Hot carrier optoelectronics with titanium nitride

Brock Doiron[1], Nicholas A. Güsken[1], Alberto Lauri[1], Yi Li[1], Andrei Mihai[2], Takayuki Matsui[1], Ryan Bower[2], Ludwig Huettenhoffer[3], Anna Regoutz[2], Stefano Dal Forno[2], Sarah Fearn[2], Peter K. Petrov[2], Emiliano Cortés[1,3], Lesley F. Cohen[1], Neil M. Alford[2], Johannes Lischner[2], Peter Petrov[2], Stefan A. Maier[1,3], Rupert F. Oulton[1]*

1 The Blackett Laboratory, Department of Physics, Imperial College London, London SW7 2AZ, United Kingdom.
2 Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom.
3 Hybrid Nanosystems Institute, Fakultät für Physik, Ludwig-Maximilians-Universität, 80799 München, Germany.
* r.oulton@imperial.ac.uk

Abstract: Titanium oxynitride enables a range of plasmonic and optoelectronic functionality using long-lived photo-generated hot carriers. We explore the time scale of hot carriers in TiN and their use in photochemical reduction and Schottky detectors.

OCIS codes: (250.0040) Detectors; (240.6670) Surface Photochemistry; (320.7130) Ultrafast Processes in Condensed Matter; (160.3900) Metals.

Plasmonic devices allow unprecedented control of light on the nanoscale [1] and highly-sensitive molecular detection [2] through the increased interaction between a conductor's free carriers and light via surface plasmon resonances. Although plasmonic modes decay on the order of tens of femtoseconds [3], much of the energy remains in excited carriers that relax ultimately through lattice interactions over picosecond timescales. Exploiting the energy that remains in these carriers has evolved into so-called 'hot-carrier' applications. Due to the low absorption of gold in the red and infrared, nanoparticles are needed to enhance absorption but this comes at the cost of more expensive fabrication. Transition metal nitrides provide an advantage in such situations due to their strong broadband absorption [4] as well as the ability to tune their electronic and optical properties by deposition conditions [5].

Titanium nitride (TiN) is a ceramic with tunable stoichiometry and is known to have a high free carrier density such that it exhibits optical properties similar to gold in the visible and near-infrared regimes [6]. Additionally, titanium nitride has been shown to achieve enhanced hot electron harvesting relative to gold, [7,8] and indeed is reported to have long-lived hot carriers [9], although the physical origin of this phenomenon is poorly understood. TiN is also expected to be resilient to high operating temperatures [10]. The physical properties of TiN are extremely sensitive to the substitution of oxygen within its lattice, enabling also the tuning of its optical response. Previously we have shown that titanium oxynitride (TiON) films exhibit intermediate properties between titanium nitride and titanium dioxide, including the emergence of two tunable epsilon near zero (ENZ) points [11].

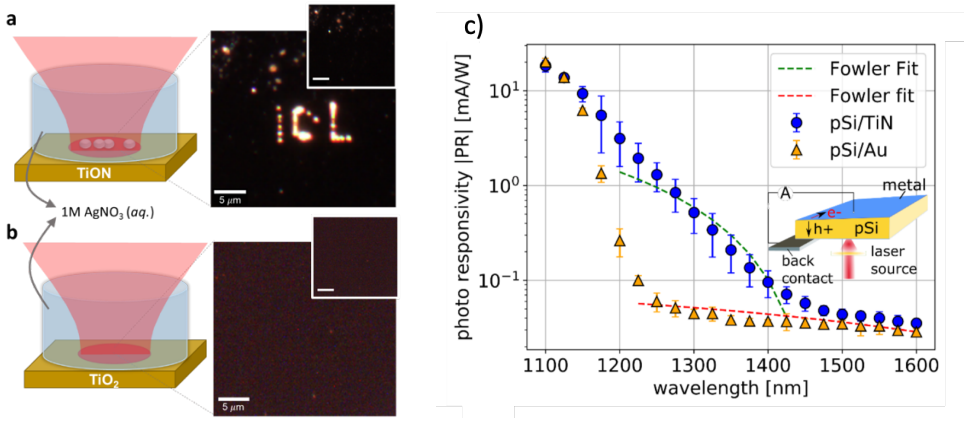

Fig. 1: (a) Diagram illustrating silver reduction mechanism where free carriers created via optical absorption in titanium oxynitride populate the TiO_2 surface oxide layer and reduce Ag+ ions from solution, which leads to nucleation of Ag colloids on the film surface. Inset shows dark field images of the titanium oxynitride surface immersed in the Ag solution prior to laser illumination. Selective formation of silver clusters on the surface of the film under laser-excitation is clearly seen. (b) Diagram and dark-field images for the same experiment but using only a TiO_2 film as substrate. c) Responsivities of Au/p-Si and TiON/p-Silicon Schottky detectors.

In this work, we compare the electron extraction efficiency across Au/TiO2 and titanium oxynitride/TiO2-x interfaces, where in the latter case the spontaneously forming oxide layer (TiO2-x) creates a metal-semiconductor contact. Time-resolved pump-probe spectroscopy is used to study the electron recombination rates in both cases

[12,13]. Unlike the nanosecond recombination lifetimes in Au/TiO2, we find a bottleneck in the electron relaxation in the TiON system, which we explain using a trap-mediated recombination model. We thus investigate the tunability of the relaxation dynamics with oxygen content in the parent film. An optimized film ($TiO_{0.5}N_{0.5}$) exhibits the highest carrier extraction efficiency ($N_{FC} \approx 2.8 \times 10^{19}\ m^{-3}$), slowest trapping and largest hot electron population reaching the surface oxide ($N_{HE} \approx 1.6 \times 10^{18}\ m^{-3}$). To demonstrate hot carrier generation at the TiO_2 surface, we also show direct photochemical reduction of Silver ions on TiON thin films (Fig. 1a,b). Our results demonstrate the productive role oxygen can play in enhancing electron harvesting and elongating electron lifetimes of titanium oxynitride.

We have also considered titanium nitride (TiN) thin film coatings on silicon for CMOS-compatible sub-bandgap photo-detection [14]. Here the titanium nitride serves as an adjustable broadband light absorber with high mechanical robustness and strong chemical resistivity. Backside illuminated TiN on p-type Si (pSi) constitutes a self-powered and refractory alternative for photodetection providing a photo responsivity of about ~1 mA/W at 1250 nm and zero bias while outperforming conventional metal coatings such as gold (Au). Our study discloses that the enhanced photo response of TiN/pSi in the near infra- red (IR) spectral range is directly linked to the trap states in the TiO2-x interfacial interlayer, which forms between TiN and Si. We show that a pSi substrate in conjunction with a few nm thick amorphous TiO2-x film can serve as a platform for photo current enhancement of various other metals such as Au and Ti. Moreover, the photoresponse of Au on a TiO2-x/pSi platform can be increased to about 4 mA/W under 0.45 V reverse bias at 1250 nm, allowing for controlled photo switching. A clear deviation from the typically assumed Fowler-like response is observed and an alternative mechanism is proposed to account for the metal/semiconductor TiO2-x interlayer, capable of facilitating hole transport.

References:

[1] Gramotnev, D. K. & Bozhevolnyi, S. I. "Plasmonics beyond the diffraction limit" Nat. Photonics 4, 83–91 (2010).

[2] Anker, J. N. et al. "Biosensing with plasmonic nanosensors" Nat. Mater. 7, 442–453 (2008).

[3] Anderson, A., Deryckx, K. S., Xu, X. G., Steinmeyer, G. & Raschke, M. B. "Few-femtosecond plasmon dephasing of a single metallic nanostructure from optical response function reconstruction by interferometricfrequency resolved optical gating. Nano Lett. 10, 2519–2524 (2010).

[4] Li, W. et al. "Refractory plasmonics with titanium nitride" Adv. Mater. 26, 7959 (2014).

[5] Guler, U. et al. "Local heating with lithographically fabricated plasmonic titanium nitride nanoparticles" Nano Lett. 13, 6078 (2013).

[6] Naik, G. V. et al. "Titanium nitride as a plasmonic material for visible and near-infrared wavelengths" Opt. Mater. Express 2, 478 (2012).

[7] Naldoni, A. et al. "Broadband Hot-Electron Collection for Solar Water Splitting with Plasmonic Titanium Nitride" Adv. Opt. Mater. 5, 1601031 (2017).

[8] Ishii, S., Shinde, S. L., Jevasuwan, W., Fukata, N. & Nagao, T. "Hot Electron Excitation from Titanium Nitride Using Visible Light" ACS Photonics 3, 1552 (2016).

[9] Ferguson, H. et al. "Hot Electron Relaxation in Thin Titanium Nitride Films" in CLEO:2016 FF2D.1 (2016).

[10] MP Wells et al "Temperature stability of thin film refractory plasmonic materials" Optics Express 26, 15726 (2018)

[11] Braic, L. et al. "Titanium Oxynitride Thin Films with Tunable Double Epsilon-Near-Zero Behavior for Nanophotonic Applications" ACS Appl. Mater. Interfaces 9, 29857 (2017).

[12] B Doiron et al "Optimizing hot electron harvesting at planar metal-semiconductor interfaces with titanium oxynitride thin films" arXiv:1807.03702 (2018)

[13] B Doiron, et al "Plasmon-Enhanced Electron Harvesting in Robust Titanium Nitride Nanostructures" J. Phys. Chem. C 123, 18521 (2019)

[14] NA Güsken et al "TiO2–x-Enhanced IR Hot Carrier Based Photodetection in Metal Thin Film–Si Junctions" ACS Photonics 6 (4), 953 (2019)