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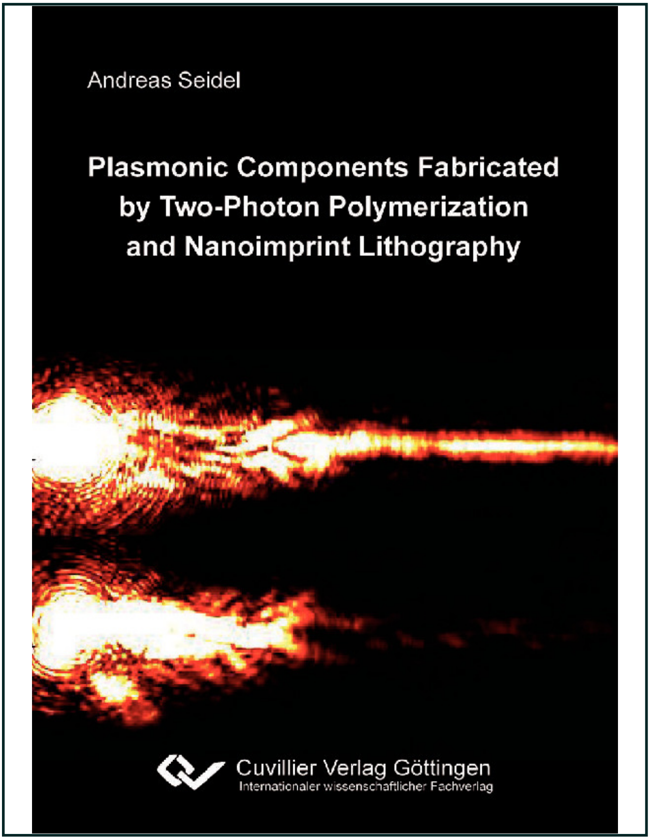
Plasmonic Components Fabricated by Two-Photon Polymerization and Nanoimprint Lithography



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1 Introduction

The introductory section of this thesis aims to provide insight and introduction into the field of research of surface plasmonics in general and dielectric-loaded surface-plasmon polariton waveguides in particular. The motivation for this research is given by illuminating the background and the history of the field.

1.1 A Brief Introduction to the History of Optics & Plasmonics

Optics is, beyond any doubt, one of the main drivers behind a revolution in the world of science and technology today, and has been for the past decades [1, 2, 3, 4]. But the story of optics is an incredibly old one, older than man, older even than the Solar System. In order to shed some light on this issue, we will divide the story of optics into two parts - the part where humans actively shape and control light, and the part where optical phenomena and devices appeared and developed without the influence of man. We will deal with the latter part first.

Beyond any doubt, the oldest and by far the largest lenses in existence are the astrophysical gravitational lenses, composed of stellar bodies (from individual stars up to galaxy clusters) whose gravitational field warps space so that light travelling through them becomes distorted as if it were passing through an optical lens. These lenses were first considered by Albert Einstein in 1936 [5], and have been put to very good use since, despite Einstein's skepticism concerning their utility. We will leave these lenses aside. We will also leave aside the plethora of primeval astrophysical masers (coherent microwave beam sources), of which an ever-increasing number has been discovered since 1965 [6, 7], and even the much rarer astrophysical lasers, which are a comparatively recent discovery [8]. While these subjects are fascinating, the content of this thesis will remain closer to Earth, and closer to optics applications which all humans may one day use.

Biological development of optical devices, however, still precedes human involvement by some five hundred million years, with the "invention" of the first image-forming eye around 543 million years ago in trilobites, a group of extinct marine arthropods [9]. It has been suggested that nature's developing of this first image-forming device sparked the Cambrian Explosion in evolution, as the size, shape, colour, and behaviour of animals were revealed, and tremendous evolutionary pressure was created to evolve hard external parts as defences, as well as limbs for swimming and clasping, either to catch prey or to escape [10]. Over the course of millions of years since the "invention of the eye", nature continued to evolve ever more specialized optical components. Diffraction gratings, narrow- and broadband reflectors, liquid crystals, anti-reflection coatings, and photonic crystals including photonic crystal fibres have all been found both in prehistoric and extant animal and plant species, sometimes in surprisingly distinct forms [10]. Human research, it seems, is only slowly catching up to what nature developed long ago.

It is not known how or when man gained consciousness or started to think abstractly about his surroundings. But it is very likely that his eyesight had a major part in the origin of his consciousness. When man first gazed at the heavens and pondered on their origins, when he first conceived simple forms of astronomical observation and religious worship of heavenly bodies, he was, in fact, already laying the foundations for optics. One could make a case that the first optical instruments were the vast neolithic monuments at Stonehenge and elsewhere [11, 12]. The real history of optics, that is the manipulation of light to serve humanity's needs, begins with the first lens-making activity by the ancient Egyptians [13] and Assyrians [14]. While the precise use of the lenses fabricated in antiquity is not always entirely clear, and their everyday occurrence has been questioned [15], it is hardly conceivable that their remarkable optical properties escaped notice.

But man was never a pure experimentalist. He soon discovered that all things in nature, including all things optical, can be described in laws and mathematics. The law of refraction, first discovered in its correct form by Ibn Sahl in 984 and rediscovered by Snellius in 1621 [16, 17, 18] was one of the earliest optical laws to be discovered. When the telescope was invented, credited today to the German lensmaker Hans Lippershey, and improved by Galileo Galilei a short time later, this was the beginning of a revolution both in science and our view of the world as a whole [19].

Since that moment, optical science has progressed in leaps and bounds as a multitude of linear and nonlinear optical processes were discovered, characterized, and formulated as scientific laws, to be harnessed in applications or used to enable further discoveries. In 1861 and 1865, James Clerk Maxwell published two papers, in which he concluded that light was an electromagnetic wave and also laid down four fundamental equations, known today as "Maxwell's Equations" that form the basis of all modern attempts at electromagnetic and optical engineering [20, 21].

The latest revolution in optics could be said to have started when Theodore H. Maiman built the first working laser in 1960 [22]. This "solution without a problem" soon became the most vital instrument in modern research and has also become a ubiquitous tool in our everyday lives, be it in our computer, DVD player, or simply the provider of communications signal when we make a long-distance telephone call.

As the field of optics continues to evolve, with feature sizes steadily decreasing in efforts to miniaturize and economize, new factors come into play. Materials change their properties at short length scales, and on the nano-scale, significantly so [23]. The next big challenge, which may lead to the next revolution in optics and science as a whole, is to harness the electromagnetic characteristics of materials at the nanoscale, and the key to this is plasmonics.

The history of plasmonics probably begins with the Lycurgus Cup, which today is in the British Museum in London, shown in figure 1.1. The cup is highly unusual in many respects, but from a physical (and plasmonic) point of view, most interesting of all are its optical properties. The cup is made of glass which contains gold and silver nanoparticles [24]. The nanoparticles have a strong influence on the scattering of the

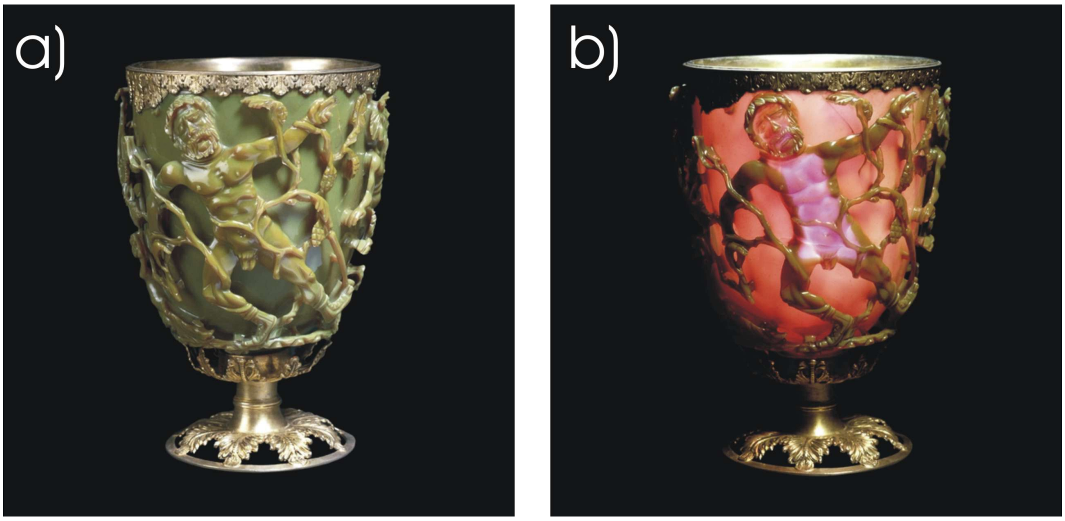

Figure 1.1: The Lycurgus Cup. Late Roman, 4th century AD. Probably made in Rome. A dichroic glass cup with a mythological scene. Source of images and caption: British Museum

light so that the cup looks opaque green when viewed in reflection and translucent red to pink when viewed in transmission. The Romans presumably knew about this effect, because the cup is thought to be designed not for drinking but as a lamp, and in this role the glass cup would display its properties at their best. Several other fragments of similar glass from Roman times have been found, but no whole vessels. It seems likely that the art of making this kind of colloid-coloured glass was lost, since no evidence of continued production has been found. It seems possible that the knowledge was constrained to one single glass workshop, and perhaps even only one single master glass-maker, an explanation that has also been proffered for a rare group of Islamic lustre ceramics with similarly spectacular metal-based optical effects [25]. An alternative explanation is that there was only one lucky block of raw glass, which was created with these properties accidentally.

In Europe, research or work of any kind involving colloidal gold began again only at the end of the 16th century [26]. At the same time, it should be emphasized that the use of silver and copper in glass colouring and glazing was commonplace since antiquity and remained so [25]. Medieval stained-glass church windows, insofar as they have been investigated, are not coloured with colloidal gold. All examples of red stained-glass from this period that have been analyzed were found to be either clear glass coloured with a thin overlay of copper or painted red [24, 27].

The resurgence of colloidal gold was possibly inspired by Islamic use of gold-ruby glass [28], but certainly Georgius Agricola mentioned a ruby-red colour to be obtained by dissolving gold in a liquid in his works [26]. The great German alchemist and father of modern chemistry Andreas Libau (a.k.a. Libavius) mentions the same thing in his most well-known work Alchemia, published in 1597 [29]. Johann Rudolf Glauber takes up the idea and proposes rebuilding the German economy (devastated by the Thirty Years' War) by, amongst other things, large-scale production of high-quality glassware using gold-based red as the colourant, and gives a recipe for it as well [30]. Following early experiments with gold colloid solutions by Andreas Cassius [31] and Johann Christian Orschall [32], the breakthrough discovery of a repeatable and controllable process for using gold nanoparticles to colour glass are made by Johann Kunckel in the early 18th century [33], who at the time was the chief glass-maker of Friedrich Wilhelm of Brandenburg. The process quickly became widely popular, with the largest centres of ruby glass production later to be found in Bohemia and Victorian Britain.

Gold colloid solutions were also rapidly adopted as an enamel paint for porcelain, used in Meissen no later than 1719 and in China a mere four years later [26], possibly introduced through German Jesuits [28]. However, due to the lack of high-resolution microscopes at the time, none of the aforementioned early scientists really knew the exact physical nature of the gold solution they were using. It was not until the very late 19th century that the full explanation was finally given by Richard Adolf Zsigmondy, who was able to show that the colour was due to the absorption spectrum of gold nanoparticles, and who became the first person to measure what we know today as the "plasmon resonance" [34].

The connection between the absorption behaviour of colloidal gold and electromagnetic waves was established only slowly. The German physicist Paul Drude developed a model to explain the electric conductivity of metals [35, 36]. This model was later refined by Arnold Sommerfeld, who applied quantum mechanics and replaced the Maxwell-Boltzmann statistics of the model with Fermi-Dirac statistics [37, 38]. This model has established itself as the "free electron model" today and can be used to describe a situation involving non-bound electrons that are freely movable in metals or plasmas. Doubtless, this model was of some use to the American Irving Langmuir, who discovered and analyzed oscillations of electrons in plasma a short time later in 1929 [39]. Such oscillations of electrons can not only take place in plasmas, or nanoparticles, but also on conducting surfaces.

Initial interest in electromagnetic surface waves came from wireless telegraphy at the beginning of the 20th century, as scientists such as Jonathan Zenneck and Arnold Sommerfeld considered the effect of the ground (be it water, earth or a good conductor such as metal) on radio signals [40, 41]. Consequently, Zenneck was originally called onto this field of research in the year 1900 to replace a seasick post-doctoral researcher on the steamer Silvana and was introduced to electromagnetic waves by steaming about the North Sea taking measurements [42]. This certainly seems more entertaining than most research in electromagnetic surface waves today, which is conducted in blacked-out laboratories in order to contain laser radiation.

The first deliberate excitation of electromagnetic surface waves was performed rather more directly, by using fast electrons and shooting them at a target. Electric excitation of plasma oscillations was proposed by Bohm and Pines in the early 1950s [43, 44] and confirmed experimentally in 1955 by analyzing the losses of an electron beam passing through a thin metal film [45]. While some people believed these losses to be due to interband transitions of conduction band electrons in the metal, instead of the generation of plasmons, these doubts were laid to rest after the early results were expanded upon and generalized briefly afterwards [46]. In the year 1968, a study on the excitation of plasmons in metal particles, the exact phenomenon that had fascinated glass-workers from the Romans until the Victorian era, was presented by Fujimoto and Komaki, which also included a section on the optical effects we now associate with plasmons [47].

In the 1950s, people began considering electromagnetic surface waves as useful for the characterization of the surface quality of metal parts. This motivated the early research by Otto and Kretschmann, who were the first to deliberately excite plasmon waves on metal surfaces at optical frequencies using prisms [48, 49].

With the coming of improved microscopy techniques, such as electron beam microscopes and confocal microscopy, this field too receded and faded away. What launched the current wave of research in plasmonics was really the ground-breaking discovery by Ebbesen, which he made in 1989 and published nine years later in 1998 when he could finally explain it [50]. He had made a thin gold film perforated with holes a couple of hundred nanometers wide, which according to scientific opinion at the time should not have transmitted measurable quantities of light. Not only did the film transmit light - more light was transmitted than actually struck the holes. Surface plasmons were the answer [51]. This amazing discovery sparked a wide range of investigations into plasmonic phenomena, which is still continuing [52].

1.2 Introduction to Surface Plasmon-Polaritons

In physical terms, a plasmon is the quantum of plasma oscillations [43, 46], analogous to the photon as the quantum of electromagnetic wave oscillations, or the phonon as the quantum of mechanical oscillations in a crystal lattice. The easiest way to understand what a plasmon is, is to consider a metal nanoparticle that is struck by an electromagnetic wave. The free electrons in the metal particle form something like a free electron gas and this, of course, reacts to the electric field of the electromagnetic wave. What ensues is a driven harmonic oscillator, with the electromagnetic field driving the oscillation of the electron gas. Like any other harmonic oscillator, the electron gas oscillation has a resonance frequency (which is mostly dependent on the geometry of the particle). If broadband (white) light is used to excite the oscillations, a peak will appear in the absorption spectrum where the energy of the photons is transformed into electron oscillations. This is known as the plasmon resonance. Plasmons may also occur on surfaces. In this case they are called surface plasmon-polaritons (SPPs) and may be understood as longitudinal electron density waves, which can propagate along a metal surface. The phenomenon of plasmon resonances and SPPs has attracted a large amount of interest in recent years [53, 54].

The difficulty of exciting a propagating SPP wave on a metal surface is best illustrated by looking at the dispersion relations of light and SPPs, shown in figure 1.2. The dispersion curve of light is a straight line, while the dispersion curve of an SPP is curved. For low values of wavelength and k-vector the two curves appear

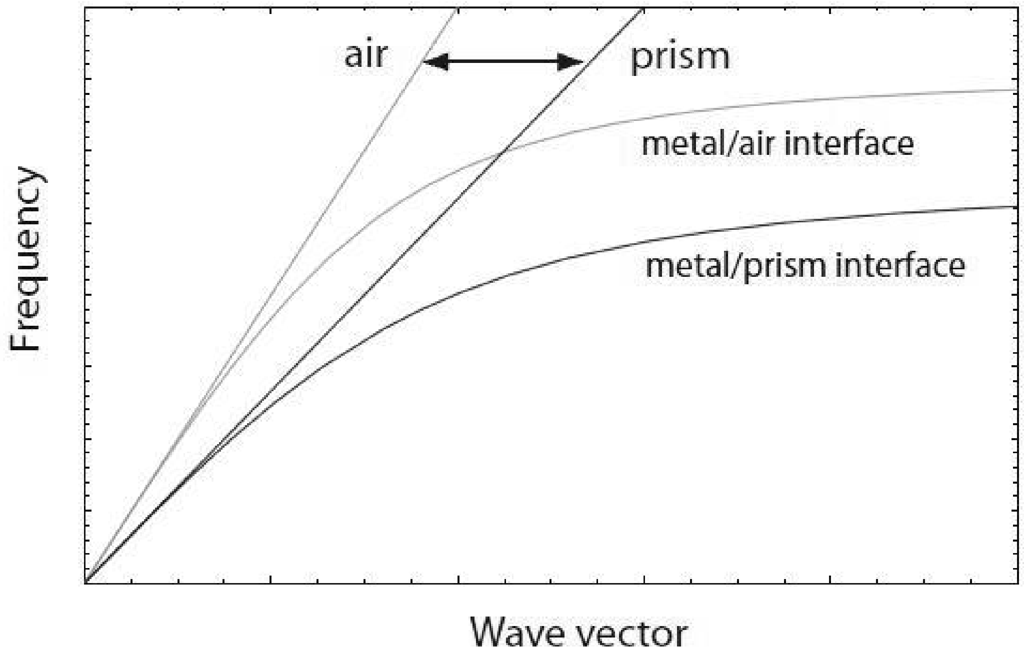

Figure 1.2: Prism coupling and SPP dispersion. Only propagation constants between the light lines of air and the prism (usually glass) are accessible, resulting in additional SPP damping due to leakage radiation into the latter: the excited SPPs have propagation constants inside the prism light cone. Source: [53]

to be colinear. However, this is not true. There is no point where the two curves intersect or are tangential, except the origin, which is of course of no practical use.

To excite an SPP wave, some trick must be used to compensate for the k-vector mismatch. The graph in figure 1.2 illustrates how this may be done using a glass prism, the method proposed by both Otto and Kretschmann [48, 49]. The prism configurations exploit the fact that the dispersion curve for light in an optically dense medium is shallower than in vacuum. Consequently, there is an intersection between the light line in the prism and the SPP dispersion curve at the metal/air interface, which allows direct excitation of a plasmon. This is precisely what happens in the Otto and Kretschmann configurations, with the configurations differing only in details.

Another method is the one used most frequently in this thesis - the coupling by grating or a surface defect [55]. That a grating can impart an additional k-vector component to an incoming light wave is well known [56, 57]. When contemplating the k-vector mismatch between the dispersion curves for light and SPPs, the idea that a grating could be used to couple light into SPPs, analogous to the way it is done with, for example, slab waveguides and photonic crystal slabs [58, 59, 60, 61, 62, 63], is not too far-fetched.

On the other hand, scattering by a surface defect is a similar mechanism, but much simpler to realize experimentally, because it is much less wavelength-specific than a grating. The efficiency of scattering by a surface defect is of course lower, and it was first explored in the context of light scattering problems involving rough metal surfaces where roughness-induced excitation of SPP's naturally occurs [64, 65]. The subject quickly matured into a field of research in its own right, with special attention paid to surface defects that scattered SPPs themselves [66, 67].

The connection between plasmonics and optical gratings did not first arise out of the intention to couple light into an SPP wave via a grating, but the opposite way round, when surface plasmon resonance effects were discovered in grating diffraction [68]. It was some years before it was recognized that an SPP propagating across a grating experienced losses, although an early theoretical study failed to draw the conclusion between the radiation losses and a potential coupling method [69]. The first study to propose and demonstrate grating coupling of light into SPPs as an alternative to the Otto configuration aimed to improve the measurement of the optical properties of metals [70], and presumably the authors did not realize - as is very common in physics in general - that their new discovery could be put to use in the telecommunications field many years later.

Once grating coupling of SPPs was discovered, it rose continuously in popularity. Not long after the initial discovery, grating-coupled surface plasmons at microwave frequencies were reported [71], followed by terahertz frequencies [72] and the near infrared (NIR), where they were even used for direct imaging of the SPP [73]. Coupling into SPPs using an elastomeric grating has been shown [74] as well as the integration of a grating SPP coupler into a metallic photonic crystal [75]. Today, the relationship between gratings and plasmons continues to evolve. Recent results include efforts to excite SPPs on gold coated single mode optical fibres [76] and a proposal for broadside input and output coupling of long-range plasmons [77].

That gratings are useful in connection with dielectric-loaded surface plasmon-polariton waveguides was already well-known before this thesis was even begun, but the manner of SPP excitation inside the waveguides was not published formally until 2008 [55], and it was also published that the grating can in practice be simplified to just one single ridge or even just the edge of one ridge.

A technology for the excitation of plasmons that has been called highly influential in the field of SPP research [78] is excitation by the use of a surface near-field optical microscope (SNOM). In this method the optical probe of a SNOM is used as a point source of SPPs on gold and silver films [79, 80]. A detailed description of this excitation and characterization method is given in section 4.4 of this thesis.

Somewhat more exotic is the proposal to excite SPPs by means of X-rays [81]. This was not used in this thesis, but it is mentioned here for the sake of completeness.

1.3 Motivation for DLSPPW

In the year 1965, in his article in *Electronics* [82], the now globally famous co-founder of Intel Gordon E. Moore made a claim that surpassed his own expectations in veracity. He wrote: "*The complexity for minimum component costs has increased at a rate of roughly a factor of two per year*". Ten years later, he altered this claim [83] to a doubling every two years, instead of each year.

While the original 1965 article (now also available in reprint [84]) is visionary in several other ways as well, as it forecasts consumer retailing of computers and the still-revolutionary phased-array radar [82], it is the forecast of computing power doubling every two years that has stuck and become widely-known as "Moore's Law". In both articles, however, the horizon he gives his own forecast is limited. The 1965 article focuses on the trend only until the year 1970, and in his second version ten years later, presumably when Moore realized he had been a bit optimistic, he reduced the speed of the increase but again made his forecast only until 1980. This time, however, the forecast was spot-on, and has taken on a life of its own, becoming one of the guidelines of the semiconductor industry [85]. So, somewhat ironically, what was once a description of the rate of technological development in the semiconductor industry has now become the target that is set by the industry itself. The graph in figure 1.3 illustrates this trend and the future plans of the semiconductor industry until the year 2022.

By limiting his forecast to the next five to ten years only, Moore was able to ignore physical limits insofar as they interfere with his hypothesis. He writes himself in the 1975 paper: "With respect to dimensions, in these complex devices we are still far from the minimum device sizes limited by such fundamental considerations as the charge on the electron or the atomic structure of matter. Discrete devices with submicrometer dimensions show that no basic problems should be expected at least until the average linewidth and spaces are a micrometer or less." [83]

Today we are no longer in the position to ignore the fundamental changes that

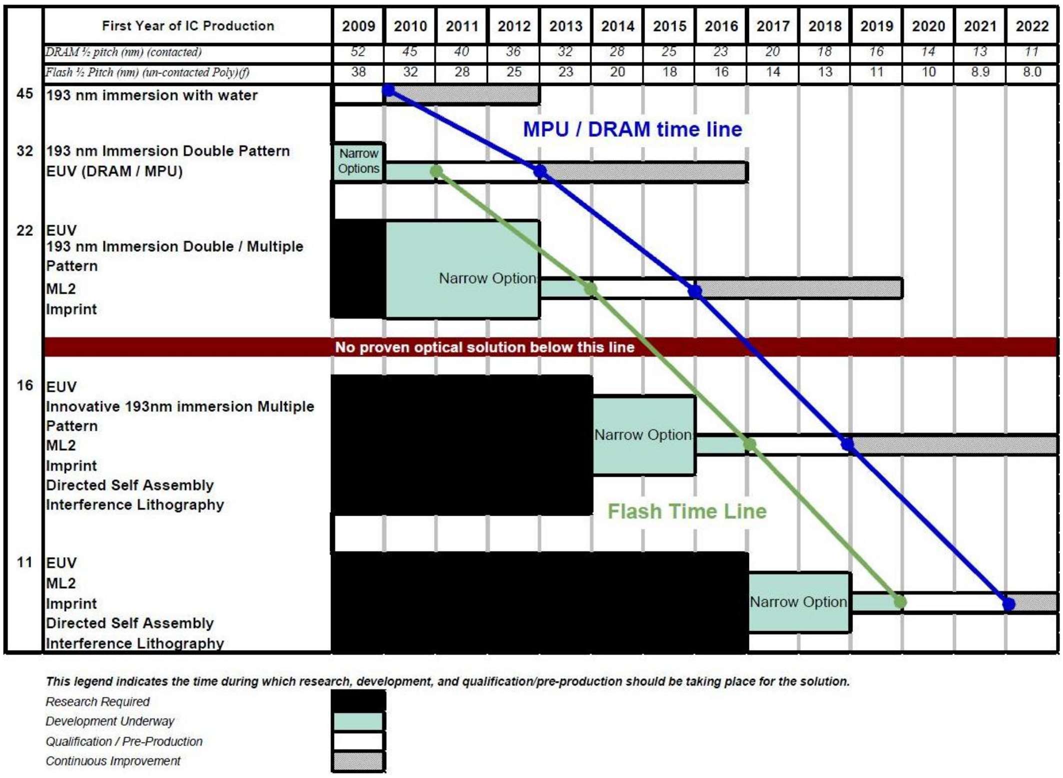

Figure 1.3: Graph showing the targets of the semiconductor industry for future pitch sizes and potential lithography solutions. Source: [85]

occur at short length-scales, even though we have remained unaffected by them for far longer than Moore suspected. It turned out that by improving fabrication techniques, the semiconductor industry was able to avoid the problems at the one-micrometer-linewidth, and has in fact progressed considerably beyond that stage. Today, state-of-the-art devices are fabricated with feature sizes on the order of 45 nm, and devices using this technology have played a considerable part in this thesis (by performing valuable service either in support of experiments or word-processing).

Today, the charge of the electron and the atomic structure of matter have become major problems for the semiconductor and electronics industry. For more than thirty years now, there has been talk of photonics and optics as a possible supplement or replacement for electronics [86, 87, 88, 89, 90, 91], frequently hailed first as "integrated optics" [92] and later in its more elaborate form as "integrated photonics" [93, 94]. While there has been considerable progress in the field [3, 95], considering its thirty-year history progress has been relatively slow, at least when compared to the rapid development of the electronics sector. This may seem surprising, and to explain this we must examine the reasoning behind the switch from electronics to photonics.

The reasoning is, in fact, closely linked to Moore's Law [96]. Thanks to the overwhelming success of Moore's Law, and its adoption by the semiconductor industry as a development roadmap, computers are now expected to become twice as capable every two years, and if possible also cheaper. Until now this could be achieved by making components smaller and increasing their quality to allow them to operate faster. But in recent times, the electron and the structure of matter itself have increasingly become the main stumbling blocks, and it has become clear that the physical limits Moore was talking about will soon be reached. Thus one of the main points of attack for research efforts has become an attack on the electron itself, and a quest to find a replacement.

The advantages of photonics over electronics are so great that optical computers have always been expected to exceed the performance of even the most powerful electronic ones [86]. Optical data transmission has already replaced electric wires in all long-haul and many short-haul communications applications due to its enormous bandwidth and the low noise of data transmission. The large bandwidth is due entirely to the much higher frequency of electromagnetic waves in the optical range when compared to the radio frequency signals of electronic data transmission. Since frequency modulation requires a fixed portion of frequency-space to operate correctly, it transpires that much more information can be sent optically. Noise is the limiting factor, since a high noise level requires a stronger signal, a more strongly-modulated signal or the multiple sending of a signal, which can then be checked for errors. All this subtracts from the bandwidth available, so it is little wonder that noise reduction was the main focus of optical communications research for a long time and that Charles K. Kao was awarded the Nobel prize in physics in 2009 for groundbreaking achievements concerning the transmission of light in fibres for optical communication.