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ABSTRACT

The possibility of using sputtered metals as mask materials for deep anisotropic chemical etching in silicon was investigated. Sputtered films of chrome, nickel and tungsten were all found to be chemically resistant to potassium hydroxide (KOH) and tetramethyl ammonium hydroxide (TMAOH). However as expected, these metals had poor adhesion to the silicon substrate. By comparison sputtered titanium was found to have excellent adhesion properties, and was chemically resistant to TMAOH but not to KOH. Resistance to KOH was achieved by thermal oxidation of the titanium film, at temperatures between 600 and 900°C. Following oxidation, etch depths more than $200\mu m$ were readily achieved in KOH etching. This makes sputtered titanium a potential alternative to the conventional mask material, silicon nitride, for the application of deep anisotropic etching. The reduction in etch rates due to a galvanic effect of conductive metal masks on silicon-on-insulator wafers was also investigated. It was observed that this effect was also overcome by thermal oxidation of the titanium mask.

Keywords: Anisotropic etching, masks, thin films, titanium, titanium dioxide, galvanic effects.

1. INTRODUCTION

Wet anisotropic etching in silicon can be performed in a variety of alkaline solutions, the most well known being potassium hydroxide (KOH), tetra-methyl ammonium hydroxide (TMAOH) and ethylene diamine pyrocatechol (EDP).[1] KOH has the problem of being incompatible with CMOS fabrication, but the advantage of being low cost and having high selectivity of all crystal directions over the {111} planes. EDP is CMOS compatible but highly toxic. TMAOH has relatively low toxicity and is CMOS compatible, but is more expensive and difficult to dispose of than KOH, and has lower etch rates.

The conventional masks for wet anisotropic etching are thermally grown SiO_2 and low stress CVD Si_3N_4. Thermal growth of SiO_2 is a low cost and widely available process, however in KOH the selectivity over silicon is relatively low, and so etch depths are limited by oxide thickness. Thick SiO_2 films for deep silicon etches are difficult to produce, as the film thickness is approximately an inverse paraboloid with respect to thermal growth time.[2] TMAOH has much higher selectivity for etching Silicon over SiO_2 compared to KOH. Deep etching with oxide masks in TMAOH is possible with reasonable oxide thicknesses.

The etch rates of Si_3N_4 are usually lower than SiO_2, but the rates for both films depend on the film density and stress, and therefore the method of deposition.[3] SiO_2 masks are obtained by thermal growth or LPCVD.[4] APCVD SiO_2 has pinhole problems and lower film density, therefore faster etching.[5] For deposition of Si_3N_4, LPCVD provides a much better mask than PECVD.[5]

Some other possibilities have been demonstrated include silicon carbide,[6,7] a 3nm fluorocarbon layer on top of SiO_2[8] and sputtered metals,[9] especially gold with a chrome adhesion layer.[5,10-12] The spin-on polymer divinylsiloxane bisbenzocyclobutene (BCB) has been successfully used as backside protection,[13] and is photo-definable, but according to the manufacturer[14] fine patterns peel off under long KOH etches due to stress generated during the curing process.

The aim of this paper is to present some convenient, low cost alternative masks to SiO_2 and Si_3N_4 for the application of deep anisotropic etching, that will allow greater flexibility in the design of MEMS processes.


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1.1. Silicon etching mechanisms

The alkaline etching of silicon is not completely understood. The process involves several intermediate chemical and electrochemical steps,[15,16] and exact form of the reactions are influenced by many factors, including electric currents, doping concentrations, pH, temperature and light levels.[15,17] It is generally agreed that the hydroxide ion plays an active role and that the reaction involves the oxidation of silicon and reduction of water. The redox pair for this first step according to Sidel *et al.*[18,19] is given by

$$Si + 2OH^- \longrightarrow Si(OH)_2^{++} + 4e^-$$

$$4H_2O + 4e^- \longrightarrow 4OH^- + 2H_2. \tag{1}$$

In the following steps the silicon hydroxyl complex being dissolved in water, leading to the overall equation given by

$$Si + 2OH^- + 2H_2O \longrightarrow SiO_2(OH)_2^{--} + 2H_2. \tag{2}$$
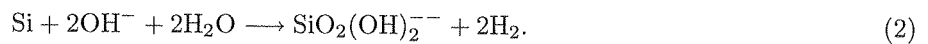
The effects of applying an electric bias to the silicon sample with respect to the solution have also been studied in some detail.[15,16] If an anodic current flows to the exposed silicon surface a different oxidation reaction is able to take place in alkaline solution, causing the growth of SiO_2 on the surface.[11]

$$Si + 4OH^- + 4h^+ \longrightarrow SiO_2 + 2H_2O \tag{3}$$
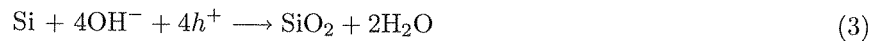
Reaction (3) does not occur in n-type silicon in darkness, where there would be no thermally excited holes present, which suggests that holes (h^+) may be more critical to the process than electrons.[16] The resulting SiO_2 on the surface must be dissolved, therefore the overall etch rate is reduced. If the voltage is increased to a point V_{pp} such that SiO_2 grows faster than it can be dissolved, the surface is passivated, and etching of silicon is completely halted. Further increases in voltage do not result in increased current.
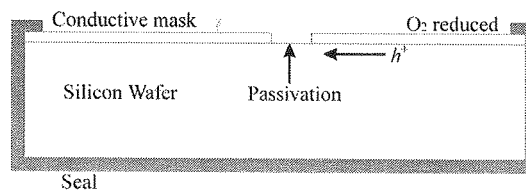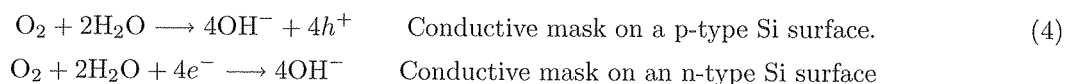

Figure 1. The passivation of silicon in alkaline etching.

Under some conditions this process may occur without externally applied bias, this is caused by the formation of a galvanic cell,[12] shown in figure 1. The metal mask forms the cathode, this end electrons are consumed or holes are created by an oxidising agent, thought to be dissolved oxygen,[11,20] as in equations 4.

$$O_2 + 2H_2O \longrightarrow 4OH^- + 4h^+ \qquad \text{Conductive mask on a p-type Si surface.} \tag{4}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad \text{Conductive mask on an n-type Si surface}$$

If sufficient current flows to the exposed silicon area (anode) the surface is passified and no etching occurs.

2. SPUTTERED METAL FILMS AS MASKS

Metal films are occasionally used as masks for etching of silicon in KOH, TMAOH and EDP.[9, 21] Here they were investigated because they were readily available, and would provide a much lower cost process than the other alternatives. In most cases the mechanism for failure is related to poor adhesion to the substrate. The metal layer sometimes allows the etchant to creep underneath the edges causing the mask to peel or bubbles off.[9] In localized areas where small contaminants exist on the substrate surface large blisters form. Only pinholes would occur with SiO_2 or Si_3N_4 masks.

Experiments were carried out using gold, chrome, nickel tungsten and titanium in both TMAOH and KOH etchants. The metals were deposited by a variety of sputtering systems and etched under various conditions in the hope of finding suitable materials for etch masks.

Aluminium has been previously shown to withstand TMAOH under some conditions,[3, 22, 23] as has tantalum but neither was investigated here. Tantalum was not readily available, and aluminium is known to be highly reactive with KOH.

Nickel, chrome and tungsten all behaved as masks in similar ways. Adhesion to the substrate was the problem rather than chemical attack. The effect of blistering caused by poor adhesion of nickel to silicon is shown in figure 2(a) for a $200\mu m$ high mesa etched in KOH. The square symmetry of the defects are a result of the well known phenomenon that when any exposed pit is allowed to etch for long enough it will be be finally limited by $\{111\}$ crystallographic planes.[24] Figure 2(b) shows a $140\mu m$ high mesa etched in KOH using a tungsten mask. In both cases the blistering of the masks has exposed large fractions of the surface area they were protecting. Protection with a gold film on nickel and chrome was tried, but with no observed improvement to the resilience of the films.
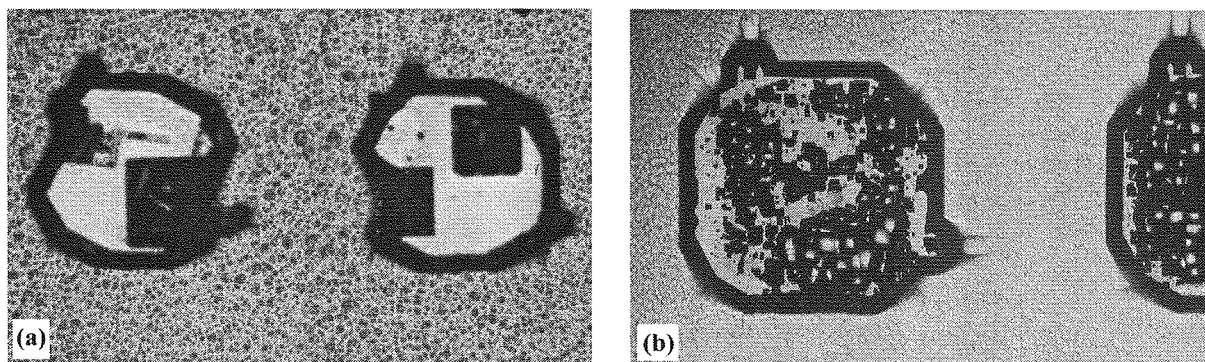

Figure 2. (a) $200\mu m$ high mesa using sputtered nickel as a mask. (b) $140\mu m$ mesa using a tungsten mask.

The only critical factor in minimising the occurrence of blistering was the quality of the sample cleaning process. The samples in figure 2 were washed with acetone, de-ionised (DI) water, isopropyl alcohol, DI water water, 10% hydroflouric acid and then DI water.

Etching conditions made little difference to the integrity of the mask. Neither did an intermediate oxide layer, or the deposition onto the unpolished back side. For short etches of the order of tens of μm or for backside protection nickel, chrome, and tungsten may make suitable masks. However for deep etches the poor adhesion and subsequent blistering made them highly problematic.

3. TITANIUM MASKS

Titanium has previously been reported for dry etching of $GaAs$[25] and for wet etching of GaN in KOH.[26] For the wet etching of silicon it proved different from the other metals in two respects. Firstly it was extremely adhesive. There was never any problem blistering or peeling, and pinholes were less common. However the second difference was that in some cases it was found to be vulnerable to attack from KOH and TMAOH.

Two mechanisms were identified in this process. Firstly it was found that at temperatures above 80°C the film failed in both KOH and TMAOH. This is in agreement with metallurgical studies of titanium by Schutz and Thomas,[27] where it was suggested that the native oxide becomes vulnerable to attack in alkaline conditions above this temperature. This was no serious problem so long as the etch solutions were kept below 80°C.

Etching in TMAOH (25% by volume, at temperatures below 80°) proved quite successful. Structures with depths of hundreds of μm were reliably achieved. Titanium therefore makes a potential low cost rival to Si_3N_4 and SiO_2 masks for etching in TMAOH. Figure 3 shows a 220μm mesa made using a 150 nm sputtered Ti film in an argon plasma at 110W RF power.
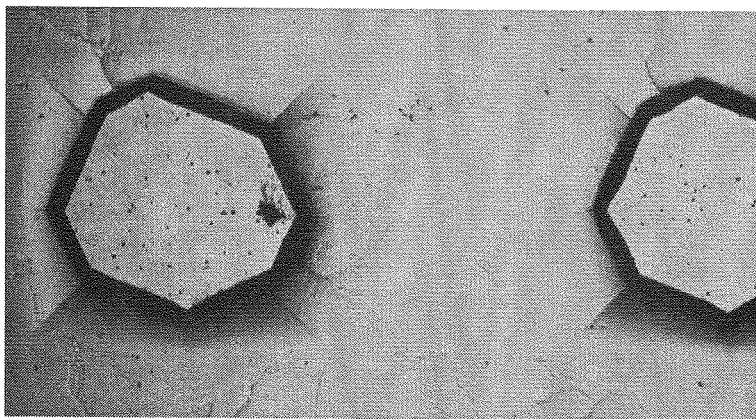

Figure 3. 220μm high mesa using sputtered Ti as a mask for TMAOH etching.

The second failure mechanism was thought to be film stress, as has been previously noted by Schutz and Thomas,[27] where mechanical stress was claimed to increase corrosion. In KOH the titanium film was usually attacked even at low temperatures. Further investigation was performed to try and find conditions under which titanium was able to reliably withstand KOH. Stocker et al.[26] reported the successful use of titanium as a mask for KOH etching of GaN, so it would be reasonable to expect such conditions to exist for silicon etching.

Stress in sputtered films can be controlled by the sputtering conditions especially DC bias, which is related to chamber geometry, working gas pressure, choice of working gas, and RF power.[28] It has also been shown that at sufficiently low temperatures the RF power can determine stress properties in metals without any DC bias.[29] Compared with other metal films, sputtered titanium is known to have high intrinsic compressive stress which changes to tensile stress only at relatively low DC bias.[30]

A small DC sputtering system was able to produce some successful titanium films for KOH etching. Etch depths of more than 100μm were achieved on several occasions, sputtering with sputtering conditions of 150mA, and 6mTorr argon pressure. However this system broke down part way through the project and was never restored to sufficiently high vacuum to sputter titanium. The dependence on D.C. sputtering conditions was therefore not thoroughly investigated.

Three RF sputtering systems were tried, with a variety of pressures, temperatures and RF powers. DC biases between -75V and -130V were tried, by adjusting RF power and argon pressure, but none made KOH resistant masks. Lower than -75V produced poor quality films, presumably due to the high argon pressure used to obtain this DC bias. A 300nm E beam evaporated film was tried, but this was also not resistant to KOH. Post deposition annealing in a nitrogen atmosphere at 800° for three hours was tried but this did not make any difference.

Attempts were also made to reduce the aggressiveness of KOH, by adjusting etch temperatures, concentrations, addition of IPA, and variable stirring rates. Concentrations between 40% to 60% by mass, and temperatures from 60° to 90° were tried. No significant changes in attainable etch depth were observed.

Sputtered films with Ti thicknesses ranging from 40nm to 500nm were tried, but there appeared to be no correlation between film thickness and the time taken for it to be removed in KOH. The 500nm film was dissolved after only $2\mu m$ of etching in 50% KOH solution, whereas most films lasted between $5\mu m$ and $30\mu m$. This is an indication that the main factor protecting the film from the etchant is the native oxide.

It was thought that the previously discussed galvanic effects in silicon etching might be resulting in the electrochemical reduction of the native TiO_2, rather than the reduction of dissolved oxygen, as in reaction 3. This theory was tested by first growing a 100nm thermal oxide prior to titanium deposition, to provide electrical insulation. However no improvement to resistance to KOH was observed. So it was concluded that electrochemical effects were not influencing the dissolution of titanium.

Another possibility is to use titanium only as an adhesion layer for other metals such as nickel, chrome or tungsten, as is done for metalization layers in microelectronics.[31] This was reasonably successful for shallow etches, however there was some attack of the Ti film at the edges, negating any advantage of the improved adhesion.

3.1. Patterning of Ti films

Titanium is easily patterned with standard positive photoresist, and etched in a solution of HF, H_2O_2 and water. However a residue is sometimes left behind. This was avoided by adding ammonium solution. The ratios $H_2O:H_2O_2:HF:NH_4OH$ used were 40:2:2:1 by volume. This was found to etch nickel also, which was convenient if nickel was being used as a mask with titanium as an adhesion layer.

Patterning can also be achieved in a reactive ion etching system with the same chlorine based gas mixtures used for etching aluminium.[32]

4. TITANIUM DIOXIDE MASKS

TiO_2 has been well studied, owing to a wide variety of applications in biotechnology, microelectronics, photo-voltaics and pigments in paints.[33] Research for photo-voltaics has shown that TiO_2 is chemically resistant to most of the RCA cleaning steps, and also to short NaOH etch steps. It also has another useful property, that high temperature steps do not contaminate the furnace.[34] The film may also be applied by low cost spray coating methods and yet retain good chemical resistance.[35] No investigation has yet been made into spray coated TiO_2 for deep alkaline etching.

Three common crystalline forms of TiO_2 exist, anatase, rutile and brookite with rutile being the more dense and chemically stable. The most common method for forming thin films of TiO_2 is by sputtering or CVD. Generally the deposited films are amorphous but form the crystalline phases on annealing. The selection between the three phases depends on the deposition conditions and annealing temperature. CVD films are known to form the anatase state, but this changes to the rutile state at deposition temperatures over 400°.[36] Sputtered TiO_2 films change to single phase rutile with annealing at 700-900°C.[37]

It was recently shown that TiO_2 films, in the rutile phase are also easily formed by thermal oxidation of sputtered titanium temperatures above 550°.[37] This method was tried here as a mask material, and proved quite successful. Following titanium metal deposition step by e-beam evaporation or RF sputtering the sample was heated in air to allow the TiO_2 layer to grow. This oxide, also brightly coloured, proved to be an excellent mask, suitable for KOH or TMAOH etches to depths of hundreds of microns. A $200\mu m$ mesa is shown in figure 4. It formed relatively quickly, compared to SiO_2 at low temperatures. The colour was dependent on film thickness, ranging through brown, blue, purple, yellow/green.

Thermal oxidation of titanium is thought to be diffusion limited, forming layers with decreasing oxygen content with increasing depth.[38] The TiO_2 film thickness for high temperatures is given by[37]

$$d = \frac{A(Dt)^{\frac{1}{2}}}{(1-W)}.$$

(5)

Where D is the temperature dependent diffusion constant, given as $10^{-12}cm^2s^{-1}$ at 700°, t is the growth time, A is the exposed area ($1cm^2$, but necessary to for the correct units) and W is the mass fraction of oxygen
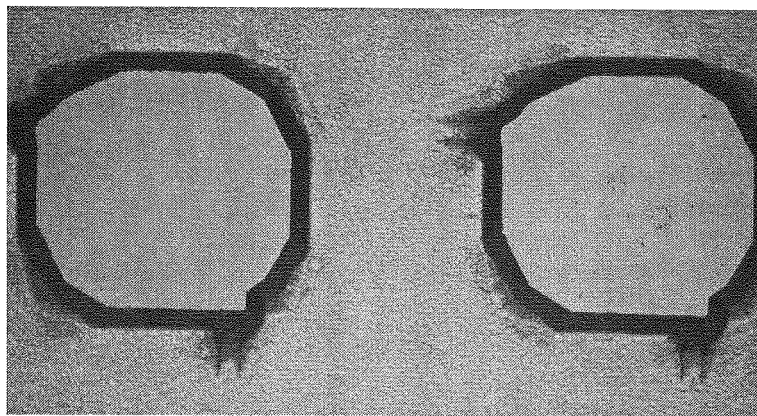
Figure 4. 200μm high mesa using TiO$_2$ as a mask.

with $W = 0.36$ for an oxygen partial pressure of 0.2 (air). Substituting these values we arrive at figure 5 for the expected film thickness for oxidation time t.
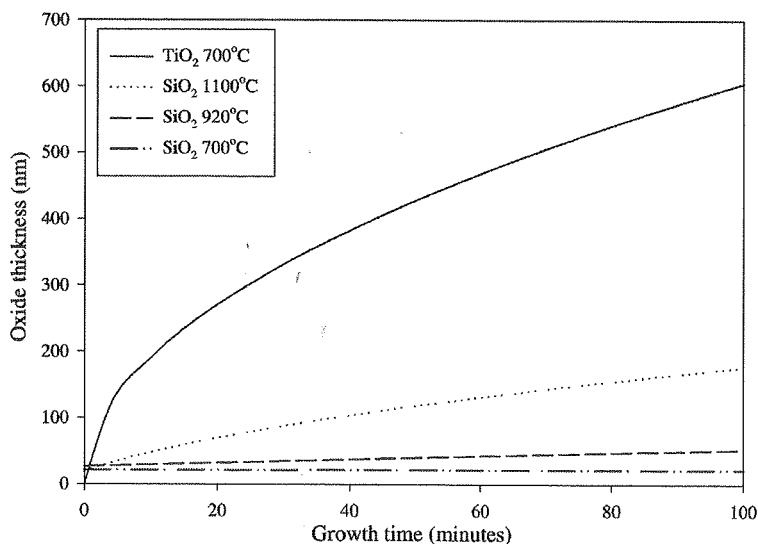

Figure 5. Thermal oxidation of silicon with data from Sze[2] and titanium with the diffusion constant from Ting *et al.*[37]

Two different initial titanium films were experimented with, the first was a 300nm E beam deposited film and the second was 150nm, formed by RF sputtering at 110W. Both were successful as etch masks after thermal oxidation, achieving etch depths of over 200μm with no significant damage to the film, except for a small number of pinhole defects in the sputtered case. However when the initial film thickness was increased to to 300nm the mask failed. It also failed when deposited onto the back unpolished side of the wafer. These two observations suggest that the quality of the oxide was still dependent on properties of the original titanium film, in agreement with other authors' observations.[39]

One major disadvantage was observed, when compared with other masks. The overhanging mask caused by lateral etching had no structural integrity. It dissolved or broke off in chunks, thus exposing new silicon to the solution at the edge. Again this may be dependent on the crystal quality, and could possibly be solved. In any case it was not significant enough to cause significant structural change. It did however cause roughening of sidewalls by the formation of small terraces on deep etched overhanging structures.

4.1. Electrical resistivity of Ti/TiO$_2$

Of particular interest was the resistivity of the film. Conducting masks were found to have problems for etching SOI, discussed in section 5. Experiments were performed to investigate the dependence of resistivity on thermal oxidation.

Measurements of resistivity were made using a four point probe. The initial sheet resistance of the films (native oxide only) varied from 3 to 20 $\Omega/\square$. At 500°C in air the film gradually increased in resistivity for 5 hours before going off the scale of the four point probe ($10^6\Omega/\square$). At 600°C this process took only 10 minutes. Presumably the oxide thickness was the main factor determining the resistance, but note that the phase of the TiO$_2$ crystal structure changes from anatase to rutile at 550°C[37] and the different crystal phases vary in resistivity so this may have also been important.

4.2. Patterning of TiO$_2$ films

It has been previously reported that TiO$_2$ may be patterned by a RIE with a CF$_4$ plasma. TiO$_2$ and Si had equal etch rates, 100nm/minute with an RF power of 100W and pressure of 0.12Torr.[40]

As RIE facilities were not available at the time a search was made for wet etch chemicals. The etch solution for Ti was tried but was not able to pattern for the thermally grown TiO$_2$. Sulphuric acid has been reported to attack TiO$_2$ at 200°C.[41] Also an alkaline mixture of H$_2$O$_2$,NH$_4$OH,H$_2$O in ratios 1:1:5 has been shown to attack non annealed spray coated TiO$_2$.[34] Both of these solutions were tried at 25°C-75°C but with no success. Nitric acid, standard aluminium etchent (CH$_3$COOH, H$_2$O$_2$, HNO$_3$,H$_2$O, 16:1:1:2), BHF and Ammonium Solution, all failed to make any noticeable attack on the film at room temperature. Further investigation could be done at high temperatures, although this may be harsh on the photoresist. The alkaline solution was also tried at 75°C for five hours without any change in the film.

The film was removed rapidly in concentrated HF. However it was not the film being dissolved but rather the interface between the film and the substrate. Therefore this method can only be used as a final step, not as a patterning step for lithography. Large samples took longer to process than smaller ones.

Lack of a wet etch solution does not prevent TiO$_2$ from being used as a mask, as the sputtered Ti was easily patterned prior to oxide growth. The oxide can'then be grown without growing a significant SiO$_2$ film on the exposed parts, as can be seen in figure 5. However further investigation to find a wet etch solution that attacks TiO$_2$ selectively over Si, SiO$_2$ and Si$_3$N$_4$ would be worthwhile. Such a solution, if it could be found, would increase the flexibility of using TiO$_2$ in conjunction with SiO$_2$ and Si$_3$N$_4$ in multiple mask processes.

5. METAL MASKS FOR ETCHING SILICON-ON-INSULATOR

When metal masks were used on silicon-on-insulator (SOI) wafers rather than bulk silicon the etch rates were often drastically reduced, TMAOH etches were sometimes completely halted. This was attributed to the formation of a galvanic cell, as was introduced in section 1.1. The wafers consisted of an 11μm thick, 61.4-61.8 Ω·cm n-type silicon device layer, on a buried 1μm SiO$_2$ layer. The effect of the buried oxide was to electrically isolate the patterned device layer from the bottom surface, and thus reduce the effective area of exposed silicon to only what is on the top.

Although galvanic etch stops have been put to good use for the fabrication of thin membranes,[11] in the case of this project it was undesirable, preventing or halting the intended etching.

To prevent the effect the anodic current per unit area to the exposed silicon surface must be sufficiently reduced. This can be achieved by reducing the quantity of dissolved oxygen or the ratio between exposed silicon, and the conductive mask.[10] This second option could only work in practice if there were areas of the wafer that could be sacrificed by opening extra windows to expose more silicon.

Another way, suggested here, is to increase the resistivity of the Ti mask. As was previously described, the resistivity of Ti increases after thermal oxidation. The same effect as oxidising the Ti could presumably be achieved by using a SiO$_2$ buffer layer between the metal and silicon. However this would be problematic if the mask is being used in conjunction with an existing SiO$_2$ mask in a multi mask process. While patterning the Ti/SiO$_2$, the SiO$_2$ mask would also be attacked.

Figure 6 shows silicon etch rates with nickel, Ti and TiO_2 masks in KOH and TMAOH with coverage areas ranging from 2% exposed Si to 85%.
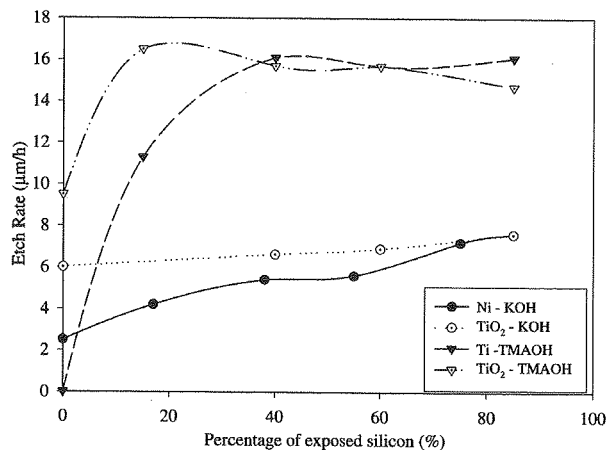

Figure 6. The etch rates of silicon with metal masks with respect to mask coverage area

In the case of TMAOH, the metal masks did not significantly reduce the etch rate, except for very high coverage area, where etching was completely halted. This is in reasonable agreement with previous results.[10] After oxidation of the titanium film a more practical etch rate of $9.5\mu mh^{-1}$ was obtained with the 2% exposed pattern.

In the case of KOH the effect was reasonably linear with respect to mask area. The etch rates with high coverage of TiO_2 were again significantly higher than for a conductive metal. Figure 6 shows $2.5\mu mh^{-1}$ with Ni, compared with a more practical $6\mu mh^{-1}$ with TiO_2, with 2% exposed silicon.

Care should be taken in interpreting the KOH results, as the native SiO_2 layer was not removed on those samples prior to etching, (at the time there was concern that BHF might attack the metal films). Therefore the rates include the time it took to etch through the native oxide. The differences could therefore be a result of the native oxide being removed more slowly due to the anodic current, rather than a change the final silicon etch rate. This experiment should be repeated with the native oxides removed prior to etching, as was done in the TMAOH case.

6. CONCLUSION

The possibility of using sputtered metals as masking materials was investigated, and it was found that titanium is very useful for this application, as it had excellent adhesion properties to silicon, compared with the other metals investigated: nickel, chrome, tungsten and gold.

After thermal oxidation, the titanium film was successful as an etch mask in both KOH and TMAOH, with reliable adhesion and no measurable etch rate. It has the advantages of being a relatively low temperature and low cost process. No wet chemical etchant was found for patterning purposes. However this is easily is overcome by dry etching, or patterning the titanium prior to oxide growth.

Without the oxidation step titanium was only reliable in TMAOH. On some occasions it was successful in KOH, but the necessary conditions for reliable use were not established.

In SOI there was a new problem of a galvanic effect due to the conductive mask, which reduced the etch rates in structures with only small areas of exposed silicon. However this problem was also solved by converting the titanium to TiO_2.

Further work is needed to find how the titanium film can be used with KOH, but without oxidation. Reducing the pH with a weak acid may be one such possibility. A wet etch solution for patterning the TiO_2 film would

also be useful, and the sputter conditions for the original titanium film should be optimised to minimise film stress.

ACKNOWLEDGMENTS

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