Advances in Colloid and Interface Science 206 (2014) 5–16

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Plasmonic films based on colloidal lithography

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ARTICLE INFO

Available online 23 November 2013

Keywords:
Plasmonic films
Surface plasmon resonance
Colloidal lithography

ABSTRACT

This paper reviews recent advances in the field of plasmonic films fabricated by colloidal lithography. Compared with conventional lithography techniques such as electron beam lithography and focused ion beam lithography, the unconventional colloidal lithography technique with advantages of low-cost and high-throughput has made the fabrication process more efficient, and moreover brought out novel films that show remarkable surface plasmon features. These plasmonic films include those with nanohole arrays, nanovoid arrays and nanoshell arrays with precisely controlled shapes, sizes, and spacing. Based on these novel nanostructures, optical and sensing performances can be greatly enhanced. The introduction of colloidal lithography provides not only efficient fabrication processes but also plasmonic films with unique nanostructures, which are difficult to be fabricated by conventional lithography techniques.

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1. Introduction

Surface plasmons (SPs) are coherent oscillations of conduction electrons on a metal surface excited by electromagnetic radiation at a metal–dielectric interface. This growing field of research on light-metal interactions is known as "plasmonics" [1–3]. It has attracted much attention and one key topic rests in fabricating various metal nanostructures for clarity of the fundamental mechanism and improved applications. In view of the previous reports, two types of structures – nanoparticles and films – are considered to cover the main plasmonic structures, of which the latter one is defined as plasmonic films. Recently, more research has focused on the films with concave/convex nanostructures, sharp tips and adjoining nanostructures on the surface, which constitute one of the most explored platforms for miniaturized optical devices, sensors, and photonic circuits with special focus on medical diagnostics and therapeutics [4–8]. These plasmonic materials offer a large range of advantages compared to nanoparticles, including facile surface chemistry for the immobilization of molecular recognition elements [9]; the possibility of a small (subwavelength) sensing area [10,11]; the potential for massive multiplexing (detection of several different chemical species at the same time) [12]; easy integration with microfluidics [13], leading to

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http://dx.doi.org/10.1016/j.cis.2013.11.010

small device footprint; high sensitivity, excellent stability and ease of use. All these favorable properties justify the high research activity aimed at the development of different types of SP-based films.

Plasmonic films are a highly active area due, in part, to recent advances in nanofabrication methodologies. These methodologies, including electron beam lithography [14,15], focused ion beam lithography [16] and colloidal lithography (CL) [17], have led to the realization of structured films with nanoholes [18], slits [19], gratings [20], cones [21], and other components [22] with precisely controlled shapes, sizes, and spacing. In particular, CL, as a fast developing unconventional lithographic technique, makes the fabrication process more efficient and further provides unique advantages in fabricating three-dimensional nanostructures. Monodisperse microspheres with sizes ranging from tens of micrometers to tens of nanometers, can easily be synthesized by conventional emulsion polymerization or sol–gel synthesis techniques. Owing to the size and shape monodispersity, they can self-assemble into two-dimensional (2D) and three-dimensional (3D) extended periodic arrays, coined as a colloidal crystal [23–26]. The interstitial array in a colloidal crystal was used as a mask for etching or deposition to create 2D patterns on a substrate. This patterning process is preferentially referred to as CL, paving a simple and low-cost route for patterning with a flexibility of scaling down the feature size below 100 nm.

This review briefly introduces the design and fabrication of CL-based plasmonic films, followed by placing the emphasis on the strategy of utilizing CL to fabricate periodic structured films. These plasmonic films will be also reviewed with a brief update on advancements of optical and sensing performance, as well as novel properties based on various surface morphologies. Finally, challenges and outlook are offered to inspire more exciting developments in this still young yet very promising field in the future.

2. Plasmonic films

Conduction electrons of a metal act like a plasma and can support surface waves, the quantum of which is known as a surface plasmon (SP). SPs have been described as light trapped at the metal surface and, in that sense, can be considered as two-dimensional light. Two types of surface plasmon resonances (SPRs) are exhibited in metal structures: (i) propagating surface plasmon polaritons and (ii) nonpropagating localized SPRs. Localized SPRs are excited when the incident photon frequency is resonant with the collective oscillation of the conduction electrons confined in the volume of the nanoparticles. The spectral position and magnitude of the localized SPRs depend on the size, shape, composition, and local dielectric environment [27,28]. This property has been exploited for label-free optical sensing where adsorbate-induced refractive index changes near or on plasmonic nanostructures are used to monitor binding events in real time [29], which has been discussed by several reviews and books published in the past few years [30–32].

Propagating surface plasmon polaritons are excited on metal films by the coupling between a light wave and a surface plasmon at a metal–dielectric interface [33]. These metal films showing SP features are defined as plasmonic films. However, resonance cannot be created on a smooth metal surface by direct optical excitation [34]. The reason is that the SP momentum is larger than that of a free photon, and direct light-to-SP conversion is forbidden. Therefore, special coupling schemes, which are used to increase the wave vector of light to match that of the surface plasmon, need to be devised to allow for SP generation. The most common couplers used at first include a prism coupler, a waveguide coupler, and a grating coupler. Prism couplers represent the most frequently used method for optical excitation of surface plasmons [35–37], of which the most common configuration is the one proposed by Kretschmann and Raether [35]. In this case, the evanescent field from the totally reflected light from the prism side extends through a thin metal film (about 50 nm) to launch SPs on the other side of the film.

Grating couplers have not been used as widely as the prism couplers. However, their compatibility with mass production (in particular, replication into plastic) makes a grating coupler an attractive approach for fabrication of low-cost SPR sensing structures. Furthermore, the grating couplers enable a strategy of preparing the films with corrugated structures to achieve the coupling between light and a surface plasmon by the films themselves. With further research, these corrugations are extended to various types, such as periodic arrays or random distributions of subwavelength holes (nanoholes) perforated in a metal film [38], rough structured continuous films [39–41], with a few examples shown in Fig. 1, and these novel structured plasmonic films constitute the focus of this review.

The geometric characteristics of the structures (type of corrugation, shape, and periodicity [42]) can be tailored to control the characteristics (resonance energy) of the SPs. Not limited to one SPR mode, both SPPs and localized SPRs might play a role in a particular system, offering opportunities to yield surprising optical effects, which result in unique transmission, reflection, extinction or surface enhanced Raman scattering (SERS) spectra. These remarkable properties open up a colorful future for the next generation of optical devices, sensors and other relevant applications.

The great process in the field of plasmonic films is, in part, due to the advances in nanofabrication methodologies. Scanning beam lithography techniques, such as electron beam lithography and focused ion beam lithography, are the main choices to fabricate metal structured films. While these conventional lithography techniques are capable of precise control over the size, shape, and spacing of metallic nanostructures, more recent research has focused on unconventional lithographic techniques that are capable of patterning large areas in parallel at low cost. In particular, the colloidal lithography technique, possessing the advantages of a low-cost and flexible fabrication process, has been more frequently used in preparing plasmonic films. The following section will describe in more details the colloidal lithography technique.

3. Colloidal lithography

The periodical array of a close-packed microsphere monolayer was first used as a mask in 1981 for the deposition of platinum by Fischer and Zingsheim [43]. After that, this new technique has been extended by large impressive efforts, and meanwhile has diverse names such as natural lithography, nanosphere lithography, and colloidal lithography [44–48]. Following extensive work, colloidal crystals are recognized as low-cost, flexible, and easily adoptable masks for growing new nanostructures with diverse structural complexity. For now, colloidal lithography is known as an important unconventional fabrication technique relying on using colloidal crystals as masks or templates for etching and deposition. This technique includes two types of masks—disordered colloid particles and ordered colloidal crystal. The latter one, which has attracted much more attentions, constitutes the focus of this review. Two main procedures of preparation and modification of colloidal crystals, and colloidal crystal assisted operations are included in the technique. By flexibly controlling these procedures, various nanostructures on planar and nonplanar substrates can be fabricated. Some examples are shown in Fig. 2. Besides, the CL technique has unique advantages in fabricating 3D structures due to the variable height of the spheres in vertical direction. The following sections will describe in more details the two main procedures.

3.1. Preparation and modification of colloidal crystals

The success of using colloidal crystals as masks for surface patterning is based on the capability of directing self-assembly of colloidal particles and manipulating the crystal packing structures. Up to date a variety of colloidal crystallization techniques have successfully been developed to implement colloidal crystallization in a controlled fashion, and each technique possesses unique advantages and limitations. For example,