Galvanic Deposition of Gold on GaAs: A Tip-Induced Lithography Approach

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A lithography technique based on reduction of metal ions on localized regions of GaAs surfaces is demonstrated. In this technique, an atomic force microscopy (AFM) tip was used to create localized defect patterns on a GaAs surface while operated in air. Subsequent exposure of the semiconductor surface to an Au(III) solution results in the deposition of gold by galvanic displacement reaction on pre-patterned defect areas. Random formation of gold islands outside of the pattern is eliminated by restricting the contact time between the Au(III) solution and GaAs semiconductor to approximately 5 minutes.

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Deposition of metals on semiconductors is practically important because of their potential applications in optoelectronics, nanoelectronics, biochemical and chemical sensors.1–3 Metal structures on semiconductor surfaces have been produced using techniques such as photolithography,7 electron beam lithography,7,8 micro-contact printing,9,10 nanoinprint lithography,11,12 soft lithographic nanopatterning.33 Scanning probe-based lithography techniques such as superlattice nanowire pattern transfer,14 dip pen15 and static/dynamic plow lithography16–20 have been demonstrated as useful approaches in the fabrication of metal structures on various surfaces.

The metallization of semiconductor surfaces via the galvanic displacement reaction has been intensively investigated.2,23–25 Galvanic displacement deposition is a relatively simple redox reaction in which noble metal ions in solutions are reduced by the substrate resulting in growth of metal deposits with various surface morphologies. The surface morphology of electroless deposited metals depends on the substrate, composition of the electrolyte, including pH and conditions of deposition eg. temperature, stirring etc.24,25 Metallization of semiconductors via galvanic displacement leads to the deposition of metal over the entire surface. Therefore, masking of the surface of semiconductors with specific polymers is required in order to fabricate desired metallic patterns. Use of polymer masks to restrict reduction of gold on a specific area has been applied in most of static/dynamic plow lithography techniques.16–19

In this work a simple three step process for a deposition of 50 nm wide and 10 nm high gold nanowires on GaAs semiconductor is described. This technique may allow the direct deposition of noble metals such as Au, Ag, or similar on GaAs semiconductor surface.

Experimental

Commercially available n-type GaAs (100) semiconductor wafers (Wafer world Inc, Florida) cut into 1 cm² pieces were used as substrates in the present experiments. In order to confirm the deposition of gold onto GaAs via the galvanic displacement reaction, the substrates were cleaned with ethanol and then simply immersed into 5 mM gold chloride trihydrate (HAuCl₄·3H₂O) solution for one hour. All experiments were performed at room temperature (about 22 ºC). After one hour of immersion, GaAs wafers were removed from the Au-containing solution, carefully washed with distilled water and then with ethanol. The substrates were stored under ethanol for the future scanning electron microscopy (SEM) and X-ray diffraction (XRD) examinations.

For the tip-induced lithography on GaAs semiconductor, the following experiments were performed. The substrates were first cleaned with deionized water and sonicated in 95% ethanol solution for 2 minutes to remove the contaminations. The substrates were then dried by blowing N₂ gas and subjected to the three step lithography process. 0.01% Br₂ dissolved in CH₃OH (BrMeOH) solution was used to clean the GaAs substrate prior to gold deposition.

Commercially available diamond coated AFM-tip (DT-NCHR, Nanoworld) with radii of curvature 100 nm and spring constant 60 N/m was used for indenting into the GaAs substrate with a known applied force. Nanoman software (Bruker nano Inc.) was used for fabricating patterns on the substrate. The patterned surface was then taken out of the AFM and a drop (50 µL) of 100 µM HAuCl₄·3H₂O solution was placed at the region of indented lines for 5 minutes. The whole process of the lithography technique is schematically presented in Figure 1, according to the described steps. After the deposition of gold was observed (approximately 5 minutes), the substrate was rinsed first with distilled water, then with 95% ethanol and finally dried with N₂ gas. The imaging of the metal patterns is performed using OTESPA (Bruker nano Inc.) tips with radii of curvature of 7 nm in the scanasyst mode. The images are analyzed using the SPM software gwyddion (v 2.3).

Results and Discussion

Deposition of gold onto GaAs semiconductor.— Upon immersion of GaAs substrate in Au(III) containing solutions, the deposition of gold was visually observed about 40 minutes after the wafers were placed into solution. The SEM images of gold deposited on GaAs substrates are shown in Figure 2. As can be seen from Figure 2, the GaAs substrates are relatively well covered with gold. Some spots, as

![Figure 1. Steps involved in the lithography process (a) BrMeOH etching, (b) Indentations into GaAs using diamond tip, (c) Incubation with 100 µM HAuCl₄ solution for 5 minutes (d) Finally produced pattern of deposited gold.](image)
seen from Figure 2 suggest the presence of pores in the Au deposit, as reported by others.21–23 For similar systems, the shape of gold particles deposited on GaAs are similar to those reported for the case of Ge semiconductor substrates.21 The size of the largest gold particles is estimated at about 400 nm. The thickness of gold deposited onto GaAs substrate is estimated according to SEM to be about 500 nm. The XRD pattern of the deposited gold on GaAs substrates is given in Figure 3. As can be seen from the pattern in Figure 3, only Au peaks are identified, confirming the visual observation of the deposition of gold.

In the galvanic displacement reactions, the reduction of ions of a more noble metal is achieved by the less noble metal (substrate) leading in this way to the deposition of the more noble metal. These systems are well studied for the case of metals e.g. Au/Cu, Cu/Al, Cu/Fe etc.25,26 Similar behavior was observed with the semiconductor substrates.16,21–24 When the semiconductors are used as substrates they may then act as the reducing agents of the ions of noble metals such as Ag, Au or similar. Deposition of gold on GaAs surface is a consequence of the galvanic displacement reaction which can be presented as follows:

\[
2\text{GaAs} + 2\text{AuCl}_4^- + 10\text{H}_2\text{O} \rightarrow \text{Au} + 2\text{H}_2\text{AsO}_4^- + 2\text{Ga(OH)}_2^+ + 6\text{H}^+ + 8\text{Cl}^- + 3\text{H}_2
\]

with \(\Delta G^\circ = -441.6704 \text{kJ/mol}\).

Another possible reaction describing the deposition of gold on GaAs can be written as:

\[
2\text{GaAs} + 2\text{AuCl}_4^- + 8\text{H}_2\text{O} \rightarrow \text{Au} + 2\text{H}_2\text{AsO}_4^- + 2\text{GaOH}_2^+ + 4\text{H}^+ + 8\text{Cl}^- + 3\text{H}_2
\]

with \(\Delta G^\circ = -481.2264 \text{kJ/mol}\).

Both reactions 1 and 2 predict the oxidation of As\(^{3-}\) to As\(^{5+}\) while Au\(^{3+}\) is reduced to Au\(^{0}\). As well, both reactions are thermodynamically possible, since \(\Delta G^\circ < 0\) and they include the hydrogen evolution. Some very small gas bubbles at the surface of GaAs wafers were noticed upon their immersion into Au(III) solutions. On the other hand it is obvious that both reactions as well predict acidification which was experimentally confirmed. In the present work a decrease in pH of the Au (III) containing solution from 5 to about 3 was observed. Considering the fact that the presence of GaOH\(^{3+}\) at this pH is more likely it can be postulated that the reaction 2 describes the deposition of gold on GaAs under the experimental conditions of the present work more realistically.

As reported above, the deposition of gold on GaAs was observed approximately 40 minutes after its immersion into Au(III) containing solution. Although the galvanic deposition on metallic substrates under room temperature conditions and from properly chosen electrolytes appears almost immediately, a delay in gold deposition as observed in the present work is a consequence of the presence of an oxide film at the surface of GaAs wafer. It is reasonable to state that the oxidation of the surface of GaAs takes place as soon as it is in contact with air.

The XRD pattern of the GaAs substrate (as received) is shown in Figure 4. Peaks at 2\(\theta\) 53° and 55° are from GaAs planes (400) and (311) respectively. Convoluted broad peak at 2\(\theta\) 31° is from base centered monoclinic Ga\(_2\)O\(_3\) (002) and (202) planes. In this way, based on the results presented in Figure 4, Ga\(_2\)O\(_3\) was detected at the surface of GaAs wafers. In order to achieve the deposition of gold on GaAs wafers it is necessary that the oxide film present at its surface must be dissolved. The thickness of Ga\(_2\)O\(_3\) was not measured in the present work. Based on the qualitative observations the dissolution of oxide film is a time dependent process, since the deposition of gold was observed approximately 40 minutes upon the immersion of GaAs into Au(III)-containing solution. In addition, the deposition of gold was observed only on polished side of the GaAs substrate and not on the back (unpolished) side, even after 120 minutes upon immersion. Considering the higher surface roughness of the back side of the GaAs wafer the observations suggest the presence of a thicker oxide layer at the surface.

![Figure 2. SEM images of gold deposited on the surface of GaAs (Magnifications: 10.8 kX left and 27.1 kX right).](image)

![Figure 3. XRD pattern of gold deposited on GaAs.](image)

![Figure 4. XRD pattern of “as received” GaAs.](image)
Tip-induced lithography on GaAs semiconductor.— The root mean square roughness of the polished side of the bare GaAs semiconductor surface was found to be around 0.3 nm. An arbitrary scratched pattern on GaAs wafers composed of squares and a circle in the middle, as shown in Figure 5 with white color, was exposed to Au(III) ions containing solution. Figure 5 shows a collection of AFM topography images formed at different indentation force. The defects in these images were made at a speed of 0.5 μm/sec with the diamond coated tip having a spring constant of 60 N/m and radii of curvature of 100 nm. It is interesting to observe that Au(III) ions were reduced preferentially only at the scratched patterns created by the diamond coated tip and not at any other place on the substrate. This observation strongly suggests that the scratching with the diamond coated tip removes the Ga2O3 oxide film formed at the GaAs surface. Obviously, gold was preferentially deposited onto scratched areas. However, some white dots are as well visible in the images presented in Figure 5, suggesting that the Ga2O3 oxide film was dissolved chemically (within the time frame of this experiment, 5 minutes), allowing the reduction of Au(III) ions and a consequent deposition of gold. At low indentation forces, the gold nanowires formed are very uniform and continuous on the defect patterns. The geometry of the AFM tip plays an important role in creating uniform patterns at a given force and its effect is clearly evident at higher indentation forces. The diamond shaped patterns are about 10 μm in dimension and spaced at certain distances from each other. It should be noted that the patterns were imaged individually and then combined together for high resolution and clarity.

The use of high tip force also results in a removal of the oxide film from the surface that is larger than the tip contact area resulting in an increased width of nanowires. Figure 6 shows a dependence of the width and height of the metallic nanowire structures on indentation force. An application of higher tip forces can result in the formation of larger structures as shown in Figure 6.

At lower indentation force from 0.2 μN to 0.75 μN the width of the nanowires is ranging from 50–60 nm while its height is around 10–12 nm. However, at higher indentation force (>1.9 μN) the width of the nanowire increases up to 80 nm, while its height is almost constant (around 6–7 nm). This shows that higher indentation force creates more nucleation sites for the gold ions to reduce laterally than compared in the vertical direction. Also, it is reasonable to expect that the larger indentation forces remove the Ga2O3 film more efficiently, leading to an increase in the width of the deposited nanowires. Figure 6 also confirms the importance the applied indentation force in creating such pre-patterned defects on the GaAs substrate where Au(III) preferentially reduces Au+.

This lithography technique is based on the galvanic displacement deposition of gold form solution preferentially on area where surface oxide i.e. Ga2O3 is removed and by controlling the contact time with the Au(III) containing solution. This was successfully achieved in the present work by mechanically pre-patterned area. A mechanical treatment of the GaAs wafers with the diamond coated AFM-tip, as described in the Experimental section leads to a significantly faster deposition of gold at the patterned area. As found, the deposition of gold on GaAs appeared after 5 minutes upon Au(III) solution was applied on the patterns. This further strongly suggests that the native oxide film at the surface of the GaAs wafer was successfully removed by the mechanical treatment. Consequently, by limiting the time of exposure of GaAs surface to the Au(III) containing solution it is possible to restrict the galvanic displacement reaction to scratched sites preferentially. Since the galvanic deposition of gold on a non-scratched area proceeds with much slower rate, random formation of nanoparticles is significantly suppressed, within the time frame of the AFM-related experiments. For a full implementation of this method in the practice, perhaps the nature of the oxide film and the surface morphology must be investigated in details.

This lithography technique may have many advantages over other scanning probe based lithography techniques. The described technique is rapid, versatile simple and it can be performed at ambient temperature, without using masks or extensive chemical modifications of the semiconductor substrate. Metallic nanostructures can be fabricated directly on the semiconductor substrate such as GaAs and does not involve steps like lift off or photo-etching of any surface bound chemical agents which may further modify surface chemistry at the nanoscale levels. Finally, this technique offers control of the width and the height of the fabricated features by controlling force used to mechanically remove the oxide film and time of exposure to solution. The limitation of the described technique is the use of proper fabricated diamond coated tips with known specifications and geometry to indent into the GaAs surface. All the tips used in the present experiments are calibrated for its sensitivity and spring constant prior to indenting the surface.

Figure 5. Collage of AFM topography images of diamond shaped Au metallic structures with indentation force of 0.2 μN (left), 1.1 μN (middle) and 5.7 μN (right).

![Figure 5](image-url)

Figure 6. Dependence of the full width at half maximum (FWHM) and height of the metallic nanowire structures on indentation force.

![Figure 6](image-url)
Figure 7. AES spectra of the bare GaAs wafer (black) and Au nanowire (gray). The star and the triangular symbols shown in the SEM image correspond to the locations for bare GaAs and Au nanowire where the spectrum is collected.

The galvanic displacement reaction of gold ions on GaAs surface is thermodynamically favorable, as soon as the surface oxide film is removed. Hence, indenting the surface of GaAs results in the physical removal of the surface oxide film. This surface oxide film is relatively softer compared to the rigid diamond probe.

In order to confirm the presence of gold on the scratched pattern, AES electron spectroscopy (AES) and imaging were used to identify the elements. Figure 7 shows Auger elemental analysis on a lithographic structure. AES spectra of the bare GaAs wafer (black) and Au nanowire (gray) given in Figure 7 clearly show the presence of Ga and As (black spectrum) and Au (gray spectrum). The “star” and “triangle” symbols shown in the SEM image in Figure 7 correspond to the locations for bare GaAs and Au nanowire, respectively, where the spectrum is collected. On the region marked by the star, only peaks corresponding to Ga and As were detected while on the region marked with the triangle, peaks corresponding to Au appeared to be dominant. These results indicate that the nanowires are composed of gold. The experimental observation suggest that the approach described in the present work should further be explored not only onto GaAs, but, as well, on other semiconductors, i.e. Si, Ge etc.

Conclusions

Deposition of gold on GaAs substrates proceeds via the displacement galvanic reaction. Using this relatively simple process, the gold nanowires were produced by exposing the scratched surface of the GaAs with the diamond coated AFM-tip to Au(III) solution. It was clearly shown that the gold nanowires formed at the sites were the surface oxide was mechanically removed are the consequence of the galvanic displacement reaction between Au(III) ions in solution and GaAs wafer. The height and width of the nanowire structures depend on the applied tip force. The width and the height of the formed nanowires are 50 nm and 10 nm respectively. The advantages of the presented method include simplicity and speed. The applications may include sensors, catalysts and electronics packaging.

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