Stefan Alexander Maier

Plasmonics

Fundamentals and Applications

等离子体光学: 原理与应用

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PLASMONICS: FUNDAMENTALS AND APPLICATIONS

STEFAN A. MAIER

Centre for Photonics and Photonic Materials Department of Physics, University of Bath, UK



Stefan A. Maier Centre for Photonics & Photonic Materials Department of Physics University of Bath Bath BA2 7AY United Kingdom

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For Harry Atwater, with thanks for the great time.

Foreword

It was the autumn of 1982 and my final year undergraduate project was on surface plasmons. I had no idea that this topic would still have me fascinated almost a quarter of a century later, let alone have become a life-time career. Time really does fly. The invitation to write a foreword to this book with the instruction that it include a historical perspective set me thinking of my own first encounter with surface plasmons. My project supervisor was Roy Sambles - little did I realise how lucky I was. Without knowing it I became hooked on physics; not just studying it but doing it - I was off. The field of surface plasmons has changed enormously in the intervening years; indeed, in its new guise as plasmonics, interest has soared and many more people have joined the field.

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But for those new to the topic, where to begin? A good book can act as a guide and companion - it can make all the difference. When I started in 1982 the newest book was a monster, a compilation called "Electromagnetic Surface Waves", edited by Alan Boardman. Together with Kevin Welford, I had joined Roy Sambles to do a PhD - as beginners we found this book a daunting yet valuable resource – we plundered it, before long the pages became dog-eared and the covers fell off. I left things plasmonic in 1986, not to rejoin until 1992. In the meantime Hans Raether published "Surface Plasmons". With his wonderful combination of simplicity and insight, especially in the introductory sections, a classic emerged. Now almost twenty years later it is still very much in use but, inevitably, it has become increasingly out of date as the field continues to rapidly expand. Whilst several specialist volumes have emerged, we have been acutely aware of the need for a more up-to-date introduction and overview of the field at a glance. Now we have it - thank you Stefan.

But what is plasmonics? "You just have Maxwell's equations, some material properties and some boundary conditions, all classical stuff - what's new about

that?" Well, would you have predicted that just by imposing appropriate struc-ture on a metal one could make a synthetic material that would turn Snell's law

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on its head? Or that you could squeeze light into places less that one hundredth of a wavelength in size? No new fundamental particles, no new cosmology but surprises, adventure, the quest to understand - yes, we have all of those, and more.

It seems that four elements underlie research in plasmonics today. The first is the ready availability of state-of-the-art fabrication methods, particularly for implementing nanostructure. Second, there are a wealth of high-sensitivity optical characterisation techniques, which one can buy pretty much off-the-shelf. Third, the rapid advance in computing power and speed have allowed us to implement powerful numerical modelling tools on little more than a laptop computer. The fact that many researchers can gain access to these things enables the expansion of the field of plasmonics, but what has motivated that expansion?

The cynic might argue fashion. However, the fourth element, the one missing from the list above, is the wide range of potential applications - solar cells, high-resolution microscopy, drug design and many more. Applications are indeed strong motivators, but I think there is more to it than that. I know I am biased, but for me and I suspect many others it's the adventure, the role of the imagination, the wish to be the one to find something new, to explain the unexplained - in short its science, simple as that. Perhaps amazingly there are still many topics in which one can do all of these things without the need to observe gravity waves, build particle accelerators, or even work out how the brain that loves to do such things works. Plasmonics is one of those small-scale topics where good people can do interesting things with modest resources, that too is one of the lures.

Roughly speaking the field is a hundred years old. Around the turn of the last century the same four elements as described above applied - albeit in a different way. The relevant state-of-the-art fabrication was that of ruled diffraction gratings, optical characterisation was provided by the same gratings - to give spectroscopy. Computation was based on, among others, Rayleigh's work on diffraction and Zenneck's and Sommerfeld's work on surface waves - all analytical, but still valuable today. There was in addition an improved understanding of metals, particularly from Drude's treatment. So what was missing? Perhaps most importantly these different activities were not really recognised as having a commonality in the concept of surface plasmons. Now we are in a very different situation, one in which the relevant underlying science is much better understood - but where, as we continue to see, there are still many surprises.

Looking back it seems clear that the 1998 paper in Nature by Thomas Ebbesen and colleagues on the extraordinary transmission of light through metallic hole-arrays triggered many to enter the field. With an avalanche of developments in spectral ranges from the microwave, through THz, IR and visible, and into the UV the need for an entry point has become more acute. Well, here it is.

Foreword

It can't possibly be comprehensive, but Stefan Maier's addition gives an up-todate introduction and a great overview of the present situation. Who knows what new concepts might emerge and where the important applications will be? Maybe none of us know yet, that's the beauty - it could be you.

> Bill Barnes, School of Physics, University of Exeter, June 2006

Preface

Plasmonics forms a major part of the fascinating field of *nanophotonics*, which explores how electromagnetic fields can be confined over dimensions on the order of or smaller than the wavelength. It is based on interaction processes between electromagnetic radiation and conduction electrons at metallic interfaces or in small metallic nanostructures, leading to an enhanced optical near field of sub-wavelength dimension.

Research in this area demonstrates how a distinct and often unexpected behavior can occur (even with for modern optical studies seemingly uninteresting materials such as metals!) if discontinuities or sub-wavelength structure is imposed. Another beauty of this field is that it is firmly grounded in classical physics, so that a solid background knowledge in electromagnetism at undergraduate level is sufficient to understand main aspects of the topic.

However, history has shown that despite the fact that the two main ingredients of plasmonics - surface plasmon polaritons and localized surface plasmons - have been clearly described as early as 1900, it is often far from trivial to appreciate the interlinked nature of many of the phenomena and applications of this field. This is compounded by the fact that throughout the 20th century, surface plasmon polaritons have been rediscovered in a variety of different contexts.

The mathematical description of these surface waves was established around the turn of the 20th century in the context of radio waves propagating along the surface of a conductor of finite conductivity [Sommerfeld, 1899, Zenneck, 1907]. In the visible domain, the observation of *anomalous* intensity drops in spectra produced when visible light reflects at metallic gratings [Wood, 1902] was not connected with the earlier theoretical work until mid-century [Fano, 1941]. Around this time, loss phenomena associated with interactions taking place at metallic surfaces were also recorded via the diffraction of electron beams at thin metallic foils [Ritchie, 1957], which was in the 1960s then linked with the original work on diffraction gratings in the optical domain [Ritchie

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et al., 1968]. By that time, the excitation of Sommerfeld's surface waves with visible light using prism coupling had been achieved [Kretschmann and Raether, 1968], and a unified description of all these phenomena in the form of surface plasmon polaritons was established.

From then on, research in this field was so firmly grounded in the visible region of the spectrum, that several rediscoveries in the microwave and the terahertz domain took place at the turn of the 21st century, closing the circle with the original work from 100 years earlier. The history of localized surface plasmons in metal nanostructures is less turbulent, with the application of metallic nanoparticles for the staining of glass dating back to Roman times. Here, the clear mathematical foundation was also established around 1900 [Mie, 1908].

It is with this rich history of the field in mind that this book is written. It is aimed both at students with a basic undergraduate knowledge in electromagnetism or applied optics that want to start exploring the field, and at researchers as a hopefully valuable desk reference. Naturally, this necessitates an extensive reference section. Throughout the book, the original studies described and cited were selected either because they provided to the author's knowledge the first description of a particular effect or application, or due to their didactic suitability at the point in question. In many cases, it is clear that also different articles could have been chosen, and in some sections of the book only a small number of studies taken from a pool of qualitatively similar work had to be selected.

The first part of this text should provide a solid introduction into the field, starting with an elementary description of classic electromagnetism, with particular focus on the description of conductive materials. Subsequent chapters describe both surface plasmon polaritons and localized plasmons in the visible domain, and electromagnetic surface modes at lower frequencies. In the second part, this knowledge is applied to a number of different applications, such as plasmon waveguides, aperture arrays for enhanced light transmission, and various geometries for surface-enhanced sensing. The book closes with a short description of metallic metamaterials.

I hope this text will serve its purpose and provide a useful tool for both current and future participants in this area, and will strengthen a feeling of community between the different sub-fields. Comments and suggestions are very much appreciated.

STEFAN MAIER

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I wish to thank my colleague Tim Birks for all his efforts in proof-reading an early draft of this book and his helpful criticism, and David Bird for his encouragement to undertake this project. Thanks also to my student Charles de Nobriga for working through a more advanced version of this text, and of course to my wife Mag for all the lovely distractions from writing ...

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