

# STUDY OF SELECTIVE WET ETCHING OF TITANIUM TOWARDS COPPER IN HYDROFLUORIC FREE ETCHANT

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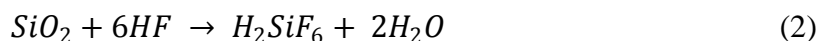
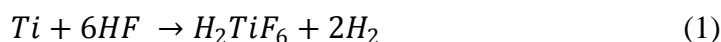
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## 1. Introduction

Titanium and copper thin films have various applications in microfabricated devices such as interconnects or through-silicon vias (TSV) [1-3]. Copper is finding increasing use as an interconnect material and is replacing aluminium in high performance integrated circuits. Due to its electrical conductivity which is almost 60 percent higher and its significant larger electromigration resistance compared to aluminium it is more attractive [3]. However, the major drawbacks of copper are its low adhesiveness to the substrate and its high diffusion ability. To overcome these problems, titanium-copper multilayers are used in microfabrication. Titanium shows good adhesion to a substrate, low diffusivity and good barrier properties [4]. Consequently, finding an etchant which allows selective etching of titanium in presence of copper becomes essential.

Hydrofluoric acid and its combination with nitric acid or hydrogen peroxide are common solutions used for wet etching of titanium. However, hydrofluoric acid shows low selectivity towards silicon dioxide which is often used as a barrier layer for microelectronics and therefore not suitable for instances of Ti/SiO<sub>2</sub> interfaces (Eq.(1) and Eq.(2)).



Furthermore, hydrofluoric acid is a highly hazardous chemical, requiring safety procedures and caution in handling.

The present work investigates the possibility of selective wet etching of titanium towards copper in hydrofluoric free solutions. Corrosion behaviour of titanium and its alloys in orthophosphoric and sulphuric acids has been subject of investigations of several research groups [5-9]. Other non-hydrofluoric titanium etchants based on hydrogen peroxide or its mixture with ammonia are mentioned in literature [10-14]. The use of acids (H<sub>3</sub>PO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub>) as well as a mixture of H<sub>2</sub>O<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O for etching titanium in microfabrication was studied. It is shown that the use of the referred acids leads to a formation of sidewall ridges at the edge of Ti-structures. This makes the surface quality of the microstructures unsuitable for microfabrication.

## 2. Experimental Details

Two different wafer types were used in the present work. Titanium films of 100nm thickness as well as Ti/Cu/Ti multilayers with a thickness of 50nm/1µm/40nm, respectively, were deposited onto Pyrex wafers. Titanium and copper films were deposited by reactive magnetron sputtering using Oerlikon (Balzers, Principality of Liechtenstein) LLS EVO sputtering device equipped with AK 515 sputtering cathodes. Titanium targets of 99.9% purity and copper targets of 99.995% purity from Umicore (Balzers, Principality of Liechtenstein) at plasma power of 1.5 kW were used.

After deposition the wafers were structured using photolithography. Lithography was carried out on a SUSS MA6 Mask Aligner (Süss Microtech AG, Germany). Photoresist AZ 1518 from AZ Electronic Materials (Merck) was used. Adhesion promoter AZ Ti-Prime purchased from Microchemical GmbH, Germany was applied. The wafers were spin-coated with adhesion promoter (AZ Ti-Prime), followed by a positive tone photoresist (AZ 1518) with a final thickness of 2.4  $\mu\text{m}$ . A soft bake step of 80 seconds on a 100°C hot plate was performed. The exposure took place on a SUSS Mask Aligner MA6 with a broadband illumination and an intensity of 30  $\text{mJ}/\text{cm}^2$ . The wafer was then developed in AZ 726 MIF for 45 seconds in single puddle mode on an EVG 101 and then rinsed with deionized (DI)water and spin dried.

Scanning electron microscopy (SEM)images were obtained using Jeol JSM-7100F (Japan) equipment. Thickness measurements were performed with a profilometer Dektak 8 (Bruker, USA).

Acid solutions of different concentrations were prepared by dilution of concentrated acids with DI-water. The influence of temperature was investigated between 70°C and 90°C in phosphoric acid and between 65°C and 85°C in sulphuric acid. Etching of Ti/Cu/Ti multilayers was performed in a mixture of ammonia, hydrogen peroxide and water at room temperature. Copper layers were etched with a CupraEtch™ DE Solution from Atotech (Atotech Deutschland GmbH, Germany) at about 40°C. The etch rates (nm/min) of the etched samples were calculated by dividing film thickness (nm) by the etching time (min).

### 3. Results and Discussion

The Pyrex substrate was coated with a titanium layer (100 nm thick) and structured with 2.4  $\mu\text{m}$  thick photoresist. In a subsequent step the wafer was diced into fragments of approximately 2  $\text{cm}^2$  pieces for both experimental series. The samples were etched in orthophosphoric acid and in sulphuric acid. Solutions of various concentrations were prepared to investigate the influence of acid concentration on etch rate of titanium. Additionally, the influence of temperature on etch rate was studied. To find out optimal etching conditions the value of the etch rate, the impact on photoresist degradation and the size of the under-etching were taken into account. It was shown that an increase in acid content as well as an increase in temperature leads to a rise of the etch rate but amplifies photoresist degradation at the same time.

Tab. 1. *Experimentally determined etch rates of titanium in orthophosphoric acid of different concentrations and at the different temperatures.*

Concentration of $\text{H}_3\text{PO}_4$ , %	Etch rate of titanium at different temperatures, nm/min		
	70 °C	80 °C	90 °C
50	7.5	15.3	30.3
61	9.2	18.5	48.8
66	10.6	21.4	75.0
70	14.5	34.1	-
75	14.9	35.9	-

The results of Ti etching in orthophosphoric acid are summarized in Table 1. The samples etched at 90°C in  $\text{H}_3\text{PO}_4$  of various concentrations show strong degradation of photoresist. Therefore no etching experiments were performed at this temperature with highly concentrated  $\text{H}_3\text{PO}_4$ . The optimal results were achieved using 61%  $\text{H}_3\text{PO}_4$  at 80°C. These

conditions enable the combination of an acceptable etch rate with a minimum photoresist erosion. The average size of the under-etching at these conditions is about 1.7 $\mu\text{m}$ .

The etch rate of titanium in sulphuric acid is significantly higher than in orthophosphoric acid. For example a Ti etch rate of 63.2 nm/min in 46%  $\text{H}_2\text{SO}_4$  at 80°C was achieved. The size of under-etching at these conditions is approx. 3 $\mu\text{m}$ . At the same temperature the etch rate of Ti in 50%  $\text{H}_3\text{PO}_4$  is just 15.3 nm/min.

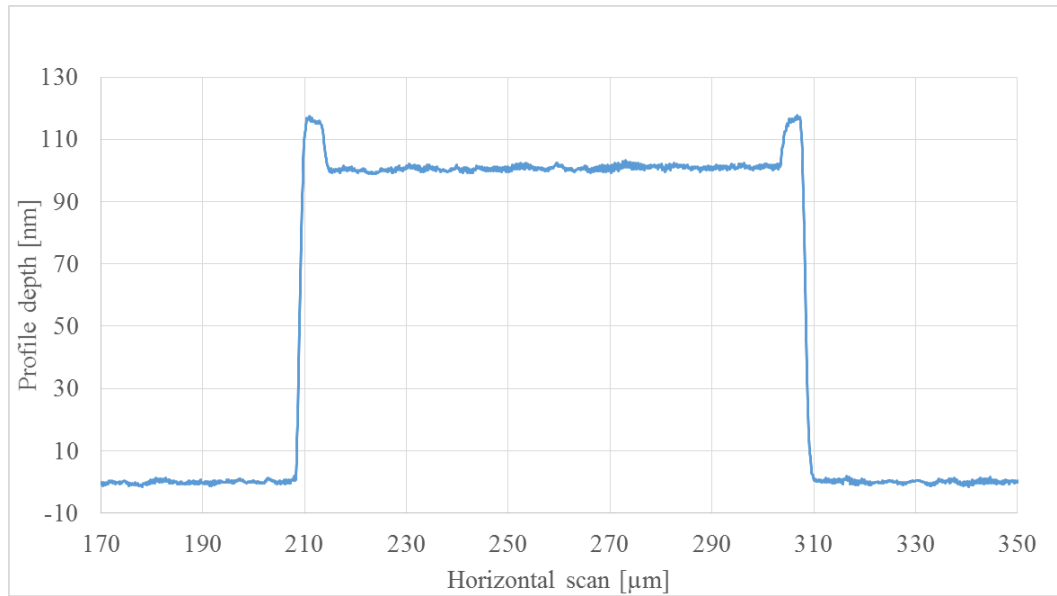
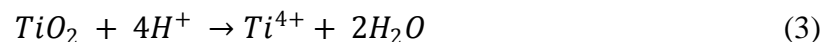


Fig.1: Profile of 100  $\mu\text{m}$  wide structure of Ti after etching in 61%  $\text{H}_3\text{PO}_4$  at 80°C.

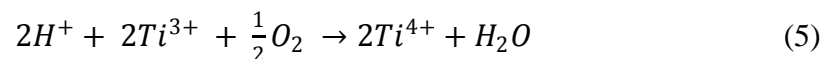
Surface investigation of the samples etched in both acids was performed. Independently from the etching conditions, formation of sidewall ridges at the edges of the structures was observed for all samples under investigation (Fig. 1). For explanation of this phenomenon the behavior of titanium in acid solutions should be considered. Devilliers et al. [12] have summarized the chemistry of titanium etching in acid media. It is known that the surface of titanium films is covered with a thin passivation layer of titanium dioxide which forms under air atmosphere [7, 9, 12, 15]. Therefore, the first step of etching titanium is dissolving of the  $\text{TiO}_2$  film (Eq.(3)).



When the protecting  $\text{TiO}_2$  layer is completely removed from the surface titanium starts to react with acid and  $\text{Ti}^{3+}$  ions are formed (Eq.(4)).

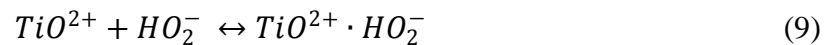
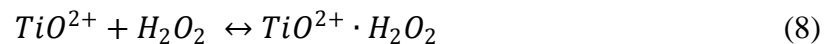
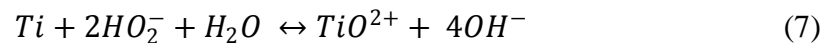
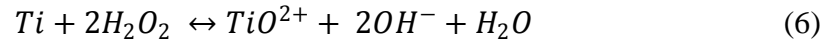


In aerated solutions,  $\text{Ti}^{3+}$  is oxidised to  $\text{Ti}^{4+}$  [12] (Eq.(5)).



It can be assumed that the oxygen which is dissolved in acid solution causes oxidation of titanium to  $\text{TiO}_2$  at the edge of the microstructures. It leads to expansion of titanium lattice and to formation of side wall ridges. Because of that the use of orthophosphoric acid as well as sulfuric acid for titanium etching in microfabrication is not suitable. The subsequent coating of the wafer with another metal or for example with a  $\text{SiO}_2$ -layer would lead to unacceptable quality of the surface.

No formation of sidewall ridges at the edge of the structures was observed when etching titanium in a mixture consisting of ammonia, hydrogen peroxide and water in a ratio of 1:3:5 at room temperature. This etching solution is widely used for a selective wet chemical etching of Ti towards silicon dioxide, silicon nitride, silicon and titanium silicide [14]. The composition of this solution corresponds almost to the composition of SC-1 “standard clean” solutions [2]. Verhaverbeke et al. [16] have noted that in presence of ammonia oxidizing agent in SC-1 solution is not only  $H_2O_2$  but  $HO_2^-$  – ions as well. The oxidation reactions of titanium with both oxidants are given in Eq.(6) and Eq.(7) [16]. Once  $TiO^{2+}$ -ion is formed, it reacts further with either oxidant, to form peroxytitanate complexes (Eq.(8)) and Eq.(9) [16].



Since etching of both Ti and Cu may occur in this solution this etchant is unsuitable for the etching of Ti/Cu/Ti multilayers. The SEM image in Fig. 2a shows the surface of the Ti/Cu/Ti-microstructure after etching in  $NH_3/H_2O_2/H_2O$  solution with a ratio of compounds 1:3:5. The edges of the microstructure show, that the oxidation of Cu occurs in this solution. The oxidizing species,  $HO_2^-$  – ions, oxidize Cu to  $Cu^{2+}$  (Eq.(10)).  $Cu^{2+}$ -ions in turn react with ammonia to a soluble copper-ammonia complex (Eq.(11)).

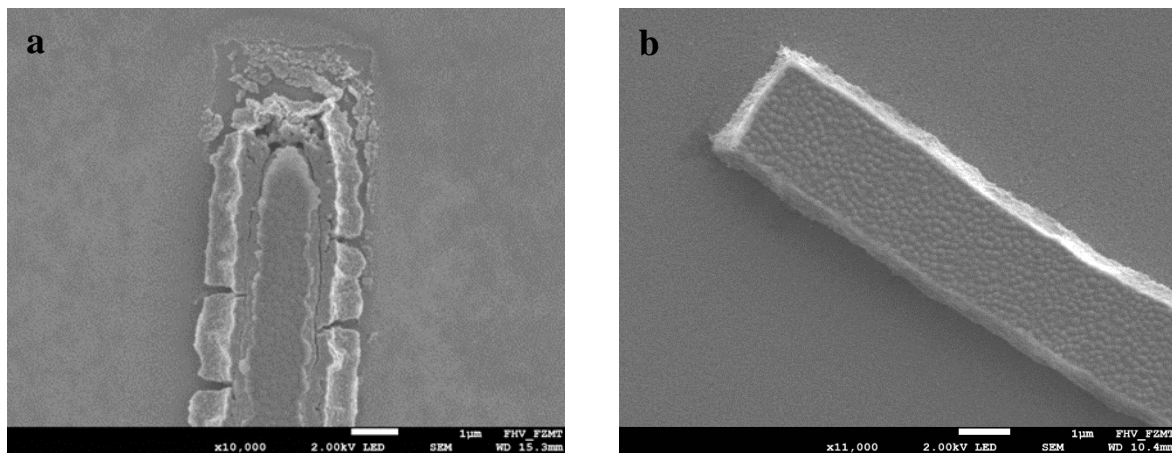
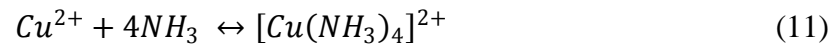
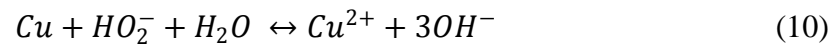


Fig.2: SEM images of Ti/Cu/Ti-microstructures on Pyrex substrate etched in  $NH_3/H_2O_2/H_2O$  solution mixed in a ratio of: a) 1:3:5; b) 0.01:2:8.

Richard et al. [17] have reported that etch rate of Cu in a mixture of ammonia and hydrogen peroxide depends from the pH value of the etching solution. The copper etch rate increases drastically for  $pH \geq 10$ . The etchant containing one part of  $NH_3$ , three parts of  $H_2O_2$  and five parts of water has a pH value above 10. Therefore it was predicted that a decrease of the pH value below 10 would lead to a slowdown of the copper etch rate.

Ti/Cu/Ti multilayers with a thickness of 50nm/1 $\mu$ m/40nm, respectively, deposited onto Pyrex were etched in a mixture consisting of ammonia, hydrogen peroxide and water in a ratio of 0.01:2:8 (pH=8.5). For these experiments 4-inch wafers were used. An etch rate of about 1.6 nm/min for Ti-film at room temperature was observed. Despite a low etch rate, this

solution shows a high selectivity in the etching of Ti towards Cu in Ti/Cu/Ti multilayers. No damages at the edges of the microstructures were observed (Fig. 2b).

#### 4. Summary and Conclusions

Selective wet etching of structured titanium films in presence of copper was investigated. Thin films of Ti as well as Ti/Cu/Ti multilayers were deposited onto Pyrex wafers using sputter deposition. Orthophosphoric acid, sulphuric acid and mixtures consisting of ammonia, hydrogen peroxide and water with different concentration ratios were used for etching of titanium. It was shown that etching of titanium in orthophosphoric and sulphuric acids leads to the formation of sidewall ridges at the edges of the microstructures. Formation of sidewall ridges makes the use of orthophosphoric and sulphuric acids for etching of titanium unsuitable for microfabrication. The use of a mixture consisting of ammonia, hydrogen peroxide and water in a ratio of 1:3:5 for titanium etching shows no formation of sidewall ridges at the edge of the structures. However, this etchant shows a low selectivity towards copper in titanium–copper multilayers and an undesired oxidation of copper. It was shown that a selective etching of titanium in presence of copper can be achieved by etching with the same compounds but in a mixture ratio of 0.01:2:8 (pH=8.5).

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