# NANOPHOTONICS FORESIGHT REPORT



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## **About this Report**

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This document is the report of a Nanophotonics Foresight Workshop held in November 2010 in Barcelona, Spain. The purpose of the workshop, facilitated by the Nanophotonics Europe Association, was to inform long-range research and development planning at the European level. The views, ideas, conclusions and recommendations presented in this report are those of the workshop participants.

## Nanophotonics Europe Association

The Nanophotonics Europe Association (NEA) is a not-for-profit organisation created to promote and advance European science and technology in the emerging area of nanophotonics. The goals of the association are fourfold:

- 1.To promote research in nanophotonics by coordinating the efforts of the various players involved, and, in particular, by encouraging collaboration between academic institutions and industry.
- 2. To create a common interest group that represents member's interests with national and transnational scientific government funding agencies, technology platforms, professional associations and the general public.
- 3.To integrate the resources and strategies of its members.
- 4. To facilitate the exchange of information, ideas and data.

More information can be found on the NEA website: www.nanophotonicseurope.org

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## PREFACE

The purpose of the Nanophotonics Foresight Workshop was to examine the trends and opportunities of nanophotonics science as applied to existing photonic technologies. For this, the workshop assembled science and technology leaders from across Europe to assess the road ahead for nanophotonics and map the potential industrial impact. The result is a snapshot of the state of the art in nanophotonics as well as research and development (R&D) topics that are likely to offer important benefits for the photonics industry, society and the research community.

Photonics is a critical area of R&D for society and the economy. It is seen as a key enabling technology (by the European Commission) to address the 'grand challenges' in healthcare, climate change, information technology, among others. At the European level, the technology platform Photonics21 helps define the priorities for scientific research, technology and development in the mid- to long-term. In January 2010 the platform published its second Strategic Research Agenda (SRA) addressing the application/research areas where photonics will have the biggest impact: Information and Communication; Manufacturing and Quality; Healthcare and Life Sciences; Lighting and Displays; Safety and Security; and Optical Components and Systems.

At the same time, nanophotonics, where optical nanomaterials can slow down, trap, enhance and manipulate light at the sub-wavelength scale, has become a major research area and is making important advances towards optical communications, (nano)imaging and sensing applications. Researchers are also turning their attention to photovoltaics and light emission to tackle energy issues. However in translating academic nanophotonics research to industry many practical roadblocks have to be overcome, for example, nanofabrication, manufacturability, cost etc. With these challenges in mind, the workshop was organised to solicit inputs from the research community regarding the contribution and impact of nanophotonics within the application areas identified by Photonics21 (Work Groups). The two-day meeting consisted of plenary sessions in which the sub-disciplines of nanophotonics were defined, the expectations of the European Commission discussed as well as actual research trends. Breakout sessions were organised around the topics of the Work Groups. In these sessions, participants considered application opportunities for nanophotonics within each of the core photonic sectors; they evaluated the state of the art of several nanophotonic concepts, materials, processes and technologies, and identified technological challenges and research barriers to be overcome.

This report summarises the discussions and findings of the group as well as opportunities and priorities for nanophotonics. Any views, ideas, conclusions or recommendations presented here are those of the workshop participants. The report is intended to provide insertions points for nanophotonics to the *Photonics21* SRA within the work groups, as well as research directions for scientists and policy makers.

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## Nanophotonics A FORWARD LOOK

While nanophotonics has emerged as a dynamic and prolific research area, concerned with the generation and manipulation of light at the nanoscale, translating research success into next generation photonic devices remains a challenge.

Photonics, the science and technology of light, plays an increasingly important role in today's society, in reducing energy consumption in lighting, building high speed internet systems and developing novel biomedical sensors. Yet by squeezing light down to the nanoscale to exploit optical phenomena, nanophotonics can challenge existing technological limits and help to deliver superior photonic devices. Opportunities range from telecommunication to health and energy: photonic circuits that are not only smaller but faster and consume less energy; nano-optical sensors able to detect the chemical composition of molecules at ultralow concentrations and even single molecules; new solar-cell designs for enhanced light absorption.

Encompassing areas such as metamaterials, plasmonics, quantum nanophotonics and functional photonic materials, nanophotonics is often perceived as a basic research field. Indeed scientific output in nanophotonics has been prolific in recent years, however research advances are often hidden in other disciplines or technologies, for example, optoelectronics, nanotechnology, imaging, and photonics in general. Despite the academic appearance, progressively examples emerge where curiosity-driven nanophotonics research is moving out of the lab.

### **INFORMATION STORAGE**

One of the most inspiring nanophotonic developments so far, in terms of commercial applications, is the use of plasmonic nanostructures for high density (light-assisted) magnetic data storage. Most methods in use today have a capacity of a few hundred gigabits per square inch thanks to perpendicular recording. However, hard disk systems are encountering a storage density ceiling, and to keep up with our ever growing demand for information storage, new approaches are needed. Researchers from Hitachi and Seagate have recently proposed a nanophotonics solution using plasmonic near-field transducers to store data at densities of up to one terabit per square inch, and beyond.

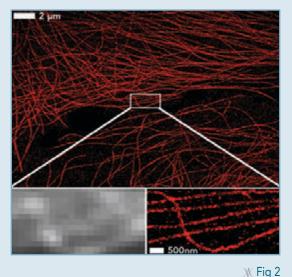
### **EMERGING TOOLS FOR BIOLOGISTS**

Nanophotonics has also contributed to the recent advances in optical microscopy and nanoscopy. Biologists are now able to observe cellular structures at the nanoscale, structures not resolvable with conventional fluorescence microscopy (see Figure 2). By working around the diffraction limit, optical resolution below 50 nm and even down to 20 nm, are achieved. Super-resolution microscopy can reveal intracellular compartments and cellular networks, all in the context of living cells or even organisms. The new non-invasive nanophotonic technology is revolutionising the understanding of molecular biology, as one can now directly follow the signalling pathways leading to immune diseases, neurological disorders, cancer and an enormous amount of other pathologies. Though still costly, super-resolution imaging systems are now commercially available for laboratory research.

### **NEW OPTICAL MATERIALS**

Though often associated to futuristic applications as "cloaking" and "perfect lensing", metamaterials are making their way to concrete applications. Specifically, efficient broadband absorbers for energy collection in photovoltaic cells, novel sensing materials, broadband waveplates for IR polarisation control and active metamaterials for switching and frequency conversion are materialising.

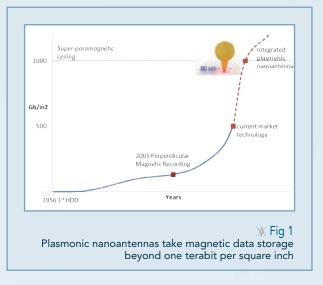
Graphene research is experiencing a real boom due to the combined aspect of nanoelectronic and nanophotonic control. Interestingly concrete applications such as graphene optical detectors, ultrathin transparent conductive films and non-linear absorbers for ps-laser mode-locking have already been put forward.



Inset compares conventional fluoresce (grey) and STORM (red) © ICFO

### **MARKET UPTAKE**

These examples, selected from the report, illustrate the promise of nanophotonics in terms of enhanced performance, better resolution, increased sensitivity and improved efficiency and the close links between basic research and technology. However, in the drive towards commercialisation and entry to the photonics market, a concerted effort both from the research community and photonics industry is crucial if emerging nanoscale techniques are to be taken up to address current technological roadblocks.



### **FUTURE PATTERNS**

Many of the recent developments in nanophotonics have been aided by an array of tools which have become available for nanoscale fabrication and characterisation. These enabling techniques, which include nanoimprint lithography (NIL) and 3D direct laser writing, are now being commercially exploited. NIL, which can print 10 nm patterns without the need for expensive equipment, is being explored as a manufacturing technique for a wide variety of photonic applications such as hard disk drives, lab-on-chip systems and high brightness LEDs. 3D direct laser writing has developed into a reliable fabrication tool, where 3D nanostructures with sub-100 nm feature sizes can be achieved with commercially available instruments. 3D writing is a crucial technique to manufacture metamaterials. Inspired by super-resolution techniques researchers are investigating novel writing schemes and sizes of a few tens of nanometres may soon be a reality.

This report highlights 10 nanophotonics research areas which are expected to have a disruptive impact on the major photonic industries, as defined by *Photonics21*, over the next 5-10 years. Based on the potential economic and social benefits, the group behind this report (leading European researchers in nanophotonics) recommend that these nanophotonics topics are seen as key insertion points in European (nano)photonics research agendas.

### FURTHER RECOMMENDATIONS

- Nanophotonics research is booming, with potential applications across a wide range of subjects - yet the connection to industry is weak.
- The nanophotonics community needs to work together with bodies such as *Photonics21* to build a cohesive R&D plan for nanophotonics in Europe.
- Support for curiosity-driven research is essential, and funding mechanisms should allow for the unexpected.
- European industry is in a strong position to exploit nanophotonics and deliver novel technological solutions.

Photonics21 Work Groups	nation & ion	WG2 - Industrial Production, Manufacturing & Quality	WG3 - Life Sciences & Health	WG4- Emerging Lighting, Electronics & Displays	WG5- Security, Metrology & Sensors	WG6 - Design & Manufacturing of Components & Systems
Photonics Topics	WG1 - Information & Communication	WG2 - Indus Manufacturii	WG3 - Life S	WG4- Emerc Electronics 8	WG5- Securi Sensors	WG6 - Desig Components
Nanoscale Quantum Optics	+++					++
All Optical Routing	+++					
Plasmonics for Data Storage	+++					++
Diagnosis, Therapy and Drug Delivery using Light			+++			
Nanoscale Imaging		++	+++			
Molecular-scale Sensors			++		+++	
NanoTagging			++		+++	
Light Distribution at the Nanoscale				+++		++
New Processing Techniques		+++				++
Nanophotonic Materials with Tailored Optical Properties				+		+++

## Nanophotonics HIGHLIGHTS

#### APPLICATIONS

Nanoscale light sources Faster non-classical information processing

### 1. Nanoscale Quantum Optics

Quantum informatics and quantum optics both constitute new paradigms for photonics applications. One involves the transport and processing of quantum information, the other can provide either the basis for optical q-bits, a quantum state used for information processing—an analogue of a bit in classical communications, or designer sources of quantum information in the form of entangled or heralded photons. To date, with some notable exceptions, quantum optics and quantum informatics have involved bulk optics, macroscopic lasers and free-space light beams. Nanoscale quantum optics will allow both the implementation *on-chip* of existing concepts and the emergence of novel phenomena, some of which may be anticipated but some of which will be new.

Quantum dot excited states have been entangled with photon states in photonic crystal cavities.<sup>1</sup> Potentially, these results will lead to scalable, coupled optical q-bits. Quantum information, antibunching<sup>2</sup> and entanglement<sup>3</sup> have been transported with a plasmonic nanowire and through a metallic nanohole array. These experiments prove that the quantum states can survive the lossy nature of plasmonic nanostructures. A quantum Controlled NOT (CNOT) gate and quantum signal processing have been demonstrated on-chip with conventional integrated optics components.<sup>4</sup> Nanophotonics should allow the integration of the laser source on the chip and achieve an increase of functionality per unit of surface area. The emission of single quantum emitters has been manipulated and directed with plasmonic nanoantennas.<sup>5</sup> Control of emission with nanostructures can provide new sources for quantum optics, but it can already improve the properties of more conventional solid state light emitting diodes (LEDs) and vertical-cavity surface-emitting laser (VCSELs). Recently, an optical transistor was demonstrated based on a single molecule.<sup>6</sup> Such ultimate control of optical logic with single quantum systems opens many new avenues of quantum information processing, and applications in security and cryptography.

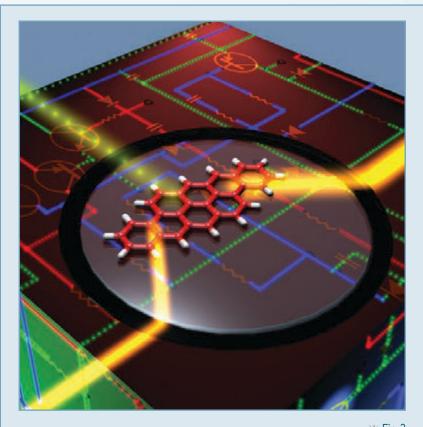
At present it is hard to anticipate the figure-of-merit for such an emerging topic. One may think of: the insertion loss of single photons in specific modes, the degree of entanglement (after transport), loss of degree of entanglement per unit length, quantum efficiency enhancement or the directionality of light emission of single photons.

Several key goals can be identified. Nanoscale control of light emission with highly spatially structured fields would allow the violation of conventional quantum selection rules for absorption and emission, thus offering a manifold of new prospects for applications. Another is the creation of an on-chip source of entangled photons.

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### 2. All Optical Routing

APPLICATIONS All-optical signal processing transparent optical networks In order to harness the full available bandwidth of optical and data communications and to overcome the bandwidth limitation of electronic components, it is imperative to minimise the optical-electrical/electrical-optical conversion of information. Processing of optical information by all-optical means allows the full available bandwidth to be exploited and to reduce the energy loss. Nanophotonics has key benefits to improve all-optical signal processing. Obviously nanophotonics allows a decreasing of the on-chip footprint of the individual components. More importantly, nanophotonics allows a profound engineering of the light-matter interactions that are required to achieve all-optical signal processing. Increasing the strength of those interactions minimises the required output intensity of the controlling light source to obtain a desired functionality.



✗ Fig 3 A single-molecule optical transistor. Courtesy of MPI Science for Light

Several clear boundary conditions can be established: on the one hand the bandwidth of the processing step needs to be maximised, on the other the power consumed for the same step, the required output power of the controlling light source and the on-chip footprint per component should all be minimised. From this point of view, both all-optical modulation and all-optical wavelength selective routing are the challenges to address. In the latter, device footprint and network integration can be substantially mitigated employing nanophotonic approaches. In the former, ultrafast and increased nonlinearity is essential.

Three distinct, but sometimes related, routes exist to obtain the desired enhanced light-matter interactions. At present, all routes have already demonstrated proof-of-concept optical data processing.

- First, ultralow nanophotonic resonators have been achieved, for example, on the basis of two-dimensional photonic crystals. These structures have an on-chip footprint of roughly a wavelength squared and the resonant nature of the structure reduces the index change required to switch the light. Femtojoule (fJ) light switching has been demonstrated. Clearly, resonator structures need to find a balance between low actuation power and bandwidth.
- Secondly, slow light in photonic or plasmonic structures has an enhanced light-matter interaction, similar to the light trapped in a nanophotonic resonator. This allows ultrasmall add/drop filters to be fabricated. A plasmonic switch 5 microns long and with a switching time of less than 200 fs has been demonstrated.<sup>7</sup> Slow light needs to balance the slowdown factor with bandwidth, a compromise governed by the Kramers-Kronig relations.
- Thirdly, plasmonic structures allow nonlinear processes to be greatly enhanced due to the achievable electric field enhancements.<sup>8,9</sup> This allows efficient enhancement of second- and third-order optical nonlinearities and thus controlling light with light in plasmonic waveguides, plasmonic crystals and using metamaterials to achieve switching below 1 ps timescale in few 100 nm size devices.<sup>10,11</sup> Plasmonics has a very high inherent bandwidth.

Challenges are the intrinsic losses and CMOS compatibility, and transition from individual devices and components to all-optical circuits and systems.

<sup>7.</sup> K.F. MacDonald, Z.L. Sámson, M.I. Stockman & N.I. Zheludev, Nature Photon., 3, 55, (2008)

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<sup>10.</sup> G.A. Wurtz & A.V. Zayats, Laser Phot. Rev., 2, 125 (2008)

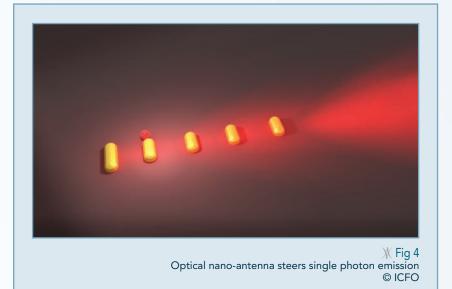
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APPLICATIONS High speed read/write High density data storage

### 3. Plasmonics for Enhanced Magnetic Storage

Magnetic data storage has gone through tremendous down scaling. In fact the surface area of individual magnetic bits has shrunk 8 orders of magnitude since the hard disk was first commercialised. Magnetic disk drives now store most of today's worldwide information. Unfortunately, conventional perpendicular magnetic recording is expected to scale by only another factor of two, reaching about one terabit/inch<sup>2</sup>.

To scale conventional recording beyond one terabit/inch<sup>2</sup>, magnetic media grain size must be reduced below 7 nm, requiring switching fields beyond the maximum flux density of known materials. One way to improve writeability is to temporarily heat the medium, to lower the switching field of high-anisotropy small grain media. After the media is written, it cools rapidly (~1 ns) for long-term storage. Because the size of the region to be heated in the media is well below the optical diffraction limit, such a writer must use a near-field device such as a nanophotonic antenna (gold, silver, copper) with a size and shape optimised for creation of surface plasmons.<sup>12</sup> The intense near-field pattern causes a localized heating of a disk placed in close proximity. Indeed recently several prototype plasmonic antennas have been designed: an integrated 'lollipop', a 'nanobeak' and an E-antenna, in which high speed writing (over 100Mb/sec) achieved densities up to 1 Tb/inch<sup>2</sup> with ~20 nm island size.<sup>13,14</sup> In all these designs a resonant antenna structure, either sphere or rod shaped, is combined with a local notch (10-30 nm in size) which concentrates the incident optical field. Ideally, the re-



cording medium consists of individually addressable and non-interacting entities, by patterning the media, in contrast to continuous media. Indeed recent improvements in track width and optical efficiency were obtained using antennas with advantageous near-field optical effects on patterned media.

A challenge is to find or produce even higher-density patterned media, with a track pitch similar to the width of the plasmonic antenna tip. With superior higher-anisotropy materials such as FePt, data density could, in principle, be further increased. Obviously high read/write speed is very demanding for reader technology and write synchronization.

So far Seagate<sup>13</sup> and Hitachi<sup>14</sup> are

taking the lead on this enhanced magnetic data storage. It is important for European industry not to lose track of the exploitation of plasmonic devices to confine and enhance optical fields for recording purposes.

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Plasmon-based cancer therapy Nanoplasmonic sensing Drug delivery

### 4. Diagnosis, Therapy and Drug Delivery using Light

**APPLICATIONS** The interaction of light with nanoscale matter provides new opportunities for highly targeted medical diagnostics and therapy. Of particular promise is plasmon-based cancer therapy, where nanoscale noble metal nanoparticles are used for targeted destruction of tumour tissue. This is enabled by a combination of surface chemistry - "finding" the malignant tissue leading to aggregation of the particles around the tumour - and careful design of the optical properties of the nanoparticles. Resonant light absorption of the particle occurs in a spectral regime (near-infrared) where human tissue is transparent, leading to heat-induced apoptosis of the malignant tissue. These studies, pioneered at Rice University, have already reached clinical trials for common cancers such as that of the prostate. This particular success story can be extended by a move towards multi-shell particles including magnetic layers, which would simultaneously allow for their use as contrast reagents for magnetic resonance imaging.<sup>15</sup> This would spearhead a move towards theranostics, using the same nanophotonic unit (multi-shell metal nanoparticles) both for diagnosing and at the same time treating the malignant tumour.<sup>16</sup> Advances in nanoscale material synthesis, biochemical targeting, and our understanding of how the optical properties of nanoparticles can be tuned are expected to result in major breakthroughs in this area of biomedicine over the coming 3-5 years.

> Other research questions which should receive major attention include the targeted release of drugs delivered via nanoparticle or molecular complexes to specific sites within the human body. A promising concept for light-induced drug release - the opening of "cages" delivering the drug - lies in the exploitation of changes in conformation of complex biomolecules induced by ultraviolet light.<sup>17</sup> A particular challenge here is to improve the response of molecular systems to lower energy radiation, thereby limiting harmful side-effects on cells in the immediate vicinity of the illumination spot.

> Lastly, exploiting the sensitivity of plasmon resonances to the local environment, metallic nanoparticles can be engineered on a surface to monitor very low concentrations of tiny biomolecules in solution. When combined with microfluidic circuits, nanoplasmonic sensing opens new opportunities to develop novel analytical platforms able to detect, from a single drop of blood, diseases such as cancer at an earlier stage and perform treatment monitoring.

> Nanophotonic platforms such as the systems described here can be expected to become a major vehicle in the move towards personalised healthcare allowing highly focused therapies while minimising harmful side effects.

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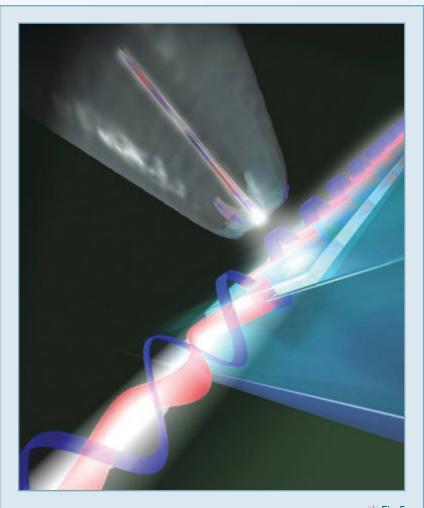
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### 5. Nanoscale Imaging

### APPLICATIONS

Biological imaging Single-molecule imaging Inspection tools for nanofabrication and quality control Biological/cell tags Modern optical microscopy has gone through a revolution in the last decade. The new so-called super-resolution techniques surpass the diffraction limit for visible light and allow researchers to resolve objects at the nanometre scale. Several approaches can be identified with a variable degree of maturity and commercialisation.

The most versatile super-resolution methods still rely on high numerical aperture (NA) lenses and far field operation, where the point-spread function is engineered to break the diffraction limit. Particularly, Stimulated emission depletion (STED)<sup>18</sup> has convincingly reached 20 nm by a combination of spatial focus engineering and non-linear de-excitation. STED is dominantly targeted for nanoscale biological imaging, yet STED could also play a role in technical inspection and quality control in nanofabrication. Unfortunately STED needs scanning. In order to overcome the need



✗ Fig 5 An optical nanoprobe scans a photonic nanostructure © AMOLF

18. V. Westphal & S.W. Hell, Phys. Rev. Lett. 94, 143903 (2005)

of scanning, a large-area enhanced resolution can be achieved by structured illumination, where a dedicated spatial amplitude/phase scan provides sub-wavelength image information. Finally at the level of sparse imaging (*i.e.* limited sources, such as single molecules) localisation microscopy can be employed. Methods such as PALM<sup>19</sup> and STORM<sup>20</sup> exploit photon-statistics and far-field microscopic spatial response to reconstruct high resolution images with details below 50nm and with sensitivity down to photon counting level.

All these far field super-resolution approaches are nondestructive. For industrial applications the new methods are scalable, typically to wafer size, low cost and compatible with state-of-the-art mass nanofabrication methods. A challenge is to find the right non-bleaching contrast media and suitable fluorophores and photoresists for STED imaging and manufacturing, respectively.

Most super-resolution methods depend on the detection of suitable luminescent labels. Besides the classical dye-labels and fluorescent proteins, the controlled tagging of cells/biological tissue with quantum dots for in vitro biomedical studies has reached a certain maturity. Quantum dots are superior (high brightness and photostability) compared to the traditional organic molecular fluorophores in terms of the absence of quenching. Yet important research questions remain, such as control over blinking, toxicity issues for in vivo studies and high quality near infrared (NIR) dots for deeper tissue penetration.<sup>21</sup>

#### Other promising nanoscale imaging systems include:

- Optical nanoantennas, which have enabled imaging of single molecules in relatively high concentrations. Several prototypes of optical antennas (bow-tie, monopole, C-shape) have been demonstrated to operate at 25 nm scale in imaging and sensing with speed up to 100Mb/sec.<sup>22</sup> The strong local evanescent field confinement and enhancement provide both improved sensitivity and specificity for a wide range of inspection purposes. Reproducible fabrication of nanoantennas and their robustness in operation remains a big challenge.
- Tip-enhanced scanning microscopy using lowfrequency radiation down to the THz regime. Initial demonstrations have focused both on semiconductor systems<sup>23,24</sup> (quality control of field effect transistors) and biomedical studies (imaging of a single virus). A particular merit of this approach is its scalability in frequency, allowing nanoscale imaging with a wavelength of choice, which can be tailored to specific resonances of the material systems under study.
- Super-oscillation that removes the need for evanescent fields.<sup>25</sup> Examples of sub-wavelength localizations of light generated by a nanohole array have been demonstrated which may be used as a focusing device as well as a super-resolution imaging device.

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### **APPLICATIONS**

Disease diagnosis Treatment monitoring Mobile sensors Monitoring pollution in water and soil Monitoring chemical exposure Detection of pathogens in food products

## 6. Chemical and Biological Sensors at the **Molecular Scale**

Next generation nano-optical sensors will be able to detect chemical and biological species at the molecular scale, and simultaneously detect multiple analytes. These sensors will be user-friendly and applicable to a wide range of environments such as food safety, pollution control and medical diagnosis.

Over the last years nanophotonic elements have shown real potential for their use as the transducing element in biochemical sensors exploiting concepts such as: optical nanoantennas and surface enhanced Raman spectroscopy (SERS) for increased light-matter interaction; surface plasmon resonance and surface enhanced mid-infrared absorption spectroscopy for higher sensitivity. 26,27

The sensitivity of nanophotonic sensors can be characterized by a figure of merit, defined as a shift compared to the width in surface plasmon resonance. Figures of merit reach almost 10 for sensors based on isolated plasmonic particles and about 50 for sensors based on extended metallic film supporting surface plasmon polaritons (SPP). Here though, latest advances in nano-optics and especially in plasmonics and metamaterials offer new strategies to design much more sensitive sensors with figures of merit of several hundreds.<sup>28</sup>

Research challenges lie in increasing the sensitivity down to single-molecule detection, particularly in the IR where good spatial overlap is inherently more difficult, and ensuring that only targeted molecules are detected, i.e. rejecting false positives. The latter requires attention in terms of surface functionalisation of the sensing site and integration with microfluidic delivery systems.

Nanophotonic sensing sites generally only show significant electromagnetic field enhancement in a narrow spectral range. The design of sensing sites showing field-enhancement in spectrally separate windows, e.g. the optical and Thz regime remains a major obstacle. Such a development would enable 'molecular fingerprinting' of complex molecules via interrogation of their rotational, vibrational, and electronic resonances on the same sensing site and would allow simultaneous multispectral imaging of different molecular species.

In the application of nanophotonics to sensing systems, integration will need to be addressed in order to move to point-of-care and roadside portable detection devices that will be easy to operate by non-specialists. This includes work at the interface with traditional microscale photonic and electronic units, particularly the parallel addressing of densely packed nanophotonic-sensing sites, e.g. surfaces patterned with an array of metallic nanoresonators.

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### 7. NanoTagging

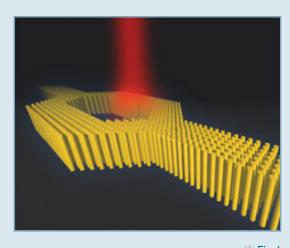
APPLICATIONS Anti-counterfeiting

Food safety tags Medical diagnostics Recent developments in nanophotonics show promise for applications in tagging and anti-counterfeiting technologies. Arrays of nanoscale optical resonators and/or metamaterials allow the creation of novel optical responses such as negative refraction, highly enhanced light scattering in spectrally narrow windows, nanoscale bar codes, and micronscale radiofrequency (and hence deep sub-wavelength) active tags.

Research strands currently exploited in the framework of transformation optics for the generation of optical cloaks and broadband light concentrators could very well find application in future tagging technologies. The challenge will lie in the balance between a suitably elaborate nanoscale surface structure leading to a distinct optical response visible to either the naked eye or a diode scanner and the associated cost of fabrication.

The definition of a figure of merit for nanotagging is far from straightforward, but necessary in terms of determining an appropriate standard. Clearly, cost will be a major issue, in addition to physical quantities such as coding depth/area, required read-out power, and signal/background noise ratio. The latter is particularly relevant for passive tags.

Another major challenge lies in the development of suitable fabrication strategies applicable to flexible substrates such as textiles or bank notes. Patterning of material systems such as organic layers – organic metamaterials – might allow knowledge transfer from the area of plastic electronics in order to create cheap tags on flexible substrates amenable to planar or solution processing.



high capacity nanophotonics tagging technique for bio-medical bead based assays, based on the use of nanostructured barcodes.<sup>29</sup> The high encoding capacity of this technology along with the applicability of the manufactured bar codes to multiplexed assays will allow accurate measurement of a wide variety of molecular interactions, leading to new opportunities in diverse areas of biotechnology such as genomics, proteomics, high-throughput screening, and medical diagnostics.<sup>30</sup>

An example of current research is a new non-contact

∦ Fig 6 Active Plasmonics © Kings College London

29. S. W. Birtwell, G. S. Galitonov, H. Morgan, & N. I. Zheludev, Opt. Comm., 281, 1789 (2008)

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## 8. Manipulation of Light Distribution at the Nanoscale

### 8.1. OPTIMISING EMISSION EFFICIENCY

### APPLICATIONS

Light generation Light harvesting High efficiency and high colour purity phosphors Polarised colour-converters for LED TVs and backlighting Custom-designed nanostructures induce strong modification of the light emission kinetics in luminescent materials. The light emission can be suitably controlled for increased emission efficiency, spatial manipulation (for localisation), angular distribution (for directionality), polarisation (for anisotropy), spectral linewidth, *etc.* by:

- Emission kinetics can be modified by exciton-plasmon coupling; metallic nanostructures provide localised plasmons with resonances tuned by the material, shape and size and act as optical nanoantennas in close proximity of emitters.
- Exciton-exciton coupling can play a role; quantum confined emitters are placed in close proximity, with proper spectral matching for nonradiative energy transfer from donor to acceptor (e.g. between quantum dots or between nanowires and nanocrystals). The nonradiative mechanism is essential to control the excitation energy flow.
- Strongly coupled exciton-photon systems can radically change the emission and lasing properties of devices. These devices have shown Bose-Einstein condensation<sup>31</sup> and room temperature polariton lasing<sup>32</sup>.

With the current nanofabrication techniques available various coupled nanosystems have been demonstrated. Emitter decay rates have increased over 20 times, intensity enhanced up to 1000 times and emission directed into narrow cones.<sup>33</sup> The important question is: what are the limits to emission modification using plasmonics and excitonics.

The distribution of light on a surface is usually controlled by nanostructuring the local surface to create efficiently emitting surfaces, or vice versa, efficiently capture the incident light. For this it is important to couple the enhanced emission efficiently to the far field.

For emitting devices, such as LEDs, the emission at grazing incidence, beyond the critical angle, is trapped in the device or coupled in a top-guide layer, resulting in a narrow escape cone for the emitted light. Particularly for high index materials used in inorganic LEDs, such as GaAs, GaP and to a lesser extent in GaN, the extraction efficiency of an unstructured GaAs surfaces is less than 5%.

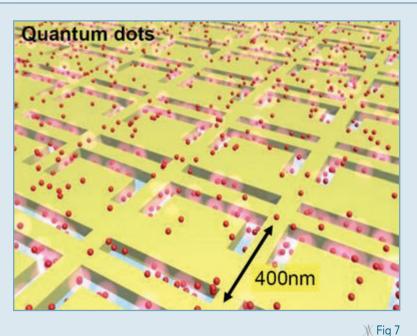
<sup>31.</sup> J. Kasprzak, M. Richard, S. Kundermann, A. Baas, P. Jeambrun, J.M.J. Keeling, F.M. Marchetti, M.H. Szymańska, R. André, J.L. Staehli, V. Savona, P.B. Littlewood, B. Deveaud & Le Si Dang, Nature, 409 (2006)

<sup>32.</sup> J.J. Baumberg, A.V. Kavokin, S. Christopoulos, A.J.D. Grundy, R. Butté, G. Christmann, D.D. Solnyshkov, G. Malpuech, G. Baldassarri Höger von Högersthal, E. Feltin, J.F. Carlin & N. Grandjean, Phys. Rev. Lett., 101, 136409 (2008)

A.G. Curto, G. Volpe, T.H. Taminiau, M.P. Kreuzer, R. Quidant, N.F. van Hulst, Science, 329, 930 (2010);
 S. Kühn, U. Håkanson, L. Rogobete, V. Sandoghdar, Phys. Rev. Lett., 97, 017402 (2006)

Nanostructuring of the LED surface opens up the escape cone to allow efficient emission over a large angle. To this end several periodic structures and various photonic crystal lattices have been designed. The photonic crystal band gap inhibits spontaneous emission within the plane of the slab - which is the wrong direction for light extraction - while the semiconductor continues to emit light normal to the slab and into free space.<sup>34,35,36</sup> Periodicity and symmetry are optimised to enhance the emission in the "right" direction. For broadband emission non-periodic or even random structures are preferred. Dielectric materials are used to avoid losses. High extraction efficiencies have been reached (over 60% in the red and 80% in the blue) and the technology is already finding its way to the consumer market with LEDs having optical efficiencies close to 50% now on the market.<sup>37</sup>

Although there have been huge advances in OLED technology the route to high brightness large area high efficiency and long life OLEDs is still very much open. Interblending of the optical material that makes up the active region can be enhanced through nanostructuring. The coupling of the molecular emission levels to resonant plasmon structures and antennas can improve both radiative and extraction efficiency.



Semiconductor quantum dots in a plasmonic array © Centre for Photonic Metamaterials, Univ. of Southampton

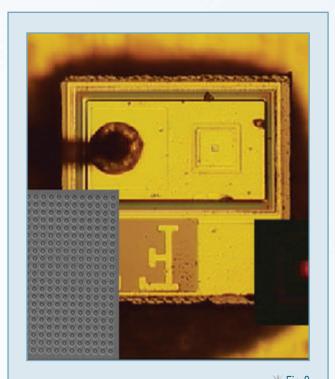
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<sup>34.</sup> S. Fan, P. R. Villeneuve, J.D. Joannopoulos, & E.F. Schubert, Phys. Rev. Lett., 78, 3294 (1997)

### 8.2. OPTIMISING LIGHT ABSORPTION

In reciprocity nanostructured surfaces are equally fit for efficient light capture. In solar cells the light should be absorbed in the active photovoltaic layer. As absorbance is generally relatively small, nanostructuring is important to increase the absorbance and guarantee trapping of light in thin film solar cells. Here metallic nanostructures supporting plasmons are of great advantage:

- Metallic nanoparticles can act as sub-wavelength scatterers or resonant antennas to trap and couple the incident light to the thin photovoltaic layer.
- Alternatively a nanocorrugated metallic film at the back surface of the solar cell can efficiently convert light to surface plasmons which couple to the photovoltaic layer.
- Interestingly the metallic nanostructuring can also be combined with the electrodes to collect the photocurrent.



💥 Fig 8 Plasmonic crystal LED © Kings College London & OSRAM Opt-Semiconductors, FP6 Project PLEAS The application of plasmonic structures in solar cells is currently developing at a tremendously high pace. The active layer can be shrunk to below 100 nm, providing physically thin, but optically thick photovoltaic absorbers.<sup>38</sup> Although factors of 2 in efficiency enhancement have been obtained several challenges lay ahead: optimal geometry, replacement of expensive gold by cheaper materials, large scale fabrication and suitable transparent electrodes.

Another research method is to control the incident light, by tailoring phase or polarisation distribution of broadband pulses, and thus achieve coherent control over the spatial light distribution, optimised for any complex nanosystem.<sup>39</sup> A desired nanoscale light hot-spot can be engineered simply by adjusting the far-field spatial profile of an incoming coherent light beam. By modifying the spatial phase profile of the incident beam the nanoscale hot-spots can be moved, providing an efficient technique for a sub-wavelength scale optical control.<sup>40</sup> So far hot-spot engineering has been rather academic, yet with suitable phase plates or LCD arrays one can imagine low-cost alternatives with potential commercial applications.

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### **CHALLENGES**

A challenge for both LED and solar cell applications is the availability of optically thin transparent electrodes which is crucial to aid efficiency and extraction. Obviously indium tin oxide (ITO) is being exploited, however ITO has its limitations: it is expensive and fragile and therefore not compatible with flexible devices. Other issues include film roughness, surface conductivity and transparency. Recently ultrathin (2-5 nm) metal films are being explored as an alternative. Finally also application of graphene sheets could be a future route. In both cases suitable fabrication of large area high quality sheets is the main challenge.

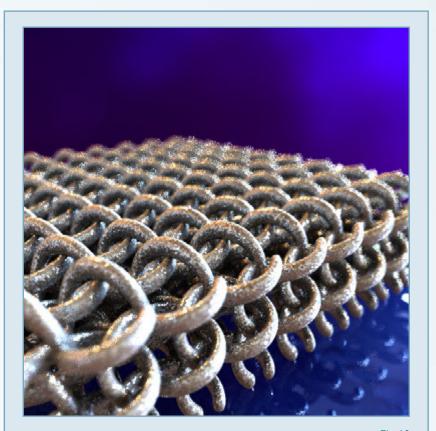


₩ Fig 9 Nanophotonics at imec Ghent © imec

### 9. New Processing Techniques for Prototyping

(Nano)photolithography is the main technique behind the semiconductor manufacturer's roadmap and routinely achieves 30 nm resolution on 300 mm silicon wafers. In principle, all methods from today's semiconductor industry, such as large-area fabrication and metallisation, stacking, as well as planarization, alignment and vertical vias can be utilized for prototyping of plasmonic circuitry, metamaterials, *etc.* The problem is rather the availability and access to such high-tech fabrication methods for nano-optic applications, and the fact that such techniques are only economically viable in large scale production scenarios.

A large variety of low cost, high resolution techniques have been developed for prototyping of nanophotonics components. Interestingly, several of these new processing techniques can be scaled up while maintaining low cost, speed and fidelity.



✗ Fig 10 Helix Crystal © University of Stuttgart

### 9.1. 3D DIRECT LASER WRITING LITHOGRAPHY

### APPLICATIONS

Low-cost rapid 2D and 3D prototyping Novel components for future alloptical Tb/sec networks Novel sensors All-optical quantum devices for secure quantum communication 3D direct laser writing (DLW) has moved rapidly from a mere concept to a practicable and reliable laboratory tool over the last 5 years (e.g. Nanoscribe GmbH). Improving mostly laser stability, mechanical stability, phase masks for voxel shaping, and in particular the writing algorithms to improve speed and performance, the manufacturing capability has developed into a very competitive alternative to holographic lithography and 3D electron beam lithography.

Very recently, Stimulated Emission Depletion (STED) lithography was added to the spectrum of direct laser writing, in combination with newly developed photoresists.<sup>41,42</sup> This pushed structure sizes down to 65 nm, which allowed manufacturing of the first true 3D photonic bandgap material in the visible wavelength range.<sup>43</sup> Different materials, such as chalcogenide glasses, or ormocers, are also available. Full automation and process control allows writing over many days with very high precision.<sup>44</sup>

3D Direct Laser Writing (DLW) allows 2D and 3D carpet cloaks in the nearinfrared to be created which are spectrally broadband. Objects on the order of several micrometers could be cloaked. Recently, this carpet cloaking has even been pushed towards the visible.<sup>44</sup>

Research priorities focus mainly on the development of new photoresist materials that are custom-tailored towards 3D DLW lithography with potential for sub 10-nm features. This includes in particular high-index materials, as well as STED-suitable resists. New spatial and polarisation filters would allow for more special voxel shapes. High-power, low-cost novel femtosecond oscillators will enable multi-focus imaging.

41. L. Li, R.R. Gattass, E. Gershgoren, H. Hwang, & J.T. Fourkas, Science, 324, 910 (2009)

- 42. T.F. Scott, B.A. Kowalski, A.C. Sullivan, C.N. Bowman, & R.R. McLeod, Science 324, 913 (2009)
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- 44. T. Ergin, N. Stenger, P. Brenner, J. B. Pendry & M. Wegener, Science 328, 337 (2010)

### 9.2. NANOIMPRINT LITHOGRAPHY

#### **APPLICATIONS**

Direct patterning of passive photonic components Microcavities Band edge lasers Waveguides Memories Metamaterials Optofluidic and lab-on-a-chip devices Organic and inorganic solar cells OLEDs and OFETs In principle, nanoimprint lithography (NIL) can be used as a low-cost, large-area, parallel mass production fabrication technique. Moreover, using appropriate overlay and stacking techniques, many multiple layers can be processed. NIL has passed the 30 nm level in industrial applications, especially in the area of magnetic recording and diffractive optical devices. Structuring polymer materials down to the 10 nm level has already been reported.<sup>45</sup> Furthermore, overlay accuracy using, for example, Moiré interferometry has reportedly achieved levels down to 30 nm.<sup>46</sup>

One major achievement has been the printing of 300 mm wafers using UV-NIL with a throughput of 20 wafers per hour, cf. 80 wafers per hour in the semiconductor industry.<sup>47</sup> In the context of nanophotonics, nanoimprinted plasmonic crystals for light extraction, where the photoluminescence emission intensity is increased by more than a factor of 10, due to plasmonexciton coupling, has recently been reported.<sup>48</sup> The possibility to realise 3D patterns by NIL is currently being investigated.

Key issues in NIL are stamp size and cost, with wafer size currently up to 300 mm; stamp wear, currently at over 1000 prints before physical wear sets in, in the absence of an anti-adhesive coating layer, as well refinement of specific processes for particular applications concerning, for example, demolding forces.<sup>49</sup> The design rules depend strongly on the arrangement of the pattern on the stamp and need to be simulated.

Research is needed on new printable functionalised polymer materials, as well as tools and protocols for nanometrology suitable for NIL. A huge benefit can be derived from combined approaches, such as NIL and self-assembly, which is virtually unchartered.

<sup>45.</sup> For a review see, eg., H. Schift, J. Vac. Sci. Technol. B, 26, 458 (2008)

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R.Hershey, M.Miller, C.Jones, M.G.Subramanian, L.Xiaoming, G. Doyle, D.Lenz & D.LaBrake, Proc. SPIE Microlith, 6337-20, (2006)

<sup>48.</sup> V. Reboud, N. Kehagias, T. Kehoe, G. Laveque, C. Mavidis, M. Kafesaki & C.M. Sotomayor Torres, Microelectronic Eng. 87 (5-8) 1367 (2010)

<sup>49.</sup> J. Ahopelto & H. Schift, Eds. "NaPa Library of Processes" www.napanil.org (2008)

### 9.3. SELF-ASSEMBLY OF NANOPARTICLES

### APPLICATIONS

Heterogeneous integration Opto-biotechnology Environmental sensors Medical sensors Artificial nano-scale materials Bio-circuits Artificial tissues and organs Energy harvesting Self-assembly techniques or bottom-up nanostructuring offers an alternative to top-down methods such as electron-beam lithography and interference lithography, as far as fabrication of periodic patterns are concerned. Colloidal methods assemble cm<sup>2</sup> size defect free areas with nanoparticle spheres. The use of silicon patterned substrates to engineer the capillary flow has resulted in the self-assembly of 3D photonic crystals in a process which is fully scalable and compatible with silicon fabrication<sup>50</sup>. Moreover utilising the pinholes for metal beam lithography, structure sizes down to 40 nm and gap sizes around 10 nm have been achieved, after annealing of the nanoparticle lattice.<sup>51</sup>

First applications of plasmonic oligomers which were produced by colloidal angle-shadow lithography have arisen. In particular, their use as sensors based on plasmonic Fano resonances or plasmonic induced transparency have become feasible.<sup>52</sup> These sensors offer sensitivities comparable to the best localized surface plasmon resonance sensors at very small sensing volumes in the attoliter range.

Bottom-up techniques such as DNA- or protein-linked metal nanoparticles have succeeded in manufacturing dimers, trimers, or more complex nanoparticle oligomers. Mostly, due to their inhomogeneous broadening, these structures suffer from worse optical properties compared to lithographic structures. However, DNA scaffolds have already shown very good structural quality. The combination of top-down pre-structuring with subsequent bottom-up methodologies should increase the optical quality significantly.



Waveguide and 3D photonic crystals by self-assembly © VTT/ICN A particular challenge to self assembly is the quantification of order. Without methods for such a task, there is little chance to come up with metrology and standards for industrial up-take in large-scale manufacturing. Also liquid-based processes are seen as inherently unreliable and require further research, in particular, into the role of convection forces and surface energy.

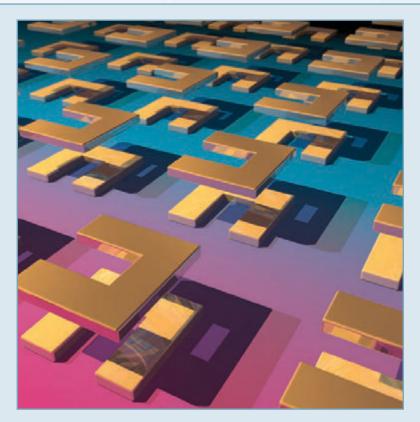
<sup>50.</sup> S. Arpiainen, F. Jonsson, J.R. Dekker, G. Kocher, W. Khunsin, C.M. Sotomayor Torres, J. Ahopelto, Adv. Func. Mater. 19, 1247 (2009); Patent: FI/02.03.07 FIA 20075153 and US-2008-8220-0220159-A1.

<sup>51.</sup> N. Liu, M. Mesch, T. Weiss, M. Hentschel, & H. Giessen, Nano Lett., 10, 2342 (2010)

<sup>52.</sup> M. Hentschel, M. Saliba, R. Vogelgesang, H. Giessen, A. P. Alivisatos, & N. Liu Nano Lett., 10, 2721 (2010)

## 10. Nanophotonic Materials with Tailored Optical Properties

By dedicated nanostructuring new types of nanophotonic materials with exceptional optical properties can be crafted: nano-arrays with extraordinary transmission, perfect absorbers, switchable and tuneable materials, media with huge non-linear response, novel polarising elements and even negative refractive materials.<sup>53</sup> Below we mention a few selected examples with more direct connections to concrete applications.



✗ Fig 12 3D Metamaterials © University of Stuttgart

### APPLICATIONS

Compact waveplates for low cost circular dichroism studies in the IR fingerprint regime

### 10.1. METAMATERIALS AS BROADBAND WAVEPLATES IN THE INFRARED

So far, it has been nearly impossible to obtain broadband circular polarisers for light. Now, using direct laser writing with two-photon polymerisation and subsequent gold electroplating, 3-dimensional metamaterials working as polarisers have been fabricated.<sup>54</sup> The waveplates show a transmission selectivity of more than 90:10 for left-handed vs. right-handed circularly polarised light between 3.5 and 8  $\mu$ m wavelength and are only a few microns thick. It should be possible to create such a metamaterial over large areas (cm<sup>2</sup>) using phase holography.

Utilising 3D direct laser writing with two-photons and subsequent electroless silver plating, it is also possible to generate 3D bichiral plasmonic crystals, which show broadband circular dichroism from 3.5-5  $\mu$ m wavelength with very little angle dependence.

A remaining challenge in this area is to produce metamaterial waveplates for the visible regime.

### **10.2. INFRARED ABSORBER APPLICATIONS**

### APPLICATIONS

Detectors Biochemical sensing Non-reflective coatings Perfect absorbers are nano-optical structures which achieve near 100% absorption over a broad spectral bandwidth, a large angular range and are mostly polarisation independent. The working scheme of such absorbers is based on a stacked plasmonic geometry which consists of a thick metal layer with a dielectric spacer layer and a nanoplasmonic top structure. The thick metal layer has two purposes, first, it makes sure that transmittance through the structure is reduced to zero. Second, in combination with the spacer layer and the nanostructure, it leads to image charges which allow for perfect impedance matching of the absorber to the incident medium and hence represent a broadband anti-reflectance coating.<sup>51</sup>

Using Si<sub>3</sub>N<sub>4</sub> and Al as metal, it is possible to tune this absorber to the 3-5  $\mu$ m and 8-12  $\mu$ m spectral regions. Hence it is fully compatible with CMOS technology for focal plane array mid-infrared detection. Furthermore, satellites can be coated with perfect absorbers that absorb Gigahertz (Radar) radiation as well as infrared radiation in order to avoid spurious reflections.

Perfect absorbers can also be used as sensors. Without the sensing agent, they are perfectly black and do not reflect any light. Upon presence of the sensing agent, they change from dark to bright and the reflected light can be detected.<sup>52</sup>

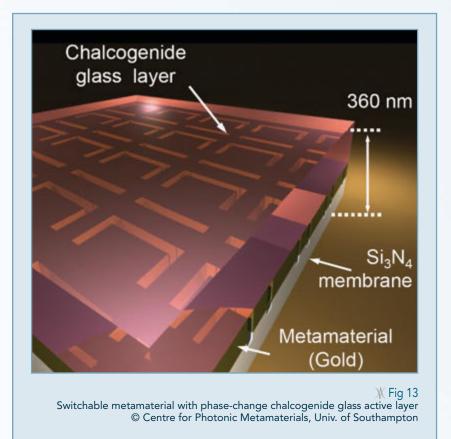
<sup>54.</sup> J.K. Gansel, M. Thiel, M. S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden, & M. Wegener, Science 325, 1513 (2009)

### **10.3. NONLINEAR AND SWITCHABLE METAMATERIALS**

### **APPLICATIONS Optical** switching Data processing Frequency conversion

For the development of all-optical data processing circuits the availability of fast and highly responsive nonlinear media is crucial. Such nonlinear materials, with light-driven change of index and absorption, are difficult to deliver in nanoscale devices, using merely electronic or molecular nonlinearities. The optical path through the nonlinear medium is shorter than the wavelength of light, and moreover stronger responses come at the expense of longer reaction times.

Particularly strong nonlinear response have been reported from nanostructured metal surfaces, caused by the combination of strongly resonant local field enhancement and high non-linear coefficients for metals.<sup>55</sup> Metals have long been discarded for non-linear applications, due to their high intrinsic losses, yet at the nanoscale the enhanced response dominates over the losses, opening new directions in switching and frequency conversion.



The presence of a metamaterial layer can strongly enhance the ultrafast nonlinear response of silicon. For example, a layer of single-wall semiconductor carbon nanotubes, deposited on a metamaterial, shows an order of magnitude higher nonlinearity due to a resonant plasmon-exciton interaction.<sup>56</sup> In another example, the transition between different metastable phases in polymorphic elemental gallium leads to dramatic change in dielectric and plasmonic properties, making it another candidate for use in switchable metamaterials.

"Phase-change" materials are prime agents for switching: chalcogenide glasses have been used in rewritable optical disk technology for several decades, providing fast and reproducible changes in optical properties in response to excitation. A nanoscale metamaterial electro-optical switch using chalcogenide glass has already been demonstrated. The recently demonstrated magnetic control of plasmons in layered structures of ferroelectric and noble metals can also be engaged to tune metamaterials.

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Zheludev, Phys. Rev. Lett., 104, 153902 (2010)

### **10.4. OPTICAL FILTERS USING NANOSTRUCTURES**

### APPLICATIONS

Hyperspectral imaging in surveillance and remote sensing

In a wide range of medical, microscopic, remote-sensing or surveillance applications, high-resolution images are required, and in much more than just three bands of colours: a large set of spectral bands extending far into the infrared, so-called hyperspectral imaging, is needed. Today, in hyperspectral imaging, both a real spatial image and a spectrum for each pixel are recorded, resulting in large three-dimensional spectral-image data cubes. Current approaches for generating this data rely on scanning the detection area, or the use of colour filter arrays or even multiple cameras. None of these techniques allow the ideal single exposure acquisition of a full spectral image with direct spectral separation at each image pixel. Nanostructuring for optical image sensors provides an alternative.

By nanostructuring a surface with a periodic index or even a photonic crystal structure the transmission and reflection spectra can be strongly modified and controlled. Exploiting metallic surfaces and excitation of plasmon modes phenomena such as extraordinary optical transmission can be achieved; for a hole surrounded by periodic grooves, the light is collected from a larger area, converted to a surface plasmon and guided to the hole.

By combining many overlapping groove areas, each with a different period each colour of the incident light can be directed. In contrast to the classical Bayer filter approach, in principle all of the light is harvested and the colour is sorted through plasmon resonances. Moreover, the use of a single nanostructured metal film enables very compact colour selection.<sup>57</sup>

### **10.5. GRAPHENE PHOTONICS**

### APPLICATIONS

Solar cells LEDs Touch screens Photodetectors Ultrafast lasers Graphene has recently been identified as a novel material combining both optical and electronic properties. The carrier density in graphene can be controlled by applying an external voltage, such that the electromagnetic reaction results in a tuneable spectral response. Graphene promises to add electro-optical capability to metamaterials, in particular in the IR and terahertz domains. Moreover by proper tuning graphene offers the potential of even larger field enhancement than in the case of metals.<sup>58</sup>

Recently the first graphene detectors have been presented; and even graphene has been proven to act efficiently as a saturable absorber in femtosecond mode-locked fiber-laser. Most importantly graphene promises to become the material of choice for transparent conducting films, replacing ITO and ultrathin metal films. First solar cell and capacitive touch screens have been fabricated both relying on a transparent graphene electrode.

57. E. Laux, C. Genet, T. Skauli & T.W. Ebbesen, Nature Photon., 2, 161 (2008) 58. F. Bonaccorso, Z. Sun, T. Hasan, & A. Ferrari, Nature Photon., 4 (9), 611 (2010)



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