Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures

Balling, P.; Christiansen, J.; Christiansen, R. E. ; Eriksen, E.; Lakhotiya, H.; Mirsafaei, M.; Møller, S. H.; Nazir, A.; Vester-Petersen, J.; Jeppesen, B.R.

Total number of authors:
17

Published in:
Optical Materials

Link to article, DOI:
[10.1016/j.optmat.2018.06.038](https://doi.org/10.1016/j.optmat.2018.06.038)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Balling, P., Christiansen, J., Christiansen, R. E., Eriksen, E., Lakhotiya, H., Mirsafaei, M., Møller, S. H., Nazir, A., Vester-Petersen, J., Jeppesen, B. R., Jensen, P. B., Hansen, J. L., Ram, S. K., Sigmund, O., Madsen, M., Madsen, S. P., & Julsgaard, B. (2018). Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures. *Optical Materials*, 83, 279-289.
<https://doi.org/10.1016/j.optmat.2018.06.038>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Improving the efficiency of solar cells by upconverting sunlight using field enhancement from optimized nano structures

P. Balling^{a,b,*}, J. Christiansen^a, R. E. Christiansen^d, E. Eriksen^a, H. Lakhotiya^a, M. Mirsafaei^e, S. H. Møller^a, A. Nazir^a, J. Vester-Petersen^c, B. R. Jeppesen^b, P. B. Jensen^{a,b}, J. L. Hansen^{a,b}, S. K. Ram^{a,b}, O. Sigmund^d, M. Madsen^e, S. P. Madsen^c, B. Julsgaard^{a,b}

^a*Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark*

^b*Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark*

^c*Department of Engineering, Aarhus University, Inge Lehmanns Gade 10, DK-8000 Aarhus C, Denmark*

^d*Department of Mechanical Engineering, Technical University of Denmark, Nils Koppels Alle, 404, DK-2800 Lyngby, Denmark*

^e*SDU NanoSYD, Mads Clausen Institute, University of Southern Denmark, Alsion 2, 6400-Sønderborg, Denmark*

Abstract

Spectral conversion of the sunlight has been proposed as a method for enhancing the efficiency of photovoltaic devices, which are limited in current production by the mismatch between the solar spectrum and the wavelength range for efficient carrier generation. For example, the photo current can be increased by conversion of two low-energy photons (below the band gap of the absorber) to one higher-energy photon (i.e. upconversion). In this paper, we will review our ongoing activities aimed at enhancing such spectral-conversion processes by employing appropriately designed plasmonic nanoparticles. The nanoparticles serve as light-concentrating elements in order to enhance the non-linear upconversion process. From the theoretical side, we approach the optimization of nanoparticles by finite-element modelling of the plasmonic near fields in combination with topological optimization of the particle geometries. Experi-

*Corresponding author
Email address: balling@phys.au.dk (P. Balling)

mentally, the nanostructures are formed by electron-beam lithography on thin films of Er^{3+} -containing transparent materials, foremost TiO_2 made by radio-frequency magnetron sputtering, and layers of chemically synthesized NaYF_4 nanoparticles. The properties of the upconverter are measured using a variety of optical methods, including time-resolved luminescence spectroscopy on erbium transitions and spectrally resolved upconversion-yield measurements at $\sim 1500\text{-nm}$ -light excitation. The calculated near-field enhancements are validated using a technique of near-field-enhanced ablation by tunable, ultrashort laser pulses.

Keywords: Upconversion, photovoltaics, plasmonic enhancement

1. Introduction

Much of the energy from the Sun is lost in photovoltaic devices because of the spectral mismatch between the sunlight and the absorption region of the solar cell. In the present paper, we will review recent activities in the SunTune
5 project, aimed at improving the efficiency of solar cells by upconverting the low-energy (long-wavelength) part of the sunlight [1, 2, 3, 4]. A specific optically active system, embedded in an appropriate host, allows for the absorption of two photons each with energy below the band gap of the absorber and subsequent emission of one photon above the band gap, which is directed into the
10 solar cell for increased current production. Combining upconversion processes with crystalline-silicon-based solar cells raises the theoretical efficiency from $\sim 30\%$ [5] to $\sim 40\%$ [6]. Different material systems have been proposed, and as discussed in greater detail in Ref. [7], the most efficient host materials have a low phonon energy in order to minimize non-radiative (multi-phonon) decay
15 channels, with prominent examples being $\beta\text{-NaYF}_4$, $\text{Gd}_2\text{O}_2\text{S}$ and BaY_2F_8 . The active ions are often chosen among the lanthanides, as these offer rich spectra of atomic-like transitions that can be used for upconversion in different spectral regions. Much effort has been dedicated to Er^{3+} in various hosts [8, 9, 10, 11], partly because this ion provides upconversion in a spectral region of high im-

20 portance for crystalline-silicon solar cells.

As upconversion requires merging the energy from two low-energy photons into one photon of higher energy, it inherently exhibits a non-linear dependence on intensity. Since the upconversion process typically occurs with fairly low probability at intensities corresponding to those of sunlight on the surface of the Earth ($\sim 1 \text{ kW/m}^2$), different approaches to enhancing the efficiency of up-
25 conversion have been examined. In addition to the obvious solution of external concentration, many groups have considered nano-optical engineering as a tool for local field enhancement. An approach based on embedding the upconverter inside a Bragg stack was recently proposed [12], and several groups have em-
30 ployed variations of plasmonic near-field enhancement [13, 14, 15, 16, 17]. Along these lines, we recently demonstrated that a single layer of plasmonic gold nanodiscs, produced by electron beam lithography (EBL) on an Er^{3+} -doped TiO_2 film, could enhance the upconversion luminescence by a factor of 7 [1].

The current activities are directed towards optimizing such enhancement
35 factors by employing optimization of the geometry and topology of the nanoparticles. The performance of plasmonic systems has previously been tuned by numerically scanning parameters defining the size, shape, and arrangement of different metal nanoparticles [18, 19, 1] and metallic grating couplers [20]. While the nature of parameter-based search-methods is simple and easy to un-
40 derstand, less freedom is given in the tuning process. In the current project, density-based topology optimization [21] is used to obtain designs tailored to enhance the electric field at wavelengths within the absorption band of erbium, without imposing any unnecessary geometric constraints on the design. Using this method, multiple excitation wavelengths, incidence angles as well as several
45 design realizations are considered simultaneously in the optimization process, aiming for a robust, broadband, optimized nanoparticle design.

2. Approaches to fabrication of materials

The SunTune project focuses on Er^{3+} as the upconverting ion, hosted in two different matrices. Thin films of TiO_2 are very well suited for basic investigations of the upconversion process and the flat samples facilitate nanostructuring by EBL. However, the deposition rates are fairly low, and a better choice for industrial applications are thus upconverting nanoparticles produced by chemical methods.

In the following subsections, we will review the fabrication methods for the two complementary hosts, and we will describe the possibilities and limitations of using EBL for defining the geometry of plasmonic nanoparticles. Finally, in a separate subsection, we will review upconversion applied for organic solar cells.

2.1. Upconverter materials

Fabrication of Er^{3+} -doped TiO_2 thin films was carried out by a radio-frequency magnetron sputtering system from AJA Orion ATC [22, 23, 1]. The targets were commercially produced (Able Targets) by mixing powders of TiO_2 and Er_2O_3 in desired ratios to achieve 1.3 at% to 6.1 at% of Er^{3+} ions [23]. The deposition was performed under 3 mTorr pressure of Ar with 2 % O_2 at 350 °C temperature. The sputtering power was set to 100 W for a steady deposition rate of around 0.1 Å/s to develop films with different thicknesses. Films ranging from 5 nm to a couple of hundred nanometers were fabricated showing surface roughness around 0.5 nm for thinner films and up to 5 nm, as measured by ellipsometry (Sentech SE850 PV Spectroscopic Ellipsometer) and atomic force microscopy (AFM) imaging (Bruker Edge). Cross-sectional images of the films were obtained by transmission electron microscopy (TEM) images (FEI Talos F200X) of samples prepared by focused-ion-beam milling, in order to analyze the compactness and the continuity of the films even for the thinnest samples. The crystallinity of the films was analyzed with X-ray diffraction using Cu $K\alpha$ radiation, in the Bragg–Brentano geometry (Bruker D8 Discover). Rutherford backscattering spectrometry was performed on several films to ensure the sto-

ichiometric composition of the host TiO_2 and the concentration of the dopant Er^{3+} ions [23].

As an alternative host, we are investigating Er^{3+} -doped NaYF_4 nanoparticles fabricated by chemical synthesis of core-shell ($\text{Er}:\text{NaYF}_4\text{-NaLuF}_4$) nanoparticles deposited by drop-cast-assisted spin coating on fused quartz substrates. Synthesis of Er^{3+} -doped $\beta\text{-NaYF}_4$ nanocrystals was performed by a solvo-thermal method with some modifications [24] within a size range of 8.0 ± 0.7 nm to 40 ± 1.4 nm and with Er^{3+} -dopant concentrations in the range of 4 mol % to 20 mol %.

The 20 mol % Er^{3+} -doped $\beta\text{-NaYF}_4$ nanocrystals were used as a core for fabrication of optically inert shells of $\beta\text{-NaLuF}_4$ around the structures by mixed sequential injection and independent injection of precursor concentrations [25, 26, 27]. After the reaction, all the samples were washed with ethanol and suspended in toluene solvent at room temperature.

The sizes of the core and core-shell nanocrystals were measured by transmission electron microscopy (Technai G2 Spirit Twins). We synthesized core nanocrystals with diameter of 19.7 ± 0.7 nm and introduced shells of NaLuF_4 with thicknesses from 0.8 ± 0.8 nm to 10.3 ± 1.3 nm, see Fig. 1. X-ray diffraction techniques (Rikagu diffractometer) verified the phase and crystalline size of all samples, which was in good agreement with TEM measurements. Inductively-coupled-plasma optical-emission spectroscopy (ICP-OES) showed a 17.2 mol % Er^{3+} concentration with small (± 2 mol %) variations over all samples.

Once the particles were synthesized, drop-cast-assisted spin coating of the structures were performed to fabricate thin films on quartz substrates. The films were prepared by introducing a drop of solution on the quartz substrates and spinning afterwards with a speed of 3500 rpm for 40 seconds in a spin-coater. The thickness of the films was varied by tuning the concentration of the colloidal solution to form monolayers to multilayers with a couple of hundred of nanometres thickness.

Figure 2 (a) shows the compact and homogeneous coverage of the nanoparticles in the monolayer. All the monolayers were heated to 150 °C for 15 minutes in uniform heating to evaporate the residuals of toluene. Figure 2 (b) depicts

Figure 1: Er^{3+} -doped $\beta\text{-NaYF}_4$ core nanocrystals of mean diameter 19.7 nm (left panel) and 40.2 nm mean diameter core-shell nanocrystals grown with two-step epitaxial growth of $\beta\text{-NaLuF}_4$ around the core (right panel).

EBL-defined Au disks buried by the core nanocrystals. The same work is currently in progress for all the $\text{Er}^{3+}:\text{NaYF}_4\text{-NaYF}_4$ core-shell structures with an aim to deposit Au disks with a surface-plasmon resonance at 1500 nm wavelength on top of the monolayer via an EBL process.

2.2. Electron-beam lithography

Electron beam lithography (EBL) is a fundamental tool for direct writing on the nanoscale by depositing a required amount of energy in a desired pattern into an electron-sensitive layer using an electron beam (e-beam). The designed nanostructures can be realized after patterning by metallization/etching and removal of the unwanted resist. The fabrication principle is essentially the same as in photolithography but with the key advantage of overcoming the optical diffraction limit, which is on wavelength scale in optical lithography systems. Major advantages and key challenges involved in the EBL-fabrication process are well reported in the literature [28, 29, 30]. In general, the two main issues in the nanofabrication via EBL are: (i) throughput, which becomes important when large-area fabrication is required, and (ii) proximity effects, where the surplus

Figure 2: Drop-cast-assisted spin coated $\text{Er}^{3+}:\text{NaYF}_4$ nanocrystals on (a) a quartz substrate and (b) on EBL-defined Au nanodisks on top of quartz. Air gaps between nanocrystals are visible as black and white areas in panels (a) and (b), respectively. Au nanodisks are fully covered with nanocrystals and placed randomly on the substrate.

dose from scattering of electrons inside the material limits the resolution. The significance of these factors depends on the design and density of the exposed patterns, and here we will focus on the main issues encountered during the EBL-fabrication process in the current activities. Various nanostructures were fabricated mainly on top of the erbium doped TiO_2 -coated quartz substrates.

The process flow of the adopted fabrication scheme is shown in Fig. 3. An FEI Magellan 30 kV scanning electron microscopy (SEM) system, equipped with a Raith pattern generator, was employed. The well-established electron-sensitive resist polymethylmethacrylate (PMMA) [31, 32] was used as a mask for the e-beam patterning. A mixture of methyl isobutyl ketone (MIBK) and isopropanol (IPA) was used for dissolving the patterned part of the resist and pure IPA was used as a stopper. An e-beam-gun source in a physical-vapor-deposition system was used to deposit the gold (Au) through the patterned mask. Finally, the unexposed resist was dissolved in acetone and Au nanodisks of size ranging between 100 nm to 600 nm were realized. Two different strategies were adopted for fabricating Au nanodisks arranged in periodic arrays, denoted PD (periodic discs), over large areas (a few mm^2). With the first strategy, PD

Figure 3: The EBL fabrication process in systematic stages. In the first step, substrates are spin coated with the electron-sensitive resist. In the second step, the resist is exposed to the patterned e-beam and the exposed part is subsequently dissolved (positive tone) in the solvent. In the next step, metal is deposited on the produced mask, followed by the removal of unexposed resist along with the unwanted metal, hence resulting in the patterned structures on the substrate.

of various sizes were obtained by simply employing an “area-exposure” scheme. In principle, the process is rather straightforward as by changing only the disk diameter in the design, one can achieve the required fabricated disk size after implementing the correct electron-dose values. However, in this approach the total exposure time may be a point of concern, as the area-exposure is realized by partitioning the design into multiple dot-exposures, defined by the step-size of the e-beam path. In the second strategy, the similarity between the shape of the disk (circular) and the e-beam was exploited by implementing a single-dot-exposure scheme. Figure 4 shows SEM images of samples, where Au nanodisks with different densities were fabricated on large areas using the dot-exposure technique. The disk size can be controlled by selecting the optimum current value (or aperture) and variable dose. However, dose values can be increased only up to a certain limit before an area is overexposed, resulting in an inversion of the response (tone) of the resist, i.e. from positive to negative. The total exposure time can be significantly reduced by adopting the latter

Figure 4: SEM images of periodic Au nanodisks with 50 nm height, fabricated using single-dot exposure with different densities [periods of 700 nm in (a) and 1000 nm in (b)] on top of the 100 nm thin Er^{3+} -doped TiO_2 -coated quartz substrates.

155 strategy, which is thus in general advantageous for fabricating PD at a large scale. However, it can also be problematic in some cases, as detailed below.

It is noteworthy that the optical properties of metallic nanodisks in a periodic arrangement are critically dependent on the incidence angle due to diffraction effects. If it is desirable to minimize this angle dependence, random arrangements of disks (RD) can be useful [33]. In the fabrication of RD, the single-dot-exposure scheme can be challenging, particularly when large disk sizes and therefore higher doses are required; in this case proximity effects become important. The irregular inter-particle distances cause an asymmetrical contribution of excess dose from the neighbors. In Fig. 5, this effect is clearly seen: RD, which are closely spaced, end up with larger size (i.e. overexposed) as compared to others, which are placed with larger inter-particle spacing. The proximity effect can be reduced by assigning the dose close to the clearing-dose range and controlling the disk diameter rather by varying the development time or using a strong developer. Furthermore, the disk size can be increased, without significant proximity contributions, by an additional step of plasma etching: After e-beam exposure and development, the patterned mask is etched to the desired thickness, which also increases the size of patterned features, i.e. the diameters

160
165
170

Figure 5: SEM image of fabricated randomly spaced Au nanodisks on top of the 100 nm thin Er^{3+} -doped TiO_2 coated quartz substrate.

of the disks in the present case. Figure 6 (b) demonstrates this technique, as RD
of size as large as ~ 600 nm were successfully achieved by adopting the plasma
175 etching route rather than relying on electron-dose values to control the disk size.
In Fig. 6 (a), on the other hand, it can be seen that the proximity effect was
unavoidable, even for comparatively smaller disk sizes, when the conventional
dose-variation technique was chosen in dot-exposure.

The single-dot-exposure scheme can, however, not be implemented in the
180 case of complex structural designs. In order to meet the throughput issue for
area-exposure cases, highly sensitive electron resists can be an option. For
instance so called semi-chemically amplified resist (CSAR) is one of the good
choices [34]. The proximity effect remains an issue and its contribution becomes
even more complex in irregular designs containing sub-50 nm features. There
185 are several commercial tools available, which implement various computational
proximity-correction methods such as dose correction, geometrical correction,
and background-exposure correction. In the past, several studies have been
conducted on this topic [35, 36, 37, 38, 39], and we have recently proposed
an optimization-based proximity-effect-correction (PEC) scheme for nanoscale

Figure 6: SEM images of fabricated randomly spaced Au nanodisks on top of the 100 nm Er^{3+} -doped TiO_2 film on a quartz substrate. When controlling the diameters by the e-beam dose, proximity effects occur (a) while these are avoided by controlling the size through the development time and assisted plasma etching (b).

lithography [40]. Leveraging concepts from the field of topology optimization [41], the proposed method enables PEC with nanometer resolution on a modern PC in minutes. For the EBL system considered in this work, the PEC method was able to reduce the minimum resolvable feature size by more than a factor of two. A combined topology-optimization and PEC approach, which integrates manufacturing constraints and thus ensures realizability, is described in Refs. [42, 43].

2.3. Upconversion in organic solar cells

The unique properties of organic semiconductors, and their use in development of low-cost, lightweight and flexible organic photovoltaic (OPV) devices has led to significant research and development investigations over the last decade. Currently, however, the still relatively low power-conversion efficiency of OPV limits their viability for cost competitive commercial production. OPV cells with a band gap of around 2 eV have up to around 75 % loss of photons, due to the photon energies being below the absorption threshold [7], which places a great need for developing more advanced innovative light-harvesting techniques to increase the absorption range in the near-infrared (NIR) region. To date,

several approaches have been developed to harvest the NIR and IR region of the solar spectrum in OPV, including synthesizing new low-band-gap donors [44], using inorganic nanocrystal sensitizers [45], developing ternary or tandem OPV [46], and utilizing upconversion materials [7, 47].

Although upconversion materials have a lot of promise for OPV applications, their integration in these cells requires different design considerations and strategies. The upconverter layer can for example be applied at the back of a device (the back contact should be transparent), or it can be integrated inside the device structure [48], for which different integration requirements must be met. In 2011, Wang et al. reported the potential of using commercial upconversion phosphors based on yttrium fluoride hosts doped with ytterbium and erbium to improve the NIR response of P3HT:PC₆₀B OPV [47]. The photocurrent density of 16.5 $\mu\text{A}/\text{cm}^2$ was obtained under laser illumination intensities of around 25 mW/cm². Also MoO₃:Yb³⁺/Er³⁺ have been used as an up-conversion layer in these cells with less than 1 % short circuit current (J_{sc}) improvement under 1 sun illumination due to the upconversion effect [49]. Adikaari et al. reported on upconversion in PCDTBT-based OPV [50], where the upconversion layer was placed behind the solar cell structure using transparent electrodes [50]. Schulze et al. showed the use of photochemical upconversion based on triplet-triplet annihilation upconverter materials for inverted semitransparent OPV [51], resulting in current enhancements of up to 0.2 % measured at 19 suns. W. Chen et al. demonstrated that NaYF₄:Yb³⁺/Er³⁺ hexagonal nanoplates can be embedded in PMMA matrices, providing J_{sc} of 450 $\mu\text{A}/\text{cm}^2$ under 975 nm laser diode illumination, leading to around 0.1 % pure upconversion power-conversion efficiency [52]. Although several research efforts have been made to enhance the photocurrent after combining the upconverters in OPV, the efficiency increase obtained is, however, still relatively low, and further improvements are needed before this can become a viable integration route [53]. The sub-bandgap photocurrent response and the upconversion efficiency in OPV could be further improved by using e.g. non-luminescent doping, plasmonic metallic nanostructures [54, 1, 2] or photonic crystals [53, 55].

Figure 7: (a) Absorption spectrum of ITO/PFN/P3HT:PC₆₀BM/MoO₃/Ag OPV extracted experimentally from diffuse reflection and transmission. The inset shows a scanning electron microscope image of the grating stripes consisting of approximately 11 Au nanoparticles across each stripe. (b) FDTD-calculated device absorption comparing cells with a grating structure to cells with integrated periodically arranged Au NPs. Adapted from Ref. [56].

In general, plasmonics provide a promising approach for obtaining improved device performances in OPV, and using the plasmonic effect with upconverting materials could further boost the absorption of NIR photons in OPV. We investigated experimentally and theoretically the effect of integrated metal nanostructures in OPV, such as integrated surface-ordered Au nanoparticle arrangements fabricated from a lithography-free stamping technique [56]. Light absorption enhancement from the periodically arranged nanoparticles demonstrated a broad-band absorption enhancement, which can be explained by the strong near field originating from the local plasmon resonance of the Au nanoparticles, together with the diffraction effect of the grating structure. The simulation results show light absorption enhancement in the wavelength range of 550 nm to 600 nm for solar cells with the silver (Ag) grating structures (grating period of 700 nm); a stronger optical enhancement is seen between 450 nm and 625 nm due to light scattering in combination with the plasmon resonance of the Au nanoparticles. Figure 7 shows the measured and theoretically calculated absorption in the organic solar cell. Discrepancies within the absorption range of the active layer blend (up to around 650 nm) between the experimentally measured and theoret-

Figure 8: (a) Calculated optical absorption of the flat and nanostructured cell (calculated via the FDTD method and labelled FDTD absorption), employing the same active layer height, and thus less active layer material for the nanostructured cell. (b) Modelled device performances of reference cell (black), nanostructured cell without absorption enhancement (blue), and nanostructured cell with absorption enhancement (red). Adapted from Ref. [59].

ically calculated absorption (in the experimental case calculated and plotted as 1-R-T) can be explained by small variations in the real nanostructure/grating size and shape, as compared to the theoretical model. Above 650 nm, parasitic absorption appears in the experimental measurements. It should be emphasized that as the applicability of this technique extends to all material combinations, it shows a general pathway towards device integration, including cost-effective up scaling [56].

Modifications of the electrical properties, alongside the optical ones, become relevant when integrating nanostructures inside OPV [57, 58]. This is due to the integrated light-trapping nanostructures being likely to affect photophysical processes such as charge-carrier losses, transport, and collection. To address the issue of tracing the electrical device properties upon nanostructure integration more precisely, we have theoretically studied the electrical properties of three-dimensional OPV with a back contact grating structure [59]. As a result, we find a significant fill-factor enhancement (18 %) in the investigated nanostructured OPV, which arises due to an increased interfacial area and thus improved charge-collection efficiency in the OPV cells. The results are highlighted in Fig. 8.

Our results confirm that, by implementing nanostructured gratings in OPV, we are able to increase the power-conversion efficiency of the cells by up to 28.5 % compared to the planar reference cells, due to a concurrent enhance-
 275 ment of both the electrical and optical cell characteristics [59]. In future work, similar studies on the optical and electrical properties of nanostructured OPV should be combined with integration of upconverter materials, in order to improve the absorption and power-conversion-efficiency enhancements obtained from upconverter layers integrated inside or outside OPV cells.

280 **3. Approaches to modelling**

Detailed modelling of the response of the upconversion process serves as important guidelines for the fabrication and for validating the interpretation of experimental results. The modelling must account for the important electric field distribution inside the upconverter materials, including also plasmonic
 285 near fields. In the following two subsections, we will provide a brief review of approaches to electric-field modelling in photovoltaics, followed by a short introduction to topology optimization with emphasis on its applications to the SunTune project.

3.1. Electric field calculations

290 In their simplest form, solar cells consist of stacks of planar layers, which, from an optical perspective, can be modeled efficiently using one-dimensional approaches such as the transfer matrix method (TMM) [60]. Modern solar cells incorporate light trapping strategies to increase the efficiency. The most common example is texturing of the front surface, which can improve light
 295 incoupling and increase the effective path length in the absorber [61]. The typical length scale of the textures is in the micrometer range, i.e. larger than the wavelength of the incident light, meaning that they can to a good approximation be treated within the framework of geometrical optics. Systems incorporating such textures can be modeled using statistical ray tracing [62]. Due to the

300 combination of low computational complexity and high flexibility with respect
to both the texture geometry and the solar cell composition, ray-tracing is
among the most successful optical modelling methods within academia as well
as industry [63].

The addition of plasmonic elements to the solar cell introduces a new level
305 of complexity. Since the characteristic length scale of plasmonic structures is
well below the wavelength of the incident light [64], geometrical optics no longer
applies. For most structures of practical interest, however, the feature size is
large enough (greater than ≈ 10 nm) that quantum corrections can be neglected
[65], so that they can be treated with the macroscopic Maxwell's equations and
310 simple constitutive relations.

Analytical solutions to Maxwell's equations exist only for a few simple ge-
ometries, among which the Mie solution for spheres is the most well known [66],
but arbitrary geometries can be treated using numerical methods. This topic has
received significant attention in the past decades, resulting in the development of
315 a broad variety of techniques. Among the most popular are the discrete-dipole
approximation (DDA) [67], the finite-difference-time-domain method (FDTD)
[68], the finite-element method (FEM) [69], and the boundary-element method
(BEM) [70]. Each method has particular advantages and disadvantages, which
makes the best choice highly problem dependent. For geometries obtained by
320 topology optimization, which can potentially be highly asymmetric and incorpo-
rate small and/or sharp features (see Sec. 3.2), FEM is particularly well suited.

To enable integration in the solar cell complex, the plasmonic element should
be sheet-like. A sheet-like design is typically formed by repeating a unit geom-
etry periodically, or by distributing a particle ensemble across a surface. The
325 periodic design can be modeled by considering a unit cell domain to which
boundary conditions that enforce the appropriate translational symmetry are
applied. The non-periodic case is significantly more complicated. An exact
solution using FEM can be obtained only by discretizing the complete sheet,
which is not computationally feasible. Elegant solutions have been proposed for
330 ensembles of spheres [71] and spheroids [72], but the general case of arbitrary

particle geometries continues to be a challenge. If the particles are randomly distributed and the spacing is sufficient, particle-particle couplings can be neglected and the ensemble response can be approximated using a one-particle model [73]. We recently demonstrated that an improved accuracy can be achieved via a two-
335 particle model [3], which additionally enables an assessment of the validity of the one-particle model for a particular system.

In solar modules, utilizing plasmonically-enhanced upconversion, the solar cell complex will include both nano-sized structures, micrometer-sized textures as well as planar layers, where the absorber layer thickness can be several hun-
340 dreds of micrometers. The different length scales make it hard to identify one technique suitable for all cases. Hybridization methods such as OPTOS [74] address this issue by dividing the solar cell complex into elements. The elements are processed individually into a matrix representation using the most efficient method available, e.g. FEM for the plasmonic structures and ray tracing for
345 surface textures. The element matrices are subsequently coupled incoherently to yield the optical response of the complete system.

3.2. Topology optimization

Topology optimization [21] was originally developed in the late 1980's for applications within solid mechanics [75]. Since the early 2000's, the method
350 has been successfully applied to wave-governed design problems, such as acoustics [76, 77, 78], sub-wavelength antennas [79], nano-photonics [80, 81, 82], and plasmonics [83, 84, 2]. The wide adoption is attributable to the method's versatility, a growing numerical toolbox as well as advances in nanoscale production methods.

The fundamental goal of topology optimization is to identify a spatial mate-
355 rial distribution that maximizes the performance of a given system. The design problem is recast as an optimization problem, where the material distribution is optimized with respect to an objective function describing the physical properties in question, while satisfying a set of design constraints. Examples of such
360 constraints are: a maximum allowed material volume, a restriction on the size

of the smallest design features within production limitations, and a maximum allowed field intensity in a given region of space [85]. To allow for a numerical solution of the optimization problem, the design is represented in a discrete raster format using pixels (2D) or voxels (3D), often chosen to coincide with
365 the FEM or FDTD discretization, with material type in each pixel (or voxel) being a design variable. The distribution of material is expressed by assigning a value between 0 and 1 to each design variable and using the design variables to interpolate between the relevant properties of material A and B, with a value of 0 corresponding to material A and a value of 1 to material B. Hereby, the
370 otherwise discrete task of distributing the material constituting the design, is reformulated as a continuous optimization problem with each pixel representing a relative material density. The continuous-density formulation may obviously introduce intermediate densities (between 0 and 1), representing an unphysical mix of both materials making the designs non-realizable in practice. The presence of the intermediate densities can be mitigated using standard penalization
375 tools [86, 87, 88] ensuring a final design consisting of pure materials A and B.

Because of this voxel-based description, the design is allowed to change during the optimization process without any predefined geometrical constraints, such as those imposed by parameter-based shape and size optimization. Efficient topology optimization relies on the availability of gradient information for
380 the objective function, a calculation which is enabled by the continuous design variable description using adjoint sensitivity analysis [89, 82]. The access to gradient information, in turn, allows the method to solve ultra-high resolution design problems with a recent example reaching $\sim 10^9$ design variables [90].

For the current project, extensive studies using simplifying 2D assumptions
385 have been conducted as this enables significantly faster design and evaluation cycles, which in turn allows more research and knowledge to be obtained. Although full 3D-designs are likely to differ from their 2D counterparts, the knowledge gained in 2D is anticipated to lower the amount of work needed to obtain
390 the final 3D-designs for the nanoparticles.

We recently considered a periodic array of two-dimensional Au nanostrips

embedded in an Er^{3+} -doped TiO_2 thin film deposited on top of a fused quartz
 (SiO_2) substrate [2]. In total, four optimization cases were considered, investi-
 gating the influence of optimizing for a combination of multiple incident wave-
 lengths and/or multiple incident angles for both TM and TE polarized light.
 The polarization-averaged electric-field enhancement for each design was evalu-
 ated over an 80 nm wavelength range and ± 15 -degree incident angle span. The
 best performing design was obtained when simultaneously optimizing for three
 incident wavelengths (1480 nm, 1520 nm, 1560 nm) at normal incidence. The
 polarization-averaged field enhancement of this design was > 42 , relative to the
 situation without Au nanostrips embedded in the film. All designs were also
 optimized for robustness towards near-uniform geometric perturbations of ± 5
 nm. A performance variation of maximum 2 % was observed for the best design
 at the three considered wavelengths compared to a 70 % performance degra-
 dation of a parametrically optimized reference design. All designs obtained
 in this study were highly non-intuitive and simple design-parametrizations are
 thus not easily conceived, demonstrating the strength of density-based topology
 optimization.

A similar two-dimensional study considers a stratified setup, in which the
 design of a gold nanoparticle is optimized when deposited on top of a 320 nm
 thick $\text{Er}^{3+}:\text{TiO}_2$ film [91]. The study investigates the impact of optimizing the
 design near (and away from) conditions of diffractive incoupling to waveguide
 modes in the film, resulting in significant electric-field enhancement for the final
 topology-optimized design.

With the aim of mitigating ill-convergence issues for plasmonic problems, a
 new non-linear interpolation scheme for use in topology optimization of metallic
 micro- and nanostructures for electromagnetic applications was recently devel-
 oped and investigated in [92]. By optimizing the energy amplification of nano-
 scale metallic antennas, this new interpolation scheme is compared to schemes
 previously used in the literature. The non-linear scheme shows superior prop-
 erties from the ultraviolet to the near-infrared wavelength regime, resulting in
 ultra-high performing designs compared to designs obtained with the previous

Figure 9: Initial 3D result: gold nanoparticle optimized for electric field enhancement considering three incident wavelengths (1480 nm, 1520 nm, 1560 nm) at normal incidence. The plot shows the 100 nm thick gold design (black) as well as the polarization-averaged field enhancement in the 320 nm thick $\text{Er}^{3+}:\text{TiO}_2$ film. The transverse dimensions of the film are 1000 nm $\times$ 1000 nm. Left panel: Center cut through the xz -plane. Right panel: The full periodic particle.

interpolation schemes.

The transition to fully three-dimensional optimizations is currently on-going. A preliminary 3D design is shown in Fig. 9, along with the polarization-averaged field enhancement in the film. This design was obtained by designing for three wavelengths (1480 nm, 1520 nm, 1560 nm) at normal incidence.

Several 3D studies will in the near future follow this initial result, exploring the possible performance gain of applying topology optimization as a design tool while respecting the production limits set by the EBL equipment available to the project. Long-term objectives include optimization of embedded nanoparticles, possibly in a more advanced setup using multi-layered design-domain configurations.

4. Experimental validation of plasmonic near-field calculations

In order to validate rigorous electric-field calculations of plasmonic nanostructures experimentally, it is necessary to probe the near fields with nanometer resolution. It is impossible for standard optical techniques to achieve this resolution due to the diffraction limit. Therefore, scanning near-field optical

microscopy (SNOM) [93] and electron-microscopy techniques such as electron
440 energy loss spectroscopy (EELS) and cathodoluminescence (CL) [94, 95] are typ-
ically used. However, the electric near-field amplitudes are not easily deduced
from these [94], so other techniques are needed for quantitative comparison.

The technique, which is pursued here, utilizes ultrashort-laser-pulse excita-
tion for causing permanent change in some medium surrounding the plasmonic
445 nanostructures. The laser-induced change can for instance be ablation (ma-
terial removal) [96, 97, 98, 4], phase-change [99, 100], or polymerization of a
photoresist [101, 102]. In all cases, the change is abrupt, implying that a cer-
tain threshold must be reached. The threshold is often expressed in terms of
incident laser fluence (pulse energy per unit area), denoted by F_{th} [103]. This
450 means that upon irradiating the nanostructures below the threshold, say by the
fluence F , no change is caused in the medium, except in locations where the
electric field (and hence the absorption) has been sufficiently enhanced above
the threshold. The boundary between the changed and unchanged material
represents a line (or surface) where the fluence F was increased to the threshold
455 value, F_{th} . Thus, the associated near-field enhancement (NFE) can be extracted
simply as $\text{NFE} = (F_{\text{th}}/F)^{1/2}$ (as the fluence is proportional to the square of the
electric field). By varying the incident fluence F , different lines (or surfaces) of
constant NFE can be mapped out. Since most laser beams are Gaussian in cross
section, each pulse contains all fluences ranging from zero to the peak value in
460 the center of the beam. A single pulse illuminates many nanoparticles with dif-
ferent distances to the center of the beam and thus probes, in principle, all the
possible values of NFEs. Since the induced change is permanent, the resulting
structures can be imaged with high spatial resolution in SEM and AFM.

Recently, electric near-field enhancements of isolated gold nanostars, placed
465 on top of a $\text{Er}^{3+}:\text{TiO}_2$ thin film with localized surface-plasmon resonances
around 1550 nm, were measured by near-field ablation and compared to simu-
lations [4]. The technique supported the near-field calculation to a reasonable
degree, but systematic differences were observed near hotspots of high NFE.
This was attributed to the physical processes preceding ablation, such as, but

not limited to, carrier diffusion, which tends to smear out the initial energy distribution. Consequently, for rigorous validation of the near-field calculations, additional simulations of the dynamics leading to ablation must be supplied using appropriate models for short-pulse excitation of metallic [104, 105, 106, 107] or dielectric [108, 103, 109, 110] samples. Note that the ablative near-field-marking technique is especially advantageous since no additional steps of sample preparation are required.

Near-field marking by ablation is limited to images of NFEs only in the substrate surface. An approach for experimentally achieving 3D maps of NFEs is currently being pursued by embedding the nanoparticles inside a polymer (SU-8). Here the near-field marking is achieved by photo-polymerization via multiphoton excitation [102, 111]. SU-8 is a negative resist, meaning that the non-polymerized SU-8 can be washed off in a post-processing step. The remaining polymerized SU-8 will stick to the plasmonic nanostructures due to NFE. The boundaries of the polymerized structures can then be related directly to surfaces of constant NFE. The procedure is illustrated in Fig. 10 (a)–(b). By combining SEM and AFM, part of the surfaces can be traced, hence making 3D mapping possible. The first results, demonstrating feasibility of this approach, are shown in Fig. 10 (c)–(e).

5. Modelling the upconversion process by rate equations

As mentioned previously, the current investigation employs Er^{3+} as the up-converting system. The lowest-lying energy levels in trivalent erbium are shown in Fig. 11 (a), and several physical mechanisms are involved in the coupling between these levels and hence in the properties of the entire upconversion process. Two different excitation mechanisms contribute to the upconversion process: (i) Ground-state absorption followed by excited-state absorption (ESA), and (ii) energy-transfer upconversion (ETU), where two excited erbium ions interact via resonant Förster energy-transfer [112]. It is our aim to make a confident determination of all the physical parameters governing the upconversion

Figure 10: Procedure for 3D marking of the optical near fields by multiphoton polymerization. (a) A plasmonic gold nanostar on top of a $\text{Er}^{3+}:\text{TiO}_2$ film is covered by a layer of SU-8 (approximately $1\ \mu\text{m}$ thick). Irradiation by a femtosecond (fs) laser polymerizes part of the SU-8 due to NFE. (b) The polymer is developed, leaving only the polymerized SU-8 behind. (c) AFM image of nanostars subjected to the near-field-marking procedure, showing SU-8 at the tips where significant NFE occurs. The arrow denotes the direction of increasing laser fluence (hence the mapping of decreasing NFE). (d) Close up of the two nanostars labelled 1 and 2 together with the corresponding values of NFE. Simulations of NFE in the upper layer of the $\text{Er}^{3+}:\text{TiO}_2$ are shown in panel 3 (truncated to values of 3.0). (e) Comparison between simulated near-field distribution with contours (dash-dotted and solid corresponding to nanostar 1 and 2, respectively) along the line shown in panel 3 in (d).

process, which is work in progress. Below we will give a qualitative exemplifica-
500 tion of these efforts by assessing the relative significance of the ETU and ESA
processes.

The upconversion dynamics in an ensemble of erbium ions can be described
by a rate-equation model [113]. The model must involve physical parameters
describing absorption, stimulated emission, spontaneous emission (radiative and
505 non-radiative) and energy-transfer upconversion (including the inverse process
sometimes referred to as cross-relaxation). In Ref. [113] the authors approached,
with great success, the determination of these physical parameters by a combi-
nation of measuring absorption coefficients and fitting the remaining parameters
of the model to measurements of quantum efficiency using samples of varying
510 concentration and varying excitation power. Another approach, the one that
we are pursuing, is to determine the individual parameters more directly by
time-resolved luminescence spectroscopy along the lines of Ref. [114]. There
are drawbacks in either case: for the fitting approach the inter-dependence of
the involved multiple fitting parameters complicate the intuition and may even
515 lead to parameters which are not physically meaningful. On the other hand,
experimentally determining the parameters more directly is an immense task
and still requires some level of modelling, since the observed decay dynamics
still depends on combinations of various physical processes.

In our work, the luminescence from various excited states is detected as
520 a function of time after excitation by a pulsed laser. A tunable femtosecond
pulse, generated by an optical parametric amplifier (TOPAS) pumped by a 35 fs
Ti:sapphire laser, is utilized to excite the various Er^{3+} transitions and a 1-ns-
resolution single-photon detection system undertakes the ensuing fluorescence
measurements. From these time-resolved measurements, the total decay rates
525 from each level are directly accessible. More indirectly, information about the
ETU rates can be gained when luminescence is observed at shorter wavelength
than used for the excitation. This is exemplified in Fig. 11, where the $^4I_{13/2}$
level is excited by a 1520 nm laser pulse while the luminescence centered at 980
nm from the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition is monitored. Since ESA is occurring

Figure 11: (a) The lowest-lying energy levels of Er^{3+} . Time-resolved fluorescence spectroscopy is exemplified using an initial pump-laser pulse at 1520 nm (red arrow) while detecting the ensuing luminescence on the 980 nm transition (blue arrow). (b) Luminescence decay curves obtained at the 980 nm transition for various excitation fluences [see (c)]. The data is fitted (black solid lines) to an exponential decay after an initial rise, $f(t) = [1 - A_R \exp(-g_R t)] A_D \exp(-g_D t)$, where the A and g parameters are amplitudes and rates, respectively, describing the rising (R) or decaying (D) part of the curve. The initial rise in the decay curve indicates that the ETU is dominant. (c) Fitted rise times for each decay curve plotted as a function of the laser-excitation fluence.

530 only during the very short laser-excitation pulse, the excitation of the ${}^4I_{11/2}$
 level (via ESA through the ${}^4I_{9/2}$ level and fast decay to the ${}^4I_{11/2}$ level) occurs
 essentially instantaneously. On the other hand, ETU from the ${}^4I_{13/2}$ level will
 occur on a slower time scale characteristic of the ETU process, which is in fact
 seen as the initial rising behavior of the curves in Fig. 11 (b). When the fluence
 535 of the excitation laser is increased, the probability that two nearby Er^{3+} ions
 are simultaneously excited increases, which in turn increases the probability
 for ETU. This is indeed observed in Fig. 11 (c), where the rise time is seen
 to decrease with increasing laser-excitation fluence. We thus have direct proof
 that upconversion is mainly due to ETU, and an estimate for the typical time
 540 scales of ETU (tens of microseconds) at the investigated level of excitation can
 be obtained.

The task of determining the rate-equation parameters is thus attacked through
 different time resolved experiments, e.g. by varying the transition of excitation
 and of fluorescence detection, and also by studying different samples with dif-
 545 ferent Er^{3+} concentration.

6. Experimental validation of the total upconversion yield

Since one of the main goals in the SunTune project is to increase the effi-
 ciency of the upconversion process, it is important to establish that the use of
 metal nanoparticles on the upconverting materials indeed improves the perfor-
 550 mance. Upconversion luminescence (UCL) of Er^{3+} -doped TiO_2 thin films has
 been experimentally recorded for excitations at 1503 nm, 980 nm and, 800 nm
 [1, 19], exemplifying a very common tool for assessing the upconversion per-
 formance. The upconverter materials are typically excited by continuous-wave
 laser beams, and the emission can be acquired either directly from the sample
 555 or collected independently of the specific emission pattern by placing the sam-
 ple inside an integrating sphere. While the former approach has the highest
 sensitivity, the latter method is needed for quantitative measurements of the
 upconversion yield.

We have previously studied the dependence of the upconversion luminescence
 560 on the concentration of Er^{3+} from 1.3 at% to 6.1 at% in the TiO_2 films while
 keeping the thickness constant; we observed an increase in UCL up to 4.5 at%
 concentration, and a sudden drop at 6.1 at% [22]. More recently, we investigated
 Au-nanodisk-enhanced upconversion in 100 nm Er^{3+} -doped (5.1 at%) TiO_2 films
 [1]. The UCL intensity at 980 nm was clearly enhanced in the presence of the Au
 565 nanodisks, and the enhancement factor depended on the size of Au nanodisks
 and attained its maximum value of 7 when the spectral position of the surface-
 plasmon resonance was matching the 1520 nm $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition of
 Er^{3+} . The variations of the UCL enhancement factors with nanodisk diameter
 was in qualitative agreement with finite-element calculations.

570 7. Conclusion and outlook

Upconversion remains a promising extension to the current state of the art
 in photovoltaics. The potential of achieving several percentage points in overall
 cell-efficiency improvements motivates investigations by several research groups.
 The current review serves to provide a status of the current developments in
 575 the SunTune consortium. Many promising results have been obtained, many
 experimental challenges have been solved, and the theoretical framework for
 optimization of the upconversion process has been established. Our work con-
 tinues, and new results, both improving our understanding and suggesting new,
 improved designs, will hopefully soon be available.

580 This work was supported by Innovation Fund Denmark through the SunTune
 project.

References

- [1] H. Lakhotiya, A. Nazir, S. P. Madsen, J. Christiansen, E. Eriksen,
 J. Vester-Petersen, S. R. Johannsen, B. R. Jeppesen, P. Balling, A. N.
 585 Larsen, B. Julsgaard, Plasmonically enhanced upconversion of 1500nm

light via trivalent Er in a TiO₂ matrix, APPLIED PHYSICS LETTERS
109 (26) (2016) 263102. doi:10.1063/1.4972785.

- [2] J. Vester-Petersen, R. E. Christiansen, B. Julsgaard, P. Balling, O. Sigmund, S. P. Madsen, Topology optimized gold nanostrips for enhanced
near-infrared photon upconversion, APPLIED PHYSICS LETTERS
111 (13) (2017) 133102. doi:10.1063/1.4998552.

- [3] E. H. Eriksen, B. Julsgaard, S. P. Madsen, H. Lakhotiya, A. Nazir, P. Balling, Particle-particle interactions in large, sparse arrays of randomly distributed plasmonic metal nanoparticles: a two-particle model, OPTICS
EXPRESS 25 (16) (2017) 19354–19359. doi:10.1364/OE.25.019354.

- [4] S. H. Møller, J. Vester-Petersen, A. Nazir, E. H. Eriksen, B. Julsgaard, S. P. Madsen, P. Balling, Near-field marking of gold nanostars by ultrashort pulsed laser irradiation: experiment and simulations, APPLIED
PHYSICS A-MATERIALS SCIENCE & PROCESSING 124 (2) (2018) 210. doi:10.1007/s00339-018-1615-4.

- [5] W. Shockley, H. J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, Journal of Applied Physics 32 (3) (1961) 510–519. arXiv:9809069v1, doi:10.1063/1.1736034.

- [6] T. Trupke, A. Shalav, B. Richards, P. Würfel, M. Green, Efficiency enhancement of solar cells by luminescent up-conversion of sunlight, Solar
Energy Materials and Solar Cells 90 (18) (2006) 3327–3338.

- [7] J. C. Goldschmidt, S. Fischer, Upconversion for Photovoltaics a Review of Materials, Devices and Concepts for Performance Enhancement, Advanced Optical Materials 3 (4) (2015) 510–535. doi:10.1002/adom.201500024.

- [8] B. S. Richards, A. Shalav, Enhancing the near-infrared spectral response of silicon optoelectronic devices via up-conversion, IEEE Transactions on Electron Devices 54 (10) (2007) 2679–2684.

- [9] C. Strümpel, M. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Švrček, C. Del Cañizo, I. Tobias, Modifying the solar spectrum to enhance silicon solar cell efficiency - An overview of available materials, *Solar Energy Materials and Solar Cells* 91 (4) (2007) 238–249.
- [10] S. Fischer, J. Goldschmidt, P. Löper, G. Bauer, R. Brüggemann, K. Krämer, D. Biner, M. Hermle, S. Glunz, Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization, *Journal of Applied Physics* 108 (4) (2010) 044912.
- [11] S. Fischer, E. Favilla, M. Tonelli, J. C. Goldschmidt, Record efficient upconverter solar cell devices with optimized bifacial silicon solar cells and monocrystalline $\text{BaY}_2\text{F}_8:30\% \text{Er}^{3+}$ upconverter, *Solar Energy Materials and Solar Cells* 136 (2015) 127–134. doi:10.1016/j.solmat.2014.12.023.
- [12] C. Hofmann, E. Eriksen, S. Fischer, B. Richards, P. Balling, J. Goldschmidt, Enhanced upconversion in one-dimensional photonic crystals: a simulation-based assessment within realistic material and fabrication constraints, *Optics Express* 26 (6) (2018) 7537–7554. doi:10.1364/OE.26.007537.
- [13] H. Mertens, A. F. Koenderink, A. Polman, Plasmon-enhanced luminescence near noble-metal nanospheres: Comparison of exact theory and an improved Gersten and Nitzan model, *Physical Review B* 76 (2007) 115123. doi:10.1103/PhysRevB.76.115123.
- [14] E. Verhagen, L. Kuipers, A. Polman, Field enhancement in metallic sub-wavelength aperture arrays probed by erbium upconversion luminescence, *Optics Express* 17 (17) (2009) 14586–14598. doi:10.1364/OE.17.014586.
- [15] S. Fischer, F. Hallermann, T. Eichelkraut, G. V. Plessen, W. Karl, D. Biner, H. Steinkemper, M. Hermle, J. C. Goldschmidt, Plasmon enhanced upconversion luminescence near gold nanoparticles - simulation and analysis of the interactions, *Optics Express* 20 (1) (2012) 271–282.

- [16] S.-M. Lee, W. Li, P. Dhar, S. Malyk, Y. Wang, W. Lee, A. Benderskii, J. Yoon, High-Performance Flexible Nanostructured Silicon Solar Modules with Plasmonically Engineered Upconversion Medium, *Advanced Energy Materials* 5 (21) (2015) 1500761–n/a. doi:10.1002/aenm.201500761.
- [17] S. Fischer, D. Kumar, F. Hallermann, G. V. Plessen, C. Goldschmidt, Enhanced upconversion quantum yield near spherical gold nanoparticles - a comprehensive simulation based analysis, *Optics Express* 24 (6) (2016) A460–A475. doi:10.1364/OE.24.00A460.
- [18] S. P. Madsen, S. R. Johannsen, B. R. Jeppesen, J. V. Nygaard, P. B. Jensen, J. Chevallier, B. Julsgaard, P. Balling, A. N. Larsen, Optimizing Plasmonically Enhanced Upconversion, *Energy Procedia* 77 (2015) 478–486. doi:10.1016/j.egypro.2015.07.068.
- [19] S. R. Johannsen, S. P. Madsen, B. R. Jeppesen, J. V. Nygaard, B. Julsgaard, P. Balling, A. N. Larsen, Up-conversion enhancement in Er³⁺-doped TiO₂ through plasmonic coupling: Experiments and finite-element modeling, *APPLIED PHYSICS LETTERS* 106 (5) (2015) 053101. doi:10.1063/1.4907415.
- [20] J. Lu, C. Petre, E. Yablonovitch, J. Conway, Numerical optimization of a grating coupler for the efficient excitation of surface plasmons at an Ag-SiO₂ interface, *J. Opt. Soc. Am. B* 24 (9) (2007) 2268–2272. doi:10.1364/JOSAB.24.002268.
- [21] M. P. Bendsøe, O. Sigmund, *Topology Optimization – Theory, Methods and Applications*, Springer, 2004. doi:10.1007/978-3-662-05086-6.
- [22] S. R. Johannsen, S. Roesgaard, B. Julsgaard, R. A. S. Ferreira, J. Chevallier, P. Balling, S. K. Ram, A. N. Larsen, Influence of TiO₂ host crystallinity on Er³⁺ light emission, *OPTICAL MATERIALS EXPRESS* 6 (5) (2016) 1664–1678. doi:10.1364/OME.6.001664.

- 670 [23] S. R. Johannsen, L. R. Lauridsen, B. Julsgaard, P. T. Neuvonen, S. K. Ram, A. N. Larsen, Optimization of Er³⁺-doped TiO₂-thin films for infrared light up-conversion, THIN SOLID FILMS 550 (2014) 499–503. doi:10.1016/j.tsf.2013.10.123.
- [24] Z. Li, Y. Zhang, An efficient and user-friendly method for the synthesis of hexagonal-phase NaYF₄: Yb, Er/Tm nanocrystals with controllable shape and upconversion fluorescence, NANOTECHNOLOGY 19 (34) (2008) 345606. doi:10.1088/0957-4484/19/34/345606.
- 675 [25] N. J. J. Johnson, A. Korinek, C. Dong, F. C. J. M. van Veggel, Self-Focusing by Ostwald Ripening: A Strategy for Layer-by-Layer Epitaxial Growth on Upconverting Nanocrystals, JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 134 (27) (2012) 11068–11071. doi:10.1021/ja302717u.
- 680 [26] X. Li, D. Shen, J. Yang, C. Yao, R. Che, F. Zhang, D. Zhao, Successive Layer-by-Layer Strategy for Multi-Shell Epitaxial Growth: Shell Thickness and Doping Position Dependence in Upconverting Optical Properties, CHEMISTRY OF MATERIALS 25 (1) (2013) 106–112. doi:10.1021/cm3033498.
- 685 [27] S. Fischer, N. D. Bronstein, J. K. Swabeck, E. M. Chan, A. P. Alivisatos, Precise Tuning of Surface Quenching for Luminescence Enhancement in Core-Shell Lanthanide-Doped Nanocrystals, NANO LETTERS 16 (11) (2016) 7241–7247. doi:10.1021/acs.nanolett.6b03683.
- 690 [28] M. A. Mohammad, M. Muhammad, S. K. Dew, M. Stepanova, Fundamentals of Electron Beam Exposure and Development, Springer Vienna, Vienna, 2012, pp. 11–41. doi:10.1007/978-3-7091-0424-8_2.
- 695 [29] M. Altissimo, E-beam lithography for micro-/nanofabrication, BIOMICROFLUIDICS 4 (2) (2010) 026503. doi:10.1063/1.3437589.

- [30] C. Vieu, F. Carcenac, A. Pépin, Y. Chen, M. Mejias, A. Lebib, L. Manin-Ferlazzo, L. Couraud, H. Launois, Electron beam lithography: resolution limits and applications, *Applied Surface Science* 164 (2000) 111–117. doi:10.1016/S0169-4332(00)00352-4.
- [31] W. Chen, H. Ahmed, Fabrication of 5-7 Nm Wide Etched Lines in Silicon Using 100 Kev Electron-Beam Lithography and Polymethylmethacrylate Resist, *Applied Physics Letters* 62 (13) (1993) 1499–1501. doi:10.1063/1.109609.
- [32] S. Yasin, D. G. Hasko, H. Ahmed, Fabrication of < 5 nm width lines in poly(methylmethacrylate) resist using a water : isopropyl alcohol developer and ultrasonically-assisted development, *Applied Physics Letters* 78 (18) (2001) 2760–2762. doi:10.1063/1.1369615.
- [33] E. M. Hicks, S. L. Zou, G. C. Schatz, K. G. Spears, R. P. Van Duyne, L. Gunnarsson, T. Rindzevicius, B. Kasemo, M. Käll, Controlling plasmon line shapes through diffractive coupling in linear arrays of cylindrical nanoparticles fabricated by electron beam lithography, *Nano Letters* 5 (6) (2005) 1065–1070. doi:10.1021/nl0505492.
- [34] R. Andok, A. Bencurova, K. Vutova, E. Koleva, P. Nemec, P. Hrkut, I. Kostic, G. Mladenov, Study of the new CSAR62 positive tone electron-beam resist at 40 keV electron energy, *Journal of Physics: Conference Series* 700 (1) (2016) 012030.
URL <http://stacks.iop.org/1742-6596/700/i=1/a=012030>
- [35] M. Parikh, Corrections to proximity effects in electron beam lithography. I. Theory, *Journal of Applied Physics* 50 (6) (1979) 4371–4377. doi:10.1063/1.326423.
- [36] M. Parikh, Corrections to proximity effects in electron beam lithography. II. Implementation, *Journal of Applied Physics* 50 (6) (1979) 4378–4382. doi:10.1063/1.326424.

- 725 [37] M. Parikh, Selfconsistent proximity effect correction technique for resist exposure (SPECTRE), *Journal of Vacuum Science and Technology* 15 (3) (1978) 931–933. doi:10.1116/1.569678.
- [38] G. Owen, P. Rissman, Proximity effect correction for electron beam lithography by equalization of background dose, *Journal of Applied Physics* 730 54 (6) (1983) 3573–3581. doi:10.1063/1.332426.
- [39] L. D. Jackel, R. E. Howard, P. M. Mankiewich, H. G. Craighead, R. W. Epworth, Beam energy effects in electron beam lithography: The range and intensity of backscattered exposure, *Applied Physics Letters* 45 (6) (1984) 698–700. doi:10.1063/1.95361.
- 735 [40] E. H. Eriksen, A. Nazir, P. Balling, J. Vester-Petersen, R. E. Christiansen, O. Sigmund, S. P. Madsen, Dose regularization via filtering and projection: an open-source code for optimization-based proximity-effect-correction for nanoscale lithography, In preparation.
- [41] M. Jansen, B. Lazarov, M. Schevenels, O. Sigmund, On the similarities 740 between micro/nano lithography and topology optimization projection methods, *Structural and Multidisciplinary Optimization* 48 (4) (2013) 717–730. doi:10.1007/s00158-013-0941-6.
- [42] M. Zhou, B. S. Lazarov, O. Sigmund, Topology optimization for optical projection lithography with manufacturing uncertainties, *Appl. Opt.* 745 53 (12) (2014) 2720–2729. doi:10.1364/AO.53.002720.
- [43] M. Zhou, B. Lazarov, O. Sigmund, Topology optimization for optical microlithography with partially coherent illumination, *International Journal for Numerical Methods in Engineering* 109 (5) (2017) 631–647. doi:10.1002/nme.5299View.
- 750 [44] W. Li, K. H. Hendriks, W. S. C. Roelofs, Y. Kim, M. M. Wienk, R. A. J. Janssen, Efficient Small Bandgap Polymer Solar Cells with High Fill Fac-

tors for 300 nm Thick Films, *Advanced Materials* 25 (23) (2013) 3182–3186. doi:10.1002/adma.201300017.

- [45] J. A. Chang, S. H. Im, Y. H. Lee, H.-j. Kim, C.-S. Lim, J. H. Heo, S. I. Seok, Panchromatic Photon-Harvesting by Hole-Conducting Materials in Inorganic/Organic Heterojunction Sensitized-Solar Cell through the Formation of Nanostructured Electron Channels, *Nano Letters* 12 (4) (2012) 1863–1867, pMID: 22401668. doi:10.1021/nl204224v.
- [46] T. Ameri, P. Khoram, J. Min, C. J. Brabec, Organic Ternary Solar Cells: A Review, *Advanced Materials* 25 (31) (2013) 4245–4266. doi:10.1002/adma.201300623.
- [47] H.-Q. Wang, M. Batentschuk, A. Osvet, L. Pinna, C. J. Brabec, Rare-Earth Ion Doped Up-Conversion Materials for Photovoltaic Applications, *Advanced Materials* 23 (22-23) (2011) 2675–2680. doi:10.1002/adma.201100511.
- [48] L. T. Su, S. K. Karuturi, J. Luo, L. Liu, X. Liu, J. Guo, T. C. Sum, R. Deng, H. J. Fan, X. Liu, A. I. Y. Tok, Photon Upconversion in Hetero-nanostructured Photoanodes for Enhanced Near-Infrared Light Harvesting, *Advanced Materials* 25 (11) (2013) 1603–1607. doi:10.1002/adma.201204353.
- [49] H.-Q. Wang, T. Stubhan, A. Osvet, I. Litzov, C. J. Brabec, Up-conversion semiconducting MoO₃:Yb/Er nanocomposites as buffer layer in organic solar cells, *Solar Energy Materials and Solar Cells* 105 (2012) 196 – 201. doi:10.1016/j.solmat.2012.06.005.
- [50] A. A. D. Adikaari, I. Etchart, P.-H. Guring, M. Brard, S. R. P. Silva, A. K. Cheetham, R. J. Curry, Near infrared up-conversion in organic photovoltaic devices using an efficient Yb³⁺:Ho³⁺ Co-doped Ln₂BaZnO₅ (Ln = Y, Gd) phosphor, *Journal of Applied Physics* 111 (9) (2012) 094502. doi:10.1063/1.4704687.

- 780 [51] T. F. Schulze, J. Czolk, Y.-Y. Cheng, B. Fckel, R. W. MacQueen,
T. Khoury, M. J. Crossley, B. Stannowski, K. Lips, U. Lemmer, A. Colsmann, T. W. Schmidt, Efficiency Enhancement of Organic and Thin-Film Silicon Solar Cells with Photochemical Upconversion, *The Journal of Physical Chemistry C* 116 (43) (2012) 22794–22801. doi:10.1021/
785 jp309636m.
- [52] W. Chen, Y. Hou, A. Osvet, F. Guo, P. Kubis, M. Batentschuk, B. Winter, E. Spiecker, K. Forberich, C. J. Brabec, Sub-bandgap photon harvesting for organic solar cells via integrating up-conversion nanophosphors, *Organic Electronics* 19 (2015) 113 – 119. doi:10.1016/j.orgel.2015.01.
790 036.
- [53] Y. Shang, S. Hao, C. Yang, G. Chen, Enhancing Solar Cell Efficiency Using Photon Upconversion Materials, *Nanomaterials* 5 (4) (2015) 1782–1809. doi:10.3390/nano5041782.
- [54] W. Zhang, F. Ding, S. Y. Chou, Large Enhancement of Upconversion Luminescence of NaYF₄:Yb³⁺/Er³⁺ Nanocrystal by 3D Plasmonic Nano-Antennas, *Advanced Materials* 24 (35) (2012) OP236–OP241. doi:10.
795 1002/adma.201200220.
- [55] C. M. Johnson, P. J. Reece, G. J. Conibeer, Slow-light-enhanced upconversion for photovoltaic applications in one-dimensional photonic crystals, *Opt. Lett.* 36 (20) (2011) 3990–3992. doi:10.1364/OL.36.003990.
800
- [56] M. Mirsafaei, A. L. F. Cauduro, C. Kunstmann-Olsen, A. M. Davidson, S. Hassing, M. A. B. Hedegaard, H.-G. Rubahn, J. Adam, M. Madsen, Periodically arranged colloidal gold nanoparticles for enhanced light harvesting in organic solar cells, Vol. 9898, 2016, pp. 9898 – 9898 – 11. doi:10.1117/12.2227867.
805
- [57] B. Ray, M. R. Khan, C. Black, M. A. Alam, Nanostructured Electrodes for Organic Solar Cells: Analysis and Design Fundamentals, *IEEE Jour-*

nal of Photovoltaics 3 (1) (2013) 318–329. doi:10.1109/JPHOTOV.2012.2220529.

- 810 [58] S.-W. Baek, G. Park, J. Noh, C. Cho, C.-H. Lee, M.-K. Seo, H. Song, J.-Y. Lee, Au@Ag CoreShell Nanocubes for Efficient Plasmonic Light Scattering Effect in Low Bandgap Organic Solar Cells, ACS Nano 8 (4) (2014) 3302–3312, pMID: 24593128. doi:10.1021/nn500222q.
- [59] M. Mirsafaei, A. H. Fallahpour, P. Lugli, H.-G. Rubahn, J. Adam,
815 M. Madsen, The influence of electrical effects on device performance of organic solar cells with nano-structured electrodes, Scientific Reports 7 (1) (2017) 5300. doi:10.1038/s41598-017-05591-8.
- [60] E. Centurioni, Generalized matrix method for calculation of internal light energy flux in mixed coherent and incoherent multilayers, Applied Optics
820 44 (35) (2005) 7532.
- [61] J. Zhao, A. Wang, M. A. Green, F. Ferrazza, 19.8% efficient honeycomb textured multicrystalline and 24.4% monocrystalline silicon solar cells, Applied Physics Letters 73 (14) (1998) 1991–1993.
- [62] E. Yablonovitch, Statistical ray optics, J. Opt. Soc. Am. 72 (7) (1982)
825 899–907.
- [63] S. C. Baker-Finch, K. R. McIntosh, M. L. Terry, Isotextured Silicon Solar Cell Analysis and Modeling 1: Optics, IEEE Journal of Photovoltaics 2 (4) (2012) 457–464.
- [64] D. K. Gramotnev, S. I. Bozhevolnyi, Plasmonics beyond the diffraction
830 limit, Nature Photonics 4 (2) (2010) 83–91.
- [65] F. J. G. de Abajo, Microscopy: Plasmons go quantum, Nature 483 (7390) (2012) 417–418.
- [66] G. Mie, Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen, Annalen der physik 330 (3) (1908) 377–445.

- 835 [67] M. A. Yurkin, A. G. Hoekstra, The discrete dipole approximation: an overview and recent developments, *Journal of Quantitative Spectroscopy and Radiative Transfer* 106 (1) (2007) 558–589.
- [68] Y. Kane, Numerical solution of initial boundary value problems involving maxwell’s equations in isotropic media, *IEEE Transactions on Antennas and Propagation* 14 (3) (1966) 302–307. doi:10.1109/TAP.1966.1138693.
- 840 [69] J.-M. Jin, *The Finite Element Method in Electromagnetics*, John Wiley & Sons, 2014.
- [70] S. Kagami, I. Fukai, Application of Boundary-Element Method to Electromagnetic Field Problems (Short Papers), *IEEE Transactions on Microwave Theory and Techniques* 32 (4) (1984) 455–461.
- 845 [71] Y.-l. Xu, Electromagnetic scattering by an aggregate of spheres, *Applied Optics* 34 (21) (1995) 4573.
- [72] M. I. Mishchenko, L. D. Travis, D. W. Mackowski, T-matrix computations of light scattering by nonspherical particles: a review, *Journal of Quantitative Spectroscopy and Radiative Transfer* 55 (5) (1996) 535–575.
- 850 [73] I. Zorić, M. Zäch, B. Kasemo, C. Langhammer, Gold, platinum, and aluminum nanodisk plasmons: Material independence, subradiance, and damping mechanisms, *ACS Nano* 5 (4) (2011) 2535–2546.
- [74] J. Eisenlohr, N. Tucher, O. Höhn, H. Hauser, M. Peters, P. Kiefel, J. C. Goldschmidt, B. Bläsi, Matrix formalism for light propagation and absorption in thick textured optical sheets, *Optics express* 23 (11) (2015) A502–A518.
- 855 [75] M. P. Bendsøe, N. Kikuchi, Generating optimal topologies in structural design using a homogenisation method, *Computer Methods in Applied Mechanics and Engineering* 71 (2) (1988) 197–224.
- 860

- [76] M. B. Dühring, J. S. Jensen, O. Sigmund, Acoustic design by topology optimization, *Journal of Sound and Vibration* 317 (3-5) (2008) 557–575. doi:10.1016/j.jsv.2008.03.042.
- 865 [77] R. E. Christiansen, O. Sigmund, Experimental validation of systematically designed acoustic hyperbolic meta material slab exhibiting negative refraction, *Applied Physics Letters* 109 (10) (2016) 101905. doi:10.1063/1.4962441.
- 870 [78] R. E. Christiansen, O. Sigmund, Designing meta material slabs exhibiting negative refraction using topology optimization, *Structural and Multidisciplinary Optimization* 54 (3) (2016) 469–482. doi:10.1007/s00158-016-1411-8.
- 875 [79] A. Erentok, O. Sigmund, Topology Optimization of Sub-Wavelength Antennas, *IEEE Transactions on Antennas and Propagation* 59 (1) (2011) 58–69. doi:10.1109/TAP.2010.2090451.
- [80] P. I. Borel, A. Harpøth, L. H. Frandsen, M. Kristensen, P. Shi, J. S. Jensen, O. Sigmund, Topology optimization and fabrication of photonic crystal structures, *Optics Express* 12 (9) (2004) 1996. doi:10.1364/OPEX.12.001996.
- 880 [81] J. Jensen, O. Sigmund, L. Frandsen, P. Borel, A. Harpoth, M. Kristensen, Topology design and fabrication of an efficient double 90/spl deg/ photonic Crystal waveguide bend, *IEEE Photonics Technology Letters* 17 (6) (2005) 1202–1204. doi:10.1109/LPT.2005.846502.
- 885 [82] J. S. Jensen, O. Sigmund, Topology optimization for nano-photonics, *Laser and Photonics Reviews* 5 (2) (2011) 308–321. doi:10.1002/lpor.201000014.
- [83] J. Andkjær, S. Nishiwaki, T. Nomura, O. Sigmund, Topology optimization of grating couplers for the efficient excitation of surface plasmons, *Journal*

- of the Optical Society of America B 27 (9) (2010) 1828. doi:10.1364/JOSAB.27.001828.
- [84] M. B. Dühring, N. Asger Mortensen, O. Sigmund, Plasmonic versus dielectric enhancement in thin-film solar cells, Applied Physics Letters 100 (21) (2012) 211914. doi:10.1063/1.4719203.
- [85] O. Sigmund, J. Sondergaard Jensen, Systematic design of phononic band-gap materials and structures by topology optimization, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 361 (1806) (2003) 1001–1019. doi:10.1098/rsta.2003.1177.
- [86] J. K. Guest, J. H. Prévost, T. Belytschko, Achieving minimum length scale in topology optimization using nodal design variables and projection functions, International Journal for Numerical Methods in Engineering 61 (2) (2004) 238–254. doi:10.1002/nme.1064.
- [87] F. Wang, B. S. Lazarov, O. Sigmund, On projection methods, convergence and robust formulations in topology optimization, Structural and Multidisciplinary Optimization 43 (6) (2011) 767–784. doi:10.1007/s00158-010-0602-y.
- [88] R. E. Christiansen, B. S. Lazarov, J. S. Jensen, O. Sigmund, Creating geometrically robust designs for highly sensitive problems using topology optimization: Acoustic cavity design, Structural and Multidisciplinary Optimization 52 (4) (2015) 737–754. doi:10.1007/s00158-015-1265-5.
- [89] D. A. Tortorelli, P. Michaleris, Design sensitivity analysis: Overview and review, Inverse Problems in Science and Engineering 1 (1) (1994) 71–105. doi:10.1080/174159794088027573.
- [90] N. Aage, E. Andreassen, B. S. Lazarov, O. Sigmund, Giga-voxel computational morphogenesis for structural design, Nature 550 (7674) (2017) 84–86. doi:10.1038/nature23911.

- [91] J. Vester-Petersen, S. P. Madsen, O. Sigmund, P. Balling, B. Julsgaard, R. E. Christiansen, Topology optimized gold nanostrips for enhanced up-conversion: Influence of the conditions for phase-matched waveguide excitation, Submitted.
- [92] R. E. Christiansen, J. Vester-Petersen, O. Sigmund, S. P. Madsen, Non-linear material interpolation for design of metallic nano-particles using topology optimization, Submitted.
- [93] J. Krenn, A. Dereux, J. Weeber, E. Bourillot, Y. Lacroute, J. Goudonnet, G. Schider, W. Gotschy, A. Leitner, F. Aussenegg, et al., Squeezing the optical near-field zone by plasmon coupling of metallic nanoparticles, Phys. Rev. Lett. 82 (12) (1999) 2590.
- [94] A. Merlen, F. Lagugné-Labarthe, Imaging the optical near field in plasmonic nanostructures, Appl. Spectrosc 68 (12) (2014) 1307–1326.
- [95] T. Coenen, D. T. Schoen, B. J. Brenny, A. Polman, M. L. Brongersma, Combined electron energy-loss and cathodoluminescence spectroscopy on individual and composite plasmonic nanostructures, Phys. Rev. B 93 (19) (2016) 195429.
- [96] P. Leiderer, C. Bartels, J. Koenig-Birk, M. Mosbacher, J. Boneberg, Imaging optical near-fields of nanostructures, Appl. Phys. Lett. 85 (22) (2004) 5370–5372.
- [97] J. Fiutowski, C. Maibohm, O. Kostiučenko, J. Kjelstrup-Hansen, H.-G. Rubahn, Mapping of gold nanostructure-enhanced near fields via laser scanning second-harmonic generation and ablation, J. Nanophotonics 6 (1) (2012) 063515–1.
- [98] S. Dickreuter, J. Gleixner, A. Kolloch, J. Boneberg, E. Scheer, P. Leiderer, Mapping of plasmonic resonances in nanotriangles, Beilstein J. Nanotechnol. 4 (2013) 588.

- [99] P. Kühler, F. J. G. de Abajo, P. Leiprecht, A. Kolloch, J. Solis, P. Leiderer,
945 J. Siegel, Quantitative imaging of the optical near field, *Opt. Express*
20 (20) (2012) 22063–22078.
- [100] C. David, P. Kühler, F. J. G. de Abajo, J. Siegel, Near-field nanoimprint-
ing using colloidal monolayers, *Opt. Express* 22 (7) (2014) 8226–8233.
- [101] C. Deeb, R. Bachelot, J. Plain, A.-L. Baudrion, S. Jradi, A. Bouhelier,
950 O. Soppera, P. K. Jain, L. Huang, C. Ecoffet, et al., Quantitative analysis
of localized surface plasmons based on molecular probing, *ACS Nano* 4 (8)
(2010) 4579–4586.
- [102] T. Geldhauser, A. Kolloch, N. Murazawa, K. Ueno, J. Boneberg, P. Lei-
derer, E. Scheer, H. Misawa, Quantitative measurement of the near-field
955 enhancement of nanostructures by two-photon polymerization, *Langmuir*
28 (24) (2012) 9041–9046.
- [103] P. Balling, J. Schou, Femtosecond-laser ablation dynamics of dielectrics:
basics and applications for thin films, *REPORTS ON PROGRESS IN
PHYSICS* 76 (3). doi:10.1088/0034-4885/76/3/036502.
- [104] K. Vestentoft, P. Balling, Formation of an extended nanostructured metal
960 surface by ultra-short laser pulses: single-pulse ablation in the high-fluence
limit, *APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING*
84 (1-2) (2006) 207–213. doi:10.1007/s00339-006-3602-4.
- [105] B. H. Christensen, K. Vestentoft, P. Balling, Short-pulse ablation rates
965 and the two-temperature model, *APPLIED SURFACE SCIENCE* 253 (15,
SI) (2007) 6347–6352, 5th International Conference on Photo-Excited Pro-
cesses and Applications, Charlottesville, VA, SEP, 2006. doi:10.1016/
j.apsusc.2007.01.045.
- [106] J. Byskov-Nielsen, J.-M. Savolainen, M. S. Christensen, P. Balling, Ultra-
970 short pulse laser ablation of copper, silver and tungsten: experimental

data and two-temperature model simulations, APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING 103 (2) (2011) 447–453. doi:10.1007/s00339-011-6363-7.

- 975 [107] J.-M. Savolainen, M. S. Christensen, P. Balling, Material swelling as the first step in the ablation of metals by ultrashort laser pulses, PHYSICAL REVIEW B 84 (19). doi:10.1103/PhysRevB.84.193410.
- [108] B. H. Christensen, P. Balling, Modeling ultrashort-pulse laser ablation of dielectric materials, PHYSICAL REVIEW B 79 (15). doi:10.1103/PhysRevB.79.155424.
- 980 [109] K. Waedegaard, M. Frislev, P. Balling, Femtosecond laser excitation of dielectric materials: experiments and modeling of optical properties and ablation depths, APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING 110 (3) (2013) 601–605. doi:10.1007/s00339-012-7136-7.
- 985 [110] K. Waedegaard, D. B. Sandkamm, L. Haahr-Lillevang, K. G. Bay, P. Balling, Modeling short-pulse laser excitation of dielectric materials, APPLIED PHYSICS A-MATERIALS SCIENCE & PROCESSING 117 (1) (2014) 7–12. doi:10.1007/s00339-014-8231-8.
- [111] M. Farsari, M. Vamvakaki, B. N. Chichkov, Multiphoton polymerization of hybrid materials, Journal of Optics 12 (12) (2010) 124001.
- 990 [112] T. Förster, Zwischenmolekulare Energiewanderung und Fluoreszenz, Annalen der Physik 2 (1948) 55.
- [113] S. Fisher, H. Steinkemper, M. Löper, M. Hermle, J. C. Goldschmidt, Modeling upconversion of erbium doped microcrystals based on experimentally determined Einstein coefficients, Journal of Applied Physics 111 (2012) 013109.
- 995 [114] R. Martin-Rodriguez, F. T. Rabouw, M. Trevisani, M. Bettinelli, A. Meijerink, Upconversion Dynamics in Er^{3+} -Doped Gd_2O_3 : Influence of Ex-

citation Power, Er^{3+} Concentration, and Defects, *Advanced Optical Materials* 3 (2015) 558–567.

LaTeX Source Files

[Click here to download LaTeX Source Files: Latex-Source-Files-Resubmission.zip](#)