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Roughness and uniformity control during wet etching of molybdenum

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Abstract

In this work the wet etching of molybdenum thin films was investigated for applications requiring controlled recess without roughening or pattern loading. First, continuous etching of Mo in alkaline and oxidative peroxide solutions was studied. Then, additives like glycine and diethylenetriamine were used and their effect on etch rate and roughness was assessed. Finally, we evaluated if the requirements for a stepwise etching approach for Mo recess using peroxide or ozonated water as the oxidizing step and ammonia as the oxide dissolution agent were met.

Introduction

Most metals used in interconnects, like W, Cu, Co, ... are polycrystalline with randomly oriented grains. The grain size, grain size-distribution and grain boundaries depend on deposition as well as on annealing conditions. The random distribution of grains and associated grain-boundaries as well as their potential random orientation pose a huge challenge on wet etching processes. Such polycrystalline surfaces typically become rougher and rougher as a function of recess depth. A huge problem for sub-10nm applications requiring almost nanometric etching precision in confined spaces uniformly across the wafer and within die.

Conventional, *wet* continuous etching processes, if not kinetically controlled, are prone to etching non-uniformities due to diffusion effects. Furthermore, *dry* plasma etching processes can create unwanted redeposition of reaction byproducts. Therefore, other etching concepts like atomic layer etching (ALE) might have a big impact on enabling metal integration in sub-10nm nodes. ALE is unique because it is making use of self-limiting reactions that only modify the thin top surface layer of the material. Different types of chemical modification reactions are conceivable, the crucial requirement being that the final modified surface layer is of a well-defined thickness (not necessarily “one” atomic layer). DeSalvo et al. reported one of the first *wet* ALE approach for GaAs and other III–V semiconductor materials using oxidation in solution followed by selective dissolution of the oxidized layer [1].

In this work we will focus on molybdenum, since it has potential to be used in interconnects, and more particularly for the fully self-aligned via's (FSAV) or buried power rails (BPR), two scaling boosters for which well-controlled metal recess is needed [2-4]. Other applications that might need this process is the lateral recess of the metallic word lines in 3D NAND multi layers [5]. In this work “wet-ALE or stepwise etching” will be compared with “continuous etching” of molybdenum.

Results and discussion

Continuous etching of Mo in ammonium peroxide mixtures (APM). In this first section, continuous wet etching of Mo will be discussed. Mo is in general well resistant to both acidic and alkaline solutions, however, when an oxidant is added, Mo is etched. In diluted ammonium peroxide mixtures (APM) for example, the Mo layer is not stable and etches. Figure 1 shows the change in resistance of different types of Mo films after exposure to different alkaline oxidative solutions. The pH value of all alkaline oxidative solutions, including the TMAH/H₂O₂ and TEAH/H₂O₂ solutions was kept constant (~pH 10.2). The resistance of the as-deposited Mo samples without anneal, as well as the N₂- and H₂-annealed samples show the same trend: an increase of the resistance of the metallic

layers. This increase in resistance can be due to etching, oxidation and/or roughening of the Mo film. This increase is much less pronounced for the forming gas (FG) annealed samples. This can be explained by the formation of Mo nitride. It is known that Mo, when annealed in forming gas, forms nitrides but *not* in just nitrogen gas [6]. These Mo nitrides form a kind of passivation layer that is less easily dissolved by APM compared to Mo oxides.

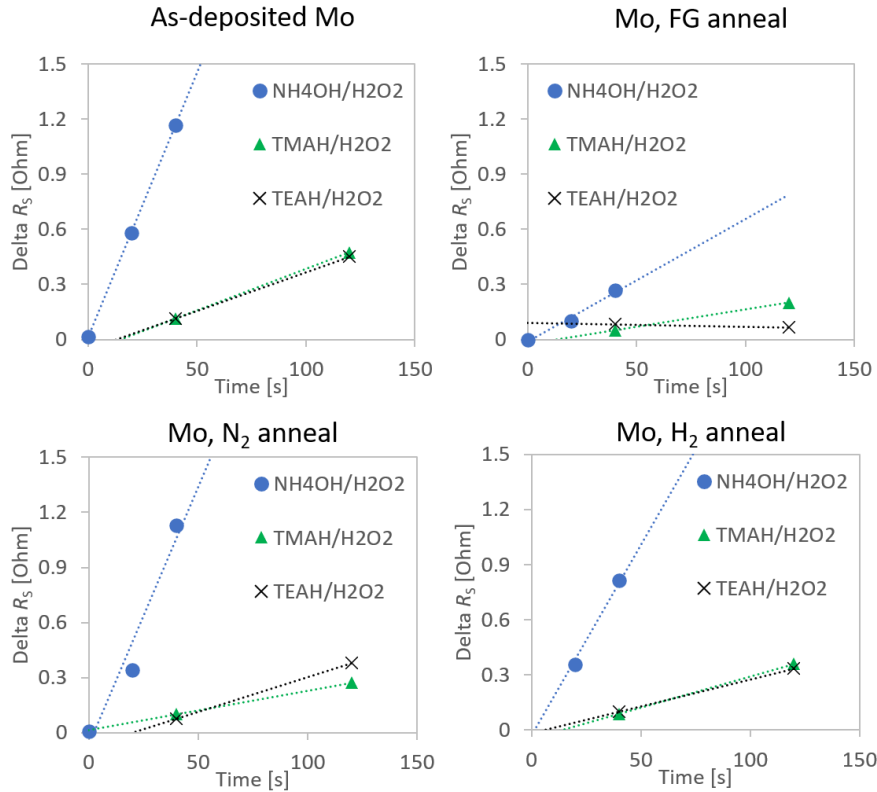
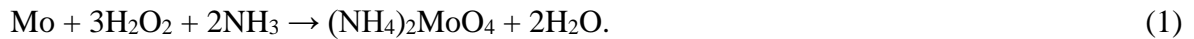


Figure 1: The graphs show the increase in sheet resistance of thin Mo films, annealed at 650°C in different gases, as a function of time of exposure to different chemical etching solutions. The pH of all OH/H₂O₂ solution is 10.

Another observation is that the resistance of Mo increases less in the TMAH/H₂O₂ and TEAH/H₂O₂ solutions, even if the total [OH⁻] is the same as in the APM solution. This apparent lower etch rate of TMA⁺ and TEA⁺ compared to NH₄⁺ containing solutions might be due to complex formation: NH₄⁺ forms a soluble complex with the oxidized Mo, (NH₄)₂MoO₄ (eq.1), which accelerates the etching process [7].



The effect of pH was also evaluated. Figure 2 shows the change in resistance of different types of Mo films after exposure to APM solutions with decreasing pH. The pH was made more acidic by the addition of citric acid. The resistance of the Mo increases slower going to less basic (pH ~8) and finally slightly acidic (pH ~6) H₂O₂-containing solutions. This can be explained by the formation of a passive MoO₂ film at lower pH or due to the reduced solubility of MoO₃ in acidic solutions: MoO₃ requires [OH⁻] ions to dissolve as molybdate (MoO₄²⁻) as shown in equation (2) [8].



Since the pH was adjusted with citric acid, one could argue that the citrate ions could also affect the etching of Mo. Citric acid will be present as free di- or trivalent citrate ions at pH values > 6 and can form highly soluble citrate complexes with Mo(VI) [9]. However, we do not notice an increase in the

oxidation or etching rate of Mo with increasing concentration of citric acid/citrate, but the opposite. Citrate is neither expected to adsorb to the surface and block the etching of Mo since it is negatively charged and will experience repulsion from the negatively charged Mo surface at pH >2 [10]. Thus, in summary, the citrate ion or ligand is not expected to increase, neither decrease the etching of Mo in above conditions and we conclude that $[\text{OH}^-]$ dominates the oxidation and etching behavior of Mo.

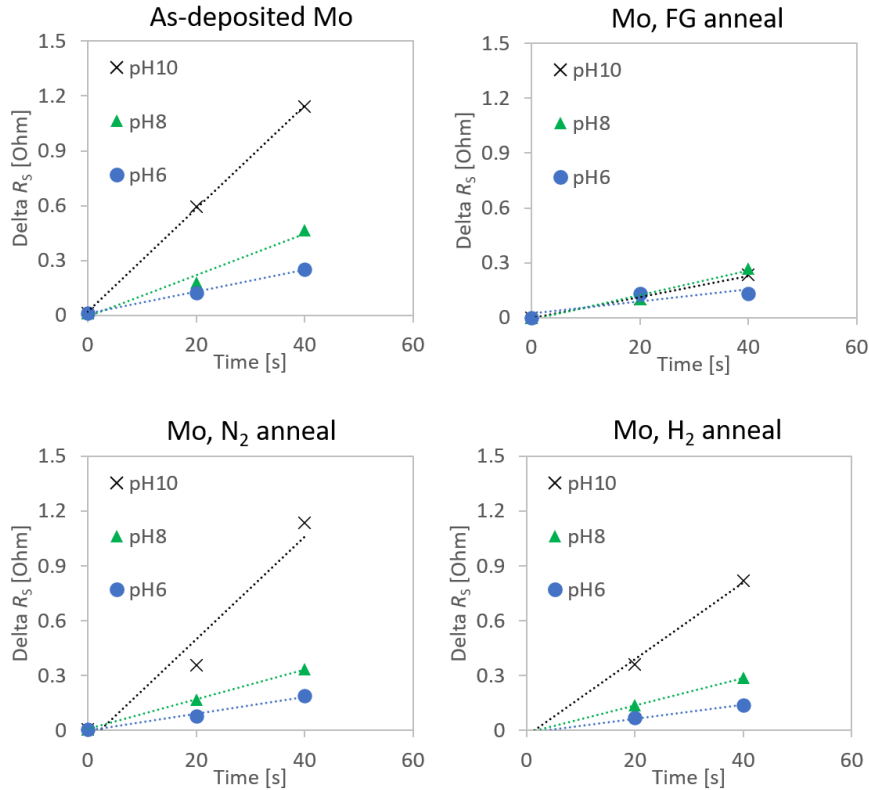


Figure 2: The graphs show the increase in sheet resistance of thin Mo films, annealed at 650°C in different gases, as a function of time of exposure to APM solutions for which the pH was adjusted by addition of citric acid.

As indicated in the introduction, roughness is *the* critical parameter to assess whether a solution can be used for those metal recess applications mentioned in the introduction. As a first verification, tilted and cross-section SEM images of the samples were done. Figure 3 shows a Mo film before and after treatment with a TMAH/H₂O₂ solution.

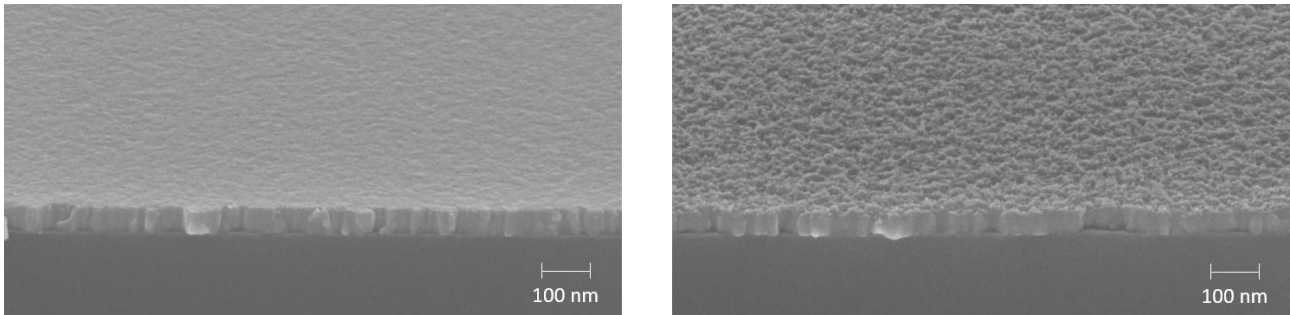


Figure 3: Tilted SEM of Mo before (left) and after (right) wet etching in TMAH/H₂O₂.

The roughness of the sample increased after 2 min. etching in this solution. This unwanted roughness increase was also observed for all other solutions described above. Moreover, when thickness loss was measured based on these XSEM images, it did not match the loss measured by R_s measurements, the loss measured by R_s being consistently higher. Therefore, delta R_s vs. time and not thickness loss vs. time was plotted in Figures 1 and 2. This mismatch between both measurements could be related

to (1) an “intrinsic” resistivity increases due to surface and/or grain boundary scattering effects, (2) a resistivity increase due to roughening and/or (3) a resistivity increase due to oxidation. In order to mitigate surface roughening, the use of additives and stepwise etching was attempted, and the results will be discussed in next two sections.

Effect of additives on the etch rate and roughness of Mo. In a first set of experiments, the additives glycine (Gly) and diethylene triamine (DETA) were added to solutions of ammonium peroxide (APM). Both additives result in lower Mo metal loss compared to the APM solution without additives, as observed by the smaller change in resistance (Fig. 4, left graph). The effect is more pronounced for DETA, for which a very small concentration already results in a significant decrease in Mo metal loss. DETA possesses three pK_b values and can exist as four different species in solution dependent on the pH [11]. In APM, the prominent species will be the singly protonated $DETA^+$. The positively charged $DETA^+$ might experience electrostatic attraction towards the Mo since its surface is negatively charged for $pH > 2$ [10]. This can result in the formation of an adsorbed layer of DETA molecules, blocking the H_2O_2 and thus resulting in a slower oxidation of the Mo and a lower loss. For glycine, the situation is different: glycine will be in its zwitterionic form: $^+{}^3HN-CH_2-COO^-$ and subjected to less electrostatic attraction. Only by increasing the concentration of glycine, the blocking effect becomes noticeable.

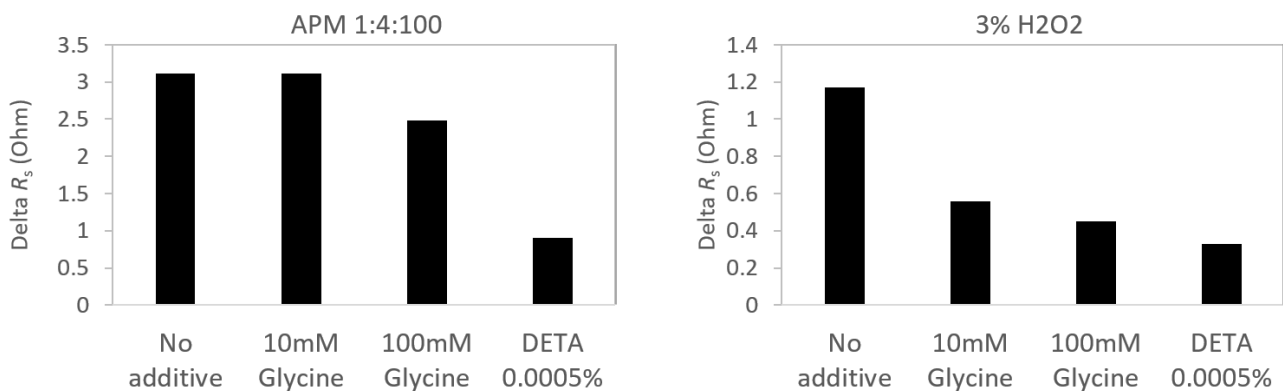


Figure 4: Evaluation of the effect of the additives DETA and Gly on Mo etching: the left graph shows Mo etching in an APM solution and the right graph Mo etching in a peroxide solution.

In a second set of experiments, the additives glycine (Gly) and diethylene triamine (DETA) were added to a neutral solution of peroxide (Fig. 4, right graph). DETA again resulted in lower Mo metal loss compared to the peroxide solution without additives, as observed by the smaller change in resistance. Note that the absolute ΔR_s is higher for the samples treated with APM compared to the ones treated in peroxide only, even if the total peroxide concentration is higher for the latter (3 wt.% vs. 1.3 wt.% H_2O_2 in APM). This is due to pH, as explained in the previous section. The pH difference will also explain the more pronounced blocking effect of glycine in a peroxide solution compared to an APM solution: glycine will have more positive charges in the neutral peroxide than in the more alkaline APM solution and thus experience more attraction towards the negatively charged Mo surface in the peroxide solution. The goal of the use of these additives was to evaluate if roughness could be mitigated. Figure 6 at the end of the last section shows the roughness plotted against equivalent Mo loss for various conditions wherein additives were used. There is an overall trend in increase in roughness as a function of recess depth. This increase is too high for applications mentioned in the introduction. In summary, it can be concluded that the additives adhere to some extent to the surface, but that surface roughening of the metal is not mitigated by this adsorbed layer of molecules.

Evaluation of a stepwise etching sequence for controlled Mo recess. In this last section, wet etching of Mo in a stepwise manner will be discussed. A stepwise process using a sequence of an oxidation (step 1) followed by an oxide-dissolution (step 2) was evaluated in a similar manner as previous studies with Cu and Co [12,13]. The main requirements for wet-ALE etching are that step 1 is self limiting and step 2 selective. First, the oxidation step (step 1) was evaluated by a gradual increase of its step time. The conditions of step 2 were kept constant (30s dilute NH_4OH). This is shown in Figure 5 where R_s was monitored for a stepwise etching process with peroxide as the oxidant (Fig. 5, right) or ozonated water (Fig. 5, left) in step 1.

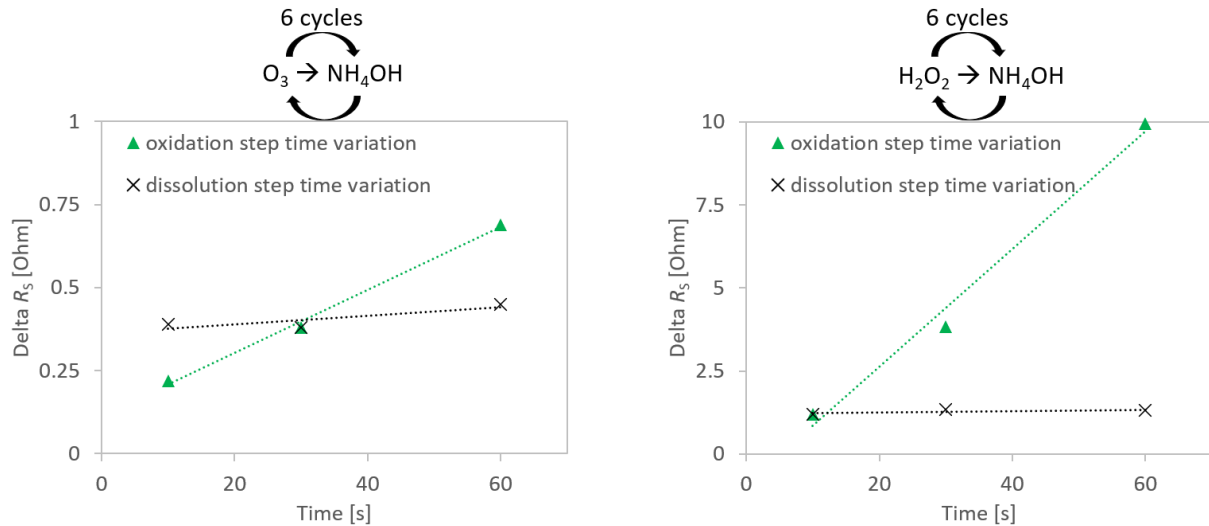


Figure 5: Evaluation of an etch process comprising 6 cycles (see schematic) by increasing the step time of only one of the two steps of each cycle: oxidation (triangles) or dissolution (crosses). Left graph shows Mo etching using ozonated water during step 1, the right graph using dilute peroxide during step 1. Both (left + right) sequences use dNH₄OH during step 2.

The resistance increases continuously with the time of step 1 due to oxidation and eventually etching of the film. However, the overall reaction is not self-limiting, neither in dilute peroxide nor in ozonated water. Second, the oxide-dissolution step (step 2) was evaluated, also by a gradual increase of its step time, while the conditions of step 1 were kept constant (30s dilute H₂O₂ or 30s ozonated water). For the oxide dissolution step dilute ammonia was chosen since it is selective to the Mo *metal*. As seen in Figure 5, no significant increase in resistance as a function of step time 2 was observed. This proves that the selectivity requirement is met: no etching of the underlying molybdenum metal.

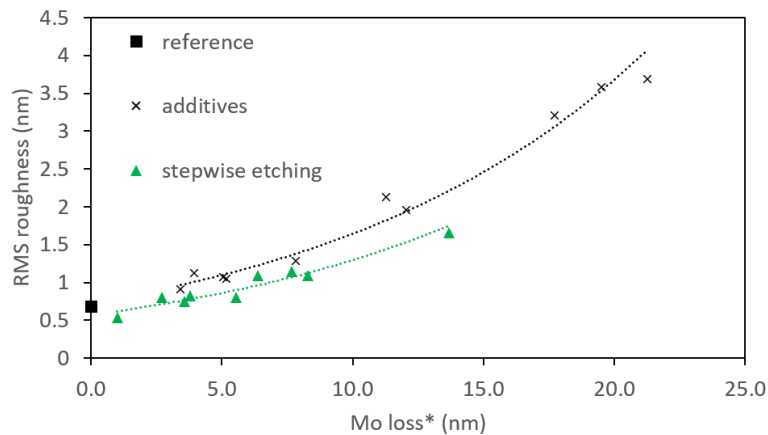


Figure 6: RMS roughness vs. Mo loss (*calculated with R_s) for various etching conditions described in this paper.

However, we do not know if there was even oxide left after step 1 *or* if the oxide is not able to dissolve in dilute ammonia. We suspect the former since previous results (see first section), point towards

increased oxide solubility with ammonia concentration. Consequently, etching (oxidation + dissolution) only happens during step 1, implying that wet-ALE etching was not possible with these oxidizing solutions. This can be attributed to the trans passive characteristics of the Mo(IV) oxide [14]: once the Mo is oxidized to Mo(IV) (e.g. in step 1 in H₂O₂), it immediately further oxidizes to Mo(VI) and forms the soluble product H₂MoO₄. The formation of other, insoluble oxides, like MoO₃, could potentially overcome this issue. In summary, Figure 6 shows the roughness plotted against equivalent Mo loss for various stepwise etching processes. There is an overall trend in the increase of the roughness as a function of recess depth. The increase is slightly smaller compared to the increase of roughness observed for the additives but still too high for the critical applications mentioned in the introduction.

Summary and conclusions

Mo etch for recess applications was evaluated in alkaline and oxidative solutions. Higher pH resulted in faster etching and, additionally it was found that NH₄⁺ assists in the dissolution of the oxidized Mo. No significant differences in wet etching behavior were observed for Mo samples annealed in N₂ or H₂ at 650°C compared with the as-deposited PVD Mo. Mo annealed in forming gas at 650°C (Mo_xN_y) however, etched significantly slower. In order to mitigate surface roughening, the use of additives was evaluated in peroxide and APM solutions. It could be concluded through etch rate change and by electrostatic attraction/repulsion trends that the additives adhere to some extent to the surface, but that the surface roughening of the metal was not mitigated by this adsorbed layer of molecules. Finally, the potential of wet-ALE or stepwise etching was evaluated for molybdenum. The self-limiting requirement of the oxidation step was not achieved. This is probably due to the trans-passive behavior of the so-formed MoO₂ oxide. The formation of oxides with Mo in a higher oxidation state, could potentially overcome this issue.

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