Australian Research Council
Nanotechnology Network

Nanotechnology in Australia

Showcase of Early Career Research

EDITED BY
DEBORAH KANE
ADAM MICOLICH
JAMES RABEAU

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Nanotechnology in Australia: Showcase of Early Career Research

The book that follows is the culmination of a project developed and supported as an activity of the Australian Research Council Nanotechnology Network (ARCNN). To quote from the ARCNN website [1]:

> The Nanotechnology field is one of the fastest growing areas of research and technology. The Australian Research Council Nanotechnology Network (ARCNN) is dedicated to substantially enhancing Australia's research outcomes in this important field by promoting effective collaborations, exposing researchers to alternative and complementary approaches from other fields, encouraging forums for postgraduate students and early career researchers, increasing nanotechnology infrastructure, enhancing awareness of existing infrastructure, and promoting international links.

One of the key aims of the research network is to support professional and research skill development in postgraduate research students and early career researchers. As an innovation in postgraduate/postdoctoral research skills and networking education, this book has been produced to a "formula" and format that is described below. We commend the process by which this book has been produced to others seeking to improve the quality of a book with multiple contributors. Workshopping the chapters collectively results in improved writing and ease of reading of the final copy. Doing a refresher course on scientific writing, before application to a writing task, also improves the writing outcomes. Some of the participating authors had never studied scientific writing as a research skill. The feedback from the participants in this book project affirms that the opportunity to participate has been of particular value to postgraduate students, late in their candidature, and to early career scientists who have recently completed postgraduate studies.

Given the focus on professional development, expressions of interest for chapters on any area of nanotechnology were sought in the first phase of this project. The areas covered in the book reflect many of the research strengths in Australian nanotechnology. Australia has a long tradition in optics, optoelectronics, and photonics which has seen research in nanophotonics grow in a natural way. This area within Australia is perhaps underrepresented in this book, but Chapters 1 and 2 describe two different programs in plasmonics research—the first reporting primarily theoretical design of plasmonic circuit elements, the second on improving infrared light trapping in solar cells using layers of metal nanoparticles of optimized design. Chapter 3 is on theoretical nanoscale design of selfcleaning coatings. It describes modelling the chemistry, morphology, and stability of the surface to show the interdependencies involved in creating a surface that resists the adhesion of contaminant particles.

There is a strong focus on nanomaterials in the book. This reflects a large materials science community, in part supporting and supported by Australia's booming mining industries. Australia holds many of the world's major mineral and metal deposits, and research that leads to value-added manufacturing in this sector is a priority. Australia is contributing strongly to the world effort on nanodiamond research. One groups' research is described in Chapter 4. Chapters 5–8 discuss production and applications of nanoparticles of various materials. Vanadium compound nanorods for electrochemical energy storage, metal nanoparticles produced by laser ablation, hollow silica nanoparticles produced by chemical synthesis methods, and bulk synthesis of graphene are described sequentially in these four chapters. Chapter 9 also covers production of superparamagnetic nanoparticles to be used as MRI contrast enhancing agents. It bridges the research topics into nano-bio-medical subjects.

The final three chapters are on nano-bio-medical science. Chapter 10 discusses luminescent nanobioprobes for bioassays and bioimaging. Chapter 11 discusses using nanomorphology of metal nanoparticles to achieve enhanced fluorescence. Last, but certainly not least, Chapter 12 describes advances in biomimicry of olfactory biosensing, in a sense creating an artificial nose.

The chapters collectively represent a sample of Australian nanotechnology research. A lot more is going on than is represented in the book. The program of the flagship conference supported by ARCNN —the International Conference on Nanoscience and Nanotechnology —for example [2], shows the range of nanotechnology research in Australia more completely. The chapters give interesting contrasts in physical and chemical approaches to nanoparticle production and characterisation. The multidisciplinary nature of nanotechnology is well illustrated with the chapters showing nearly all combinations of physics, chemistry, and biology in their subject matter.

The editors have had an excellent insight into the talent, work ethic, and professional development of the participants through the pre-workshop, workshop, and post-workshop phases of the book project. The participants have been provided with feedback from their assigned editor on how their chapter has been judged to have improved from initial draft to final copy. Eleven of the 12 chapters were judged to have evolved significantly through the phases of the project. A process of further improvement would still be possible, but there are diminishing returns in this. Experience dictates individuals lose motivation beyond two to three rounds of feedback and response. One of the biggest writing challenges that remains is to get scientists to write shorter sentences. The guilt for this writing sin spreads beyond the book project participants. As scientists, many of us are inconsistent and challenged writers. Continuing to work to improve as writers requires our continuing attention.

As we trust that others will be interested to know more about our format for the book project, the following sections give more detail of how this book has been produced. In the pre-workshop phase, those interested in being particpants as “first authors” responded with an expression of interest via a process described in “Information for Applicants”. The expressions of interest were ranked by a committee, and those offered a place at the workshop were required to submit a draft of their chapter in advance of the workshop. This early submission facilitated feedback to authors where the chapter required significant further work. For the majority of authors, who submitted acceptable drafts, it established a period of disengagement from the writing so that they could read their own writing with a fresh perspective at the workshop.

In the section “Workshop Program”, the schedule and activities followed during the nine-day on-campus workshop are described briefly. The final word is given to the participants in “Comments from Participants”. This project has involved an enormous amount of effort and work on the part of the organizer and editors. However, the results demonstrate categorically that such a program, combined with the motivational carrot of a published book chapter, is well worth the effort for more than 90% of late stage PhD students and early career researchers who participate.

Information for Applicants

This nanotechnology book project will lead to a book that will be published by Pan Stanford Pte. Ltd. Those who are successful in having their chapter proposal accepted for development and inclusion in the book will travel to Macquarie University, Sydney, to participate in a nine-day workshop. This will involve working with the editors and the collective of authors to “workshop” the book chapters. The workshop will cover a range of key professional development areas, in addition to the strong focus on high-quality scientific writing and communication.

Who should apply?

If you have nearly finished or recently finished your PhD thesis, then this is an opportunity you should consider carefully—you are the optimum applicant. If you are a PhD student and you have not yet started writing your thesis, and/or you have not published any refereed journal articles, it is too soon for you to apply. If you are completing or have completed your PhD with examination by a thesis that is a collection of refereed papers, this may be an opportunity for you to develop your writing skills for the format of a book chapter. But please do not underestimate how much time this may require. If you completed your PhD thesis in the last three years and you work at a university or ARCNN-affiliated organisation, you may apply, if your current work commitments permit. However, every chapter in the book must make reference to the relevant literature in the field up to the present.

What is the preferred format for the book chapter?

Each chapter should include all or most of the following:

(i) An introduction and review of the relevant field of research. This should give appropriate care and attention to fully acknowledging the work of others that precedes and informs the research being communicated. It should also demonstrate the significance of the original research you and your co-workers have completed.

(ii) A "tutorial"-style coverage of concepts, methods, and theory required to understand, interpret, and analyse the new science. This book is intended to give readers clear and significant insights and understanding of the science.

(iii) Some of the original research from your PhD research. Note that permission will be required to use any figures and graphs that have appeared in copyright materials. However, the workshop will also address how you might achieve higher visual and scientific impact in the way these materials are presented.

What sort of a book do we want to produce?

One with excellent scientific writing, reporting excellent nanoscience and nanotechnology. This is an opportunity for early career researchers working in Australia to show the world the quality and capability of their science and science writing. Appropriate acknowledgement of co-workers (including co-authorship when appropriate) must also be given.

What are the copyright issues?

The publisher will be the copyright holder of the book chapter. Thus, you should not submit any research that you plan to publish in substantially the same form, at a later date, in an archival journal or other copyrighted form. The chapter should also be substantially different from any journal papers already published. Figures and graphs can be reproduced from previously published work provided the appropriate permission is obtained from the publisher holding the copyright. Documentation of such permissions will be required by the book publisher. Such permissions are normally granted.

What will participants get from the project?

A lot! They will collaborate closely within the group and learn how to build task-focused, cooperative working relationships quickly. They will have an excellent motivation to write a review/new results chapter from their PhD thesis research to an exceptionally high standard, in a higher-profile publication than is normally achieved at this early career stage. They will have the opportunity to produce an excellent book that will be valued widely and that will garner respect and acknowledgement for what ECRs' can achieve. They will have a high-quality learning experience—they will get to learn about each others' research and learn from each other, and the editors in the discussion process around improving their own and others' writing and illustration. This will be done in part by formal instruction on, and discussion of, high-quality scientific writing. They will contribute to an experiment in professional skills development for PGs and ECRs. The success of this experiment will be largely in the minds and hands of the contributors. The book will be distributed in Australian government and science policy-making circles to show the talent in early career scientists that is to be supported.

Workshop Program

The workshop ran in the computing laboratory maintained and shared by the Departments of Physics, and Mathematics, at Macquarie University, Sydney, Australia. Access to such a facility is needed. Access to additional quiet space is also advantageous for participants.

Each of the three editors was assigned four chapter authors before the workshop. The editors started their chapter reviewing ahead of the workshop. Within each group, two participant reviewers were assigned to each chapter. The main focus of the first two days of the workshop was for participants to act as reviewers of the writing of others. They did this after being pre-conditioned to have heightened awareness of writing structure and quality, engendered through presentations and informational handouts. This, in turn, heightened their sensitivity to their own writing style and quality when they returned to their own chapter on day 3 of the workshop. They also had three reviews of their chapter at that stage. Feedback from one participant after the workshop identified training in reviewing, and feedback on the quality of participant reviews could be added to future workshops.

The participants were also coached on the importance of the visual impact of figures and graphics in their chapter. A motivating hook was "How do you get your research onto the front cover of Nature Nanotechnology or Small?" To introduce the participants to a new skill in 3D graphics, a tutorial on "Introduction to Blender and Luxrender" [3] was given on day 2 by Iwan Kartiko, a specialist in using this software. Expert support to assist learning and using this software was provided by Mr Kartiko throughout the workshop. There was no compulsion for participants to engage with learning this software during the workshop. About a third of the participants selected this as a priority for their time during the workshop. Another third spent some time gaining some familiarity with the software, and the remainder focused on the structure and content of their chapter only. Allowing the participants to choose their own priorities from the activities being promoted worked well. In hindsight, the introduction of the computer graphics element would have been better if it were delayed until after the feedback discussions occurred on day 3. It detracted from participants focusing on their second review task, which had different motivation and focus than the first.

There are many resources that are suitable for postgraduates and ECRs to use in developing their writing and presentation skills. For the workshop two approaches were presented. We see these as having elements that are complementary and worthy of separate presentation. A traditional approach was presented on day 1. Robert Day's book [4] and Vernon Booth's book [5] are suitable examples to represent the traditional approach. The style guides of journal publishers are also useful resources [6]. After being pre-conditioned by a presentation drawn from "Day" and "Booth" the participants reviewed a chapter. On day 2 they had a presentation drawn from Lebrun's book [7]. This more recent approach to scientific writing explicitly addresses that readers are time poor. Thus, writers need to write in anticipation of the reader's requirements if they are to gain and hold the reader's attention. Lebrun also has an excellent approach to analysing the structure of writing as an extra tool for diagnosing what may be dysfunctional for the reader. The participants were asked to pay particular attention to analysing the structure of the second chapter they reviewed, following the methods of Lebrun. Consideration has been given to whether, or not, research skill education is adequately serviced by using Lebrun alone. Different views exist. It was hoped that analysis of the reviews of the chapters by participants would help in answering this question. However, the participants did not assimilate the approach of Lebrun sufficiently, within the structure and time constraints of the workshop, for this to be possible. Further analysis of the reviews is planned and may be reported elsewhere.

By day 3 there was enormous anticipation of the feedback to be received. Everyone was geared up to get on with improving their chapter. The remainder of the workshop saw the participants hard at work improving the writing and visual presentation of their chapter. Additional presentations addressed issues of copyright and authorship and using mind maps to plan research and writing. Each author was given up to two pages in the colour page section of the book in which to promote their book chapter visually. A suggestion of a book/journal cover design, plus two landscape-format presentation slides, was made. The various approaches of the authors can be seen in the final colour section of the book. Overall, the workshop involved intense work, carried out within a relaxed and positive group atmosphere. The success of the project relied in large part on the constructive and supportive group dynamic that prevailed.

Summary of Workshop Program

Day 1	Presentation: Introduction to "how to read and write high-quality scientific writing" Task: To critically appraise another participant's chapter.
Day 2	Presentation: Introduction to the "Lebrun" approach to "what readers are looking for" and "what writers' are trying to achieve"—including structure analysis. Presentation: Introduction to Blender and Luxrender as software that can be used to produce high-impact visuals to illustrate research. Task: To critically appraise a second chapter based on a "Lebrun" approach. Start learning "Blender" etc if chosen as an activity.
Day 3	Presentation: "The big picture and important small details" —feedback on points that were common to many chapters —to be acted upon in redrafting chapters. Advice on being resilient in the face of well-intentioned review comments. Task: Feedback discussions—each reviewer/editor discusses his or her feedback and suggestions for redrafting with chapter authors. Each author receives three lots of feedback to inform redrafting and starts acting upon them. Ongoing professional support for learning and using Blender and Luxrender. Ongoing clarification of components of the chapter, the two-page colour section, copyright permissions, etc.
Day 4	Redrafting/graphics workday. Discuss work with editors and other participants as needed. Further discussion of two-page colour insert for each chapter.

Day 5	Presentation on authorship and copyright issues and protocols. Ongoing redrafting/graphics workday. Presentation on "mindmaps" as a way to structure a written article, including an example.
Days 6 & 7, weekend	Time for relaxation, reflection, further work by individual choice. The two-page colour spread for each chapter to be published.
Day 8	All participants present their colour section to the group. Collective decision on the strongest visuals that are to be forwarded to the publisher for consideration for the front cover. Redrafting/graphics workday.
Day 9	Redrafting/graphics workday. Tour of local research labs. Close of workshop.

Comments from Participants

"The ARCNN book workshop challenged me to give my opinion on the writing of others and accept the opinion of others about mine. It exposed me to research of other early career researchers from around the country. It provided me with the opportunity to learn new skills with tutoring in graphics software. The process was good practice at meeting deadlines. It will be a rewarding experience to see the book come together."

Kelly Bailey, ECR

"The book writing workshop provided a forum to rethink and discuss scientific writing styles. It was very useful at this point in my career."

Fiona Beck, PhD student

"The workshop has been a great experience. It has been intense, sometimes tiring, but always enjoyable. Honestly, I can't believe how much I have learnt and how much I have gotten from it. Definitely thumbs up!!"

Carlo Bradac, PhD student

"The workshop was thoroughly enjoyable, and the feedback I received from the editors and other authors was extremely helpful. The opportunity to develop my writing skills for a more general readership was very rewarding, and I would highly recommend this workshop to others."

Matt Carroll, PhD student/ECR

"In order for science to have an impact, it must be communicated effectively. This workshop helped to do just that, and at the same time increasing my confidence to report my area of research to a much broader community, both in Australia and abroad."

Mohammad Choucair, PhD student

"I strongly support this type of workshop and book project to continue in the future, say, once a year. Our PhDs and postdocs will benefit a lot from writing skills, networking and accelerating Australian research to the cutting edge internationally"

Jin Dayong, ECR

"This workshop gave me a deep impression. I learned a lot of things about writing a high-quality paper. In addition, I also learned about some research skills from other people who gave a pretty good presentation. I highly recommend my co-workers attending such workshop."

Wei Deng, PhD student

"This workshop will be of great benefit to all early career researchers! I learnt valuable scientific writing skills that are valuable not only to my book chapter, but to journal papers as well. The structure of how to write a journal paper was of particular interest to me, as well as how to write catchy titles, achieve good image quality and how to keep a reader entertained. The hands-on aid with developing figures was particularly useful!"

Kristy Vernon, ECR

"The ARCNN Book Workshop was a unique experience which I enjoyed immensely. Thought provoking, challenging, exciting and always fun, I strongly recommend ECRs to participate in this once-in-a-lifetime opportunity. I've learnt a great deal during this workshop in regard to scientific writing, editing/reviewing, graphical imaging and the publication process."

George Yiapanis, PhD student

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Deborah M. Kane, Adam P. Micolich, and James R. Rabeau

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Chapter 1

PLASMONIC CIRCUITS: MANIPULATING LIGHT ON THE NANOSCALE

Kristy Cherie Vernon
CSIRO Materials Science and Engineering, Private Bag 33,
Clayton South MDC, Victoria 3169, Australia
Kristy.Vernon@csiro.au

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Nanotechnology in Australia: *Showcase of Early Career Research*
Edited by D. M. Kane, A. P. Micolich, and J. R. Rabeau

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Abstract

Technology decreases in size and increases in speed every year, because of the continuing decrease in size of electronic components. However, the size of electronic components is now reaching a fundamental limit. To continue the advancements in technology, a way of overcoming this fundamental limit or, alternatively, a replacement for electronics must be found. One such electronic alternative is plasmonics. Plasmons are a hybrid between light and electrons and enable light to be manipulated on the nanoscale. By using plasmonics it would be possible to build a circuit with potentially faster speeds than electronics. To achieve this task three components are necessary: waveguides for propagating the plasmon around the circuit, nano-focusing devices for efficiently coupling light into the circuit and active components capable of performing Boolean operations. In this book chapter we discuss the progress in creating these three components. We review the seminal works in the field as well as our work towards this goal: the creation of the plasmonic circuit. We begin the chapter by introducing the basic properties of plasmons and methods of excitation. In the next section, we discuss stripe, nanowire, V-groove, wedge and gap plasmon waveguides. We illustrate the main properties of these waveguides which make them useful for plasmonic circuits. Nano-focusing devices are then discussed, followed by the progress in the new field of "active plasmonics". This chapter is intended to be a review of the latest progress in the field, including our own, and to provide you, the reader, with an accessible introduction to the world of plasmonic circuits.

1.1 AN INTRODUCTION TO PLASMONICS

In 1947 Bell Labs created the world's first transistor, which resulted in a technological revolution. It would be hard to imagine the world today without the invention of the transistor. The electronics in the car, radio, television, computer, microwave—everything is based on the transistor.

The size of transistors has reduced dramatically over the years, thereby enabling more transistors per chip and faster processor speeds. The number of transistors per chip doubles every two years following Moore's law. In 1971 the Intel 4004 processor had 2300 transistors and processor speeds of 92,000 operations per second. The modern transistor can be as small as tens of nanometers, with ~2 billion transistors per chip, resulting in processor speeds of ~2 GHz, or billions of operations per second. The rapid reduction in the size of electronic components has pushed ahead the technology revolution, resulting in smaller computing devices with greater processing speeds.

However, the size of the transistor is approaching a fundamental limit [1]. As the transistor size approaches that of several nanometers, the interactions of individual atoms must be taken into account. These are known as quantum effects. To overcome this fundamental limit and continue reducing the size and increasing the speed of technology, alternatives to electronics would be advantageous. Since light photons can travel faster than electrons, optics is a possible alternative. However, there is a major drawback in using optical devices. Conventional devices like optical fibres are generally diffraction limited. This limits the useful minimum size of a conventional optical device to $\sim\lambda/2n$, where λ is the wavelength of light and n is the refractive index of the medium [2, 3]. Conventional waveguides can be created with dimensions smaller than are allowed by the diffraction limit, but the light will be poorly confined. For example, take a glass cylinder of index 1.5 and diameter 150 nm. The diameter of this cylinder is smaller than 210 nm for an excitation wavelength of 633 nm ($\lambda/2n$), so the device is smaller than is allowed by the diffraction limit. As can be seen from the field distribution (Fig. 1.1a), a cylinder of these dimensions for this wavelength cannot guide the light, and the light leaks out of the cylinder and into the surrounding environment.

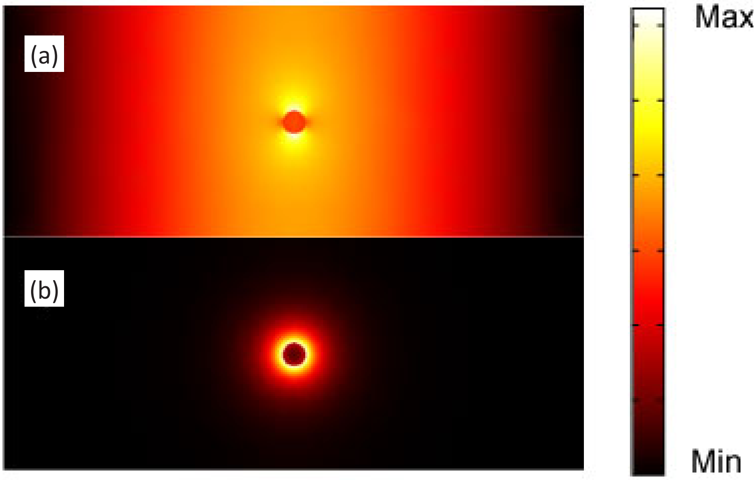

Figure 1.1 (a) The norm of the electric field of the wave propagating along a dielectric cylinder of diameter 150 nm and material refractive index 1.5 for an excitation wavelength of 633 nm and (b) a plasmon propagating along a silver cylinder of diameter 150 nm and excitation wavelength of 633 nm. The confinement of the light is stronger using a metal nanostructure. Conventional dielectric waveguides are diffraction limited. See also Colour Insert.

Since conventional optical devices generally exhibit poor confinement on the nanoscale, it is not possible to fit 2 billion optical devices in a processor, unless new technology is developed. In recent years, there has been much research into nano-photonics, which involves devising nanostructures that guide and manipulate light on the nanoscale. A promising field of endeavour is plasmonics, which uses the interaction of light with the conduction electrons of a metallic nanostructure, which can result in nanoscale confinement of the light [3, 4] (Fig. 1.1b).

1.1.1 History of Plasmons

Plasmonics is a field of research which has existed since the turn of the twentieth century and has blossomed as a highly important area of research in nano-photonics. Plasmonics research has resulted in the development of surface-enhanced Raman spectroscopy (SERS) for detecting traces of chemicals [5, 6], near-field scanning optical microscopy (NSOM) for imaging nanostructures [2, 3], and improved efficiency of solar cells [7, 8] and sensors for the detection of diseases and biological substances [9, 10].

A plasmon is the interaction of light with the conduction electrons or plasma of a metal structure. The light interaction results in coherent oscillations of the electrons along the metal surface, forming an electron wave. Plasmons are a hybrid between electrons and light.

There are two main types of plasmon, the localized surface plasmon resonance (LSPR) associated with metallic nanoparticles [7, 10, 11] and the surface plasmon (SP) associated with flat metal–dielectric interfaces [2, 3]. The LSPR has been observed since ancient Roman times, but the true nature of the effect was not understood until the early 1900s. The Romans used the LSPR effect for the creation of stained-glass windows and artworks. Metal nanoparticles in solution produce different colours when sunlight shines through the solution. The colour depends on the type of metal, size of particle, and the surrounding environment. Scientific investigations into the colours produced by metallic particle solutions can be dated back to 1857 and the works of Faraday [12]. Today, LSPRs have found applications in sensing, solar cells, and the development of certain types of plasmon waveguides known as nanochains [13].

The LSPR is the coherent oscillation of the conduction electrons of a metallic nanoparticle, such as a sphere. It is highly confined to the metal surface. It is non-propagating. A snapshot in time of the electron distribution of an LSPR of a sphere is shown in Fig. 1.2a. The electrons move towards one side of the sphere (dark) leaving a positive charge on the other side of the sphere (light). This LSPR is known as a dipolar LSPR. There are an infinite number of possible LSPRs that the sphere can support. The two common LSPRs are shown in Fig. 1.2.

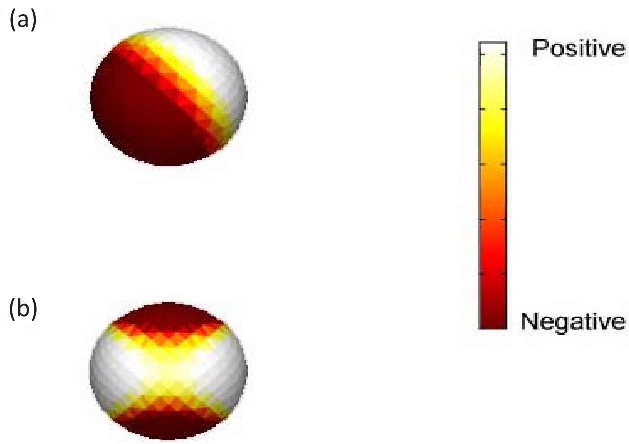

Figure 1.2 Snapshot in time of the charge distribution of (a) dipole LSPR and (b) quadrupolar LSPR. The white regions are regions of positive charge, and the dark regions show regions of electrons. Images created using Maxem©, founder T. J. Davis.

The LSPR wavelength is highly dependent on the particle shape, type of metal, and the permittivity of the surrounding environment [14, 10, 15]. An increase in the permittivity of the surrounding environment causes the resonance to red-shift, or move towards longer wavelengths. The resonance of spheres and ellipsoids can be predicted using the Mie theory, developed in 1908 [11]; the resonances of complex shapes such as rods and nanostars must be predicted using numerical methods [10]. My colleagues and I have devised a method for predicting the resonance of nanoparticles on a substrate, which is applicable to complex nanoparticle shapes [15]. We believe this work should find applications in solar cell and sensing research.

Unlike the LSPR, the SP is a propagating plasmon. It was first detected in the visible regime by Wood in 1902 when analysing the spectra of light reflected from a metal grating [16]. However, Wood did not realize he had detected a plasmon. The actual results of his work were explained 39 years later by Fano [17]. Though the plasmon was an interesting phenomenon, it was not possible to systematically fabricate metallic nanostructures at this time or predict complex plasmon behaviour. Such technology was not developed until the 1990s, and it was in the 1990s that the importance of plasmonics for biomedical and green energy applications began to be realised.

1.1.2 Overarching Purpose

Plasmonics has a wide range of applications, and it is not possible to cover all these applications in a single book chapter. This chapter will focus on the use of SPs for the development of an all-optical nanocircuit, an alternative to electronics. For such a circuit to become a working reality, several key ingredients are required:

- a means of propagating light around the circuit
- a method to efficiently couple light into the circuit
- switches and active components for the development of logic gates and performing Boolean operations

These key ingredients are shown schematically in Fig. 1.3. We will discuss the advances towards the development of the plasmon circuit by reviewing seminal works in this area as well as our own progress. A plasmonic circuit has not been developed as yet, but there has been much progress in terms of coupling light into the circuit and controlling the light propagation. This work is commonly performed using SPs, as these are a propagating plasmon. To fully understand and devise circuit components, knowledge of SPs is essential. The chapter will cover the basic plasmon properties and excitation techniques, as well as refer you to some excellent text books and review articles.

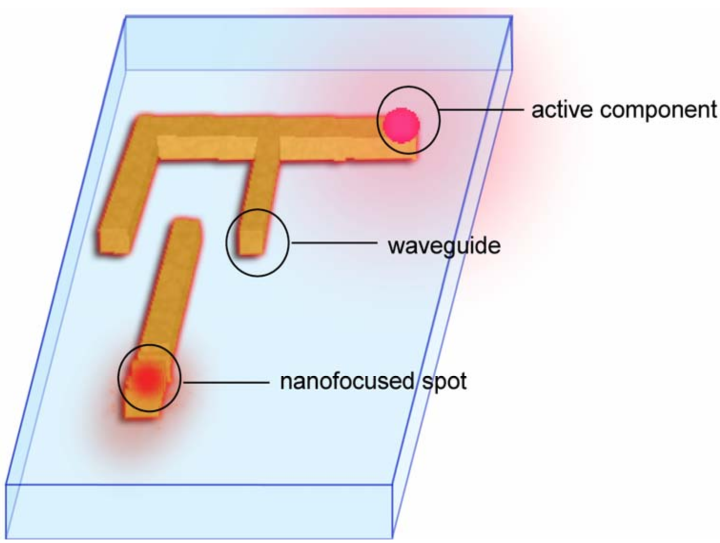

Figure 1.3 Schematic of a plasmon circuit containing the three vital components: waveguide (method of propagating plasmon around circuit), nanofocused spot (method of efficiently coupling light into circuit), and active component for performing Boolean operations.

1.1.3 Properties of Surface Plasmons

The SP is a surface transverse magnetic (TM) wave confined along an interface [4, 2, 3]. The SP will propagate along an interface if the dielectric permittivities of the two isotropic media in contact are opposite to each other, e.g., a metal–dielectric interface—$\varepsilon_2 < 0$ and $\varepsilon_1 > 0$ (Fig. 1.4). The magnitude of this negative dielectric permittivity must be larger than the permittivity of the other medium (dielectric): $|\varepsilon_2| > \varepsilon_1$. This is known as the existence condition of the SP and will be clarified further when we derive the SP dispersion relationship later in this section.

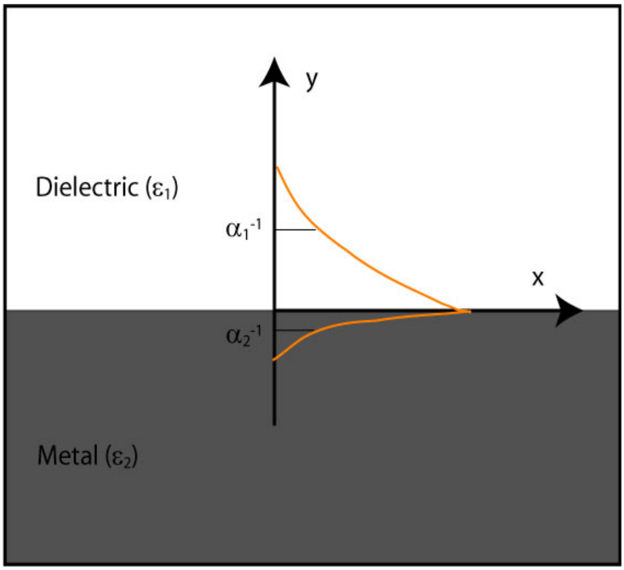

Figure 1.4 Schematic representation of an SP on a dielectric–metal interface. The metal extends into the (x, z) plane, and the SP propagates along the x axis. α_2^{-1} and α_1^{-1} are the penetration depths of the wave into the metal and dielectric, respectively.

The SP can be excited on the metal–dielectric interface using several excitation techniques such as attenuated total reflection and grating coupling. These techniques will be discussed in detail in Section 1.1.4. For now we will focus on the properties of SPs.

SPs are confined to the guiding interface, meaning their electric field is maximum along the interface, exponentially decaying into both the media in contact [4, 2, 3]. This is shown schematically in Fig. 1.4. The typical penetration depths $\alpha_{1,2}^{-1}$ of the plasmon into the dielectric and metal, respectively, can be vastly different. The penetration depth is the distance from the interface at which the maximum of the SP field is reduced by a factor of *e*. It gives an indication of the confinement of the plasmon to the interface. The smaller the penetration depth, the more confined the plasmon is to the interface. Typically the penetration depth into the metal is smaller than into the dielectric.

Since SPs belong to the special category of waves known as TM, they have only one component of the magnetic field which is non-zero, and this component is perpendicular to the interface, or in the y direction (Fig. 1.4). Using Maxwell's equations and rewriting them to contain only the magnetic field, one can describe the magnetic field of the SP in the two media, the metal (2) and the dielectric (1) [2]:

$$\frac{\partial^2 H_{1,2}}{\partial x^2} + \frac{\partial^2 H_{1,2}}{\partial y^2} + \frac{\omega^2}{c^2}\varepsilon_{1,2}H_{1,2} = 0, \tag{1.1}$$

where H is the y component of the magnetic field, c is the speed of light, and ω is the angular frequency. The solutions to the wave equations in (1.1) are sought in the form of a surface wave propagating along the x axis and exponentially decaying in both the media:

$$H_1 = H_0 \exp\{ikx - i\omega t - \alpha_1 y\}, \tag{1.2}$$

$$H_2 = H_0 \exp\{ikx - i\omega t - \alpha_2 y\}, \tag{1.3}$$

where k is the wave number of the plasmon, t is time, and α_1 and α_2 are the reciprocals of the penetration depths into the dielectric and metal, respectively. The equations for the reciprocal penetration depths are obtained by substituting the solutions of Eqs. (1.2) and (1.3) into the wave equations (1.1):

$$\alpha_1 = \sqrt{k^2 - \frac{\omega^2}{c^2}\varepsilon_1} > 0; \quad \alpha_2 = \sqrt{k^2 - \frac{\omega^2}{c^2}\varepsilon_2} > 0.$$

The dispersion relationship for an SP is determined from the conventional boundary conditions at the metal–dielectric interface that should be satisfied by the solutions of Eqs. (1.2) and (1.3). Using these conditions, the wave number k for SPs is [2–4]:

$$k = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}}. \tag{1.4}$$

If ε_2 is negative and larger (in magnitude) than ε_1, which is the SP existence condition, then k is positive, real, and larger than

$$k_{\mathrm{d}} = \frac{\omega}{c}\sqrt{\varepsilon_1}. \tag{1.5}$$

k_d is the wave number of a wave propagating in the dielectric. Thus, we have a surface wave confined to the metal–dielectric interface, i.e., an SP. The dispersion relationship is shown graphically in Fig. 1.5. The dispersion curve is below the light line, which means the plasmon cannot leak into light waves travelling in the dielectric medium. Neither can the SP be generated by light waves from the dielectric striking the smooth metal interface [2–4].

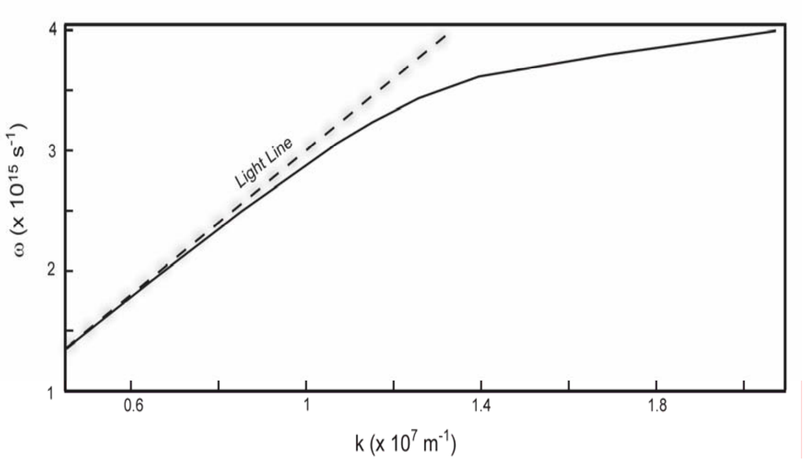

Figure 1.5 Dispersion of a surface plasmon propagating along a gold–air interface.

If the metal half-space in Fig. 1.4 is replaced with a thin metal film, then SPs can exist on both sides of the film. If the film is sufficiently thin, the SPs can interact and couple to form film plasmon modes (Fig. 1.6) [18, 19]. This structure is known as an insulator–metal–insulator waveguide. When the dielectric permittivity is the same on both sides of the film, the SPs couple to form two plasmon types, symmetric and anti-symmetric (Fig. 1.6) [18, 19]. One of the characteristic differences between these plasmons is the distribution of their magnetic field. An anti-symmetric film plasmon is characterised by a zero of the magnetic field in the middle of the film, i.e., an anti-symmetric field distribution (Figure 1.6) [18]. A symmetric film plasmon has a minimum of the magnetic field in the middle of the film, i.e., a symmetric distribution (Fig. 1.6).

The dispersion relations for the anti-symmetric and symmetric plasmons for a metal film of permittivity ε_m and thickness h surrounded by a dielectric with permittivity ε_d (Fig. 1.6) may be derived using Maxwell's equations and conventional boundary conditions and seeking a solution in the form of surface waves propagating on the metal–dielectric interfaces (full details are given in [2]):

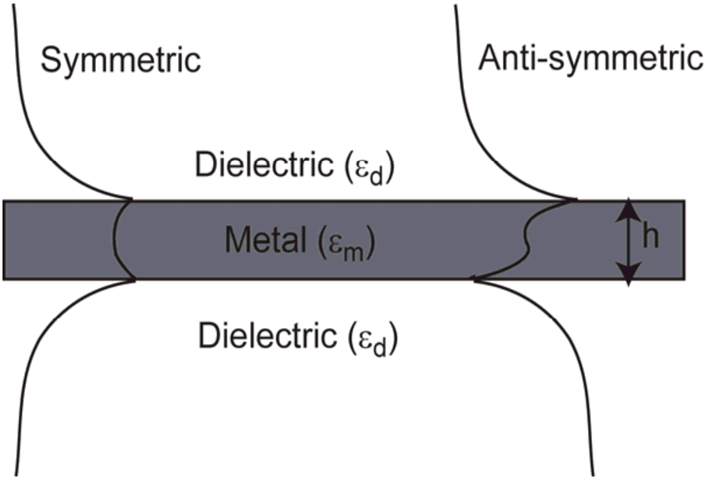

Figure 1.6 Thin metal film (ε_m) of thickness *h* in a dielectric medium (ε_d). The film supports a symmetric and anti-symmetric film plasmon. The magnetic field distribution of each plasmon is depicted.

$$\tan h\left(\frac{\alpha_m h}{2}\right) = -\frac{\alpha_m \varepsilon_d}{\varepsilon_m \alpha_d}, \tag{1.4}$$

$$\tan h\left(\frac{\alpha_m h}{2}\right) = -\frac{\alpha_d \varepsilon_m}{\varepsilon_d \alpha_m}, \tag{1.5}$$

where

$$\alpha_d = \sqrt{k^2 - k_0^2\,\varepsilon_d}, \quad \alpha_m = k^2 - k_0^2\,\varepsilon_m, \tag{1.6}$$

and $k_0 = \omega/c$ is the wave number in vacuum. The dependency of the plasmon wave number on film thickness is given in Fig. 1.7 for the anti-symmetric and symmetric plasmon. As the film thickness is decreased, the wave number of the anti-symmetric mode increases, as does its confinement to the metal–dielectric interface. The wave number of the symmetric mode tends towards that of a wave in the dielectric with decreasing film thickness [18].

Symmetric and anti-symmetric modes also exist in the thin dielectric film sandwiched between two metal half-spaces. These waves are known as gap plasmons. In this case the symmetric mode becomes more localised as the dielectric film thickness is reduced [20], i.e., it behaves similarly to an anti-symmetric film plasmon. As for the anti-symmetric gap plasmon, as the thickness of the dielectric film is reduced, the wave number will decrease to that of a conventional dielectric waveguide mode guided between the two metal plates [18].

Film and gap plasmons are plasmons typically seen in plasmon waveguides and focusing devices. Their applications will be discussed thoroughly in later sections.

1.1.4 Excitation of Surface Plasmons

Since SPs propagating along a metal-dielectric interface have a wave number greater than that of a wave in the dielectric, they cannot be generated by simply shining light onto a flat metal interface. To circumvent this problem, a variety of plasmon excitation methods have been developed: attenuated total reflection (ATR), grating excitation and end-fire excitation [2, 3].

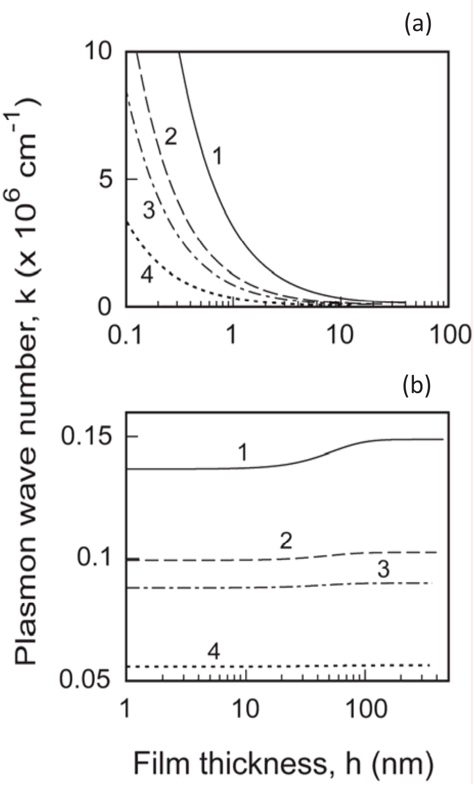

Figure 1.7 Wave number of the (a) anti-symmetric and (b) symmetric film plasmon as a function of film thickness for a silver film at different excitation wavelengths and in different environments: (1) air and wavelength 459.2 nm, (2) air and wavelength 632.8 nm, (3) glass and wavelength 1127 nm, and (4) air and wavelength 1127 nm. Reproduced, with permission, from D. K. Gramotnev and K. C. Vernon, "Adiabatic nano-focusing of plasmons by sharp metallic wedges," *Appl. Phys. B*, 86, 2007, 7–17 [32].

There are two main ATR geometries: Kretschmann and Otto [3]. The Kretschmann geometry consists of a thin metal film on the base of a glass prism (Fig. 1.8a). An incident wave travels through the prism at an angle greater than the critical angle, resulting in internal reflection. For the correct incident angle θ, the tangential component of the incident wave vector, k_{It} will equal the k of an SP on a metal–air interface. Then the field from total internal reflection will generate the SP on the thin metal film [3].

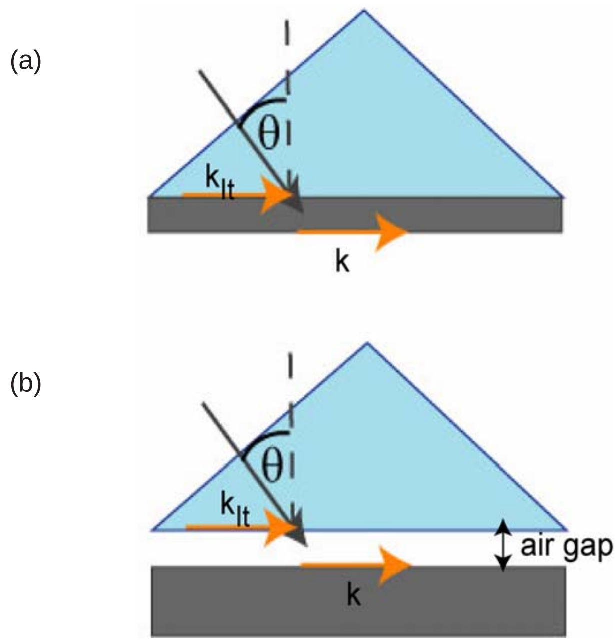

Figure 1.8 SP generation via (a) ATR using Kretschmann geometry and (b) Otto geometry. k_{It} is the tangential component of the incident wave, and k is the wave number of the SP.

Otto geometry is implemented for generating SPs on a thick metal slab (Fig. 1.8b). The geometry consists of a glass prism and metal slab separated by an air gap. Light is incident onto the prism with an angle of incidence greater than the critical angle. The light strikes the bottom of the prism, generating an evanescent wave in the gap and a reflected plane wave in the prism. The evanescent wave induces an SP on the metal–air interface. The amplitude of the SP will be maximal if the tangential component of the incident wave vector, k_{It}, is equal to the wave number of the SP [3].

An alternative excitation approach is to use grating coupling. Light is shone onto a grating with a certain periodicity. This periodicity enables k_{lt} to match that of the SP, resulting in the SP being generated. The gratings can be as simple as an array of holes [21] or rectangular indents [22] in the metal surface, and they need not be metal. Dielectric gratings can also be used [23].

However, one of the simplest ways to generate SPs is to simply shine the laser onto a surface defect or discontinuity, such as a bump in the metal surface, the edge of the metallic nanostructure of interest, and so on. This technique is known as end-fire excitation and is efficient for generating long-ranging surface plasmon polaritons (LRSPPs), though the coupling efficiency into other types of sub-wavelength plasmonic modes is normally quite low [3, 22]. To focus the light more efficiently onto the discontinuities, optical fibers may be implemented, or SPs can be generated in conical tapers and light focused to the discontinuity (Section 1.3) [2]. Near-field scanning optical microscopes operated in the transmission mode can also generate SPs. Their fiber tip focuses light to a small nanoscale area, and the small tip aperture results in a large range of wave numbers, encompassing that of the SP [2]. Using near-field excitation (like near-field scanning optical microscopes and nano-focusing), it is possible to generate plasmons at specific locations with nanoscale accuracy.

Generating SPs on flat metal–dielectric interfaces results in sub-wavelength localisation in only one dimension. To achieve high integration of nano-optical devices for the plasmonic circuit, it is necessary to use plasmon waveguides, capable of confining the plasmon to a sub-wavelength scale in two dimensions.

1.2 PLASMON WAVEGUIDES

In conventional optics, waveguides are used to transport light to the desired area. However, such waveguides cannot be scaled down to the nanoscale, as the light will be poorly confined (Section 1.1). The development of plasmonic waveguides is integral to the development of a nanoscale optical circuit as the waveguides will propagate light around the circuit, provide sub-wavelength confinement in two dimensions, and enable high integration of nano-optical devices. One of the first plasmonic waveguides capable of sub-wavelength guidance is nanochains, developed in 2000. These waveguides consisted of closely spaced metallic nanoparticles [13,24, 25]. An LSPR was excited in the first member of the nanochain, inducing an LSPR in the next member of the chain, and so forth. The chain was capable of localising the plasmon on a sub-wavelength level (~10 nm), but provided a very limited propagation distance of the order of 1/10 of a wavelength, which may prove too small for creating nanoscale optical devices [25].

Larger propagation distances (several micrometers) can be obtained using SPs. The sub-wavelength confinement of SPs in two dimensions, while maintaining significant propagation distances, can be achieved using unique metallic waveguides. The types of plasmon waveguides commonly used for developing circuit components are

- the V-groove waveguide, which consists of a sharp triangular groove in a metal substrate [26–28]
- the wedge waveguide, which consists of a triangular metal wedge [29, 30]
- the gap plasmon waveguide (GPW), which consists of a rectangular gap between two closely spaced metallic films [31–33]
- metal nanowires, which consist of metal cylinders of nano-sized cross-sections [34–36]
- metallic stripes, which consist of metal films of nano-sized cross-sections [37–39]

Each waveguide listed above has its own niche in the nano-optical environment. Some of the waveguides are easier to fabricate, while others can guide plasmons around sharp 90^{o} bends with little scattering. Some waveguides are almost impervious to structural imperfections or can operate single mode, i.e., supporting only one type of plasmon. The properties of each of these waveguides will be discussed in the following sub-sections, and their benefits to plasmonic circuits reviewed.

1.2.1 Stripes and Wires

The metal stripe waveguide is simply a nano-sized rectangular metallic bar surrounded by dielectric [37–39]. A stripe with sub-wavelength thickness but large width (i.e., larger than the wavelength) in a uniform dielectric supports an LRSPP mode (Fig. 1.9). The LRSPP experiences less attenuation and less confinement as the stripe thickness decreases, similar to the symmetric film plasmon (Section 1.1.3).

Since stripes have a finite width the symmetry of the plasmon must be discussed along both the thickness (*x*) and the width (*y*) of the stripe (Fig. 1.9). The symmetry is always discussed in terms of the symmetry of the dominant electric field component. The LRSPP plasmon is known as ss_b^0 as it is a fundamental (^{0}), bound ($_b$) mode, with a symmetric distribution of the predominant electric field component along both *x* and *y*. The distribution of the predominant electric field component of the LRSPP mode is given in

Fig. 1.9 for a 1 μm wide silver stripe with thickness 100 nm and excitation wavelength 532 nm. The surrounding environment has a permittivity of 2.25.

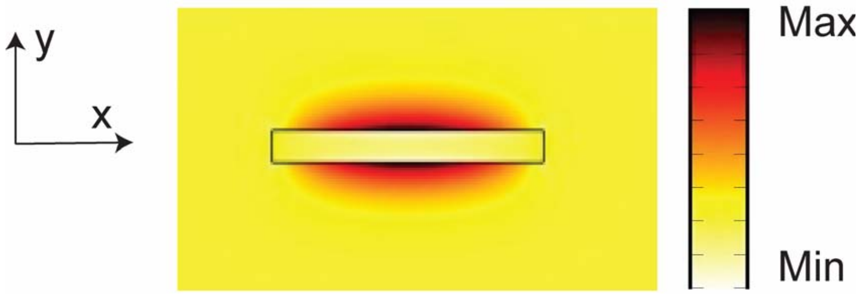

Figure 1.9 The field distribution of the *y* component of the electric field of the fundamental LRSPP mode of a 1 μm wide stripe of thickness 100 nm.

Besides the LRSPP, the stripe waveguide supports three other types of plasmon: as_b, sa_b, and aa_b. The aa_b plasmon is similar to the anti-symmetric plasmon supported by a thin film of infinite width and can exhibit sub-wavelength confinement [38, 40–42]. The as_b is a weaker LRSPP exhibiting a cut-off thickness and width. If a stripe is fabricated with dimensions smaller than the cut-off thickness/width, the as_b will not be supported [41, 42]. The sa_b and aa_b have increasing attenuation and confinement with decreasing thickness and do not exhibit a cut-off [42].

By decreasing one of the stripe dimensions it is possible that only the ss_b^0 plasmon will exist after sufficient propagation lengths. Thus, the stripe waveguide is capable of single-mode operation. This is useful for nanocircuit design. Having only one plasmon greatly simplifies the signal emitted by the circuit [38, 42].

Plasmons supported by stripes were first demonstrated experimentally in 2000 [40]. Since then, they have been utilised in the development of S bends, Y junctions, Mach–Zehnder interferometers, and couplers for nanocircuits [41–43]. The LRSPP was used to create these devices because of its relatively large propagation distance compared with other stripe modes. However, one of the disadvantages of the LRSPP is that it does not experience sub-wavelength confinement and is sensitive to structural imperfections. The other disadvantage is that it experiences significant bend losses. It scatters and radiates significantly as it propagates around sharp, 90° bends [41, 42]. This can be a problem for achieving dense integration in the nanocircuit. To overcome this, bends of large radius of curvature can be used. However, this is also disadvantageous for high integration as it increases the size of the circuit [41, 42]. The bend losses can be reduced by placing the stripe on an embedded dielectric core. In this system the stripe is on a substrate consisting of two different dielectrics. Directly beneath the stripe is a core (a dielectric of high index), while the rest of the substrate consists of a dielectric of lower refractive index. Without the embedded core, fabricating a bend in the stripe leads to the LRSPP leaking out of the stripe and into the surrounding environment. Using a core, this reduces the leaky wave effect. Using this technique, Yamazaki et al. have improved the propagation loss by 0.2 dB/mm for a bending radius of 300 μm [44].

Degiron and colleagues investigated an alternative to the embedded core [45]. They proposed embedding the entire stripe in a layer of thin dielectric. The leaky waves which are emitted as the plasmon propagates around the corner experience total internal reflection from the air–dielectric interface and cannot escape the waveguiding structure. However, using this technique, they found that the optimal bend radius is 2.4 mm for a wavelength of 1550 nm, which is still large [45].

Recently, we theoretically investigated the use of evanescent coupling to connect stripes, rather than using sharp bends [43]. A Mach–Zehnder interferometer was designed on the basis of evanescent coupling between four stripe waveguides (Fig. 1.10). The plasmon is excited in the input arm and then couples to the reference and sample arm through its evanescent field. When the plasmons recombine at the output arm, there is a phase mismatch which results in a measurable drop in the intensity of the plasmon on the output arm. This change in intensity provides information on the refractive index of the sample [43]. The refractive index gives a measure of the materials the sample consists of. The sample could be a sample of water, index 1.33. If the index is different from 1.33, this could indicate contamination of the water.

Using the above design, interferometers of dimension 2.5 μm in width and 55 μm in length can be fabricated. Though not nanoscale, these are some of the first interferometers in the visible regime to come close to nanoscale dimensions [43].

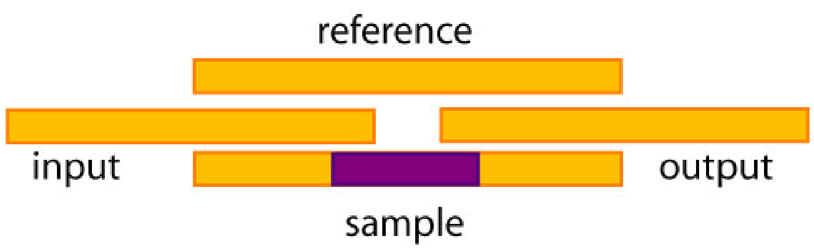

Figure 1.10 Compact interferometer design consisting of four stripe waveguides. The input and output waveguide are evanescently coupled to the reference and sample waveguide.

One of the main reasons sub-wavelength components cannot be formed from stripe waveguides is that devices are built using the LRSPP mode, which does not have sub-wavelength confinement along the width of the waveguide. Other plasmon modes, such as sa_b and aa_b, may exhibit sub-wavelength localisation [46]. For example, Krenn's group investigated a gold stripe of thickness 50 nm and width 200 nm for an excitation wavelength of 800 nm. Localisation in one of the directions was 1/7 of the wavelength in vacuum, demonstrating that sub-wavelength localisation can be obtained [46]. The propagation lengths were on the order of 2.5 μm, still longer than what can be achieved using a nanochain [46]. However, such modes are harder to excite than LRSPPs.

When considering a stripe waveguide there is always a trade-off between confinement of the guided mode and propagation distance. This trade-off also occurs for many other types of plasmon waveguides, such as the V-groove waveguide and GPW. In a recent analysis by Buckley and Berini [47] a method for calculating the figure of merit, M^{2D} (i.e., an indication of the trade-off) for 2D plasmon waveguides has been defined:

$$M_1^{2D} = \sqrt{\frac{\pi}{A_e}}\frac{1}{\alpha_z}. \tag{1.7}$$

A_e is the mode size defined as the area bounded by the $1/e$ field magnitude contour relative to the global field maximum, and α_z is the attenuation coefficient. They demonstrated that narrow thick stripes provide smaller mode area than wide thin stripes, but larger wave numbers may be obtained using wide thin stripes compared with narrow thick stripes. In terms of localisation, it is the mode area which is important. This is why the figure of merit defined by Buckley and Berini (1.7) uses mode area rather than wave number.

An alternative to metal stripes is metal nanowires, which have much of the same guiding properties as the stripe. The nanowire is a long cylindrical rod with a nano-sized diameter [25, 34, 36]. The nanowire has a circular cross-section. Nanowires are capable of providing sub-wavelength localisation of the plasmon eigenmode. When tapered, they are useful for nano-focusing (Section 1.3). To excite plasmons in a nanowire the incident wave must be polarised such that its electric field is perpendicular to the wire axis. This could lead to polarisation-sensitive switches [34, 48]. Transistors, LEDs, photodetectors, and lasers have been created using these structures [49, 50].

Nanowires can be single crystal, which minimises surface defects and provides longer propagation distances of the plasmon. Ditlbacher and colleagues investigated single-crystal, 18.6 μm long silver nanowires with a diameter of ~120 nm [25]. The plasmon propagation distances in these wires were ~10 μm. This is substantial for nano-optic applications [25]. The nanowires were then used as Fabry–Perot resonators. A plasmon was stimulated at one end of the silver nanowire using a laser beam, focused by a microscope objective and incident perpendicular to the substrate plane. The laser light is focused onto the nanowire, and scatters over a broad range of angles. Some of the scattered light will be at the right angle to produce a plasmon in the nanowire. Thus, some of the laser energy will generate a plasmon which will propagate along the nanowire and reflect from the opposite wire end [25]. The plasmon is excited at one end of the wire and is reflected from the other end with ~25% efficiency. The wire thus forms a natural Fabry–Perot cavity. The reflection of the plasmon results in periodic modulation of the plasmon intensity as the plasmon reflects back onto itself.

Nanowires also suffer strong bend losses of their guided plasmons. Though nanowires and stripes are relatively simple to fabricate, integration can be troublesome because of these bend losses. An alternative to these waveguiding structures is to use lithographic plasmon waveguides, such as the triangular plasmon devices and the GPW. Such devices support plasmon modes with low bend losses.

1.2.2 Triangular Waveguides

V-groove waveguides were originally envisaged by Lu and Maradudin in 1990 [27] and consist of triangular channels in a planar metal surface (Fig. 1.11). The V groove can support a one-dimensional plasmon known as a channel plasmon-polariton (CPP), which can experience strong sub-wavelength confinement in the groove. The plasmon can be confined in an area spanning ~100 nm above the groove tip for an excitation wavelength of 633 nm [51, 52]. The field distribution of the CPP mode is given in Fig. 1.11.

Sufficiently sharp V grooves (see [53] for more details) can be investigated using the geometrical optics approximation (GOA). GOA was discussed thoroughly by Kravtsov and Orlov in the 1990s [54]. This approach is applicable for sufficiently tapered structures such that a wave travelling in the structure does not experience a significant change in wave number as it propagates distances of about one wavelength. In other words the wavelength is small compared with the characteristic dimension of the problem.

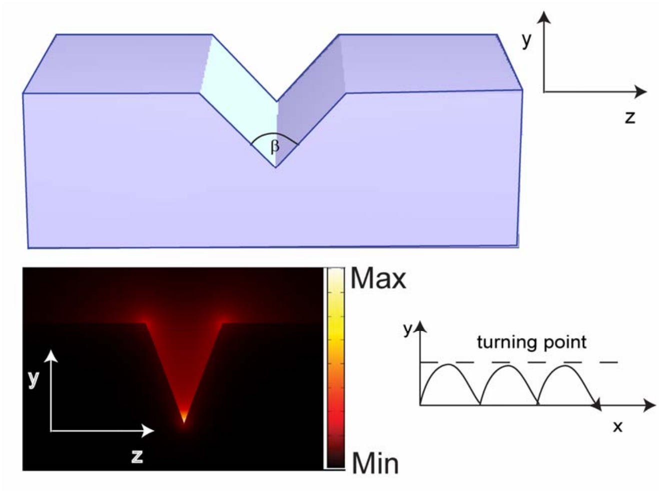

Figure 1.11 The CPP propagates in the *x* direction (i.e., along the tip of the groove of angle θ) reflecting from the tip and the turning point y_t. The $|E|$ distribution of a 45°, 200 nm deep groove in gold was calculated using COMSOL Multiphysics. Excitation wavelength was 532 nm.

Using GOA any function ϕ that is related to the wave field will take the form [55]

$$\phi = ae^{i\psi}, \tag{1.8}$$

where a is the amplitude and ψ is the phase. The time derivative of the phase gives the frequency of the wave, and the space derivative gives the wave vector of the wave, **k.**

In GOA a V groove in a metal substrate will be approximated as a thin dielectric film of slowly varying thickness between metal half-spaces [53]. The thickness of the film is slowly varying, such that the parameters of the structure do not vary significantly within distances of about one wavelength.

For example, say there is a groove with a sufficiently sharp groove angle θ such that GOA is applicable (Fig. 1.11). If you consider a certain point above the tip of the groove, the plasmon at this point will be approximately the same as a gap plasmon propagating in a uniform dielectric film of width H (the local width of the groove at the considered point) between two metal half-spaces. The CPP can thus be considered a guided gap plasmon. It propagates along the length of the groove, reflecting from the groove tip and a turning point a certain height above the tip (Fig. 1.11).

CPPs may only be guided by a groove if the groove angle θ (Fig. 1.11) lies between two critical angles [53]:

$$\beta_{c2} \leq \beta < \beta_{c1}, \tag{1.9}$$

where β_{c2} is the lower critical angle determined via GOA and β_{c1} is the upper critical angle determined via numerical approaches. If the groove angle is smaller than β_{c2}, the plasmon will no longer be reflected from the tip but may adiabatically stop as it approaches the tip experiencing nano-focusing (Section 1.3). If the groove angle is larger than β_{c1}, the CPP mode will leak into SPs, which will escape up the sides of the groove [53].

The CPP propagates along the tip of the groove and has a propagation distance of tens of micrometers in the visible spectrum, sufficient for the plasmonic circuit. Other important features of CPPs are their strong localisation, almost 100% transmission around sharp bends, high tolerance to structural imperfections, and the possibility of single-mode operation [51, 52]. The CPP mode was detected experimentally by Bozhevolyni and colleagues [26, 56]. Sub-wavelength localisation, single-mode operation, and long propagation distance of the CPP were verified.

Bozhevolyni *et al.* fabricated the V groove and used it as the basic building block behind ring resonators, Mach–Zehnder interferometers, and Y splitters [56] (Fig. 1.12). The grooves had an angle of ~25°, depth of 1.1–1.3 μm, and excitation wavelengths in the 1.4–1.6 μm range [56]. The Y splitter showed remarkably low bend loss, and the CPP was hardly affected by structural imperfections [56]. The corresponding Mach–Zehnder also showed a strong tolerance to structural imperfections [56].

To investigate the sensitivity of the CPP to the surrounding environment, we investigated the V groove for changing dielectric filling inside the groove. It was shown that by using filling it is possible to optimise the confinement and propagation distance of the plasmon and design the cut-off angles of the groove, β_{c1} and β_{c2} [57]. The confinement of the CPP mode is increased with increasing permittivity of the dielectric filling [57]. The filling also results in increasing the cut-off angles and decreasing the propagation distance. For example, a silver groove of angle 30° and excitation wavelength 633 nm, the propagation distance decreases by a factor of 4 for an increase in the filling permittivity by a factor of 2. By the same token the confinement increases by a factor of 4 [57].

We also investigated rounding of the groove tip. Rounding of the groove tip occurs when fabricating V grooves using lithography, so our investigated structure was closer to that of a real V groove [57]. Curvature of the tip affects the CPP mode properties. For a vacuum groove, changing the curvature of the tip has a minimal effect, but for grooves containing dielectric filling of a large permittivity, the radius of the tip significantly affects the CPP wave number, propagation distance, and confinement, all important properties in designing plasmonic circuits [57].

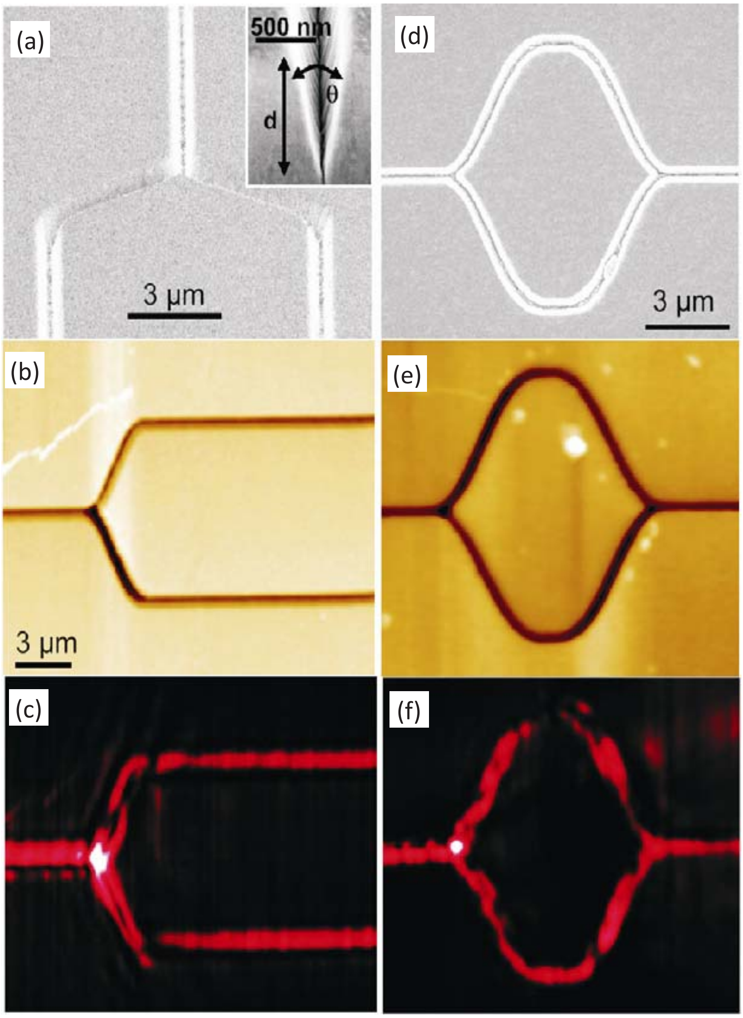

Figure 1.12 Scanning electron microscope (SEM) images of Y splitters (a,b) and Mach–Zehnder interferometers (d,e) made of V grooves. Figures (c,f) showing the wave travelling through the structures and are taken using near-field scanning optical microscopy. Reprinted, by permission, from Ref. [12].

The V groove can prove quite difficult to fabricate for small groove angles. An alternative structure is a triangular metallic wedge. These wedges support plasmon modes known as wedge plasmons (WPs) propagating along the wedge tip (Fig. 1.13) [29, 30, 58]. In GOA, the WPs can be considered film plasmons, which reflect from the tip and a turning point and propagate along the length of the wedge (similar to the description of CPPs).

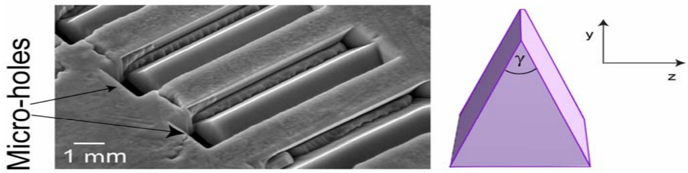

Figure 1.13 SEM image of fabricated wedges and schematic of a wedge of angle γ. A plasmon propagates along the tip of the wedge in the x direction. SEM images reprinted, with permission, from Ref. [55]. Copyright 2005, American Institute of Physics.

For sufficiently sharp wedge angles γ the wedge waveguide has a single-mode operation. The WP has significant propagation distances along the tip of the wedge with distances on the order of micrometers [30]. Such propagation distances make the wedge waveguide a promising device for nano-optics. WPs may experience strong sub-wavelength localisation, of the order of tens of nanometers for the visible regime.

Using a full numerical solution of Maxwell's equations via a finite-difference time domain (FDTD), it was found that a critical wedge angle exists, and WPs can be supported only by wedges with smaller wedge angle than the critical angle [30]. For a silver wedge at the red He-Ne wavelength (632.8 nm), this angle is $\sim 102^\circ$. If the wedge angle is larger than this value, the WP will leak into SPs travelling along the sides of the wedge [30]. A lower critical wedge angle also exists, below which a WP may not be guided. This angle is $\sim 7^\circ$ for a silver wedge at the red He-Ne wavelength [58].

Wedge structures were fabricated using focused-ion beam lithography (FIB) (Fig. 1.13) [30]. Holes were fabricated in the metal film, and laser light was shone through these holes and excited the plasmons on the wedge. Using a NSOM the near-field intensities of the WP were monitored as the WP propagated along the wedge tip [30]. It was seen that the WP modes do exhibit sub-wavelength localisation, with propagation distances of 1.5 μm for the red He-Ne wavelength [30].

1.2.3 Gap Plasmon Waveguides

Another lithographic waveguide which is simpler to fabricate than the triangular structures is the gap plasmon waveguide (GPW), which consists of a thin metal film containing a rectangular groove or slot [31–33] (Fig. 1.14). This waveguide provides two-dimensional, sub-wavelength localisation of the guided mode. It was devised by us and by two other groups, led by Liu and Veronis. All teams published their seminal works in 2005.

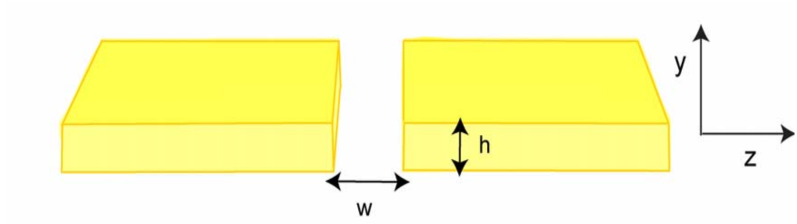

Figure 1.14 The GPW consists of a slot in a thin metal membrane of finite dimensions in the *y* and *z* directions and infinite in the *x* direction. The slot has a height *h* and a width *w*.

The papers by Liu et al. [31] and Veronis et al. [33] describe the existence of GPW modes in the form of guided gap plasmons, reflecting from the bottom and the top of the slot and propagating along the waveguide in the *x* direction (Fig. 1.14). We showed that there is another plasmon which consists of the four corners of the slot coupling together [32]. This plasmon is known as the fundamental mode.

The guided plasmons in the GPW have propagation distances in the micrometer range for sub-wavelength confinement [31, 33]. The plasmon is also efficiently guided around sharp bends—e.g. for a GPW of w = 50 nm and h = 200 nm the plasmon may be guided around a bend of radius of curvature 100 nm with a transmissivity of 77% (Fig. 1.14). This far surpasses nanowires and stripes of similar structural parameters [31].

We conducted theoretical work into coupling between the fundamental modes supported by two nearby GPW devices (Fig. 1.15) [59]. In a plasmon coupler device a plasmon is generated in one waveguide, and after a certain propagation distance, known as the coupling length, it transfers all its energy to the second waveguide. Such devices may be useful for routing light around the circuit. In the GPW coupler we showed that the coupling predominantly occurs by means of the field extending from the slots into the substrate.

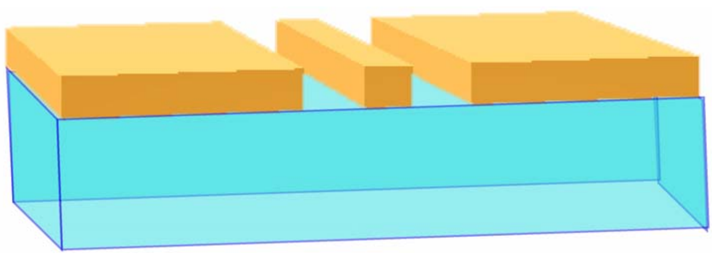

Figure 1.15 Schematic of the GPW coupler, which consists of two coupled slots separated by a metal bar.

In collaboration with the University of Tokushima, Japan, individual GPW structures were fabricated [32]. Several GPWs were etched in silver, with varying widths and heights (Fig. 1.16). The heights varied from 800 nm to 1300 nm, and the width varied from 150 nm to 300 nm. A 633 nm laser source was used to excite the GPW mode. When experiment was compared with numerical calculations, it was seen that the gap-plasmon-like GPW

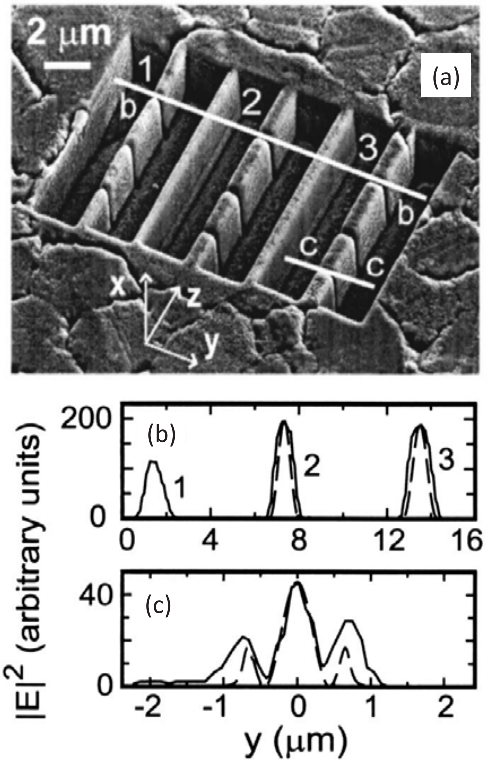

Figure 1.16 (a) SEM image of several GPWs consisting of five silver ridges of height 2.2 μm on a glass substrate. Three ridges of thickness (1) 800 nm, (2) 1200 nm, and (3)1300 nm contain gaps etched down to the glass substrate. Widths of the gaps in the *b*–*b* cross-section: At the top of the ridge w = 300 nm, at the bottom of the ridge w = 200 nm, and in the *c*–*c* cross-section w = 150 nm and w = 70 nm. A laser beam is incident onto the structure from underneath, through the glass substrate. The signal from scattering of the generated GPW modes at the tops of the ridges is registered. (b) The experimental distribution of the signal intensity (solid curves), and the corresponding theoretical curves of the intensity distribution of the GPW mode with w = 300 nm and the corresponding thicknesses of the ridge. (c) Same as b, but for the gap in the *c*–*c* cross-section with w = 150 nm. Reprinted, with permission, from Ref. [56]. Copyright 2005, American Institute of Physics.

modes (the ones detected by Liu et al. and Veronis et al.) were detected in this experiment. Unfortunately, rounded metal edges will limit the propagation of the fundamental GPW mode, so it is doubtful whether it will be seen in experiments.

The five waveguides—the V groove, wedge, wire, stripe, and GPW—are all useful for nanocircuits. The most important parameters for circuit design are confinement, low bend loss, sufficient propagation lengths, ease of fabrication, and single-mode operation. The only waveguide which does not provide low bend loss is the nanowire. Furthermore, all waveguides but the nanowire can be fabricated lithographically with nanoscale control of the waveguide position. This is currently not the case for the nanowire.

The only guide which may not find applications in plasmon waveguiding in circuits is the nanowire. Such a device cannot be used to create a complex circuit. However, the nanowire has found applications in nano-focusing, a method for taking light to the nanoscale and coupling it into the nanocircuit.

1.3 NANO-FOCUSING

Sub-wavelength waveguides will be an integral part of an optical circuit, but the next problem will be to couple light efficiently into these nanoscale devices. This may be achieved using tapered metal nanowires and tapered dielectric nanowires coated in metal [60–62]. These structures are tapered in such a way that they take on a cone-like shape. The structures focus the light to a spot of nano-sized area at the tip of the cone. In this process, it is also possible to significantly enhance the light field, creating a very intense spot on the nanoscale. This is advantageous in sensing, possibly enabling, the interaction of light with single molecules [62].

The tapered nanowires are the nano-optical equivalents of spherical lenses. The nano-optical equivalents of cylindrical lenses are the V-groove and wedge structures. These structures focus light to a strip of nano-sized width. The first experimental evidence of a nano-cylindrical lens was in 2009. The light was nano-focused, and the light field enhanced by a factor of 10. The nano-cylindrical and nano-spherical lenses will be useful for coupling light into the plasmonic circuit.

1.3.1 Nano-spherical Lenses

Nano-focusing is simply the localisation of the electromagnetic field to an area smaller than allowed by the diffraction limit—normally through a gradual adiabatic process [62]. Recent research into tapered metal nanowires has suggested that the tapered structure acts as the nanoscale equivalent of a spherical lens focusing light to a spot of nano-sized dimensions [62–64]. A theoretical paper by Stockman [62] has shown that a tapered silver nanowire with a sufficiently sharp taper angle may support a SP travelling towards the tip. As the SP approaches the tip, it adiabatically slows down with both its phase and group velocity tending to zero asymptotically. Stockman found that there is a three-order increase of the electric field intensity of the plasmon as it approaches the tip of the cone. This large field enhancement with nanoscale localisation means the tapered rod can provide a very intense light source on the nanoscale, which would prove extremely useful for sensing and coupling light into nano-sized plasmon waveguides and circuit components.

This theory was tested by Ropers and colleagues [65]. To efficiently couple light into tapered nanowires, a grating was etched above the wire tip (Fig. 1.17). The grating was illuminated, generating SPs and scattered modes, which propagated towards the tip. Ropers et al. fabricated the grating sufficiently far from the tip so that only SPs reached the tip. The distance between the grating and tip was optimised such that the excitation field was well separated from the tip, and also to reduce the required propagation distance and hence loss of the SP. They showed that generating the SP resulted in a light source at the tip with stronger confinement than in the case of shining a laser directly onto the tip (i.e., butt coupling or end-fire excitation), thus supporting Stockman's theory [62].

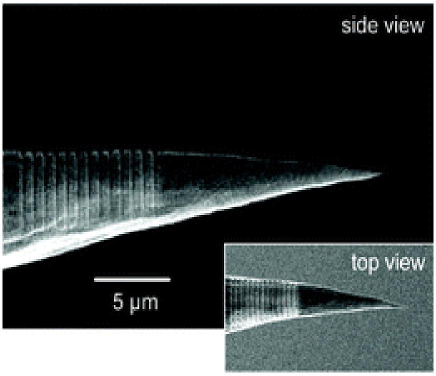

Figure 1.17 Grating etched into tapered nanowire. Laser is directed at grating producing an SP, which propagates towards the tip of the tapered nanowire and experiences nano-focusing. Reprinted, with permission, from [60]. Copyright 2007, American Chemical Society.

Besides the conical metal tip, a tapered dielectric nanowire coated in metal is also capable of focusing light to a nano-sized spot [60, 61, 66]. Plasmons can be generated in these devices by fabricating the rod on the end of an optical fiber. For example, Janunts et al. have suggested that a silver-coated glass cone at the end of an optical fiber can be used to nano-focus SPs [61]. The guided mode in the fiber should couple into SPs travelling on the outside of the silver coating. As the SP propagates towards the tip, its wavelength and speed should decrease and a large amount of energy should be concentrated at the tip [61].

Janunts et al. suggest that this fiber with a glass cone tip coated in a thin layer of silver can be used as a NSOM probe. Because of the large increase in plasmon energy at the tip, this new probe may be used to analyse non-linear responses of a sample as well as to spatially resolve second-harmonic generation and Raman scattering [61].

Surface plasmon probes for near-field microscopy were fabricated by Ashino and Ohtsu [60]. Similar to the above probe, their probe also consisted of a glass cone coated in a thin layer of metal (gold), whose thickness was about 80 nm except at the tip, where the thickness was around 30 nm. The probe had an angle around 20°. A thin layer (~1 nm) of germanium was used as an adhesive between the gold and glass. The plasmons were excited into the probe using the Otto geometry (Section 1.1.4). The probe achieved an intensity of collected light six times that of an uncoated glass probe. However, an intensity 100–200 times that of the incident light field was expected. This discrepancy is thought to be due to the thickness of the gold layer being too thick. Alternatively, the light intensity detected by the uncoated probe could be due to scattered light [60], which renders the normalised intensity inaccurate.

A theoretical study by Bouhlier and colleagues [66] has determined the optimal film thickness of the metal layer on the fiber. For a gold film (at the wavelength of 488 nm) on the fiber of permittivity 2.18, the optimal film thickness is ~60 nm. If the film is thinner than this value, though there is stronger field enhancement, the penetration of the plasmon through the layer is greater, leading to a larger far-field background signal [66]. If the thickness is greater than ~60 nm, there is less penetration, and thus less far-field background signal. However, there is also smaller field enhancement.

Bouhlier and colleagues [66] also studied the excitation of plasmons in the nano-focusing structure. To excite plasmon modes on the gold–dielectric interface, a radially polarised TM mode is required. However, fibers usually support TE and TM modes, and these modes can be decoupled only if there are no azimuthal variations of the field. This makes the generation of the pure TM mode quite difficult as it is not easily coupled to the fiber. Additionally, the polarisation will be substantially effected by bending of the fiber and the quality of injection of the mode into the fiber [66].

The focusing of light to a nanoscale spot is well established. It has been demonstrated both theoretically and experimentally. The tapered nanowire acts as the nano-optical equivalent of a spherical lens and will have its place in nano-optical circuitry. However, there is another type of lens important in optics, the cylindrical lens. It has been shown that V grooves and wedges can act as the nano-optical equivalents of cylindrical lenses. The first experimental evidence of the nano-optical cylindrical lens occurred in 2009.

1.3.2 Nano-cylindrical Lenses

A V groove in a metal substrate will act as the nano-optical equivalent of a cylindrical lens, as long as the groove angle β is sufficiently small [63, 67]. The device will focus light to a strip of nano-sized width, and with a length that of the groove. This nano-optical equivalent of a cylindrical lens should find novel applications in sensing, microscopy, and efficiently coupling light into nano-scale devices.

Using GOA, the V groove was treated as a thin dielectric film between two metal half-spaces. The thickness of the film was slowly varying such that the wave number of the gap plasmon did not change significantly as it propagated distances of about a wavelength, i.e., sufficiently sharp groove angles.

Only the symmetric gap plasmon has a wave number which increases as the thickness of film decreases, so only the symmetric gap plasmon is useful for nano-focusing [63]. Nano-focusing can occur for certain taper angles only. Gramotnev showed that if the groove angle is sufficiently small (less than 5° for a silver–vacuum groove for the 632.8 nm wavelength), a plasmon approaching the tip of the groove will experience nano-focusing, adiabatically stopping at the tip. There was a finite enhancement of the magnetic field of the plasmon near the tip and an infinite enhancement of the plasmon electric field, in the absence of dissipation. The groove will act as an extremely intense light source on the nanoscale with the light focused to a line of nanoscale width and length that of the groove.

The nano-focusing of light using V-groove structures was verified in 2009 by two separate research teams: Volkov et al. [68] and Choi et al. [69]. Volkov et al. had an innovative approach of decreasing both the groove depth and the groove angle. They began by manufacturing 28° grooves using focused ion beam lithography, and then slowly decreasing the depth and angle of groove as they etched [68]. The plasmon was excited in the 28° groove, and as it propagated along the groove of ever-decreasing angle, it experienced nano-focusing, with measured intensity enhancements of ~90 for the telecom wavelength range (1425–1620 nm).

Choi et al. used a different approach [69]. They manufactured a groove of angle 71° and then, near the groove tip, further decreased the groove angle to 17° using focused ion beam lithography. Intensity enhancements of ~10 were recorded.

There is an alternative to the groove cylindrical lens, and that is the wedge. The wedge waveguide and the V-groove waveguide have similar guiding properties. Thus we investigated the possibility of using sharp metal wedges for nano-focusing [70, 71].

We investigated nano-focusing in wedges surrounded by a uniform medium and on a dielectric substrate (Fig. 1.18). It is hoped the latter will prove even easier to fabricate and more structurally stable and robust compared with wedges surrounded by uniform media. All structures were analysed using GOA [70, 71].

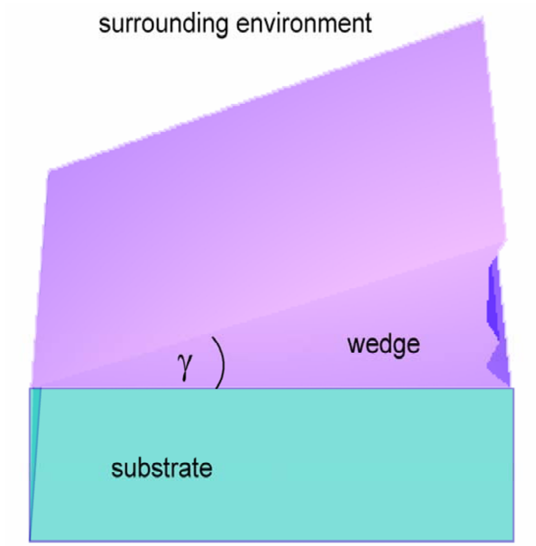

Figure 1.18 Schematic of the tapered film (metal wedge) on a dielectric substrate.

In the metal wedge surrounded by a uniform dielectric medium (permittivity of surrounding environment = permittivity of substrate = ε_c), it is the anti-symmetric film plasmon that undergoes nano-focusing near the wedge tip. The wedge angle γ must be smaller than $-2\varepsilon_c/\mathrm{Re}(\varepsilon_m)$, where ε_m is the metal permittivity and ε_c is the permittivity of the dielectric medium [70]. This gives wedge angles of less than 7° for a silver wedge in vacuum for the excitation wavelength of 632 nm. Though there is local field enhancement at the tip of the wedge, it is about five times weaker than what can be achieved with a V groove [53].