STRUCTURAL STABILITY OF MAGNETIC TUNNEL JUNCTION BASED MOLECULAR SPINTRONICS DEVICES (MTJMSD)

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ABSTRACT

Harnessing the exotic properties of molecular level nanostructures to produce novel sensors, metamaterials, and futuristic computer devices can be technologically transformative. In addition, connecting the molecular nanostructures to ferromagnetic electrodes bring the unprecedented opportunity of making spin property based molecular devices. We have demonstrated that magnetic tunnel junction based molecular spintronics device (MTJMSD) approach to address numerous technological hurdles that have been inhibiting this field for decades. MTJMSD approach is based on producing a capacitor like a testbed where two metal electrodes are separated by an ultrathin insulator and subsequently bridging the molecule nanostructure across the insulator to transform a capacitor into a molecular device. Our prior work showed that MTJMSDs produced extremely intriguing phenomenon such as room temperature current suppression by six orders, spin photovoltaic effect, and evolution of new forms of magnetic metamaterials arising due to the interaction of the magnetic a molecule with two ferromagnetic thin films. However, making robust and reproducible electrical connections with exotic molecules with ferromagnetic electrodes is full of challenges and requires attention to MTJMSD structural stability. This paper focuses on MTJMSD stability by describing the overall fabrication protocol and the associated potential threat to reliability. MTJMSD is based on microfabrication methods such as (a) photolithography for patterning the ferromagnetic electrodes, (b) sputtering of metallic thin films and insulator, and (c) at the end electrochemical process for bridging the molecules between two ferromagnetic films separated by ~ 2nm insulating gap. For the successful MTJMSD fabrication, the selection of ferromagnetic metal electrodes and thickness was found to be a deterministic factor in designing the photolithography, thin film deposition strategy, and molecular bridging process. We mainly used isotropic NiFe soft magnetic material and anisotropic Cobalt(Co) with significant magnetic hardness. We found Co was susceptible to chemical etching when directly exposed to photoresist developer and aged molecular solution. However, NiFe was very stable against the chemicals we used in the MTJMSD fabrication. As compared to NiFe, the Co films with >10nm thickness were susceptible to mechanical stress-induced nanoscale deformities. However, cobalt was essential to produce (a) low leakage current before transforming the capacitor from the magnetic tunnel junction into molecular devices and (b) tailoring the magnetic properties of the ferromagnetic electrodes. This paper describes our overall MTJMSD fabrication scheme and process optimization to overcome various challenges to produce stable and reliable MTJMSDs. We also discuss the role of mechanical stresses arising during the sputtering of the ultrathin insulator and how to overcome that challenge by optimizing the insulator growth process. This paper will benefit researchers striving to make nanoscale spintronics devices for solving grand challenges in developing advanced sensors, magnetic metamaterials, and computer devices.

INTRODUCTION

Molecules can be harnessed as the transformative devices for computer's logic and memory [1-3]. Molecular spintronics devices (MSDs), focusing on utilizing electron's spin degree of freedom, can become a highly promising platform to enable the quantum computation[4] and novel materials utilizing the spin filtering attributes of a magnetic molecule[5]. The molecular device operation depends upon manipulation of the spin degree of freedom of electron(s), requiring small energy for their manipulation[6, 7]. MSDs are expected to work with significantly low energy input, as compared to the charge-based logic and memory devices[6-8]. Novel MSDs are expected to evolve from a system of ferromagnetic (FM) electrodes and molecule with a net spin. Several intriguing phenomena have been theoretically predicted for MSDs [9-13]. For example, Petrov et al. [14, 15] predicted nearly seven orders resistance change for the molecular bridges, which were initially antiferromagnetically coupled with the electrodes. Molecules are like quantum dots. Martinek et al. [16, 17] predicted the Kondo resonance for a system enabling the interaction between the spins of FM electrodes and the spin of quantum dots.

Due to fabrication extreme difficulties in producing reliable FM contacts to the magnetic molecules and failure in performing extensive control experiments the field of MSD is still in

emergent stage after nearly 20 years of extensive research. This paper discus our magnetic tunnel junction based molecular spintronics device (MTJMSD) approach and several aspects associated with making it robust and mass producible. The MTJ based devices have progressed beyond mass production stages and currently utilized in several hard drives. It is noteworthy that MTJMSD approach is based on using magnetic tunnel junction (MTJ) as the testbed for harnessing molecule's attributes as the device or sensing elements.

EXPERIMENTAL DETAILS

MTJMSD fabrication was accomplished in several stages [18, 19].For fabrication of MTJMSD, a silicon wafer with thermally grown 100 nm silicon di oxide (SiO_2) isolation layer was used as the substrate. Prior to every photolithography step, substrates were sequentially cleaned with acetone, isopropyl alcohol and de-ionized (DI) water. Samples were then dried in nitrogen jet. The planar dimensions of top and bottom single or multilayer electrodes and AlOx insulator were defined by a conventional photolithography method. Photolithography step was accomplished with Shipley 1813 positive photoresist and a Karl Suss mask aligner. Photolithography step was important for yielding the optimum bottom electrode's edge profiles; slightly undercut profile was necessary to avoid notches on the metallic pattern after liftoff. The photoresist thickness, exposure time and developing steps were optimized to obtain a suitable edge profile, for the deposition of the first electrode [20]. Metal electrodes were sputter deposited with 100-150 W RF sputtering gun power and 1-2 mtorr argon (Ar) pressure in AJA International Multitarget Sputtering System. After the required film deposition steps, a liftoff process was carried out with a Shipley 1165 resist remover for 2-4 hours. The key highlight of the TJMD approach is that the ultrathin AlOx insulator and the top metal electrodes were deposited through the same photoresist pattern (Fig. 1b). Utilization of the same photoresist cavity, (Fig. 1b), helped matching the lateral dimensions of AlOx and top metal electrode. When lateral dimensions of AlOx and top electrodes are the same then inter-electrode gap along the junction edges is equal to the AlOx thickness (Fig. 1a-c). The second photolithography step was performed to deposit AlOx and top metal electrode. The AlOx and top metal electrodes were deposited through the same photoresist cavity. Deposition of the 2 nm thick AlOx insulator, the most important step of molecular electrode fabrication scheme, was accomplished using a multi-step process. Liftoff of photoresist produced an exposed edge tunnel junction (Fig. 1e). Other details about tunnel junction based molecular device fabrication is published elsewhere [18]. Subsequently, molecules are attached by employing an electrochemical step described elsewhere[21].

RESULTS AND DISCUSSION:

MTJMSD allows the utilization of any ferromagnet. However, the selection of thickness and type of ferromagnet must be considered by considering the potential risk of damage during the remaining fabrication steps, molecular treatment, leakage current level via bare tunnel junction, long-term stability, and intended device operation (e.g., spin-valve type operation). We initially used NiFe as the top and bottom electrode (Fig. 1a). However, we noted that the utilization of NiFe alone as the bottom electrode produced relatively high leakage current (Fig. 1a). The second limitation of NiFe was that it is one of the softest ferromagnetic alloys. When we tried to apply the magnetic field to switch the direction of only one electrode selectively, both top and bottom NiFe electrodes switched simultaneously. Interestingly, we observed spikes in the current, but no stable switching was obtained (Fig. 1b). We focused on making the bottom electrode harder to attain the selective control on the magnetization direction. For this purpose, we envisioned utilizing cobalt (Co) as the bottom electrode.

The most important challenge in incorporating a ferromagnetic electrode depends on its reactivity with the alkaline developer chemical used in the 2nd photolithography stage (Fig. 2i). We noted that a typical MF-319 developer utilized for the removal of UV exposed Shipley® positive photoresist, dissolve the Co with > 20 nm/min rate. One must consider that many metals such as aluminum, copper, cobalt are not sufficiently alkaline stable. However, this problem associated with positive photoresist developer can be solved by selecting tetramethylammonium hydroxide (TMAH) or other suitable developers. We produced MTJ testbed using Co as the bottom electrode. Interestingly, the utilization of the cobalt (Co) electrode produced ~5-10 factor smaller leakage current as compared to NiFe bottom electrode-based MTJ (Fig. 1c). However, we observed that Co-based MTJ was quite unstable with time. An MTJ showing very clean I-V and strong tunneling property started showing an increase in tunneling current and noisy transport characteristics (Fig.1d) and within few days failed to appear to become a resistor (Fig1c). Upon systematic investigation about the failure of Co bottom electrode-based MTJ, we learned that Co substrate produces sharp conical features via the AlOx tunneling barrier under the effect of the sputtering process-induced compressive stresses. Co was surprisingly the reason for several needle-like hillocks that formed under the mechanical stresses (Fig. 1e). The Co-based nanoscale needle-like features were found to be sensitive towards the mechanical stresses generated during the various AlOx growth.

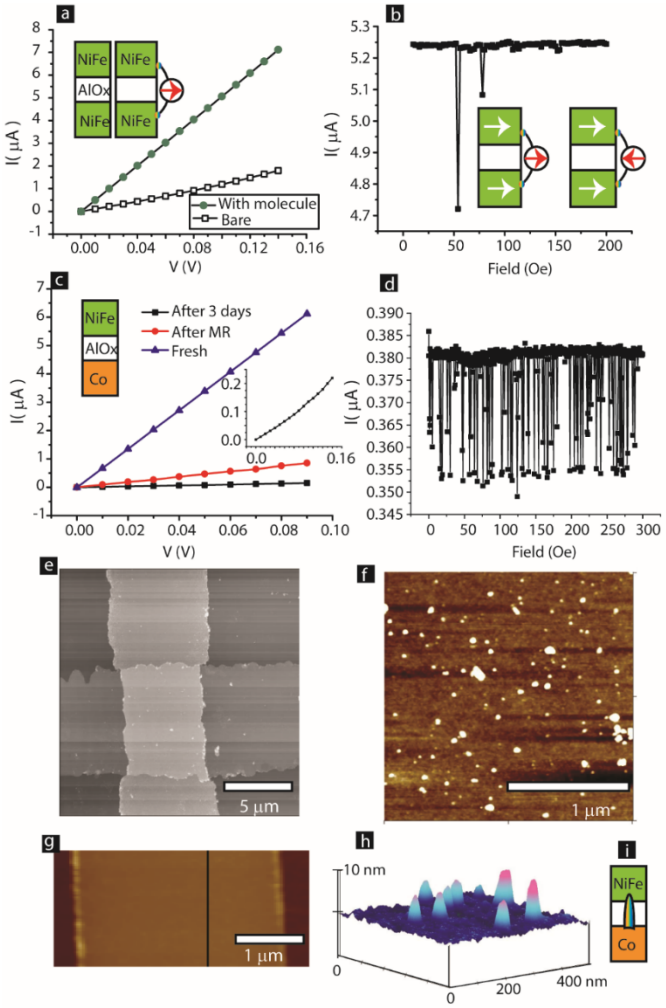

Fig.1(a): I-V of a NiFe top and bottom electrode based MTJ before and after hosting magnetic molecules. (b) Transient effect of magnetic field on NiFe based MTJMSD. (c) I-V of Cobalt based tunnel junction showing transient response with time. (d) Bare Co based MTJ showed fluctuations in transport (e) AFM of a complete MTJ testbed. (f) Hillock generation in the planar area of cobalt based MTJ test bed. (g) Freshly produced >10 nm Co without any hillocks like feature. (h) 3D image of hillocks that generate on >10 nm co based bottom electrode in the MTJ junctions. (i) Conceptual mechanism how a hillock creates short circuit between two metal electrodes.

A 10 nm thick Co-produced different types and density of needle-like features as mechanical stresses relaxed with time. These needle-like features and destroyed the tunneling property of the MTJ testbed (Fig.1f). An in-depth analysis of the mechanical stress-based tunnel junction failure mechanism has been published elsewhere [19]. The topography of the as-produced Co layer is shown in Fig.1g. There was no hillock or sharp structures in the planar area. It was noted that >10 nm Co was highly susceptible to stress-induced hillock generation (Fig. 1h). This hillock was the primary cause of AlOx tunnel barrier formation.

To solve the multiple issues such as: (a) Co nanohillocks generation causing junction failure, (b) alter the bottom magnetic electrode property with respect to top electrode to facilitate switching, (c) etching of Co with alkaline photoresist developer we started pursuing Co(5-7 nm)/NiFe(5-3 nm) bilayer. Based on the prior literature, we came to know MTJ with switchable magnetic electrode directions can be produced by the use of Co/NiFe bilayer. We also envisioned the advantage of using bilayer from the standpoint of minimizing the sharp notches along the photolithographically patterned bottom electrodes for the MTJMSD and keep utilizing the same PR developer that etches the Co metal. Thought behind the utilization of alkaline developer during the second photolithography was to expose Co/NiFe bilayer edges where the developer will etch away 20-50 nm Co. During Co etching process, NiFe along the edges will wash off due to the loss Co base. As a result, the improved bottom ferromagnetic electrode with tapered edges was expected to emerge.

Effect of Co thickness in Co/NiFe bottom electrode appeared a strong factor in the MTJMSD stability. Co thickness was maintained below 7 nm because the strength of film thickness is directly dependent on thickness. Thinner films were found to produce fewer hillocks like feature. On the other hand, when Co thickness was ~ 10 nm bottom electrode became very sensitive towards nano hillocks generation via the NiFe top layer. The most devastating part was the impact of CH2Cl2 solvent-based molecular solution towards the end when an MTJ was transformed into MTJMSD. In this paper, we have discussed the chemical stability during molecular treatment as a separate topic.

We have also elaborated on the effect of temperature and environment on the oxidation susceptibility of the ferromagnetic electrodes like Ni, Co, and NiFe. We noted that MTJMSD fabrication steps must be executed below ~90 °C[22]. One may also consider using the inert environment when MTJMSD's ferromagnetic electrodes are expected to be exposed to high temperatures. After oxidation, a ferromagnetic film is unable to form bonds with the molecules utilizing thiol functional groups. Thiol functional groups are widely used for making bonds with the ferromagnets.

CONCLUSION

This paper discussed the effect of design consideration on the stability of MTJMSDs. The selection of the ferromagnetic material type is a critical factor in governing the process parameters necessary to produce MTJ testbed. The ferromagnetic electrode materials are critical in determining the susceptibility of MTJMSD towards chemical etching related damages that may occur during the patterning stages and also during the molecule attachment process.

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