Catching Light Rays:

Refractory Plasmonics

for Energy Conversion, Data Storage and Medical Applications

Alexandra Boltasseva[1,2] and Urcan Guler[2]

[1]School of Electrical and Computer Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA.

[2]Nano-Meta Technologies, Inc., 1281 Win Hentschel Blvd, West Lafayette, IN 47906, USA.

E-mail: aeb@purdue.edu

The influence of the optical technologies on the development of modern society cannot be overestimated. Ranging from conventional mirrors, lenses, microscopes, telescopes, optical sensors and high-precision measurement systems to lasers, fiber optic communication systems and optical data storage systems, optical instruments have brought revolutionary advances and novel concepts to many disciplines including astronomy, manufacturing, chemistry, biology (particularly bio- and chemical sensors), medicine (particularly ophthalmology and optometry), various engineering fields and information technology. The rise of the new generation of optical technologies is nowadays fueled by the development of nanophotonics that investigates the behavior of light on the nanometer scale, and the interaction of nanometer-scale objects with light. In nanophotonics, one of the major focal points is on developing a new class of "plasmonic" structures and "metamaterials" as potential building blocks for advanced optical technologies. Plasmonics deals with metallic components, which can focus and manipulate light at the nanometer scale via excitation of surface plasmons – collective oscillations of free electron clouds (found in metallic materials) coupled to light (Maier, 2007). Plasmonics can "squeeze" light into tiny areas much smaller than the wavelength of light thus offering light confinement beyond the usual diffraction limit as well as extreme light enhancement in those plasmonic “hot spots” (Lindquist et al., 2013; Schuller et al., 2010). Plasmonic devices are envisioned to have a transformative effect on optoelectronics, microelectronics, on-chip optical communication and data transmission by enabling low power, nanometer scale photodetectors, fast light modulators, nanoscale, power efficient lasers and light sources. Plasmonics paves the way to optical microscopy and photolithography with the nanometer scale resolution, novel concepts for data recording/storage, improved energy harvesting through optimized, plasmonics-based light capturing techniques as well as single-molecule sensing and advanced spectroscopy. Nowadays, one can design plasmonic structures and metamaterials – artificial composite surfaces/materials using plasmonic building blocks as their functional unit cells – with versatile properties that can be tailored to fit almost any practical need.

However, to enable new plasmonic technologies, grand limitations associated with the use of metals as constituent materials must be overcome. In the devices demonstrated so far, too much light is absorbed in metals (such as silver and gold) commonly used in plasmonic structures and metamaterials. The fabrication and integration of metal nanostructures with existing semiconductor technology is challenging, and the materials need to be more precisely tuned so that they possess the proper optical properties to enable the required functionality. Moreover, metals conventionally used in plasmonics are soft materials with relatively low melting points. Thus plasmonic devices fall short in meeting the challenges that real industry applications face; particularly where high operational temperatures (such as in energy harvesting or data recording applications), high pressure and harsh chemical environments are present, making plasmonics a “what-happens-in-the-lab-stays-in-the-lab” area of research.

In order to enable practical devices utilizing plasmonic concepts, new constituent materials are needed that could both exhibit the plasmonic properties required to capture and manipulate light at the nanoscale and provide durable, chemically, mechanically and thermally stable solutions for realization of rugged optical instruments. Recently, plasmonic ceramic materials have been proposed as the basis for practical, low-loss, CMOS-compatible plasmonic devices marking a long-awaited technology-driven era for the fields of plasmonics (Naik, Shalaev, & Boltasseva, 2013). Transition metal nitrides such as titanium nitride (TiN) and zirconium nitride (ZrN) have recently been proposed as refractory plasmonic materials, i.e. sustaining high temperature (e.g., TiN melting point is 2930°C), that exhibit good optical properties, along with bio- and CMOS-compatibility, robustness, chemical stability, corrosion resistance, mechanical strength and durability (Guler, Boltasseva, & Shalaev, 2014; Guler, Shalaev, & Boltasseva, 2015). The attractiveness of TiN for practical device applications is illustrated by its extensive use in semiconductor manufacturing industry as a gate layer and a diffusion barrier, in large scale integrated microelectronics, microelectronic mechanical systems (MEMS), and in biotechnology.

Improving the efficiency of light harvesting is among the major engineering challenges for the upcoming decade where *photovoltaics* (PV) is seen as one of the most important energy supplies of the future. A variety of techniques based on plasmonic effects have been proposed over the last couple decades in order to improve solar cell efficiencies via field concentration and hot electron generation (Polman & Atwater, 2012). Plasmonic metamaterials were investigated as broadband absorbers and spectrally engineered emitters for *solar/thermophotovoltaic* (S/TPV) systems (Li et al., 2014; Molesky, Dewalt, & Jacob, 2013). Some of the problems in the field of photovoltaics are again connected to efficiency and stability degradation due to the device heating under the absorption of solar radiation. The S/TPV concept includes a perfect absorber designed for broad absorption of solar radiation while a selective emitter designed to emit light in a narrow energy band just above the semiconductor bandgap in the PV cell can be heated by the absorber through an intermediate layer or via chemical, nuclear, or waste heat sources (Bauer, 2011; Fan, 2014). The beauty of the approach is that the system can be used in a hybrid mode (hence the name "solar/thermophotovoltaics") but high temperature operation in such devices again brings material degradation into the focus (Guler, Shalaev, et al., 2015). The high operational temperatures (well above 800°C) have hindered the progress in the S/TPV field due to low melting points for noble metals and poor optical performance as well as lattice imperfections for refractory metals. Refractory plasmonic ceramics such as titanium nitride represent a unique platform for realizing practical plasmonic devices for S/TPV as an emerging energy-conversion concept, which promises efficiencies up to 85% (Guler, Shalaev, et al., 2015). TiN absorbers have been already shown to provide high optical absorption (about 95%) over a broad range while being extremely durable under exposure to heat and strong light illumination (Li et al., 2014). Figure 1 (a) gives a schematic representation of solar-thermophotovoltaic system along with exemplary absorber and emitter metamaterial designs. Figure 1 (b) shows the absorption measurements from identical plasmonic metamaterials made of TiN and Au. Titanium nitride metamaterial provides broader absorption and retains its optical properties after 8 hr annealing at 800 ^{o}C, whereas Au metamaterial has narrower resonance peaks and its absorption properties degrade after 15 minutes annealing at the same temperature (Li et al., 2014).

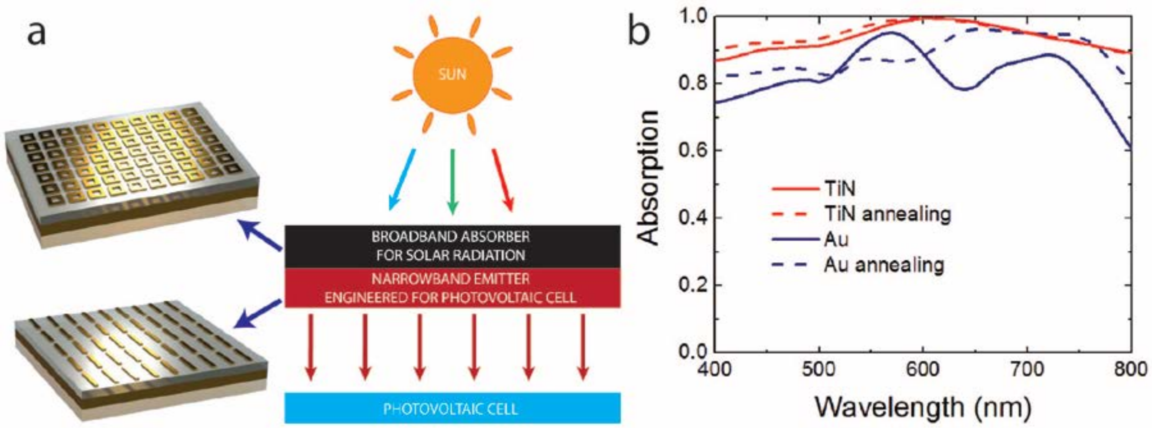

Figure 1: (a) A solar-thermophotovoltaic system consists of a broadband solar absorber and a spectrally selective emitter engineered to match the bandgap of a photovoltaic cell. Adapted with permission from (Guler, Shalaev, et al., 2015). Copyright (2015) Elsevier. *(b) TiN metamaterial provides better absorption compared to an identical Au absorber and it retains its properties after exposure to high temperatures (800 ^{o}C).* Adapted with permission from (Li et al., 2014). Copyright (2014) John Wiley & Sons, Inc.

Durable, refractory TiN also holds a great promise to enable efficient, TPV-based *waste heat recovery* (Bauer, 2011). Efficient heat energy harvesting could have a transformative effect on a number of industries including metal casting, aerospace and gas & oil industries by providing fossilfuel based power generation (including diesel- and gas engines), radioisotope-based cells, fuel-fired cells and portable power generators for civil and military needs. TiN properties are also well suited for *solar thermoelectric* generators (Kraemer et al., 2011), plasmon-mediated *photocatalysis* (Clavero, 2014), and plasmon assisted *chemical vapor deposition* (Boyd, Greengard, Brongersma, El-Naggar, & Goodwin, 2006).

Another heat-generating application of plasmonic nanoparticles is in healthcare. *Photothermal therapy* utilizes a unique property of metallic nanoparticles to concentrate light and efficiently heat a confined nanoscale volume around the plasmonic structure (Loo et al., 2004). Thus, nanoparticles delivered to a tumor region can be heated via laser illumination at near-infrared wavelength located in the biological transparency window. Hyperthermia is known to induce cell death in many tissues and has been shown to increase local control and overall survival in combination with radiotherapy and chemotherapy in randomised clinical trials. Gold nanoparticles are emerging as promising agents for cancer therapy and are being investigated as drug carriers, photothermal agents, contrast agents and radiosensitisers. While having many attractive properties for use in therapy, gold nanoparticles resonate at the specific light wavelengths that lie outside the biological transparency window thus requiring larger dimensions and complex geometries such as nanoshells and nanorods (Huang, Jain, El-Sayed, & El-Sayed, 2008). In turn, larger sizes affect nanoparticles' pharmacokinetics, biodistribution and in vivo toxicity. TiN nanofabricated particles have been shown to exhibit plasmonic resonance in the biological transparency window and higher heating efficiencies than gold (Guler et al., 2013). More importantly, TiN dispenses the need for complex geometries and provide simple, small-size particles solution that is critical in optimizing cellular uptake and clearance from the body after the treatment (Guler, Suslov, Kildishev, Boltasseva, & Shalaev, 2014). Figure 2 (a) shows the high resolution transmission electron microscope image and optical transmittance data taken from colloidal single crystalline TiN sample. Lattice parameters of the nanoparticle matches well with the tabulated single crystalline bulk values of TiN samples and the optical transmittance data has the plasmonic extinction dip located at the biological transparency window. Figure 2 (b) shows a comparison between the calculated absorption efficiencies of Au and TiN nanodisks. The dipolar resonance peak of Au is located around 520 nm where the excitation light is strongly attenuated in biological samples. Titanium nitride dipolar resonance peak located around 800 nm allows the use of small particles. Since TiN is a very contamination safe material and widely used in surgical tools, food-contact applications and medical implants, TiN colloidal particles could become a next generation solution for tumor-selective photothermal therapy, medical imaging as well as other bio-medical applications.

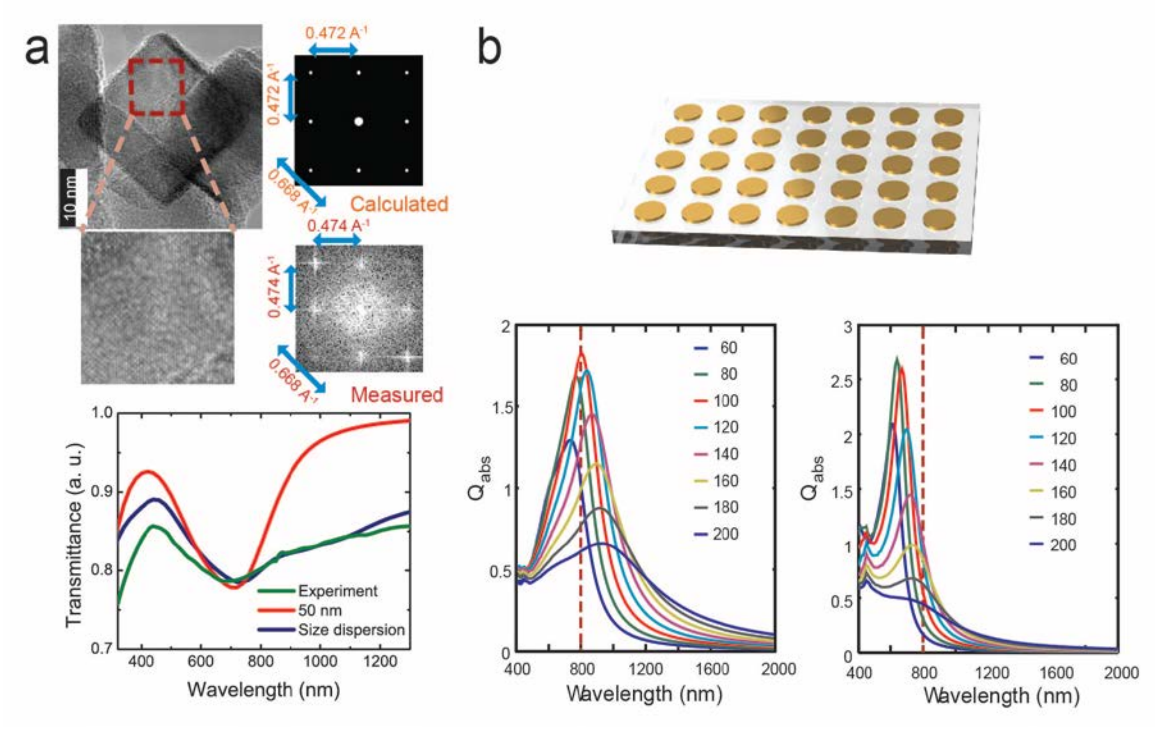

Figure 2: (a) Lattice parameters of single crystalline TiN nanoparticle match well with the tabulated values obtained from bulk TiN samples. Transmittance data obtained from colloidal TiN sample has a plasmonic extinction dip located at the biological transmittance window. Adapted from (Guler, Suslov, et al., 2014). (b) Absorption efficiencies calculated for TiN and Au nanodisks. Small TiN nanodisks provide enhanced absorption at 800 nm while large nanodisks of Au are required at the same wavelength due to spectral mismatch. Adapted with permission from (Guler et al., 2013). Copyright (2013) American Chemical Society.

Refractory plasmonic materials are seen as the best candidates for applications utilizing nanometer-scale field enhancement and local heating. An example of such application is a next generation data recording technology, namely *heat-assisted magnetic recording* (HAMR) (Challener et al., 2009). This is a nanophotonic approach that promises to significantly increase the amount of data on a magnetic disk by using a laser light tightly focused on a magnetic material where the tight focusing into a subwavelength spot is achieved via a plasmonic nanoantenna. In contrast to noble metals that are prone to deformations such as melting and creep due to material softness and melting point depression in nanostructures, any degradation of refractory plasmonic materials can be avoided with the proper material integration (Guler, Kildishev, Boltasseva, & Shalaev, 2015; Li et al., 2014). Titanium nitride antennae have recently been shown to satisfy the stringent requirements for an optically efficient, durable HAMR near field transducer paving the way to the next-generation data recording systems (Guler, Kildishev, et al., 2015).

More generally, the realm of tip-based applications including near-field scanning optical microscopes and other local field enhanced signal measurements can be greatly expanded by the use of refractory plasmonic ceramics opening up measurement schemes in previously unavailable frequency ranges and operational regimes (Boltasseva & Shalaev, 2015; Guler, Boltasseva, et al., 2014).

The durability and refractory properties of TiN and ZrN could also make them the only material building block for high-temperature, harsh environment optical *sensors* and *flat photonic components* such as ultra-thin lenses, and spatial light modulators using the concepts of the emerging field of *metasurfaces*. Refractory flat optical components last longer in harsh environments, provide more reliable data, and offer ultra-compactness combined with planar fabrication process. In oil and gas industries, ultra-compact, extremely durable plasmonic sensors could replace electrical sensors and enable novel measurement concepts for pressure, flow, drill bit temperature and breakage detection.

Thermal, mechanical and chemical stability of TiN along with its high conductivity and corrosion resistance makes it an ideal material for *nanofabrication*. TiN can be used for making ultra-durable imprint stamps with unparalleled hardness and resistance to wet chemistry processes. When combined with emerging plasmonic nanolithography schemes TiN films can be used to create durable multiple-use master molds and novel fabrication concepts for large-scale sub-10-nanometer resolution patterning.

CMOS-compatible refractory plasmonic materials are also seen as a platform for the next-generation on-chip hybrid photonic-electronic devices such as subwavelength photodetectors, optical interconnects and modulators with unprecedented compactness, speed, and efficiency (Kinsey, Ferrera, Shalaev, & Boltasseva, 2015).

Having an excellent combination of hardware performance properties, appealing optical properties, durability and contamination safety, plasmonic ceramics in general and TiN in particular, hold a promise of enabling highly robust, ultra-compact, CMOS-compatible optical devices capable of addressing numerous application-specific challenges. Plasmonic ceramic materials are seen as promising building blocks for advanced optical technologies, including data processing, exchange and storage; a new generation of cheap, enhanced-sensitivity sensors; nanoscale-resolution imaging techniques; new concepts for energy conversion including improved solar cells, as well as novel types of light sources.

References

Bauer, T. (2011). *Thermophotovoltaics: Basic Principles and Critical Aspects of System Design*. Berlin, Germany: Springer-Verlag.

Boltasseva, A., & Shalaev, V. M. (2015). All that glitters need not be gold. *Science* , *347* (6228), 1308–1310. Retrieved from http://www.sciencemag.org/content/347/6228/1308.short

Boyd, D. A., Greengard, L., Brongersma, M., El-Naggar, M. Y., & Goodwin, D. G. (2006). Plasmon-Assisted Chemical Vapor Deposition. *Nano Letters*, *6*(11), 2592–2597. doi:10.1021/nl062061m

Challener, W. A., Peng, C., Itagi, A. V, Karns, D., Peng, W., Peng, Y., … Hsia, Y.-T. (2009). Heat-assisted magnetic recording by a near-field transducer with efficient optical energy transfer. *Nature Photonics*, *3*(4), 220–224.

Clavero, C. (2014). Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat Photon*, *8*(2), 95–103. doi:10.1038/nphoton.2013.238

Fan, S. (2014). Photovoltaics: An alternative "Sun" for solar cells. *Nat Nano*, *9*(2), 92–93. doi:10.1038/nnano.2014.9

Guler, U., Boltasseva, A., & Shalaev, V. M. (2014). Refractory Plasmonics. *Science (New York, N.Y.)*, *344*(6181), 263–264. doi:10.1126/science.1252722

Guler, U., Kildishev, A. V., Boltasseva, A., & Shalaev, V. M. (2015). Plasmonics on the slope of enlightenment: the role of transition metal nitrides. *Faraday Discussions*, *178*, 71–86. doi:10.1039/C4FD00208C

Guler, U., Ndukaife, J. C., Naik, G. V., Nnanna, A. G. A., Kildishev, A. V., Shalaev, V. M., & Boltasseva, A. (2013). Local heating with lithographically fabricated plasmonic titanium nitride nanoparticles. *Nano Letters*, *13*(12), 6078–6083.

Guler, U., Shalaev, V. M., & Boltasseva, A. (2015). Nanoparticle plasmonics: going practical with transition metal nitrides. *Materials Today*, *18*(4), 227–237. doi:http://dx.doi.org/10.1016/j.mattod.2014.10.039

Guler, U., Suslov, S., Kildishev, A. V, Boltasseva, A., & Shalaev, V. M. (2014). Colloidal Plasmonic Titanium Nitride Nanoparticles: Properties and Applications. *arXiv Preprint arXiv:1410.3920*.

Huang, X., Jain, P., El-Sayed, I., & El-Sayed, M. (2008). Plasmonic photothermal therapy (PPTT) using gold nanoparticles. *Lasers in Medical Science*, *23*(3), 217–228. doi:10.1007/s10103-007-0470-x

Kinsey, N., Ferrera, M., Shalaev, V. M., & Boltasseva, A. (2015). Examining nanophotonics for integrated hybrid systems: a review of plasmonic interconnects and modulators using traditional and alternative materials \[Invited\]. *J. Opt. Soc. Am. B*, *32*(1), 121–142. doi:10.1364/JOSAB.32.000121

Kraemer, D., Poudel, B., Feng, H.-P., Caylor, J. C., Yu, B., Yan, X., … Chen, G. (2011). High-performance flat-panel solar thermoelectric generators with high thermal concentration. *Nature Materials*, *10*(7), 532–538. doi:10.1038/nmat3013

Li, W., Guler, U., Kinsey, N., Naik, G. V, Boltasseva, A., Guan, J., … Kildishev, A. V. (2014). Refractory Plasmonics with Titanium Nitride: Broadband Metamaterial Absorber. *Advanced Materials*, *26*(47), 7959–7965. doi:10.1002/adma.201401874

Lindquist, N. C., Jose, J., Cherukulappurath, S., Chen, X., Johnson, T. W., & Oh, S.-H. (2013). Tip-based plasmonics: squeezing light with metallic nanoprobes. *Laser & Photonics Reviews*, *7*(4), 453–477. doi:10.1002/lpor.201209044

Loo, C., Lin, A., Hirsch, L., Lee, M. H., Barton, J., Halas, N., … Drezek, R. (2004). Nanoshell-enabled photonics-based imaging and therapy of cancer. *Technol Cancer Res Treat*, *3*(1), 33–40. doi:d=3018&c=4130&p=12032&do=detail [pii]

Maier, S. A. (2007). *Plasmonics: Fundamentals and Applications*. Springer. Retrieved from http://books.google.com/books?id=yT2ux7TmDc8C

Molesky, S., Dewalt, C. J., & Jacob, Z. (2013). High temperature epsilon-near-zero and epsilon-near-pole metamaterial emitters for thermophotovoltaics. *Optics Express*, *21*(S1), A96–A110. doi:10.1364/oe.21.000a96

Naik, G. V, Shalaev, V. M., & Boltasseva, A. (2013). Alternative plasmonic materials: beyond gold and silver. *Adv Mater*, *25*(24), 3264–3294. doi:10.1002/adma.201205076

Polman, A., & Atwater, H. A. (2012). Photonic design principles for ultrahigh-efficiency photovoltaics. *Nat Mater*, *11*(3), 174–177. Retrieved from http://dx.doi.org/10.1038/nmat3263

Schuller, J. A., Barnard, E. S., Cai, W., Jun, Y. C., White, J. S., & Brongersma, M. L. (2010). Plasmonics for extreme light concentration and manipulation. *Nat Mater*, *9*(3), 193–204. doi:10.1038/nmat2630 nmat2630 [pii]