Customized Chemical Compositions Adaptable for Cleaning Virtually All Post-Etch Residues

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Abstract

A post-etch residue cleaning formulation, based on balancing the aggressiveness of hydrofluoric acid with its well-known residue removal properties is introduced. In a series of investigations originally motivated by the cleaning challenge provided by high-k dielectric-based residues, a formulation platform is developed that successfully cleans residues resulting from the plasma patterning of tantalum oxide and similar materials while maintaining metal and dielectric compatibility. It is further shown that the fundamental advantages of this solution can be extended to the cleaning of other, more traditional post-etch residues, with no sacrifice in compatibility, as demonstrated by measurements on blanket films and through SEM data.

Introduction

The types of formulations employed in the cleanup of post-plasma etch residues (PER's) have evolved dramatically since the advent of plasma patterning for semiconductor interconnect. Before plasma etching grew to prominence, wet chemical processes in the semiconductor industry were largely confined to photoresist stripping, wet etching and standard cleans. The appearance of plasma-generated residues based (mostly) on patterning of Al, W and silicon oxide necessitated the creation of new classes of cleaning materials, some of which were derived from solvents and etchants, and others of which were based on entirely new reaction chemistry, such as PER cleaning chemistries based on hydroxylamine, and other highly-engineered formulated blends [1,2].

Similarly, and driven by product performance demands, the semiconductor industry has employed an ever-increasing number of materials in its products. Thus, the variety of PER's that need to be cleaned during semiconductor manufacturing has increased over time, but most rapidly in the last decade or two. What has not changed is the set of requirements for a PER cleaning chemistry, which simply stated involve the removal of unwanted residues in the presence of frequently-sensitive metal and dielectric materials. This removal needs to be accomplished quickly, at moderate temperatures, using benign ingredients that allow for easy rinsing, drying and chemical disposal – all at reasonable cost.

The proliferation of materials and process demands might then lead to a wide array of cleaning chemistries, different classes of which are highly tuned for highly-specific processes such as Al line cleaning, via clean, Cu damascene post-etch cleans, Ti etchant/clean combinations, cleans needing compatibility with "exotic" metals such as Co or Ru, and so on. And to some extent this cleaning product proliferation has been observed.

Especially challenging is the cleaning of PER's created during plasma etching of high-k materials such as tantalum, zirconium and hafnium [3]. These challenges were observed during early work on patterning of metal oxides and silicates for use as replacement gate dielectrics for silicon oxide, and persist today with increasing use of these kinds of materials in MIM (Metal-Insulator-Metal)

decoupling and other capacitors and other circuit elements [4]. These are notoriously resilient and difficult to remove, a challenge that is exacerbated when other materials, especially metals such as aluminum, are present during the cleaning process.
Thus, the cleaning challenge related to refractory metal oxides is the removal of PER in the presence of more chemically-reactive metals and potentially delicate dielectric materials; and more ambitiously, to extend chemical formulations capable of meeting this challenge to successfully achieve other cleaning demands such as those mentioned above.

Recent work addressing these challenges demonstrated dramatic improvements in the state of the art, and established highly selective wet chemical cleaning products for refractory metal-based residues through precise control of hydrofluoric acid aqueous solvation in combination with water and polar aprotic solvents. As a result, diluted hydrofluoric acid (DHF) is frequently employed as an active ingredient in these cleaning processes Table I.

stack	Standard industry Cleaners for post PER residues removal			
Al, Ti, W	Hydroxylamine	Acid mix	Organic solvents/ Fluoride	Diluted Sulfuric Peroxide
Cu, TaN, Ta		Organic acid	organic acid / DHF	DHF
Si, Hf, Ta, Nb, Zr			H_2SO_4/HF	DHF

Table I: standard post dry etch residues cleaners

With the fundamental underpinnings of this success better understood, the objective of the work presented here is to generalize the cleaning efficacy for high-k residues to Al, Cu and other types of plasma byproducts created during the manufacture of advanced semiconductor products. This can be achieved by manipulation of the three key chemical formulation variables mentioned here– water, fluoride, aprotic solvent concentrations and solution pH.

Experimental

Blanket & patterned wafers were obtained from the different customer's sources.
Patterned wafers:

- Metal interconnection:
  - Al/Cu – Ti/TiN barrier after BCl_3/Cl_2 dry etch and CF_4/ O_2 ashing
  - W lines on Ti/TiN barrier after dry etch SF_6/Ar or NF_3 / N_2 ashing
- CAP MIM (PAD & lines)
  - USG/Al/TiN/Ta_2O_5 after etch and ashing (process not disclosed)
  - Cu/TaN/Ti/Al/TEOS after etch and ashing (process not disclosed)
- Piezoelectric Filter
  - Al alloy after etch and ashing (process not disclosed)

Etch rates of metals were measured by 4-point probe, and dielectrics using an Ocean Optics NANOCALC reflectometer. Scanning electron micrographs were generated on a Hitachi 4500. The cleaning process where performed at LETI and other partners on different single wafer tool platforms.

Results and Discussion

The studies were focusing on developing a selective clean that is simultaneously capable of the removal of resilient high-k PER's and traditionally less tenacious residues formed in the presence of metals such as Al and Cu while preserving metal integrity. Since the composition of PER's tend to have similarity with metal oxides, especially after ashing, it is instructive to think of a cleaner's chemical selectivity in terms of its ability to dissolve amorphous metal oxides – such as those created during an O2 ashing step – while limiting attack on their corresponding polycrystalline metal oxides [5].

This work illustrates the possibility to do so, through careful control of i) solution pH; ii) water content and iii) the judicious choice of spectator counter ions present when formulating with weak acids and bases for the provision of common active species (mostly hydronium ion, H_3O^+ and fluoride, F^-).

Determination of optimal pH and counter ion effect.

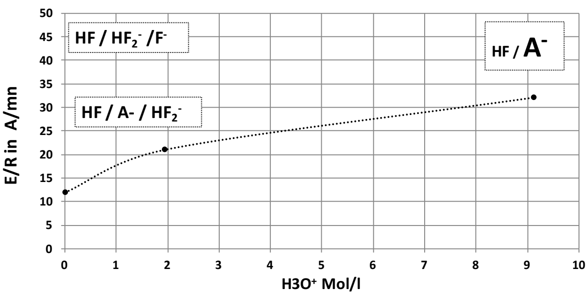


Figure 1: HfO2 ER with acid mol/l

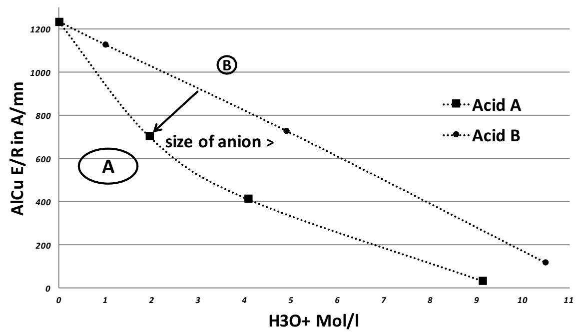


Figure 2: Al/Cu ER with acid mol/l- Impact of the acid counter ions A & B on ER

Further investigations and chemical screening allowed to confirm the great ability of some strong acids to be able to drift the pH to very acidic region enhancing etch rate of high-k based PER and conjointly improving overall Al compatibility (Figure 1& 2). In addition, it was also observed that depending of the nature, property and size of the acid's counter ions, extra performance in terms of metal compatibility and selectivity could be reached.

Etch Rates and Cleaning Performance in Low-Water Environments. The etch rate behavior of low-water-content solutions containing hydrofluoric acid (HF) on HfO_2 and SiO_2 has been described and monitored for different densities and doping doses; for example, is reported in the literature [6] indicating 12nm/min for TEOS and 25-70nm/min for sputtered oxide at 35C in a 7/1 DHF [7]. For comparison HfO2 in BOE 10% HF is etched around 3-5nm/min while aluminum by more than 100nm/min, the new formulation and ingredients fine tuning allowed to maintain the etch rate of HfO2 while hindering Al attack in DHF blends (Table II: Al ER < 1,5nm/min).

In order to expand the application space for this formulation set, similar data have been generated for Ti and TiO_2 (Figure 3) and other common materials (Table I) in a solution now known commercially as TechniClean IK 73 at 25 °C.

The Ti and TiO_2 data are very interesting and illustrative of the selectivity afforded by IK 73 and the determination of a process window available for cleaning of Al/Ti-based residues. The red line shows the removal of blanket Ti, and indicates that no removal of passivation-type Ti occurs for just over 60 sec. By contrast, the removal of as-deposited TiO_2 starts occurring almost immediately, so in this case (where the thicknesses of the Ti and TiO_2 are x and y, respectively) there is an available process window (shown by the vertical dotted blue lines) during which complete removal of TiO_2 takes place prior to erosion of Ti passivation. While these data are on blanket surfaces, they indicate, in combination with the values in Table II, the applicability of this approach to cleaning applications normally considered more sensitive than those involving high-k materials

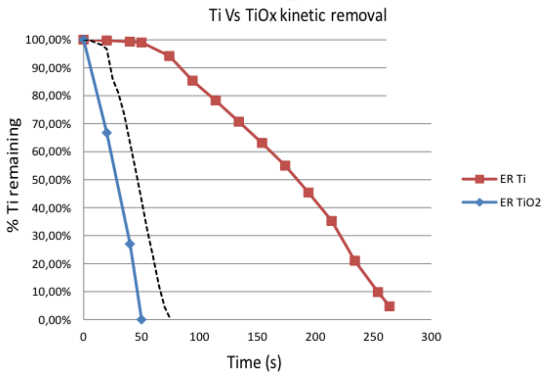


Figure 3: Ti and TiO_2 etch rates in IK 73

Material	Etch Rate (nm/min) 25°C
HfO_2	1
Ta_2O_5	0.6
thermal SiO_2	1.2
TiO2	8
PVD Al	< 1,5
CVD Cu	<2

Table II: Etch rates in IK 73

This has been verified as illustrated by SEM (Figure 4), showing effective residue removal in a conventional Al/Cu/Ti/TiN/SiO_2 line application.

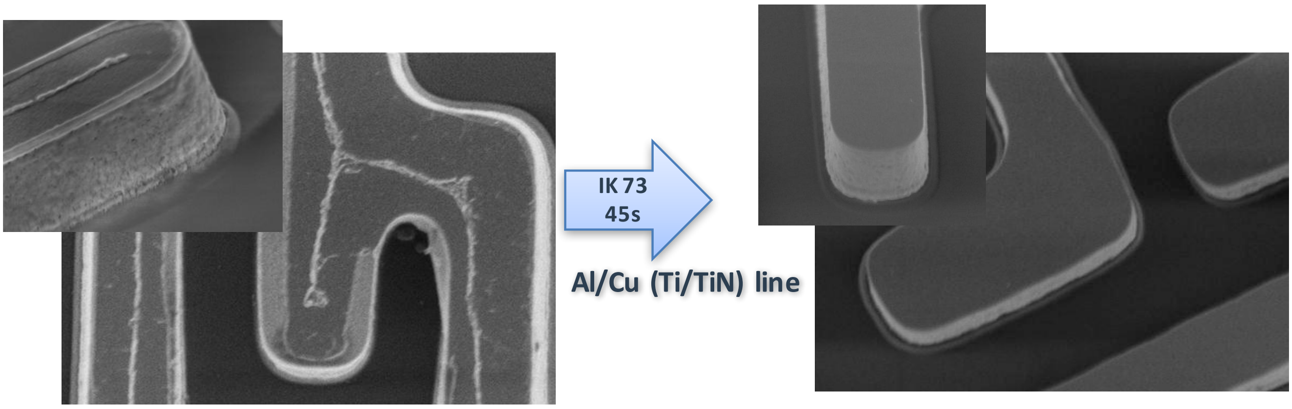
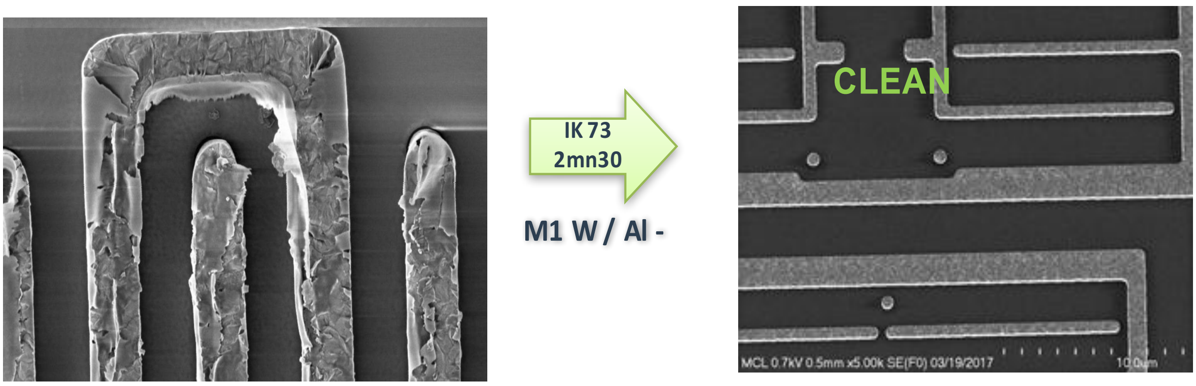


Figure 4: Al/Cu line cleaning 0,5µm width (25 °C, single-wafer application)

Etch Rates and Cleaning Performance through careful increase in [H_2O]. The effectiveness of the base formulation technology in IK 73 can be highlighted by the careful manipulation of the ratios of the three primary components. In this example, formulation tuning leads to a cleaning solution that at 20 °C and over a period of few minutes provides excellent cleaning and selectivity to the metal stack over several different metal and barrier features (Figure 5).



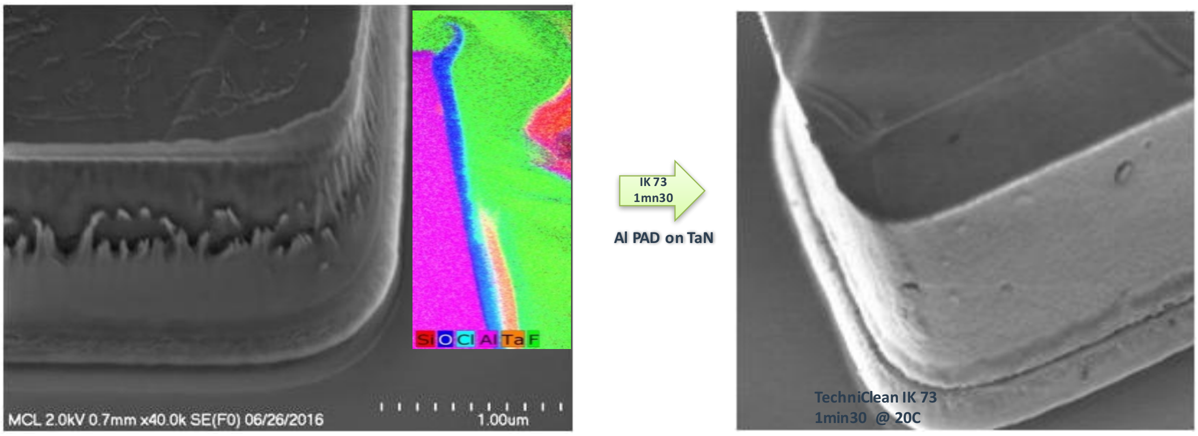


Figure 5: SEM images showing residues created after plasma etch (W, Al/TaN) and effective cleaning after 3 min, 20°C in single wafer tools.

Conclusions

Traditionally, the aggressiveness of hydrofluoric acid in semi cleans has been controlled by lowering its concentration in water, as demonstrated by the wide applicability of dilute HF (dHF and dHF+), BOE and a wide variety of proprietary cleaning products based on HF.
This novel semi-aqueous formulated HF approach appears to be extendable and tunable to virtually all semiconductor stacks and interconnect technologies. TechniClean IK73 delivers clear advantages based on cleaning ability (especially of chemically inert residues made from Ta, Hf, Zr based) with high selectivity to sensitive substrate materials such as Cu and Al. Additionally, the solution offers very high selectivity between amorphous and as-deposited high-K oxide and metals, improving the overall residues cleaning performance, feature cleanliness and integrity.

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