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Philip A. Thomas

Narrow Plasmon Resonances in Hybrid Systems

Doctoral Thesis accepted by
the University of Manchester, Manchester, UK

Springer

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Their minds sang with the ecstatic knowledge
that either what they were doing was
completely and utterly and totally impossible
or that physics had a lot of catching up to do.
Douglas Adams

Supervisor’s Foreword

In the last two decades, the field of plasmonics has attracted a lot of attention. Plasmonics is devoted to studies of the interaction of light with subwavelength objects that contain free-electron plasma. There are two main reasons for the increased interest in plasmonics. First, developments in nanofabrication have allowed the fabrication of various artificial materials which are capable of carrying optical plasmons. These artificial materials formed the basis for a new experimental field of investigation (optical metamaterials) promising a whole set of new phenomena: light compression into subwavelength regions, electromagnetic field enhancement, perfect lensing, negative refraction, topological darkness, etc. Second, being the last relatively unexplored branch of optics, plasmonics carries the torch of optics which is always set not only to unveil exciting new science but also to deliver important applications useful for society and the general public. Indeed, optics was the first useful physical discipline (the laws of light refraction and reflection, fibre optics and lenses without distortion were established as early as the tenth century AD) and has continued to bring forth a variety of useful tools and installations: glasses, lenses, polarizers, lasers, interferometers, optical fibres, nonlinear frequency doublers, etc. Plasmonics has continued the long-standing tradition of optics and delivered applications in the areas of ultrasensitive biosensing, materials with the designed optical response, nonlinear optics, etc.

The efforts of many groups and advances in our understanding of the interaction of light with subwavelength plasmonic materials have allowed unique optical responses to be tailored at the nanoscale. In particular, it was recently found that metal nanostructures (capable of supporting surface plasmons) can be designed to possess spectrally narrow plasmon resonances, which are of particular interest due to their exceptional sensitivity to their local environment. Combining plasmonic nanostructures with other materials in hybrid systems enabled this sensitivity to be exploited in a broad range of applications. In this thesis, Philip Thomas explores two different approaches to attaining narrow plasmon resonances: in gold nanoparticle arrays by utilising diffraction coupling and in copper thin films covered by a protective graphene layer. The performances of these resonances were evaluated for a number of applications. For example, nanoparticle arrays along with an atomic heterostructure were used as elements in a nanomechanical electro-optical modulator, capable of strong, broadband light modulation. Strong coupling between diffraction-coupled plasmon resonances in a gold nanoparticle array and guided modes in a dielectric slab was applied to construct a hybrid waveguide. The extreme phase sensitivity of graphene-protected copper was utilised to detect trace quantities of small toxins in solution far below the detection limit of commercial surface plasmon resonance sensors. One can expect that Philip Thomas' thesis is the first real step towards combining the extraordinary properties of plasmonics and 2D materials into smart hybrid optical devices, promising the realisation of valuable new applications.

Manchester, UK
April 2018

Prof. Alexander N. Grigorenko

Abstract

Surface plasmons are collective oscillations of free electrons excited at a metal–dielectric interface by incident light. They possess a broad set of interesting properties including a high degree of tunability, the generation of strong field enhancements close to the metal's surface and high sensitivity to their adjacent dielectric environment.

It is possible to enhance the sensitivity of plasmonic systems by using narrow plasmon resonances. In this thesis, two approaches to narrowing surface plasmon resonances have been studied: diffraction coupling of localised surface plasmon resonances in gold nanoarrays and the use of graphene-protected copper thin films. Applications of these approaches in hybrid systems have been considered for modulation, waveguiding and biosensing.

Arrays of gold nanostripes fabricated on a gold sublayer have been used to create extremely narrow plasmon resonances using diffraction coupling of localised plasmon resonances with quality factors up to a value of $Q \sim 300$, among the highest reported in the literature. The nanostructures were designed to give the narrowest resonance at the telecommunication wavelength of 1.5 μm, allowing for this array geometry to be used in hybrid systems for proof-of-concept optoelectronic devices.

The gold nanostripe array was used in a hybrid nanomechanical electro-optical modulator along with hexagonal boron nitride (hBN) and graphene. The modulator was fabricated with an air gap between the nanoarray and the hexagonal boron nitride/graphene. Applying a gate voltage across the device moves the hBN towards the nanoarray, resulting in broadband modulation effects from the ultraviolet through to the mid-infrared dependant on the motion of the hBN instead of graphene gating.

The deposition of a 400-nm hafnium(IV) oxide film on top of the gold nanoarray created a structure capable of guiding modes at 1.5 μm. The hybrid air–dielectric–stripe waveguide is capable of guiding modes over a distance of 250 μm.

Copper thin films have stronger plasmon resonances and higher phase sensitivity than gold thin films. Transferring a graphene sheet on the copper prevents oxidation of the copper. A feasibility study of this hybrid system has shown that phase-sensitive graphene-protected copper biosensing can detect HT-2 mycotoxin with over four orders of magnitude greater sensitivity than commercially available gold-based surface plasmon resonance biosensing systems.

In summary, two methods of attaining narrow plasmon resonances have been demonstrated and their promise in modulation, waveguiding and biosensing has been demonstrated.

Acknowledgements

This thesis is the culmination of a series of adventures and near-misadventures. The successes have far outnumbered the failures during this Ph.D., something that can only be attributed to the kindness and generosity shown to me over the past few years by a large number of people.

I was lucky to start my Ph.D. when Ben Thackray was finishing his own Ph.D. Ben's work provided an excellent starting point for my own research, and his help with measurements in the early days of the project was greatly appreciated. Vasyl Kravets has been a guide and mentor through all aspects of clean room and measurement work. I am greatly indebted to his patience and selflessness on any number of occasions throughout the Ph.D. It has been a pleasure to collaborate on so many projects with Gregory Auton, who has always been exceptionally generous with his time, helping out with e-beam lithography and 2D material work. Fran Rodriguez, Owen Marshall, Dmytro Kundys and Yang Su have all helped me out at various stages with measurements, fabrication and general pearls of wisdom.

My time in the clean room has transitioned from initial unadulterated terror to a genuine pleasure (especially on hot humid days). In addition to Vasyl, Greg and Fran, I must thank Fred Schedin, Jack Warren and Chris Berger for training, tips and general help around the clean rooms. I am also indebted to Richard O'Connor, Fran Lopez-Royo, Alex Lincoln and all others working to keep the CMN and NGI well-stocked and smoothly running.

The final year of my Ph.D. has primarily been devoted to the biosensing results described in Chap. 7. For a dyed-in-the-wool physicist, this was a strange world to enter into, but I have been very grateful to Harry Warner, Andrei Kabashin, Henri Arola, Miika Soikkeli and Philip Day for helping me feel surprisingly comfortable talking about biostuff. I must especially thank Fan Wu for her industrious help in sample fabrication and measurements.

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I must also thank Irina Grigorieva, Tom Thomson and all at the Graphene-NowNano Doctoral Training Centre for providing such a great environment in which young, foolish researchers such as myself can become slightly less young and slightly less foolish. The number of people who have provided advice, patiently endured my rants and/or organised super-amazing conferences is far too great to mention here.

I am very grateful for having survived the Ph.D. process and must thank my friends, family and the good saints of Holy Trinity Platt for help in preserving my sanity.

And finally, I thank you, dear reader, for having read this far. This thesis is as long as *A Christmas Carol*, and although this thesis is lacking in sentimental talk of goodwill to all, it does at least contain four fewer ghosts than the aforementioned novella.

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Abbreviations

AOI	Angle of incidence
ATR	Attenuated total reflectance
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
HPWG	Hybrid plasmon waveguide
IPA	Isopropyl alcohol
LSPR	Localised surface plasmon resonance
NA	Numerical aperture
NS	Nanostripe
SEM	Scanning electron microscopy
SPP	Surface plasmon polariton
SPR	Surface plasmon resonance
TE	Transverse electric
TM	Transverse magnetic
VASE	Variable angle spectroscopic ellipsometry