

Nanoscale Pattern Generation for use in Surface Plasmon Resonances

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The creation of patterned metal films on the nanoscale for use in surface plasmon resonance has potentially useful applications, particularly as a biosensing technique which provides a sensitive means for molecular analysis. Nanosphere lithography has been identified as a cost effective and time saving procedure for generating nanoparticle arrays; this method has polystyrene-latex microbeads behave like a mask for peak formation and has been tested using a variety of substrates (glass, mica, polystyrene). The results from this experiment were substrate dependant and quite varied. Other pattern generation techniques were explored as well, including perforated film creation with a Formvar-water-chloroform emulsion and electron beam lithography. Although all three aforementioned patterning techniques met some degree of success during experimentation, e-beam lithography seems to hold the most promise.

Introduction

An evanescent field is produced when total internal reflection occurs for an air-glass prism configuration. If a thin metal film is introduced to the air-glass interface, at some point the collective electron oscillations on the metal surface will begin to resonate with the evanescent field. This surface plasmon resonance (SPR) is marked by a reduction in the intensity of the reflected light.

Because the surface interface is sensitive to changes, the SPR phenomenon has been applied as a bioanalysis method. When molecules are deposited and immobilized onto the surface interface, a resonance shift occurs and can subsequently be seen by noting a change in the SPR angle. The primary advantages of using this method as a sensing device are that it provides a label free, nondestructive means to monitor a sample in real time (Szabo). In addition, SPR is highly sensitive and capable of detecting up to a single layer of molecules as small as 180 Daltons, the size of an amino acid.

Typically, planar gold or silver films are used to excite the surface plasmon resonance; however, this experiment is concerned with creating patterned metal

surfaces that contain periodic peaks or sharp edges. The electric field strength will be higher at these peaks or sharp edges, and should result in a higher SPR tunability as well as sensitivity. Nanosphere lithography can be used to create one such aforementioned pattern (Jensen). With this method, polystyrene-latex microbeads function as a mask for peak formation; the gaps within a single layer of hexagonally close-packed microbeads will be filled with evaporated metal. The microbeads will subsequently be removed with an organic solvent, leaving patterned peaks behind.

Experimental Section

Substrate Preparation. Coverslips (18x18mm from VWR) and freshly peeled mica were piranha cleaned, then sonicated in a 4:1:1 water, ammonium hydroxide, and hydrogen peroxide solution for 10 minutes. Optical plastic and polystyrene petri dishes (Falcon brand) were cut into squares, rinsed with isopropanol, and air-dried as well.

Microbead Preparation. Microbeads (Polyscience) were centrifuged so that the water in the solution could be removed; the beads were subsequently resuspended in a surfactant solution (1:400 TritonX and Methanol solution).

Peak Formation. The microbeads were spincoated onto the substrate at 1700 rpm for 20 seconds. After spincoating, the samples were placed into a Sharon thermal evaporator and a thin layer of gold or silver was deposited onto the substrate. Chromium was eventually added as an intermediate metal layer to increase the adhesion of the noble metals to the substrate.

Bead liftoff was accomplished using organic solvents (namely dichloromethane). The sample was placed into solution for a few minutes; sonication was occasionally required.

Results and discussion

The experiment initially began with the deposition of 1 micrometer polystyrene beads and a 40 nanometer silver film onto a glass substrate. Bead deposition, though single layered, contained patchy surfaces throughout the slide (Figure 1). Liftoff procedure utilized dichloromethane. As evidenced in Figure 2, the solvent removed the microbeads, as well as the majority of the peaks (remaining peaks are circled in white). The noble metal clearly experiences difficulty in bonding with the substrate.

A series of mica samples were prepared with 1 micrometer polystyrene beads and a 40 nanometer silver film as well. Patchy areas are still prevalent throughout the slide (Figure 3); moreover, the beads on the mica substrate exhibit double layering, an effect which prevents peak formation (Figure 4). For the bead removal procedure, dichloromethane was again used as a solvent. Nothing remained after the liftoff procedure.

Since the metal did not bond well with the substrates, 4 nm of chromium was evaporated as an intermediate layer to help improve the adhesion of the noble metal to the substrate surface.

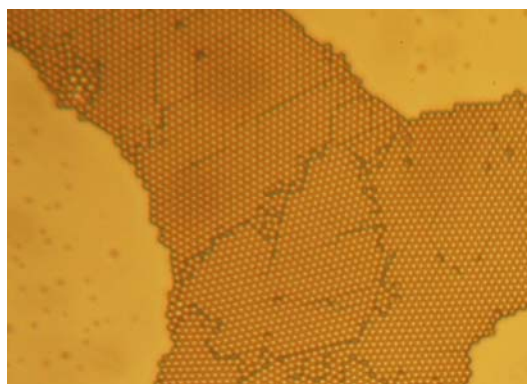


Figure 1. Glass substrate with 1 micrometer beads, 40 nm Ag, pre-liftoff.

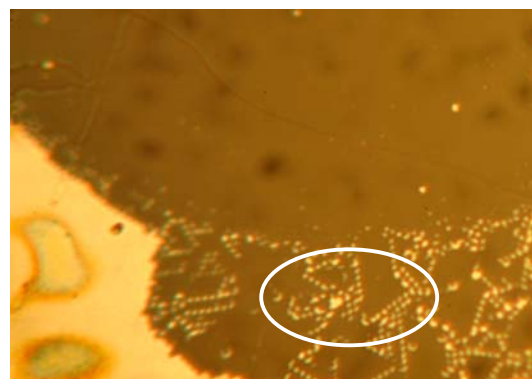


Figure 2. Glass with 1 micrometer beads, 40 nm Ag, post-liftoff. Remaining peaks are encircled in white.



Figure 3. Mica substrate with 1 micrometer beads, 40 nm Ag, pre-liftoff.

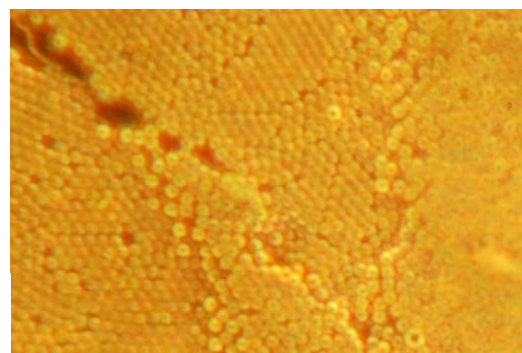


Figure 4. Mica substrate with 1 micrometer beads, 40 nm Ag, pre-liftoff. Double Layering Effect.

The effects of the intermediate chrome layer on the glass substrate are apparent, as evidenced by the post-lift-off image shown in Figure 5. Although some beads still remain from the dichloromethane removal procedure, there is a marked increase in the amount of remaining peaks. The majority of these peaks are randomly distributed; ideally, nanosphere lithography would produce a large array of periodic patterns, which is shown on a small scale in Figure 6.

For mica, the deposition of chromium as an intermediate layer does not improve the adhesion of the metal to the substrate surface. As post-lift-off image shows in Figure 7, the bulk of the beads and peaks have been removed by the dichloromethane despite the additional chromium layer. Clearly, substrate choice is essential in determining the success rate of peak formation.

A polystyrene substrate was tested for peak formation also, since noble metals bonded well to the surface during thermal evaporation (Takei). From Figure 8, it can be seen that the microbead distribution on the substrate is very even throughout the bulk of the sample. Lift-off procedures for this substrate varied from the glass and the mica, since dichloromethane is known to dissolve polymers. Isopropanol was used as a solvent instead, and resulted in some degree of success; however, due to time constraints, no further experiments were conducted on this particular substrate.

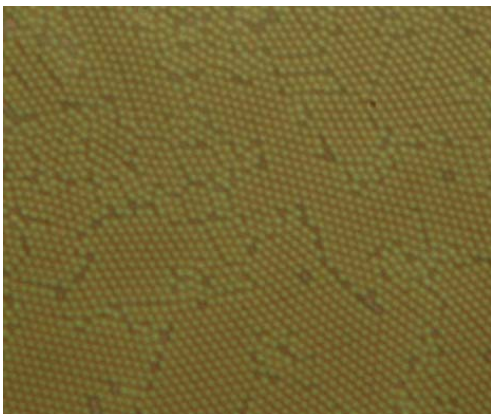


Figure 8. Polystyrene substrate with .75 micrometer beads. ore – evaporation.

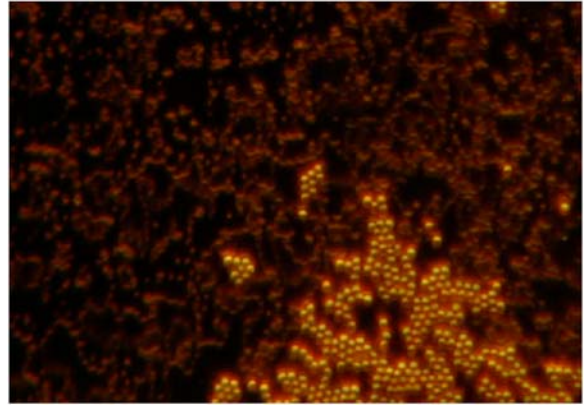


Figure 5. Glass substrate with 1 micrometer beads 40 nm Au, post-lift-off. Remaining peaks can be identified by the dark spots.

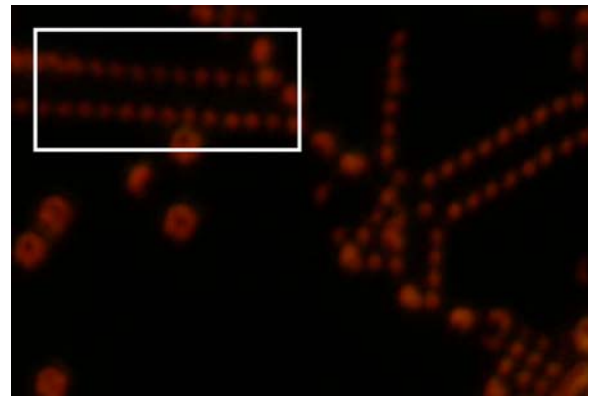


Figure 6. Glass substrate with 1 micrometer beads 40 nm Au, post-lift-off. Periodic peaks are highlighted.

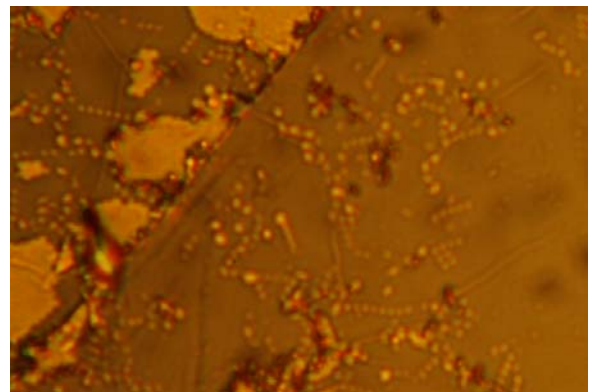


Figure 7. Glass substrate with 1 micrometer beads 40 nm Au, post-lift-off.

While the nanosphere patterning has been successful to some extent, there still remain some challenges, specifically in obtaining a uniform bead distribution during spincoating and periodic peak formation from the liftoff procedure. Consequently, this experiment explored other methods of patterning.

One such endeavor involved the use of a chloroform, Formvar, and water emulsion solution to create a perforated film on a glass substrate. The perforated film functioned as a mask during thermal evaporation and was dissolved thereafter so that only metal peaks remained. Figure 9 shows an image of the sample after thermal evaporation and film removal. Although the peaks appear in high density throughout the sample, their distribution is still largely random.

Because a highly regular pattern is desirable, this experiment diverged once again and began to investigate the capabilities of mainstream nanofabrication methods such as electron beam lithography. For this method, a pattern of peaks was not used; rather, the design consisted of a 50x50 array of deformed hexagons with sharp corners on either end (Figure 10). The actual e-beam written pattern can be seen in Figure 11, and is comparable to the computer-generated pattern. As Figure 12 also shows, there is high regularity in the pattern even after the metal deposition and developing procedures.

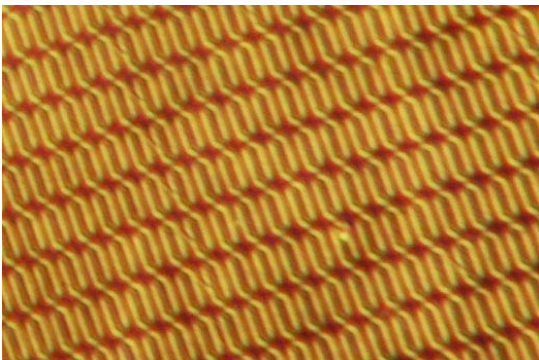


Figure 12. E-beam written pattern after gold evaporation, developing, and acetone rinse.

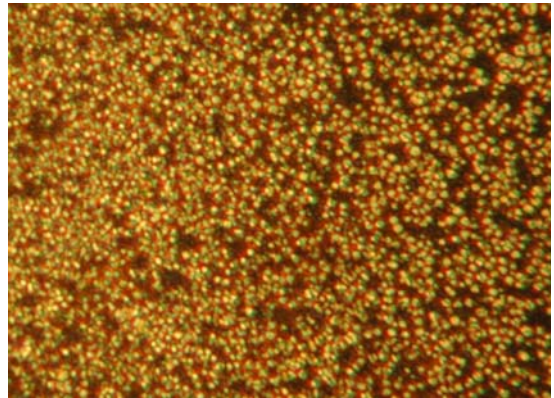


Figure 9. Formvar film method after thermal evaporation of 40nm Au and film liftoff.

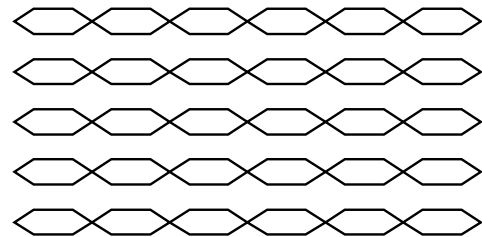


Figure 10. Sample computer designed pattern for electron beam lithography. Dimensions for 1 hexagon: 3.5x1 micron.



Figure 11. E-beam written sample, 20x magnification

Substrate Testing

Once the patterned surfaces were fabricated, they were tested for surface plasmon resonance. One setup that was used for testing contained a light source [He-Ne Laser, 633 nm], a polarizer that oriented light to a p-polarization, a prism mounted on a rotating stage, and the sample itself (to be attached to one face of the prism with index matching oil).

With nanosphere lithography, only the glass and polystyrene substrates were successful in producing a patterned surface containing peaks. When tested for SPR, the glass substrate demonstrated a very slight and broad resonance; this could be attributed to the lack of periodicity in the film pattern. The polystyrene substrate exhibited a broad resonance as well. However, this could also be attributed to the difference in the indices of refraction between glass and polystyrene, which are approximately 1.51 and 1.55, respectively.

The e-beam written sample was tested for resonance using a slightly different configuration. This setup required the use of a fluorescence microscope, fluorophores, a light source [He-Ne Laser, 633 nm], a polarizer, prism, and the sample itself (which was again attached to one face of the prism with index matching oil). The idea is that when surface plasmon resonance occurs, the fluorophores that have been deposited on the patterned surface will broadcast the enhancement of the surface plasmon resonances around the sharp corners within the pattern.

Conclusions

Nanosphere lithography is capable of generating nano-patterned metal surfaces for the purpose of surface plasmon resonance testing. A number of different substrates were tested with this method, and the quality of the patterned peak formation was dependant on substrate choice. Glass

displayed the best performance, followed by the polystyrene substrate.

Although there were initial challenges with bead distribution, metal-substrate bonding, and bead liftoff, this experiment has successfully achieved uniform bead distribution and metal-substrate bonding; bead liftoff procedures, though met with some success, remains unpredictable and still must be refined.

This research explored other successful methods for small-scale pattern generation as well. The use of a Formvar-water emulsion produces excellent perforated films that can be used as a mask for metal evaporation. Electron beam lithography is also another effective means for creating patterned metal surfaces; though time consuming, this alternative method creates remarkably precise and periodic patterns.

The ability to create nanoscale patterned metal surfaces for use in surface plasmon resonance is significant in that it could result in a higher SPR tunability and local electromagnetic field enhancement. Although such developments could potentially lead to superior biosensing capabilities, further research must still be conducted before such applications can be realized.

Acknowledgements

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