

Development of Methanol Based Reactive Ion Etching Processes for Nanoscale Magnetic Devices

M. T. Moneck* and J.-G. Zhu*

*Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA, mmoneck@andrew.cmu.edu

ABSTRACT

As feature sizes shrink to sub-50 nm for spin transfer torque (STT) devices and to sub-10nm for ultra-high density bit patterned media (BPM), anisotropic, defect free etching becomes difficult with conventional techniques, such as ion milling. Instead, reactive ion etching (RIE) must be used to meet the challenge. In this work, we present research on the development of a methanol based RIE technique for anisotropic etching of nanoscale magnetic and nonmagnetic STT and BPM related device structures with enhanced selectivity, minimal redeposition, and less faceting than similar structures etched with Ar ion milling. Using methanol RIE, we demonstrate magnetic film etch rates as high as 40nm/min and features as small as 20nm. These results, the promises of such a technique and the feasibility of etching sub-10nm dimensions are discussed in detail throughout the paper.

Keywords: methanol RIE, reactive ion etching, spin transfer torque, bit patterned media, ion milling

1 INTRODUCTION

Over the past decade, significant advancements have been made in the areas magnetoelectronics and hard disk drive (HDD) recording. Two of the most notable have been the realization of spin transfer torque (STT) devices for low power magnetoresistive random access memory (MRAM) and the development of bit patterned media (BPM) for ultra-high density magnetic recording beyond 1 Tbit/in² [1-2]. The main factor enabling such advancements has been the ability to scale feature sizes well below 100nm. Continued advancement now requires feature sizes to reach sub-50nm for STT devices and sub-10nm for BPM [1-2]. At these small length scales, anisotropic defect-free etching of magnetic films becomes difficult with conventional ion beam etching techniques, particularly at high aspect ratio where defects include faceting, erosion, ion beam shadowing, and material redeposition [3-7]. Instead, advanced reactive ion etching (RIE) techniques must be developed to meet the challenge.

In this work, we present research on the development of a methanol based RIE process for etching magnetic and non-magnetic STT and BPM device structures using single and dual layer nonvolatile mask layers composed of SiN_x, Ta, and Ti. First introduced by Anelva Corporation, the process

relies on the formation of volatile carbonyl byproducts combined with physical sputtering to etch magnetic alloys composed of Co, Fe, and Ni, as well as non-magnetic Cu, Pt, Ru, and more with enhanced selectivity, minimal redeposition, minimal shadowing, and less faceting or erosion relative to conventional Ar ion milling [3-5]. Using this process, we demonstrate the ability of methanol RIE to produce etch rates as high as 40nm/min and features as small as 20nm. By adding Ar to the methanol chemistry, one can achieve even further enhancement of etch rate, selectivity, and anisotropy. These results and the promises of using such a technique to achieve sub-10nm high aspect ratio features will be discussed in detail throughout the paper.

2 SAMPLE PREPARATION & ETCHING

Three types of samples containing combinations of materials commonly found in STT and BPM device structures were prepared and etched in methanol according to the process flow of Figure 1. For STT applications, the etched structures, include test films of Si/Ta (3-5nm)/NiFe (20-120nm), as well as giant magneto-resistive (GMR) film stacks composed of Si/SiO₂(1 μ m)/Ta(5nm)/Cu(80nm)/Ta(5nm)/CoFe(10nm)/Cu(3nm)/CoFe(1nm)/NiFe(2nm)/CoFe(1nm)/Cu(20nm)/Pt(10nm), where NiFe refers to Ni₈₁Fe₁₉ and where CoFe refers to Co₉₀Fe₁₀. Each film was deposited via DC or RF magnetron sputtering from elemental or alloy targets. For BPM applications, the test samples consist of commercial 2.5" perpendicular magnetic recording (PMR) media having the structure Glass Disk/Underlayers/Ru(20nm)/CoCrPt+Oxide(10-11nm)/CoCrPt(5-7nm)/DLC(1.5-3nm), where underlayers refers to a proprietary stack of magnetic and non-magnetic seed layers, where CoCrPt refers to a proprietary media alloy, and where DLC refers to diamond-like carbon.

Patterned features ranging in size from ~20nm to greater than 100nm were generated on the above sample structures using electron beam lithography with polymethyl methacrylate (PMMA) positive resist or hydrogen silsequioxane (HSQ) negative resist in a FEI Sirion scanning electron microscope (SEM) running J. C. Naby Nanometer Pattern Generation Software. Transfer of the positive and negative resist patterns into various mask layers was accomplished through the direct etch and liftoff techniques illustrated in Figure 1. In the case of direct etch processing, mask layers, such as SiN_x, and Ta/SiN_x were

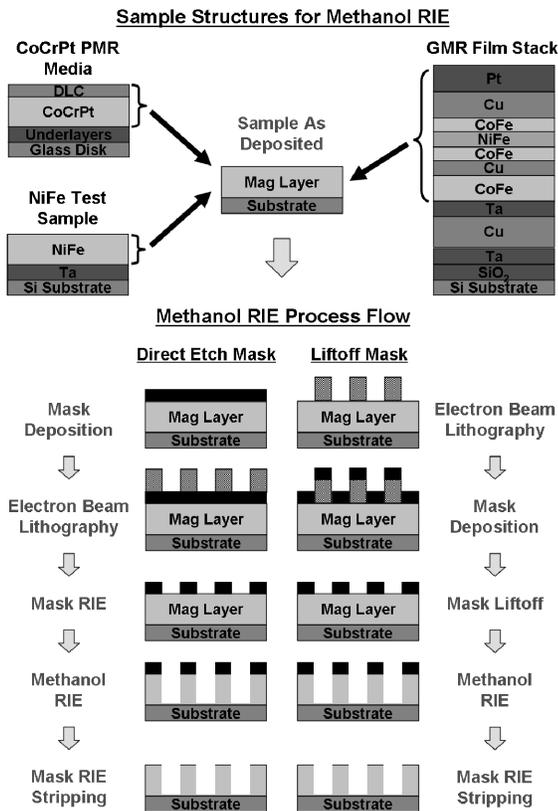


Figure 1: Schematic diagram of methanol RIE test sample structures and the corresponding process flow.

sputter deposited on the samples prior to lithography. Following lithography, the patterns were transferred to the mask layers using a Plasma Therm 790 RIE system with gas combinations that include CF_4 , CHF_3 , and/or SF_6 . In the case of liftoff processing, less volatile mask layers, such as Ta or Ti are deposited on top of lithographically patterned PMMA via DC magnetron sputter deposition or electron beam evaporation. Following deposition, the samples are placed in an acetone ultrasonic wash to lift off the PMMA, leaving behind the patterned Ta or Ti mask structure.

Methanol RIE of the aforementioned NiFe, GMR, and PMR media samples was performed in pure CH_3OH or $\text{CH}_3\text{OH}/\text{Ar}$ (25-30% Ar by flow) environments using the parallel plate Trion Phantom II RIE or the inductively coupled plasma (ICP) based STS Aspect RIE systems depicted in Figure 2. Samples etched in the Trion system were processed on a water cooled platen with powers ranging from 40W to 100W and pressures ranging from 5-20mTorr at a total gas flow ($\text{CH}_3\text{OH}+\text{Ar}$) of 20 sccm. DC bias voltages generated under these conditions are unknown due to a lack of instrumentation. In the STS system, samples were processed on a He backside cooled chuck with platen powers ranging from 200W to 800W, coil powers ranging from 1kW to 2kW, and pressures of 5-10mTorr at a total gas flow ($\text{CH}_3\text{OH}+\text{Ar}$) of 20sccm. Under such conditions, DC bias voltage was found to range between 360V and 725V.

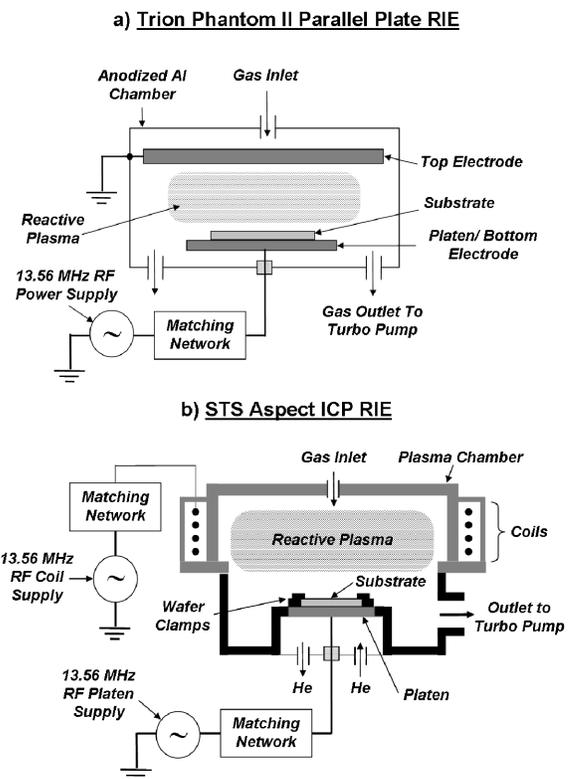


Figure 2: Schematic diagrams of the (a) Trion Phantom II parallel plate and the (b) STS Aspect ICP RIE systems used for methanol RIE.

The final step illustrated in Figure 1 is the removal of any mask material remaining after RIE in methanol. This step is optional and not performed in all cases, particularly for Ta and Ti masks. More discussion of this matter will be included in the next section. In the event mask removal is necessary, the same fluorine based RIE processes used to define the mask can be used to remove the mask.

3 RESULTS & DISCUSSION

NiFe test films were etched as a general means of evaluating the Ta, Ti, and Ta/SiN_x mask structures and to compare the parallel plate and ICP methanol RIE processes described in the previous section. The results are depicted in Figure 3. Based on these images and bulk film selectivity tests, Ta was found to be the most effective mask material for methanol RIE, with selectivities (defined as the ratio between film etch rate and mask etch rate) greater than 20:1 for NiFe and 90:1 for Cu [3]. Such high selectivity is most likely attributed to the formation of hard to remove Ta carbide during exposure to the methanol plasma [3,8]. The effectiveness of Ta is particularly evident in Figure 3(a) where 10nm thick Ta masks (6nm of SiN_x was used as an etch mask to RIE the Ta) were used to etch 100nm NiFe islands to depths greater than 40nm with sidewall angles of 75-80° and sharp corners having virtually no faceting.

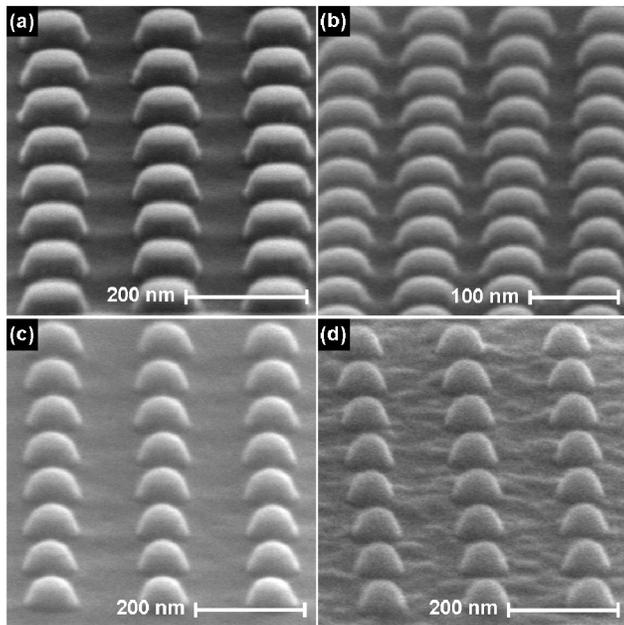


Figure 3: SEM images of NiFe islands etched in parallel plate methanol RIE processes using (a)-(b) direct etch Ta/SiN_x and (c) Ta liftoff masks. NiFe islands etched in an (d) ICP methanol RIE process using Ti liftoff masks are included for comparison. The etch masks remain on the islands in all cases.

Using the same direct etch Ta/SiN_x mask structure, Figure 3(b) depicts the ability of methanol RIE to etch small gaps approaching 30nm in width; although, some faceting can be detected due to the effects of physical sputter etching.

In cases where liftoff masks are required, Ta and Ti have both proven to be robust and effective. Figures 3(c) and 3(d) show a comparison between between 80-85nm NiFe island arrays etched in parallel plate and ICP RIE processes using 17.5nm Ta and 25nm Ti liftoff masks respectively. The thicker Ti was necessary given that Ti has a tendency to undergo more physical erosion than Ta [3]. Nonetheless, the parallel plate and ICP etches produced similar etch profiles at the same etch depth of 40-45nm. Perhaps more significant is the fact that the ICP etch was completed 20 times faster than the optimized parallel plate etch, demonstrating the superior efficiency of the ICP process. Figure 4(a) shows a plot of the ICP etch rates obtained for NiFe films at platen powers of 200-800W and coil powers of 1-2kW. Given the same platen power, etch rates achieved in the ICP system represent a 400% increase over the etch rates produced by the parallel plate reactor. Figure 4(b) indicates the addition of 25-30% Ar to the process can enhance etch rate another 20%, resulting in ICP rates as high as 40nm/min for NiFe. In addition to faster rates, the ICP configuration offers higher density plasmas at lower operating pressures and independent control of ion bombardment, making it more suitable for directional etching of the high aspect ratios and narrow gaps required in STT and BPM device applications [3,9-10].

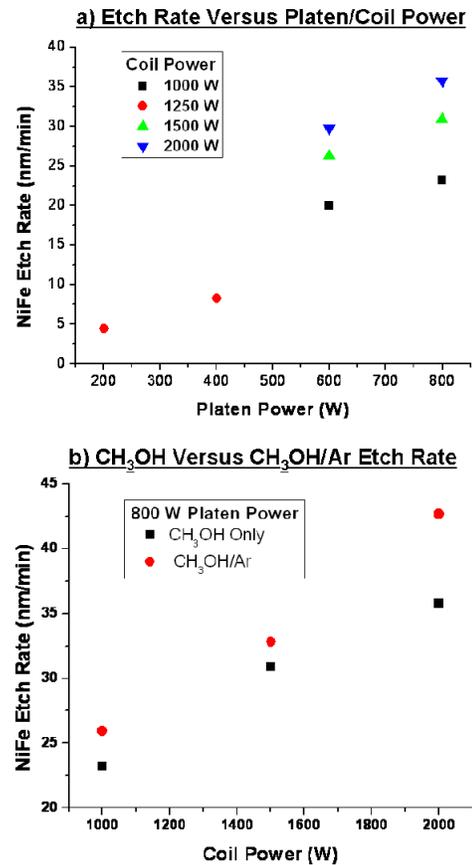


Figure 4: Plots of methanol based ICP RIE NiFe etch rates for various platen and coil powers (a) with pure CH₃OH and (b) with CH₃OH combined with 25% Ar by flow.

3.1 Methanol RIE for STT Device Structures

Utilizing the results of the NiFe film tests, methanol RIE was applied to the GMR film stacks of Figure 1 using 25nm Ti liftoff masks. The etches were conducted at 5mTorr using CH₃OH and CH₃OH/Ar based ICP RIE with 600W platen power and 1kW coil power to produce the 60-80nm structures depicted in Figure 5. In both cases, the etch was carried through the top Cu/Pt layers and through each of the magnetic films, stopping at the highly selective 5nm Ta interlayer adjacent to the CoFe. Immediately evident is the large anisotropy difference between the pillars of Figures 5(a) and 5(b), particularly in the Cu/Pt region at the top of the pillars. Given the similar etch conditions and etch depths between the two samples, the results suggest the addition of Ar to the CH₃OH plasma produces a significant increase in directionality. Additional testing, confirms that Ar can also enhance selectivity by up to 10%, leading to bulk film selectivities as high as 96:1 for Cu, 70:1 for Pt, 23:1 for NiFe, and 13:1 for CoFe relative to Ta and Ti masks [3,9-10]. However, the same mechanism that leads to high selectivity can also be a drawback in some applications. Recall that Ta and Ti are believed to form hard to etch carbides during exposure to the CH₃OH plasma

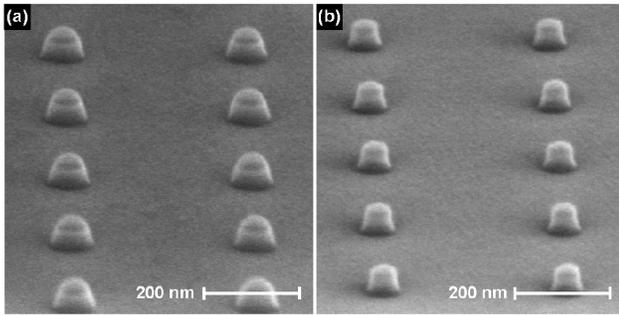


Figure 5: SEM images of GMR film stacks etched in ICP methanol RIE using Ti masks with (a) pure CH₃OH and (b) CH₃OH/Ar gas combinations.

[3,8,11]. These carbides help to increase mask selectivity, but they also make post-etch mask removal difficult. In STT applications, conductive materials, such as Ta and Ti may be incorporated into the device structure, eliminating the need for removal, but in other applications difficulty in mask removal may pose a problem [2]. Nonetheless, ICP RIE with CH₃OH/Ar shows a great deal of promise for STT device applications.

3.2 Methanol RIE for Bit Patterned Media

BPM applications require that a magnetic recording head be flown only a few nanometers from the media surface, making post-etch mask removal a critical consideration [2]. Given the difficulty in removing Ta and Ti, less reactive SiN_x masks were pursued instead. Figures 6(a) and 6(b) depict two sets of discrete data tracks etched into CoCrPt PMR media using a parallel plate CH₃OH/Ar etching process with 45nm and 40nm thick SiN_x direct etch masks respectively. The sample of Figure 6(a) was etched the majority of the way through the CoCrPt+Oxide/CoCrPt media layers, while the sample in Figure 6(b) has an unknown etch depth. In both cases, the media was etched with minimal faceting, erosion, or material redeposition, suggesting methanol RIE with thick SiN_x can be effective, despite having a bulk film selectivity approximately 6 times lower than Ta or Ti [3]. Following CH₃OH/Ar etching, the SiN_x masks were able to be removed via the RIE processes described in Section 2, leaving behind a clean media surface, with no residual mask layer. These results suggest that methanol RIE with SiN_x does show promise for BPM applications. In particular, the sub-20nm etch gaps achieved in Figure 6(b), suggest the process is scalable, especially if using a more directional, faster etching ICP RIE process. However the authors would like to note that the RIE results obtained in this work are only preliminary. The CoCrPt PMR media used in the above tests provides some insight into the etching process, but the media structure is not magnetically optimal for BPM or structurally optimal for methanol RIE due to the presence of low selectivity Cr and oxide. Moving forward, the process must be applied to more suitable CoPt, CoPd, and FePt BPM media alloys [2].

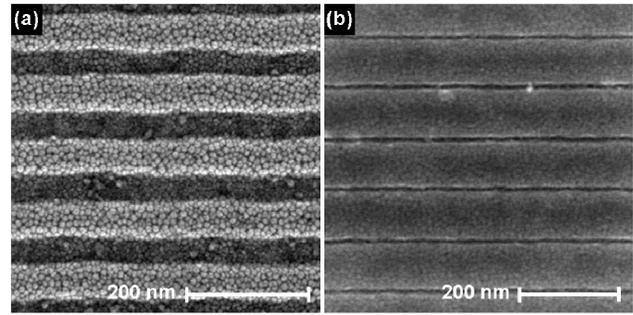


Figure 6: SEM images of (a) 55-60nm discrete tracks and (b) sub-20nm narrow gaps etched into CoCrPt PMR media using methanol RIE with removable SiN_x masks.

Employing such alloys into an ICP methanol RIE process is a more suitable route to achieving sub-10nm etching.

4 SUMMARY & CONCLUSIONS

Utilizing parallel plate and ICP based methanol RIE processes, we have demonstrated sub-20nm etching of CoCrPt PMR media and highly anisotropic etching of 60-80nm GMR film stacks. The ICP configuration, was shown to enhance the process, producing etch rates as high as 40nm/min for NiFe. Further enhancement of etch rate, selectivity, and anisotropy was achieved by adding Ar to the CH₃OH plasma. Taking these achievements into account, ICP RIE using methanol based plasmas shows a great deal of potential for etching high aspect ratio and/or narrow gaps required in STT and BPM device applications.

REFERENCES

- [1] J. A. Katine and E. E. Fullerton, *J. Magn. Magn. Mater.*, 320, 1217-1226, 2008.
- [2] B. D. Terris, *J. Magn. Magn. Mater.* 321, 512, 2009.
- [3] M. T. Moneck and J.-G. Zhu, *Proc. of the SPIE*, 7823, 78232U, 2010.
- [4] Y. Otani, H. Kubota, A. Fukushima, H. Maehara, T. Osada, S. Yuasa, and K. Ando, *IEEE Trans. Magn.* 43, 2776, 2007.
- [5] Y. Kodaira and T. Hiromi, *United States Patent Number 7,060,194 B2*, 2006.
- [6] Y. Kamata, A. Kikitsu, H. Hieda, M. Sakurai, and K. Naito, *J. Appl. Phys.*, 95, 6705, 2004.
- [7] J. M. Shaw, S. E. Russek, T. Thomson, M. J. Donahue, B. D. Terris, O. Hellwig, E. Dobisz, and M. L. Schneider, *Phys. Rev. B*, 78, 024414, 2008.
- [8] Y. Kuo., *Jpn. J. Appl. Phys.* 32, 179, 1993.
- [9] J. K. Bhardwaj and H. Ashraf, *Proc. SPIE*, 2639, 224, 1995.
- [10] H. Jansen, H. Gardeniers, M. de Boer, M. Elwenspoek, and J. Fluitman, *J. Micromech. Microeng.* 6, 14, 1996
- [11] K. Blumenstock and D. Stephani., *J. Vac. Sci. Technol. B*, 7, 627, 1989.