Thickness-controlled Metal Nanoscale Etch for Proposed Metal Nanowires Fabrication

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ABSTRACT

A novel nanoscale etch process of metallic structures, the metal peel-off method(MPOM), is developed. The etching area can be defined photolithographically on the exposed substrate. Utilizing galvanic displacement as well as selective etching process after photolithographic process, we simply and uniformly achieve self-controlled etch rate of 32.2±2.1nm/times through whole wafer level. MPOM provides a high throughput and low temperature etching process which is compatible with conventional semiconductor process. We also propose a novel top-down fabrication process, from the MPOM to the metal peel-off lithography(MPOL) for the patterning and formation of metal nanowires.

Keywords: nems, nanoscale etch, metal nanowires, galvanic displacement, selective wet etching

1 INTRODUCTION

Recently, the need of nanoscale metallic structures has imposed increasingly widespread preparation of metallic features with reduced dimensions. Higher-order architectures and devices for technologically relevant applications such as arrayed nanosensor, nanogap devices for molecular electronics, highly dense nanowires for ultra-large-scale integration(ULSI) interconnects, and NEMS devices can be achieved using the efficient patterning and utilization of these structures[1-3]. In order to obtain these nanoscale metallic devices, etch-related issues such as precise controllability of the geometry, etching depth, aspect ratio, and surface morphology have to be resolved. In addition, each application will require complicated and unparalleled precision without sacrificing throughput or cost effectiveness[4]. Current metal etch technology using reactive ion etching does not have precise etch rate controllability and selectivity between the materials. In the case of conventional chemical wet etching, the selectivity of the etching materials has been provided accurately. But still the etch profile is isotropic and may lead to the non-uniformity in etch rate of local position. This, in turn, leads to poor control of feature size under micrometer scale. Therefore, to achieve these two goals at the same time for nanoscale devices, neutral beam and focused ion beam etching have been investigated by many researchers[5-6]. However, these process equipments are expensive and take much time to fabricate the nanoscale devices.

From this perspective, we have proposed a metal peel-off method(MPOM) for simple and uniform patterning and etching of 3 dimensional metallic nanostructures. We also suggest an idea of metal peel-off lithography(MPOL) as one of the MPOM applications for metal nanowire fabrication.

2 EXPERIMENTAL METHODS AND MATERIALS

MPOM consists of photolithography, galvanic displacement and selective etching process. As explain below, MPOM is accomplished in four fundamental operations[7]:

(1) deposition of metal film onto a substrate,
(2) application of patterned polymer resist onto metal film,
(3) immersion of the substrate into an electroless plating solution(diluted metal salt), where REDOX process makes displacement of each metal[8],
(4) final selective peel-off or removal of displaced metal through metal etchant.

Figure 1 illustrates schematic process of MPOM for generating a metal nanoscale structure. The substrate material used in this experiment was p-type Si(100) wafer.(Fig. 1(a)) As shown in Fig. 1(b), Ti(200Å) and Ni(2000Å) metal layers were deposited by thermal evaporator onto Si substrate. Ti layer was operated as an adhesive layer. We used Ni layer, because of its high ionization tendency which makes REDOX process easy and conventional utility in semiconductor process. After metal deposition, AZ6612K photoresist was patterned by MA6 aligner to conceal Ni layer.(Fig. 1(c)) We can easily and precisely define the etching area and position by lithographical methods on the substrate. In other words, the lithographical resolution constrains the lateral etching accuracy. Subsequently, an immersion of the substrate into electroless plating solution which contained dilute Au metal salt($KAu(CN)_2$(aqua)) made the exposed Ni atom

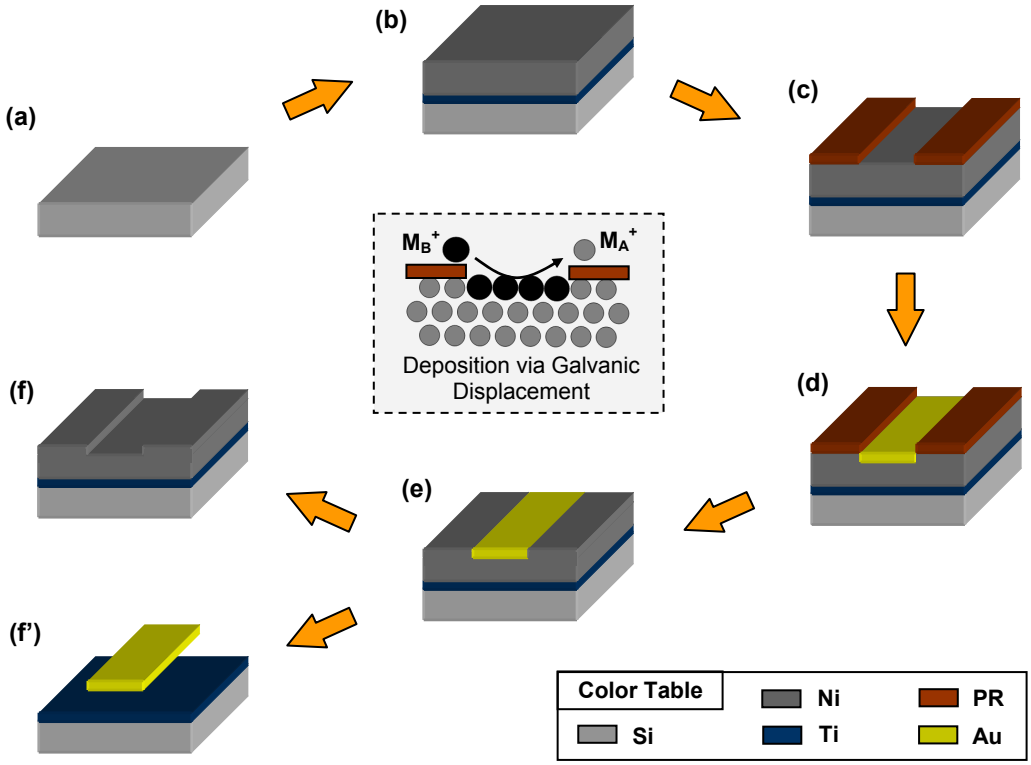

Figure 1. Schematic process of the metal peel-off method(MPOM).

layer replaced by Au metal layer.(Fig. 1(d)) The electroless plating solution, provided by CNCtech Co.,Ltd., contained 2g/L of Au metal into ELECTLESS FX basic solution and pH was adjusted to 4.7 by pH Basic-A solution. Dipping into this solution, galvanic replacement of each metal atom occurred. The replacement time was 3min and the process temperature was 75°C. The photoresist was removed by acetone.(Fig. 1(e)) Finally, the selective Au etchant(Au-5) removed Au replaced layer whose etch stop and etching depth were physically self-controlled.(Fig. 1(f)) We used diluted Au-5(Au-5 : Deionized water = 1:10) to etch the displaced Au layer for 30sec. On the other hand, using Ni etchant enabled the fabrication of Au thin film or suspended structures shown in Fig. 1(f')

3 RESULTS AND DISCUSSION

Figure 2 shows scanning electron microscope(SEM) images of each process. As shown in Fig. 2(a), patterned Ni layer was displaced by Au thin film. AZ 6612K photoresist had a hemisphere shape because of the omission of hard baking process. Though the cross-sectional shape of photoresist was changed due to the plating temperature, the contact area with photoresist and exposed area remained the same. After removing the photoresist by acetone, we investigated that the Au ions displaced the Ni layer and the Au layer thickness was higher than the displaced depth of Ni layer.(Fig. 2(b)) Fig. 2(c) and 2(d) show the results after selective etching process. We tried to zoom in the step-like etching area with SEM, but only the grain size of metal was shown due to the limitation of the field of view and the SEM resolution. Through Fig. 2(c), (d) SEM images, the area masked by the photoresist was clearly brighter than the etching site. Since we cannot measure and explore the exact SEM images, we concluded the etching depth was controlled within 50nm. Moreover, to verify the selectivity of Au-5 etchant, we immersed the Ni(2000Å) sample deposited on the Si substrate into diluted Au-5 for about one day at room temperature. As a result, Ni and Ti layer were found to be inert with Au-5 etchant[9].

Figure 3 describes atomic force microscope images after Au electroless plating and selective etching. A contact mode of atomic force microscope(XE-100, PSIA) was used to measure the etching depth or etch rate of MPOM and check the surface roughness. The etching depth of MPOM was 32.3±2nm on an average. The surface roughness after MPOM seems deteriorated, but from the SEM images we check that this is an error of the AFM tip.(Fig. 3(b)) The surface root-mean-square(RMS) roughness of etched area and original Ni surface were measured as 6.9±2nm and 9.5±2nm, respectively. We can consider that MPOM made the smooth surface. The reason for the smoothening effect was inferred from the mechanism of electroless plating. Ni metal dissolved into the solution and became metal ions. This dissolution process generated electrons that reduce the Au ions from the solution. The reduced Au film was deposited on the substrate. From this exchange of electrons, it is possible to grow ideally as an atomic grain size.

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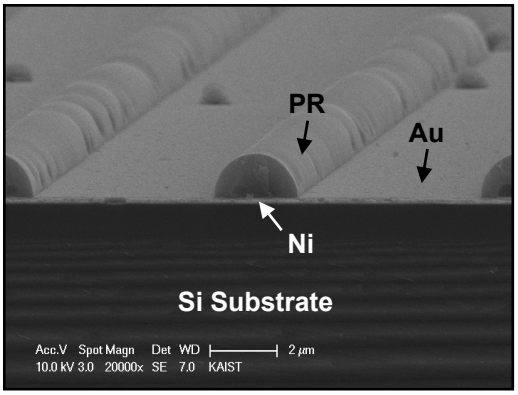
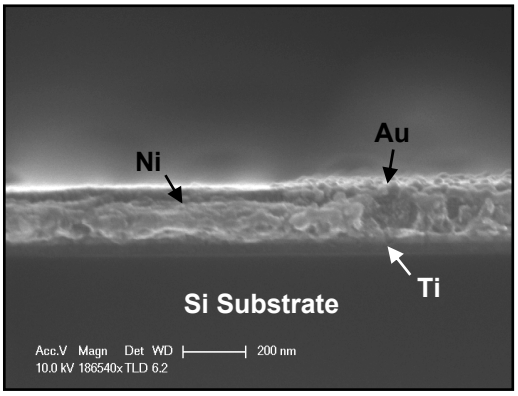
Therefore, the bigger grain size of Ni surface can be reduced by displacement of Au atom.

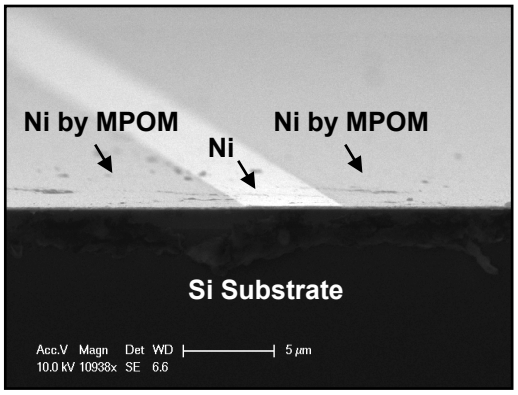
Likewise, the etching depth of MPOM can be adjusted by the electroless plating mechanism. Since galvanic displacement between Ni atoms and Au^{3+} ions occurred, the open Ni surface was getting closer by Au film. The replacement of Ni atom by Au film finished when Au film completely covered the open surface. Based on this mechanism, we can precisely control the etch depth of Ni structure because it saturated automatically by consuming whole Ni surface atom.



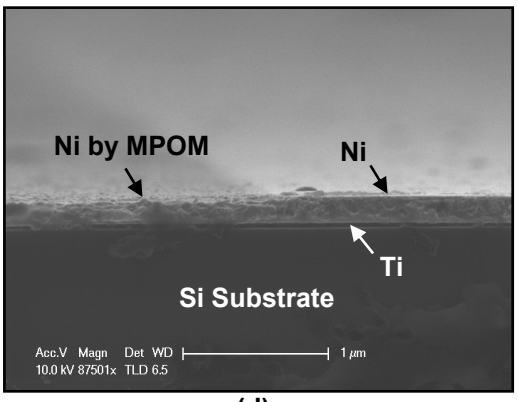
(a)



(b)

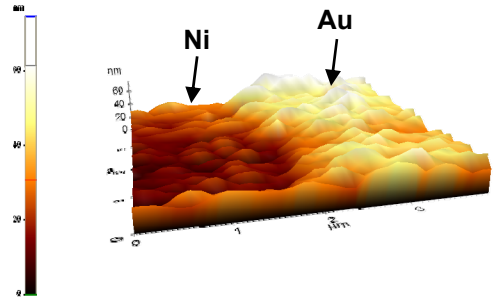


(c)

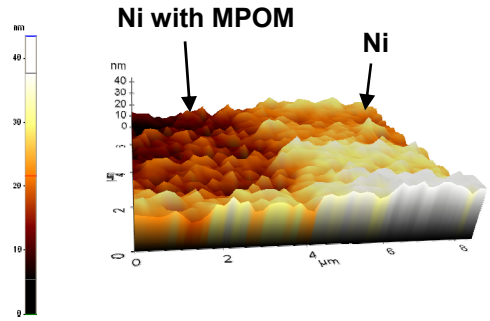


(d)

Figure 2. (a) SEM image of photoresist molds and electroless plated Au on Ni. Scale bar, 2μm. (b) Electroless plated Au displaced Ni surface through the photoresist opening patterns. Scale bar, 200nm. (c),(d) Displaced Au was etched by selective etchant, peeled off the electroless plated metal. Scale bar, (c) 5μm and (d) 1μm..



(a)



(b)

Figure 3. 3D atomic force microscope(AFM) images (a) after Au electroless plating and (b) after selective etching.

A size reduction process to make 3-dimensional metallic nanostructures from microscale structures by utilizing the self-saturated etching thickness is suggested. For this purpose, we repeated MPOM process and measured the etch rate per MPOM times. Figure 4 demonstrates the results of MPOM times versus etching depth. The samples of this measurement data were

fabricated without photoresist patterning. The etching depth was calculated by subtracting the remaining thickness from the original thickness. When the etch rate is plotted with respect to number of times of MPOM, we obtained a linear curve by fitting the measurement data which was 32.2±2nm/times. Therefore, constant etching rate per number of times of MPOM shows that the displacement thickness by electroless plating is self-controlled by fixing the time and the process temperature.

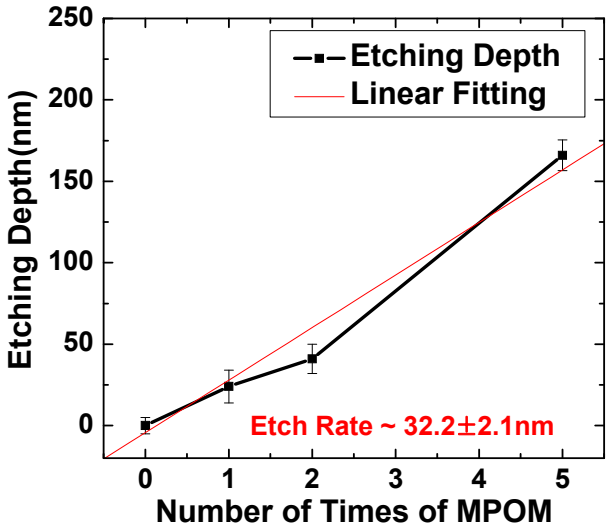


Figure 4. Number of Times of MPOM versus Ni etching depth after Au selective etching.

Figure 5 illustrates the main idea to form metallic nanowires as a size reduction process using MPOM. This is one of the possibilities for the application of MPOM. In addition, MPOM process will provide a controllable location of nanowires, which will be a mask to form and pattern the underlying layer. Proposed method is called metal peel-off lithography(MPOL). A novel idea of nanolithography to fabricate metallic nanowires is in progress.

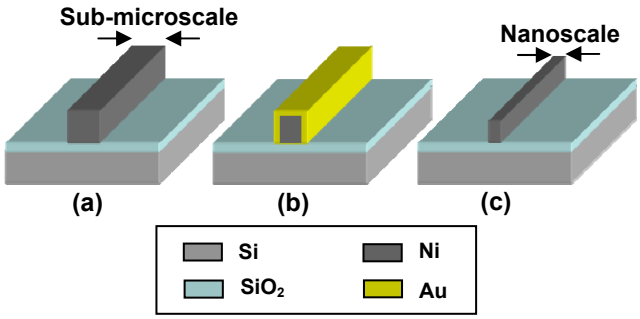


Figure 5. Schematic process of proposed metal peel-off lithography(MPOL) for metal nanowires.

4 CONCLUSION

Novel metal peel-off method(MPOM) and its potential application are introduced in this paper. We successfully and uniformly etch Ni metal layer at nanoscale which exhibits the possibility of 3D metal nanopatterning. MPOM provides a controllable etching depth, about 30nm/times, by repeating the process. Moreover, proposed method would be easily and widely applied to enable various new 3D metal nanostructures and metal nanolithography. Hence, metal peel-off method would prove to be a simple and cost-effective process.

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