Selective Alkaline Wet Etching of Al and AlCu Using a Phosphoric and Nitric Acid Free Formulation

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Introduction

Wet chemical metal etching presents a viable alternative to dry etching techniques in semiconductor processing. It is commonly performed using acid-based solutions in the presence of oxidizing agents. The PAN-etchant –a mixture of phosphoric, acetic, and nitric acids in aqueous solution– has been employed for aluminium etching [1] and has also proven effective for metals like nickel and copper [2]. In microelectromechanical systems (MEMS) fabrication, aluminium and nickel layers can be exposed simultaneously to the same etchant, making the solution's selectivity a critical parameter [3]. Furthermore, phosphoric acid waste management poses significant challenges [4]. At the CEA-Leti facility, these chemistries are handled through strict protocols, with liquid waste and emissions subject to environmental monitoring. Regional restrictions on nitric acid usage further complicate this application [5]. Alkaline etching, as predicted by Pourbaix diagrams [6], offers a potential alternative and has been developed in other engineering contexts [7]. However, in semiconductor manufacturing, the high pH of such solutions often renders them incompatible with photoresist (PR) materials used in photolithography.

Experimental

Representative 200mm wafers of pure aluminium (Al, 100%) and aluminium-copper (AlCu, 0.5%Cu) have been prepared by physical vapor deposition (PVD) in full-sheet and patterned wafers to evaluate alkaline wet etching solutions. Pure Al has been deposited at 200 and 350°C, with a 200nm thickness, while AlCu at 200 and 450°C, with a 440nm thickness. Patterned wafers have been structured using PR masks, either I-Line (365nm) or a DUV (248nm), with features sizes (critical dimensions, CDs) ranging from 500nm to 50µm. Pattern types included lines/spaces, and pillars/holes geometries. This study has focused on structures ≈1µm. Depending on the integration scheme, some technologies require "low temperature" (200°C) processes due to thermal budget constraints, while others allow "high temperature" processing (350, 450°C). This wafer set enables a comprehensive evaluation of Al and AlCu etch behaviour under varying thermal and patterning conditions.

An extensive screening of alkaline solutions, including quaternary ammoniums, tertiary amines, and alkali salts, has been carried out to assess their performance in etching Al and AlCu wafers. Beaker tests have been performed using small coupons (2cm x 2cm) cut from full-sheet and patterned wafers, immersed in 25mL of solution at varying conditions: immersion time, temperature, stirring speed, and solution pH. After treatment, deionized water has been used for rinsing and clean dry air (CDA) for drying. Partial etch rates (ER) have been determined by surface resistivity measurements and complete metal layer etching by time to clear (TTC).

An alkali salt has been used to study the AlCu TTC while simultaneously assessing compatibility with DUV PR as a function of pH. Optical and scanning electron microscopy (SEM) have been employed to characterize these coupons (Table I). A screening of chelating agents and surfactants has also been conducted to evaluate the solution's ER and wetting properties (Table II). Based on these initial findings, a formulated solution has been prepared. The effect of deposition temperature and presence of Cu on full-sheet coupons has been examined through ER measurements (Figure 1, A). The solution's compatibility with Ni, as well as other metals and dielectrics, has been assessed by ellipsometry and surface resistivity measurements (Figure 1, B). The solution's ER has also been evaluated after 6h at 50°C, and as a function of concentration of AlCu dissolved. Finally, immersion tests have been performed on Al and AlCu patterned coupons using TechniEtch D-BAL220, before and after PR stripping (Figure 2).

Results

At $pH>13$, the ER of AlCu has increased significantly, but the PR has also been removed. As a result, the AlCu under the mask has been exposed, and the solution has etched the entire metal film. At $pH<12$, AlCu has not been fully etched, even after 30min of immersion. A favourable balance between PR compatibility and AlCu etching has been achieved in the pH range of $12<pH<13$. Some chelating agents have increased the ER of the solution which in turn has decreased the immersion time and the PR exposure. The selected chelator has not altered the colour of the initial solution and is compliant with wastewater regulations. Generally, surfactants have decreased the solution's contact angle; however, some also have affected the PR. In presence of these surfactants, the PR has been partially dissolved and its structure modified. At low deposition temperature, the ER of pure Al is lower than that of AlCu. This difference in ER is not observed at high deposition temperatures. For AlCu, the ER at low deposition temperature is higher than that at high temperatures. This effect may be attributed to the increased formation of Cu agglomerates. The additives identified have significantly improved the solution's performance at low pH. The solution has proven compatible with Ni, Cu, and other evaluated materials. The solution has also proven stable at 50°C for at least 6h and after 186.5mg of AlCu/L have been dissolved. When evaluated on patterned wafers, the resulting features have exhibited vertical sidewalls and minimal undercut. The etching process has shown to be anisotropic and well-controlled. These features have been consistently reproduced on both Al and AlCu. The solution has also successfully etched other aluminium alloys, including AlN, and AlScN.

Conclusions

The proposed alkaline solution, TechniEtch D-BAL220, has been formulated with carefully selected additives to optimize etching performance and material compatibility. It delivers equivalent etch performance to conventional PAN-based chemistries for Al and its alloys, while demonstrating significantly lower etch rates on Ni and Cu. This enhanced selectivity improves process control in multi-metal integration schemes. In addition to its technical advantages, the solution is free from phosphoric and nitric acids, offering a more environmentally sustainable alternative. It also exhibits excellent thermal stability, high metal loading capacity, and enables the formation of well-defined, anisotropic features. Full-wafer immersion tests on patterned substrates are ongoing to evaluate its suitability for industrial-scale deployment.

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Table I. Immersion tests of AlCu (440nm, 450°C) with alkali salts at different pH. Etching performance and resist compatibility have been reported by TTC and characterized by optical (x100, except pH13 x1k) and scanning electron microscopy (x20k) imaging on full-sheet and patterned coupons.

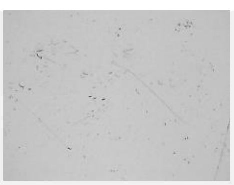
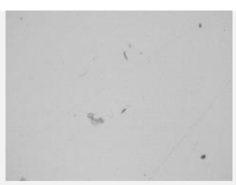
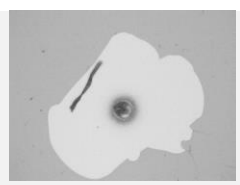
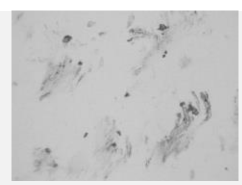
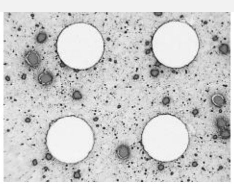
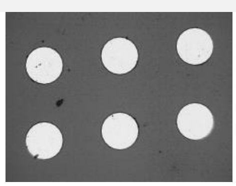
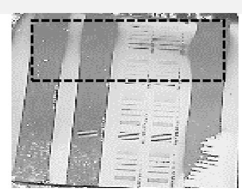
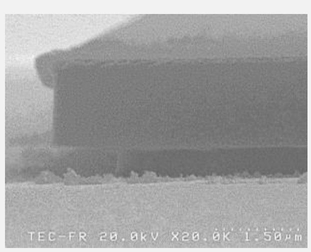
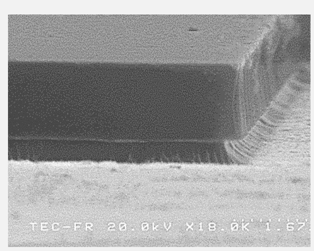
pH of solution	*11*	*12*	*13*	*14*
Immersion time	30 min	6 min 48s	2 min 41s	45s
Etch rate	< 14.7 nm/min	64.7 nm/min	164.2 nm/min	586.7 nm/min
Full-sheet optical images				
Patterned optical images				
Scanning electron microscopy	-			-
Comments	Incomplete etching.	Slow ER but complete. PR starts to be affected.	Good ER, but some areas of PR exhibit blisters.	High ER but PR is dissolved.

Table II. General tendencies of selected chelating agents and surfactants when added to the alkali-based solution. Etch rates and wetting properties are reported for AlCu (440nm, 450°C).

Formulation	*Solution w/o additives*	*+ Chelating agent*	*+ Surfactant*
Etch rate [nm/min]	106	200-250	150-180
Contact angle [°]	80	60-80	40-60

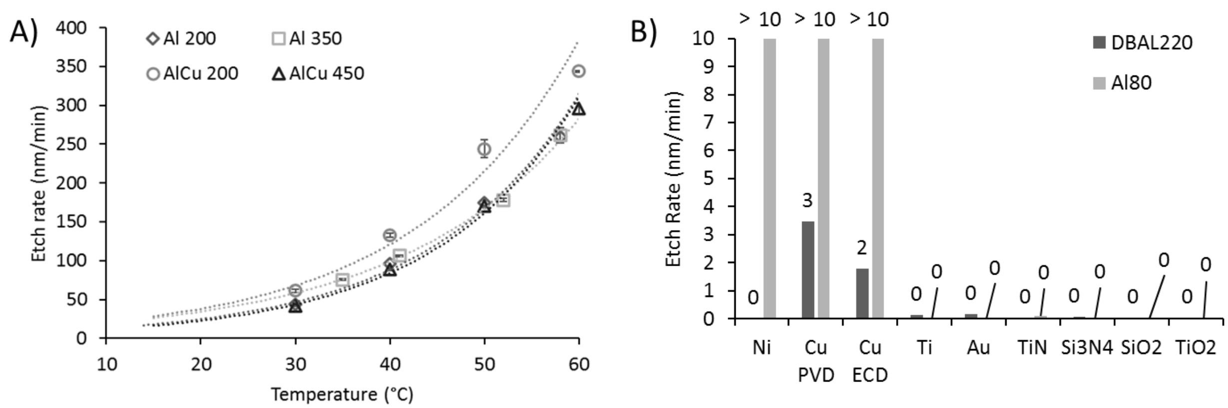


Figure 1. Etch rates of TechniEtch D-BAL220 on A) Al (200 or 350°C) and AlCu (200 or 450°C) substrates as a function of temperature, and B) metals and dielectrics at 50°C compared to TechniEtch Al80 (PAN-etchant).

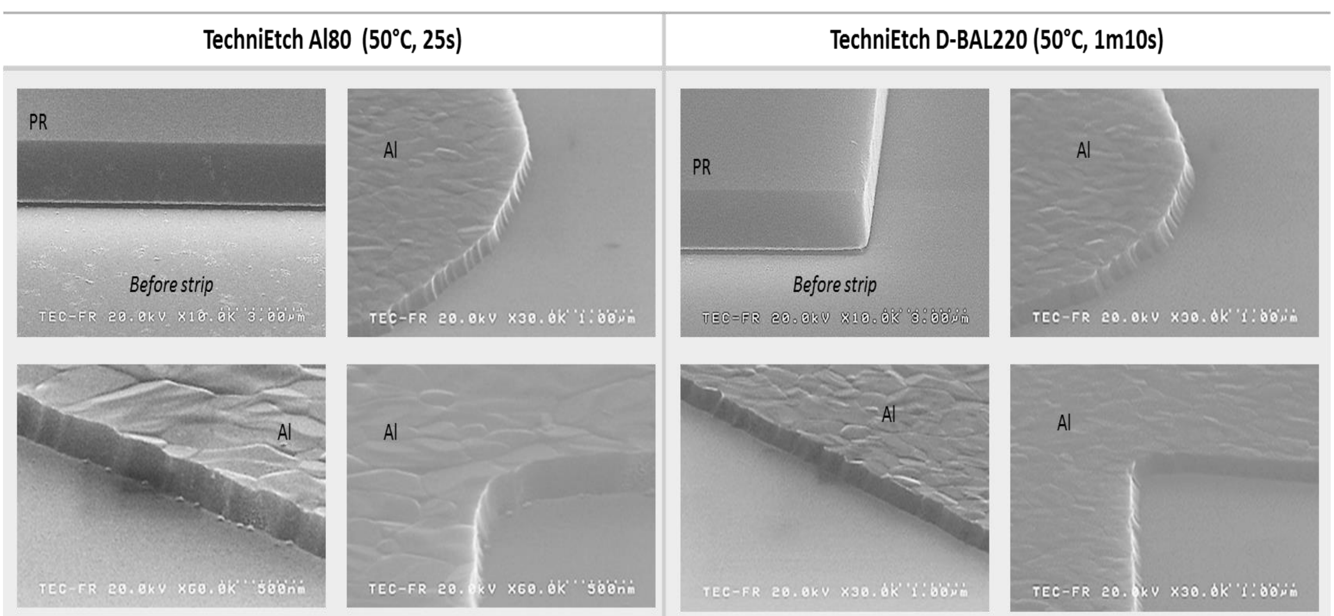


Figure 2. SEM images after treatment of Al patterned coupons at beaker level with TechniEtch D-BAL220 and TechniEtch Al80 (PAN-etchant) at 50°C before and after stripping of PR material.