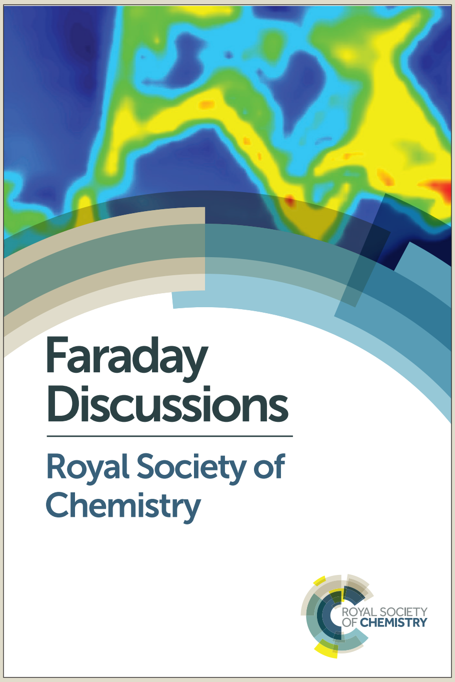
Faraday
Discussions
Royal Society of
Chemistry
ROYAL SOCIETY OF CHEMISTRY

Plasmonics on the slope of enlightenment: the role of transition metal nitrides

Urcan Guler[a], Alexander V. Kildishev[ab], Alexandra Boltasseva[ab] and Vladimir M. Shalaev[ab]*

DOI: 10.1039/b000000x

The key problem currently faced by plasmonics is related to material limitations. After almost two decades of extreme excitement and research largely based on the use of noble metals, scientists have come to a consensus on the importance of exploring alternative plasmonic materials to address application-specific challenges to enable new functional devices. Such a change in the motivation will undoubtedly lead to significant advancements in plasmonics technology transfer and could have a revolutionary impact on nanophotonic technologies in general. Here, we report on one of the approaches that, together with other new material platforms, mark an insightful technology-driven era for plasmonics. Our study focuses on transition metal nitrides as refractory plasmonic materials that exhibit appealing optical properties in the visible and near infrared regions, along with high temperature durability. We take heat-assisted magnetic recording as a case study for plasmonic technology and show that a titanium nitride antenna satisfies the requirements for an optically efficient, durable near field transducer paving the way to the next-generation data recording systems.

1 Introduction

It was the pioneering work by Michael Faraday that reported the "*great power of action*" metal nanoparticles have on light and the effect of parameters such as the nanoparticle dimensions on the plasmonic resonance.[1] In this quintessential lecture he described gold (Au) as "*especially fitted for experiments*" for several reasons mostly based on the ease of observation. Following the same reasoning, noble metals such as Au and silver (Ag) have been widely used over the last few decades for a broad range of activities in the field of plasmonics.[2-11] With the advancement of nanofabrication techniques, the field of plasmonics experienced a burst in research activities, leading to great expectations on outcomes for daily applications mostly associated with optics and photonics. However, between the pioneering report of Faraday and the hype in the field, it was the electron beam techniques that revealed plasmonic resonances of metals. In 1959, Powel and Swan reported the observation of bulk and surface plasmon resonances from an aluminium (Al) thin film via electron energy loss spectroscopy (EELS).[12] As a low cost material with plasmon resonance covering the UV and visible regions, Al is again attracting attention of the plasmonics community.[13]

Although other traditional metals, such as copper and aluminium,[14,15] have been utilized for plasmonics applications, their room temperature oxidation and strong dependence of the resonance quality on the oxide remain limitations for their widespread adoption. Similarly, Ag has been claimed as the highest quality

---

[a] *Nano-Meta Technologies, Inc., 1281 Win Hentschel Blvd, West Lafayette, IN 47906, USA.*
[b] *School of Electrical and Computer Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA. E-mail: shalaev@purdue.edu*

plasmonic material that exhibits resonances through the entire visible spectrum, but the use of the material has been hindered due to strong room temperature oxidation and sulfidation; both processes are significantly enhanced when material is nanostructured.[16,17] The development of chemically stable and bio-compatible Ag nanostructures is an exciting challenge with intensive ongoing effort.[18,19] Among the widely used plasmonic metals, Au has attracted a significant amount of attention due to its chemical stability and relatively good plasmonic properties, despite the fact that the resonance quality of Au is significantly lower compared to Ag and Al.[20] However, even this comparison of Au against Ag shows that the parochial approach, which concentrates simply on the resonator strength when evaluating materials, could be misleading in a particular application. In fact, the entire field of plasmonics has reached a stage where the overall functional material properties should be considered instead of plasmonics-only evaluations.

2 Assessment

As a research field that attracted great attention over the last two decades, giving birth to numerous application proposals, plasmonics is now subject to grand expectations on the deliverables. Relying on the maturity of the field and the fact that technology products are soon expected, here we discuss the brief history of breakthroughs and the current state of the technology from our interpretation of the Gartner Hype Cycle methodology (HCM). The HCM has been successfully used for a variety of technologies over the last decade and claims to be an efficient way to adopt them to real industrial problems.[21]

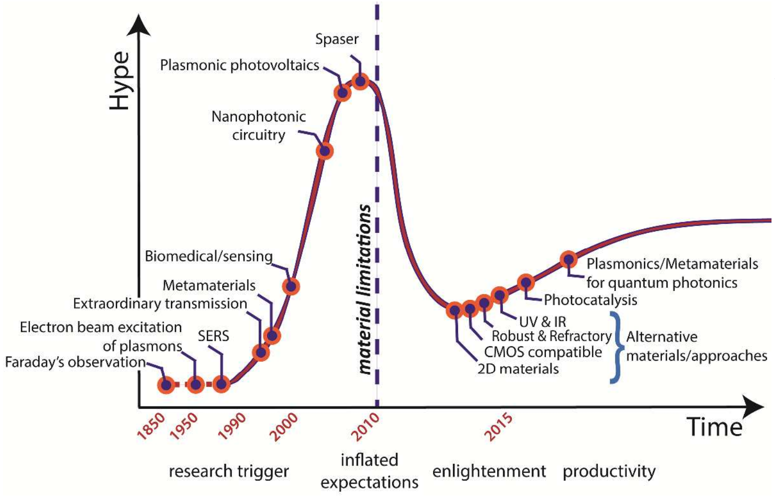

Fig. 1. The Hype Cycle for the field of plasmonics from the authors' point of view. After a decade of high expectations, material limitations are delaying the realization of the proposed concepts and technology transfer. Merging plasmonics with materials science and chemistry could provide new solutions and bring technological advances across many application spaces.

Figure 1 shows the authors' view on the main milestones in plasmonics that generated a great deal of attention over the past decade. Although the first observations of plasmonic effects are quite old, [22] the systematic investigation of the interaction of light with nanoscale metallic particles clearly starts with the work performed by Faraday in 19th century.[1] After a relatively long period of theoretical studies performed by leading scientists,[23,24] characterization of electron-beam-excited plasmons are considered the leading experimental efforts in the field.[12,25] Surface enhanced Raman scattering (SERS), first observed in 1974 by Martin Fleischman et al.[26] and attributed to enhanced electric field by David Jeanmaire and Richard Van Duyne in 1977,[27] is perhaps the very first systematic application of plasmonic effects. Soon after the first experimental results were reported, the clear relation between the localized surface plasmon resonance (LSPR) and the enhanced SERS signal was proposed by Martin Moskovits.[28,29] With the advancement of nanofabrication methods and their widespread availability, breakthrough results such as extraordinary transmission of light through plasmonic nanoholes,[30] and plasmonic metamaterials created a strong impact.[31]

Sensing and biomedical applications have long been the flagship of the field due to wide range of exciting opportunities offered by bio-compatible, plasmonic nanostructures.[32-34] With a solid research record over the past two decades, a wide variety of sensing and biomedical devices based on the plasmonic effects were expected to enter production lines. However, technology transfer has thus far been slow compared to the level of expectations.[35] Beyond biomedical applications, interest in the field was substantially nourished by several recent proposals to develop sub-wavelength, hybrid nanophotonic components that have optical and electronic functionalities,[4,9,36-49] and plasmonic photovoltaics where metal nanoparticles were used as E-field concentrators in thin films devices for enhanced photocurrent generation. [50-54]

In our opinion, the peak of expectations in the field of plasmonics was reached with the breakthrough concept of spaser,[55] the plasmonic counterpart of a laser at nanoscale, that could potentially be the key towards many nanoscale applications such as all-optical circuitry, lithography, probing and microscopy.[56,57] Compensation of losses in plasmonic nanostructures with semiconductor quantum dots,[58] and demonstration of a spaser based on sub-wavelength resonators made of gold nanoparticles surrounded by a dye-doped silica shell operating in the visible spectrum was reported soon after the proposal.[59] However, despite extensive experimental efforts, losses in metal nanostructures arising from electron scattering have been the major limiting factor for the spaser and the field of plasmonics in general.[60,61] This absorption of electromagnetic energy due to material losses is inherently affecting technologies relying on the field enhancement and lossless propagation of energy, which span the entire list of breakthroughs positioned at the peak of expectations.

The metamaterials research, a field highly correlated with plasmonics, has followed a similar trend over the last decade. Triggered by the negative index materials and superlens,[31,62-64] excitement and expectations peaked with the idea of cloaking and transformation optics.[65,66] In authors' opinion, after the recognition of material limitations such as losses and scalability, the field is experiencing an enlightenment period with approaches incorporating alternative materials with realistic design parameters.

We believe the breakthroughs that led to the peak of somewhat inflated expectations are now evolving and bringing solutions to earlier problems. For example, the concept of harvesting solar energy using the enhanced interaction of plasmonic nanostructures with light has expanded to the generation of hot electrons for efficient heating, and plasmon induced photocatalysis.[67,68] Mubeen et al. recently reported an approach where metal in a plasmonic photovoltaic device is not a field enhancing antenna as in previous concepts, but instead, plays a role of the light absorber that generates carriers.[69] Another approach to beat the metallic losses is to use high refractive index dielectric nanostructures as light trappers.[70] Nanophotonic circuitry is now leaning towards the integration of plasmonics with newly emerging research on 2D materials such as graphene and MoS_2 and quantum photonics.[71-74] Plasmonic metamaterials research is concentrated on alternative materials with application specific characteristics such as low loss, tunability, refractory properties, and CMOS compatibility.[37,75-77] Research into alternative materials for spectral ranges out of the visible are other examples of application-specific efforts in the field of plasmonics.[78,79] In this work, we consider one of the approaches that, together with other new material platforms including semiconductors, 2D materials, phase-changing and ceramic materials, marks an insightful technology-driven era for plasmonics on the slope of enlightenment.

3 Results & Discussions

In this Paper, we report on a case study for plasmonics technology that could enable the next-generation data recording systems. In particular, we focus on the potential of refractory plasmonic materials as nanoantennas for field enhancement and local heating. Refractory plasmonic materials provide two unique properties: good plasmonic performance in the visible and near infrared regions, and durability at high temperatures.[76] Although the definition varies with the level of devoutness, we will use the term refractory to describe materials with melting points above 2000 ^{o}C. Mechanical hardness and chemical stability are other common features of refractory materials, while metals with refractory properties generally suffer from oxidation at high temperatures.[80] Thus, oxidation is considered as an exception to chemical inertness when classifying refractory metals. Self-passivation of the oxide slows down the process for bulk metals, but nanoscale structures are often too small to accommodate a protective oxide layer.

In contrast to structural deformations such as melting and creep that are usually encountered in the case of soft metals, oxidation of refractory plasmonic materials can be avoided with the integration of optically transparent materials with higher oxidation temperatures. Thus, for applications with extreme operational conditions, refractory plasmonic materials with comparable optical properties can replace noble metals,[81] with the help of optically transparent, oxidation resistant thin layers, and new technologies can be developed.

Refractory metals provide high melting temperatures and hardness along with metallic properties that imply their potential use for plasmonic applications. They have been the material of choice where metallic optical properties and high temperature stability are desired such as spectrally selective photonic crystal emitters for thermophotovoltaic devices.[82,83] However, for applications where enhanced interaction of a sub-wavelength structure with electromagnetic radiation is essential, the requirements go beyond the metallic behaviour and necessitate good plasmonic properties.[77] Although the metrics for a good plasmonic material are functions of a variety of parameters mostly depending on the application,[84] it is usually considered acceptable to reduce the formulation to simplified terms.[77,85] Here, we will limit the discussion to LSPR where nanoparticles are employed as sub-wavelength field enhancers. One such application which has been quite popular over the last few years is the heat assisted magnetic recording (HAMR).[86] In the HAMR approach, magnetic grains made of high coercivity materials, which require intense magnetic field to be written, are locally heated in order to facilitate the writing process. The requirement of a high coercivity material is simply a result of the motivation to achieve higher density data storage, which causes the use of smaller grains and introduces instabilities.[86] After the writing is accomplished at an elevated temperature, the grain is cooled down to lower temperatures where it can retain the data. It was initially proposed that local heating could be achieved under focused laser illumination.[87] Despite a successful demonstration, laser heating was naturally limited by the diffraction limit which resulted in a spot much larger than the sizes imposed by the dense storage motivation.

In order to achieve sub-wavelength focusing of electromagnetic radiation, plasmonic nanostructures can be used in the system as near field transducers (NFTs).[86] In this scenario, the excitation light is guided onto a plasmonic nanostructure with a resonance around 830 nm, where cost-effective diode lasers are available, and the enhanced near-field is used as a concentrated source of energy for local heating of the magnetic layer. Noble metals are the natural candidates for NFTs as they exhibit strong plasmonic oscillations in the visible region of the electromagnetic spectrum. Although the plasmonic properties of silver (Ag) are superior to Au, chemical instability and consequent performance degradation is a major concern for HAMR and many other applications. Therefore, owing to its chemical stability, Au was used as the plasmonic NFT material in the very first demonstrations of HAMR technology where the idea has been successfully demonstrated.[88,89] However, Au is a soft material with a relatively low bulk melting temperature which is further reduced due to the nanostructured geometries and sharpened edges required for better field confinement.[90] Although operational temperatures around 400 ^{o}C are required at the nanoscale near the magnetic grain, NFTs made of pure Au show degradation in mechanical properties at temperatures around 100 ^{o}C.[91] Mechanical instability of Au NFTs under conditions imposed by HAMR's operational principles has been one of the major problems which has slowed the progress towards a reliable product.[92] Among several methods to resolve the problem, alloying and doping of the plasmonic NFT material with a harder dopant, at the expense of lowered optical performance, have attracted attention.[91,93] Although the refractory metals can be used as the hard dopants to improve the mechanical properties of plasmonic metals, their use as the plasmonic NFT material has so far not been possible due to poor optical properties.

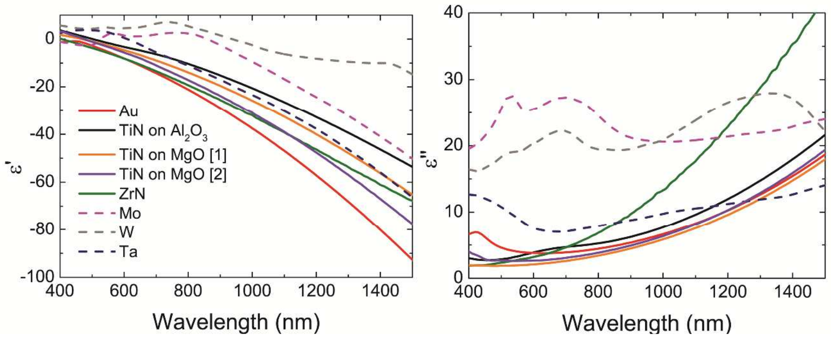

Fig. 2. Dielectric permittivities of refractory transition metal nitrides, refractory metals, and gold. Gold is given as a reference plasmonic material. Transition metal nitrides, which are refractory materials durable at high temperatures, exhibit optical properties similar to gold. Refractory metals, on the other hand, are plasmonic in the near infrared region and exhibit larger losses.

Transition metal nitrides are refractory materials with high melting points and mechanical hardness. They have been widely used as protective coatings in applications where mechanical strength is desired. In addition to their superior mechanical properties, it has been demonstrated that titanium nitride (TiN) and zirconium nitride (ZrN) exhibit plasmonic properties similar to Au, explaining their golden luster.[84,94,95] In fact, these materials have been used in imitation jewellery as a cheaper and more durable replacement to Au.[96] As a bio-compatible material, the use of TiN is common in bio-medical implants.[97,98] Consequently, TiN has been one of the most frequently used transition metal nitrides which has resulted in good understanding of the deposition techniques, including CMOS compatible processes.[99,100] The optical properties of transition metal nitrides strongly depend on the deposition conditions and can be optimized to nearly match the optical properties of Au. [84,101,102]

Figure 2 shows the real and imaginary parts of the dielectric permittivities of different metals along with transition metal nitrides. Gold is presented as a reference since it has been widely used as the plasmonic material in many applications, including HAMR demonstrations. Here we use permittivities experimentally retrieved from Au thin films deposited on a sapphire substrate as described elsewhere.[95] Although the bulk permittivities reported by Johnson and Christy are frequently used in comparison tables, in practice, thins films of metals exhibit optical properties inferior to bulk values.[103] Transition metal nitride films were also experimentally retrieved from thin films deposited on sapphire and MgO substrates while the permittivities of refractory metals were taken from tabulated data.[77,95,104] Not surprisingly, the magnitude of the real part (ε') is largest for the case of Au. In addition, the imaginary part of the permittivity (ε'') is also one of the smallest among the materials listed. The use of Au as the NFT material would be unquestionable if the plasmonic properties were the only concern. However, as stated earlier, the ductility of Au prevents the use of the material for a long period without further processing which degrades its optical properties. On the other hand, refractory metals, which would naturally resolve many issues related to material deformations, do not exhibit plasmonic properties in the spectral region of interest. Tungsten (W) and molybdenum (Mo) are barely plasmonic in the infrared region, however their permittivities are positive in the visible. Tantalum (Ta), on the other hand, has a permittivity zero cross-over near 610 nm, making the material plasmonic around HAMR operational wavelengths. However, the imaginary part of the permittivity is still significantly higher that Au, although it is much smaller than other refractory metals. For the case of transition metal nitrides, the optical properties are closer to plasmonic metals – representing a significant opportunity to resolve the complications arising due to harsh operational environment. Both ε' and ε'' values of ZrN are very close to Au, especially in the visible region, making it a potential candidate to replace noble metals. Figure 2 presents three different TiN data retrieved from samples grown on sapphire and MgO. Sapphire supports local epitaxial growth of TiN and reduces the losses in the film while MgO provides even better lattice matching, leading to an even higher quality epitaxial thin film. Titanium nitride films grown on sapphire substrates have a negative permittivity in the visible region and a loss factor in the same range as the Au film. Thin films of TiN deposited on MgO substrates exhibit plasmonic properties better than the sample grown on sapphire and losses even smaller than the Au film.

The figure of merit (FOM) of a plasmonic nanostructure totally depends on the specific application in mind.[77] The high level of interest in identifying proper plasmonic materials has resulted in a comprehensive collection of reports comparing different material classes for metamaterial, transformation optics, superlens, surface plasmon polariton and LSPR applications.[77,105-107] The general consensus for LSPR applications is to set the ratio of the real and imaginary parts of the dielectric permittivity of a plasmonic material as a FOM.[77,105-107] For a nanoparticle in the quasistatic limit, when the size of the particle is very small compared to the wavelength, the FOM can be conveniently defined as ε'/ε'' where the real part of permittivity implies a good resonator and the imaginary part represents the loss factor. However, as the particle size becomes comparable to the wavelength of the incident light, the quasistatic approximation loses its validity, and so does the FOM. A straight modification to increase the accuracy of the FOM is to include the size factor which would take into account missing effects such as the existence of the higher order modes, interference effects arising from the multi-modal system, penetration depth of the excitation light through the nanoparticle, etc. In addition, even for the case of a single field such as LSPR, there are a variety of operational modes which require different features such as maximized absorption in the particle and subsequent efficient local heating or hot electron generation,[11,108] enhanced field in the near zone for energy confinement,[59,109] or scattering to far zone for several other applications.[110,111] Previously we have shown that a more comprehensive, yet still convenient, FOM for LSPR applications is the optical cross-section which can be obtained through the Mie formalism.[84] Comparison between the scattering efficiencies of transition metal nitrides and Au shows that the field enhancement at the surface, or at an infinite distance from the particle, for TiN and ZrN are indeed comparable to Au when the nanoparticles are out of the quasistatic regime.[84] Here, we will follow the general consensus and apply the simplified FOM with the quasistatic approximation to compare the LSPR efficiencies of transition metal nitrides, refractory metals, and Au, which is the reference material due to its wide use in the field. In HAMR technology, an NFT is expected to focus electromagnetic energy to a confined volume in the magnetic layer with minimal loss in the plasmonic particle itself. We note that recently reported comparisons between transition metal nitrides and Au employed the FOM in the quasistatic approximation and TiN's optical properties that were not yet optimized for plasmonic applications.[85,112]

Table 1. Permittivity values for refractory metals, refractory transition metal nitrides, and gold at 830 nm. The figure of merit is defined in the quasistatic regime. Titanium nitride samples grown on MgO substrate outperform other refractory materials and become prominent for high temperature plasmonic applications in the visible and near infrared spectrum.

Material	Permittivity (real)	Permittivity (imaginary)	FOM (|ε'|/ε'')
Au	-23.39	4.67	5.01
TiN (Al_2O_3)	-11.73	5.47	2.14
TiN (MgO) [1]	-15.57	3.68	4.23
TiN (MgO) [2]	-19.08	4.11	4.64
ZrN	-21.15	7.64	2.77
Mo	1.43	23.16	NA
W	4.21	19.41	NA
Ta	-12.89	8.15	1.58

Table 1 shows the dielectric permittivity values for gold, refractory metals, and refractory transition metal nitrides at 830 nm wavelength. Dielectric permittivities retrieved for TiN thin films deposited on c-sapphire and MgO substrates are given to illustrate the variation of the optical properties based on the deposition parameters, (and hence, crystallinity and the amount of defects) and their effect on the FOM. It should be noted that the comparison of real part to imaginary part is reasonable due to the fact that i) the real part illustrates the resonator properties which determines the field enhancement, and ii) the imaginary part factors in the losses which degrade the resonance and increase the internal heating of the NFT, an undesired effect.[85] Table 1 shows that the experimental data retrieved from the Au thin film deposited on sapphire substrate has the best FOM among all samples. The TiN film deposited on sapphire has a FOM value of 2.14 which is less than half of the Au film, but still better than the previously reported FOM values for TiN.[112] When grown on MgO, TiN films with enhanced optical properties can be achieved due to the better lattice matching between the film and the substrate which promotes epitaxial growth.[102] The TiN samples deposited on MgO have FOMs significantly larger than that of the TiN sample grown on sapphire, values very close to Au. Zirconium nitride has a large normalized real permittivity, however the FOM value is degraded due to large losses. Refractory metals, on the other hand, are either not plasmonic in the spectral region of interest, or exhibit very poor properties, ruling them out for LSPR applications in the visible and near infrared region of the electromagnetic spectrum.

According to the FOM values given in table 1, TiN thin films grown on MgO substrates exhibit plasmonic properties close to Au, with only 16 % and 7 % reduction in the optical FOM. However, as a refractory plasmonic material, TiN possesses material properties such as hardness, a high melting point, CMOS-compatibility, and chemical stability that are of significant importance for applications that require extreme operational conditions. Heat assisted magnetic recording, for example, is one such application that employs plasmonic elements successfully, but suffers from ductile material limitations.[92]

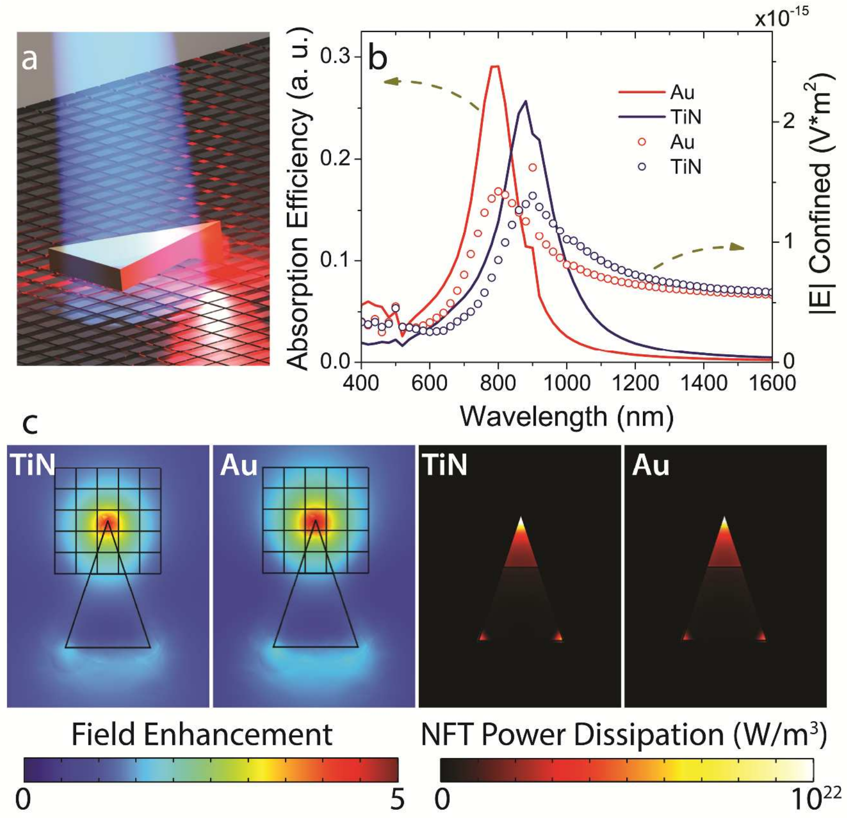

Fig. 3. (a) Illustration of a "nanobeak antenna" design used in simulations where titanium nitride and gold are compared. (b) The absorption efficiencies of gold and titanium nitride nanobeak antennas and corresponding electric field magnitude |E| confined in a 25 x 25 x 10 nm^3 volume in the dielectric layer 5 nm below the antenna tip. Dashed arrows indicate the corresponding scale. (c) Electric field magnitude |E| in the dielectric layer and heat dissipation density inside the nanoantennas for the peak wavelengths of each material; 880 nm for TiN and 800 nm for gold. Permittivity values are taken from the sample: TiN on MgO [1], as given in figure 2.

Figure 3 shows FEM simulation results for a "nanobeak antenna" that was previously suggested as an efficient design for near-field generation for HAMR.[113] Here we use this design in order to take a step further in the comparison between TiN and Au. Although the TiN film on MgO substrate labelled with [2] has a better FOM, we proceed with the data from the sample [1] in our simulations. The calculated absorption efficiencies of the same antenna made of Au and TiN (sample on MgO [1]), and the corresponding electric field enhancement in a dielectric layer located 5 nm below the NFT are given in Fig. 3(b). Due to the compact design of the NFT and magnetic head, overheating of the plasmonic antenna is an undesired side effect of local heating for HAMR devices.[114-117]

Heat generation inside the plasmonic antenna is a direct result of the absorption of the electromagnetic energy.[118] Thus, for an NFT design, large field enhancement in the magnetic medium is desired while the absorption inside the antenna should be kept minimal. Calculations show that the identical "nanobeak" design with Au and TiN gives comparable field enhancement in the magnetic grain and absorption in the antenna. This result is in agreement with the FOM values given in Table 1 for the quasistatic regime. Figure 3 (c) shows the electric field enhancement in a dielectric layer located 5 nm below the tip of the "nanobeak" antenna. The enhanced field peak is confined within a 25 x 25 nm^2 area for both TiN and Au antennas. Power dissipation densities inside the antennas are concentrated at the corners, as expected, which illustrates the importance of material durability on the nanometer scale. Calculation results presented in figure 3 clearly indicates that a TiN NFT would generate heating in a very similar way as a Au NFT does. In addition to comparable optical properties, TiN offers hardness and high temperature durability. In fact, TiN is already a material of interest as a diffusion barrier between the NFT and the magnetic lip.[119] Therefore, a TiN NFT is a reliable solution to multiple high temperature based problems.

Refractory metals are defined chemically stable at high temperatures, but the oxidation at elevated temperatures is always an exception.[80] This is a problem for transition metal nitrides as well.[120] A self-passivating thin native oxide of thickness around 1-2 nm is present at the surface of TiN at room temperatures. Two stages of oxidation, so called as initial and normal stages, were observed with an order of magnitude difference in rate constants.[121] Further investigation revealed that the TiO_2 changes from amorphous to crystalline in time, and faster with higher temperatures.[122] For the case of plasmonic applications, where subwavelength nanostructures are the building blocks, the effects of even a thin oxide layer on the performance of the plasmonic component would be significant. The temperatures at which oxidation starts to play a significant role are in the range where plasmonic NFTs in HAMR devices operate (~500 °C).[85] Fortunately, the oxidation is easier to handle compared to other structural problems arising from the softness of Au.[120] Here, we suggest an optically transparent, thin overcoat as an oxidation barrier which provides long term durability at elevated temperatures.[120] Dielectric ceramics are natural candidates as oxidation resistant protective layers over plasmonic transition metal nitrides. Figure 4 shows reflectance measurements and numerical simulations for thin TiN films grown on a c-sapphire substrate. An overcoat layer with 10 nm thickness is applied as an oxidation resistant barrier. Figure 4 (a) shows the reflectance measurements of a bare TiN film and a sample with a dielectric overcoat. The bare film reflectance matches well with the simulation where a 2 nm native oxide is included. Figure 4(b) shows the reflectance data for the protected sample after exposure to high temperatures in air for several hours. The sample was cooled down to room temperature after each treatment for optical measurement and heated up to the next level for further testing. The measurements show that the film retains its optical properties at least up to 525 ^{o}C which is at the upper limits of proposed HAMR operational temperatures. Figure 4(c) shows the reflectance data of the bare TiN film before and after exposure to 375 and 425 °C in air. The optical properties of the sample degrade significantly due to oxidation. Simulation results given in figure 4(d) takes the oxide layer into account and matches well with the experimental data. For the case of 425 °C heating, the intensity of the simulated dip shows a deviation from the experimental data likely due to an intermediate oxynitride formed between the oxide and nitride due to oxygen diffusion and nitrogen displacement. Further discussion on the effect was studied earlier by Saha and Tompkins. [122]

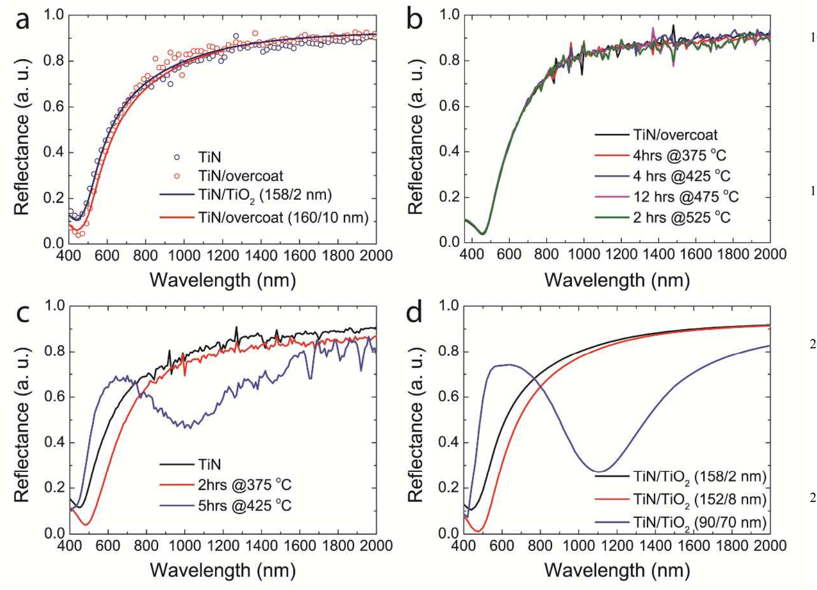

Fig. 4. (a) Reflectance measurements and simulations for TiN thin films with and without an overcoat. (b) Sample with dielectric overcoat shows significant resistance against oxidation. (c) Bare TiN thin films oxidize at temperatures above 350 °C which causes severe degradation of optical properties. (d) Changes in the optical properties with increasing temperature can be replicated in simulations by introducing oxide layers with increasing thicknesses.

Conclusions

The field of plasmonics is facing challenges due to materials' limitations. However, we believe that this research field is now entering its technology-driven enlightenment period, exploring alternative materials for application-specific needs and new device concepts. Novel material platforms such as semiconductors, 2D materials, phase-changing and ceramic materials mark a new era for plasmonics and are expected to bring advancements to various photonic technologies such as information and communications, imaging and sensing, healthcare, energy, manufacturing, and national security. Among many plasmonic materials, transition metal nitrides are particularly appealing because they exhibit good plasmonic properties along with excellent refractory characteristics and thus, they could perform well when noble metals fail because of their softness and low melting points. In this work, we take heat assisted magnetic recording as one of the important examples of high temperature plasmonic applications and compare the properties of refractory transition metal nitrides, refractory metals, and gold. Simulation results show that titanium nitride can perform very similar, in terms of its plasmonic properties, to gold but provides indispensable advantages due to its excellent refractory characteristics. We also show that the oxidation of titanium nitride at high temperatures can be fully avoided through the use of optically transparent, thin ceramic overcoats. Therefore, we believe that refractory plasmonic transition metal nitrides are the key to next generation durable, compact photonic devices. Our findings directly impact the technology of heat-assisted magnetic recording for data storage and could provide harsh-environment capable solutions for the defense, intelligence, information technology, aerospace, energy, and oil & gas industries.

Acknowledgements

The authors acknowledge generous support from NSF SBIR grant IIP-1416232, ONR MURI grant N00014-10-1-0942, and NSF MRSEC grant DMR-1120923. We would like to thank Nathaniel Kinsey for his help in preparation of this manuscript.

References

1. M. Faraday, *Philosophical Transactions of the Royal Society of London*, 1857, **147**, 145-181.
2. W. L. Barnes, A. Dereux and T. W. Ebbesen, *Nature*, 2003, **424**, 824-830.
3. E. Ozbay, *Science*, 2006, **311**, 189-193.
4. H. A. Atwater, *Sci Am*, 2007, **296**, 56-63.
5. S. A. Maier, *Plasmonics: Fundamentals and Applications*, Springer, 2007.
6. S. Lal, S. Link and N. J. Halas, *Nat Photon*, 2007, **1**, 641-648.
7. J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White and M. L. Brongersma, *Nat Mater*, 2010, **9**, 193-204.
8. D. K. Gramotnev and S. I. Bozhevolnyi, *Nat Photon*, 2010, **4**, 83-91.
9. V. J. Sorger, R. F. Oulton, R.-M. Ma and X. Zhang, *MRS Bull.*, 2012, **37**, 728-738
M723 - 710.1557/mrs.2012.1170.
10. M. Kauranen and A. V. Zayats, *Nat Photon*, 2012, **6**, 737-748.
11. G. Baffou and R. Quidant, *Laser Photonics Rev.*, 2013, **7**, 171-187.
12. C. J. Powell and J. B. Swan, *Physical Review*, 1959, **115**, 869-875.
13. M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander and N. J. Halas, *ACS Nano*, 2013, **8**, 834-840.
14. G. H. Chan, J. Zhao, E. M. Hicks, G. C. Schatz and R. P. Van Duyne, *Nano Lett.*, 2007, **7**, 1947-1952.
15. G. H. Chan, J. Zhao, G. C. Schatz and R. P. V. Duyne, *The Journal of Physical Chemistry C*, 2008, **112**, 13958-13963.
16. U. Guler and R. Turan, *Opt Express*, 2010, **18**, 17322-17338.
17. M. D. McMahon, R. Lopez, H. M. Meyer, III, L. C. Feldman and R. F. Haglund, Jr., *Appl. Phys. B*, 2005, **80**, 915-921.
18. A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman and T. P. Bigioni, *Nature*, 2013, **501**, 399-402.
19. G. A. Sotiriou, G. D. Etterlin, A. Spyrogianni, F. Krumeich, J.-C. Leroux and S. E. Pratsinis, *Chem. Commun.*, 2014.

20. M. G. Blaber, M. D. Arnold, N. Harris, M. J. Ford and M. B. Cortie, *Physica B*, 2007, **394**, 184-187.
21. J. Fenn and M. Raskino, *Mastering the Hype Cycle: How to Choose the Right Innovation at the Right Time*, Harvard Business Press, 2008.
22. I. Freestone, N. Meeks, M. Sax and C. Higgitt, *Gold Bull.*, 2007, **40**, 270-277.
23. G. Mie, *Ann. Phys.*, 1908, **330**, 377-445.
24. J. C. M. Garnett, *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character*, 1904, **203**, 385-420.
25. Y.-Y. Teng and E. A. Stern, *Phys. Rev. Lett.*, 1967, **19**, 511-514.
26. M. Fleischmann, P. J. Hendra and A. J. McQuillan, *Chem. Phys. Lett.*, 1974, **26**, 163-166.
27. D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **84**, 1-20.
28. M. Moskovits, *The Journal of Chemical Physics*, 1978, **69**, 4159-4161.
29. M. Moskovits, *Notes and Records of the Royal Society*, 2012, **66**, 195-203.
30. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio and P. A. Wolff, *Nature*, 1998, **391**, 667-669.
31. J. B. Pendry, *Phys. Rev. Lett.*, 2000, **85**, 3966-3969.
32. L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, B. Rivera, R. E. Price, J. D. Hazle, N. J. Halas and J. L. West, *Proceedings of the National Academy of Sciences*, 2003, **100**, 13549-13554.
33. C. Loo, A. Lin, L. Hirsch, M. H. Lee, J. Barton, N. Halas, J. West and R. Drezek, *Technol Cancer Res Treat*, 2004, **3**, 33-40.
34. A. M. Gobin, M. H. Lee, N. J. Halas, W. D. James, R. A. Drezek and J. L. West, *Nano Lett.*, 2007, **7**, 1929-1934.
35. P. D. Howes, R. Chandrawati and M. M. Stevens, *Science*, 2014, **346**.
36. R. F. Oulton, V. J. Sorger, D. A. Genov, D. F. P. Pile and X. Zhang, *Nat Photon*, 2008, **2**, 496-500.
37. A. Boltasseva and H. A. Atwater, *Science*, 2011, **331**, 290-291.
38. R. Zia, J. A. Schuller, A. Chandran and M. L. Brongersma, *Mater. Today*, 2006, **9**, 20-27.
39. M. L. Brongersma and V. M. Shalaev, *Science*, 2010, **328**, 440-441.
40. S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, J.-Y. Laluet and T. W. Ebbesen, *Nature*, 2006, **440**, 508-511.
41. T. W. Ebbesen, C. Genet and S. I. Bozhevolnyi, *Phys. Today*, 2008, **61**, 44.
42. R. Charbonneau, C. Scales, I. Breukelaar, S. Fafard, N. Lahoud, G. Mattiussi and P. Berini, *J. Lightwave Technol.*, 2006, **24**, 477.
43. A. Silva, F. Monticone, G. Castaldi, V. Galdi, A. Alù and N. Engheta, *Science*, 2014, **343**, 160-163.
44. P. Berini and I. De Leon, *Nat Photon*, 2012, **6**, 16-24.
45. J. R. Krenn, M. Salerno, N. Felidj, B. Lamprecht, G. Schider, A. Leitner, F. R. Aussenegg, J. C. Weeber, A. Dereux and J. P. Goudonnet, *Journal of Microscopy*, 2001, **202**, 122-128.
46. K. F. MacDonald, Z. L. Samson, M. I. Stockman and N. I. Zheludev, *Nat Photon*, 2009, **3**, 55-58.
47. A. G. Curto, G. Volpe, T. H. Taminiau, M. P. Kreuzer, R. Quidant and N. F. van Hulst, *Science*, 2010, **329**, 930-933.
48. M. Abb, P. Albella, J. Aizpurua and O. L. Muskens, *Nano Lett.*, 2011, **11**, 2457-2463.
49. M. Staffaroni, J. Conway, S. Vedantam, J. Tang and E. Yablonovitch, *Photonics Nanostruct. Fundam. Appl.*, 2012, **10**, 166-176.

50. H. R. Stuart and D. G. Hall, *Appl. Phys. Lett.*, 1998, **73**, 3815-3817.
51. D. M. Schaadt, B. Feng and E. T. Yu, *Appl. Phys. Lett.*, 2005, **86**, -.
52. D. Derkacs, S. H. Lim, P. Matheu, W. Mar and E. T. Yu, *Appl. Phys. Lett.*, 2006, **89**, -.
53. H. A. Atwater and A. Polman, *Nat Mater*, 2010, **9**, 205-213.
54. A. Polman and H. A. Atwater, *Nat Mater*, 2012, **11**, 174-177.
55. D. J. Bergman and M. I. Stockman, *Phys. Rev. Lett.*, 2003, **90**, 027402.
56. M. I. Stockman, *Nat Photon*, 2008, **2**, 327-329.
57. N. I. Zheludev, S. L. Prosvirnin, N. Papasimakis and V. A. Fedotov, *Nat Photon*, 2008, **2**, 351-354.
58. E. Plum, V. A. Fedotov, P. Kuo, D. P. Tsai and N. I. Zheludev, *Opt. Express*, 2009, **17**, 8548-8551.
59. M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong and U. Wiesner, *Nature*, 2009, **460**, 1110-1112.
60. J. B. Khurgin and G. Sun, *Appl. Phys. Lett.*, 2010, **96**, 181102-181102-181103.
61. D. Pile(Interviewer) and J. Krenn(Interviewee), *Nat Photon*, 2012, **6**, 714-715.
62. V. G. Veselago, *Soviet Physics Uspekhi*, 1968, **10**, 509.
63. R. A. Shelby, D. R. Smith and S. Schultz, *Science*, 2001, **292**, 77-79.
64. V. M. Shalaev, W. Cai, U. K. Chettiar, H.-K. Yuan, A. K. Sarychev, V. P. Drachev and A. V. Kildishev, *Opt. Lett.*, 2005, **30**, 3356-3358.
65. J. B. Pendry, D. Schurig and D. R. Smith, *Science*, 2006, **312**, 1780-1782.
66. U. Leonhardt, *Science*, 2006, **312**, 1777-1780.
67. O. Neumann, A. S. Urban, J. Day, S. Lal, P. Nordlander and N. J. Halas, *ACS Nano*, 2012, **7**, 42-49.
68. S. Linic, P. Christopher and D. B. Ingram, *Nat Mater*, 2011, **10**, 911-921.
69. S. Mubeen, J. Lee, W.-r. Lee, N. Singh, G. D. Stucky and M. Moskovits, *ACS Nano*, 2014, **8**, 6066-6073.
70. M. L. Brongersma, Y. Cui and S. Fan, *Nat Mater*, 2014, **13**, 451-460.
71. K. M. Goodfellow, R. Beams, C. Chakraborty, L. Novotny and A. N. Vamivakas, *Optica*, 2014, **1**, 149-152.
72. N. P. de Leon, M. D. Lukin and H. Park, *Selected Topics in Quantum Electronics, IEEE Journal of*, 2012, **18**, 1781-1791.
73. F. J. García de Abajo, *Science*, 2013, **339**, 917-918.
74. P. Alonso-González, A. Y. Nikitin, F. Golmar, A. Centeno, A. Pesquera, S. Vélez, J. Chen, G. Navickaite, F. Koppens, A. Zurutuza, F. Casanova, L. E. Hueso and R. Hillenbrand, *Science*, 2014, **344**, 1369-1373.
75. N. Strohfeldt, A. Tittl, M. Schäferling, F. Neubrech, U. Kreibig, R. Griessen and H. Giessen, *Nano Lett.*, 2014, **14**, 1140-1147.
76. U. Guler, A. Boltasseva and V. M. Shalaev, *Science*, 2014, **344**, 263-264.
77. G. V. Naik, V. M. Shalaev and A. Boltasseva, *Adv Mater*, 2013, **25**, 3264-3294.
78. C. Langhammer, M. Schwind, B. Kasemo and I. Zorić, *Nano Lett.*, 2008, **8**, 1461-1471.
79. A. Frölich and M. Wegener, *Opt. Mater. Express*, 2011, **1**, 883-889.
80. H. O. Pierson, *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps*, William Andrew, Incorporated, 1996.
81. W. Li, U. Guler, N. Kinsey, G. V. Naik, A. Boltasseva, J. Guan, V. M. Shalaev and A. V. Kildishev, *Adv. Mater.*, 2014, 10.1002/adma.201401874.
82. V. Rinnerbauer, Y. X. Yeng, W. R. Chan, J. J. Senkevich, J. D. Joannopoulos, M. Soljacic and I. Celanovic, *Opt. Express*, 2013, **21**, 11482-11491.

83. K. A. Arpin, M. D. Losego, A. N. Cloud, H. Ning, J. Mallek, N. P. Sergeant, L. Zhu, Z. Yu, B. Kalanyan, G. N. Parsons, G. S. Girolami, J. R. Abelson, S. Fan and P. V. Braun, *Nat Commun*, 2013, **4**.

84. U. Guler, G. V. Naik, A. Boltasseva, V. M. Shalaev and A. V. Kildishev, *Appl. Phys. B*, 2012, **107**, 285-291.

85. N. Zhou, X. Xu, T. Hammack Aaron, C. Stipe Barry, K. Gao, W. Scholz and C. Gage Edward, *Nanophotonics*, 2014, **3**, 141-155.

86. M. H. Kryder, E. C. Gage, T. W. McDaniel, W. A. Challener, R. E. Rottmayer, G. Ju, Y.-T. Hsia and M. F. Erden, *Proc. IEEE*, 2008, **96**, 1810-1835.

87. W. Challener, C. Mihalcea, C. Peng and K. Pelhos, *Opt. Express*, 2005, **13**, 7189-7197.

88. W. Challener, C. Peng, A. Itagi, D. Karns, W. Peng, Y. Peng, X. Yang, X. Zhu, N. Gokemeijer and Y.-T. Hsia, *Nat. Photonics*, 2009, **3**, 220-224.

89. B. C. Stipe, T. C. Strand, C. C. Poon, H. Balamane, T. D. Boone, J. A. Katine, J.-L. Li, V. Rawat, H. Nemoto, A. Hirotsune, O. Hellwig, R. Ruiz, E. Dobisz, D. S. Kercher, N. Robertson, T. R. Albrecht and B. D. Terris, *Nat Photon*, 2010, **4**, 484-488.

90. Q. Jiang, S. Zhang and M. Zhao, *Mater. Chem. Phys.*, 2003, **82**, 225-227.

91. T. Zhao, M. C. Kautzky, W. A. Challener and M. A. Seigler, Google Patents, 2013.

92. N. C. Lindquist, J. Jose, S. Cherukulappurath, X. Chen, T. W. Johnson and S.-H. Oh, *Laser Photonics Rev.*, 2013, **7**, 453-477.

93. *United States Pat.*, 20120127839, 2012.

94. G. V. Naik, J. L. Schroeder, X. Ni, A. V. Kildishev, T. D. Sands and A. Boltasseva, *Opt. Mater. Express*, 2012, **2**, 478-489.

95. U. Guler, J. C. Ndukaife, G. V. Naik, A. G. A. Nnanna, A. V. Kildishev, V. M. Shalaev and A. Boltasseva, *Nano Lett.*, 2013, **13**, 6078-6083.

96. *United States Pat.*, 4589917, 1986.

97. A. Wisbey, P. J. Gregson and M. Tuke, *Biomaterials*, 1987, **8**, 477-480.

98. S. Dong, X. Chen, L. Gu, L. Zhang, X. Zhou, Z. Liu, P. Han, H. Xu, J. Yao, X. Zhang, L. Li, C. Shang and G. Cui, *Biosens. Bioelectron.*, 2011, **26**, 4088-4094.

99. T. E. Tang, W. Che-Chia, R. A. Haken, T. C. Holloway, L. R. Hite and T. G. W. Blake, *Electron Devices, IEEE Transactions on*, 1987, **34**, 682-688.

100. H. Wakabayashi, Y. Saito, K. Takeuchi, T. Mogami and T. Kunio, *Electron Devices, IEEE Transactions on*, 2001, **48**, 2363-2369.

101. G. V. Naik, J. Kim and A. Boltasseva, *Opt. Mater. Express*, 2011, **1**, 1090-1099.

102. G. V. Naik, B. Saha, J. Liu, S. M. Saber, E. A. Stach, J. M. K. Irudayaraj, T. D. Sands, V. M. Shalaev and A. Boltasseva, *Proceedings of the National Academy of Sciences*, 2014.

103. W. Chen, M. D. Thoreson, S. Ishii, A. V. Kildishev and V. M. Shalaev, *Opt. Express*, 2010, **18**, 5124-5134.

104. X. Ni, Z. Liu and A. V. Kildishev, nanohub.org/resources/3692, 2008.

105. P. R. West, S. Ishii, G. V. Naik, N. K. Emani, V. M. Shalaev and A. Boltasseva, *Laser Photonics Rev.*, 2010, **4**, 795-808.

106. M. G. Blaber, M. D. Arnold and M. J. Ford, *J. Phys. Condens. Matter*, 2010, **22**, 143201.

107. M. G. Blaber, M. D. Arnold and M. J. Ford, *The Journal of Physical Chemistry C*, 2009, **113**, 3041-3045.

108. C. Clavero, *Nat Photon*, 2014, **8**, 95-103.

109. V. M. Shalaev, *AIP Conference Proceedings*, 2001, **560**, 237-258.

110. E. Stratakis and E. Kymakis, *Mater. Today*, 2013, **16**, 133-146.

111. R. Bardhan, S. Lal, A. Joshi and N. J. Halas, *Acc. Chem. Res.*, 2011, **44**, 936-946.

112. *United States Pat.*, 20130279315, 2013.
113. T. Matsumoto, K. Nakamura, T. Nishida, H. Hieda, A. Kikitsu, K. Naito and T. Koda, *Appl. Phys. Lett.*, 2008, **93**, 031108.
114. S. Xiong, J. Kim, Y. Wang, X. Zhang and D. Bogy, *J. Appl. Phys.*, 2014, **115**, 17B702.
115. S. Bhargava and E. Yablonovitch, Proc. SPIE, 9201, 2014.
116. X. Baoxi, T. Yeow Teck, C. Cheow Wee, L. Jianming, Z. Jing, Y. Kaidong and A. Chengwu, *Magnetics, IEEE Transactions on*, 2012, **48**, 1789-1793.
117. B. X. Xu, Z. J. Liu, R. Ji, Y. T. Toh, J. F. Hu, J. M. Li, J. Zhang, K. D. Ye and C. W. Chia, *J. Appl. Phys.*, 2012, **111**, -.
118. A. O. Govorov and H. H. Richardson, *Nano Today*, 2007, **2**, 30-38.
119. J. A. Katine, V. P. S. Rawat, N. L. Robertson and B. C. Stipe, Google Patents, 2013.
120. *WO Pat.*, PCT/US14/38561.
121. H. G. Tompkins, *J. Appl. Phys.*, 1992, **71**, 980-983.
122. N. C. Saha and H. G. Tompkins, *J. Appl. Phys.*, 1992, **72**, 3072-3079.