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(http://iopscience.iop.org/0022-3727/48/18/184002)

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Fabrication of aluminium nanostructures for plasmonics

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Received 15 August 2014, revised 24 October 2014
Accepted for publication 10 November 2014
Published 15 December 2014

Abstract

Metallic nanostructures are the building blocks for nanoplasmonics and for subsequent applications in nano-optics. For several decades, plasmonics have been almost exclusively studied in the visible region by using nanostructures made of noble metals exhibiting plasmonic properties in the near infrared to visible range. This notwithstanding, emerging applications will require the extension of nanoplasmonics towards higher energies, particularly in the UV range. Therefore, alternative metals, often described as poor metals are emerging to achieve that goal. Among all these metals, aluminium appears to be one of the most appealing for extending plasmonics towards ultraviolet energies. Aluminium is cheap, widely available, compatible with optoelectronic devices and exhibits plasmonic properties over a wide range of energies, from the infrared to the deep UV. Our aim is to present a review of current research centred on the fabrication of aluminium nanostructures. Mastering the geometry of aluminium nanostructures is extremely important in order to tune their plasmonic properties and target a given application. First we give an introduction to the nanofabrication of aluminium nanostructures within the context of plasmonics. The review then focuses on the possible geometries that such structures may take when fabricated with specific fabrication techniques. Each technique is detailed and the plasmonic properties of the aluminium nanostructures are briefly described. When possible, an example of an application is given. Finally, the future applications of aluminium plasmonics are highlighted and a conclusion with perspectives is given.

Keywords: aluminium, plasmonics, nanofabrication

(Some figures may appear in colour only in the online journal)

1. Introduction

When excited at an adequate energy, metallic nanostructures support localized surface plasmon resonances (LSPRs) due to the coherent, collective oscillation of their surface conduction electrons [1]. Due to LSPRs, the electromagnetic (EM) field is strongly enhanced and locally confined in the vicinity of a metallic nanostructure, which intensively absorbs and scatters light. The fundamental properties of LSPRs, energy and line-width (or Full Width at Half Maximum, FWHM), depend on the intrinsic properties of the metal (electronic band structure, dielectric function), its geometry, and the refractive index of the surrounding medium. Accordingly, metallic nanostructures exhibit extremely interesting optical properties leading to various applications such as metal-enhanced fluorescence [2], ultra-sensitive sensing [3] and surface enhanced Raman spectroscopy (SERS) [4], to name only a few. For several decades plasmonics have been almost exclusively studied in the visible and near-infrared portion of the electromagnetic (EM) spectrum by using nanostructures made of gold or silver. However, these noble metals have inherent limitations hindering the development of plasmonic devices towards the blue and ultraviolet (UV) parts of the EM spectrum. Gold does not exhibit plasmonic resonances at wavelengths shorter than 520 nm due to its interband transitions. Silver nanostructures exhibit LSPRs down to 350 nm but suffer from strong oxidation and lose their plasmonic properties over time. To overcome those issues, aluminium (or AL) plasmonics is now emerging. Due to its intrinsic properties, such as its high plasma energy of 15.6 eV, aluminium behaves like a metal
up to energies located in the deep UV, while keeping relatively low losses, except within a relatively narrow energy range centred at 1.5 eV where interband transitions are active [5]. Although plasmonic resonances in aluminium nanostructures have been observed since the early eighties [6] thanks to electron energy loss spectroscopy (EELS), aluminium plasmonics has truly begun in recent years [7–16]. In contrast to noble metals, aluminium is cheap and widely available as it is a very abundant material on Earth. This is a tremendous advantage for industry related applications which could have a strong impact in terms of economic benefits. For instance, aluminium is compatible with optoelectronic devices and CMOS technology. Therefore, aluminium opens avenues for plasmonic engineering of the optical properties of wide bandgap semiconductors such as ZnO [17] or GaN related alloys [18], which could create a new market in the field of optoelectronics. On a broader level, aluminium plasmonics is very appealing for a lot of applications: surface enhanced Raman spectroscopy in ultraviolet [19, 20], metal enhanced fluorescence [21], label-Free biosensing applications [22], non-linear plasmonics [23], light harvesting devices [24], photodetection [25], photocatalysis [26] or high data density storage [27]. Nevertheless, studies of LSPRs in the UV region have been sporadically reported, implying that aluminium for plasmonics is still in its infancy. Of paramount importance in the development of future aluminium plasmonic applications is the capability to fabricate well defined aluminium nanostructures in order to fine-tune their plasmonic properties. This article aims to give an overview of current research centred on the fabrication (and to a lesser extent, the optical properties) of aluminium nanostructures. The review mainly focuses on the feasible geometries that such nanostructures may take when fabricated with specific methods. Each method is therefore described and the plasmonic properties of the fabricated aluminium nanostructures are briefly described. More precise information concerning the plasmonic properties of aluminium nanostructures is available in [28], which is published in the same issue. Finally, the potential applications of aluminium plasmonics are highlighted and a conclusion with perspectives is given.

2. Lithography

This review devotes a first and large section to the different types of lithographic methods used for the fabrication of aluminium nanostructures. Indeed, in order to investigate their optical properties as a function of features like their size, shape, height, or dielectric environment (substrate, encapsulating layers), lithography appears as an obvious choice, as it allows for a precise control of the nanostructure’s geometry.

2.1. Electron beam lithography

Electron beam lithography (EBL) is a very efficient tool for the fabrication of plasmonic nanostructures [29]. The main steps involved in EBL are described in figure 1. The first step consists of exposing a positive resist (spin coated on a substrate beforehand) using a scanning electron beam, allowing one to write down the desired pattern shape in the resist. The electrons interact with the resist breaking its polymeric chains as illustrated by the inset in figure 1(a). The resist is then developed in a selective solvent as the exposed areas contain smaller chains with higher solubility compared to non-exposed areas. Then the entire sample is metallized using for instance, evaporation techniques. Before the evaporation of the metal, it is important to get an inverted profile in the resist as illustrated in figure 1(b). Indeed, the discontinuity between the metal deposited onto the substrate and the resist (figure 1(c)) is mandatory for the final step of resist removal, or lift-off (figure 1(d)). Moreover, a minimum ratio of 1:3 for the metal:resist thickness is used to prevent any contact. In
the last step, the sample is dipped in a solvent dissolving the remaining resist and lifting up the unwanted metallic areas.

At this point, it should be specified that aluminium can be evaporated by using either electron-beam or thermal evaporation, with a typical deposition rate between 0.1 nm s⁻¹ and 0.2 nm s⁻¹ and a base pressure between 10⁻⁹ and 10⁻⁷ Torr. These experimental conditions are of importance in order to keep a relatively smooth surface. However, there is a difficulty inherent in the evaporation of aluminium due to its tendency to nucleate in the early stage of growth. This prevents a very smooth surface of the Al nanostructures, which exhibit large grain size leading to distorted shapes. These features are more or less visible on the SEM (scanning electron microscopy) images of lithographed aluminium nanostructures presented in this review.

The goal here is to give a relevant list of studies involving EBL for the fabrication of aluminium nanostructures. EBL has proven to be a very efficient tool for the fabrication of aluminium nanostructures aiming at the rigorous study of their plasmonic properties. Indeed, the size and shape of metallic nanostructures are easily tunable when fabricated by EBL, with dimensions ranging from a few tens of nm to some μm. Such full parametric studies are very interesting in order to investigate the fundamental properties of aluminium plasmons such as their energy dispersion relation or their extinction, absorption and scattering efficiencies.

Let us begin with a recent example where the plasmonic properties of simple structures consisting of aluminium nanodisks are studied by Knight et al [14]. The Al nanodisks fabricated by EBL are shown in figure 2(b). Individual scattering spectra have been measured and theoretically calculated on each Al nanodisk as is visible in the graphs in figures 2(a) and (c). Obviously, the radiative properties of LSPRs sustained by the Al nanodisks range from the visible to ultraviolet wavelengths. The main peak visible in the ultraviolet (for the smallest nanoparticle) is the signature of typical Lorentzian dipolar plasmonic resonance. When the diameter of the nanoparticle increases, the LSPR is red-shifted and becomes broader. This effect is due to phase delay across the nanoparticle decreasing the lifetime (or increasing the linewidth) of the plasmonic resonances [30]. Due to phase delay, additional peaks with lower wavelengths and lower relative intensities appear in the dark field spectra. These peaks actually correspond to the signature of high order plasmonic resonances (quadrupolar resonance, for instance) sustained by larger Al nanodisks. In this study they particularly pointed out that the aluminium plasmonic resonances are remarkably sensitive to the presence of the native oxide ((Al₂O₃) or alumina) within the metal. The percentage of alumina in the nanodisks is retrieved by comparing the experimental resonances with the resonances calculated by numerical simulations where the amount of alumina is taken into account in the dielectric function. At this point, it is important to remember that aluminium does not oxidise in depth but passivates with a stable alumina shell, roughly equal to 3 nm [7], keeping Al plasmonic properties over time even for nanostructures with surfaces exhibiting relatively large grain size. For instance, the evolution of the plasmonic properties of aluminium surfaces during their oxidation is investigated in [31] while the mechanisms of aluminium nanoparticle oxidation are investigated in [32].

In an earlier study, Knight et al also thoroughly studied the radiative properties of individual Al nanoantennas (or nanorods) made by EBL thanks to spatial resolved cathodoluminescence [11]. Plasmonic resonances sustained by EBL-made aluminium nanodisks have also been investigated by Zorić et al [30]. They wrote down a specific pattern shape in the resist leading to large area and two-dimensional patterns of randomly distributed nanodisks with well-defined size and shape, narrow size distribution and tunable interparticle distance. Thanks to the characterization of these samples by extinction spectroscopy and theoretical calculations, they studied the radiative and non-radiative damping mechanisms of dipolar plasmonic resonances sustained by Al (and also gold and platinum) nanodisks, and linked the results to the specific electronic band structure of the considered metal. Note that the same group thoroughly investigated the plasmonic properties of Al nanodisks earlier (2008), but the method of fabrication was different (hole-mask colloidal lithography, or HCL) [7], and this work will be discussed later.

Lecarme et al have recently worked on Al nanostructures made by EBL [15]. This study focused on the plasmonic properties of Al nanorods in the infrared to visible region of the EM spectrum. Here the structures consist of nanorods with varying dimensions as shown in figures 3(b) and (c). The spectra (figure 3(a)) correspond to extinction measurements
under unpolarized illumination of ordered arrays of 20 nm thick Al nanorods with a constant aspect ratio (length divided by width) of 2. Both the longitudinal (L) and transversal (T) plasmonic modes sustained by the nanorods are naturally red-shifted when the dimensions of the rod are increased. Interestingly, an additional feature around 800 nm appears on the spectra for all the nanorods. Indeed, a more or less visible third peak appears between the L and the T mode peaks. This feature is clearly visible for the smaller nanorod (black curve) and actually results from coupling between the LSPR and the energy-localized IT of Al. This coupling can be adjusted thanks to EBL parameters (as the plasmonic resonance depends on the geometry of the nanorod), and used to switch from highly scattering particle arrays to absorbing particle arrays as is shown quite nicely in the article. A large number of other parameters have been varied in this work. For instance, the influence of the distance between each nanorod on their optical properties has also been studied. Indeed, in a two-dimensional lattice, the usual choice for EBL fabrication, the nearest-neighbour interactions have to be taken into account to fully understand the optical properties of metallic nanoparticle arrays. This study demonstrates again that EBL-made samples make possible the thorough study of precise mechanisms such as IT-plasmon interactions in aluminium nanostructures.

Another complete parametric study involving EBL can be retrieved in [33] where arrays of Al and gold (Au) nanorods are fabricated. By combining their experimental results with discrete dipole approximation calculations, the optical properties of Au plasmonic structures are compared with similar Al structures, and solar cell light-trapping applications are discussed. It is shown that Al nanoparticles are interesting for amorphous silicon solar cells, but their application for polycrystalline solar cells is limited by the presence of the IT mentioned above. In [34], EBL was used to fabricate aluminium nanoantennas with various aspect ratios and their plasmonic properties have been studied by EELS. In this work, the multipolar plasmonic resonances sustained by the nanoantennas have been mapped at the nanometer scale and their damping mechanisms have been studied. More particularly, it is shown that in the blue-UV spectral range, high order plasmonic modes present a quality factor roughly two times higher than low order plasmonic modes at the same energy. EBL has also been used to fabricate aluminium nanoantennas with various aspect ratios and their plasmonic properties have been studied by EELS. In this work, the multipolar plasmonic resonances sustained by the nanoantennas have been mapped at the nanometer scale and their damping mechanisms have been studied. More particularly, it is shown that in the blue-UV spectral range, high order plasmonic modes present a quality factor roughly two times higher than low order plasmonic modes at the same energy.

A very nice example of an application exploiting the plasmonic properties of EBL made aluminium nanostructures is the colour generation for printing applications [35]. As aluminium is a low cost material and exhibits plasmonic properties from the infrared to the ultraviolet when nanostructured, high-resolution plasmonic colour printing appears as a direct industry-related application, such as security tagging, cryptography, and information storage. Here, EBL has been used in order to fabricate plasmonic nano-pillars with varying diameters on a silicon substrate. The nano-pillars are made of negative-tone resist (which is patterned during the electronic irradiation and the subsequent development), subsequently capped with aluminium, resulting in the plasmonic nano-pillars. Then, matrices of pixels are designed, each pixel consisting of four plasmonic nanopillars. By varying the size of the nanopillars and the distance between them in each pixel, they were able to reproduce all the colour and tone variations of a reproduction of Monet’s Impression, Sunrise, as is nicely demonstrated in the article.

A second example of structural colouration using aluminium nanostructures can be found in [36]. Without going into detail, the nanostructures consist of coupled aluminium nanodisks and nanoholes. Here the hybridization between LSPR modes in the nanodisks and nanoholes is used to design...
and fabricate bright angle-insensitive colours tunable across the entire visible spectrum. This method has tremendous potential for large scale implementation of structural colours in plastic products for daily use, as explicitly stated in the corresponding article. As a final example, Al nanorod arrays made by EBL have also been used by Olson et al for the fabrication of plasmonic pixels [37]. In this study, the plasmonic properties of the pixels are intensively investigated and are proved to be very appealing for future display technologies.

2.2. Colloidal lithography

Colloidal lithography (CL), also known as nanosphere lithography (NSL) is based on the self-organization of colloidal particles (for instance polystyrene beads) on surfaces to form 2D or 3D evaporation (or etch) masks [38]. This method is cheaper than EBL and less demanding in terms of facilities. A well-known version of NSL is the use of organized 2D colloidal crystals with a hexagonal close-packed pattern as an evaporation mask, often in combination with reactive ion etching. The subsequent evaporation through the mask defines the resulting metallic pattern, and the material deposition conditions such as the evaporation angle or specific deposition technique (electron beam deposition, sputtering, epitaxial growth, thermal deposition) enable the variation of the final pattern. A very simple schematic illustrating NSL (here for the fabrication of silver nanotriangles) is visible in figure 4 from [39].

The critical step in CL is to form a well organized 2D colloidal layer with as few defects as possible (such as dislocations in the colloidal crystal, or vacancies). The formation of the colloidal crystal can be achieved by arranging the colloids contained in commercial solutions onto the substrate. To achieve that end, several methods are commonly used [40]: drop-coating, spin-coating, dip-coating, electrophoretic deposition, or self-assembly at the gas–liquid interface. A surfactant can be added to the solution to assist the colloids in wetting the substrate, or functionalized colloids are purchasable to avoid aggregates and to form a homogeneous thin layer. The functionalization of the substrate, making it hydrophilic is also a solution to enhance the wetting of the colloids [10]. Assuming a good and homogeneous wetting between the colloids and the substrate (which has to be highly hydrophilic), the final thickness of the colloid’s layer (e.g. monolayer, bilayer, ...) is tunable by varying the concentration of the colloidal solution and the volume spread onto the substrate. Actually, such methods of coating involve a complex dynamic process associated with the evaporation of the colloidal solution (which is time and solvent dependent) and its viscosity gradients. NSL has been used to fabricate aluminium nanoparticles [9, 26, 41]. An example of NSL leading to aluminium nanotriangles is shown in figure 5, taken from reference [9]. Here the hexagonal 2D pattern of polystyrene beads has been used as the evaporation mask leading to the nanotriangles of aluminium. By varying their width (typically from 95 to 230 nm for a constant 50 nm height), such aluminium nanotriangles sustain LSPRs tunable from 350 nm to 800 nm as proved by UV-visible extinction measurements and confirmed by theory. In this work, the native alumina shell has been characterized by combining scanning electron microscope and atomic force microscopy. It is demonstrated that the presence of the alumina layer, especially on the tips of the nanotriangles, results in a significant red shift of the LSPR maximum \( \lambda_{\text{max}} \). By merging the samples in different solvents, it is also experimentally shown that the plasmonic resonances sustained by aluminium nanotriangles have a refractive index sensitivity equal to 0.405 eV per refractive index unit (0.405 eV per RIU). The plasmonic properties of unoxidised triangular nanoparticles of similar size and geometry have been calculated showing that the refractive index sensitivity is significantly decreased by the oxide layer.

CL has two inherent limitations. First, the size of the metallic nanostructures are completely determined by the diameter of the colloids used for the mask. One can easily imagine that achieving ultrasmall aluminium structures (in order to tune their plasmonic resonances into the deep UV) would need very small colloids, with diameters typically less than or equal to 200 nm. Such small colloids (as polystyrene nanospheres available in commerce) are very difficult to deposit and align in well-ordered crystals over large areas.
Secondly, as the available diameters of colloids are limited, the continuous tuning of the metallic nanostructures’ size (and consequently of their plasmonic properties) is not trivial. In [10], in order to fabricate tunable aluminium nanostructures by NSL, a method is proposed to tune the gap between the polystyrene microbeads (mean diameter 336 nm) with a hexagonal closely-packed arrangement. To achieve this, the beads are heated under a microwave, resulting in the shrinking of the spaces between them as illustrated in figure 6. The spaces are thus tuned by changing the heating time and the following evaporation step leads to aluminium nanostructures with a typical size tunable from 80 to 50 nm. Note that the shape of the nanostructures gradually changes from triangles to spheroids. Finally, the localized plasmonic resonances are tuned from 342 to 270 nm, as illustrated in figure 6. By using different bead diameters, this method is therefore very appealing for tuning the plasmonic properties of aluminium nanostructures from the visible to the mid UV.

Another version of CL, called sparse CL (SCL) [42] has also been used for the fabrication of aluminium thin films perforated with nanoholes [43]. In contrast to NSL, the evaporation mask used in SCL is defined by a sparse monolayer of colloidal particles. This method enables the production of large areas of features like nanoholes in thin films, with sizes down to 20 nm and which occupy 10–50% of the total surface area. In [43], propagating surface plasmon polaritons (SPP), LSPR and interactions between Al IT and LSPR have been thoroughly studied in aluminium (but also in gold) thin films perforated with nanoholes. The last version of CL related here is hole mask CL (HCL), which has been developed by Fredriksson et al and detailed in [44]. The main difference in HCL is the presence of a sacrificial layer combined with a thin film containing nanoholes (the hole-mask) used as a mask template during the evaporation (or etch) steps to define the pattern. The hole-mask is removed after processing thanks to the sacrificial layer. HCL has been used by Langhammer et al [7] to fabricate well defined aluminium nanodisks randomly distributed on the substrate combined with relatively large particle–particle separation. Thus, both far and near field optical coupling are avoided (such as Bloch modes or Woods anomaly). Consequently, plasmonic resonances tunable from the infrared to the ultraviolet sustained by HCL-made aluminium nanodisks have been thoroughly studied in this pioneering work in the field of aluminium plasmonics, as illustrated in figure 7.

Let us finish with a NSL-based method proposed in [45] allowing for the fabrication of crescent-shaped aluminium
Figure 7. SEM micrographs of Al nanodisks with a mean diameter (a) $D = 61$ nm and $h = 20$ nm and (b) for $D = 115$ nm and $h = 20$ nm. (c) Measured extinction efficiencies for Al nanodisks for a range of disk diameters $61 \text{ nm} < D < 492 \text{ nm}$ at constant height $h = 20$ nm. Reprinted from [7]. Copyright 2008 American Chemical Society.

nanoantennas. Even if no samples have been fabricated in this study, the plasmonic properties of such nanocrescents in the UV-VIS region are thoroughly analysed with calculations. Interestingly, higher-order modes sustained by these structures exhibit intense and controllable hot spots suitable for applications in the UV regime, such as SERS.

2.3. Interference lithography

Laser interference lithography (LIL or IL) is an alternative method for the fabrication of metallic nanostructures on dielectric substrates. Even if IL allows for the realization of periodic (or quasiperiodic) nanostructures, it has obvious advantages as it is maskless, low-cost, low time-consuming and large-scale compatible. Let us briefly recall the principle of IL. Interference patterns between two or more coherent light waves are printed in a layer of photosensitive resist. During the development step after exposure, the illuminated areas are dissolved in a selective solvent and the patterns are printed in the photosensitizer. The inherent limitation of IL is the resolution which is roughly defined by half of the wavelength of the laser source (but also by the resolution of the photosensitive resist) meaning that very short wavelengths are needed in order to achieve nanostructures with such a method. Consequently, extreme ultraviolet IL (EUV IL), which is the combination of IL with extreme ultraviolet light from undulators at synchrotron radiation facilities, has been developed [46, 47]. The main drawback of EUV IL is obviously the source, which relies on complex facilities that are seldom available. Using EUV IL, arrays of aluminium nanoparticles with sizes down to 40 nm and well-defined geometries have been deposited over large areas [8] as illustrated in figure 8. In this work, EUV IL has been used to create arrays of nanoholes in the resist, and the subsequent evaporation led to the aluminium nanoparticle arrays. These nanoparticles exhibit strong and sharp plasmonic resonances in the near and mid-UV spectral regions as confirmed by experiments and theory.

The same group has also developed another method based on EUV IL and thermal evaporation for the fabrication of large area, free-standing aluminium nanohole arrays [48]. Here, the method consists of (1) the deposition of the resist layer on a thin Si$_3$N$_4$ membrane, (2) the creation of hole (110 nm depth) arrays in the layer of resist by EUV IL exposure (and the subsequent resist development) and (3) Al evaporation at an oblique angle while the substrate is rotated around the normal direction. Due to a self-shadowing effect during the film evaporation, the holes in the photore sist are still open after the aluminium deposition. This results in nanohole arrays in the aluminium film. The Si$_3$N$_4$ membrane and the resist are then removed by reactive ion etching from the backside during the last step, resulting in a free-standing aluminium nanomesh as shown in [48]. The UV plasmonic properties of the aluminium nanomesh are characterized using optical transmission measurements. A final example of aluminium nanostructures made by EUV-IL can be found in [20]. Here, aluminium nanodisks sustaining dipolar and quadrupolar plasmonic resonances located in the near and mid UV, respectively, are used for SERS operating at 257.2 nm.

A simpler IL setup, particularly for the source, can be used for the fabrication of aluminium nanostructures [16]. Its principle is described in figure 9(a): A laser beam (operating at 266 nm) is expanded and then spatially filtered. Using a Lloyds mirror setup, the beam is divided in two parts. The first one is directly incident on the sample and the second one is reflected by a mirror which is perpendicular to the substrate. Consequently, light interferences are generated, which create a sinusoidal distribution of the irradiation with a given periodicity in the resist. This periodicity is adjustable by changing the angle of incidence $\theta$ of the laser beam. The resist is then developed, resulting in nanohole arrays which will serve as the evaporation (or etch) mask. This method is more convenient that the previous one (EUV IL) as the optical setup, particularly the source, is more straightforward and available. With this method, they produced aluminium nanostructures of various geometries: disks, quadratic and elliptic forms. The size of the nanostructures are larger compared with those obtained using EUV IL, with a typical minimum dimension equal to 120 nm. Consequently, the plasmonic properties of such Al nanostructures are located in the visible region, at least for their dipolar resonances. However, the nanostructures are very regular and uniform, and are consequently suitable for full systematic study. There are many optical characterizations in this work, and here we show only an example of transmission measurements performed on elliptic aluminium nanoparticles exhibiting polarization-dependent plasmonic resonances as illustrated in figures 9(b) and (c).
2.4. Nanoimprint lithography

Nanoimprint Lithography (NIL) relies on the mechanical deformation (and its subsequent patterning) of the resist material when pressed via a structured stamp [49]. Unlike EBL or IL, the desired pattern does not rely on the chemical modification of the resist when irradiated by electrons or photons. A schematic illustrating NIL is shown in figure 10. NIL is very appealing for industrial applications as this technique can produce nanostructures over very large areas on the substrate in a very short time. Indeed, the advantage of using nanoimprinting rather than other lithography methods to generate nanostructures is the production of stamps that are reusable many times and well suited for integrating into large-scale rollers in a roll-to-roll process. Some studies have focused on the use of NIL for the fabrication of aluminium nanostructures for plasmonic purposes.

The first example of Al nanostructures fabricated thanks to NIL is given in [50]. Here, large scale Al nanovoid-type substrates for UV-SERS detection purposes are fabricated. The method of fabrication combines nanoassembly, ion milling, nanoimprinting and e-beam evaporation. Each nanovoid measures typically 180 nm in diameter and 20 nm in depth. The nanovoid arrays cover a very large area onto the substrate (>1 cm²). In this work, it is shown that the plasmonic field localized at the edges of the nanovoids (and also inside) enhances the UV Raman signal (with a laser excitation source at 244 nm) of adenine by more than three orders of magnitude compared to planar metal substrates. Such UV-SERS plasmonic substrates are of tremendous interest for highly sensitive sensing or biochemical applications.

In a second example, by using nanoimprinted aluminium nanoparticle hexagonal arrays, the light emission of a dye-doped polymer layer capping the arrays is strongly shaped [51]. Here, by tuning the separation between aluminium nanoparticles in the arrays, the emission from the random distribution of dye molecules has an enhanced directionality in a narrow spectral range. The authors therefore claim that such structures will provide a wealth of new opportunities for the design and optimization of solid-state lighting devices.

In [52], aluminium gratings with a period of 200 nm have been demonstrated by combining reactive ion etching with NIL. This study just focused on the fabrication issues. In [53], the authors used such aluminium gratings in order to achieve a polarizer made of Al nanowires. Thanks to the optical properties of the aluminium gratings, the polarization extinction ratio reaches 38 decibels (dB) at a wavelength of 1550 nm. Let us finally point out that NIL is certainly an avenue to be explored further for mass production of plasmonic nanostructures. One can imagine the economic impact, for instance, of mass production of substrates containing aluminium.
nanostructures for printing applications, as already demonstrated by using EBL [35].

3. Self assembled thin films

In this section, more or less straightforward methods are discussed based on self-organization approaches for the fabrication of aluminium nanostructures. Simple metal evaporation, followed by rapid thermal annealing (RTA), can lead to the formation of well-separated nanostructures over large areas by thermal-induced dewetting. This method has been widely used to generate nanoparticles made of various metals. When aluminium thin films are evaporated on quartz substrates without any subsequent annealing, their morphology is thickness dependent [54] and nanostructured features are generated as illustrated in figure 11. The SEM images show the morphology of the aluminium layers with thicknesses varying from 2 to 80 nm. For the thinnest layer (2 nm), even if the film contains nanoparticles, no clear plasmonic resonances are visible on the corresponding absorption spectrum (not shown here). The nano-sized features become larger when the thickness is increased and tend to coalesce and disappear for the thicker films which are becoming almost continuous. Nevertheless, even if the aluminium thin films do not exhibit clear plasmonic resonances here, they have been successfully used as fluorescence enhancers in the ultraviolet-blue region of the EM spectrum. The fluorescence enhancement factor

Figure 10. Schematics of nanoimprint processes: (a) the originally proposed nanoimprint lithography process where a resist layer is used for further pattern transfer, as in standard lithography, and (b) a method where the patterned layer is directly used (shown here with the deposition process as the last fabrication step). Reprinted from [49]. Copyright 2009 Institute of Physics.

Figure 11. SEM images of (a) 2 nm, (b) 5 nm, (c) 10 nm, (d) 20 nm and (e) 80 nm-thick thermally evaporated Al films on quartz substrates. Reprinted from [54]. Copyright 2007 American Chemical Society.
strongly depends on the thickness of the aluminium films, reaching a maximum value of 8 for an aluminium thickness of about 10 nm.

In [55], another example of aluminium surface plasmon-assisted fluorescence in the near UV region is given. Here, the fluorescence (near 350 nm) appears almost completely p-polarized, unveiling the origin of the fluorescence enhancement which is due to the coupling between SPP sustained by aluminium films and the emitters.

As mentioned above, a dewetting step can be added by annealing the thin films in a rapid thermal annealing furnace, for instance. The objective of this step is to transform the thin metallic film into well shaped and separated quasi-spherical nanoparticles or nanoislands. Unfortunately, this technique is not efficient when directly applied to aluminium. Indeed, when aluminium thin films are annealed without any specific conditions (which are discussed below), they do show some nanostructuring. However, these structures are not separated into well-defined aluminium nanoparticles and do not exhibit clear plasmonic resonances. There are two main reasons offered which may explain the poor dewetting of aluminium. The first one is related to the high adhesion coefficient of aluminium [56], which considerably hinders the dewetting process, yielding poor-quality aluminium nanostructures. The second one is related to the natural oxidation layer of alumina which rapidly forms around any aluminium feature. During the dewetting step, the alumina layer may limit the mobility of aluminium on the surface of the substrate, hindering the formation of well-separated particles even at high temperatures.

In [57], the dewetting of thin aluminium films evaporated on silicon substrates has been dramatically improved. The dewetting issue related to the oxidation of aluminium is overcome by annealing the samples inside the deposition chamber. Thus, aluminium is thermally evaporated onto substrates at temperatures varying from 200 to 400 °C and then annealed for 60 min while keeping the vacuum in the evaporation chamber. The average particle size is controlled by adjusting the thickness of the deposited aluminium, as illustrated in figure 12. The mean particle diameter ranges from 20 to 130 nm, and increases with the deposited thickness, which is typically set to 7–20 nm. Due to the relatively broad size distribution of the obtained particles, transmission measurements (not shown here) on ensembles revealed more or less large dips centred at 320 nm and 450 nm for a deposited thickness of 7 nm and 14 nm, respectively. These optical features are rightfully attributed to LSPRs sustained by the aluminium particles in the UV-VIS region of the EM spectrum. Finally, it is proved that such particles can be used for enhancing the efficiency of thin Si solar cells by increasing their external quantum efficiency up to 15%.

An older study focused on the optical absorption in aluminium nano-islands formed on a large area is detailed in [58]. Here the substrate was also annealed during aluminium deposition leading to separated aluminium particles with typical sizes ranging from 5 to 200 nm. This study particularly emphasised the influence of aluminium particle size on their absorption related to IT. As a reminder, the main IT of aluminium is located in a relatively narrow range of energies centred at 1.5 eV. Therefore, the LSPR sustained by the aluminium nanoparticle can be tuned (or detuned) to the same energy as the IT.

As mentioned earlier, aluminium exhibits a high adhesion coefficient on various substrates, which considerably hinders the dewetting process, yielding poor-quality aluminium nanostructures. To circumvent this issue, a substrate preparation method that dramatically decreases the adhesion of aluminium to the substrate is proposed in [59]. A well-chosen chemical functionalization leads to a super-repellent substrate and allows for the efficient dewetting of aluminium. More precisely, perfluorosilane molecules (1H,1H,2H,2H-perfluorodecyltrichlorosilane) are grafted onto the surface of the substrate, after being activated in a piranha solution. This drastically changes the surface wettability as verified by measuring the contact angle of a water droplet on the surface. Following the functionalization, a thin layer of aluminium is thermally evaporated onto the substrate and is then annealed by RTA for 10 min at 800 °C. The RTA is performed under primary vacuum followed by a 25 sccm argon flux to prevent oxidation of Al. During annealing, quasi-spherical aluminium droplets are formed due to the super-repellent property of the substrate as illustrated in figure 13, on the bottom of the right panel. The crucial role played by the surface functionalization is emphasized in this figure showing two SEM images of a 5 nm aluminium film after annealing without (left column) and with (right column) the surface functionalization step. When the surface is functionalized, well-defined quasi-spherical

![Figure 12. SEM images showing (a), 7 nm, (b), 14 nm and (c) 20 nm thermally evaporated aluminium on Si substrate annealed at 300 °C inside the deposition chamber. Reprinted from [57]. Copyright 2013 Institute of Physics.](Image 120x655 to 480x777)
nanoparticles of relatively homogeneous sizes are obtained. A complete characterization of the morphology of the nanostructured film is given in the article for three different initial evaporated thicknesses (2.5, 5 and 8 nm). The nanoparticle diameters have a Gaussian distribution. The 2.5 nm film gives rise to Al-NPs with a mean diameter of 5.1 nm and a relatively narrow distribution width (FWHM = 2.1 nm). When the film thickness increases, the mean diameter increases (6.9 nm for the 5 nm thick film and 11.6 nm for the 8 nm thick film) and the size distribution becomes broader. Interestingly, these aluminium nanoparticles sustain localized plasmonic resonances down to 210 nm as shown by extinction measurements and confirmed by Mie theory, by taking an effective refractive index taking into account the alumina shell and the substrate.

Another very efficient method for the fabrication of small aluminium nanoparticles sustaining plasmonic resonances in the deep ultraviolet has been developed by Maidecchi et al [12]. This method follows the procedure sketched in the top part of figure 14 and is succinctly discussed in the following. First, flat LiF(1 1 0) crystals (used as a substrate), are flashed at 700 K in a vacuum chamber with a base pressure of 1.5 × 10⁻⁸ mbar in order to clean them efficiently. Crystalline LiF is transparent up to 11.5 eV and is thus very convenient for deep UV transmission measurements. Then a 240 nm LiF layer is homo-epitaxied on the substrate heated to 590 K. Due to complex surface kinetics during the epitaxial growth, a regular one-dimensional nanoridge-valley pattern with a periodicity roughly equal to 25 nm is formed at the LiF surface. Each nanoridge is defined by two side walls with particular crystallographic orientations as illustrated in the schematic in figure 14. In the next step, a thin aluminium layer is deposited by molecular beam epitaxy at grazing incidence in order to deposit aluminium only on the side walls defined by a specific crystallographic orientation (i.e. on one and the same side of all the nanoridges). Finally, the samples are flashed at a temperature of 670 K in vacuum for 5 min to activate the dewetting of aluminium and are cooled down under oxygen flux. This method leads to well-shaped, small and spheroidal aluminium nanoparticles aligned along the LiF nanoridges (see figure 14). Their mean size can be gradually increased with increasing the thickness of aluminium during the evaporation, and typically range from 12 to 25 nm in width and 12 to 15 nm in height for the metallic part of the nanoparticles, as proved by high resolution x-ray photoelectron spectroscopy. Indeed, the thickness of the alumina shell surrounding the Al nanoparticles has been thoroughly studied by this method of characterization. They particularly studied the dependence of the oxide/metal XPS peak intensity ratio as a function of the Al nanoparticles metallic-core radius. Finally, as shown by extinction measurements and confirmed by calculations, such arrays of aluminium nanoparticles sustain sharp LSPR up to very high
energies (up to 5.8 eV), and are thus very appealing for deep ultraviolet plasmonics. In this study, optical characterizations and calculations are very much complete and deeply analysed, but as we focus on the fabrication in this review all the details can be retrieved in the corresponding [12].

A final example of self-assembled Al structures is given in [60]. Here, evaporation-induced rapid self-assembly of microwires made of Al nanoparticles (commercially purchased under the form of Al powder) was demonstrated under microwave heating. By using different surfactant-solvent formulations, the microwires are formed on the substrate at the contact line between the solvent containing the powder and the air due to stick-slip dynamics during the heating. These mechanisms are very well described in the paper. The typical width of the microwires is 1–20 \( \mu \text{m} \), and the distance between the microwires is typically 50–300 \( \mu \text{m} \).

4. Laser ablation

Historically, it appears that one of the first developed techniques for the mass production of Al nanoparticles is the pulsed laser ablation (PLA) technique. In addition, this technique, well known and well documented, has been widely used in different communities, including nanooptics, to generate nanoparticles of various materials [61]. This technique relies on the interaction of a pulsed laser beam with a solid target. The ablation takes place in several steps which are summarized in figure 15. (i) the first one is the generation of a plasma induced by the laser on the surface of the target. (ii)
Conclusively, the chemical synthesis of Al nanoparticles is not

5. Chemical synthesis

Colloidal chemistry of Au or Ag, based on salt reduction, is widely used for numerous applications in nanooptics. Contrarily, the chemical synthesis of Al-nanoparticles is not
popular due to the fact that the reduction of aluminium salts is complicated [67]. This is because the reduction of Al halide is achieved using lithium or sodium. These two reductors are strongly reactive (particularly with water) and the reaction could be dangerous. Moreover, the production of Al nanoparticles is accompanied by the formation of by-products. The final separation implies various steps of washing. Nevertheless, another method for the chemical synthesis of Al nanoparticles has been developed. The synthesis is based on the catalytic decomposition reactions of alanes [67–70]. Haber et al
J Martin and J Plain have shown the possibility of reducing AlCl₃ with LiAlH₄ according to the reaction presented in figure 20. Haber et al claim that the reaction presented in figure 20 proceeded by the intermediate formation and decomposition of alanes, AlH₃.

Thus, they show the possibility of obtaining Al nanoparticles by the direct decomposition of alanes with or without a catalyst precursor according to the reaction shown in figure 21.

In both strategies, the final particles are quite large, exhibiting a wide distribution of size ranging from several hundreds of nm to 2 µm. Then, Jouet et al [68] and Foley et al [69] developed strategies to passivate the obtained Al particles by the decomposition of alanes. Finally, Meziani et al have realized a systematic study of the alanes’ decomposition under various experimental conditions [70]. As a result, they show that an appropriate balance between the alanes’ decomposition and the timing in the introduction of the passivation agent is critical to control the final morphology of the nanoparticles. The results in terms of size and shape are shown in figure 22 for two different experimental conditions. The particles with a size lower than 100 nm present a spherical shape and no clear evidence of crystallinity (no obvious peak in the XRD spectra, not presented here). On the contrary, the biggest ones (>200 nm) are crystalline Al nanoparticles and exhibit various shapes as evidenced in figure 22(b). It clearly appears that the choice of the alane, the temperature of reaction, the solvent and the passivation agent are critical parameters that control the final product.

6. Conclusion and perspectives

We have presented here a review of techniques for the fabrication of aluminium nanostructures within the context of plasmonics. For each technique, we have focused on the feasible geometries that the nanostructures may take and we have also given a succinct description of their plasmonic properties when possible. It turns out that the fabrication of aluminium nanostructures paves the way toward a new generation of plasmonic functionalities, tunable from the infrared to the deep ultraviolet. Even if the present review has not been exhaustive, we hope that we have given the reader a good idea of the different tools available for the fabrication of aluminium nanostructures exhibiting plasmonic properties. Moreover, we have introduced techniques such as pulsed laser ablation or chemical synthesis which have not been developed for plasmonic applications. As for noble metal plasmonics, some issues are the mass production and the large scale patterning and we think that these techniques could be very good candidates to overcome such challenges. Furthermore, it seems that there is an opportunity to develop chemical routes allowing for a control of the size and shape of aluminium nanoparticles in solution as in the case of gold or silver.

Acknowledgments

JM and JP thank D Gérard for useful discussions. The authors acknowledge the Région Champagne-Ardennes, the Conseil général de l’Aube, and the FEDER funds through their support of the regional platform Nanomat. JM acknowledges support from the DRRT (project PlasmUV).

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