Novel light-trapping structures for thin-film solar cells

Pavel Voroshilov
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**Abstract**

The thesis is devoted to the development of novel broadband light-trapping structures based on regular arrays of nanostructures and microstructures often referred in the modern literature as metamaterials. Our suggested light-trapping structures offer the gain in the optical efficiency of thin-film solar cells of several types without damaging their operational characteristics. These types of photovoltaic devices include thin-film solar cells based on amorphous silicon, organic and perovskite materials.

In the first part, we present a metal light-trapping structure based on arrays of nanoantennas and report its theoretical and experimental studies. We reveal unusual eigenmodes in arrays of metal elements with domino-like proportions and show that in the optical range of frequencies they may composite a broad frequency band comparable with the operation band of a realistic solar cell. We experimentally confirm the existence of these modes and theoretically prove their light-trapping functionality. We design the optimal array of metal nanoantennas supporting these modes and theoretically demonstrate the enhancement of the useful absorption for a realistic organic solar cell. Finally, we present experimental results demonstrating an increase of the overall power conversion efficiency granted by our light-trapping structure compared to the reference solar cell with a conventional design.

In the second part, we discuss novel all-dielectric light-trapping structures and report the results of full-wave numerical simulations. For amorphous silicon-based thin-film solar cell, we study the suppression of both reflection and transmission granted by the following systems: a flat antireflection coating, an array of densely packed polystyrene nanospheres, and arrays of nanovoids (cylindrical and tapered shape, both in the PMMA layer). We optimize the geometrical parameters to obtain the highest absorption in the photovoltaic layer and reveal light-trapping properties of these structures. Finally, we suggest and study a universal light-trapping structure for solar cells of 3rd generation. The structure consists of an array of dielectric truncated cones serving as the tapered optical waveguides for the incident light and optically connected to the thin-film solar cell through the holes in the metal film (e.g., Au). We theoretically show the advantages of our solution with respect to known analogs: it grants a gain in the PV absorption both in case of the organic thin-film SC (more significant) and perovskite thin-film SC (less significant but still noticeable). The existing techniques allow us to fabricate such a structure rather simply and quickly without involving expensive materials or processes. We believe that the presented results are helpful for the further development of thin-film solar cells of these three types.

**Keywords** Solar cells, light-trapping, nanoantennas, metamaterials

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This doctoral thesis would not have been possible without strong encouragement from Prof. Pavel Belov. I sincerely thank him for setting me on the right path and keeping me covered during my doctoral studies. He is a great leader working with tireless dedication and continuous excitement. His reliable support, mentoring and enthusiasm helped me to move forward with confidence.

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I am most thankful to my parents, relatives and all my friends who supported me a lot during many years of my studies. Finally, I take this opportunity to profoundly gratitude my beloved Kristina for her patience and care. This thesis is dedicated to her.

Espoo, August 8, 2018,

Pavel Voroshilov
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>1</td>
</tr>
<tr>
<td>Contents</td>
<td>3</td>
</tr>
<tr>
<td>List of Publications</td>
<td>5</td>
</tr>
<tr>
<td>Author's Contribution</td>
<td>7</td>
</tr>
<tr>
<td>List of Abbreviations</td>
<td>9</td>
</tr>
<tr>
<td>List of Symbols</td>
<td>11</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>13</td>
</tr>
<tr>
<td>1.1 From solar light to electricity</td>
<td>13</td>
</tr>
<tr>
<td>1.1.1 History</td>
<td>13</td>
</tr>
<tr>
<td>1.1.2 Prospects</td>
<td>14</td>
</tr>
<tr>
<td>1.2 Solar cells</td>
<td>15</td>
</tr>
<tr>
<td>1.2.1 Three generations</td>
<td>15</td>
</tr>
<tr>
<td>1.2.2 Main characteristics</td>
<td>18</td>
</tr>
<tr>
<td>1.2.3 Overall efficiency</td>
<td>20</td>
</tr>
<tr>
<td>1.3 Light management</td>
<td>21</td>
</tr>
<tr>
<td>1.4 Objectives and contribution of this thesis</td>
<td>25</td>
</tr>
<tr>
<td>2. Metal light trapping structure</td>
<td>26</td>
</tr>
<tr>
<td>2.1 Theoretical analysis of the broadband light-trapping effect</td>
<td>27</td>
</tr>
<tr>
<td>2.1.1 Leaky domino-modes in arrays of silver nanobars</td>
<td>29</td>
</tr>
<tr>
<td>2.1.2 Light trapping effect</td>
<td>37</td>
</tr>
<tr>
<td>2.2 Experimental verification of our simulations</td>
<td>41</td>
</tr>
<tr>
<td>2.3 Nanoantennas for organic solar cell</td>
<td>45</td>
</tr>
<tr>
<td>2.3.1 Suggested structure and its numerical simulations</td>
<td>47</td>
</tr>
<tr>
<td>2.3.2 Fabrication and measurements</td>
<td>51</td>
</tr>
</tbody>
</table>
### Contents

2.3.3 Conclusions ........................................ 58

3. **All-dielectric light trapping structures** 59

3.1 Numerical study of two light-trapping structures for a-Si thin-film solar cells ........................................ 61

3.1.1 Normal incidence of light ............................. 63

3.1.2 Oblique incidence of light ............................ 70

3.1.3 Conclusions ........................................ 71

3.2 Universal light-trapping structure for organic and perovskite solar cells ........................................ 71

3.2.1 Design solution ....................................... 73

3.2.2 An example of an organic solar cell ............... 75

3.2.3 An example of a perovskite solar cell ............. 76

3.2.4 Fabrication ........................................... 78

3.2.5 Conclusions ........................................ 79

4. **Conclusions of the thesis and future work** 80

References .................................................... 81

Publications ................................................... 89
List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Leaky domino-modes in regular arrays of substantially thick metal nanostrips”

The initial idea of the paper was suggested by Prof. C. Simovski. The author performed all the calculations and was responsible for writing the paper draft. The work was carried under the supervision of Prof. C. Simovski.

Publication II: “Demonstration of unusual nanoantenna array modes through direct reconstruction of the near-field signal”

Author performed the simulations. I. Sinev, I. Mukhin, A. Denisyuk, M. Guzhva and A. Samusev were responsible for experimental part. All authors contributed to editing the text. The work was guided by Dr. P. Belov and Prof. C. Simovski.

Publication III: “Nanoantennas for enhanced light trapping in transparent organic solar cells”

The work was mainly done by the author. The author did the calculations was responsible for writing the publication. Dr. P. Belov and Prof. C. Simovski supervised the work.

The author performed simulations, fabrication, measurements, and wrote the manuscript draft. V. Ovchinnikov and A. Papadimitratos assisted in fabrication. All authors contributed to editing the text. Profs. Anvar Zakhidov and Constantin Simovski supervised the work.

Publication V: “Light-trapping and antireflective coatings for amorphous Si-based thin film solar cells”

The initial idea for the paper was proposed by Dr. A. Shalin. The author performed the numerical simulations. All authors contributed to editing the text. Dr. Pavel Belov and Prof. Constantin Simovski supervised the work.

Publication VI: “Affordable universal light-trapping structure for third-generation photovoltaic cells”

The initial idea for the paper was proposed by Prof. C. Simovski. The author performed all the calculations and was responsible for writing the paper draft. Prof. Constantin Simovski supervised the work.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic-force microscope</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>APFO</td>
<td>Alternating polyfluorene copolymer</td>
</tr>
<tr>
<td>ARC</td>
<td>Antireflection coating</td>
</tr>
<tr>
<td>AVT</td>
<td>Averaged visible-light transmittance</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminium-doped zinc oxide</td>
</tr>
<tr>
<td>BCP</td>
<td>Bathocuproine</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline silicon</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium selenide</td>
</tr>
<tr>
<td>CIS</td>
<td>Copper indium selenide</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CTL</td>
<td>Charge transfer layer</td>
</tr>
<tr>
<td>CZTS</td>
<td>Copper zinc tin sulfide</td>
</tr>
<tr>
<td>eV</td>
<td>Electronvolt</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite-difference time-domain method</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FF_{SQ}</td>
<td>Shockley–Queisser limit of fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LTE</td>
<td>Light-trapping efficiency</td>
</tr>
<tr>
<td>LTS</td>
<td>Light-trapping structure</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
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<tr>
<td>mA</td>
<td>Milliampere</td>
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<tr>
<td>mc-Si</td>
<td>Multicrystalline silicon</td>
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### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>mW</td>
<td>Milliwatt</td>
</tr>
<tr>
<td>NA</td>
<td>Nanoantenna</td>
</tr>
<tr>
<td>nc-Si</td>
<td>Nanocrystalline silicon</td>
</tr>
<tr>
<td>Nd:YAG</td>
<td>Neodymium-doped yttrium aluminum garnet</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NSOM</td>
<td>Near-field scanning optical microscope</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaics</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>Carbazole-based copolymer</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>PML</td>
<td>Perfectly matched layer</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic(s)</td>
</tr>
<tr>
<td>SC</td>
<td>Solar cell</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SQ</td>
<td>Shockley-Queisser efficiency</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric</td>
</tr>
<tr>
<td>THz</td>
<td>Terahertz</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$a$</td>
<td>Bar length</td>
</tr>
<tr>
<td>$A$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$b$</td>
<td>Bar width</td>
</tr>
<tr>
<td>$c$</td>
<td>Period of an array of parallel nanobars along $x$-axis</td>
</tr>
<tr>
<td>$d$</td>
<td>Period of an array of parallel nanobars along $y$-axis</td>
</tr>
<tr>
<td>$D$</td>
<td>Period of nanoantenna array</td>
</tr>
<tr>
<td>$dV$</td>
<td>Volume element</td>
</tr>
<tr>
<td>$e$</td>
<td>Array period of oligomers of four nanobars</td>
</tr>
<tr>
<td>$e_{\alpha\beta\gamma}$</td>
<td>Levi-Civita symbol</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$g$</td>
<td>Geometrical parameter of nanoantenna</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
</tr>
<tr>
<td>$I_{mp}$</td>
<td>Current at maximum power</td>
</tr>
<tr>
<td>$I_s$</td>
<td>Photovoltaic spectral response</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>$J$</td>
<td>Current density</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>$J_{SQ}$</td>
<td>Shockley–Queisser limit of short-circuit current density</td>
</tr>
<tr>
<td>$m$</td>
<td>Magnetic dipole moment</td>
</tr>
<tr>
<td>$M$</td>
<td>Normalized magnetic dipole moment</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
</tr>
<tr>
<td>$o$</td>
<td>Electric octupole moment</td>
</tr>
<tr>
<td>$O$</td>
<td>Normalized electric octupole moment</td>
</tr>
<tr>
<td>$p$</td>
<td>Electric dipole moment</td>
</tr>
<tr>
<td>$P_m$</td>
<td>Power of the incident light</td>
</tr>
<tr>
<td>$P_{max}$</td>
<td>Maximum power</td>
</tr>
<tr>
<td>$q$</td>
<td>Electric quadrupole moment</td>
</tr>
<tr>
<td>$Q$</td>
<td>Normalized electric quadrupole moment</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>( r )</td>
<td>Radius-vector</td>
</tr>
<tr>
<td>( R )</td>
<td>Reflection coefficient</td>
</tr>
<tr>
<td>( R_s )</td>
<td>Solar irradiance</td>
</tr>
<tr>
<td>( s )</td>
<td>Magnetic quadrupole moment</td>
</tr>
<tr>
<td>( S )</td>
<td>Normalized magnetic quadrupole moment</td>
</tr>
<tr>
<td>( T )</td>
<td>Transmission coefficient</td>
</tr>
<tr>
<td>( V )</td>
<td>Voltage</td>
</tr>
<tr>
<td>( V_{mp} )</td>
<td>Voltage at maximum power</td>
</tr>
<tr>
<td>( V_{oc} )</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>( V_{SQ} )</td>
<td>Shockley–Queisser limit of open-circuit voltage</td>
</tr>
<tr>
<td>( x, y, z )</td>
<td>Cartesian position coordinates</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Axial component of wave vector</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>Thickness</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Skin-depth</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Permittivity</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>Free-space permittivity</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>Free space permeability</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Angular frequency</td>
</tr>
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1. Introduction

1.1 From solar light to electricity

The Earth receives a huge amount of energy from the Sun every day. This energy is free and inexhaustible. Mankind has always used some of this energy directly in everyday life – for drying and heating. Striving for knowledge of the world allowed to make a step forward. Humans understood that nature handles sunlight through the process of photosynthesis by its conversion to chemical energy. Eventually, they have also discovered other prospective ways to utilize solar energy indirectly under own control. One such method is called Photovoltaics (PV) which is a compound of two words: photo meaning light, and volt – the unit of electromotive force.

1.1.1 History

The idea of conversion of solar light into electricity appeared long ago. It has been almost 180 years since French experimental physicist Edmond Becquerel in 1839 first discovered a photovoltage when he illuminated chloride coated platinum electrodes submerged in an aqueous nitric acid electrolyte solution by a light beam [1]. At that time, this concept was perceived as a curious scientific observation which had vague prospects. Although the generated power was minuscule and not sufficient for any practical usage, in fact, it was the first ever PV device.

Next essential contributions to the development of PV technology were made in the 1870-1880s. In this period, several researchers actively studied the element selenium and its properties. In 1873 English electrical engineer Willoughby Smith found that the selenium is photoconductive [2]. He measured the resistance of selenium bars under different conditions
Introduction

and discovered that the value depends on the intensity of incident light. Four years later British scientists William Grylls Adams and Richard Evans Day at Cambridge observed the PV effect illuminating a junction between solid selenium and platinum without any electrolyte [3]. Next, in 1883 American engineer Charles Fritts made the first selenium-based solar cell with a remarkable efficiency of 1% in converting solar energy into electrical energy [4]. This device consisted of millimeter-thick selenium layer covered by a semitransparent gold film on a platinum substrate. Finally, in 1888 Alexander Stoletov revealed the direct proportionality between the induced photocurrent and the absorption of incident light in the bulk of selenium layer [5]. These experimental studies clarified the crucial role of the semiconductor in recently discovered PV process and attracted the attention of many scientists.

Further progress would be impossible without a deep understanding of fundamentals of the PV mechanism. Breakthrough contribution to this area was made by Albert Einstein, who elaborated the theory of PV effect on a quantum basis [6]. Combined with the discovery of the electron, a new description of light explained that incident photons knock out electrons from their atomic orbits in materials like selenium and released electrons flow through attached wires resulting in an electrical current. For this work, he was awarded the Nobel Prize in 1921. His research spawned and paved the way for the development of solar photovoltaics.

Nevertheless, new obstacles awaited researchers. Despite many years of extensive work, they couldn’t surpass a maximum efficiency of 1% obtained in 1883. The idea of practical implementation in a foreseeable future met with considerable skepticism. But with the beginning of silicon breakthrough, in 1954 Daryl Chapin, Calvin Fuller and Gerald Pearson from Bell Laboratories fabricated the first practical silicon p-n junction solar cell with an efficiency of around 5% that revolutionized the PV industry [7]. This event marked the beginning of a new era for humankind – harnessing the solar energy with its conversion into electricity.

1.1.2 Prospects

The level of the technological development determines the structure of the energy sector. Nowadays, our civilization heavily relies on carbon-based fuel (oil, natural gas, and coal) whose share is about 85% in global energy production. However, traditional energy resources are limited and distributed nonuniformly on the Earth. Moreover, they will run out by
the end of the current century taking into account growing appetite for energy. Public concerns about the negative impact of fossil fuels on the environment and oil crises encouraged researchers to develop reliable renewable energy resources.

Solar energy that reaches the Earth is thousands of times as much as the current total energy consumption by humans on our planet. The solar industry is rapidly growing. However, its share is still quite small – about 1% in total commercial electricity production. Solar PV offers the ability to generate electricity in a safe, reliable, cheap and convenient way. In contrast to nuclear power plants or hydroelectric power station, solar-powered energy production does not require complicated infrastructure and can be realized directly at consumers’ place. According to the consensus view, an increase of the share of solar PV up to 15% is possible by 2030 if the certain advances are accomplished in the coming years.

At the end of the last decade, a committee of experts, consisting of outstanding engineers and researchers, convened at the request of the U.S. National Academy of Engineering, announced 14 grand challenges for engineering in the 21st century. One of these challenges is to make solar electric energy affordable and accessible. Considerable progress has been made in crystalline silicon solar cell development that resulted in achieving more than 26% efficiency for traditional single-junction elements compared to 5% at the beginning of silicon revolution 60 years ago [8]. Recent achievements in emerging low-cost and highly efficient PV has received significant attention in the public [9, 10]. Further significant efforts in science and technology can make solar PV economical in the near future. Continued decreasing of solar PV price while enhancing solar cell performance will make this human’s dream come true.

1.2 Solar cells

1.2.1 Three generations

Solar cell (SC) technologies are traditionally classified into three generations. Conventional crystalline silicon (c-Si) wafer-based single-junction SCs belongs to the first generation of PV technology [11]. The fabrication process of c-Si panels is well developed, and they are the most widely available on the market with a share of about 90% among other PV tech-
nologies [12]. This type of SCs demonstrates high stability when exposed to weather conditions and good performance over the years while the efficiency is quite high exceeding 20%. However, up to the most recent time the requirement of the high purity of c-Si together with the substantial thickness of the PV layer implied high cost and a significant amount of toxic waste. Therefore, the price of electricity generated by such SCs was still high. This stimulated the development of next two generations of solar PV.

The second generation aimed to drastically decrease the cost of the solar electricity making it more accessible [13]. This category of solar PV comprises SCs based on amorphous silicon (a-Si) [14], micro- and polycrystalline silicon [15], tandem SCs comprising a-Si and microcrystalline Si called micromorph SCs [13], SCs based on semiconductor compounds III-V (GaAs, InP, GaP), II-VI (CdTe), and multi-component compounds abbreviated as CIS [16], CIGS [17] and CZTS [18]. The typical overall efficiency of these SCs is 10-15%, and the typical thickness of the PV layer is few microns (for polycrystalline Si – even submicron). In spite of lower performance, these SCs have chances to compete with c-Si solar PV promising (after commercialization) lower prices and incomparably lower amount of the PV material per unit area.

Flexible thin-film SC is a particular example that illustrates potential advantages of the second generation. They are based on a-Si and have the p-i-n structure of the PV layer that is backed by a metal foil (bottom electrode) electrically connected to a-Si via an intermediate (conductive paste or amorphous conductive composite). Such SCs can be transported in rolls, located on any support as conformal surfaces and their fabrication steps are compatible with the roll-to-roll processing [13]. Due to these advantages, they were widely commercialized at the beginning of 21 century in spite of their low efficiency (4-4.5%). This efficiency is so low due to the dilemma of either optical losses or recombination losses. The mean free path of the photocurrent carriers in a-Si is close to 300 nm. If the thickness of the PV layer noticeably exceeds this value, a significant part of carriers recombine that results in the low photocurrent. From other hand, the sunlight is fully absorbed in a-Si over the depth of 1 μm. If the PV layer is noticeably thinner than 1 μm and an antireflective coating suppresses the reflection losses, a significant portion of sunlight is lost. It transmits into the bottom electrode and heats it instead of being usefully absorbed in the PV layer. This optical loss results in the similar
decrease of the photocurrent compared to the ideal case. The ideal case is that where the thickness of the PV layer is optimal but optical losses are suppressed by a perfect light-trapping structure (see below). In this case, the efficiency of flexible a-Si SC could be raised up to 10% – that of the best thin-film SC based on a-Si with the bottom electrode of polished metal [19]. In reality, companies producing flexible a-Si SCs with thin (300-500 nm) or thick (1 μm) PV layer paid for the flexibility by the twofold reduction of efficiency [12]. Among other drawbacks of a-Si SCs is the drastic decrease of efficiency at diffused solar illumination (clouds) and 30-40% decrease of efficiency after nearly one year of exploitation [20] called the Staebler-Wronski effect (degradation of doped a-Si after a solar exposure whose origin is not yet exactly known).

The third generation includes a range of alternatives to conventional PV technologies. These alternatives include SCs with solar spectrum splitting (most known are multi-junction SCs), frequency-conversion solar PV systems, SCs with hot-carrier effects, and other advanced techniques. Some thin-film technologies often described as emerging PVs – organic SCs, quantum dot SCs, dye-sensitized SCs, and perovskite SCs are also included in this category. Multi-junction cells based on high-performance semiconductors show the record values of the overall efficiency (45-46%), but they are very expensive limiting their use to aerospace and military applications [21]. Other third-generation technologies are currently subjects of active research, especially thin-film SCs, but they have not been industrially adapted [12]. Such PV cells promise easily accessible (portable, flexible, etc.) and potentially cheap production of electricity.

Five years ago thin-film solar PV was at the peak of development being of highest interest for both industry and research institutes. Of course, the commercialized c-Si solar photovoltaics with its daytime-averaged 20% efficiency was 4-5 times more efficient than the thin-film solar panels of 2nd and 3rd generations. However, these solar panels were much more expensive, incomparably more heavy and not conformal. In 2011, the difference in prices per unit area of a c-Si SC and a flexible a-Si SC produced with the roll-to-roll technique was 20 times not in favor of a c-Si PV. In spite of the 5-fold lower efficiency, this low price together with the flexibility and light weight made a-Si solar PV competitive, and many companies produced such solar panels [13]. However, in 2011-2014 a technique of manufacturing silicon crystals from silicon waste accompanying the production of telecom devices [12] was adapted for PV manufacturing. As
a result, the price of c-Si (per unit area with the appropriate thickness) dropped by an order of magnitude. Once the difference in prices of c-Si and a-Si solar PV became twofold, the flexibility and other advantages of a-Si solar PV cannot anymore compensate for its low efficiency. In 2013-2014 all companies producing a-Si solar PV collapsed [12]. Simultaneously, because of growing production of c-Si solar panels, the start of the mass production of SCs of 3rd generation is postponed.

However, the industrial collapse of a-Si solar PV does not mean that we have to stop scientific research in this field. Imagine that we have eliminated all optical losses for a flexible a-Si SCs in an affordable way suitable for manufacturing. It means that the efficiency will increase twice and becomes only 2.5 times smaller than the efficiency of c-Si solar panels. Together with flexibility, it will restore the competitiveness of these SCs, and the corresponding industry will revitalize [22]. Similarly, fresh ideas that appear in the field of applied electromagnetism, modern achievements in nanotechnology, that make them cheaper and more accessible, and, finally, current progress in material science make the scientific research in the field of 3rd generation SCs actual and promising [19].

1.2.2 Main characteristics

![Figure 1.1. Characteristics of a solar cell.](image)

The performance of any SC is commonly characterized by its power conversion efficiency (PCE). PCE is a comprehensive parameter used to compare different SCs. However, it is not the only important parameter and should be complemented at least by three characteristics described below.

Short-circuit current ($I_{sc}$) is the maximal current which is created in a
SC under illumination when the voltage across the device is zero (see in Fig. 1.1). $I_{sc}$ is determined by the number of charges generated due to the PV absorption and reaching the electrodes. Most often, this parameter is normalized to unit area meaning current density ($J_{sc}$ in mA/cm²). For a unit area of the SC and the standard illumination conditions, the value of $I_{sc}$ depends on the so-called collection probability and the optical efficiency of the SC. The collection probability is determined by recombination losses that depend on the charge carriers mobility, their lifetime, and the thickness of the PV layer if it exceeds the mean free path of carriers. Also, for SCs whose top electrode is defined as a grid of metal fingers (the surface of the PV layer between these fingers is exposed to the sunlight), there is a so-called surface recombination. Then the collection probability depends on the quality of the top surface passivation. As to optical efficiency, it is the percentage of sunlight (at frequencies above the semiconductor band-gap) absorbed in the PV layer. For a SC with the metal top electrode, the fingers usually occupy about 10% of the area resulting in the corresponding inevitable optical loss. Another implementation of the top electrode is of a transparent conductive material (some metal oxides and polymers). In this case, the top metal contact has a negligible area compared to that of the SC and the surface recombination in the PV layer prevented. However, there are losses at non-ideal contact interfaces and optical losses in the top electrode itself because it is not ideally transparent.

Open-circuit voltage ($V_{oc}$) is the maximal voltage that can be achieved from a SC when the current is zero (see in Fig. 1.1), i.e., there is no external circuit. $V_{oc}$ is mainly determined by the semiconductor band-gap, however also depends on the recombination loss, on the series resistance (ohmic loss in the bulk of the PV layer) and the shunt resistance of the p-n junction (in the ideal junction the shunt resistance is infinite). Notice, that besides SC of the diode type there are also so-called excitonic SCs, in which the role of the semiconductor band-gap is played by the energetic gap between so-called HOMO and LUMO molecular orbitals [22]. For a given gap $V_{oc}$ is influenced by the resistance of the ohmic contacts between electron-transporting and hole-transporting layers and current-collecting electrodes.

Fill factor (FF) is a ratio between the maximal output power from the SC and the product of $I_{sc}$ and $V_{oc}$, i.e., maximal attainable power. FF describes the squareness of the IV curve, that is evidently favorable for maximal overall efficiency (see in Fig. 1.1). For usual SCs (ultrabroad-
band photodiodes) the squareness characterizes the non-linearity of the diode and depends on the series (ohmic) and the shunt (p-n junction) resistances [20].

The product of these three parameters defines PCE:

\[
PCE = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}},
\]

(1.1)

where \(P_{in}\) is the total power of the incident light.

### 1.2.3 Overall efficiency

![Fraction of Shockley-Queisser detailed-balance limit for voltage and current achieved by record cells](image)

**Figure 1.2.** Fraction of Shockley-Queisser detailed-balance limit for voltage and current achieved by record cells [reproduced from [23]].

The efficiency of power conversion in a conventional single-junction SC is fundamentally restricted by the Shockley-Queisser (SQ) limit which was theoretically calculated in 1961 [24]. According to the SQ limit, the maximal achievable value of PCE is around 33.7% [25] for a SC with an optimal band-gap of the active layer measured under standard illumination conditions. Such low value is mainly due to the relaxation loss factor. The solar spectrum is very broad, and many absorbed photons have the excessive energy that is converted into the kinetic energy of the photoinduced carriers. It finally results in the heating, i.e., ohmic losses. Also, photons whose energy is below the band-gap, do not contribute to electric power generation and their absorption is either absent or parasitic. If the band-gap frequency is low, the relaxation loss factor is very high. If this frequency is high, the sub-band loss becomes very high. This dilemma is partially resolved in the multijunction SCs having several PV layers each
of them absorbing photons in the corresponding frequency ranges. It is also resolved in the advanced thermal PV cells where the narrow-band thermal emitter replaces the sun, in the PV systems utilizing the non-linear conversion of photons (so-called up/down conversion) and in some other advanced SCs of the third generation [19, 22, 26]. For SCs of the 1st and 2nd generations the limit 33.7% is unavoidable [12, 13, 16]. Among other harmful factors reducing the efficiency of a SC, we have to mention the recombination loss already discussed above (for SCs of the diode type with eliminated surface recombination and PV layer thinner than the mean free path of carriers the typical value of this loss is 10%). Notice, that the non-radiative part of the recombination loss decreases $V_{oc}$ compared to the value corresponding to the bandgap. Also, there are contact losses due to the non-ideal ohmic junction of the PV layer with the electrodes. This resistance together with the ohmic resistance of the SC affects the FF. Finally, parasitic effects such as heating by solar radiation result in the thermal radiation from a SC (typically 6-8% is lost in this way).

All these losses are intrinsic for a SC and do not include optical losses that are usually considered in terms of the optical efficiency of an antireflective coating or (for thin-film SCs) of a light-trapping structure. Optical losses are noticeable especially for SCs which do not follow the sun (absolute majority of SCs for terrestrial applications). So, in practical SCs, the efficiency is significantly lower than the fundamental SQ limit for a given band-gap. The plot shown in Fig. 1.2 demonstrates how much of the record performance SCs made of different well-known PV materials is limited either by optical or by electrical factors. Based on the analysis performed in [23], c-Si, GaAs, and GaInP SCs are found to be the most optimal among other SCs reaching more than 25% overall efficiency (75% of 33.7% limit). The remaining (including thin-film SCs) industrially relevant SCs are far from being so efficient since they suffer from poor light management and low collection of generated carriers. So, there is still much room for further improvement that stimulates researchers.

### 1.3 Light management

As it has been already mentioned in the previous sections, optical losses represent a crucial issue in the further advancing of thin-film SCs. There were many attempts to decrease the negative impact of this detrimental
effect by using nanostructures. This structures can be classified into two categories: antireflective coatings and light-trapping structures.

**Antirefection**

An antireflective coating (ARC) implements the reduction of the undesirable reflection from beneath the surface. ARCs utilize thin films of dielectric material which thicknesses are chosen to produce interference effects. The simplest case is a single-layer ARC of a thin transparent material with the refractive index equal to the square root of the substrate effective refractive index. The thickness of the coating is dependent on the wavelength incident on the dielectric material. In air, the reflectance vanishes for a quarter-wavelength coating thickness. Reflectance is also strongly decreased in a broader band around this central wavelength.

Using multilayer structure, it is possible to obtain the total reflectivity as low as 4-5% in the operation band of the silicon solar PV (360-1000 nm). However, this is achieved only for the normal incidence. Since the daytime concept adopted in solar PV implies high incidence angles up to 70° at which such ARCs are not efficient, they are currently not in use in SCs for terrestrial applications. Some ARCs implement the gradient-index idea, i.e., are non-uniform composite layers whose effective refractive index smoothly decreases from its bulk value to unity at the top surface. Such ARCs are, as a rule, nanotextured surfaces with regular protrusions [27, 28]. Sometimes, this functionality is performed by a textured top electrode [29]. Moreover, in SCs with the top electrode composed of metal fingers, random nanotexturing of the PV layer offers similar or even better reduction of the reflection losses. The most known example is the so-called black silicon [30]. Some of these nanotextured SCs have been already commercialized [12]. Notice, that none of them offers a complete suppression of the integral reflection loss averaged over the daytime. The best omnidirectional ARCs known by 2011 only reduced this loss by 10% [31]. This is so because for the incidence angles 60-70° the idea of the gradient index does not work and the reflection loss in the best cases attains about 30-35% [31]. The same refers to composite ARCs based on optically dense arrays, e.g., arrays of densely-packed nanospheres of low-index material [32–35]. Such arrays mimic a multilayer ARC [19].

**Light-trapping**

As it was already discussed, the antireflection coatings do not resolve the problem of low optical efficiency of thin-film SCs. The thickness of the PV
layer in thin-film SCs, including the a-Si solar cell is usually smaller than
needed for the complete absorption of incident light [20, 36, 37]. Some-
times – e.g., in polycrystalline SCs and in organic SCs even two passages
of sunlight through the PV layer are not enough for absorption. Then the
polished metal rear electrode of the SC does not help to prevent the re-
flection losses, and the ARC nicely transmits the radiation reflected from
the rear electrode backward to free space. Sometimes the polished metal
rear electrode is impractical (flexible thin-film SCs), and the transmitted
light is absorbed beneath the PV layer.

Many suggestions for increasing the absorption in SCs are based on the
use of light-trapping structures (LTSs). Such structures may reduce both
the reflection from the SC and the transmission through its PV layer. The
last function can be achieved, e.g., due to the conversion of the incident
wave into a package of evanescent waves for which Abbe diffraction limit
is not valid. These waves can be localized into high-intensity hot spots
in the volume of the PV layer [38–45]. These LTSs are usually based
on plasmonic nanoparticles. However, in some of them, dielectric res-
sonator cavities exploring whispering gallery resonances and high-order
(e.g., quadrupole) Mie resonances are used [38, 46, 46]. Such cavities be-
ing coupled to incident plane waves can be called dielectric nanoantennas
(NAs).

Alternatively, one may one prepare the PV layer as a photonic crystal
and convert the incident light into its staggered modes [47,48]. Some SCs
implementing the gradient-index idea, e.g. using optically dense regular
arrays of semiconductor protrusions are also capable to trap the light cap-
tured in the gaps between the protrusions and guided downwards [49,50].
These SCs, as well as black silicon, cannot be referred as thin-film SCs
since an essential part of their PV layer is a substantially thick composite
layer of protrusions. In this work, we will not consider such SCs.

Some plasmonic LTS prepared as regular plasmonic nanostructures con-
vert the incident plane wave into waveguide modes propagating in the
plane of the PV layer  [40,44,51–53]. Such LTSs mimic an optical facet –
phase diffraction grid built in as a textured coating. These phase diffrac-
tion grids are inefficient for trapping the light in the PV layers of amor-
phous or organic thin-film SCs when the thickness of the layer, as a rule,
does not exceed 400 nm [54–56].

Meanwhile, regular plasmonic grids, especially combined with the bot-
tom electrode or incorporated into the PV layer implement this functional-
ity very well due to the effect of so-called Wood's diffraction anomaly [57]. Such LTSs require a separate ARC on top of the SC.

Let us now discuss the disadvantages of LTSs mentioned above. LTSs based on random arrays of plasmonic nanoparticles grown by chemical means are rather cheap but inefficient due to losses in metal elements inherent to localized surface plasmon resonances. They also possess noticeable backscattering that increases the reflection loss, especially if the metal nanoparticles are located on top of the PV layer or incorporated into it. As a result, such LTS can not improve any SC with an optimal internal design [19]. LTSs based on regular arrays of dielectric NAs [46] are also inefficient compared to textured ARCs. This is a correct comparison because the dielectric resonators are in all practical cases located on top of the PV layer and are aimed to perform also the antireflecting functionality. Since they constitute a diffraction grid their reflection losses are higher than that of the conventional ARC and the modest gain due to the narrow-band light-trapping effect does not overcompensate this shortage [19]. Photonic crystal LTSs combined with the PV layer are efficient, but they are technologically reasonable only for thin-film SC with the crystalline structure of the PV layer, such as polycrystalline silicon. For other types of thin-film SCs these LTSs are not suitable.

Similar limitations are applied to polycrystalline SCs with pyramidal micro-texturing [49,50]. Such a SC consists of an array of densely packed pyramids of 2-5 micron heights and submicron thickness and represents the historically first and most known LTS. To decrease the scattering losses a usual bilayer ARC covers the surface of such the SC. Here, the normally incident light is trapped in the PV layer because it experiences four passages in it. This effect is achieved due to mirror effect of the back electrode. The light reflected from one pyramid impinges the adjacent one due to the presence of the back electrode. As a result, the total path of the light turns out to be sufficient for absorption. Unfortunately, due to technological reasons, this method of light-trapping is either not suitable for other thin-film SCs or would result in a too expensive fabrication [19].

As to regular arrays of plasmonic elements converting the incident light into the horizontally guided modes, besides of high costs (a general drawback of all LTSs with regular structure) their drawback is a lack of efficiency. Though an 18% increase of efficiency compared to a conventional ARC has been demonstrated in [58] for an a-Si SC, it seems to be too modest for the studied case of a conventional SC (with a back electrode operat-
ing as a reflector). For flexible SCs a similar gain was, to our knowledge, never reported. Moreover, to stress the positive effect of such LTSs some authors take the PV layer thinner than the optimal one, e.g., instead of 300 nm one takes 150-200 nm [44,51,53] or even 80 nm [43] for a-Si. For optimally designed thin-film SCs the gain of most known regular nanoarrays is very modest because of the resonant nature of the light-trapping effect. The same concerns applies to any array of nanoantennas including dielectric NAs [46]). Even if several resonances of the array of NAs are used as in [44,59] the light-trapping effect remains narrow-band compared to the operation band of the SC. Such LTSs bring a very modest gain that cannot justify their fabrication cost.

1.4 Objectives and contribution of this thesis

The thesis is devoted to the development of novel broadband light-trapping structures based on regular arrays. It includes the results published in six journal papers. It consists of two main parts. In the first part (Chapter 2), we present a metal light-trapping structure based on arrays of metal nanoantennas and report its theoretical and experimental studies. The second part (Chapter 3) discusses novel all-dielectric light-trapping structures supported by numerical simulations.
2. Metal light trapping structure

As we have discussed, many LTSs for thin-film SCs such as a-Si and organic SCs are built of the arrays of silver or gold nanoparticles. If they exploit the localized surface plasmon resonances of a single particle or a cluster of particles, the response of a random array with the variations in the particle shapes and locations is composed of overlapping resonances of the array components yielding a broad overall resonance of absorption. This resonance can cover the whole operational band of the SC (for a-Si it corresponds to wavelengths 400-700 nm). However, in this case, nearly one-half of the absorption coefficient originates from the plasmonic dissipation in metal nanoparticles and only one-half of the incident light is usefully absorbed in the PV layer. The parasitic absorption in the bottom electrode of a thin-film SC without an LTS is replaced by the similar parasitic absorption in the LTS itself. At least, this is the case if the thickness of the PV layer is optimal [19].

Regular arrays of metal nanoelements transform the incident wave field into evanescent waves or waveguide modes (this functionality is nothing but that of a receiving antenna). They support collective resonances which are not dipole plasmonic resonances. At these resonances, the hot spots can be formed in the bulk of the active layer, and its intersection with the NA can be very small. For the first time, the possibility of such a resonance was noticed in [44]. However, this result appears to be an outlier. In the literature, LTSs based on metal NAs even with a multifrequency operation (2-3 resonances) still have a relatively small bandwidth that is not sufficient for a drastic improvement of the useful absorption. This situation motivated us to develop a new technical solution where the resonances of the NA array would occupy a substantial part of the operation band of a SC.
2.1 Theoretical analysis of the broadband light-trapping effect

![Diagram showing geometries of arrays supporting domino modes](image)

Figure 2.1. Geometries of some arrays supporting domino modes (top view). (a) – Chain of parallel metal bars from work [60]. (b,c) – Two structures supporting optical leaky domino modes studied in the present work.

Interesting approach to collective resonances in arrays of metal elements suitable for light trapping was proposed in [60]. In that paper, the low-loss infrared waveguide was formed by a chain of parallel metal bars of micron sizes and a rectangular cross-section. This chain carried tightly confined electromagnetic modes referred to as domino plasmons or domino modes. An advantageous property of domino plasmons was low attenuation because the electric field penetrated into the metal to a depth smaller than the skin-depth. Therefore the electric field was mainly concentrated in the gaps between the micro-bars and the waveguide mode propagated to a long distance, much longer than in the most of the discrete optical guides. Since the guided mode is an inherently collective propagating oscillation, domino-modes belong to the class of so-called spoof plasmons [61]. The dispersion was nearly the same as that of a surface plasmon-polariton and modified slightly when the chain period $d$ increased up to a certain threshold. When $d$ exceeded this threshold, the electromagnetic interaction between adjacent elements became insufficient, and the mode vanished.

The bars proposed in [60] were parallel to one another and vertically oriented (Fig. 2.1a). The length $a$ of the bars was comparable with the wavelength in free space, and the thickness $\Delta$ significantly (5-6 times) exceeded the skin-depth $\delta$. In [60] the spoof plasmon propagated in a chain of silver, gold or copper elements in the far and mid-IR ranges. Later in work [62], similar waveguide modes were found in the chain of parallel nanobars operating at the near IR frequencies. The orientation of the unit element of the chain was modified keeping the same ratios of its geometrical parameters as in [60] – now the bars were placed in-plane.
The conditions of the spoof plasmon remained the same as those found for the vertical domino elements: period of the chain should be smaller than 1.2a, where a is the bar length, thickness Δ of the domino element should be substantial (at least twofold skin-depth δ), and the thickness of the bar should be several times smaller than the width. Further, in [63] one found several high-order dispersion branches in both surface-wave and leaky-wave domains of the phase space. These branches arise at higher frequencies than the waveguide regime. The leaky modes can be excited at several eigenfrequencies by incident plane waves.

Performing numerical simulations as a part of my doctoral studies I established the essential features of the leaky domino modes. These features are low attenuation, an efficient concentration of E in the gaps between the metal elements with very weak penetration depth, high density of these modes over the frequency axis and correspondence of these modes to the multipole resonances. At the multipole resonances, the multipole moments of a metal bar become more important than the dipole moment. This property is tightly related to the small penetration depth and is a prerequisite of the low losses in the metal at frequencies of these modes. Also, the density of these dispersion branches over the frequency axis increases when the chain is placed on a dielectric substrate.

These peculiarities allowed us to suggest that the excitation of these modes can be utilized for broadband light-trapping in thin-film SCs. Although leaky modes were previously found only for a 1D array – chain – of domino-elements, we assumed that these modes might exist in a 2D planar array. We also suggest that the electromagnetic interaction of such elements in a planar array might lead to the overlapping of these resonances and formation of a solid band of domino modes, especially on the substrate where the dispersion branches overlap. Next, we suggest that in the presence of a lossy substrate the resonant reflection in this band is substituted by resonant absorption. All we needed for it was keeping the subwavelength field concentration in the gaps between the nanobars in the case of the lossy ambient.

To confirm our guesses, I performed an extensive numerical study reported below. This study enabled the suggested application of leaky domino-modes excited by incident plane waves in the optical range.
2.1.1 Leaky domino-modes in arrays of silver nanobars

The goal of the research reported in Publication I was to prove the existence of leaky domino modes in a 2D array of parallel nanobars, to explain the physics of the corresponding regime and to expand this concept to the case of a lossy substrate. First, I have performed a rigorous numerical study of the structure of identical parallel bars depicted in Fig. 2.1b.

Array of parallel nanobars

In this part, we calculate the dispersion diagrams of the array of nanobars of Ag located in free space and analyzed its TE and TM leaky eigenwaves. Then, we determine the frequencies where these dispersion branches start (Bloch vector $\beta = 0$). This regime corresponds to the leakage of the eigenwave in the normal direction. Due to the reciprocity, the same multipoles that correspond to the eigenwave with $\beta = 0$ at a given frequency must be excited by a normally incident plane wave of the same frequency. Next, we calculate the multipole moments induced in an element of the array by a normally incident plane wave in the frequency ranges centered by the frequencies where the leaky domino-modes start. Normalizing these multipoles as it is described below we make all of them dimensionless to compare them. This way we find which multipoles dominate in every bar for a given dispersion branch. We also analyze the spatial distribution of the electric fields and polarization currents. Polarization currents are proportional to the electric field calculated inside the bar with the factor $(\varepsilon_{Ag} - 1)$. We find the evidence of these multipoles in the distributions of the polarization currents and notice the following trend: the higher is the order of the dominating multipole moment the smaller is the penetration depth of the electric field into the domino bar. Zero order multipole corresponds to the electric dipole, first order to the magnetic dipole, second – to the electric quadrupole, third – to the magnetic quadrupole, etc. [64]. Polarization currents corresponding to high-order multipoles are surface currents. It is not surprising that the power absorption decreases along with the order of the multipole dominating at a given frequency.

The geometrical parameters of the array are as follows: period along the $x$-axis is equal $c = 600$ nm, period along $y$ is $d = 300$ nm, sizes of the bar along these axes are $a = 500$ nm and $b = 200$ nm, respectively. The material of the elements in these simulations is silver, whose complex permittivity was taken from [65]. $\Delta = 50$ nm, whereas $\delta$ at 300-600 THz does not exceed 22 nm. Simulations of the dispersion diagrams were done in
the range 50-600 THz using the commercial package Lumerical FDTD Solutions, which allows all eigenfrequencies to be found using the method of transparent sources [66]. A cloud of randomly oriented dipoles is used in this software to find eigenfrequencies for any value of the Bloch vector $\beta$ of a periodic array. For calculation of electric and magnetic field distributions, we applied both Ansoft HFSS and CST MWS softwares which gave very close results.

![Figure 2.2](image)

**Figure 2.2.** Dispersion diagrams for the structure depicted in Fig. 2.1b located in free space. (a) – Propagation along $x$, (b) – that along $y$.

The dispersion diagrams of the eigenwaves propagating along the axes $x$ and $y$ are shown in Fig. 2.2a and 2.2b, respectively. Besides of two guided domino-modes which exist at $f < 210$ THz (propagation along $x$) and at $f < 180$ THz (propagation along $y$) and straight lines (eigenmodes of free space) we have found several leaky branches with starting point $\beta = 0$ at frequencies 360, 445, 455 and 495 THz. Both TE and TM eigenwaves starting from 445 THz have $\langle E_x \rangle = 0$ (here brackets denote the averaging over the unit cell). These eigenmodes can be excited by a plane wave with $y$-polarized electric field. The corresponding dispersion branch shown in Fig. 2.2a is a TE-polarized wave of the forward-wave type. The mode shown in Fig. 2.2b is a TM-wave of the backward-wave type. On the contrary, the eigenmodes starting at 455 THz have $\langle E_y \rangle = 0$ and can be excited by $x$-polarized electric field. The corresponding mode in Fig. 2.2a is the TM-wave and in Fig. 2.2b it is the TE-wave (both are forward waves). The modes starting at 360 THz are $x$-polarized in Fig. 2.2a and $y$-polarized in Fig. 2.2b.

The next important step in our study was to identify multipoles, which resonate at frequencies of leaky domino-modes in these planar arrays. The dipole mode obviously has the spot partially covering the metal that results in substantial losses. Higher order multipoles may lead to the localization of the electric field outside the metal. How significant are
multipole moments compared to the dipole ones? To clarify this point, we have performed the calculation of multipole moments of the unit cell—electric and magnetic dipoles, electric and magnetic quadrupoles, and electric octupoles. Multipole moments were calculated using standard definitions \[64\] through the polarization current \( \mathbf{J} = i\omega\varepsilon_0(\varepsilon_{\text{metal}} - 1)\mathbf{E} \) induced in the metal element of our array by a normally incident wave:

\[ p_\alpha = \frac{1}{j\omega} \int J_\alpha dV, \]
\[ m_\alpha = \frac{1}{2} e_{\alpha\beta\gamma} \int r_\beta J_\gamma dV = \frac{1}{2} \int [\mathbf{r} \times \mathbf{J}]_\alpha dV, \]
\[ q_{\alpha\beta} = \frac{1}{j\omega} \int r_\alpha J_\beta dV, \]
\[ s_{\alpha\beta\gamma} = \frac{1}{4} e_{\alpha\gamma\delta} \int r_\beta r_\gamma J_\delta dV = \frac{1}{4} \int ([\mathbf{r} \times \mathbf{J}]_\alpha r_\beta + [\mathbf{r} \times \mathbf{J}]_\beta r_\alpha) dV, \]
\[ o_{\alpha\beta\gamma\delta} = \frac{1}{j\omega} \int r_\alpha r_\beta J_\gamma dV. \]

Here \( r_\alpha \) is the radius-vector referring to the center of the unit cell and \( e_{\alpha\beta\gamma} \) is the Levi-Civita symbol allowing to express the vector product in the coordinate notation. Downward from the top, formulas (2.1) refer to the dipole, magnetic dipole, electric quadrupole, magnetic quadrupole, and electric octupole moments. Repeating indices imply summation. In fact, we have calculated only diagonal components of tensorial multipoles since the electric and magnetic fields produced by the off-diagonal components of an electric (magnetic) multipole of the \( N \)-th order is not distinguishable from that produced by a magnetic (electric) multipole moments of the \((N - 1)\)-th order \[64\]. For example, the electric quadrupole component \( q_{xy} \) creates the electromagnetic field which cannot be distinguished from that produced by \( m_z \). Similarly, the field produced by the off-diagonal octupole components is not distinguishable from that of magnetic quadrupole components.

The dipole moment calculated for both \( x \) and \( y \) orientations of the incident electric field turned out to be not resonant at all frequencies of interest. The normally incident plane wave excites some dipole-type resonances above 600 THz. This spectral domain (green and higher-frequency light) is out of the scope of the present study. The frequency region of our interest is 320-500 THz. In this range the induced dipole moment is weakly dispersive. To compare different multipole moments with it and with each other we have normalized them using the absolute value of the dipole moment \( p \) as the basis. Since the magnetic multipoles in the definition (2.1) do not contain \( \mu_0 \), we normalized the magnetic moment.
components induced by the incident wave as follows: \( M_{y,z} = m_{y,z}/\omega|p_x|c \), \( S_{yy,zz} = s_{yy,zz}/\omega|p_x|^2 \) for the case when the incident electric field is \( x \)-polarized and \( M_{x,z} = m_{x,z}/\omega|p_y|d \), \( S_{xx,zz} = s_{xx,zz}/\omega|p_y|^2 \) for the case of \( y \)-polarized incident field. Similarly, the normalized electric quadrupole and octupole moments are \( Q_{xx} = q_{xx}/|p_x|c \), \( Q_{yy} = q_{yy}/|p_y|d \), \( O_{xxx} = o_{xxx}/|p_x|^2 \), and \( O_{yyy} = o_{yyy}/|p_y|^2 \). In Fig. 2.3, we show the resonances of \( Q_{xx} \) and \( M_y \) for \( x \)-polarized incident electric field, and in Fig. 2.4 we show the resonances of \( Q_{yy} \) and \( S_{zz} \) for \( y \)-polarized incident electric field.

\[ \text{Figure 2.3. Frequency dependencies of normalized multipole components } Q_{xx} \text{ and } M_y \text{ induced in an element of our array by a normally incident plane wave with } x \text{-polarized electric field of unit amplitude.} \]

In Fig. 2.3a we see that the quadrupole moment at the resonance frequencies 460-470 THz is of the order of 1% with respect to the dipole moment and at 480-490 THz its magnitude is 0.1%. However, this does not mean that the contribution of the non-resonant dipole moment dominates in near field. The near-field of the quadrupole moment, whose normalized value is 1, is much higher than the near field of the reference dipole moment, provided both quadrupole and dipole are uniformly spread over the volume of the domino-element. This is so because the quadrupole field is more localized than the dipole field. Moreover, the octupole moment \( O_{xxx} \) also has the resonances in the same bands. This means that in the resonance bands of \( Q_{xx} \) a set of high-order electric multipoles also resonates, and the near field of this set around the domino element dominates over the near field of the dipole polarization. The same refers to the resonance band 485-490 THz. At frequencies 480-490 THz the normalized magnetic moment \( M_y \) depicted in Fig. 2.3b resonates and achieves 6% of the dipole moment. In this situation the series of resonances of high-order magnetic multipoles become comparable or even exceed the dipole moment.

The same observation is valid in the case when the array is excited by the \( y \)-polarized electric field. In the range 435-450 THz, the magnetic
quadrupole $S_{zz}$ represents the main multipole moment of the resonant set of higher-order magnetic multipoles. Electric quadrupole $Q_{yy}$ has multiple resonances which are accompanied by resonant octupoles (and, obviously, higher electric multipoles). In Fig. 2.5 we observe resonances of $M_z$ produced by the incident wave with either $x$-polarized or $y$-polarized electric field. In both cases, the resonance band is 350-360 THz. The general conclusion is as follows: in the broad frequency region 320-500 THz there are several bands where the electromagnetic interaction of adjacent domino-elements is governed by their resonant multipoles (magnetic dipole moment in the theory of artificial magnetism is a multipole of the first order) and not by their electric dipole because the last one over the whole frequency region is not resonant.

So, all leaky modes depicted in Fig. 2.2 are linked to multipole resonances. The modes whose starting point $\beta = 0$ corresponds to 360 THz in both dispersion diagrams are linked to a set of magnetic multipoles with dominating magnetic moment $M_z$ induced by both TE and TM waves. The modes starting at 445 THz are linked to a set of magnetic multipoles with
dominating magnetic quadrupole $S_{zz}$ excited by the $y$-polarized electric field and to a set of electric multipoles with dominating quadrupole $Q_{xx}$ excited by the $x$-polarized the electric field. The modes starting at 460 THz $495$ THz are linked to a set of electric multipoles with dominating quadrupole $Q_{\alpha\alpha}$ excited by $\alpha$-polarized electric field.

It should be noted that frequency dependencies of the multipoles are not Lorentzian. This is not surprising: what we simulate are not multipole polarizabilities which, most probably, correspond to the Lorentz resonance, but multipole moments produced in a unit cell of an array by a plane wave with a unit electric field. The absolute values of these multipoles versus frequency are relevant for the location of the corresponding resonances and comparison of the resonance magnitudes. The frequency dispersion of the real and imaginary parts of these multipole moments is not very relevant.

We have thoroughly analyzed the spatial distributions of the electric field in the array and have seen that the higher is the order of the dominating multipole the weaker is the penetration depth of the electric field inside the nanobar. At frequencies of the domino-modes, the absorption of the incident plane wave is negligibly small, because high-order multipoles determine them. The detailed analysis of the microscopic polarizations in the domino-element at different frequencies is presented in Publication I.

Next, we had investigated the evolution of the leaky domino modes when the geometric parameters of the array varied. When the array periods $c$ and $d$ become larger than the certain threshold values leaky domino-modes associated with higher multipoles disappear and, simultaneously, the dipole resonances transfer to the frequency region 320-500 THz. These observations confirm the collective nature of domino-modes – they cannot be excited in an isolated bar.

The most important conclusion of this section is as follows: an array of submicron domino-elements in a broad range of optical frequencies supports several leaky modes. These modes attenuate weakly. They all result from collective resonances of high-order multipoles induced in the elements of the array. The dipole-type plasmon resonances dominate beyond this frequency region. Unlike the case of a chain of domino-elements where leaky modes are TM-polarized and represent the spoof plasmon modes, in the planar array domino-modes have both TE- and TM-polarizations.
Array of nanoantennas – oligomers of four nanobars

Next, we have analyzed the structure depicted in Fig. 2.1c that is nearly in-plane isotropic. The sizes of the bars (250x150x50 nm) are slightly smaller than those adopted above so that the unit cell (array period) would be not too large (otherwise the diffraction lobes are noticeable). Our unit cell is a square of size $\varepsilon = 850$ nm. The oligomer of four nanobars will be referred below as a metal NA.

![Dispersion diagram for the array with in-plane isotropy.](image)

In the dispersion diagram Fig. 2.6 we can (besides of the light lines and weakly distinguished guided modes) identify four leaky branches – two TM-waves and two TE-waves. One TM-branch and one TE-branch start in the band 330-350 THz and two other branches start in the band 490-500 THz. Both these bands correspond to resonances of $Q_{xx}$ (induced by the $x$-polarized incident electric field) and $Q_{yy}$ (induced by the $y$-polarized one). Magnetic moments of the element and electric octupole moments are also resonant in the same bands. The electric dipole moment is not resonant within the whole range 320-500 THz. So, for such the planar array with in-plane isotropic polarization response, the main observations of the previous subsection keep valid: leaky domino-modes are still linked to multipole resonances, and these resonances are collective modes of the array – oscillations governed by the electromagnetic interaction of its elements.

Array on a substrate

In the present part, we consider the domino-modes excited in both anisotropic and isotropic arrays located on a substrate of subwavelength thickness 100 nm and lossless (but rather high) permittivity $\varepsilon = 14$. First, we have considered the simple anisotropic array depicted in Fig 2.1b. The dispersion diagrams of TE- and TM-polarized surface waves for two propagation
Metal light trapping structure

Figure 2.7. Dispersion diagrams of the structure from Fig. 2.1b located on a highly refractive substrate. (a) – Eigenmodes propagate along the x-axis, (b) – Eigenmodes propagate along the y-axis. Modes in both plots whose dispersion branches start in the ranges 340-490 THz and at 550-560 THz are domino-modes.

directions are shown in Fig. 2.7. The location of the array on the substrate resulted in the frequency shift of the same modes which existed when the array was located in free space. Counter-intuitively, this is the blue shift of the corresponding modes. Modes which started without the substrate at 360 and 445 THz, start at 370 and 460 THz with the substrate, respectively. Also, the substrate gave rise to many new domino-modes. We have simulated the magnetic and quadrupole moments of the unit cell (for $\beta = 0$, i.e., excited by the normally incident plane wave with both x- and y-polarizations and found them resonant at the frequencies where the leaky modes reside. An important result of this study is that the multipole resonances (leaky domino modes) do not alternate with dipole resonances (leaky plasmon modes) in the band 350-500 THz. In this frequency region, every element has essentially multipole response, and at these resonances, it concentrates the local electric field outside the metal. Notice, that in the present case there is also a quadrupole resonance excited by a normally incident wave at 550-560 THz (above the one of the dipole resonances).

When the substrate thickness increases, e.g., for the thickness of 200 nm, the separate leaky modes remain in the same frequency range. However, their number nearly doubles and they become not visually distinguishable in the simulated dispersion diagram. Simultaneously, the resonances of the quadrupole, magnetic dipole, magnetic quadrupole and octupole moments in this region overlap and form a continuous band in which the high-order multipoles of the unit cell dominate over its dipole moment. The same effect occurs if we introduce optical losses into the substrate of thickness 100 nm adding to its permittivity $\varepsilon$ a sufficient
imaginary part.

Figure 2.8. Dispersion diagrams of the structure from Fig. 2.1c located on a highly refractive substrate. Numerous domino-modes dispersion branches start ($\beta_x = 0$) at frequencies between 340 and 500 THz.

Finally, we have considered an array with in-plane isotropic unit cell depicted in Fig. 2.1c with the same substrate. Here, the domino modes also experience the blue shift and their number increases even more significantly than for an array of parallel nanobars. Multipole resonances are excited by a normally incident wave at 340-350, 360-375, 375-390, 420-430 THz, and form a range of overlapping resonances at 460-500 THz. The dispersion plot in Fig. 2.8 allows us to identify the corresponding dispersion branches. Above 500 THz and below 340 THz the leaky modes seen in this plot correspond to noticeable dipole moments. At corresponding frequencies the dissipation in the metal is noticeable. Again, in the present structure, the twofold increase of the substrate thickness results in the formation of the solid band 340-500 THz filled with only domino-modes.

2.1.2 Light trapping effect

In this subsection, we discuss the light-trapping properties of our leaky domino-modes. First, we have simulated the reflection coefficient of our in-plane isotropic array located on the same lossless substrate as above (100 nm thick, $\varepsilon = 14$). Second, we considered a lossy substrate ($\varepsilon = 14 + 0.75i$) to estimate the absorption in it. The domino-modes, in this case, form a broad band of overlapping resonances 350-500 THz.

In Fig. 2.9a we compare the additional reflectance of the dielectric layer due to the presence of domino-elements. The calculation of additional reflectance allows us to get rid of the frequency dispersion in reflectance of the bare layer. On the red curve, corresponding to the lossless layer, we
can identify four bands of the resonant reflection – 340-350, 360-390, 420-430, and 460-500 THz which correspond to the previously found frequencies of multipole resonances and, respectively, the frequencies of leaky domino-modes start in Fig. 2.8.

On the blue dash-dotted line, corresponding to the case of the lossy layer, the reflection resonances disappear. The additional reflectance decreases with respect to the lossless case though remains positive – the array slightly increases the integral reflection in the band 350-500 THz. This is not surprising because the structure is not optimized for suppressing the reflection. Varying the optical losses of our substrate and its thickness we may obtain a negative value for the additional reflectance averaged over the band 350-500 THz. Here we aim to show that the light-trapping is inherent to any array supporting leaky domino-modes.

For this purpose, it is sufficient to show that the additional reflectance in the case of the lossy substrate is smaller than the additional reflectance in the case of the lossless substrate and that the absorption in the lossy substrate increases in the presence of the domino-elements. The first fact is visually evident from Fig. 2.9a. The second one is clear from Fig. 2.9b. Notice that the total absorption in the structure calculated via reflection and transmission coefficients visually coincides with the absorption in the lossy substrate shown with the solid red line in Fig. 2.9b. This means that the absorption in the domino-elements is negligibly small.
Shape adjustment

We have performed a comprehensive simulation to find an optimal geometry of the unit cell which would demonstrate the best light-trapping functionality. Our primary goal was to achieve the broadest band of the light-trapping effect in the operational range of a typical thin-film SC and to minimize the parasitic reflection caused by our metal elements. We saw in these simulations that the domino-modes could be excited in arrays of optically long bars as well as in arrays of optically short ones if the domino shape of the nanobar is maintained and the minimal size exceeds the skin-depth at least twice. However, for light-trapping purposes the length of an element must be restricted: the unit cell of the grating should not significantly exceed the operational wavelength. Otherwise, the array causes a high backscattering in the grating lobes, and the reflection loss increases drastically. Another restriction is the isotropy of the polarization response in the horizontal plane. It is required because the sunlight is unpolarized. Let us briefly discuss the design which meets the criteria mentioned above.

A unit cell performed as an oligomer of four domino-bars ensures the needed isotropy, but it means that the unit cell is more than twice longer than the nanobar. The decrease of the nanobar sizes results in the narrowing of the frequency band of domino-modes in the array. The problem is resolved reshaping the nanobar itself. Our calculations have shown that the operational band broadens and achieves the relative width 50% if the nanobar is tapered. Domino-bars should be trapezoidal as shown in Fig. 2.10 for a SC operating in the range of visible light (such as SCs based on silicon, CdTe, InP and some other PV materials) and for a SC operating in the band $\lambda = 700-1300$ nm called the inter-band range (some
organic SCs and solar cells based on some multicomponent semiconductors such as cadmium indium selenide).

Parasitic reflection from the metal is low in the band of domino-modes. Here the concept of a shadow formed by the metal elements is not applicable – it is based on the geometrical optics not applicable in the range of eigenmodes. At higher frequencies (except those of the high-order surface-plasmon resonances where the geometrical optics also does not work) the reflectance is close to that resulting from the shadow effect (geometrical optics). However, our array is geometrically sparse, and the shadow effect of the metal elements is not critical. The distance between the tapered nanobars in our optimal design is sufficiently small for the excitation of domino modes and large enough to avoid the critical reflection outside of the band of these modes. Moreover, we have checked the possibility to tune the band of domino-modes to operational bands corresponding to other real SCs. For it, the scaling of the unit cell is required, and a small adjustment of trapezoidal domino-bar dimensions is also needed.

Selection of the metal
Our initial analysis was developed for silver domino bars. Since it was found that the domino-shaped nanobars in the array display multiple collective resonances that are different from the plasmonic ones, we assumed that the same operation is possible using other metals. We have investigated the similar light-trapping effect for domino-elements of three different metals: gold, chromium, and aluminum. Gold and chromium elements do not enhance the absorption in the substrate – they absorb the light themselves. The reason for this is evident. The skin-depth of these metals is comparable with 50 nm. Therefore the arrays with the same sizes do not support the domino-modes. The increase of the element thickness to double skin-depth is not helpful, because it requires the corresponding increase of all sizes. Then the unit cell of the array becomes optically large that apparently result in high diffraction losses.

Aluminum elements of the same geometry support domino-modes at practically the same frequencies and the main properties of these modes are the same as those of domino-modes in the silver arrays. However, aluminum does not possess plasmonic properties in the range 350-500 THz. The only common feature of Al and Ag in this range is the skin-depth smaller than 22 nm. One may conclude from it that the leaky domino-modes are not plasmonic oscillations in their nature. In other words, the
leaky domino-modes are not collective oscillations of electron plasma in a nanoparticle. They are plasma oscillations which are collective for an array; they are mutually coherent oscillations in the array elements governed by the electromagnetic coupling of these elements. In our opinion, these modes represent a phenomenon that is very unusual for the optics of metal structures.

2.2 Experimental verification of our simulations

In the previous section, we have theoretically investigated the planar arrays of Ag nanobars supporting domino-modes. Unusual optical properties make the domino-modes in planar arrays extremely interesting and promising. Our simulations seem entirely reliable to us since we used different solvers giving the same results. However, for the scientific community new physical effects and other unusual results obtained by simulations do not look convincing enough without an experimental confirmation. To our knowledge, domino modes have not been demonstrated experimentally even for chains of domino bars. As to the leaky domino modes in the optical range, we have discovered them, and they hardly could be studied by other scientific groups. Therefore, the experimental validation of our simulations was an essential task. The aim of our experimental work reported in Publication II was to validate the predictions of the numerical simulations reported above and to confirm the predicted existence of these unique collective modes in the optical frequency range.

For this purpose, an array of four-element oligomers of silver nanobars (with trapezoidal shape) was fabricated by electron beam lithography on a bulk crystalline silicon substrate. Here we follow the design proposed at the end of the previous chapter. The scanning electron microscope (SEM) Zeiss Neon 40 with Raith Elphy Plus lithography attachment was employed to expose patterns in 400 nm PMMA resist. Further fabrication steps included the development of the resist, deposition of a silver layer using resistive thermal evaporation (in Edwards Auto 500) and lift-off process. We also introduced thin (45 nm) passivation layer of silicon oxide through magnetron sputtering (in Edwards Auto 500) to prevent chemical degradation of silver in NAs. The SEM image and atomic force microscopy (AFM) representation of a single NA (unit cell of the fabricated array) are shown in Fig. 2.11b,c. The period of the array equals 815 nm, while the thickness of the sputtered silver approximately equals 50 nm. To visu-
Figure 2.11. (a) Design of nanoantenna array unit cell. All values are specified in nanometers. (b) SEM image of a single silver NA from the array fabricated by electron beam lithography and covered with 45 nm silica passivation layer. (c) Perspective view of the topography of a single NA measured by AFM. (d) Schematic view of the NSOM configuration used in the experiments.

alize the distribution of the electromagnetic fields in the vicinity of the NA array, we used an aperture-type near-field optical microscope (NSOM, AIST-NT SmartSPM™) operating in the collection mode [67, 68]. Since the thick silicon substrate is opaque in the visible spectral range, we used the experimental geometry with oblique excitation of the sample in reflection mode. The schematic view of this configuration is presented in Fig. 2.11d. Here, a weakly focused laser beam was incident at 25 degrees to the sample surface, while the polarization of the beam was either TE or TM. For excitation, we used 532 nm frequency-doubled continuous wave Nd:YAG laser with the power up to 80 mW and 633 nm HeNe continuous wave laser with the power up to 35 mW. The fields induced by the NA array were collected by a metalized tapered fiber probe with an aperture diameter of about 200 nm. The signal transmitted through the aperture was detected with a photomultiplier tube (PMT, Hamamatsu H10722-01).

To avoid the near-field signal artifacts induced by the complex sample topography, we performed the measurements in constant-height mode [68]. During the scanning process, the tip moved within a plane at a distance of 100 nm from the surface of the silicon oxide layer between the NAs.
Figure 2.12. Color maps of $|E|^2$ within the unit cell of the array of nanoantennas at $\lambda = 633$ nm (top row) and 532 nm (bottom row) on silicon substrate. The first wavelength theoretically corresponds to the range of domino modes. The second wavelength refers to the range of plasmon resonances of NAs. The XZ and YZ sections are taken through the center of the NA, while the XY section is taken at 2 nm below the substrate surface. The spatial scale bar shown in each section represents 200 nm. The polarization of the TE-polarized incident light is along the X axis, the tangential component of the wavevector of the incident wave is parallel to the Y axis (see Fig. 2.11). The field intensity is normalized to the intensity of the electric field in the incident wave. For the reference, the NA and silica layer borders are shown with dashed lines on XZ and YZ sections.

(see Fig. 2.11d), which was ensured by employing the capacitive sensor feedback loop.

The numerical simulations of the electromagnetic fields distribution in the vicinity of NA array were carried out in the CST Microwave Studio®. The numerical data obtained for two experimentally available wavelengths, 532 and 633 nm, are presented in Fig. 2.12. For $\lambda = 633$ nm (Fig. 2.12a-c). One can immediately see the characteristic features indicating the excitation of domino-modes at $\lambda = 633$ nm: low penetration depth of the electric field inside the metallic elements (Fig. 2.12a,b) and localization of this field beneath the NA (Fig. 2.12c). On the contrary, the numerical data for 532 nm excitation (Fig. 2.12d-f) demonstrate rather high density of the electric energy inside the NA and low electric field beneath the NA, which corresponds to its plasmon resonance. Notice that the first wavelength, in accordance to our simulations corresponds to the range of domino modes excitation for a multilayer structure with a thin (150 nm) top layer of silicon, which once more confirms the low impact of the substrate on domino modes.

Though NSOM cannot grant us access to the structure of electromagnetic fields in the bulk of the investigated array and provide outright evidence of field localization under the NAs observed in the numerical calculation, it can offer a rich record of the fields distribution above the sample. Therefore, we were able to compare the results of rigorous numerical simulations of the investigated structure with the results of the
Figure 2.13. Comparison of experimental results (top row) and numerical calculations (bottom row) of the near-field signal patterns at a distance of 100 nm from the sample surface. The excitation wavelength is 633 nm (panels (a-d) and 532 nm (panels (e-h). The polarization of the incident beam is either TE (panels (a,c) and (e,g) or TM (panels (b,d) and (f,h). The NA contours are shown for the reference.

The experimental data are presented in the top row of Fig. 2.13 for \( \lambda = 633 \) nm (panels a,b) and \( \lambda = 532 \) nm (panels e,f).

One can see that the numerical modeling demonstrates excellent agreement with the experimental data for \( \lambda = 633 \) nm for both TE and TM polarizations. A worse agreement of numerical and experimental field patterns for \( \lambda = 532 \) nm can be explained by inaccuracies in the model of silver dielectric permittivity [69] for this band of wavelengths. Beyond the plasmon resonance of nanobars these inaccuracies are not so important. These small inaccuracies are not essential for the domino modes – above 550-560 nm. In this range, our NAs operate, roughly speaking, as perfectly conducting elements. An error in the conductivity of silver is not important if this error does not violate the main condition of the domino modes – the smallness of the skin-depth compared to the sizes of the domino-bar. However, at plasmon resonances, the inaccurate knowledge of the complex permittivity of silver results in quite significant errors. Another common reason for the disagreement is the interaction between the sample and the probe which can distort the near-field patterns. This is, most probably, the reason for the small quantitative differences in measured and simulated patterns for \( \lambda = 633 \) nm. However, qualitatively the measured and simulated color maps agree very well. In general, for the range of the domino modes, the agreement between the theory and
Metal light trapping structure simulations turned out to be good.

As to the color map for $\lambda = 532$ nm, the impact of the imaginary part of the complex permittivity is high, and it may explain the quantitative disagreement though the similarity between the simulated and measured field distributions also holds in this case. For the TE-incidence the measured signal has maxima in the same places as the theory predicts, though they are more spread – local maxima distinguished in the simulated pattern overlap in the measured pattern. For the TM-incidence the measurements show no maxima over the elements stretched along $y$-axis, however other maxima are seen well.

In the literature on the NSOM measurements, such the similarity of the measured and calculated near-field signal is usually considered as good. This result allows us to assert that the numerical model of domino modes utilizing the commercial packages stands the experimental check. The experimentally observed near-field patterns for $\lambda = 633$ nm are an indirect manifestation of the optical domino-modes present in the arrays of domino-bars.

### 2.3 Nanoantennas for organic solar cell

We have already mentioned that organic solar photovoltaics is considered as solar PV of 3rd generation and the number of publications in this field has grown continuously during past two decades. Organic photovoltaic (OPV) cells based on conducting polymers and organic molecules belong to the class of excitonic SCs. The absolute majority of such SCs are thin-film – their PV layer is of submicron thickness. Panels of OPV cells can be made flexible like a-Si solar panels. They possess high sensitivity to the non-direct (e.g., scattered by clouds or inhomogeneities of the atmosphere) and low-intensity solar irradiance. Whereas for c-Si and a-Si solar PV the cloudy weather implies a 4-5 fold drop of their electrical output, for a panel of OPV the decrease is only twofold. These advantages of OPV cells combined with low weight and low production cost potentially make them economically viable for many applications [36].

Transparency in the wavelength range of visible light is one of the exciting properties of specific OPV materials. This feature extends the applications of OPV cells beyond those pointed out in well-known books [13, 20, 36, 37]. For example, SCs operating in the infrared or ultraviolet ranges can be incorporated into a window of a residential or office building, of
an automobile, into touch-screens of smart devices, etc. The visible solar light goes through, and the infrared radiation is absorbed and converted into electricity.

Of course, this operation cannot be ideal. One may sacrifice a certain decrease of the visible light integral transmittance in favor of the electric energy generation. A typical residential architectural window transmits nearly 55% of the visible light energy whereas 30% of the integral transmittance in the visible range is sufficient for practical needs [70]. This means that the illumination is sufficient if an OPV cell transmits 54% of the visible light. Taking into account the spectral sensitivity of a human eye, this minimally allowed value can be even reduced. Currently, there are several designs of transparent SCs which transmit nearly one half of the incident solar radiation in the visible range. They are PV cells based on organic polymers [71, 72] or on so-called molecular heterojunctions [73,74]. Also, there are excitonic SCs with inorganic heterojunctions – SCs based on p-NiO and n-ZnO [75]. In this work, we concentrate on OPV cells.

OPV cells based on molecular heterojunctions may operate in the near-infrared (NIR) range where the solar power is much higher than the one in the ultraviolet. However, these cells have severe limitations in the thickness of their PV layer. In the excitonic SC, the thickness of the active layer is also restricted and this is related to the exciton lifetime. This requirement is similar to that in the case of a diode SC where the thickness of the PV layer should not exceed the diffusion length of the carriers. In most of the organic PV materials the exciton has the diffusion length 10-15 nm [76], in advanced organic PV materials it may attain 30 nm [19], and to let the exciton reach the heterojunction interface and break up into free carriers the PV layer should not be much more significant. However, the thickness of the excitonic material 30-50 nm typical for OPV cells is far from being sufficient for the efficient absorption of the visible (and moreover infrared) light in one and even in two passages. Therefore, in the absence of a suitable LTS, the overall efficiency of such a SC is very low.

Moreover, even partial transparency for the visible light is impossible if the bottom electrode is a metal layer as in conventional SCs. Therefore, for such OPV cells one develops distributed Bragg reflectors combined with the bottom electrode performed of transparent conductive oxide (TCO). The reflectance of a distributed Bragg reflector is frequency se-
lective and offers the second passage to the infrared light that increases the electric output nearly by 30% [74]. However, the Bragg reflector consists of nanolayers performed with a sub-nm precision, and its cost drastically exceeds that of the SC. The improvement of the efficiency by 30% hardly justifies the corresponding expenses.

In this section, we consider the possibility to significantly enhance the PV absorption in such SCs using LTSs of our metal NAs. The target OPV cell is based on molecular heterojunctions, and its structure is taken from work [74]. The main absorption occurs in the near-infrared (NIR) range. The mechanism of the light trapping is related to the excitation of domino modes. In the frequency range of domino modes the solar energy is transformed into a set of hot spots partially located in between the metal elements, partially in their substrate and the penetration of the enhanced electric field into the metal of NAs is negligible — the penetration depth is much smaller than the skin-depth. Since the incident light energy is practically not dissipated in the metal, the useful PV absorption dominates in the frequency range of domino-modes.

2.3.1 Suggested structure and its numerical simulations

In our research reported in Publication III, we considered the design of an OPV cell suggested in [74] which is highly transparent for the visible light. A molecular heterojunction is formed by organic molecular donors, namely chloroaluminum phthalocyanine (ClAlPc), and molecular acceptor fullerenes C_{60}. A modification of this design was suggested in [77]: where tin-phthalocyanine (SnPc) serves as a donor. We have chosen this design mainly because we have not found in the available literature optical constants for ClAlPc, whereas those of SnPc are known for both NIR and visible ranges. Also, SnPc has a maximum of absorption in the near-infrared at wavelengths $\lambda = 700$-950 nm and very low attenuation at wavelengths $\lambda = 420$-600 nm. It provides good transparency of the SC in the visible range. SCs based on SnPc enhanced by an ARC and a NIR Bragg reflector show the overall efficiency nearly equal to 2% and an averaged visible-light transmittance (AVT) that exceeds 70% [77].

The photovoltaic cell in our simulations is located on a glass substrate coated with a layer of indium tin oxide (ITO) which operates as a transparent anode. A layer of organic semiconductor bathocuproine (BCP) is placed between an acceptor C_{60} and transparent ITO cathode layers. BCP facilitates the transfer of electrons to the cathode [74, 76]. We suggested
incorporating NAs into the anode of the SC. Silver elements are assumed to be covered with a 2-3 nm thick deposited layer of SiO₂. A so thin dielectric is sufficient to prevent the ohmic contact of NAs with ITO but does not affect the electromagnetic fields and can be neglected in full-wave simulations.

A unit volume of the OPV device split in accord to the dimensions of the unit cell of our NA LTS is shown in Fig. 2.14. It is clear that SC is located on the internal side of the window. Numerical simulations for the SC with LTS were carried out using Frequency Domain Solver in commercial package CST Microwave Studio. Periodic boundaries with two symmetry planes were set in x and y directions, and open boundary conditions (PML) were put at top and bottom along the z-axis. In our calculations, the SC was illuminated by a normally incident wave with uniform power spectrum in the range \( \lambda = 400 – 1000 \) nm. We calculated the useful absorption coefficient – the power absorbed (per unit area) in the photovoltaic layer over the whole operation band of the SC (600-1000 nm) normalized to the power of the incident light. We also calculated the transmission coefficient in the range of the visible light (400-750 nm). To check the excitation of domino-modes and their contribution to the absorption we also calculated the spatial distributions of the electric field amplitude. The transfer matrix method was used to exactly calculate absorption and transmission spectra in the case of the pure SC – that is without LTS. Complex refractive indices of BCP and glass, as well as optical constants of ITO were
Metal light trapping structure
taken from [78]. Complex refractive index of SnPc was taken from [79],
that of C60 – from [80].

At first, numerical optimization of geometric parameters of NAs was
carried out to maximize the average photovoltaic absorption in the NIR
range while maintaining the acceptable transparency of the whole SC
for the visible light. On the first stage, we varied the maximal width
of tapered nanobars and the distance between them inspecting the dis-
tribution of the electric field in the layer of photoactive material and cal-
culating the NIR absorption in the photovoltaic layer. Absorption coeffi-
cients of NIR solar light as functions of the wavelength for different
horizontal parameters of NAs and relative arrangement in the unit cell
are shown in Fig. 2.15. Domino modes occupy the whole operation band
λ = 600 – 1000 nm whereas maxima and minima of the absorption coeffi-
cient correspond to constructive and destructive Fabry-Perot resonances,
respectively.

![Figure 2.15](image-url)

**Figure 2.15.** Absorption coefficients as a function of the wavelength for the initial design
parameters of NAs (solid black line), for narrowed NAs (red dash-dotted
line), and for the case when nanobars are shifted to the edges of the unit
cell (blue dotted line). These geometries are depicted in scale on the right
panel. The unit cell size and thickness of nanobars are constant for all three
cases and equal to 1000 nm and 50 nm, respectively.

The second stage of optimization was related with maximization of AVT,
for which the total area of metal elements per unit cell and their thick-
ness are critical. The light trapping is better for thicker NAs in which
the domino modes are excited more efficiently. However, the thickness
of metal elements has a negative impact on the AVT. The normalized
infrared absorbance and visible transmittance as functions of the wave-
Figure 2.16. Absorption (left) and transmission (right) coefficients as functions of the wavelength for various thicknesses of metal NAs: 30 nm, 50 nm (the same as in the case of the original design) and 70 nm.

Figure 2.17. Average absorption (left) and average visible transmission (right) coefficients as functions of the wavelength for various cathode thicknesses. The optimal thickness of the transparent ITO cathode is 150 nm for both cases.

Next, we optimized the thickness of the ITO cathode keeping the constant thickness of the ITO anode equal to 150 nm and starting from 10 nm for the cathode thickness. These initial design parameters were taken from [77]. A proper choice of the cathode thickness enables to decrease the averaged reflectance in the operational band placing constructive Fabry-Perot resonances of the overall structure inside it. These resonances also may decrease the transmittance maximizing the field in the active layer, i.e., increasing the photovoltaic absorption. We calculated the field distributions and the photovoltaic absorption in the SC for different thicknesses of the ITO cathode. It was done for both pure SC and that with
the cathode thickness from initial 10 nm reduces the AVT slightly, whereas the positive impact of this increase to the NIR photovoltaic absorption is significant. The optimal thickness of the transparent ITO cathode was found to be 150 nm for a pure SC as a trade-off between the useful absorption and AVT. In this optimal case, AVT is equal to 74%. In the presence of our LTS, the optimal thickness of the ITO cathode turned out to be equal to 150 nm, too. This result indicates that NAs practically do not contribute to wave interference processes. The AVT decreases from 74% to 50% due to the presence of NAs with optimized parameters.

Absorption and transmission spectra of the optimized structure are shown in Fig. 2.18. The total gain in the PV absorption granted by our LTS was calculated using the follow formula:

$$G_A = \frac{J_{sc}^{LTS}}{J_{sc}^{w/o LTS}} = \frac{\int I_s(\lambda)R_s(\lambda)A_{LTS}(\lambda) d\lambda}{\int I_s(\lambda)R_s(\lambda)A_{w/o LTS}(\lambda) d\lambda} = 3.6,$$

and the gain due to our LTS is more than triple. It is clear that this gain overcomes the rather modest reduction of the illumination. Notice, that in the present geometry the gain in the photovoltaic absorption is equal to the gain in the photocurrent [36] and grants rather high electric power output.

### 2.3.2 Fabrication and measurements

In the previous section, we have shown that proposed LTS increased the absorption of infrared solar light in the SnPc (donor) – C$_{60}$ (acceptor) layers of our OPV SC more than triple. Such OPV SC had two ITO
Figure 2.19. Normalized electric field intensity distributions in the horizontal planes $P_1$ and $P_2$ (top panel) and in the slightly tilted cross-sections (bottom panel) for an OPV SC containing ITO anode and cathode, $\lambda = 840$ nm (a) and for a similar OPV SC with ITO anode and Al cathode, $\lambda = 480$ nm (c). Active layer boundaries are shown as white dotted lines (bottom panel). Ag nanoantennas are located on top of ITO anode, embedded into the PV layer. In panel (b) we show the OPV SC schematics for these two cases. Horizontal planes $P_1$ and $P_2$ are shown as black dashed lines. Orange arrows show the wave incidence.

Figure 2.20. (a) Photo of the sample with our LTS. (b) Scheme of the metasurface geometry. The geometrical parameters are as follows: $D_x = D_y = 1000$ nm, $g_1 = 300$ nm, $g_2 = 150$ nm, $g_3 = 300$ nm, $g_4 = 250$ nm, $\Delta = 35$ or 50 nm (two different samples). (c) Transmission and reflection spectra were measured for 50-nm sample (LTS) and for bare ITO area (substrate).

electrodes (both anode and cathode), that made it transparent for visible light, though by a price of the low efficiency. For such thin-film SCs the triple enhancement of the absorption (assuming that the FF remains the same) promises a nearly double increase of the short-circuit current and a similar increase of PCE compared to that achieved in [74]. Meanwhile, the transmittance of visible light is kept sufficient for the effective transparency of a window into which the advanced OPV SC can be incorporated.

Unfortunately, in our experimental study reported in Publication IV,
we cannot confirm this doubling of efficiency. We could not fabricate a transparent ITO cathode, and the exact experimental implementation of the structure described in the previous section was not successful. The problem with the ITO anode was resolved by purchasing glass plates with already deposited ITO, but the deposition of ITO on our OPV SC destroyed it. We have replaced the ITO for the cathode by a foil of Al. Dropping the transparency requirement we concentrated on the experimental proof of the light trapping effect granted by our LTS. We also have studied the implications of our LTS for the characteristics of our thin-film SC.

Since in this case the transparency of the PV layer is not required, we have deviated from the initial design and added a nanolayer of CuPc combining the functions of an additional donor and the hole transport layer. It allowed us to create a double heterojunction and to increase the initial efficiency of the prototype. Our new design is also typical and corresponds to works [26] and [81]. To demonstrate the advantageous operation of our LTS, that compatible with the optimal structure of the selected SC we do not modify the design parameters of the prototype compared to these works. In this regard, our study fairly demonstrates the real enhancement granted by our LTS to a typical OPV SC.

The hole-transport layer of CuPc has maximal absorption in the visible region. Therefore, conversion of solar radiation occurs in the extended spectral range, which includes both the near-infrared (750-900 nm) part where the absorbing material is SnPc and the visible parts (550-750 nm), where CuPc absorbs. Another difference of the present design is the slight shift of the metasurface with respect to the ITO anode. Instead of embedding the NAs into ITO, we locate them on the ITO surface that allowed us to strongly simplify the fabrication.

Figure 2.21. Scanning electron microscope image of our LTS.

Although the design modifications listed above may seem insignificant,
they can drastically affect the performance of the LTS. It becomes necessary to study the influence of the Al cathode on the local electric field distribution inside the PV cell. We have performed full-wave (CST Studio) electromagnetic simulations of two PV devices: one with a transparent ITO cathode and another with an opaque Al cathode. Complex refractive indexes were taken from [78–80]. Electric field intensity distributions for these two cases are presented in Fig. 2.19. Indeed, the opaque metal film fully changes the hot spots arrangement in the bulk of the structure at all wavelengths. Obviously, in the presence of a transparent cathode, an effective Fabry-Perot cavity is formed in the structure that works together with domino-modes excited in our NAs and leads to the more advantageous location of hot spots in the near-infrared range (700-850 nm). Meanwhile, in this configuration, hot spots do not appear in the visible range, and the visible light is not trapped at all. The situation changes when Al replaces ITO as a cathode material. Now, hot spots also appear in the visible range and appear at favorable locations. Notice, that in this case hot spots corresponding to the NIR band shift away from the PV layer. In any case in the range of the domino modes, noticeable parasitic losses do not arise because the hot spots do not intersect with the metal.

In general, simulations confirmed our expectations. The enhancement of the useful absorption remains after the replacement of ITO by aluminum and this enhancement now is present in the visible light range.

We have prepared two series of samples with either 50 nm or 35 nm thick Ag nanoantennas on top of the ITO-glass substrate. These samples contain 1.5 \cdot 10^6 and 3 \cdot 10^6 unit cells of our LTS, respectively. Fabrication was done using electron-beam lithography (EBL) and electron-beam evaporation. The SEM characterization has shown a very high quality of our NA arrays, as can be seen from Figs. 2.20 and 2.21. We have measured both power transmittance $T$ and reflectance $R$ in the solar spectrum (incidence from the glass side) for a 50-nm thick LTS. The result is shown in Fig. 2.20c in comparison with those coefficients obtained for the bare substrate (glass and ITO). This comparison shows the impact of NAs. The frequency-averaged reflectance growth due to NAs is about 10%, whereas the non-transparent NAs cover 40% of the whole area. The reflectance increases much less than could be estimated using geometrical optics. This is, definitely, the effect of resonances in the NAs. In accordance with our simulations, these resonances are mainly domino-modes which occupy almost one half of the visible band.
We may estimate the impact of our LTS to the parasitic absorption $A$ in the ITO. From the energy balance, we have $A = 1 - R - T$. In the absence of our LTS, we have $\langle A \rangle \approx 0.05$, where $\langle A \rangle$ implies the averaging of $A$ in the range $\lambda = 400 - 900$ nm. In the presence of the LTS $\langle A \rangle \approx 0.08$. This increase of the absorption is due to the concentration of the trapped light in ITO. Both negative effects – 10% increase of the reflection loss and 45% increase of the parasitic absorption loss in ITO are present in our OPV SC, however, these effects are overcompensated by the concentration of light in the PV layer.

Further, we decided to additionally fabricate a variant of the OPV SC with C70 fullerene derivative instead of C60. If the impact of our LTS will be more significant for the structure with C70, it will confirm the shift of light-trapping regime (predicted by our simulations) from the IR range to the visible range for Al cathode. This should be the case because C70 has higher absorption than C60 below $\lambda = 700$ nm, whereas C60 has higher absorption at longer waves.

Our first sample with 50 nm-thick NAs has the following structure above the glass substrate: ITO anode (150 nm) / CuPc (15 nm) / SnPc:C70 (30 nm) / C70 (55 nm) / BCP (10 nm) / Al (70 nm). The corresponding schematic is shown in Fig. 2.22a. This configuration with co-evaporated phthalocyanine and fullerene leads to the formation of two donor-acceptor heterojunctions: CuPc/C70 and SnPc/C70. We illuminated our sample with an AM 1.5G solar simulator from the side of glass through a 1 mm aperture. We measured the IV dependencies of our sample illuminating either the 1 mm areas comprising our NAs or 1 mm areas free of them. In this way, we have collected sufficient statistics for a reliable measurement of two IV-curves – one for an OPV SC enhanced by our LTS and another for a bare OPV SC (with only antireflective coating). These curves are shown in Fig. 2.22 and demonstrate a noticeable increase of $J_{sc}$ caused by our
LTS. Photocurrent generated in the NA area reaches the value 5 mA/cm$^2$, whereas the structure without NAs gives 4.6 mA/cm$^2$. This means an 8% increase of the photocurrent due to our LTS.

Since domino-modes regime do not occupy the whole operating range of the OPV SC, we can estimate the shadow effect. Due to 40% of the area covered by metal NAs, the photoactive area (that photogenerates carriers and provides $I_{sc}$) is only 60% of the similar area in a reference OPV SC. Therefore the actual enhancement of $J_{sc}$, provided by the LTS is not 5 mA/cm$^2$, but $5/0.6 = 8.3$ mA/cm$^2$. Though the array of silver NAs occupies the area that does not create carriers, it creates the enhancement of the light electrical field around the NAs. In this area, we have the gain in the photocurrent density that equals to $8.3 \text{ mA} / 4.6 \text{ mA} = 1.8$, i.e., 80%. The 80% increase of the photocurrent corresponds to a higher (nearly 100%) increase of the PV absorbance due to a nonlinear current response of such OPV SC [82]. So, our LTS results in the almost double enhancement of the optical absorption of light in the photoactive area. This increase is achieved in spite of already mentioned 10% increase of the reflectance loss and 45% increase of the parasitic absorption loss brought by our LTS. If we could avoid these factors (which were minimized in our initial design), the enhancement of the useful absorption granted by our LTS would be higher than twofold. However, we have to keep the design parameters of the OPV SC corresponding to the optimal PV characteristics and cannot change them in favor of our LTS.

Moreover, we have to accept the negative features of the NAs decreasing the current-collection efficiency and transforming the 80% gain in the photocurrent density into a modest 8% enhancement of $J_{sc}$ compared to that in the reference cell. Besides the 40% reduction of the photoactive area, these negative features are leakage of carriers from Ag, quenching of excitons, and surface recombination on Ag. We cannot estimate these effects, but it is clear that due to all these negative factors, the doubling of the PV absorption apparently is not accompanied by the enhancement of the efficiency.

Though our LTS improves the FF calculated from the IV characteristic of the SC by 2.6% (see inset of Fig. 2.22c), the open-circuit voltage becomes worse. Our NAs decrease $V_{oc}$ by 0.09 V, i.e., by 25% compared to the reference OPV SC. The most probable reason for the drop of $V_{oc}$ is a quite substantial surface area of our nanobar compared with the thickness of the active layers. $V_{oc}$ in OPV SCs is directly proportional to the difference
between the Fermi levels, and the ITO electrode having the band-gap in the ultraviolet has an impact on \( V_{oc} \). Silver elements having the ohmic contact with ITO decrease the effective work function of the material of the electrode. As a result, the difference of the Fermi levels squeezes and \( V_{oc} \) decreases.

The 25% drop in the voltage overshadows the 8% gain in the current and, as a result, our LTS negatively affects the PCE. Parameters of the OPV SC with NAs and without NAs are shown in the inset of Fig. 2.22c. These data are averaged over several sample areas, as explained above.

After identifying the reason of this failure, we have decreased the thickness of our Ag elements from 50 nm (optimal for light-trapping) to 35 nm. This new thickness is a compromise between the gain in the PV absorption and the negative impact of our NAs to the open-circuit voltage. Our next design of the OPV SC is identical to the previous one but with a replacement of \( C_{70} \) by \( C_{60} \) (and thinner NAs). The new structure is shown in Fig. 2.23a. It consists of the following layers on the glass plate: ITO (150 nm) / CuPc (15 nm) / SnPc:C\(_{60}\) (30 nm) / \( C_{60}\) (25 nm) / BCP (10 nm) / Al (70 nm). Since \( C_{60} \) is less absorptive material in the visible range, the impact of our LTS on the photocurrent is also decreased compared to the previous case. Now it is only 4.6% instead of the previous 8%, as can be seen from Fig. 2.23b. However, the impact of the silver particles on the band-gap of the ITO electrode in this case is much lower. As a result, the Fermi levels and \( V_{oc} \) stay almost unchanged by the LTS. Moreover, 35 nm thick metal elements improve the FF by 19% (versus previous 2.6%). The PCE enhancement turns out to be positive, and its value averaged over all such samples equals to 18%. This value is higher than the experimentally verified gains offered by recently suggested plasmonic counterparts of our LTS designed for such OPV SCs (see, e.g., [59]).
2.3.3 Conclusions

In this chapter, we have suggested an original LTS suitable for many thin-film SCs that is based on the so-called leaky domino-modes. We have found these unusual eigenmodes in arrays of metal nanobars with domino-like proportions and have shown that in the optical range of frequencies they may occupy a broad frequency band comparable with the operation band of a realistic SC. We have experimentally confirmed the existence of these modes and theoretically proved their light-trapping functionality. We have designed the optimal array of metal NAs implementing this regime and theoretically demonstrated the triple enhancement of the useful absorption for a realistic OPV SC granted by our LTS. Next, we have fabricated some OPV SCs and have experimentally shown the increase of the photocurrent density corresponding to the double increase of the PV absorption granted by our LTS. Moreover, we have experimentally obtained the 18% gain of the overall power conversion efficiency granted by our LTS compared to the reference SC with a conventional design. This comparison is fair in the meaning that we have not intentionally worsened the structure of the OPV SC to stress the light-trapping capacities of our LTS.
3. All-dielectric light trapping structures

Inevitable dissipation losses in plasmonic light trapping, as well as high fabrication cost of regular metal NAs, have led researchers to active studies of all-dielectric LTSs. According to the belief of many authors, dielectric nanoparticles have a chance to exceed the efficiency gain granted by LTSs based on plasmonic metamaterials due to lower optical losses in a dielectric compared to any metal [83]. In addition, many dielectric nanostructures can be manufactured by relatively simple and inexpensive methods, compatible with the technology of producing thin-film SCs such as roll-to-roll technology. In the present thesis, we report our theoretical contribution in the field of all-dielectric LTSs.

Our contribution is novel since we do not exploit the conventional dominant approach to use some resonant mechanisms of trapping light in the arrays of dielectric nanoparticles [19]. Usually, these mechanisms are whispering-gallery modes [46,84,85]. The maximal gain in the optical efficiency achieved by using such LTS for a-Si thin-film SC was equal to 11% under normal incidence of light. After averaging over the daytime (when the incidence angle varies from zero to nearly 70°) this gain decreases nearly twice. The modesty of this gain has the same reason as for the most of plasmonic NAs – a narrow total band of the resonant modes. In other papers, magnetic or quadrupole Mie resonances of dielectric cavities shaped as spheroids or disks are used [86–88]. These resonances result in the light trapping since the backward scattering can be suppressed by an ARC and the light transmission can be partially substituted by the lateral scattering lobes. However, such structures are challenging for fabrication because the fabrication tolerances to the shape of nanocavities are strict and the granted gain in the optical efficiency is not higher than that of LTSs using the whispering gallery modes.

In work [89], one proposed an affordable (and easily manufactured)
All-dielectric light trapping structures

non-resonant LTS performing also the functionality of ARC due to different dimensions. It is a densely packed array of slightly submicron polystyrene spheres that attach to the surface of a PV layer due to the self-organization from colloids. In what concerns the light-trapping, the array of such spheres utilizes the mechanism of so-called photonic nano-jet. It is collimation of the incident plane wave to a wave beam with nearly $\lambda/2$ effective cross-section. This regime is implemented in a rather broad range of wavelengths comparable with the size of a dielectric sphere. For a polystyrene sphere of radius 450 nm, the regime of nanojet covers 50-70% of the visible range. The lower number refers to the location of the sphere in free space, the larger number – to its location on top of a transparent substrate with relatively high refractive index (in work [89] it was polycrystalline Si). We have already mentioned that the visible range is equivalent to the operation band of a-Si thin-film SCs. Therefore, the light concentration due to the exploited effect is sufficiently broadband and significantly increases the useful absorption in the PV substrate. In what concerns the reflection, the layer of nanospheres operates as an effectively flat layer with the favorable (rather low) refractive index. In fact, the operation of such arrays as ARCs has been known previously, in our group we only suggested to combine it with the LTS functionality and with this purpose increased the diameter of the spheres by 80-100% (compared to the optimal diameter for purely antireflective purposes that equals to 500 nm).

Next, we have analyzed the possibility of the light-trapping in another all-dielectric composite – an array of nanovoids – whose antireflective properties were studied in works [33–35]. We have found the effect of the subwavelength field concentration in these structures. As a result, arrayed nanovoids (whose size is nearly 50% increased compared to the optimum required for purely antireflective purposes [35]) perform the light trapping. This effect turned out to be resonant, but it is multi-frequency in the visible range, and the total resonance band is rather broad (see below). Both these LTSs – arrayed spheres and arrayed voids – also perform the antireflective function, whereas the structure with voids possesses lower backscattering losses than the array of spheres. It is not clear a priori which LTS is more efficient for a-Si SCs.

The goal of the study reported in Publication V was to compare two novel all-dielectric LTSs, both suggested in our group – the one based on polystyrene spheres and the one based on nanovoids, both applied to a
standard a-Si SC. The optical efficiency of the SC is numerically simulated for different angles of incidence. The gain in the optical efficiency granted by both LTSs was compared with that granted by a standard single-layer ARC optimized for the same a-Si thin-film SC.

### 3.1 Numerical study of two light-trapping structures for a-Si thin-film solar cells

We have considered the system, depicted in Fig. 3.1 and representing the three types of all-dielectric coatings under study. The first type is a layer of mutually touching polystyrene spheres (in Fig. 3.1a we show a unit cell). In accordance to [89], this structure acquires the light-trapping properties in the visible range when the diameter of a sphere exceeds 500 nm. Meanwhile, when it exceeds 1 micron, the strong backscattering makes this LTS not efficient without a special laminate. In our simulations, it was a composite layer of densely packed micron or submicron spheres whose diameter varied from 0.3 to 1 μm. This array is placed on top of the aluminum-doped zinc oxide (AZO) electrode that is nearly transparent for the visible light. The AZO layer in our simulations is 200 nm thick. This thickness is selected as a trade-off between a sheet resistance, whose reduction requires to enlarge the thickness of AZO, and a parasitic optical loss in it, that demands to shrink this thickness. The
optimal thickness of 200 nm corresponds to nearly 5% of the optical loss, integral over the visible range for a normally incident plane wave. In the presence of the LTS on top this parasitic loss may increase, and that will decrease the useful absorption. Beneath the AZO layer, a 300-nm thick layer of a-Si is placed. It is composed of a 10-nm thick p-layer, 280 nm thick i-layer, and 10 nm thick n-layer. The PV layer is sandwiched between the top AZO electrode and the bottom electrode also made of AZO and assumed to be semi-infinite. In practical cases, the bottom AZO electrode is a submicron layer supported by a non-polished metal foil on which it is deposited using an atomic layer deposition technique. However, for our purposes, the thickness of the bottom layer of AZO is not essential. In a flexible SC, mainly all the light transmitting into the back electrode is absorbed. Therefore, it is not important which absorbing material is below the submicron bottom layer of AZO – a stochastically nano-corrugated metal foil or still AZO. Other geometrical parameters of our thin-film SC are standard [90].

The density of minority carriers in both doped layers of a-Si is equal to $3 \cdot 10^{18} \text{cm}^{-3}$, Ref. [22]. Such thin-film SC may have the internal quantum efficiency up to 70%. The optical constants of materials were taken from Refs. [91–93].

The second structure is shown in Fig. 3.1b. The voids (notches) are shaped either as cylinders (disks) or truncated cones in the dielectric cover – both these geometries of a composite were suggested in works [33–35] for the broad-angle and ultra-broadband antireflective operation. A conventional homogeneous film, depicted in (Fig. 3.1c) operates in a narrower band and can suppress the reflection only in a narrow range of angles. When the parameters of the voids are optimized for antireflection, the results are evidently in favor of this array of notches. However, we want to combine the antireflection with the light trapping and increase the sizes of the voids. Therefore, the comparison with the conventional ARC remains relevant.

For both 1st and 2nd structures, the suppression of reflection occurs mostly due to the dipole polarization of inclusions [33–35,89]. Meanwhile, the concentration of light in the substrate of the notched layer may arise due to the high-order multipole moments excited in a unit cell of an array [94]. Moreover, the similar explanation corresponds to the effect of the nanojet in the dielectric spheres [89]. The difference is that in the multipoles of the spheres are almost independent on the adjacent spheres.
They weakly interact though are densely packed. In the case of voids, it is a collective effect. This makes the effect sensitive to the unit cell geometrical parameters that can require high fabrication tolerances. From another hand, the notched layer seems to be more advantageous than the LTS of spheres. The last one would, most probably, require adding a layer of the polymer glue to ensure the mechanical robustness of the spheres. The solid dielectric layer with notches on top is robust as is.

3.1.1 Normal incidence of light

Since both upper and lower contacts are flat conductive films, our SC except the LTS is a conventional a-Si thin-film SC with a homogeneous distribution of the photocurrent. In work [95] it was shown that for such a-Si thin-film SCs the photocurrent depends on the PV absorption almost linearly. In this chapter, assuming that the gain in the optical absorption is the gain in the photocurrent, we fully concentrate on the PV absorption (absorption in the layer of intrinsic a-Si).

Simulating the absorption in the PV layer for the case of the normal incidence of light on our three structures, we found the optimal parameters of the arrays of nanospheres and those of nano-voids. Here, we optimized these structures by the brute force method using both Comsol Multiphysics and CST Microwave Studio. The practical coincidence of the results convinces us in their reliability. As to the conventional flat ARC, the
reliability was confirmed even triply since a multilayer without inclusions is precisely described analytically using the transfer matrix method [20]. Our Matlab code gives the same result for the optimal parameters of the ARC as the numerical simulations: the thickness is $\Delta = 94$ nm, and the refractive index is $n = 1.36$. Notice, that polymers used as laminates of SCs with nanostructured/nanotextured surfaces to prevent their atmospheric abrasion [96] have typical refractive indices $n = 1.34 – 1.38$, and $n = 1.36$ (stable in the whole visible range) corresponds to a realistic material called ethylene-vinyl acetate [96]. In this case, the integral PV absorption enhancement granted by the ARC in comparison with non-coated thin-film SC is about 6%. More exactly, we have

$$A_{\text{ARC}}^{\text{bare}} = \frac{\int A_{\text{ARC}} \, d\nu}{\int A_{\text{bare}} \, d\nu} \approx 1.062,$$

where $A_{\text{bare}}$, $A_{\text{ARC}}$ – absorption in the i-layer of a-Si for a bare thin-film SC and for thin-film SC with a flat ARC respectively. It is not surprising that the ARC grants such a modest enhancement. The most common ARC for a-Si solar PV panels with the AZO top electrode (a film of fused silica glass of thickness $\Delta = 85$ nm [90]) grants only additional 4.6% to the PV absorption compared to the bare cell. This is so because the multilayer structure of our SC is favorable for absorption: the absorption is maximal exactly in a-Si, and the AZO layer of thickness 200 nm operates as a kind of ARC. Therefore, the potential of the enhancement is modest and refers to the light-trapping effect.

Let us now consider the dependence of the integral absorption on the parameters of the suggested LTSs. The ratio $A_{\text{spheres}}^{\text{ARC}}$ of the integral PV absorption calculated in the presence of spheres ($A_{\text{spheres}}$) to the same value $A_{\text{ARC}}$ corresponding to our ARC is shown in Fig. 3.2a. It is clear that the PV absorption is higher compared to the case of the flat ARC for sphere diameters in the interval 380-580 nm. The optimal sphere radius is equal to 250 nm when the integral absorption enhancement is 3.7% compared to the flat ARC (and 8.5% with respect to the case of the bare SC). An array of polystyrene spheres with the diameter 500 nm operates in the low-frequency part of the operational band as a composite ARC where no light-trapping effect is possible. Only at wavelengths shorter than 500-550 nm this array combines the features of an ARC and a LTS. This disagreement with our initial paper [89] where the optimal sphere radius was found equal to 450 nm and the array operated as an LTS in the whole operational band of the SC (up to $\lambda = 800$ nm) can be explained by the drastic difference of the SCs under study. In our work [89] the PV layer
Figure 3.3. Absorption spectra of the system for the following cases: pure thin-film SC (black solid line), flat ARC of fused silica glass (blue dashed line), layer of nanospheres (purple line), disk voids (green line) and tapered voids (of optimal radius and depth; red line). was that of a polycrystalline Si, and the top electrode of AZO was absent (in such SCs the top electrode is a grid of metal fingers). In the present case, we apply the array to a thin-film SC based on a-Si and the spheres are located on AZO. For this case, the optimal diameter of the spheres for the normal incidence is indeed 500 nm.

In the case of notches, the number of parameters to be optimized is greater, that makes the task difficult. We have optimized the depth of the voids, their radius, the taper angle of the truncated nanocones and the distance between the adjacent notches. Fig. 3.2b shows the plot analogous to that shown in Fig. 3.2 (a), but for several values of the depth. We show only the dependencies corresponding to the optimal value of the distance between adjacent voids (30 nm) and to the optimal angle (10°) to avoid cluttering. The presence of a small taper angle is an advantage. Notice that the material of the LTS is polymethyl-methacrylate (PMMA), it is a soft dielectric, and such slightly tapered voids can be obtained with high precision using a nanoimprint lithography technique.

As it can be seen from Fig. 3.2b, the highest PV absorption holds for the depth of voids $d =$300 nm and the radius of voids $r =$180 nm. The enhancement of the absorption is $(A_{\text{void}}^{\text{ARC}} - 1) \cdot 100 = 5.6\%$ compared to the flat ARC and $(A_{\text{void}}^{\text{pure}} - 1) \cdot 100 = 10.5\%$ compared to the bare SC. Thus, the array of nanovoids in the layer of PMMA, located on top of thin-film SC, is more efficient than the layer of polystyrene nanospheres. The PV absorption spectra for the thin-film SC enhanced by three different coatings are shown in Fig. 3.3. As can be seen from Fig. 3.3, the PV absorption
is quite small at long wavelengths, and the presence of any coating does not substantially affect its value due to a rather low optical absorption of a-Si in the range of \( \lambda \) above 650 nm. On the other hand, in accordance with Fig. 3.3 the integral coefficient of the PV absorption (the same as the optical efficiency) for the bare thin-film SC is equal 42%. It is a rather high value for a thin-film SC, but still there is a room for enhancement. In which range the PV absorbance can be noticeably enhanced?

At 500-600 nm the spectral PV absorption of a bare SC is close to the total one and cannot be noticeably enhanced. Above 650 nm it is very low, and though the room for enhancement in this range is huge, it would be very difficult to enhance such a low absorbance toward the complete one. The most realistic improvement refers to the range 400-500 nm. This band has the relative width 23% that is compatible with the idea of the resonant mechanism of light trapping. The resonances in the arrays of notches may cover this range. Taking into account the antireflective functionality of this array, this multi-resonant LTS seems to be advantageous with respect to the layer of spheres.

In Fig. 3.3 we note a significant growth of the spectral PV absorbance in this range of wavelengths granted by all our coatings. For the flat ARC, the increase of the spectral absorbance at 400-475 nm is accompanied by a decrease of it in the range 475-575 nm where the transmission losses dominate. Both LTSs offer a higher gain, and the best result for the normal incidence corresponds to the LTS of tapered voids: the optical efficiency attains 48%, i.e., increases by 14% compared to the bare SC.

As we have already noticed, our LTSs based on voids and spheres operate differently. To analyze this difference more quantitatively, we have studied separately how they affect the reflectance and transmittance spectra.

Fig. 3.4a shows dependencies of the reflectance from the thin-film SC on wavelength for all considered cases. It is obvious that the reflection is significantly lower when using ARC, spheres and tapered voids than in the case of cylindrical notches. The relative integral reflection, normalized to the reflection from the bare surface is:

\[
R_{\text{struct.}} = \frac{\int R_{\text{struct.}} \, d\nu}{\int R_{\text{bare}} \, d\nu},
\]  

(3.2)

where \( R_{\text{bare}}, R_{\text{struct.}} \) are, respectively, the power reflection coefficient from the bare surface of the SC and from the structure with coating respectively. The reflection reaches the following values:
Figure 3.4. Dependencies of the reflectance from our SC (a) and the transmittance through its PV layer (b) on wavelength for all three cases of coating.

1. $R_{\text{bared tapered voids}} = 0.607$,

2. $R_{\text{bared cylindrical voids}} = 0.748$,

3. $R_{\text{bared spheres}} = 0.643$.

4. $R_{\text{bared ARC}} = 0.539$.

The cylindrical notches are noticeably worse than the array of nanospheres, and the flat ARC offers the best suppression of the reflection. Spheres emulate a textured layer. In the previous studies [32–35,89] the array of 500 nm large spheres suppressed the reflection better than a flat ARC. However, these results were obtained for different SCs. For a standard a-Si thin-film SC, the array of spheres is a worse ARC than the flat layer, and its advantage is entirely related to the transmission suppression at short wavelengths of the visible range. Tapered voids only approach to the flat ARC in what concerns the reflection loss and are also advantageous (for the normal incidence) only due to the light trapping.

Let us now consider the parasitic transmission of power through the PV layer. As we have already mentioned, the transmission loss is what we can noticeably decrease in our SC. The dependencies of the corresponding coefficient are presented in Fig. 3.4b.

It is not so simple to adequately describe the reduction of the parasitic transmission through the PV layer accompanied by the modified reflection. In our case, the lowest integral transmittance $T$ of the incident light to the AZO substrate corresponds to the bare thin-film SC. It is not sur-
prising, because the power significantly reflects on top of the structure. Therefore, in spite of the rather low PV absorption, only a small portion of the incident power transmits to the bottom half-space of AZO. The reduction of the reflectance granted by our ARC and LTSs automatically result in the certain increase of $T$. In our situation, it is reasonable to quantify the comparison with the bare thin-film SC by a coefficient describing the parasitic transmittance. We introduce the coefficient which describes the light-trapping efficiency (LTE) for different coating structures in this comparison. This coefficient is defined as:

$$LTE_{\text{struct}}^{\text{bare}} = \frac{R_{\text{bare}} - R_{\text{struct}}}{T_{\text{struct}} - T_{\text{bare}}},$$

(3.3)

and shows how the presence of the structure modifies the parasitic transmittance. Here $R(T)_{\text{bare}}$ and $R(T)_{\text{struct}}$ are integral reflection (transmission) coefficients of the bare SC and the SC with a coating structure, respectively. The minimal increase of the transmission together with a maximal decrease of reflection indicates the best light-trapping property. This coefficient is significantly different for four coatings under study:

1. $LTE_{\text{bare}}^{\text{tapered voids}} = 2.57,$
2. $LTE_{\text{bare}}^{\text{cylindrical voids}} = 5.04,$
3. $LTE_{\text{bare}}^{\text{spheres}} = 2.54,$
4. $LTE_{\text{bare}}^{\text{ARC}} = 1.31.$

The highest values of $LTE_{\text{bare}}^{\text{struct}}$ coefficient are in the case of tapered notches. We can see that the cylindrical notches possess better light-trapping properties than the tapered ones, but the latter give the maximal gain in the PV absorption due to better antireflective operation. Notice, that the value of $LTE_{\text{bare}}^{\text{ARC}}$ is not unity, and it is not surprising. Apparently, an ARC suppresses the parasitic transmittance because it reciprocally changes the balance between the energy transmitted to the substrate and the energy reflected from the bottom interface in favor of the last one.

To understand the advantage of the tapered nano-voids compared to nano-spheres let us consider the time-averaged distributions of the electric energy density in the structure. The corresponding color map is shown in Fig. 3.5 for wavelengths $\lambda = 435, 450$ and $475$ nm, where the local field
concentration is most pronounced. It can be seen that the 500 nm large sphere transforms an incident plane wave with $\lambda = 475$ nm (the same effect keeps at shorter wavelengths) into a collimated beam, as it was in [89]. The parasitic absorption occurs in the top layer of AZO, and only a rather attenuated beam transmits to the PV layer, resulting in the formation of a hot spot in the i-layer of a-Si. This implies an increase of the parasitic absorption in AZO and determines the modest gain granted by such the LTS to the optical efficiency of our SC. In the structure with nano-voids multiple hot spots are formed over a unit cell. Besides of a parasitic absorption in AZO, still several hot spots are also formed in the i-layer of a-Si. Such multi-spot field distribution looks similar to that obtained for our metal NAs with domino-modes. First, in both these structures hot spots are located mainly in between light-trapping inclusions (in the present case – voids). Second, in both these structures, the light-trapping regime is related to the lattice, i.e., governed by the electromagnetic interaction of inclusions. The obtained effect is theoretically observed only for a specific distance between the notches. It is seen comparing Fig. 3.5a with Fig. 3.5b,c that the hot spots in the case of nano-voids are much smaller than in the case of the spheres. The smaller is a hot spot, the stronger is the absorption in it, and the light-trapping features of the notches are more pronounced than those of the spheres.

Figure 3.5. The time-averaged distributions of the electric energy density in the light-trapping structures under consideration at wavelengths where the local field concentration is most pronounced.
3.1.2 Oblique incidence of light

The dependence of the efficiency of a thin-film SC on the angle of incidence is one of the main characteristics since thin-film SC (unlike a wafer solar panel of a power station) does not rotate following the Sun. Thus, the study of the proposed LTS would not be complete without consideration of the stability of the PV absorption versus the incidence angle.

We studied the integral absorption enhancement for the optimal structures, whose parameters were found in the previous sections for the oblique incidence of light (0-30°). The results are shown in Table 3.1.

The PV absorption enhancement provided by the ARC is quite stable at these angles and only slightly decreases with increasing the angle up to 30° due to the redshift of the antireflection peak. In the case of nanospheres, the absorption rapidly decreases, and the efficiency becomes higher than in the case of ARC only at small (<20°) angles for this SC design. Nevertheless, spheres show 3.7% efficiency enhancement in comparison with a non-coated SC at the angle of 30°. Cylindrical voids show a less dramatic decrease of the absorption comparing with spheres and exceed the efficiency granted by the ARC at angles of incidence up to 28°.

In the case of the tapered voids, integral absorption is substantially more stable to the angle of incidence and the absorption averaged over the angle is maximal for this case.

The total efficiency of all these structures can be described through the angular averaging of the integral absorption that corresponds to different positions of Sun. These values normalized to the case of the pure thin-film SC are as follows:

1. \( \langle A_{\text{tapered voids}}^{\text{bare}} \rangle = 1.087 \),

2. \( \langle A_{\text{cylindrical voids}}^{\text{bare}} \rangle = 1.068 \),

Table 3.1. Values of the integral absorption (over the operating range of thin-film SC) at the presence of our LTS to the corresponding value \( A_{\text{bare}} \) for different angles of incidence of light.

<table>
<thead>
<tr>
<th>Angle, °</th>
<th>( A_{\text{tapered voids}}^{\text{bare}} )</th>
<th>( A_{\text{cylindrical voids}}^{\text{bare}} )</th>
<th>( A_{\text{spheres}}^{\text{bare}} )</th>
<th>( A_{\text{ARC}}^{\text{bare}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.105</td>
<td>1.088</td>
<td>1.085</td>
<td>1.046</td>
</tr>
<tr>
<td>10</td>
<td>1.096</td>
<td>1.082</td>
<td>1.062</td>
<td>1.046</td>
</tr>
<tr>
<td>20</td>
<td>1.075</td>
<td>1.06</td>
<td>1.046</td>
<td>1.045</td>
</tr>
<tr>
<td>30</td>
<td>1.07</td>
<td>1.042</td>
<td>1.037</td>
<td>1.044</td>
</tr>
</tbody>
</table>
3. \( \langle A_{\text{sphere}}^{\text{bare}} \rangle = 1.058 \),

4. \( \langle A_{\text{ARC}}^{\text{bare}} \rangle = 1.045 \).

Thus, the average gain over the angle has a maximum value for the LTS of tapered voids and is nearly equal 8.7\% that corresponds to 48\% optical efficiency averaged over the incidence angles.

### 3.1.3 Conclusions

In this section, we have considered all-dielectric structures offering an enhancement of the efficiency of the PV conversion in thin-film SCs based on a-Si. The suppression of both reflection and transmission were studied for the following systems: a flat antireflection coating, an array of densely packed polystyrene nanospheres, and arrays of nanovoids (cylindrical and tapered shape, both in the PMMA layer). The optimal parameters of the structures that provide the highest absorption in the PV layer were found, and it was shown that three our LTS offer the gain in the PV absorption which is more than the gain granted by the flat ARC to the bare SC. The antireflecting and light-trapping effects in our LTS are sufficiently broadband. We have found that the array of cylindrical nano-voids has the highest light trapping efficiency, whereas tapered nano-voids offer the highest integral absorption due to better antireflective operation. Polystyrene spheres are worse than both types of notches. The optimal structure grants almost 9\% of the gain in the optical efficiency averaged over the range of incidence angles 0–30°. This is a noticeable improvement and it is rather easy to implement it in practice because it is simply a notched PMMA nanolayer whose notches shapes and sizes are compatible with the standards of the nanoimprint lithography. These thin-film SCs can be fabricated using the roll-to-roll technology.

### 3.2 Universal light-trapping structure for organic and perovskite solar cells

As it is stated in [19], the absolute majority of LTSs for TFSCs is not compatible with the initial idea of cheap solar electricity. The suggested LTSs are, as a rule, expensive nanostructures whose cost is higher than that of the thin-film SC itself, and are challenging for the industrial adaptation.
An exotic application of organic SCs such as electricity from the window can, probably, justify these additional expenses. For a-Si thin-film SCs we have suggested above an affordable solution – arrays of notches in an easily deposited nanolayer of a polymer, that can be very quickly and rather easily prepared. However, it is a specific design for a-Si solar PV. What about an affordable LTS for organic and, perhaps, metal-organic SCs? Have they been suggested earlier? Are they efficient enough? Can we propose something better?

Yes, a cheap and rather universal solution for organic thin-film SCs has been known. In work [97] one suggested a LTS that should be cheap in mass production and seems to be quite universal for organic thin-film SCs. The idea of this work is to trap the light in between two golden films. One of them is perforated by tiny (few microns) holes, and the light is focused exactly in the centers of these holes so that it diverges in the spacer between the golden films. These films play the role of current collecting electrodes, and the gap between them comprises the organic SC. The focusing is performed by an array of lenses with characteristic sizes of few dozens of \( \mu \text{m} \) located on the perforated golden film and centered exactly over its holes. Since the light beam diverges beneath every hole and the hole area is relatively small compared to the unit cell area the incident light is almost fully absorbed in the SC. The idea is elegant and seems to be brilliant, especially because the structure does not require to involve nanotechnologies. Substantial sizes of the unit cell allow for the array fabrication using optical lithography and standard processes of microfabrication [97]. However, in what concerns the efficiency the result is not modest. Both numerical simulations and experiment have shown that the gain in the PV absorption and photocurrent due to the application of this LTS to a particular organic thin-film SC is nearly equal 25% [97]. The optical efficiency of the thin-film SC keeps low (below 20%) though the reflection loss is reduced by LTS. This means that the most of energy is dissipated in the LTS – basically in the golden film.

In our research reported in Publication VI, we suggest an alternative universal LTS, also as simple and cheap as in [97], but theoretically more efficient because we have determined a drawback inherent to the array of microlenses. This drawback was not found in [97] nor in further works where this LTS was applied for other thin-film SCs (with the gain 22% and lower [98]), whereas its knowledge allows one to get rid of it. We have eliminated the drawback rejecting the idea of focusing the light in the
hole. It turns out that our LTS is also suitable for improvement of metal-organic (perovskite) thin-film SCs. It is commonly believed that this type of solar PV does not need light-trapping at all because the optimal thickness of the PV layer is sufficient for the complete optical absorption. However, in all known perovskite SCs there are noticeable optical losses in the transparent conductive electrode. Our universal LTS allows us to get rid of these losses in the inverted geometry of a perovskite SC.

In this section, we theoretically study the operation of our universal LTS for both organic and perovskite thin-film SCs and demonstrate the simplicity of its fabrication reporting on an experimental sample we have manufactured.

### 3.2.1 Design solution

![Figure 3.6](https://via.placeholder.com/150)

**Figure 3.6.** (a) – A general view of our LTS, applied to a thin-film SC. A densely packed array of truncated glass cones operates as a set of practically lossless optical waveguides. The guided modes are the rays with total internal reflection. These rays beneath the holes become a set of divergent light beams creating the waveguide modes confined in the layered structure. Here and below red arrows show the direction of the solar light incidence. (b) – Two explicit examples of thin-film SCs for which this LTS can be applied: an organic heterojunction thin-film SC and a perovskite thin-film SC with inverted geometry with respect to the illumination. Charge-transport layers on both sides of the PV layer are not shown for simplicity.

The main drawback of the structures with microlenses [97] is the excitation of surface plasmons in the metal film. The analysis of the field in the focal spot located at the center of a hole in the golden film shows that the focused field strongly feels the presence of the plasmonic layer around it. It is not surprising because the focal spot and its environment (caustics) are not described by the geometrical optics. Focused field weakly attenuates beyond the focal spot. In the presence of the metal layer, the
focal spot located in the hole spreads in the hole aperture and strongly excites the surface plasmon on the hole perimeter. The frequency band of this plasmon is in the visible range and this effect results in the parasitic losses of sunlight in the perforated golden layer. The replacement of gold by a non-plasmonic metal only worsens the situation. Then the focal spot is still coupled to the hole perimeter and the conductive losses in the metal arise in the whole solar spectrum. If the focal spots were much smaller than the hole diameter, this effect could be, probably, avoided. But the diameter of the focal spot created by a microlens is a value of the order of 2 microns. To avoid the interaction with the metal the diameter of the hole must be, probably, of the order of 20 μm. However, the small ratio of the diameters hole/lens is the crucial prerequisite of the light trapping. The micro-lenses themselves in [97] and [98] have the size of the order of 20 microns. The further increase of the lens diameter will result in the drastic growth of the backscattering. Therefore, the optimal design parameters found by extensive numerical simulations in [97] reflect a trade-off between the losses in the perforated gold and the light-trapping effect.

Our structure is free of the drawback related to the plasmon in the holes because we reject the idea of focusing in the hole. Our design solution exploits the ray optics that is working in all components of the LTS. Therefore, it turns out to be more efficient. Its general view is shown in Fig. 3.6. A key component is the array of densely packed dielectric (e.g., glass) cones truncated at the bottom end. Cones may be obtained by the micro-patterning the dielectric layer (see below). An antireflection layer covers the bottom end of the glass cone. This way the cones are matched to the thin-film SC and the incident light distributed between the cones is efficiently introduced into the PV layer.

Tapering does not destroy the wave guidance since it is small enough, and the vertical size (thickness) of our LTS is substantial. Plasmons are not excited in the hollowed metal film because there light keeps inside the glass and does not feel the hole perimeter. The metal film may serve as a top current-collecting electrode. Then beneath it, a charge-transport layer is located, then the PV layer (e.g., that with the heterojunction), then the second charge transport layer, and the bottom electrode of polished gold. Since the charge transport layer has a rather high refractive index $n_{\text{CTL}}$, the matching layer (ARC) between it and the glass is needed. It is shown in Fig. 3.6b by the orange color. The condition $n_{\text{glass}} < n_{\text{ARC}} < n_{\text{CTL}}$ is satisfied e.g. for molybdenum oxide (when our LTS is applied for perovskite
All-dielectric light trapping structures

Figure 3.7. Sketch of the vertical cross section of two variants of application of our universal LTS: (a) organic and (b) perovskite thin-film SCs. In the second case, the light is incident from the opposite side – the bottom golden electrode in the conventional design. In this electrode we make micron holes and add a matching layer of molybdenum oxide.

thin-film SCs). In this geometry, we avoid optical losses in the conducting oxide serving as the top electrode in the conventional geometry. In the present case, the conducting oxide serves the bottom electrode, and the light does not transmit into it. Only a small parasitic absorption in the charge-transport layer remains unavoidable in our design.

3.2.2 An example of an organic solar cell

Figure 3.8. (a) Scheme of the organic solar cell conventionally designed without an LTS (bottom) and the variant of the application of our LTS (top). (b) Normalized spectra or the PV absorption in the active layer versus wavelength for two cases: our LTS is present (red solid line) and is absent (blue dashed line).

In our first example, we consider an organic thin-film SC with the bottom electrode of aluminum and the top electrode of indium tin oxide (ITO) from work [97]. A glass laminate of macroscopic thickness covers the prototype structure. The bulk heterojunction layer consists of a mixture of a
All-dielectric light trapping structures conducting polymer APFO Green-9 and fullerene derivative PC_{70}BM. The optimal thickness of the layer is 30 nm, that implies a very low PV absorption per one passage. Using literature data for the complex permittivities of the components of the layer [99, 100] we have found the volume fractions of these components (not indicated in [97]), that allowed us to successfully reproduce the spectrum of the PV absorption calculated in [97]. Since the structure under study consists of only flat layers, this calculation, based on the layer transfer matrices, is analytic and accurate. After that, we have simulated the absorption in the modified structure (with our LTS) using the CST Studio Suite.

The plot of the PV absorption takes into account the solar spectrum on the Earth surface (AM 1.5G). It is shown in Fig. 3.8 for two cases: 1) no LTS (analytic calculation, blue dashed line) and 2) with LTS (CST, solid red line). We see that the gain due to our LTS appears in the range 450-800 nm, whereas, at 350-450 nm, the PV absorption remains at the same level. This is the better result than that obtained in work [97], where the LTS decreased the PV absorption in the range 350-450 in favor of the dissipation in the metal film. Respectively, our overall gain in the PV absorption is equal 33% against 25% (both experiment and calculations) reported in [97].

3.2.3 An example of a perovskite solar cell

Our next example refers to a perovskite SC without a hole-conducting layer. Here, it is worth to note, that the progress in the efficiency of per-
ovskite SCs starting from the initial work [101], where the overall efficiency 3.8% was reported, to the record result 22.1% in work [102] took only six years. For instance, it is commonly accepted that perovskite SCs do not need LTS because their PV layer has optimized thickness 300-500 nm, that is sufficient for almost full absorption (95%) per one passage. However, a detailed analysis shows that optical losses in perovskite thin-film SCs are noticeable. In work [102] one has obtained that only 65% of the incident sunlight is absorbed in the perovskite layer, i.e., optical losses are as high as 35%. 4% of the incident light is reflected, 2% is absorbed in the charge-transport layers, 14% is absorbed in the top electrode (which is, as we have already mentioned, semitransparent), and 15% of light is lost due to the parasitic transmission to the bottom metal electrode which is not polished and does not reflect the light back to the perovskite. This high parasitic transmittance mainly occurs at the wavelengths above 800 nm (optical absorption of perovskites drops in the infrared range, and, therefore, the bandgap wavelength of PV perovskites is usually engineered within the interval 800-900 nm). It is easy to understand that the correct light management can noticeably increase the optical efficiency with so high optical losses.

Using the apparatus of transfer matrices, we have reproduced the results of [10] for the perovskite thin-film SC. This thin-film SC consists of the following layers: a transparent electrode of ITO (80 nm), two electron-transporting layers of PEDOT:PSS (5 nm) and PCDTBT (5 nm), a perovskite layer CH$_3$NH$_3$PbI$_3$ (350 nm), a contact material layer PC$_{60}$BM (10 nm) and bottom electrode of Au (100 nm). Here the hole-conducting layer is absent, that is harmful for the overall efficiency (near 10%) but useful for the stability of the cell. The PV absorption can be improved in such thin-film SC by inverting the structure – introducing the incident light through the holes in the gold film. Then we not only get rid of the optical losses in ITO, but we may also get rid of ITO itself, replacing it with gold. ITO is not less expensive than the gold one and since indium is a rare element its price continually grows.

In Fig. 3.9 one can see the normalized spectra of the PV absorption versus the wavelength for two cases: when the LTS is present and when it is absent and the thin-film SC is illuminated through the glass laminate. Our LTS does not influence the PV absorption at 500-750 nm, and weekly improves it at long wavelengths. However, at short waves – below 500 nm, where the ITO (we have removed) is lossier – we get the maximal
All-dielectric light trapping structures
gain, and the overall increase in the optical efficiency is equal 6%. So, our LTS is advantageous also for a perovskite thin-film SC. Moreover, there are bonuses: the static surface resistance of the gold layer is lower, and the work function is higher than that of ITO. The thickness of the gold electrode does not matter and can be arbitrarily thick (up to microns if needed).

3.2.4 Fabrication

![Fabrication Diagram](image)

**Figure 3.10.** (a) The stages of the fabrication of a microstructure with submicron precision using the optical interference lithography: (I) deposition of the azo-polymer by spin-coating, (II) the exposure of the photo-sensible polymer, (III) partial etching the polymer in order to enter the windows, (IV) dry etching of the substrate, (V) elimination of the polymer. (b) The AFM image of our first demonstration (dimensions are intentionally reduced compared to those of our LTS in order to better inspect the fabrication tolerances).

In this section, we report on our experimental sample of LTS with the purpose to prove that it is affordable. The structure was prepared using the optical interference lithography [103]. This is a commonly adopted and inexpensive method if a photosensitive material like one of the azopolymers is used as in [103], there is even no need for an optical mask. One may expose the whole substrate at once. The periodicity with the accuracy below one half of the wavelength is achieved over large macroscopic area impinged by light. Here one uses two mutually coherent laser beams formed by the Lloyd mirror optical scheme. The sinusoidal intensity profile corresponds to the interference pattern on the sample surface. The photosensitive material migrates to the dark regions that results in the formation of the profile. The obtained periodic profile is used for the dry etching of a dielectric material. After the dry etching, the photosensitive material is removed by a solvent. In this way, one may obtain large-area arrays of conical protrusions rather fast and with essentially submicron accuracy. In Fig. 3.10 we depict the main stages of fabrication (a) and
present the image of the experimental sample obtained using an atomic force microscope. The goal of this fabrication was not to reproduce the universal LTS since we have not yet acquired the facilities for fabricating organic or perovskite SCs. Our purpose was to check the accuracy of such the fabrication. Therefore, we prepared a much smaller structure than needed for trapping the sunlight. The cone base diameter, as well as the cone height, was taken equal to 500 nm, and the deviations are smaller than 50 nm as one can see in Fig. 3.10b.

3.2.5 Conclusions

In this section, we have suggested and studied a universal LTS for SCs of 3rd generation. It is mainly intended for organic thin-film SCs, however, can also be used for enhancement of perovskite SCs. Only a slight modification of design parameters is needed for the latter case. The structure comprises an array of dielectric truncated cones serving as the tapered optical waveguides for the incident light and optically connected to the thin-film SC through the holes in the metal coating (e.g., Au). We have theoretically shown that our LTS has advantages with respect to known analogs: it grants the gain in the PV absorption both in case of the organic thin-film SC (more significant) and perovskite thin-film SC (less significant but still noticeable). The existing techniques allowed us to fabricate such a structure rather simply and quickly without involving expensive materials or processes. In fabrication, it is important to avoid gaps between the output ends of the truncated cones and the thin-film SC. The needed bonding can be performed by a polymer compound.
4. Conclusions of the thesis and future work

This thesis considers the light management based on nanostructures and microstructures often referred in the modern literature as metamaterials in thin-film SCs. I report collaborative research in which I played the major role on new LTSs offering the gain in the optical efficiency of thin-film SCs of several types without damaging their operational characteristics. These types of thin-film SCs are solar cells based on a-Si, organic photovoltaic solar cells and metal-organic (perovskite) SCs. The report includes theoretical investigations based on analytical calculations (for reference structures), full-wave numerical simulations for nano- and microstructures, as well as experimental studies of a relevant physical phenomenon (leaky domino-modes) and the realistic SCs exploiting this phenomenon.

We believe that the presented results are helpful for the further development of thin-film SCs of these three types. We would like to point out some important topics for the further research work. In the planned studies of organic SCs enhanced by LTSs of our NAs, we will use NAs with proper work function contributing to the collection of holes at the side of ITO. We will further optimize the geometry of the SC so that to reduce the shading of the photocurrent. We plan to consider the design where an array of NAs is located in the middle of the photoactive layer, and not attached directly to the charge collecting areas. Hopefully, the positive impact of our NAs will be higher, since the new fabrication facilities not available during these doctoral studies will allow us to fabricate the LTS and the SC in the same clean room. Next, we will determine the effective increase of the photocurrent more accurately, combining optical and electrostatic simulations together, as it was done in [104]. Finally, we plan to perform experimental studies of all-dielectric LTSs suggested in the present dissertation.


References


References


