Chapter 1

SURFACE PLASMON NANOPHOTONICS

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1.1. INTRODUCTION

In recent years, we have witnessed a flurry of activity in the fundamental research and development of surface plasmon based structures and devices. Surface plasmons are collective charge oscillations that occur at the interface between conductors and dielectrics. They can take various forms, ranging from freely propagating electron density waves along metal surfaces to localized electron oscillations on metal nanoparticles. Their unique properties enable a wide range of practical applications, including light guiding and manipulation at the nanoscale, biodetection at the single molecule level, enhanced optical transmission through sub-wavelength apertures, and high resolution optical imaging below the diffraction limit. This book is intended for people entering this diverse and rapidly growing field, recently termed "Plasmonics". It covers the fundamentals of surface plasmon science as well as some of the exciting new applications. The contributing Authors include world-leaders in the field. Together they provide an overview of the current state-of-the art and their personal views on where the field is heading. The Editors hope that by reading this book you will get caught up in the excitement and join us to define and shape the future of Plasmonics.

1.2. SURFACE PLASMONS - A BRIEF HISTORY

Well before scientists set out to study the unique optical properties of metal nanostructures, they were employed by artists to generate vibrant colors in glass artifacts and in the staining of church windows. One of the most famous examples is the Lycurgus cup dating back to the Byzantine Empire (4 century A.D.). Some of the first scientific studies in which surface plasmons were observed date back to the beginning of the twentieth century. In the year 1902 Prof. Robert W. Wood observes unexplained features in optical reflection measurements on metallic gratings.[1] Around that same time, in 1904, Maxwell Garnett describes the bright colors observed in metal doped glasses[2] using the then newly developed Drude theory of metals, and the electromagnetic properties of small spheres as derived by Lord Rayleigh. In an effort to develop further understanding, in 1908 Gustav Mie develops his now widely used theory of light scattering by spherical particles.[3]

Some fifty years later, in 1956, David Pines theoretically describes the characteristic energy losses experienced by fast electrons traveling through metals,[4] and attributes these losses to collective oscillations of free electrons in the metal. In analogy to earlier work on plasma oscillations in gas discharges, he calls these oscillations ‘plasmons’. In 1957 a study is published by Rufus Ritchie on electron energy losses in thin films,[5] in which it is shown that plasmon modes can exist near the surface of metals. This study represents the first theoretical description of surface plasmons. Coincidentally, one year later John Joseph Hopfield introduces the term ‘polariton’ for the coupled oscillation of bound electrons and light inside transparent media.[6] In 1968, nearly seventy years after Wood’s original observations, Ritchie and coworkers describe the anomalous behavior of metal gratings in terms of surface plasmon resonances excited on the gratings.[7] A major advance in the study of surface plasmons is made in 1968 when Andreas Otto as well as Erich Kretschmann and Heinz Raether present methods for the optical excitation of surface plasmons on metal films,[8] making experiments on surface plasmons easily accessible to many researchers.

At this point the properties of surface plasmons are well known, however the connection to the optical properties of metal nanoparticles has not yet been made. In 1970, more than sixty years after Garnett’s work on the colors of metal doped glasses, Uwe Kreibig and Peter Zacharias perform a study in which they compare the electronic and optical response of gold and silver nanoparticles.[9] In their work, they for the first time describe the optical properties of metal nanoparticles in terms of surface plasmons. As the field continues to develop and the importance of the coupling between the oscillating electrons and the electromagnetic field become more apparent, Stephen Cunningham and his colleagues introduce the term surface-plasmon-polariton (SPP) in 1974.[10]

Another major discovery in the area of metal optics occurs in that same year, when Martin Fleischmann and coworkers observe strong Raman scattering from pyridine molecules in the vicinity of roughened silver surfaces.[11] Although it was not realized at the time, the Raman scattering – an exchange of energy between photons and molecular vibrations – was enhanced by electromagnetic fields near the rough silver surface due to the presence of surface plasmons. This observation led to the now well established field of Surface Enhanced Raman Scattering (SERS). All these discoveries have set the stage for the current surge in surface plasmon nanophotonics.

1.3. SURFACE PLASMONS –PRESENT AND FUTURE

Since the early days of surface plasmon optics there has been a gradual transition from fundamental studies to more application driven research. The present surge in plasmon based research is happening at a time where crucial technological areas such as optical lithography, optical data storage, and high density electronics manufacturing are approaching fundamental physical limits. Several current technological challenges may be overcome by utilizing the unique properties of surface plasmons. Thanks to many recent studies, a wide range of plasmon-based optical elements and techniques have now been developed, including a variety of passive waveguides, active switches, biosensors, lithography masks, and more. These developments have led to the notion of *plasmonics*, the science and technology of metal-based optics and nanophotonics.[12]

The growth of the field of plasmonics is clearly reflected in the scientific literature. Figure 1-1 shows the annual number of publications containing the words ‘surface plasmon’ in the title or the abstract. Since 1990 the annual number of papers on surface plasmons has doubled every five years. This rapid growth is stimulated by the development and commercialization of powerful electromagnetics simulation codes, nanofabrication techniques, and physical analysis techniques, providing researchers and engineers with the necessary tools for designing, fabricating, and analyzing the optical properties of metallic nanostructures. A major boost to the field was given by the development of a commercial surface plasmon resonance (SPR) based sensor in 1991. At present an estimated fifty percent of all publications on surface plasmons involve the use of plasmons for biodetection.

Most recently, metal nanostructures have received considerable attention for their ability to guide and manipulate “light” (SPPs) at the nanoscale, and the pace of new inventions in the area has accelerated even further. In 1997 Junichi Takahara and co-workers suggest that metallic nanowires enable the guiding of optical beams with a nanometer scale diameter,[13] in 1998 Thomas Ebbesen and coworkers report on the extraordinary optical transmission through subwavelength metal apertures, and in 2001 John Pendry suggests that a thin metallic film may act as a "perfect lens".[14,15] All these findings have motivated a tremendous amount of new research, captured in a number of exciting review articles.[16,17] It should be noted that the brief overview provided here cannot do justice to all the different research directions the field of Plasmonics. Rather making an attempt to be exhaustive, we have tried to present a short historical perspective including the fundamentals and some of the current hot topics. In the following section we highlight the various topics covered in this book. Together, these represent the true state-of-the art in the field of plasmonics.

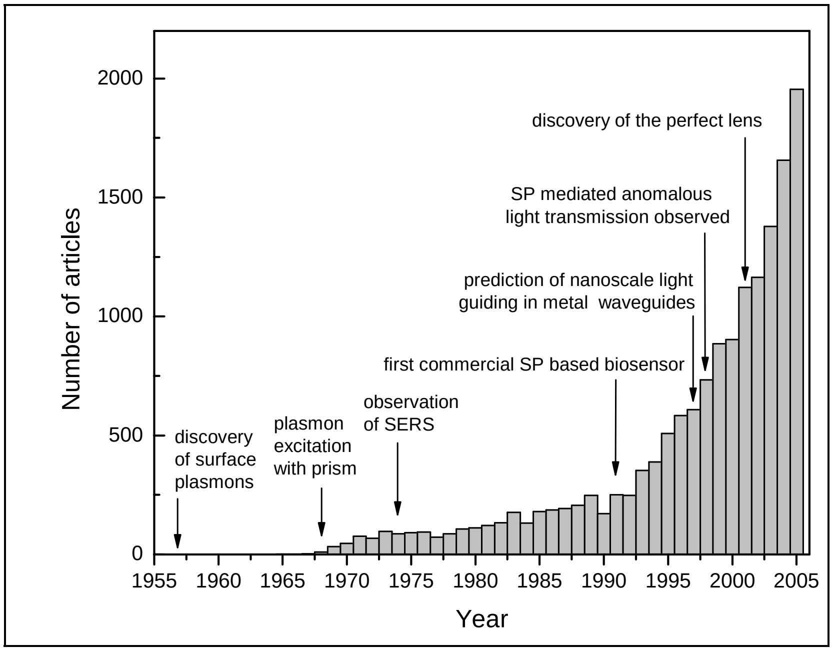

Figure 1-1. The growth of the field of metal nanophotonics is illustrated by the number of scientific articles published annually containing the phrase "surface plasmon" in either the title or abstract (based on data provided on www.sciencedirect.com)

1.4. THIS BOOK

This book contains seventeen chapters broadly divided into 5 major topical areas, which are indicated in boldface below. Although, all the chapters are self-contained, the topical areas help to provide connections between the different research directions.

Surface plasmon excitations in isolated and periodic metal nanostructures are discussed in the first two chapters. This section forms a solid basis for understanding several concepts used throughout this book.

Chapter 2 deals with the optical near-field and far-field properties of isolated metal nanoparticles and periodic metal nanoparticle arrays (Fig. 1-2). First, a qualitative introduction to surface plasmon excitations in metal nanoparticles is given and their resonant behavior is discussed in detail. In the latter part of the chapter, the properties of metallic nanoparticle arrays (extinction spectra, optical near fields, non-linear optical properties and particle interactions) are treated. Metallic nanoparticle arrays played an important role in the early days of this field and hold tremendous promise for the development of new applications, from nanoparticle-based plasmonic waveguides discussed in Chapter 7 to advanced substrates for surface enhanced Raman spectroscopy, as shown in Chapter 14. A deep understanding of the optical properties of metallic particles has also provided an intuitive vantage point from which the resonant behavior exploited in optical nanoscale antennas (Chapter 9) and tip-enhanced spectroscopy (Chapter 10) can be understood.

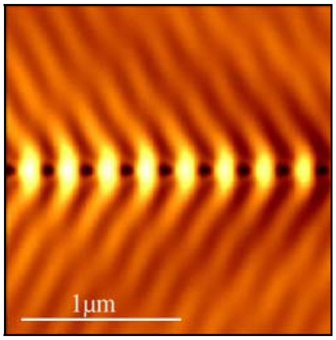

Figure 1-2. Optical near fields of metal nanoparticle chains (Chapter 2) with a grating constant of 400nm. The chains are excited under total internal reflection from the right at 800nm. The image was taken using a photon scanning tunneling microscope. The circles indicate the nanoparticles.

Chapter 3 provides the theoretical foundation of the extraordinary optical transmission (EOT) phenomenon observed in thin metallic films perforated with a two-dimensional array of subwavelength holes. It also explains the appearance of EOT in single apertures surrounded by periodic corrugations in the input side and the observation of beaming effects for the case in which the periodic corrugation is placed in the output surface. This phenomenon has given the field of plasmonics a tremendous boost in attention in recent years and the role of SPPs in this phenomenon is discussed.

Surface plasmon waveguides are analyzed in detail in chapters 4 through 7 and 15. Such waveguides can manipulate and route "light" at the nanoscale. A number of different geometries are discussed, each with their individual strengths and weaknesses.

Chapter 4 shows how near-field optical techniques can be employed to characterize the properties of SPP waveguides. It starts with an explanation of the operation of a photon scanning tunneling microscope with which the propagation of SPP patterned metal films can be imaged. The authors apply this technique to analyze straight waveguides, bent waveguides, and structures with Bragg gratings. These measurements provide a deeper understanding of the properties of patterned, stripe waveguides and will be invaluable in designing improved more complex devices, including biosensors, interferometers, and active plasmonic structures.

Chapter 5 discusses the behavior of plasmonic transmission lines consisting of metal strips embedded in an isotropic medium. To this end, a computational method is presented that relies on the use of Eigensolutions available from many commercial solvers. Particular attention is given to the long range modes supported by the strips and important practical issues such as the effect of surface roughness and smooth, curved edges on the propagation distance are analyzed. Practical device geometries such as periodically corrugated waveguides and waveguide bends are treated. These form important building blocks for plasmonic devices.

Chapter 6 demonstrates the feasibility of employing photonic band gap effects for realizing miniature photonic circuit elements by nano-patterning metal surfaces. In particular, the Authors show that SPP waveguiding and routing structures can be realized by defining line-defects in periodically corrugated metal surfaces. Numerical methods are used to simulate the behavior of these structures by solving the famous Lippmann-Schwinger equation. The reader is provided with intuitive insights into the operation of these devices and with a working knowledge on how to choose the bump spacing, height, and type of lattice for obtaining high transmission at specific operating wavelengths.

Chapter 7 discusses how metallic waveguides can be constructed that enable deep subwavelength spatial confinement of optical modes. Two waveguide types are investigated in detail, namely nanoparticle-based waveguides and metal-insulator-metal waveguides. Although the propagation distances are short (a few microns), they offer exciting opportunities for the development of truly nanoscale optical and photonic components.

Surface Plasmon Mediated Field Concentration and Imaging methods are discussed in Chapters 8 through 10. Such imaging techniques include the now famous perfect lens and the apertureless near-field optical microscope. Both optical elements rely on the use of metallic nanostructures and the excitation of SPPs to enable deep sub-wavelength operation.

Chapter 8 reviews the intriguing properties of superlenses. A superlens is an optical element capable of imaging objects of subwavelength dimensions. First the theory behind the superlens is discussed and it is shown how a thin slab of metal is capable of enhancing a broad band of evanescent waves in the wave vector spectrum. Such enhanced evanescent waves can be used to reconstruct the image of a subwavelength object. The theory is followed by a series of experiments that provide information on the transfer function of a silver superlens and show true subwavelength imaging with imaging resolution of 60 nm or $\lambda/6$. Super lenses exhibit enormous potential for commercial applications including ultra-high resolution imaging, high-density memory storage devices, and nanolithography.

Chapter 9 analyzes the intriguing properties of resonant bowtie antennas that can cause enormous field concentration (Figure 1-3a). Experimental and theoretical results demonstrate that local optical field enhancements greater than 1000 times can be obtained compared to the incident light wave. Physical explanations are given for the resonant behavior and its dependence on the dimensions of the antennas.

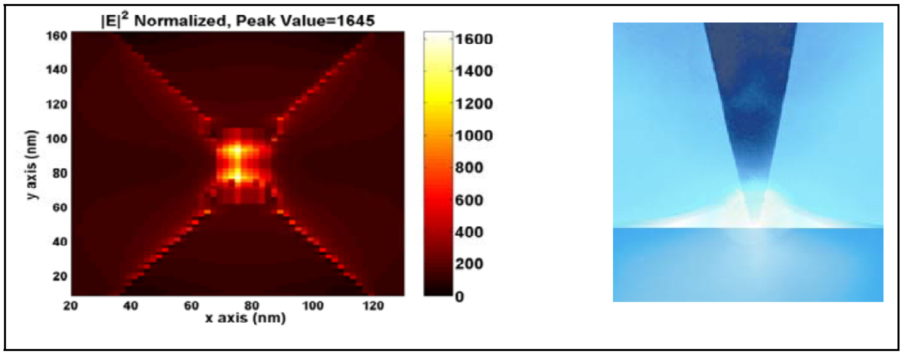

Figure 1-3. (a) Simulation of the intensity, |E|^2, enhancement in the 16 nm wide gap of a bowtie antenna, as measured 4 nm above the antenna (Chapter 9). (b) Artist impression of the optical field enhancement underneath the metallic tip used in apertureless, near-field optical microscopy (Chapter 10).

Chapter 10 reviews the application of apertureless, near-field optical microscopy for the local excitation and detection of SPPs. In such a microscope a sharp metallic tip is used for the imaging. Similar to the bow-tie antennas in Chapter 9, such tips possess the ability to convert incident free-space light waves to strongly confined fields at the end of the tip (Figure 1-3b). It is explained in detail how a combination of lightning-rod and surface-plasmon resonance effects gives rise to the localization. It is this light confinement that allows for the use of these tips as tiny (secondary) light sources with which structures can be imaged with nanoscale spatial resolution. To illustrate this, it is shown how SPP interference, decay, and scattering on patterned metal surfaces can be visualized. The strong field enhancement near the end of metal tips can give rise to a range of exciting non-linear effects, including second-harmonic and continuum generation. This is demonstrated experimentally and analyzed in theory. These microscopic techniques are expected to play a key role in the analysis of future nanoscale plasmonic devices.

Experimental characterization and simulation techniques for plasmonic structures are treated in chapters 11 and 12. Our current understanding of plasmonic devices is largely based on the development of powerful far-field and near-field optical analysis tools and numerical simulation techniques. The unique ability of SPP-based structures to manipulate light at the nanoscale has generated substantial and fascinating challenges in the analysis and prediction of their behavior. Some of these challenges and their solutions are described in the following two chapters.

In *Chapter 11* Alain Dereux discusses ways to map the optical near-field in the vicinity of nanoscale optical structures. It is shown that a true near-field measurement does not allow the simultaneous detection of the electric field and the magnetic field. Calculational methods to predict near-field distributions on scattering structures are described, and practical examples are given that prove the validity of the developed approach under specific experimental conditions.

Chapter 12 provides a valuable overview of numerical simulation techniques that are suitable for predicting the behavior of plasmonic structures and devices. The authors first describe the challenges we are faced with in the numerical modeling of metallic nanostructures. These include the arbitrary device geometries, the complicated dispersive properties of metallic materials at optical frequencies, and the rapid decay of surface plasmons away from metal-dielectric interfaces. The strengths and limitations of various techniques are highlighted and future research directions in this area are outlined.

Chapter 13 discusses a very intuitive model that can be used to predict the optical response of complex metallic nanostructures and systems. It is called the plasmon hybridization model and shows intriguing similarities to the well-established theories on molecular orbital formation from atomic orbitals. This model can predict the location of plasmon resonances in complex systems based on knowledge of the resonant behavior of elementary building blocks. It thus provides a powerful tool for optical engineers in the design of future functional plasmonic nanostructures. The basic theory is explained and applied to a number of important examples, including multilayer concentric gold nanoshells and multi-particle geometries.

Applications of surface plasmon nanophotonics are analyzed in chapters 14 through 17. In these chapters, several exciting applications of SPPs that have already been commercialized or have tremendous potential to be commercialized are discussed.

Chapter 14 is devoted to the applications of Raman spectroscopy and way to improve the power of this technique with the use of metallic nanostructures. Raman scattering spectra enable molecular “fingerprinting,” which is of great importance in the fields of molecular sensing and biology. Carefully engineered metallic nanostructures can enable surface enhanced Raman scattering (SERS) to provide a far greater detection sensitivity than conventional Raman spectroscopy. It is further shown that under special conditions, nanoparticulate silver films allow for fine rearrangement of their local structure under protein deposition, causing substantial SERS enhancements. Such newly discovered adaptive, metal nanostructures allow for new way to perform protein sensing and can be applied in protein micro-arrays.

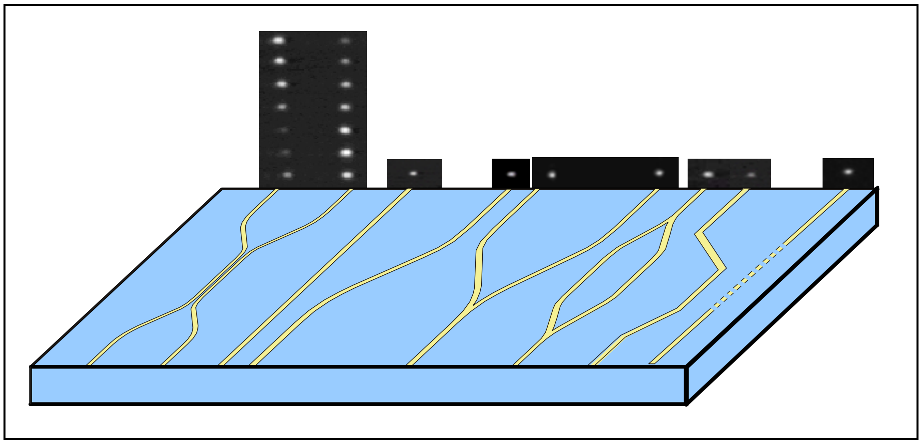

Figure 1-4. A schematic representation of several integrated optical devices based on Long Range Surface Plasmon Polaritons that are described in Chapter 15. The insets represent optical images recorded at the exit facet of a real device.

Chapter 15 introduces a variety of integrated optics components based on long-ranging surface plasmon polaritons (Figure 1-4). The current state-of-the art is reviewed, with an emphasis on passive elements including straight and curved waveguides, s-bends, y-junctions, four-port couplers, Mach-Zehnder interferometers and Bragg gratings.

Chapter 16 discusses a unique near-field based technology that can push the current limits in optical data storage. It is based on a so-called "super-resolution near-field structure" that enables the generation of strong, localized optical fields and localized surface plasmons in a thin film that exhibits a giant optical nonlinearity. The use of strongly localized fields occurring in nonlinear resonant systems could lead to optical data storage and readout with a capacity exceeding 1 terabyte.

Chapter 17 treats the use of metallic structures to modify and control the fluorescence properties of dyes. Particular attention is paid to a recently reported phenomenon that allows surface plasmon-coupled emission of excited fluorophores into a cone-like directional beam in a glass substrate. This allows for simple and efficient collection of the emitted photons. The authors expect that such near-field manipulation of light in combination with other nanophotonic technology will open new era for biophysical and biomedical applications of fluorescence.

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