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Cluster ion beam assisted fabrication of metallic nanostructures for plasmonic applications

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ABSTRACT

We report a high-throughput, single-step method for fabricating rippled plasmonic nanostructure arrays via self-assembly induced by oblique angle cluster ion beam irradiation of metal surfaces. This approach does not require lithographic or chemical processes and has the prominent advantage of possible large surface area coverage and applicability to different starting materials. The polarization dependent plasmonic property of the gold nano-ripple is due to their one dimension structure. The localized plasmon resonance frequency of synthesized *nano-ripple arrays* is tunable by changing nano-ripple dimensions that can be engineered by changing the cluster ion beam irradiation parameters. In this specific case presented, using 30 keV Ar-gas cluster ion beam, we fabricate gold nano-ripple arrays that show localized plasmon resonance in the visible range through near IR range, tunable by varying cluster ion irradiation fluence.

1. Introduction

Localized surface plasmon resonance (LSPR) effect of metal nanostructures has attracted considerable research interest because of its potential applications in several areas including sensors [1], surface enhanced spectroscopy [2,3], photovoltaics [4,5], sub-wavelength microscopy [6,7], near-field lithography [8], nano-photonics [9], bio-imaging [10], laser photo thermal therapy [11], and numerous other applications. LSPR results from coupled oscillations between the charge density of conduction electrons and their corresponding electromagnetic field in conductive nanostructures that are smaller in dimension compared to the wavelength of exciting electromagnetic radiation, which results in enhanced absorption and scattering resonances [12]. The unique plasmonic property of metals resides in the fact that their dielectric constant is a complex function of the frequency of incident light, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary component $\varepsilon_2(\omega)$ causes the resonant behavior. The LSPR peak relies greatly on the shape, size and composition of the nanostructures. Application of the LSPR effect therefore critically depends on reliable and efficient ways of controlled fabrication of metallic nanostructures.

Numerous nano-fabrication techniques are utilized in synthesizing nanostructures for utilization of the LSPR effect [13]. Wet chemical reduction is an attractive method for synthesizing noble metallic (Au and Ag) nano particles of dimensions required for LSPR applications. Because of the face centered cubic crystallization of many metals, in this approach, the nano particles inherently crystalize into a truncated octahedron shape. However, surfactants and stabilizing agents added to the reactants allow engineering of different shapes and morphology by promoting preferential growth along certain crystal facets [14]. Wet chemical reduction synthesis has the advantage of large scale, relatively rapid synthesis. However, it is impaired in reproducibility and ability to fabricate substrates with immobilized ordered nanostructure arrangements. Another attractive approach is to promote plasmonic metal nanoparticle growth in a solid solution, where the metal is infused into a solid substrate by means of ion implantation as to reach a concentration exceeding the solid solubility of the metal in the substrate [15,16]. Nano-particles formed in this process are inherently immobilized in the solid substrate with high spatial propinquity and therefore, these composites are also effective as surface enhanced Raman spectroscopy (SERS) substrates [17].

Lithographic techniques are attractive in achieving size and shape control of plasmonic nanostructures. Fabrication of nano structures via electron beam (EB) lithography and focused ion beam lithography allows high resolution and precise control of size,

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shape, and spatial distribution of nano structures [13,18,19]. Despite their advantages, they suffer from being slow processes and are limited to relatively small area fabrication [18]. Nano sphere lithography offers a cost effective method to produce large area 2D periodic arrays of plasmonic nano structures [20,21] that are also effective SERS substrates. Alterations to fabrication methodology of nano sphere lithography allows fabrication of nano structure morphologies that include nano disks, nano rings, nano holes, and even cup-like structures [22]. Nanoimprint lithography can be considered to be a next generation lithographic technique that offers high precision comparable to EB lithography, while offering high throughput suitable for large-scale patterning [13,18]. This method allows finest lithographic resolutions, however, limited by the resolution of mask fabrication [13]. Some attractive and effective alternate approaches include the fabrication of metallic plasmonic resonators by nano skiving of chemically synthesized micro-plates of gold [23,24]. In this approach, microplates of metal (gold) of nano-scale thickness are embedded in epoxy, and then sliced along with epoxy via nano skiving. This forms nano wires of well-defined dimensions that act as plasmonic resonators and plasmonic waveguides. One attractive feature is that when deposited microplates are single crystalline, the structures themselves become single crystalline, making them low-loss plasmonic resonators. The approach however is a multiple step process and is unable to produce large area nano structure arrays.

Systematic laboratory procedures with cleanroom techniques do produce effective plasmonic structures, however, industrial applications such as large-area photovoltaic module production requires inexpensive and scalable techniques for controlled fabrication of metal nano patterns [25]. Simple methods to achieve this include thermal evaporation of a thin metal film on to a substrate and heating at a moderate temperature (200–300 °C). This causes agglomeration of the metal film by surface tension that forms a random array of nanoparticles with more regularity achievable by evaporation through a porous membrane (for example porous alumina) [25–27].

To compliment such large-area high-throughput fabrication methods, in this article we discuss a method to fabricate plasmonic nano-arrays by oblique angle gas cluster ion beam (GCIB) irradiation of gold surfaces. Our method is a single step process with high throughput [28] and the capability to produce large-area fabrication (200 mm wafer processing with commercial cluster ion implanters). Further, as any ion irradiation process this method produces minimum contamination since it does not involve any chemical processes. The fabrication method is further reproducible, and can be applied to many different starting materials that include metals and non-metals [29–31].

Cluster ions are charged, bound units of thousands of atoms. Energetic flux of cluster ions makes a cluster ion beam. Interaction of cluster ions with a solid is significantly different from how monomer ions interact with a solid. This is because of comparatively very low kinetic energy per constituent atom of a cluster ion and the synergetic reaction caused by the simultaneous arrival of thousands of constituent atoms of a cluster at the target with high spatiotemporal propinquity [32,33]. The resulting nature of cluster ion–solid reactions is ideal for controlled surface modification. Gas cluster ion irradiation at normal incidence to a surface is widely used in research and industry for atomic scale smoothing of surfaces [32,34,35]. In contrast, GCIB irradiation of surfaces at an oblique angle roughens a surface, under proper conditions, producing self-assembled periodic nano-scale ripple arrays that closely resemble Aeolian sand-ripples [29–31]. Our approach utilizes this self-assembly process in order to fabricate metallic plasmonic nano structure arrays. Interestingly, with our approach, it is straightforward to control the scale and the separation of the nano-ripple structures, for example in this case of gold, to be in the range that exhibit LSPR in the visible range. In our experiment we irradiate a thin plain gold surface with ionized clusters of argon gas. Argon being an inert gas does not react with the surface and forms a one dimensional gold nano-ripple pattern due to sputtering of the gold atoms at the surface [30]. The nano-ripple wavelength depends on the number of clusters hitting the surface per unit area (centimeter square). By varying fluence of these clusters we obtain nano patterns of different sizes. In this paper we have reported the variation in the localized surface plasmon resonance frequency with the change in dimension of the gold nano-ripples and the polarization dependence of the plasmonic response of these nano-ripples on the incident electric field vector due to their one dimensional structure.

2. Experimental section

2.1. Fabrication process

We fabricate nano-ripple structures on gold surfaces (100 nm thick gold film on silicon obtained from Sigma Aldrich) by means of oblique angle irradiation (see Fig. 1) by 30 keV Ar GCIB (with 3000 mean Ar atoms per cluster ion) using an Epion cluster ion implanter. In order to control the geometry of the nano-ripple structures for the purpose of tuning the LSPR resonance frequency, we change the GCIB irradiation fluence as the variable parameter. For the cases discussed, at a base angle of incidence of 60 degrees, we irradiate the gold surface with different GCIB fluence of 1×10^{16} clusters/cm^2, 2×10^{16} clusters/cm^2 and 4×10^{16} clusters/cm^2. The cluster ion beam flux is approximately 3.9×10^{12} clusters/cm^2/s and is kept constant. The variation of irradiation fluence affects the self-assembly process such that geometric parameters of

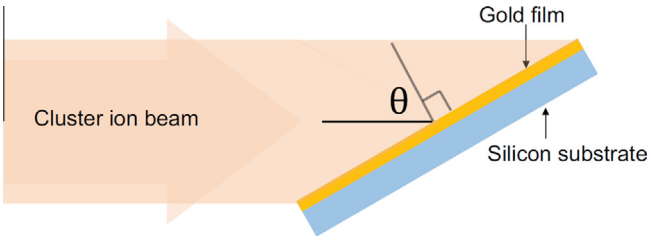

Fig. 1. A schematic of oblique angle gas cluster ion beam (GCIB) irradiation configuration used in fabrication of nano ripple array structures. In this case presented, a 100 nm thick film of gold on silicon is irradiated with argon GCIB. θ is the angle of incidence of GCIB irradiation.

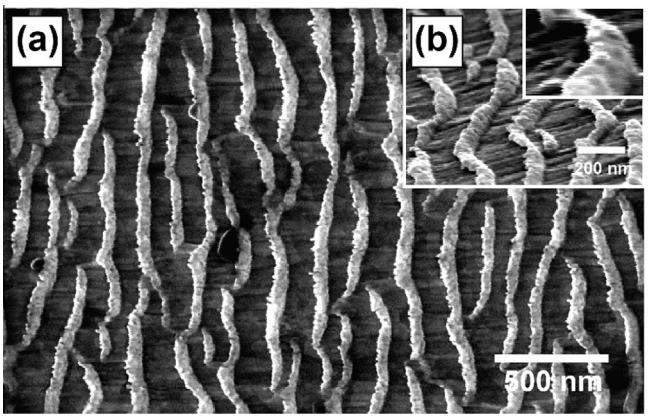

Fig. 2. (a) SEM top view image of the nano-ripple array on gold surface obtained for GCIB irradiation fluence of 4×10^{16} clusters/cm^2, for an incident angle of 60 degrees. (b) SEM image with the substrate tilted 70 degrees for better visualization of the cross-section of the ripples.