Multidimensional Metal-Dielectric Plasmonic Array

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Abstract:

We present a new multi-dimensional plasmonic array consisting of a metal-dielectric-metal interface. This array enhances plasmonic interactions between layers and exhibits tunneling effects dependent on dielectric thicknesses. Plasmon-driven growth is used to controllably fabricate the multi-layer nanogap structure. This multi-dimensional structure, which cannot be easily produced through conventional lithographic methods, takes advantage of plasmonic coupling effects and provides increased tunability of the optical resonance as well as greater enhancement of the near-field. In addition, we report high electric field focusing in the multidimensional plasmonic nanogap array, which confirms the enhancing nature of the structure and shows a potential for high sensitivity in detection applications. We demonstrate the uniformity and stability of the plasmonic structures through characterization of nanoparticle size and absorption spectra. Such a substrate can find uses in many areas, including optofluidic platforms for the detection of biological molecules such as proteins.

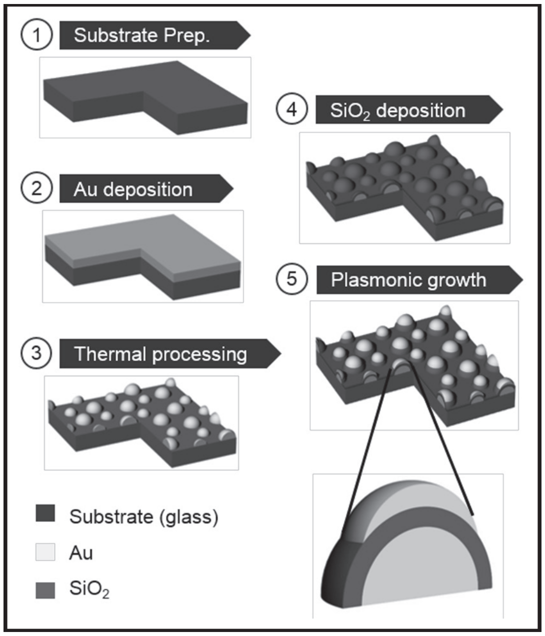

Figure 1: Schematic illustration of fabrication process for the multidimensional array.

Introduction:

In recent years there has been extended exploration of plasmonic substrates due to their uniquely enhanced optical properties that are a result of localized surface plasmon resonances (LSPRs). Such substrates have largely consisted of either isolated or ordered two-dimensional metallic nanostructures in various shapes and sizes. Some examples of shapes that have been prepared include spheres, pyramids, cubes, bowties, rods, stars, and other varied shapes [1].

Much effort has been placed into optimizing geometric properties because the optical characteristics of a plasmonic structure depend critically on features like shape, size, particle spacing, etc. [2]. However, as a result of the focus on shape alteration, relatively little work has been done on increasing the dimensionality of plasmonic structures, which can lead to new interactions and emergent phenomena.

Here we introduce a multi-dimensional plasmonic array that consists of two metal nanostructure arrays separated by an insulating dielectric layer. The increased dimensionality introduces new coupling effects that must be considered, and the solid dielectric layer (as compared to the empty space of air) means that the substrate will exhibit different field decay behavior and see a potential for tunneling and backscattering effects.

Experimental Procedure:

After thoroughly cleaning bare glass slides, gold (Au) films were deposited onto the glass through electron-beam evaporation. The samples were thermally processed by heating in a furnace to produce islands of Au, which comprised the nanogap array of the first layer of nanoparticles (NPs). Then, using SiO$_2$ as the insulator, the dielectric layer was deposited over the Au NP array through e-beam evaporation.

The second layer of Au NPs was grown on top of the SiO_2 layer through a seed-mediated, plasmon-induced method. We first immersed the samples in an Au seed solution and ensured seed adsorption by taking advantage of the electric field produced by LSPR excitations, which attracted the seeds to adhere to the surface of the previously produced NPs. Then, we grew the second layer of Au NPs on the seeds by chemical reduction of an Au precursor, attracting the Au ions in the same manner using LSPR excitations. In this way, we could direct the growth sites of the secondary Au layer.

Results and Conclusions:

We proceeded to analyze the morphological and optical properties of our plasmonic array to produce a rigorous characterization. To confirm the structure of the substrate we used scanning electron microscopy (SEM) in combination with an image analysis program, ImageJ, to visually as well as quantitatively describe the geometry of the NPs.

From Figure 2, it is evident through simple visual inspection that the number of Au NPs grown in the second metal layer, shown by the white spheres, increased from the controlled growth case to the plasmon-induced growth case. By further analysis in ImageJ, we obtained size distribution data for the particles as shown in Figure 3. The effect of introducing our plasmon-induced method to the growth process was that the size of the NPs grown with the method was increased at all SiO_2 thicknesses over the control growth.

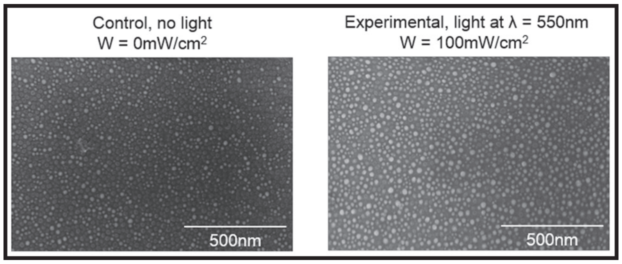

Figure 2: Growth of secondary Au layer without an excitation source (left) and with an excitation source (right).

We demonstrate that the overall size of the NPs, as well as the size difference between the control and experimental cases, decreases with increasing SiO_2 thickness. This result is expected as with a larger insulating layer, the strength of the electric field is reduced and the size of the particles grown should be smaller. With a 20 nm SiO_2 thickness, the difference between the plasmon-induced growth method and the control is almost entirely eliminated. We also see that the dielectric layer cannot be eliminated entirely, as that then results in the smallest size of NPs.

Next we characterized our substrate optically through ultraviolet-visible (UV-VIS) spectroscopy. The absorption spectra, shown in Figure 4, demonstrate a redshift of the resonance peaks with increasing silica thickness. The effect of growing the secondary Au layer, in comparison, is a blueshift of the peaks. In the dark or control growth, which produced smaller NPs than the plasmon-induced method, the blueshift is smaller than in the plasmon-induced growth, which produces larger NPs and exhibits a larger blueshift as a result.

Future Work:

Given the complete characterization of our array and its favorable properties as a plasmonic substrate, we will look to integrate it into practical devices that require the sensitivity and robustness of our substrate. Creation of an optofluidic device to allow detection of biological proteins is an application that has many practical uses, and is one in which our bioplasmonics group at the University of Michigan has experience.

Acknowledgments:

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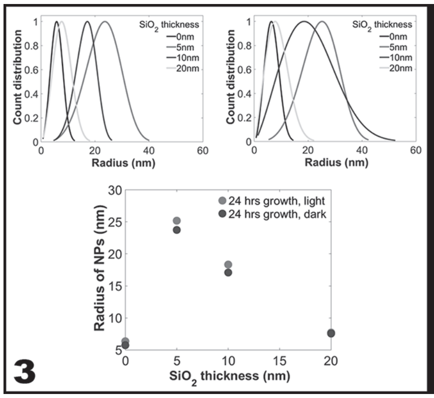

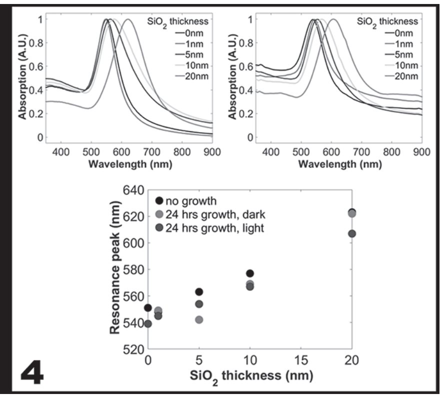

Figure 3, left: Radii of NPs grown without an excitation source (top left), with an excitation source (top right), and comparison of peak location (bottom). Figure 4, right: Absorption spectrum before growth (top left), after 24 hours growth with excitation source (top right), and comparison of peak location (bottom).

References:

[1] Sharma, Bhavya, et. al. High-performance SERS substrates: Advances and challenges. MRS Bulletin, 2013, 38, 615-624.

[2] Willets, Katharine A., and Van Duyne, Richard P. Localized Surface Plasmon Spectroscopy and Sensing. Annual Review of Physical Chemistry, 2007, 108, 267-297.