Introduction

Lithographic tools have played a pivotal role in the fabrication of metamaterials since the pioneering work of Smith, where printed circuit boards were used in structures operating at radio frequencies. However, as the dimensions and wavelengths have shrunk, the technology of printed circuit boards has been replaced by other lithographic processes, such as optical and electron-beam lithography. All three technologies share a common base - the use of a resist. Resist is a term that was originally coined in printing and dyeing processes, and refers to the patterning placed upon a material that can then be transferred into the material by the application of ink or dye. In a more conventional sense, covering a selected area of material (e.g., the copper in circuit boards, dielectrics or semiconductor materials) with resist, allows it to be processed in a different manner from that used on the rest of the material. Pattern transfer is achieved by first applying resist to the whole surface of a piece of material or substrate, then selectively removing some of the resist. A further processing step, which may be deposition of another material or etching of the existing material, transfers the pattern itself into the material.
The resist is usually a polymer and the selective removal of the resist is achieved by exposing it to either ultra violet light or electrons (X-rays and ions are also possible). Resist comes in either a positive or a negative form: positive organic resists consist of polymers, the chains of which are broken during the exposure process; conversely, in negative organic resists, the exposure to UV light or electrons causes the formation of additional cross-links between the polymer chains. Examples of commercially available positive and negative resists are polymethyl methacrylate (PMMA) and AR-N - a novolak resin based resist, respectively. After exposure, the resist is developed in a solvent. For positive resist, the chains of polymer that were broken during exposure are more soluble than the unexposed regions and are therefore dissolved in the solvent; while, for negative resist, it is the exposed areas where additional cross-links have formed that are less soluble - and the unexposed area is dissolved in the solvent. In some resists, negative tone may be obtained simply by the use of a greater exposure dose. Hydrogen silsesquioxane (HSQ), is however an atypical negative resist in that it does not use polymer cross-linking, since the exposure process is primarily conversion into amorphous silica. This key difference in its basic properties leads to the exceptionally high-resolution capability of HSQ resist. The resist exposure process is shown schematically in Figure 1.

Once the resist has been developed the next stage of processing can begin, which involves either an etching step onto previously defined metalisation or selective deposition of metal through holes developed in the resist layer.

Figure 1. Lithographic processing: Schematic representation of the exposure and development processes.
Methods of fabrication

Lithography

Optical Lithography

Optical lithography techniques have primarily been developed to enable the mass production of integrated circuits, and can be considered as the backbone of the silicon industry. With successive generations of exposure tools, the wavelength of the light has been reduced and the wafer size increased to accommodate ever-larger production volumes. The key to the success of optical lithography is the parallel nature of the process. Once the mask (or more likely the mask set) has been produced, it can be used repeatedly to produce multiple copies of the master design.

Figure 2. Trends in Optical Lithography
The historical trend of integrated circuit minimum feature-size is shown in Figure 2. To keep pace with Moore’s Law, a self-fulfilling prophecy which says that critical dimensions halve every 18 months, special techniques have been developed to achieve sub-wavelength resolution. The most significant of these are phase-shifting masks and optical proximity correction. An example of a phase-shifting technology is shown in Figure 3. For phase-shifting masks, the wave fronts between adjacent lines interfere destructively and cause a local minimum in the merged electric field. The resist is sensitive to the intensity (electric field squared) and produces a gap between the two exposed lines.

Masks are generally made using electron-beam lithography (EBL), which has been employed as the tool of choice in the fabrication of near-infrared or optical-frequency metamaterials because of its high resolution, moderate cost and flexibility (allowing designs to be easily changed). However, for mass-production of fixed designs, optical lithography is likely to prevail because of the much larger production volumes that it provides. It may eventually merge with X-ray lithography due to recent developments in X-ray lasers that offer bright coherent light sources at wavelengths such as 13 nm or 15 nm.

Electron-beam lithography

The original electron-beam (e-beam) writing tools were made by modifying scanning electron microscopes (SEMs) or transmission electron microscopes (TEMs). Nowadays, commercially available electron-beam writers use vector-scanning, which allows for far greater speed than the less efficient raster scanning previously used. In the more large-scale machines now in use, it is also possible to stitch together two writing fields with great accuracy and achieve patterns that are larger than a single field, e.g. to produce patterns that typically occupy as much as several square centimetres. The stitching error when joining two fields can be as low as 10 nm.
**Proximity correction**

Proximity correction is routinely used in both optical lithography and EBL. In optical lithography, the need for proximity correction arises from the significant diffractive spreading of the coherent light used in the exposure process. This spreading changes the dimensions of features, effectively increasing the width of the illuminated regions. As shown in Figure 4, the remedy for optical proximity effects is to add extra features with carefully limited and shaped areas at or alongside the edges of the primary features of the pattern.

In EBL, the need for proximity correction arises from variations in the number of secondary electrons per unit area arising from a given exposure level, in the space between two close features of a pattern. In EBL, proximity correction is achieved by reducing the exposure dose locally to achieve a more uniform density of the secondary electrons that actually modify the resist, physically.

**How optical proximity affects patterns**

- Line width warped due to optical proximity
- Line-end shrink
- Rounding corners

**How to correct distorted area (OPC)**

- Bias/jog
- Assist bar
- Serif/jog
- Hammerhead
- Extension/jog
- Outer/Inner serif

Figure 4. Optical Proximity Correction.

**Lift-off**

Lift-off is a process that is often used in defining patterns in metal films in situations where, for example, dry-etch processing is not possible for chemical reasons or where it could cause unacceptable damage to the underlying material. In lift-off processing, thin films of the required material are deposited on top of a resist pattern that is the inverse of the pattern required in the desired material thin-film. The resist pattern is then removed by means of an appropriate solvent, which swells the resist, causing it to tear off the thin film material that is not in direct contact with the surface of a sample. A schematic representation of the lift-off process appears as Figure 1.2 of the chapter by Linden and Wegener². The advantage of the lift-off process is that it obviates the need for an etching step; for structures with feature sizes that are smaller than one micrometre, wet-etching runs into fidelity and uniformity problems that would otherwise require the use of dry etching, which may cause significant damage to the material, because of the relatively high energy of the ions involved.
Multiple Layer Structures

A variation on the lift-off technique, which allows fabrication of multiple layers in a single lithographic step, involves the deposition of multiple layers into the same lithographically defined window. Here the structures are aligned to each other, though usually with some tapering towards the upper layer, since the hole or window fills up with material through it sticking to the side-walls. An example of a multiple-layer metamaterial structure that has shown interesting and potentially useful electromagnetic properties at optical frequencies is the grid structure featured in Figure 1.14 of the chapter by Linden and Wegener. See also Figure 5 from the work of Shalaev with arrays of double wires. This structure uses a metal-dielectric-metal sandwich, while the fabrication uses patterning via EBL, together with lift-off to remove the multi-layer in the windows of the pattern.

Arbitrary multilayer structures

For structures that do not follow the original pattern, or for which an offset between layers is required, a more complex approach is necessary, involving two key steps: alignment and planarisation. Before the structure is defined, a set of alignment marks is required to align subsequent patterns. These marks must be visible (to the EBL machine), and are generally deeply etched holes, metal squares or T-shapes. The alignment marks are usually located away from the main structure, since these areas may become exposed during the alignment process. For many layers, several sets of alignment marks may be necessary, and even the addition of an extra set may be required, after several layers have been processed. The inherent alignment precision is limited to the registration accuracy of the EBL system, which is typically around 30 nm.
Nanoimprint Lithography

The fundamental attraction of nano-imprint lithography (NIL) is that it is a parallel process for pattern transfer and so has, by virtue of its parallel nature, a significant level of comparability with optical lithography. The characteristic feature of the nano-imprint approach to lithography is that a master stamp (or template, or mould) is formed by a combination of processes, e.g. EBL followed by dry-etching – and this stamp is then pressed into a layer of resist order to transfer the required pattern into the layer into. In principle, the master stamp, or subsequent replicas of it, can be used many times with high precision, i.e. in a fashion that is somewhat similar to the re-use of the mask set in conventional optical lithography. Repeated use of a master stamp is limited by wear or damage that occurs as the stamp is imposed upon on the imprint layer – and it is essential that none of the imprinted layer material adhere to the stamp as it is removed. In analogy to optical lithography much of the effort is involved in producing the mask or stamp, which usually involves serial electron-beam writing followed by dry etching. The two processes have comparable fidelity.

As shown in Figure 7, there are at least two basic versions of the NIL process, a thermal one and one based on ultra-violet light exposure. The thermal process relies on the ability of the imprint tool to impose its surface pattern accurately on a deposited resist layer when the resist is at a high enough temperature to be soft and deform accurately in conformity with the tool pattern. At the same time, the tool must come away cleanly from the imprinted resist pattern, with no material adhering to the tool and no change in the surface topography of the resist layer, as the tool is removed. This is usually accomplished by a surfactant surface layer.
Figure 7: Two alternative nano-imprint lithography (NIL) processes, (a) Thermal process that involves heating to a temperature where the resist softens sufficiently to enable ready deformation and effective transfer of the template pattern – and (b) Process relying on ultra-violet light exposure to polymerise and imprint fluid that has been deformed by the template, thereafter retaining the form of the template.

In the second process, ultraviolet light is used to expose the positive resist layer after it has been moulded by the imprint tool, polymerising the shaped layer so that it remains as an inverted version of the pattern on the tool, after tool removal. An example of NIL for metamaterials can be found in this reference⁵.

**Focused Ion Beam Etching**

Focused ion-beam (FIB) etching was originally developed as a tool for etching cross-sectional samples for transmission electron microscopy. The technique involves scanning a focused ion beam (usually gallium) and physical bombardment of the sample to remove material. However, this technique is not without its problems. Unlike reactive ion etching (RIE), where a volatile compound is formed that can be pumped away in a vacuum system, with FIB there is a tendency for material that has been sputtered from the sample to be re-deposited on the side walls, or elsewhere on the structure.

**SRR based metamaterials in different metalisations**

Planar arrays of split-ring resonator (SRR) metal structures patterned by lift-off have been realised in a number of different alternative metals – in particular in gold (Au), silver (Ag), aluminium (Al) and copper (Cu). In most, if not all cases, the array patterns have a periodic arrangement – and therefore have the potential to exhibit band-structure for light (or electro-magnetic waves more
generally) at appropriate wavelengths. Before considering the metamaterial properties of SRR arrays – or more complicated structures that include SRRs as one of several patterns – it is appropriate to cite Soukoulis and co-workers\(^6\). Here the properties of ‘real’ metallic photonic crystal structures with spacing appropriate to produce band-structure from the infra-red through much of the visible light spectrum are analysed numerically. Although the calculations were carried out on three-dimensionally periodic arrays of metallic cubes, the insights provided remain broadly applicable for planar (two-dimensionally periodic) array patterns. A feature of the results is that structures in all four of the metals treated (Au, Ag, Al and Cu) exhibit stop-band behaviour – but that gold and silver are substantially superior to aluminium in terms both of lower absorption losses at high transmission parts of the spectrum and exhibition of a more definitive stop-band behaviour, i.e. lower optical transmission levels, in the stop-band regions.

The properties of the metallic photonic crystal structures – and of metamaterial arrays of SRRs – are both substantially determined by the two characteristic frequencies, or time-constants, of the bulk metals, the plasma-resonance frequency (which is desirably the largest for Al) and the dissipation time constant (which is undesirably much larger for Al). If the optical wavelength involved is long enough, the properties of these metals (all four of which are good electrical conductors) are sufficiently similar that the characteristic behaviour of metamaterial arrays may be related in a conceptually simple way to the geometry of the structure - and it becomes valid to describe the resonant behaviour (and associated large changes in the reactive impedance) in terms of an equivalent L-C resonance\(^7\).

**Basic Resonances**

The two principal types of resonance observable in the ‘C’ or ‘U’ shaped SRR are usually called the plasmon or Mie resonance, at shorter wavelengths, and the so-called LC resonance, at longer wavelengths. The identification of the longer wavelength resonance as an LC resonance was made by Linden et al\(^7\), with the frequency of the resonance being approximately determined by considering the SRR to be a single turn inductor in series with the capacitor formed by the gap between the SRR arms. Rockstuhl et al\(^8\) have proposed that the resonances observed may be interpreted as simply being the symmetric or anti-symmetric fundamental and higher-order plasmon resonances.

In general the wavelength of the resonances scale with the size of the SRR until visible wavelengths are approached. Beyond this point reducing the size of SRR ceases to produce a commensurate shorting of the wavelength\(^9\). This effect arises from the kinetic inductance associated with the dynamic behaviour of the electron cloud of the metal in a high (optical) frequency electro-magnetic field, which becomes progressively more important as the frequency increases. To achieve simultaneous negative \(\varepsilon\) and negative \(\mu\) at optical frequencies, it is first necessary to change the geometry from planar SRRs. Changing the geometry to double wires or the so-called ‘fishnet’ structure consisting of double-plate pairs which provide the negative magnetic permeability, and long metal wires, which act as a diluted Drude metal giving rise to negative permittivity, has allowed significant advances.

Researchers in the field of metamaterials have extended the definition of the visible spectrum to wavelengths as long as 780 nm, – in order to be consistent with the with the phrase ‘visible in the laboratory’\(^10\). A metal that had the higher UV frequency plasma-resonance of Al, but the smaller loss time-constant of Au or Ag, would presumably make it possible to penetrate well into the genuinely visible part of the optical spectrum (below 700 nm) with simultaneously negative \(\varepsilon\) and \(\mu\).
Figure 8 shows sections of SRR arrays realised in two different metals, Al and Au, with the same nominal dimensions, realised on silicon substrates. The reflection and transmission characteristics of such arrays depend on the detailed features. With sufficient spacing between the SRRs, the behaviour will be dominated by the individual characteristics of the SRRs. If the SRRs are sufficiently small, their resonant behaviour can be considered as that of a combination of an inductor and a capacitor, i.e. they exhibit classic L-C resonance behaviour, even at optical frequencies where typical metals cannot simply be regarded as good electrical conductors. If the SRRs are periodically distributed and closely packed together, their collective characteristics will differ from those of the individual elements – because of the coupling, in particular, between adjacent resonators.$^{11}$

Figure 8: Scanning electron micrograph (SEM) images of SRR arrays and individual elements fabricated using lift-off in aluminium (Al, left) and gold (Au, right)$^{12}$. 
Figure 9: Measured transmission and reflection spectra for the SRR array patterns shown from Figure 8 above. (A) and (B) were obtained on structures fabricated in gold (Al), while (C) and (D) were obtained on a nominally identical pattern fabricated in aluminium (Au).

The main spectral difference upon changing metal is a very significant blue shift of the LC resonance in going from gold (1.8 µm) to aluminium (1.2 µm) metalisation. The Mie resonance for TE is merged with the characteristic feature of the silicon band-edge at a wavelength of 1.1 µm.

Effect of substrate

A 3-D FDTD simulation has been used to calculate the effect of changing the substrate material from glass with a refractive index of 1.5 to a potentially active silicon substrate with n = 3.1. As shown in Figure 10, the change of substrate from glass to silicon results in an approximately 20% increase in the resonance wavelength. This change is substantially less than the change in the refractive index because part of the resonant electromagnetic distribution resides in the near-surface region of the metal film and part is in the air above the metal.
Synthetic opal is an important example of a self-organised photonic nanostructure. Under appropriately controlled conditions, nucleation of the solid material into the constituent spheres of opal takes place almost simultaneously at a large number of separate locations, with subsequent growth of the colloidal spheres proceeding at very nearly the same rate for all spheres. In the simplest process, for example with silica spheres, where they are significantly denser than the surrounding medium, the colloidal spheres are deposited under gravity on a flat surface, which may be merely the bottom of the vessel in which the spheres are formed. The forces of repulsion and attraction involved tend to lead to cubic close-packing of the depositing spheres on a layer-by-layer basis, and the formation of a face-centred cubic (f.c.c.) lattice. This process and the more common controlled evaporation, or capillary growth, whereby a thin film is grown on an angled substrate as the liquid of the colloidal solution is evaporated can produce growth defects. The growth defects are caused by a choice of site locations for the growing crystal and subsequent shrinkage of the spheres (and crystal) upon drying. By growing on a (100) surface the choice of site is eliminated. Furthermore, by growing on a template with pillars that are slightly larger than the sphere size, the shrinkage is distributed evenly across the crystal resulting in a slight tetragonal distortion - but producing a crack free crystal of up to 1 mm area.

Figure 11 shows an example of the formation of an opal photonic crystal structure with nearly cubic symmetry with the lattice orientation controlled by a template process (C. Jin et al)\textsuperscript{13}. Square packing in the self-organised formation of the opal is imposed by EBL patterning and development of HSQ negative resist in a square array of moderate height pillars (see inset). This approach can possibly be extended so as to produce different crystal orientations i.e. other facets than (111) (the natural orientation produced on a flat surface) or (100) shown in the figure.
Figure 11. SEM image of (001)-oriented photonic crystal grown on a square patterned template. Inset: An enlarged SEM image of the template with pillar spacing of 308 nm; the scale bar of the inset is 800 nm.

Figure 12. Electrochemical infiltration of metal (silver) into polymer sphere opal.

Although the opal system provides a periodic 3-D matrix most metamaterials rely on metals in combination with dielectrics. An exception has been the use of highly alternating layers of highly doped semiconductor InGaAs, and intrinsic AlInAs forming a metamaterial in the infrared. One method of incorporating metal into a dielectric matrix is by electrochemical deposition. Figure 12 shows a mixed metal-dielectric structure formed by a lattice of polystyrene spheres surrounded by the lighter coloured metallic silver. These are formed from the modified electrochemical deposition of silver from a solution of KI and AgNO₃ obtained from reference 15. It is possible to control the amount of infill from the deposition time and applied voltage16.

Other self-assembly approaches based on eutectics are discussed elsewhere in this volume.
Measurements

Here we mention in outline only the measurement techniques used to characterise the optical metamaterials of the type described above. Most measurements of metamaterials consist of transmission and reflection often followed by a transformation to retrieve the real and imaginary parts of \( \varepsilon \) and \( \mu \). Because the phase information can be more difficult to obtain than in say S parameter measurements in the microwave region, alternative schemes have been developed. Similarly, a wedge-shaped metamaterial in the microwave region can straightforwardly demonstrate negative refraction – this becomes more difficult in the NIR and visible with the need to obtain large area samples with several layers. For some experiments where the ultimate goal is the retrieval of \( \varepsilon \) and \( \mu \), simulations are made of the structures. The normalised S parameters retrieved from the simulations are used to extract \( \varepsilon \) and \( \mu \) via the Fresnel equations\(^{17}\) often with simplifying assumptions. Techniques for retrieving the phase include the use of phase masks\(^{18}\), angular resolved measurements\(^{14}\), ellipsometry\(^{19}\) where the ratio of TM-to-TE polarized light is plotted as a function of frequency for oblique incidence, and femto-second laser interferometry\(^{20}\) where the group and phase velocities are obtained from interferograms.

Discussion and Conclusions

In this chapter we have covered a number of different approaches to the realisation of artificially structured photonic metamaterials. The approaches described include high precision ‘top-down’ deterministic ones that are typically specified, in the first place, as a set of patterns which are transferred either directly or via a mask to the unstructured material followed by deposition and/or etching. We have also made a short foray into the territory of ‘bottom-up’ realisation in self-organised structured materials such as synthetic opal. A fairly obvious conclusion is that future work in the field of optical metamaterials will involve approaches to fabrication that may be either ‘bottom-up’ or ‘top-down’ – or a judicious combination of the two. Various examples of interesting combinations have already appeared in the literature, e.g. (i) templates generated directly via EBL patterning that are used to determine the lattice constant and orientation of synthetic opal structures\(^{13}\) and (ii) the selective removal, using EBL, of entire ‘photonic atoms’ from polymer opal\(^{21}\) and new combinations of techniques such as laser writing and chemical vapour deposition of metal.\(^{22}\)

References


2 This volume page XX


4 Three-dimensional photonic metamaterials at optical frequencies
Na Liu, Hongcang Guo, Liwei Fu, Stefan Kaiser, Heinz Schweizer and Harald Giessen
Nature Materials Vol 7 2008 pp 31-37
Optical Metamaterials at Near and Mid IR Range Fabricated by Nanoimprint Lithography
Wei Wu, Evgenia Kim, Ekaterina Ponizovskaya, Yongmin Liu, Zhaoing Yu, Nicholas Fang, Y. Ron Shen, Alexander M. Bratkovsky, William Tong, Cheng Sun, Xiang Zhang, Shih-Yuan Wang and R. Stanley Williams


Magnetic Response of Metamaterials at 100 Terahertz


Negative-index metamaterial at 780 nm wavelength G. Dolling, M. Wegener, C. M. Soukoulis, and S. Linden Optics Letters, Vol. 32, Issue 1, pp. 53-55


Optical Properties of Split Ring Resonator Metamaterial Structures on Semiconductor Substrates


Fabrication and characterization of silver inverse opals

Onn Lu Shian A Z Khokhar, Basudev Lahiri, R M De La Rue and N P Johnson, Unpublished results.

Experimental Demonstration of Near-Infrared Negative-Index Metamaterials

Terahertz Magnetic Response from Artificial Materials
T. J. Yen, W. J. Padilla, N. Fang, D. C. Vier, D. R. Smith, J. B. Pendry, D. N. Basov, and X. Zhang

Simultaneous Negative Phase and Group Velocity of Light in a Metamaterial
Gunnar Dolling, Christian Enkrich, Martin Wegener, Costas M. Soukoulis, Stefan Linden

Artificial Defect Engineering in Three-Dimensional Colloidal Photonic Crystals

Photonic metamaterials by direct laser writing and silver chemical vapour deposition
Michael S. Rill, Christine Plet, Michael Thiel, Isabelle Staude, George Von Freymann, Stefan Linden and Martin Wegener
Nature Materials Advance Online Publication May 2008