been little implementation in commercial detectors. The aim is obtain valid improvements on useful functionalities for commercial applications.

CONCEPT AND DESIGN OF PLASMON ENHANCING STRUCTURES

The state of the art in plasmonic phenomena such as enhanced transmission, beaming apertures, and simple light harvesting structures are just the start of research into plasmonic concepts that can enhance emission and photodetection. Many topics are to be addressed: what happens to enhanced transmission structures when placed on high index substrates? How do guided modes couple through sub-wavelength apertures? How can reflection losses be removed in light harvesting structures. The main differences between emitters and detectors is that plasmon enhanced structures, must be fully conductive for emitters and therefore mainly continuous structures will be considered, while for detectors the plasmon structures may be discontinuous as a conductive contact is not required.

The main topics which will be studied for emitter applications are hole arrays. For detectors light harvesting structures and circular gratings will be studied as well as field enhancing structures such as particles.

MODELLING

There were several different methods used to model light extraction and collection: i) modal-expansion method with surface impedance boundary conditions in the horizontal interfaces, ii) finite-difference time domain (FDTD) method, iii) transfer matrix method and the multiple-multipole method. Generally there is a good qualitative agreement between the results obtained with these methods.

Several structures such as harvesting structures and periodic structures have been studied and modelled for photodetectors. The aim of these structures is to improve the photodetector either by improving the signal to noise ratio or by adding functionality in polarisation and spectral filtering. Both symmetric and a-symmetric structures were modelled and it was shown that symmetric structures, i.e. ones with the same material either side of the metal generally give the best results.

A substantial amount of time was put into a reasonable normalisation method for harvesting structures as the figures quoted in the literature seem at best misleading. This is due to the fact that normalisation was often made using a sub wavelength aperture through which very little light passes. This results in very large enhancement factors; however the total light remains low, which for practical applications are of little use.

Several optimised designs have now been made and are currently being trialled for photodetectors.

The modelling for light extraction in LED technology focussed on transparent contacts and extractor filters (polarisation and colour). In order to do this we investigated hole and slit arrays with different hole shapes and nanoparticles. To obtain results which can be implemented in industry we investigated structures not only on glass but also on Gallium Phosphide (GaP) which is a high index transparent material used to test structures before transferring them to LEDs. Angular measurements were also made a high brightness is a key issue in modern lighting. Here we report on some of our results on rectangular holes, slit arrays and metal nanoparticles for light extraction.

RECTANGULAR HOLE ARRAYS

Rectangular-hole arrays were extensively studied during the first year of the project in order to understand the physical mechanisms for enhanced light transmission in these structures, as it was reported in the first *Periodic Report on Simulation and Experimental Results.* That study revealed that the transmission peak appearing near the cut-off frequency was the most convenient for light extraction in LED. During the second year of project PLEAS, the modelling work on rectangular-hole arrays has concentrated on the optimization of geometrical parameters for light extraction applications.

Rectangular-hole arrays have been simulated with both the modal-expansion method with surface impedance boundary conditions in the horizontal interfaces and FDTD methods. The main difference between the modal expansion method and FDTD is in the absorption. The modal expansion method slightly underestimates the absorption because absorption occurring within the hole walls is not included in this method. Despite this underestimation in the absorption the modal expansion method can be used for optimizing the geometrical parameters of hole arrays for light extraction applications.

The geometrical parameters of square hole arrays for light extraction were optimized by means of the modal-expansion method. The incidence is considered from the GaP substrate. Two different metals were used in the calculations: gold (results in Fig. 1) and silver (see Fig. 2 for results). As a result of the high index of refraction of the substrate, short periods and large holes should be considered in order to obtain a high transmission. Absorption is significantly lower in silver structures than in gold ones. Therefore, it is more convenient to use silver in order to have less absorption and a more efficient light extraction.

For hole arrays on GaP substrate, transmissions between 20% and 40% can be achieved. However, absorption is perhaps higher than desirable (4% in silver, the metal with less absorption). Another important issue is the low metal coverage of the optimized structures, which might be a problem for the metal film acting as an electrical contact.

Calculations were also performed for analyzing the dependence of the total transmission on the angle of incidence. For symmetric structures (where the GaP is surrounded by the same material on either side), the spectral locations of the transmission peaks do not depend much on the angle of incidence. However, for non-symmetric structures (as in the case of hole arrays on a GaP substrate), the transmission peaks present a strong dispersion with the angle of incidence. This effect is due to the electromagnetic coupling between the waveguide modes and the SPPs on the two metal-dielectric interfaces.

In conclusion although relatively high transmission (~30%) can be achieved using hold arrays on GaP the structure proposed have low metal coverage which may make them hard for contacting. Also the least angular dependent structures are those which are symmetric which are technologically challenging to make.

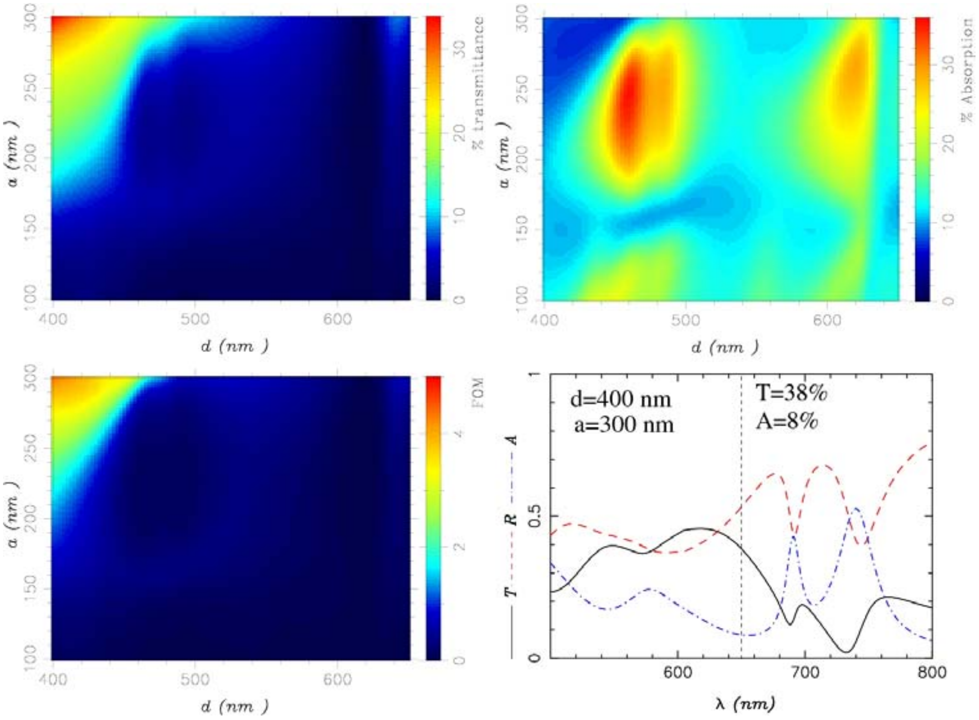

Figure 1. Transmission, absorption and FOM (figure of merit= transmission/absorption) as a function of the period *d* and the hole side *a* for a square hole array in 200nm thick gold film. Normal incidence is from the GaP substrate. The last panel shows the transmission, reflection, and absorption as a function of wavelength for period d=400nm and hole side a=300nm. Calculations were performed with the modal expansion method.

PLEAS
PLASMON ENHANCED PHOTONICS

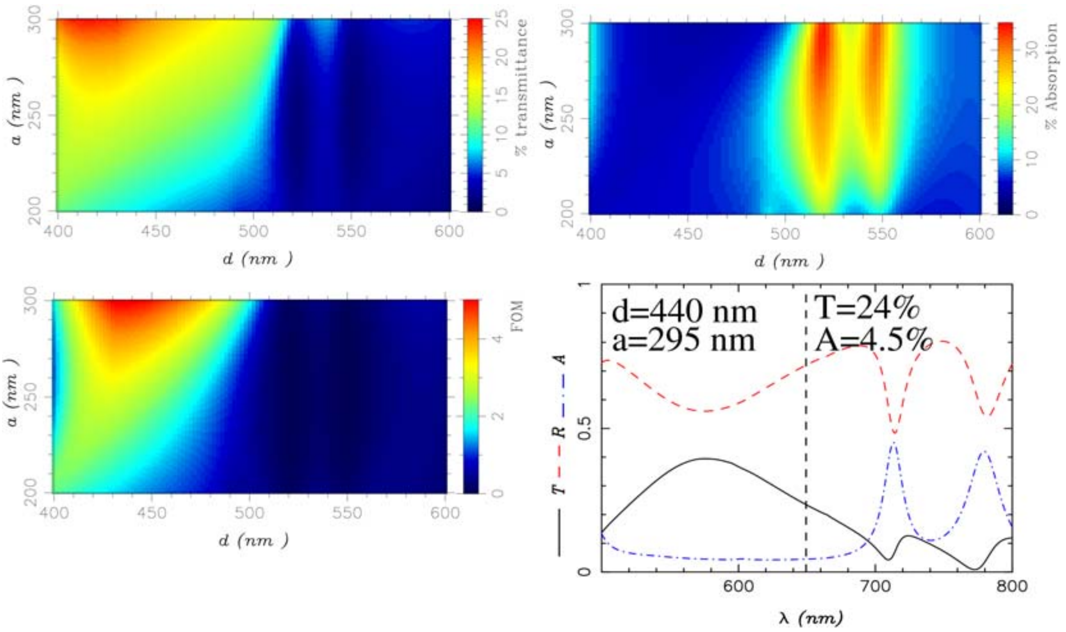

Figure 2. Transmission, absorption and FOM (figure of merit=transmission/absorption) as a function of the period *d* and hole side *a* for a square hole array in 200nm thick silver film. Normal incidence is from the GaP substrate. The last panel shows the transmission, reflection, and absorption as a function of wavelength for period *d*=440nm and hole side *a*=295nm. Calculations were performed with the modal expansion method.

SLIT ARRAYS

During the last six months the modeling work has focused on the theoretical study and optimization of slit arrays for light extraction applications. The structures that have been investigated are metal slit arrays sandwiched between ZnO slabs. In particular, in the calculations, ZnO slabs are considered as semi-infinite.

In order to study the transmission properties of these structures, three different methods have been used: i) transfer matrix method, ii) modal expansion method with surface impedance boundary conditions on horizontal interfaces, and iii) multiple-multipole method. There is a good agreement between the numerical results obtained with the transfer matrix method and the multiple-multipole method. On the other hand, the used modal-expansion method provides semi-quantitative results for real metal in the optical regime and slightly underestimates the absorption because absorption at the slit walls is not included in the method. To have a good description of the absorption is an important issue for light extraction applications and hence the analysis that is reported below has been performed by means of the transfer matrix method.

First structures with short periods are explored in order to try to get a large transmittance at the wavelength of interest (λ=650nm). The idea was to try to be in the regime where only the zero-order is propagating in ZnO. Fig. 3 shows the total transmittance and absorption for a silver slit array with period d=150nm. Even with such a short period, it was not possible to obtain a significant transmittance at λ=650nm and the absorption is rather high.

A similar analysis was performed for gold slit arrays (see Fig. 4). Transmission was very low at the wavelength of interest (λ=650nm) and absorption was higher than for the silver structure. In conclusion, the strategy of shortening the period of the slit array was not successful for achieving high transmissions at λ=650nm.

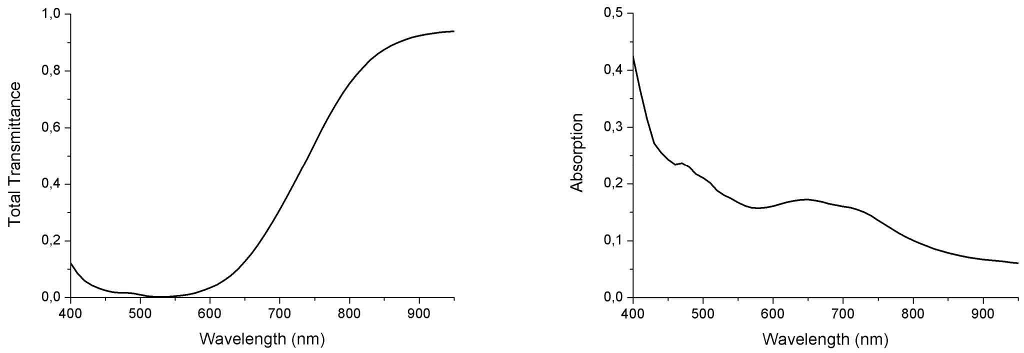

Figure 3. Total transmittance and absorption for normal incidence for a silver slit array with period d=150nm, slit width a=50nm, and film thickness h=200nm. The slit array is sandwiched between ZnO slabs. The results were calculated with the transfer matrix method.

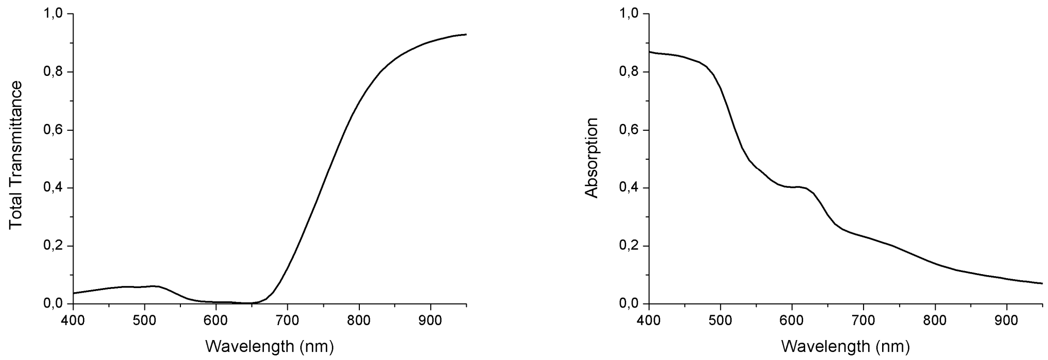

Figure 4. Total transmittance and absorption for normal incidence for a gold slit array with period d=150nm, slit width a=50nm, and film thickness h=200nm. The slit array is sandwiched between ZnO slabs. The results were calculated with the transfer matrix method.

Next, structures where several orders are propagating in ZnO were examined. Parameters such as the period and the slit width were varied and optimized in order to have a transmission peak near λ=650nm. For silver slit arrays, the optimized geometrical parameters were: period d=350nm, slit width a=100nm, and film thickness h=200nm (see Fig. 5 for total transmittance and absorption spectra). For these parameters and λ=650nm, a total transmittance at normal incidence of around 24% was achieved, with absorption of 7% (a ratio total transmittance/absorption of approximately 3.5). The absorption obtained in slit arrays (7%) is higher than the calculated absorption for the optimized hole array structure (4%). However, different theoretical approaches were used in analyzing slit arrays and hole arrays. In particular, hole arrays were simulated with the modal-expansion method, which slight underestimates the absorption in the structure.

Similar slit array structures made of gold were simulated, obtaining total transmittances near 30% but much higher absorption (27%) than for silver structures (see Fig. 6). Consequently, and in line with the findings for hole arrays, silver structures are more convenient for light extraction applications due to their lower absorption.

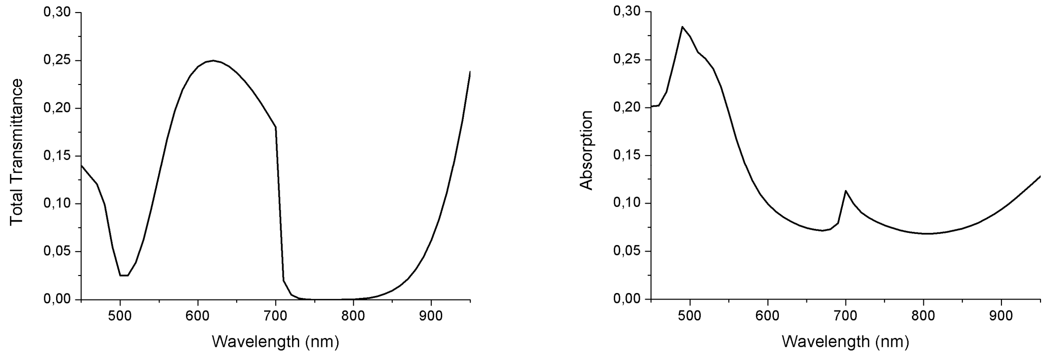

Figure 5. Total transmittance and absorption for normal incidence for a silver slit array with period d=350nm, slit width a=100nm, and film thickness h=200nm. The slit array is sandwiched between ZnO slabs. Results calculated with the transfer matrix method.

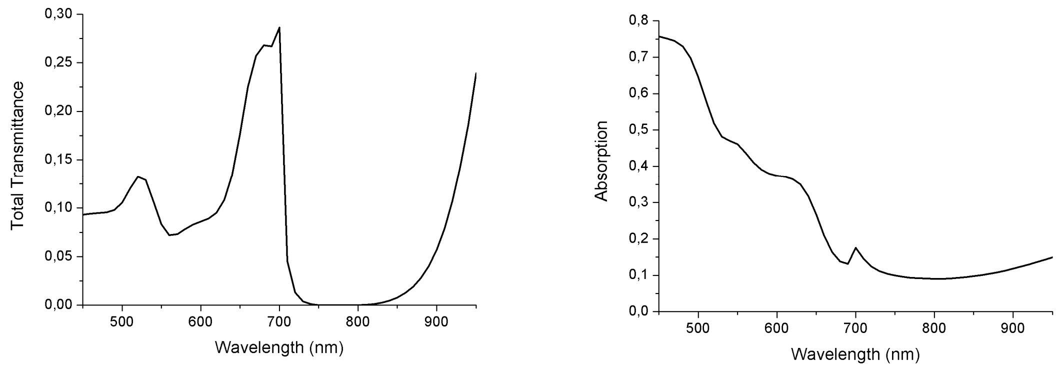

Figure 6. Total transmittance and absorption for normal incidence for a gold slit array with period d=350nm, slit width a=100nm, and film thickness h=200nm. The slit array is sandwiched between ZnO slabs. Results calculated with the transfer matrix method.

For the optimized silver slit array structure, transmission properties as a function of the angle of incidence were analyzed, as is illustrated in figure 7. The total transmittance at λ=650nm varies significantly with the angle of incidence, reaching zero for approximately 8 degrees. The transmittance is only significant for small angles of incidence; it is very low for angles near and above 8 degrees, which is a detrimental property for light extraction applications.

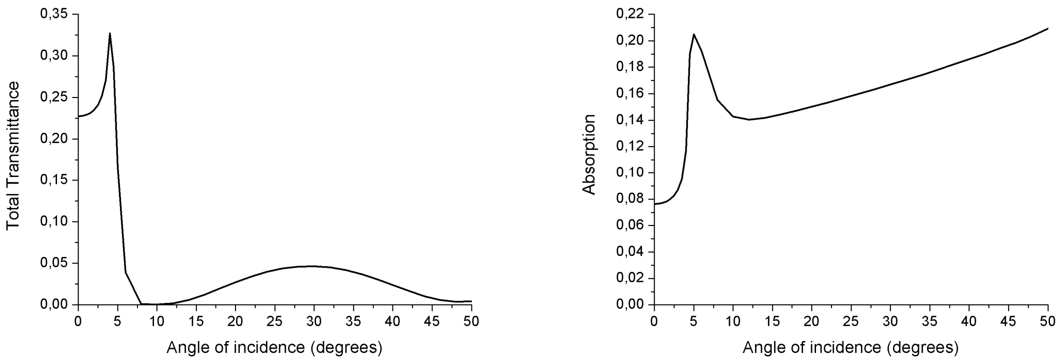

Figure 7. Total transmittance and absorption as a function of the angle of incidence for a silver slit array with period d=350nm, slit width a=100nm, and film thickness h=200nm and wavelength in vacuum λ=650nm. The slit array is sandwiched between ZnO slabs. These results were calculated with the transfer matrix method.

In order to understand the angle of incidence dependence shown in figure 7 for a fixed wavelength of λ=650nm, total transmittance spectra for different angles of incidence were calculated (see Fig. 8). The minimum initially for normal incidence at λ= d n_{ZnO} shifts to shorter wavelengths for increasing angles of incidence. Eventually, this minimum crosses the wavelength of interest (λ=650nm) for an angle of approximately 8 degrees.

In conclusion, the results so far obtained for slit arrays are not very encouraging for the utility of slit arrays in light extraction applications, especially due to the strong dependence on the angle of incidence.

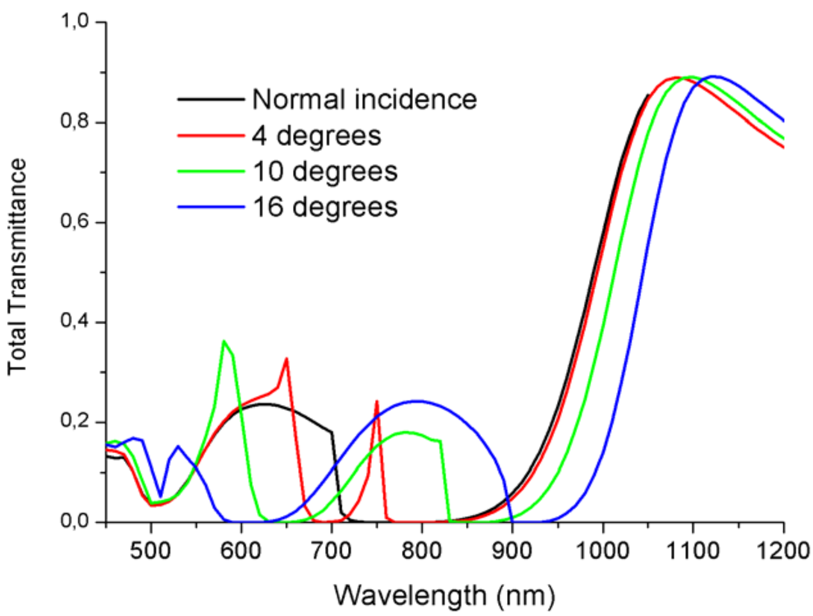

Figure 8. Total transmittance versus wavelength for several values of the angle of incidence and a silver slit array with period d=350nm, slit width a=100nm, and film thickness h=200nm. The slit array is sandwiched between ZnO slabs. There results were calculated with the transfer matrix method.

COUPLING OF A SINGLE LUMINESCENT EMITTER AND A METAL NANOPARTICLE

Field enhancement through metal nanoparticles (MNPs) is envisaged here for solid luminescent emitters consisting of GaP. In the 3-dimensional theoretical study carried out by the Technical University of Dresden (TUD) with the multiple-multiple (MMP) technique a single emitter is considered whose emission frequency coincides with the band gap of GaP, embedded in a matrix of n = 3.5, which corresponds to the refractive index of GaP. The single emitter may be placed at any position in space in order to calculate its fractional contribution to the overall emitted light flux.

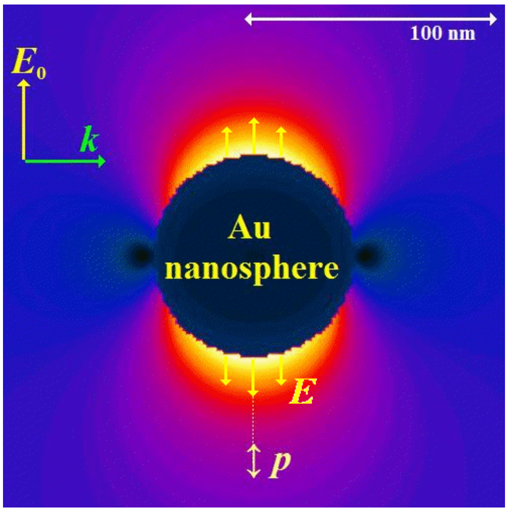

Figure 9. Electric field distribution around an 80nm Au nanoparticle illuminated with linearly polarized light at 532nm from the left.

At short distances between the emitter and the MNP the near-field of the emission dipole couples to the free-electron gas of the metal, exciting a dipole and to some extent also higher multipoles in the MNP. This dipole efficiently radiates energy to the far field, thereby acting as an antenna. As a result, the radiated power is increased compared to the situation when the emitter is far away from any MNP. This means that the energy is very efficiently extracted from the emitter, which makes MNPs promising as a means of improving the out coupling from LEDs. The effect is closely related to the field enhancement occurring at the MNP when the MNP is illuminated by light. There is a spectral dependence with a pronounced resonance depending on the material, size, and shape of the MNP, and on the surrounding medium. The relaying of the energy via the MNP is, however, also subject to loss of energy by dissipation in the MNP. We may express this latter effect as a decrease of the quantum efficiency occurring when the emitter is brought close to the MNP. In spite of this energy loss, the overall effect in a LED may still be a gain in efficiency, as the MNP is able to convert energy that would normally be lost due to total internal reflection into freely propagating light.

The coupling between the emitter and the MNP strongly depends on the relative orientation of the emission dipole, namely whether it is perpendicular or parallel to the MNP surface. In the present case, the parallel orientation is much more favourable than the perpendicular one. Both the quantum efficiency and the radiation power (see Fig. 9) are lower in the latter case.

The calculations were so far carried out for a gold MNP having a diameter of 80nm. TUD has a lot of experience with such particles. Former experiments were, however, performed with the particles embedded in media with much lower indices of refraction. Therefore, future simulations will focus on finding the optimum conditions (in particular the optimum particle size) for the high-index semiconductor environment and will also properly take into account the semiconductor/dielectric interface.

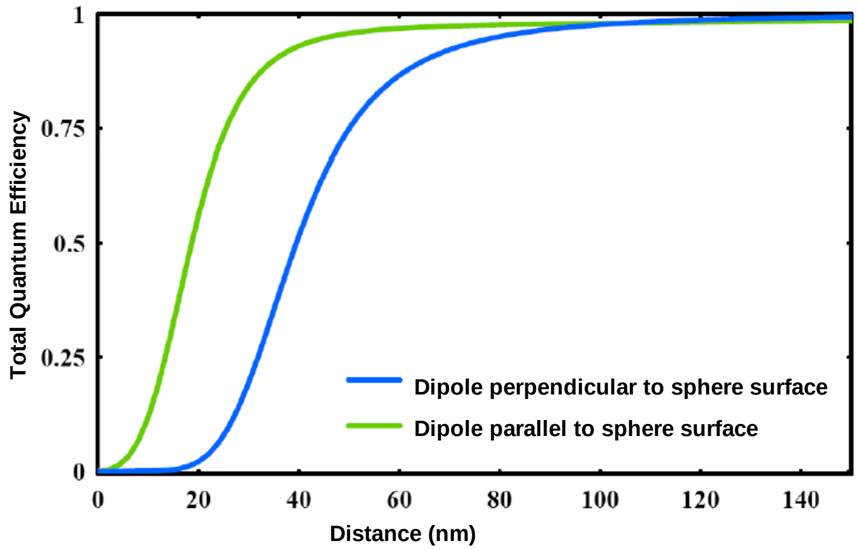

Figure 10. Total quantum efficiency calculated for a single dipolar emitter approaching the gold nanoparticle surface. Note the different behaviour of emitter dipoles lying parallel and perpendicular to the MNP surface.

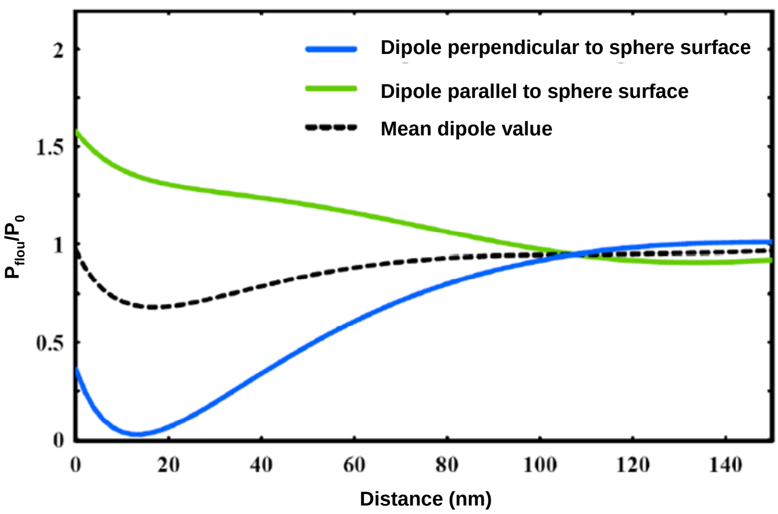

Figure 11. Shows overall normalized power flux as a function of emitter–MNP distance. As seen, dipoles emitting light being polarized parallel to the MNP surface is more efficiently enhanced, while a perpendicular polarisation rather leads to a strong quenching at short separations.

EXPERIMENT

The experiments are designed to characterise the behaviour of the plasmon enhancing structures through surface and optical measurements. Work has been undertaken by the various partners to study the chosen structures for both the LEDs and the photodetectors.

For the lighting applications, each partner studied a different type of structure (nanoparticle, hole, slit and annular hole arrays) in order to study a wider range of structures. Experimental measurements in both the near field and far field have been undertaken on glass, GaP and on working encapsulated and non-encapsulated LEDs. Spectra of the normalised transmission (with angular dependence) and polarisation have been taken. These results are currently being published so we refer the reader to the publication list on the website www.eu-pleas.org.

For the photodetectors measurements on harvesting structures and slit arrays which characterised the normalised transmission and, the spectral and polarization filtering were made. Nearfield measurements have also been made on metal nanoparticles. Work has now begun characterising plasmonic structures on CMOS fabricated detectors. Below we detail both far field results i.e. on spectral and polarization filtering and near field results i.e. when looking at metal nanoparticle interaction with emitting or absorbing object.

SPECTRAL AND POLARIZATION FILTERING

By introducing a metal film with SPP based optics in the collection process of an array of photodetectors; we could possibly collect separately different spectral components of the incident light in the same area but send them to different photodetectors. If losses are minimal, this would be advantageous for spectral and polarization sensitive imaging. Through a collaboration between ULP and Torbjorn Skauli (FFI, Lillestrom, Norway), we have looked into this issue using first Bulls Eye's as prototype structures. Figure 12. Below compares the transmission intensity of 3 Bull's Eyes with different periods, and therefore different resonance wavelengths, as they overlap more and more. A linear gradient in the groove structures of each Bull's Eye with the grooves becoming shallower for the outermost ones. This was introduced in order to minimize the perturbation of the transmission of the other Bull's Eyes.

The results are quite promising as can be seen in figure 12. since there is a drop in intensity only for overlaps larger than 70%. It shows that plasmonic structures can sort photons and redirect them to decoupling features such as the holes.

Encouraged by these results, we then tested slits surrounded by overlapping corrugations in a triangular lattice as shown in figure 13. The absolute transmission efficiency of the whole structure depends on a number of parameters, including the slit width and depth. We have found that we can reach ca. 10% absolute transmission which is quite significant when one considers that the maximum possible is 50% in view of the polarization selective nature of the structure. This property is additionally interesting for polarimetric imaging. Further optimization is still necessary and the structures should preferably be tested directly on photodetector pixels

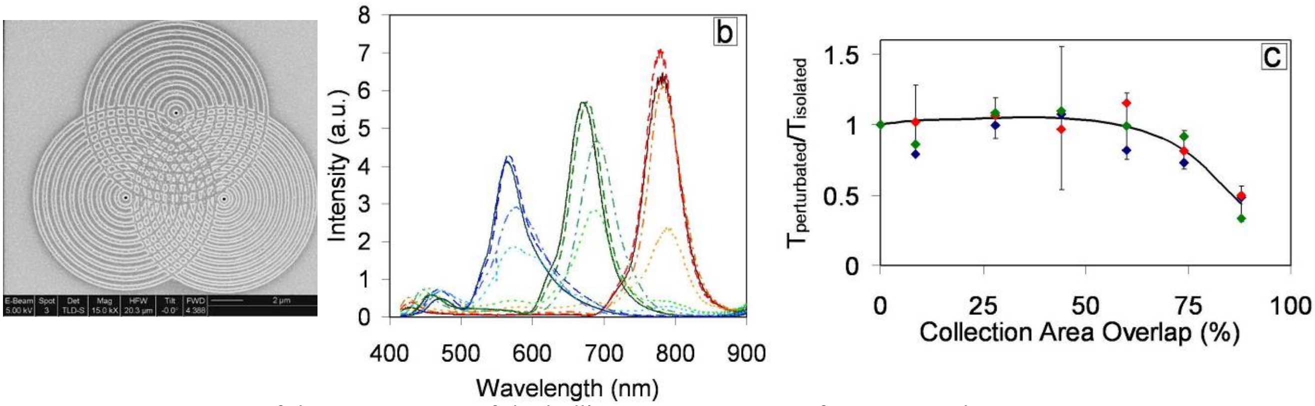

Figure 12. Comparison of the transmission of the bull's eye structures as a function overlap.

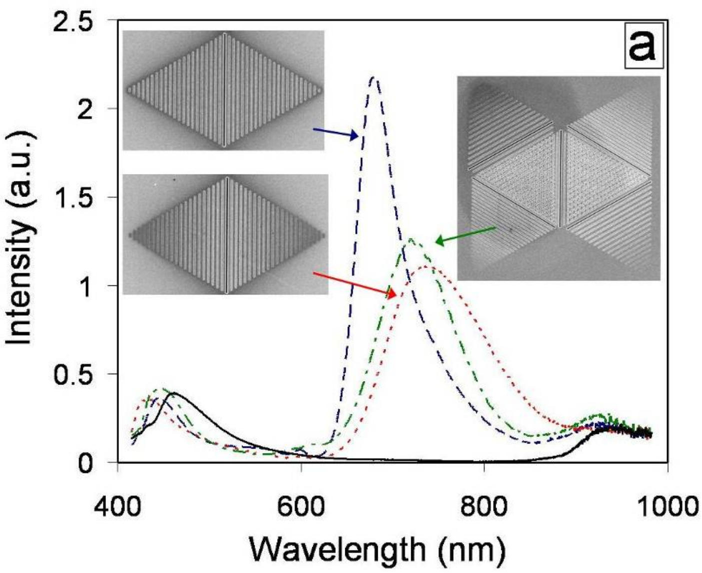

Figure 13. Slits surrounded by grooves (blue, without groove gradient, red with groove gradient and green with overlapping grooves in a triangular lattice

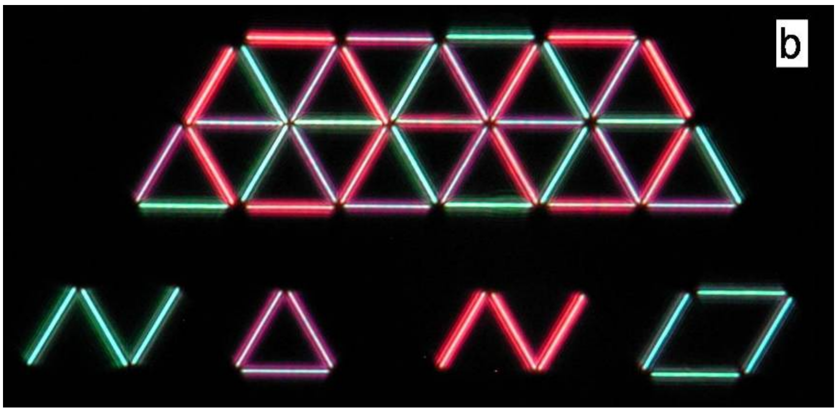

Figure 14. Microscope image of transmission through such a triangular lattice

METAL NANO PARTICLE INTERACTION WITH EMITTING OR ABSORBING OBJECT

Aiming at precise experiments on the single-particle level, TUD has developed a method which allows them to attach single gold nanoparticles to the tip of an atomic force microscope (AFM) or of a near-field optical microscope. First, particles suspended in water are deposited on a substrate and the liquid is removed by dry-blowing. Then, a particle is identified in an optical microscope by its characteristic spectrum, and the tip, after having been coated by a linker molecule such as 3-amino-propyl-trimethoxy-silane (APTMS), is lowered onto the particle. Chemical bonds are formed between the particle and the linker molecules such that the particle becomes firmly attached to the tip (fig. 15.). Such single-particle probes are ideally suited for studying the fundamental processes of the interaction between a MNP and an emitting or absorbing object. In the present context of light-out coupling from LEDs they will be used to study how particles can serve to scatter light out of a high-refractive-index substrate.

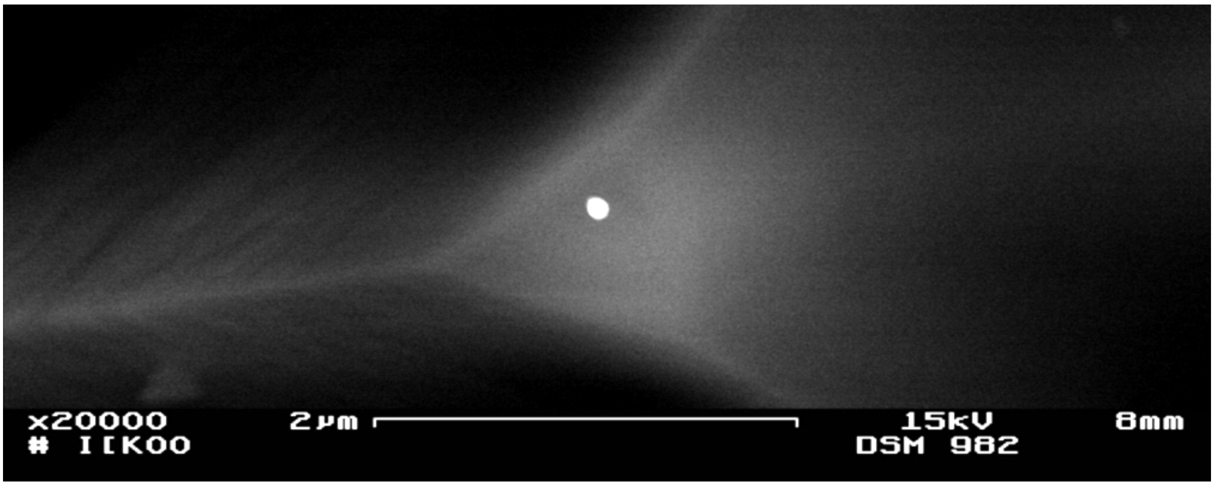

Figure 15. Electron micrograph of an 80-nm gold particle attached to an AFM tip.

To illustrate the possibilities for well-defined experiments offered by such probes, figure 16 shows a measurement of the interaction between two MNPs. The larger MNP was attached to the tip and was then moved across a second, smaller MNP that had been deposited on a substrate. The larger MNP had been covered by a monolayer of organic molecules which produced a Raman scattering signal. This signal was used to study how the field enhancement increases when the two MNPs are brought close together.

To capitalise on the field enhancement in the far field it would be necessary to scatter several particles at well defined distances. This is currently under investigation.

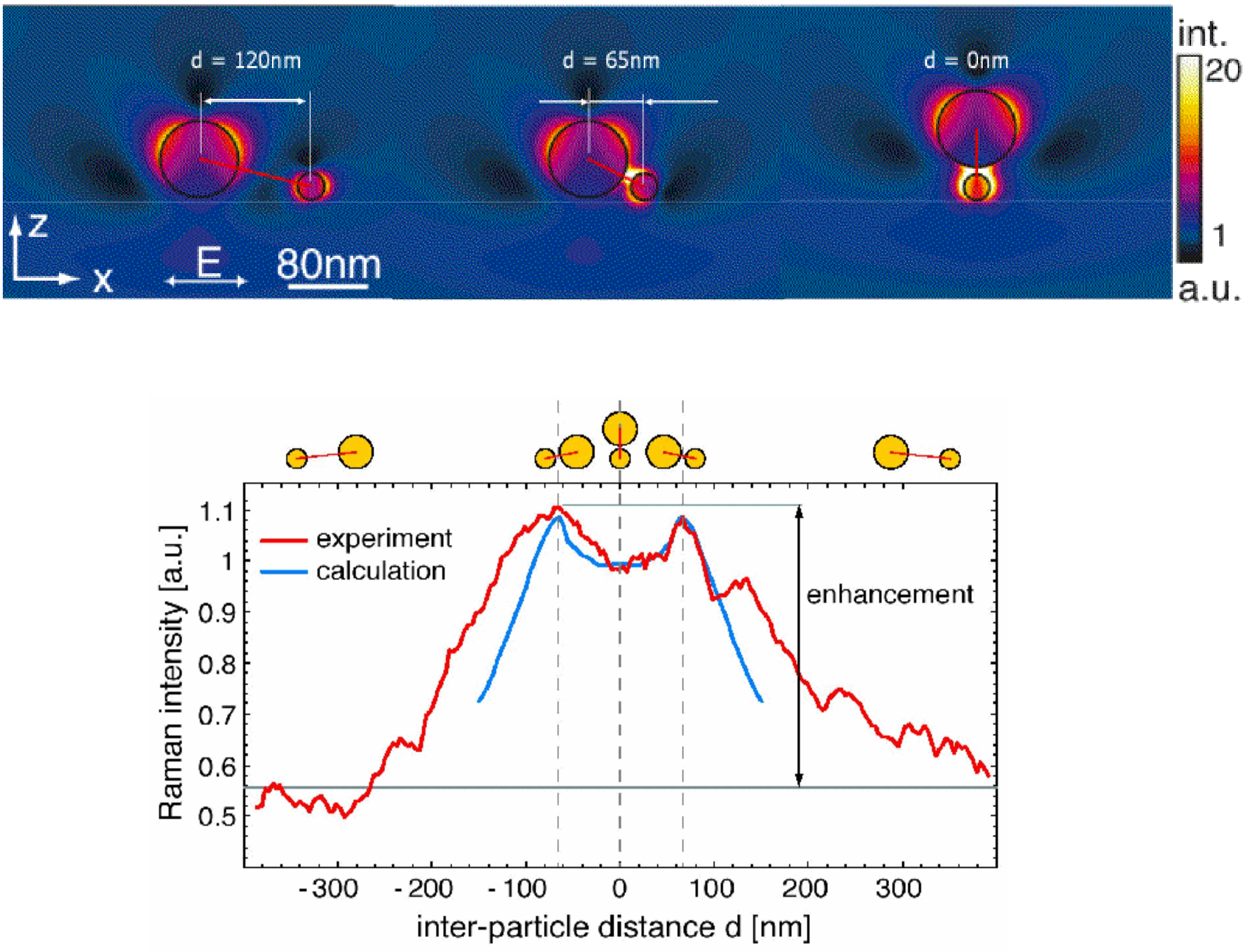

Figure 16. Interaction of two MNPs. The upper panel shows the intensity distribution calculated by MMP for three different distances between the particles. The illumination is by a plane wave from below. In the experiment, the Raman signal produced by thiol molecules deposited on one of the gold spheres was monitored while the larger particle, attached to a fibre tip, was moved across the smaller particle.

CONCLUSIONS

In this report we summarized some of the experimental and simulation work done within the PLEAS project. The main conclusions are as follows:

Rectangular hole, slit arrays and metal nanoparticles were investigated theoretically as systems to obtain good light extraction from LEDs. Several drawbacks were shown such as strong angular dependence of slit arrays, and the low metal coverage for rectangular arrays. The latter may result in increased resistance if the metal were to be used as a contact. Metal nanoparticles (MNP) were shown to give loss due to energy dissipation of the MNP, however it was also shown that the field enhancement may more than compensate this effect.

Experimental investigations into spectral structures for photodetectors were investigated. Bull’s Eye structures were shown to give good optical properties even when overlapped, with 10% full transmission and full width half maximum of 50nm. To further obtain polarisation structures slit and groove structures were also made.

The effect of MNP’s on absorption and emission of light was investigated when two such particles were brought into contact with each other and their Raman intensity was measured. Enhanced interaction has an influence not only on the LED emission but also on using a MNP as an antenna to help detection. This work is being extended to arrays of MNP’s..

Many of the challenges alluded to in the report show the importance of understanding the fundamentals of plasmons so that the engineering challenges which arise when bringing plasmons to the market place can be met. As this is only a representative sample of some of the work, the reader is referred to the website for further details and the latest publications by the consortium.

THE CONSORTIUM

The PLEAS project stretches from the fundamentals of plasmons to the industrial application and is reflected in the consortium members:

Institute	Country	Project leader
Centre Suisse d'Electronique et de Microtechnique SA (CSEM)	Switzerland	Ross Stanley (Co-ordinator)
Universidad Autonoma de Madrid (UAM)	Spain	Francisco J. Garcia-Vidal
Universidad de Zaragoza (UNIZAR)	Spain	Luis Martin-Moreno
Osram Opto Semiconductors GmbH (Osram OS)	Germany	Reiner Windisch
The Queen's University of Belfast (QUB)	United Kingdom	Anatoly Zayats
Technische Universität Dresden (TUD)	Germany	Lukas M. Eng
Université Louis Pasteur de Strasbourg (ULP)	France	Thomas Ebbesen
SAGEM Défencse Sécurité (SAGEM)	France	Eric Agostini

For more details on the consortium, and other aspects of the project please visit www.eu-pleas.org.