ANODIC SACRIFICIAL LAYER ETCH (ASLE) FOR LARGE AREA AND BLIND CAVITY RELEASE OF METALLIC STRUCTURES

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ABSTRACT

A method to release metallic structures without the addition of diffusion etch holes is presented. The method employs an anodic sacrificial layer etch (ASLE) process which allows micro-structures with large surface area substrate coverage and/or structures with sacrificial areas that are not directly exposed to etchant from the surface (blind cavities) to be released in very short times. In addition, the thickness of the sacrificial etch layer can be arbitrarily set from about 200 Å to as thick as needed for controlling the tolerances between mating surfaces. One-dimensional etch rate experiments were conducted to directly compare ASLE with standard etching. The specific system tested was nickel electroplated on a copper seed layer, which is sacrificially released in a copper (II) nitrate-based etchant. The results show that the combination of fast etching of large areas with ultra-thin sacrificial layer is achievable with the ASLE process.

INTRODUCTION

Sacrificial layer etching is an integral step in the fabrication of many sensors and actuators [1,2]. When an electroplated metal serves as the principle structural material, release techniques often rely on various sacrificial layer etches in common wet etchants [3]. In these applications, designs for large area structures of the order of millimeters are limited by the necessity of etch ports [4] and relatively thick (1 µm and greater) sacrificial layers. Manufacturing throughput is limited by the times required for the various sacrificial layer etch procedures, as is the minimum selectivity ratio between the sacrificial layer and the structure. In addition, the release from cavities or structures with irregularly shaped interfaces is impeded where etchant flow is severely restricted. A main motivation for developing the anodic sacrificial layer etch (ASLE) process is to improve on these limitations, in order to release very large, arbitrarily shaped structures on the order of centimeters, with tight, controllable tolerances. The purpose of this article is to demonstrate that the ASLE process can dramatically enhance sacrificial layer etching, by removing the limitation that diffusion of chemical species normally imposes on standard wet etching.

THEORY

The concept underlying the ASLE process is shown in Fig. 1. In the ASLE process, the sacrificial layer is made into an anode, with respect to the etchant. By applying a voltage bias (both DC and a AC voltage with DC offset can be used), an additional driving force is supplied to the reactants at the interface of the sacrificial layer and etchant. This anodically driven etch process differs fundamentally from the usual wet etch process, in that it is not inherently diffusion limited. As depicted in the inset, the etch rate is determined by the normalized concentration (C*) gradient of the ions being removed. For very small layer thickness and large etch depth L, the normal etching process quickly becomes diffusion limited, since the gradient at the interface goes to zero. For the ASLE process, the gradient at the interface is governed by the applied field at the interface, and the concentration gradient does not tend to zero. The electrochemical process occurring at the interface and in the channel is in general very complicated and is in need of further study. However, the concept underlying ASLE is fairly general and a number of different etchant and sacrificial layer systems can be developed to exploit the process. Depending on the chemistry of the materials and

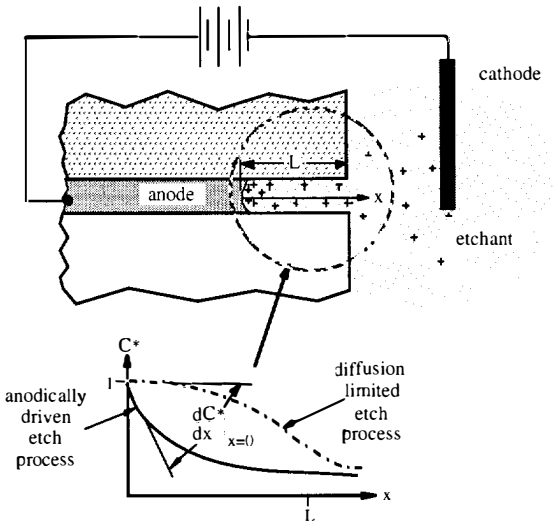

Figure 1 Concept of anodic sacrificial layer etch (ASLE) release.

etchant to be used, the anodic potential may act to increase the etch rate of the sacrificial layer with respect to the principle materials, or may drive a reaction forward that would not normally occur. Etch rate selectivity depends on both bath chemistry and applied potential. This dual dependency enables the ASLE process to independently or simultaneously etch sacrificial layers of different composition.

The sacrificial etching of a copper (Cu) layer in a bath of copper (II) nitrate and ammonium hydroxide electroplated with nickel (Ni) or permalloy ($Ni_{80}Fe_{20}$) demonstrates each of these aspects: (i) standard etching of the Cu sacrificial layer in a cupric nitrate bath can occur without any applied potential; (ii) applying an anodic AC and/or DC potential can dramatically increase the etch rate of Cu; and (iii) increasing the potential beyond a specific over-voltage initiates the etching of Ni or $Ni_{80}Fe_{20}$, the principle structural materials used in this study. Table I indicates the compositions of the etchant baths used. Standard and anodic etch rates are directly compared to demonstrate two fundamentally different limits of sacrificial layer etching: diffusion vs. reaction limited.

Normal sacrificial etching of the Cu layer with the standard etchant in Table I is primarily governed by diffusion of the reacting species. For release of thin sacrificial layers, the oxidizing species, copper (II) nitrate, must come into contact with the solid Cu, which is at the end of the effective etch channel, as shown in Fig. 1. Since two moles of copper (I) nitrate are produced for each depleted copper (II) nitrate, a net outflow occurs opposing the depletion gradient of Cu^{2+}. As the etch front recedes from the etchant bath of essentially constant concentration in Cu^{2+}, the depletion gradient decreases. Since it is this depletion gradient of Cu^{2+} that is driving the etch process, the etch rate will slow until it become diffusion limited, and the etching essentially stops. This process is complicated by subsequent thermodynamically-favored oxidation of Cu^{+} to Cu^{2+} in the channel; however, the basic concept remains.

The etching reaction changes considerably from the standard process when an electric potential is applied to the Cu. A net outflow of Cu cations from the surface occurs, as with the non-anodic etching reaction. However, unlike the case where

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Table I: Copper Bath Etchant Compositions

Component	Standard Bath*	Reduced Bath
$Cu(NO_3)_2 \cdot 2.5\ H_2O$	7.5 g	0.15 g
NH_4OH (commercial 14.8 N)	36 mL	16 mL
DI H_2O	498 mL	24 mL

**Recipe for Standard Bath from H. Guckel's U. Wisconsin web page at* http://mems.engr.wisc.edu/products.html

the reacting specie must overcome the outflow driven only by a depletion gradient, the anodic potential also acts as a body force very near the etch front, driving the anions to the Cu surface for reaction. Conversely, the positive potential also drives the cations away from the front, creating an observably higher fluid velocity away from the front, helping to bring unreacted fluid nearer to the front due to conservation of mass. The higher the applied positive potential, the stronger the body forces act near the solid, which drives the reaction harder producing accelerated etch rates.

As with standard etching, the anodic reaction becomes more complicated when the principle metals are present in the etchant. With an applied potential, the principle metals electroplated on to the Cu also assume an anodic character, and can react with the etchant directly. Depending on the concentration of the copper (II) nitrate in the bath, we observed two competing reactions: passivation of the principle metal surface, and oxidation and etching of the metals. For the standard etchant, passivation of a pure Ni wire acting as the anode occurred for potentials below 3 V. Passivation increased with added potential: less with AC than for DC of the same mean voltage. In the standard bath, bubble formation initiates at the Ni anode above 3 V, starting the removal of the passivation layer. Higher nitrate concentration appears to increase both the passivation and bubble formation rates. Above approximately 5 V, bubble formation appears to completely remove the passivation layer and etching of the Ni began. Our working assumption is that principle metal etching begins with bubble formation, since no etching is observable or measurable below the initiation potential. The formation of a passivation layer on the principle layer is, in general, undesirable, since the thickness of the layer increases with time if no bubble formation is present. As the thickness increases, the etchant channel narrows, slowing the etch process and decreasing the desired clearance. The strongest effect on passivation layer formation is the concentration of the nitrite in the etchant bath. For low concentrations, no passivation layer was observed to occur at any applied positive potential.

The limit in the ASLE reaction rate in very small channels depends on several factors: passivation layer and bubble formation, Cu precipitate formation, viscous flow, and reaction kinetics. At a high enough potential, the fluid begins to form gas bubbles in the etchant, presumably at the Ni anode surface since bubbles did not form with Cu alone. As the formation of gas bubbles increases, the etchant is forced out of the channel, and the bubbles shield the etchant reaching the Cu surface. The bubble flow dynamics can become quite complex, at times enhancing etchant flow and other times shielding, with corresponding increases and decreases observed in the etch rate. Another limit in the anodic etch rate was observed when the voltage was increased high enough in the high copper (II) nitrate etchant to form a soluble, light-blue, Cu precipitate. Our working assumption is that the Cu ion compound forms as the Cu^+ ion is oxidized further to Cu^{2+}, forming a coordinated compound with water. This precipitate could then impede the flow of ions to and from the etch front, thereby creating essentially a new diffusion limit. Several species of copper nitrates and/or hydroxides can be formed by such a process. While soluble in NH_4OH, if the reaction rate is high enough, the local formation of such compounds can exceed the local solubility, and the precipitate forms. This precipitate dissolves when left in the bulk bath for a short time, but persists inside the channel. Another possible rate limit is viscous drag imposed on the outgoing and incoming ions by the walls of the channel. We would expect that as the gap narrows and lengthens, viscous drag on the ions increases and the etch rate decreases. More work will be needed to definitively find the viscous limit for ASLE, if it exists. The final limiting case considered here is the kinetic reaction limit. The reaction limit is the desired limit, since for the ASLE process the kinetic rate is determined by the electron flow and reacting ion concentration. Thus, the etch rate can be controlled for a given concentration by adjusting the voltage, as long as one of the other limits does not occur first. Our preliminary data shows that for samples where one of the other limits was not reached, the etch rate was only a weak function of depth of etch, and depended only on the current density. Therefore, it appears that it may be possible to optimize a given ASLE process to be rate limited, to etch extremely high aspect ratio sacrificial layers.

EXPERIMENT

To determine the effectiveness of the ASLE process, one-dimensional etch rate experiments were conducted using the copper etchant described above to directly compare ASLE to standard sacrificial layer etching. A Cu sacrificial layer and the copper (II) nitrate-based etchant were chosen since the etchant can be used for both standard and anodic etching for direct comparison. Other potential anodic etchants would not etch Cu without an applied potential. Two sets of samples with Ni electroplated on a Cu sacrificial seed layer were fabricated. The samples varied in copper sacrificial layer thicknesses, with each sample having an identical counterpart in the other set.

In order to quantify our comparison, the etch front of the sacrificial layer was monitored *in situ* [5], through an ordinary pre-cleaned Pyrex microscope slide as depicted in Fig. 2. Sequential metal films of titanium (Ti) and Cu were evaporated on the slide. Ti was used as an adhesion layer to the glass and as an oxidation shield for the Cu seed/sacrificial layer. Four thicknesses of Ti/Cu/Ti were used in each set: 150/300/150 Å, 150/3000/150 Å, 300/500/150 Å, and 300/2000/150 Å. The thicker 300 Å Ti adhesion layer was used on the last two due to concerns that the roughness of the glass substrate prevented full coverage. However, no large differences were observed, save difficulties seeing through the thicker Ti layer. A rectangular photoresist mask 2 by 3.25 cm was used as the electroplating mold. Prior to electroplating, the upper layer of Ti was removed in a 1:50 HF:DI acid bath, exposing the copper layer. A standard nickel sulfamate bath was used to electroplate Ni on Cu

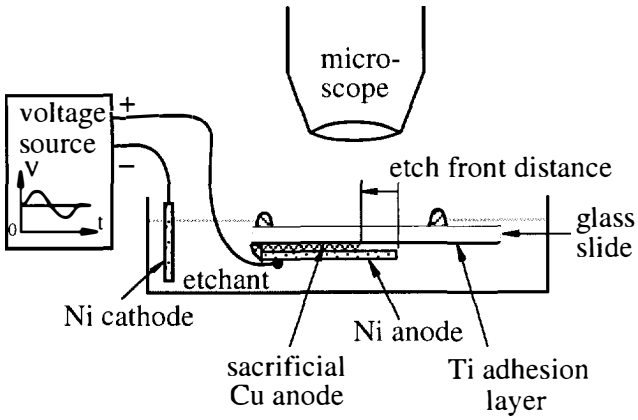

Figure 2 Experimental set-up of 1-D etch rate monitoring.

at a conventional current density of 50 mA/cm^2 for one hour. Following electrodeposition, the photoresist and the exposed upper layer of Ti was removed, and a silicone sealant was applied to three of the four sides of the nickel rectangle in order to form a one-dimensional rectilinear etch port [6]. On the back surface of each slide, additional silicone was applied to form an embankment mirroring the location of the nickel structure in order to keep etchant from flowing over this surface. The 150-300 Å Ti adhesion layer was translucent: thus we monitored the movement of the etch front of the Cu layer through the back of the glass slide using an ordinary optical microscope.

One set of 4 slides was immersed in the standard etchant and monitored at various time intervals to track the distance that the etch front moved from the edge of the Ni. The other set had electrical leads attached with conductive epoxy to one corner of the nickel structure, and then sealed with silicone. After immersion in the etchant, a DC potential was applied, with a coil of Ni wire serving as the cathode. Progression of the etch front was monitored to about 500 μm at which point the potential was removed. One sample was then used to determine the characteristics of an applied AC potential, while another was used to evaluate etch rate characteristics of a different bath chemistry.

RESULTS AND DISCUSSION

Prior to the controlled etch studies, metallic structures of large planar area and others with blind cavities were fabricated on silicon wafer substrates and released using an earlier form of the ASLE process. Chronologically, the first attempts of anodic sacrificial layer etching were performed on nickel structures using a Ti adhesion layer as the anodic layer. Buffered oxide etch (BOE) was used to etch the Ti, and a potential of 10 VDC was applied to accelerate the process. Although the nickel structure was released quickly with negligible attack on the Ni, the combination of the potential and the BOE actually etched large holes (300 μm) through the silicon! Subsequently, different metal systems and/or selective etchants [7] were investigated to find more suitable systems to anodically release over Si. The copper (II) nitrate/ammonium hydroxide bath listed in Table I, and its peculiar selectivity of copper over titanium, is one such system. To test this etchant with Ni and Fe, permalloy structures were electroplated using various well known electroplating baths and methods [8,9]. These structures were fabricated on planar silicon substrates as well as in cavities created in the silicon substrate using KOH anisotropic etch procedures. These early ASLE experiments were designed to find out how fast the etch process could go, how much area could be released without the addition of etch holes, how thin the sacrificial layer could be, and if structures plated into cavities could be released. Consequently, we used relatively high potentials (> 10 V), and we were not excessively concerned with selectivity with respect to the principle metal material, or their cosmetic appearance. Two examples of early experimental large area release samples can be viewed in Fig. 3. For both Ni and $Ni_{80}Fe_{20}$, solid plated areas of over 1 cm^2 were released in approximately 1 hr. In addition, the thickness of the seed layer could be taken down to as little as 200 Å, and release would still occur. Each aspect of high speed, large size, and ultra-thin sacrificial layer exceeded the standard methods of release we are aware of by several orders of magnitude.

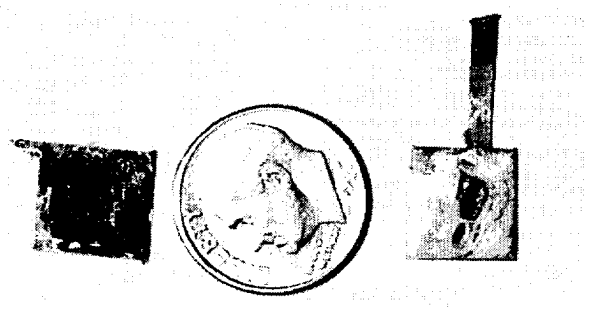

Figure 3 - Inelegant, but effective, examples of large area (~ 1 cm^2) release in about 1 hr. from an ultra-thin (< 500 Å) sacrificial layer using ASLE, without any etch holes added to enhance diffusion. On the left is permalloy approximately 25 μm thick, and the right is nickel about 80 μm thick. Both layers were plated on Ti(150 Å)/Cu(300 Å) with adhesion to the wafer stronger than the fracture strength of the underlying Si.

To quantify the results, one-dimensional etch experiments were conducted with the Cu/copper (II) etchant system. Figure 4 shows the etch front distance vs. time for Cu layers of 300 and 3000 Å thickness. In (a), the diffusion limit for the normal etch case is clearly seen as the rate goes to zero at times over 2000 min. at about 1 mm depth. The ASLE using a DC potential at 3 V for the same case shows no such limit to the same depth. In (b), the results for the 3000 Å case are plotted in log-log form to show the order of magnitude higher initial etch rate in the ASLE before the standard case becomes diffusion limited, with little drop-off in rate. The nearly constant rate is indicative of a reaction limited etch. Similar results were found for all the other samples tested. However, we did note that using the standard bath for ASLE that a Cu precipitate formed in the channels. The precipitate often clogged the channels, causing uneven etching and some rate fluctuation with distance.

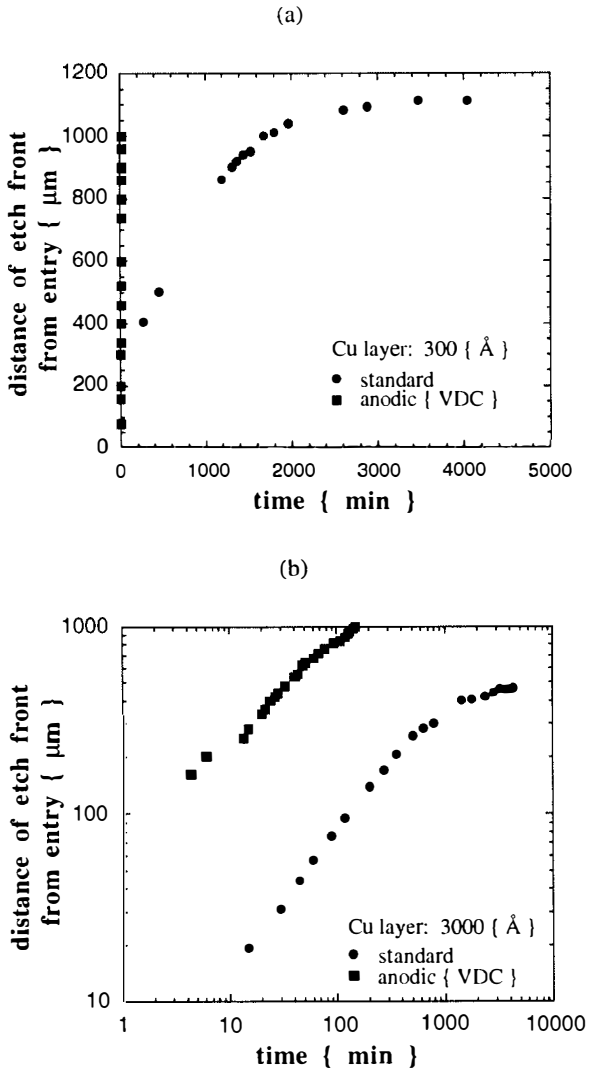

Figure 4 - Observed 1-D etch depth vs. time for (a) 300 and (b) 3000 Å thick Cu sacrificial layer. Fig. (a) shows diffusion limited behavior vs. time of standard etch, and (b) in log-log shows the initial order of magnitude higher etch rate of the anodic vs. standard before standard becomes diffusion limited.

Although the precipitate which exited the channel due to the induced flow during the anodic etch dissolved in the bulk fluid, the precipitate persisted in the channels as the depth increased, presumably due to local changes in NH_4OH concentration. In separate tests, the formation of precipitate was found to be a strong function of nitrate concentration. By dropping the nitrate concentration in the bath, the precipitation could be completely suppressed. However, the etch rate exhibited nearly a step function with respect to a minimum in copper (II) nitrate concentration. Etching proceeded extremely slowly at no to very low concentrations in copper (II). Once a minimum value, slightly below that given in Table I for the reduced bath, was reached, etching continued at the same rate as for the standard case, but without the fluctuations observed earlier, as shown in Fig. 5 for a 2000 Å thick Cu layer. The etch rate is essentially linear in this regime, and thus appears to be limited only by the reaction due to the applied voltage and thus current density. It should be noted that for the reduced concentration, no observed etching occurred without an applied potential. Therefore, the anodic potential is essential for the reaction to proceed.

In separate tests to investigate the formation of the passivation layer and bubbles on the Ni anode, we observed that applying an AC potential with a mean at the previously tested DC voltage, reduced both the passivation layer and large bubble formation, particularly at frequencies over 1 KHz, though no further changes were easily observed at higher frequencies (to 10 MHz). If the passivation layer grows too large, the channel may close off, slowing the rate. Also, if bubble formation is excessive, the etch rate may fall. Therefore, we tested a 1 KHz AC potential, where the minimum is above 0 V to avoid redeposition of Cu. As seen in Fig. 6, applying an AC potential more than doubled the etch rate over the DC case. The diffusion-limited standard etch case is included for comparison. Clearly, AC excitation and its enhancement mechanisms require further investigation.

CONCLUSION

This study is an initial investigation of the anodic sacrificial layer etch process for achieving orders of magnitude improvement in release of micro-structures. The process has yet to be optimized, but the results so far are promising and suggest several areas of future study, including: different ASLE systems, DC vs. AC, etchant concentrations, binary anodes, and limiting mechanisms. In addition, the Cu process described here can be can be integrated with an ammonium fluoride and CO_2 supercritical drying process to prevent stiction of moveable structures [10], potentially enhancing ASLE's use for releasing blind structures in-place: research currently underway at UIUC.

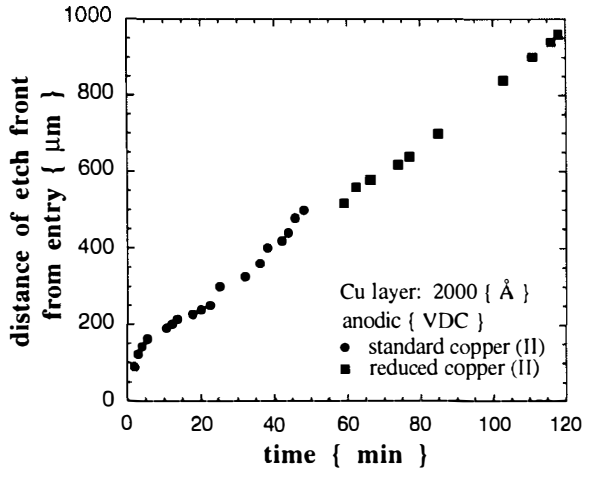

Figure 5 - Anodic etch using with the standard and reduced copper (II) nitrate etchants. Linear behavior of reduced bath suggests reaction limited etch is occurring.

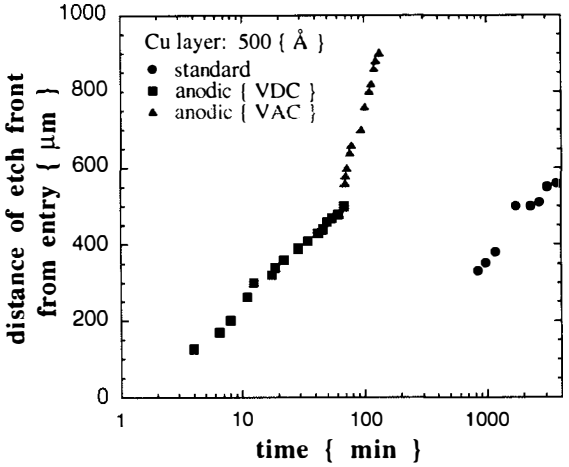

Figure 6 - Shows DC and 1 KHz AC anodic etch compared to standard etch for 500 Å Cu layer. Enhanced affect of AC excitation over DC is clearly seen for this sample.

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