Aspects of the Controlled Chemical Etching of Thin Metal Films, in Particular Multilayer Type

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Wet chemical processing plays a vital role in the microelectronics industry. A modern Fab contains a profusion of front and back-end-of-line (FEOL and BEOL) wet processing tools. BEOL wet processing has become increasingly important as the number of metal levels has increased and feature sizes have relentlessly shrunk. The presence of a metal layer generally precludes the use of the aggressive chemical steps used in the FEOL. This talk will focus on the controlled chemical etching of thin films of metals and alloys, e.g., ferromagnetic (FM) type, with emphasis on inhibition by passive films, etch selectivity, and avoidance of Galvanic effects.

The chemical etching of metals involves both localized anodic (metal oxidation) and cathodic (oxidant reduction) reactions. Corrosion is an unwanted form of metal etching or reaction. The cathodic reaction is a critical, enabling feature of metal etching (and of corrosion). It is influenced by several factors, including the following: the standard potential of the oxidant; the concentration of the oxidant in solution; rate-limiting mass transfer, which influences etching rate uniformity; in the case of Galvanic effects, the difference in, a) the area, and b) the kinetics of oxidant reduction, of the surface supporting the cathodic reactions relative to the surface undergoing etching; and, the presence of inhibition films.

Magnetic tunnel junctions (MTJ) (1) possess thin FM films. Their 20-50 Å z-direction thickness relative to the x-y dimensions of patterned MTJ elements (> 1000 - 2000 Å) makes them attractive model systems for studying thin metal film chemical etching. In the present work, MTJ stacks typically possessed the following layers: antiferromagnetic (AF) (e.g. IrMn, PtMn) / fixed-moment (pinned) FM layer (e.g. 15 Å $Co_{90}Fe_{10}$) / 12-15 Å AlO_x tunnel barrier / free FM layer (e.g. 50 Å $Ni_{81}Fe_{19}$) / capping layer (e.g. 100-200 Å Ta). Due to the thin nature of the FM films, lateral etching should be minimal, although Galvanically-enhanced etching of the pinned layer should be expected if care is not taken. The MTJ FM films ideally require weak etchant solutions in order to facilitate controlled etching, minimal lateral etching, and etch selectivity. However, with such solutions, surface passive films play a major role in the etching behavior of air- and reactive ion etch (RIE)-exposed FM films, in particular Ni-alloy layers (2).

Prior to chemically etching the soft layer, the Ta cap layer was removed using SF_6/(10 % Ar) RIE. Rapid dissolution (≃ 2 Å/s) of the freshly-exposed $Ni_{81}Fe_{19}$ layer occurred upon immersion in a dilute solution of moderately long-chain dicarboxylic acid, e.g. 0.05 mol dm^{-3} suberic (1,8-octanedioic) acid, pKa ca 5.0) (2). Following Ta removal, x-ray photoelectron spectroscopy (XPS) confirmed the presence of minute amounts of S on the surface of $Ni_{81}Fe_{19}$, which caused the passive film formed on $Ni_{81}Fe_{19}$ during RIE, mainly NiF_x, to poorly protect the Permalloy.

If the alumina tunnel barrier thickness exceeded ≥ 12-15 Å, vibrating sample magnetometry (VSM) and XPS confirmed that, etch selectivity was such that the more reactive $Co_{90}Fe_{10}$ just below the tunnel barrier remained intact (the barrier protected the $Co_{90}Fe_{10}$). The dicarboxylic acids, $HOOC(CH_2)_nCOOH$, with n = 5 or 6, which do not form energetically-favorable chelate complexes with Al^{+3}, reacted least with the tunnel barrier alumina, as compared to, e.g., malonic acid (n = 1) which can form relatively stable 6-membered ring chelate compounds. An advantage of stopping the etching at the AlO_x is that Galvanic corrosion reactions are avoided (FM alloy in contact with noble metal-based AF layer).

Chemical etching can serve as an enabling fabrication method in certain emerging technologies, such as large-area substrate fabrication which requires inexpensive, high-through-put processes. An example is the paper-like electronic display (3). Self-assembled monolayers (SAMs), deposited by micro-contact printing (μCP) using elastomeric stamps (4), are being explored as pattern-transfer masks. In the contact regions, the alkanethiol preferentially reacts with the surface, typically Au, to form a dense monolayer. The exposed Au may be chemically etched in a ferri/ferrocyanide etchant (3).

Despite having the potential for broadening the scope of chemical etching, nonaqueous etching solutions have received little attention for metal etching. An example of a relatively environmentally friendly etching process is the selective etching of Cu in the presence of Co (5), which is usually the more reactive metal in aqueous media. Cupric ion was employed as the oxidant in anhydrous isopropyl alcohol solvent. Cuprous ion, the oxidant byproduct, was stabilized by an alkene, e.g., 2-butene 1,4 diol. In an aqueous etchant, one would have to passivate the Co surface in order to selectively etch Cu in the presence of Co.

In conclusion, the chemical etching of thin metal films possesses many challenges when factors such as selectivity are important, and dissimilar metals are present. As in the past, integration with dry etching methods will continue to be a key feature of solution-based etching methods. Ever increasing pressure to come up with environmentally friendly and more cost-effective solutions will tend to drive innovation of new etching chemistries, both as replacements for existing processes and for use in emerging technologies.

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References

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