Plasmonic structures fabricated via nanomasking sub-10 nm lithography technique

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ABSTRACT

Making use of a newly established nanomasking technique, nanoscale features (sub-10 nm) have been fabricated with the potential to act as plasmonic enhancement structures. The technique makes use of a two-step lithography process to simultaneously produce many plasmonic hotspots with two-dimensional features over a large area, showing promise for mass production scalability. This technique is highly reproducible, reliably patterning multiple nanostructures and nanogaps over a potentially wafer-scale area without significantly increasing the number of steps required. Fabrication results show promise for scalability towards applications such as biosensing, photovoltaics, and enhanced spectroscopies.

Keywords: Plasmon, nanogap, sub-10nm, nanofabrication, scalable nano, electron beam lithography (EBL), Plasmonic enhancement

1. INTRODUCTION

Nanoscale fabrication is one area of research at the forefront of human technological innovation. Advances in self-assembling chemical processes, accelerating ions and particles, and deposition and etch techniques have enabled control over matter to reach down to the nanoscale, creating structures smaller than the wavelength of most ultraviolet light. These advances will help to enable new and exciting technologies that take advantage of things such as increases in surface area at the nanoscale, high density arrays of structures, and even sub-10 nm features or gaps between structures.

One such technology that makes use of the interaction of sub-wavelength features and light is the field of plasmonics. Plasmons are the collective oscillations of electrons on the surface of a metallic structure caused by the interaction between the charges and electric fields. These charge oscillations are thus caused when light is incident onto the surface of a metallic nanoparticle or a metal surface. By creating objects smaller than the wavelength of the incident light, which is typically in the visible range for many applications, light can be enhanced, focused, bent, and guided due to plasmonic effects. Sub-100 nm fabrication has allowed for the creation of various types of structures that have displayed plasmonic enhancement effects, increasing the field strength relative to the incident radiation.[1–5] Nanogaps between plasmonically active structures have been shown to increase the level of enhancement.[6–11] Prior work has shown that decreasing the width of these gaps to the 10 nm range and below causes a nearly exponential increase in the enhancement of light within the gaps relative to the incident light.[7(p-10),12–15]

Thus, to take advantage of plasmonic gaps for light enhancement, it is necessary to be able to fabricate sub-10 nm gaps between structures. The nanomasking technique is an advanced fabrication method that takes advantage of a unique lithography and deposition process to create sub-10 nm gaps adjacent to metallic nanostructures to produce plasmonic or other devices.[16–18] Preliminary results of this technique have demonstrated its ability to simultaneously fabricate sub-10 nm gaps with a density of over 500 million gaps per square cm.[17,18] Nanomasking has also been used to simultaneously create gaps in two dimensions, which is not possible with some existing gap-making methods such as electromigration,[19–23] mechanical break junctions,[24] or even ion beam lithography.[12,25–28] These techniques must create gaps serially, while the advanced technique described here creates many gaps in parallel. An additional benefit of nanomasking is that is has been shown to be capable of simultaneously fabricating *both* sub-10 nm gaps *and* adjacent

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sub-20 nm metallic structures.[17] This will allow future technology such as biosensing,[29–32] photovoltaics,[33–39] and enhanced spectroscopies[1,19,20,40,41] to make use of benefits from both nanoscale features and the gaps between them on the same scale. The geometrical control of this technique has been demonstrated as well, in that gaps can be created adjacent to structures of various shapes and sizes.

2. NANOMASKING FABRICATION

Bauman et al. have described the process in full detail for the creation of gaps and adjacent nanostructures.[17,18] Here we will briefly summarize the process, which begins with a lithography step to create the first geometrical patterns. A metal deposition fills these geometries, with the top layer being crucially a layer of Cr. The Cr layer expands upon oxidation either in a controlled environment or in ambient conditions, allowing the overhanging Cr_xO_y to act as a shadow mask during a second lithography and deposition step. The Cr mask will cause gaps between the primary and secondary structures, on the order of 10 nm in width. This width can be controlled, as demonstrated by Fursina et al., by controlling the Cr oxidation stage.[42] Etching away the Cr layer, the result is a sample containing the desired geometries overlapping one another, separated by nanogaps.

Figure 1 shows a three-dimensional sketch of the nanomasking process for clarification, demonstrated for circular patterns. As the metal used during deposition is not confined to Au, they are shown in different colors and referred to as metal one and metal two here. Figure 1(a) shows the top Cr layer having already oxidized. Thus, it is shown to have expanded over the edge of the first metal layer (colored gold). In Figure 1(b), the second lithography step has been performed, overlapping a second, larger circle with the primary pattern, and the second metal deposition has been performed. The second metal is shown in silver/white. Figure 1(c) displays the final result upon etching the Cr layer. The primary metal circle is separated from the secondary ring by a gap, a result of the Cr_xO_y deposition mask. What is unique in the nanomasking technique is that a sub-lithography limited metal nanostructure is created in addition to the nanogaps. This nanostructure is the outer ring in this case.

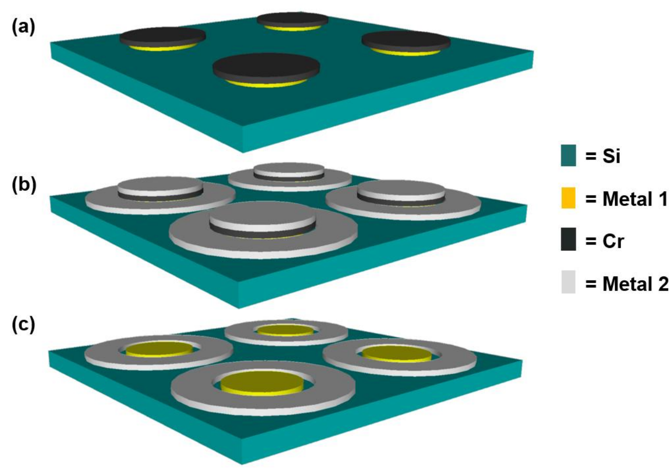

Figure 1. 3D sketch of the nanomasking technique for circular patterns. (a) Metal 1 and Cr shown to have been deposited after lithography step 1. Cr_xO_y overhangs the edge of the metal 1 disks. (b) Metal 2 shown to have been deposited, overlapping the primary structures, after lithography step 2. (c) The result after etching the Cr. Disks of metal 1 separated from rings of metal 2 by a gap.

The lithography patterns used in Figure 1 are both circles with diameters that are limited by the lithography step used. However the result is a ring with a width that is below limit of lithography. This technique has been shown for other geometries and combinations of shapes and sizes as well.[17] There are many potential devices that have not yet been created as well. Trying different combinations of parameters such as the materials used, the heights of the primary and secondary materials, and other variations are planned fabrications for future work. Some interesting results of varying the overlap of the primary and secondary patterns are shown in the Sections 2.1 and 2.2.

2.1 Sub-Lithography Limited Nanostructures

The ability of the nanomasking process to fabricate nanogaps has been demonstrated as a proof of concept for the possible large scale integration of the technique. This work also demonstrated the simultaneous fabrication of nanogaps *and* adjacent nanostructures that are *both* below the lithography resolution limit. This has been described for patterns aligned on the same center point as with the circle patterns shown in Figure 1. Varying the overlap of the two patterns, however, has the effect of changing the width of the resulting metal 2 adjacent sub-lithography limited structure.

Figure 2 shows colorized SEM images of the result of varying the overlap between a square primary pattern and a rectangular secondary pattern. Both metal 1 and metal 2 were Au in this case. One larger rectangular and one square pattern with different amounts of overlap are shown in Figure 2(a). The higher magnification image (b) shows one case in which the square pattern and rectangular pattern were overlapped so that structures formed adjacent to the gap; below the square, a 30 nm metal nanostructure was formed with features below the typical lithography limit of the EBL system used in this work (approximately 60 nm).

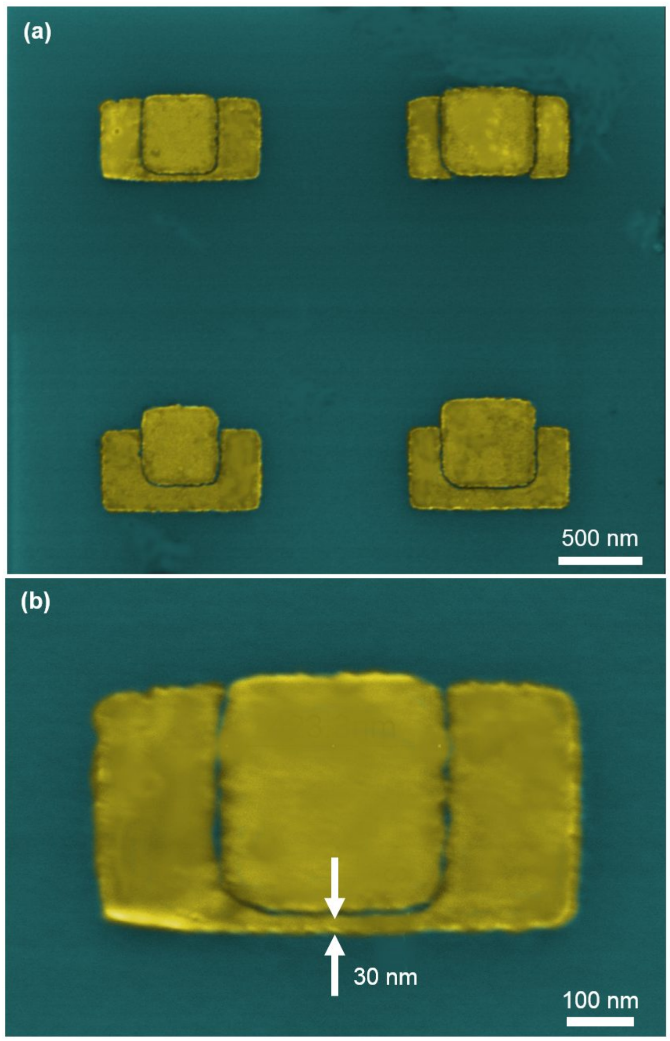

Figure 2. Colorized SEM images of the results of nanomasking fabrication for a square pattern overlapping a rectangular pattern where metal 1 and 2 were both Au. (a) The overlap between the two patterns was changed, as well as the size of the square pattern. (b) Higher magnification image showing the resulting nanostructure width.

This type of overlap variation demonstrates the control of the technique over the creation of nanostructures adjacent to nanogaps. The width of the structures, demonstrated down to sub-20 nm,[17] can be varied to optimize the devices for plasmonic resonance or other applications.

2.2 Removal of Lithography Step

The versatility of this advanced fabrication method has been demonstrated and relies on the fact that it uses lithography to create the overlapping geometries. For specific geometries, however, it is possible to obtain nanogaps adjacent to structures without need for the secondary lithography step in the process. Take a checker type pattern for instance, as shown in Figure 3. A process flow comparison between the two-lithography typical nanomasking process and a process with only the first lithography step is shown in Figure 3(a) and (b). In Figure 3(a), there are two lithography patterns that must be overlapped with one another, with a deposition step after each lithography process. The final result is a checker pattern of metal 1, with metal 2 filling in everywhere else on the substrate except for the nanogaps. This can be seen from above in Figure 3(a) and (b) as well as three-dimensionally and from the side in (c). This type of pattern was fabricated using the two-pattern process as shown in (a), but with a large overlapping cross for the second pattern. The result, shown in Figure 3(d), matched that of the result shown in the sketches. There were gaps present between metal 1 and 2 everywhere that they overlapped, but not anywhere else. Metals 1 and 2 were again Au.

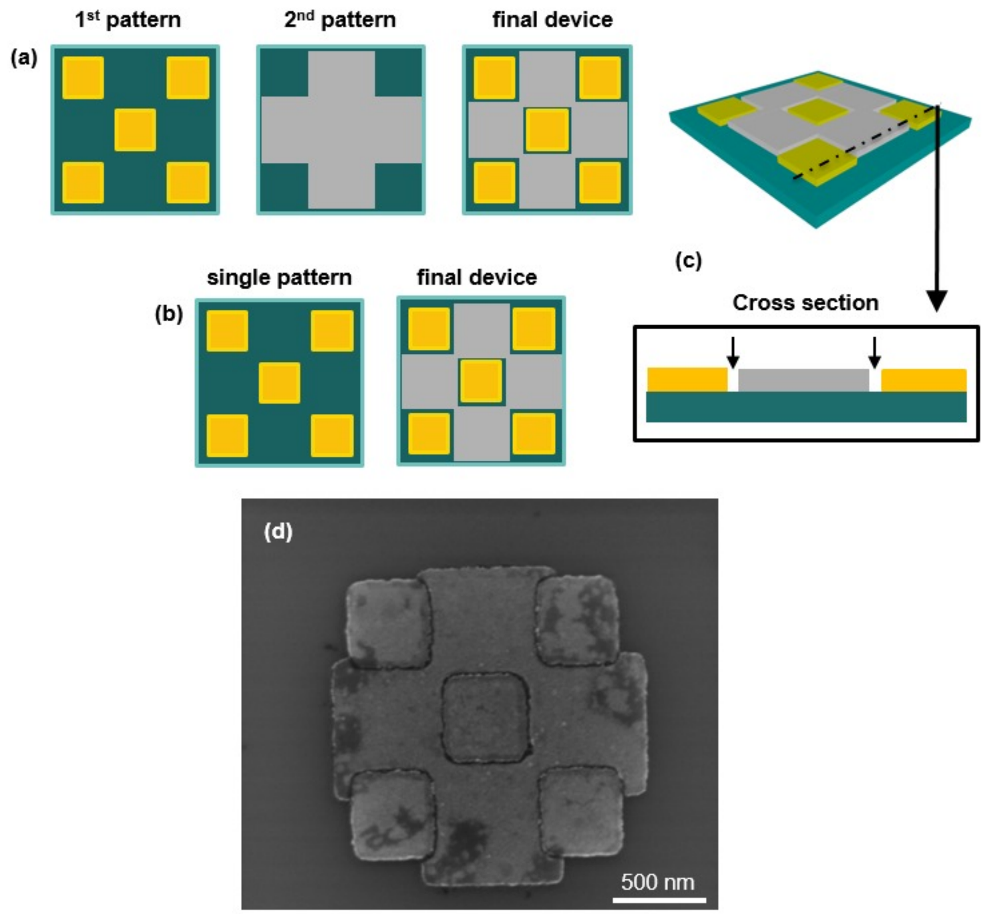

Figure 3. Nanomasking demonstrating the removal of a lithography step. (a) Top views of the first and second lithography patterns and the final result when the two are overlapped. (b) Top views of the first lithography pattern and final device when the second lithography step is removed. (c) 3D sketch and cross sectional view of the final device. (d) SEM image of the result when using the two lithography patterns shown in (a).

In Figure 3(d), the center represents a pattern that has essentially had the second lithography step skipped, as metal 2 was deposited completely over the top of this square, resulting in nanogaps on all sides. This was a successful proof of concept of the capability of creating nanogaps without the need for a secondary lithography process. The result of a larger area deposition over multiple primary structures was carried out and is detailed in Section 3.

3. BLANKET NANOMASKING

The nanomasking technique was used in the creation of an array of parallel nanowires with different widths separated by nanogaps. This was performed using a specific case of the nanomasking process referred to as blanket nanomasking. The process begins, again, with patterning a desired geometry using lithography. This was electron beam lithography in the case of the work presented here, but photolithography could be used as well for larger structures and rapid patterning. The desired metal and Cr layer are then deposited, and the Cr allowed to oxidize (under ambient conditions in this work).

Figure 4 shows the process from this point forward. Figure 4(a) shows parallel Au nanowires with an oxidized Cr layer overhanging the edge of the Au. From here, a second deposition of Au is all that is needed in order to produce more parallel nanowires, separated from the primary structures by nanogaps on both sides (Figure 4(b) and (c)). The deposition covers the entire sample area, and the Cr mask is still able to produce nanogaps adjacent to the wires. Figure 4(d) shows SEM images of the results of this type of fabrication process. The width of the primary and secondary nanowires could be controlled in a design such as this to optimize the plasmonic response to specific wavelengths of incident light.[43]

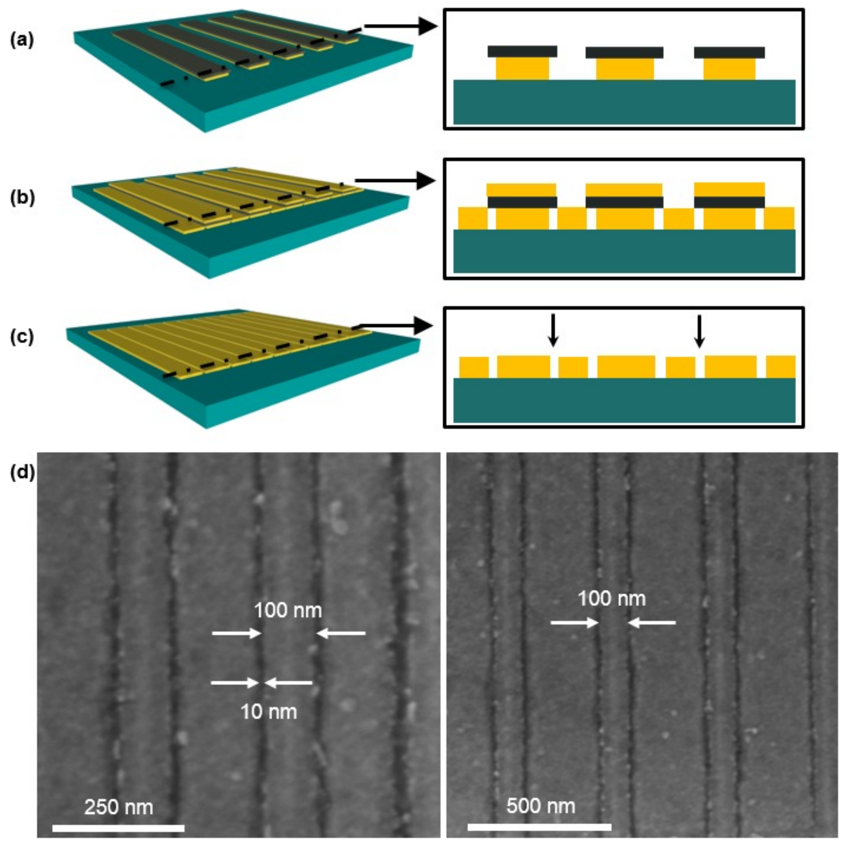

Figure 4. Blanket nanomasking of parallel nanowires. 3D sketches and cross-sectional views of (a) the result after the first lithography process, metal deposition (gold and gray), and Cr layer oxidation (gray), (b) the secondary metal deposition step, and (c) the resulting parallel nanowires separated by nanogaps. (d) SEM images of the resulting Au nanowires.

Thus, blanket nanomasking has been shown to be capable of patterning nanogap structures over a large area without the need for a secondary lithography step. The geometrical design possibilities are limited compared to the standard nanomasking process, but blanket deposition over a sample containing nanostructures may prove useful for mass production of devices.

4. CONCLUSIONS

A nanomasking fabrication was demonstrated to be capable of simultaneous fabrication of *both* nanogaps *and* nanostructures, where the width of the structures can be controlled by the degree of overlap of the two lithography patterns used in the process, and the sizes of the nanogaps *and* the nanostructures both can get below the lithography limits. The degree of overlap can be thought of as the second pattern just covering the entire sample in the case of blanket nanomasking. This has been conceptually proven to allow for the removal of the secondary lithography step from the process while still creating nanogaps adjacent to multiple structures on a substrate surface. This is another aspect of the method that makes it appear promising for mass production level fabrication. These advancements and others will continue to make this fabrication technique exciting for the development of plasmonic devices and other nanotechnology.

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