# **Grooved Bottom Electrode Based Molecular Spintronics Device**

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#### **ABSTRACT**

Mass fabrication of molecular spintronics devices (MSDs) can harness the untapped exotic properties of molecules for making the next generation of computers, including quantum computers for the common public. However, since the conceptualization of molecular devices in early 1970, no device fabrication approach has provided answers to major critical device fabrication challenges. The most pressing challenge is the lack of a commercially via ble device fabrication approach. This paper show a novel method of utilizing magnetic tunnel junction (MTJ) with a grooved bottom electrode to address MSD fabrication challenges. SMM-like molecules of interest will be bonded along the exposed edges of an MTJ to serve as a device channel. MTJ's insulator serves as an industrially massproducible spacer between ferromagnetic electrodes and is expected to give >95% MSD yield. We patented this method as P. Tyagi, "Trenched Bottom Electrode and Liftoffbased Molecular Devices. U.S. Patent Application No. 16/102,732.," 2020.

Keywords: magnetic tunnel junction, m tj msd, m ole cular spintronics devices, msd, smm

#### 1 INTRODUCTION

Molecules are the only mass-producible quantum nanostructure that can be generated with atomic-level precision[1]. Molecules are also the only nanostructures that can be designed in almost infinite ways to possess exotic quantum properties[2]. The chemistry discipline has evolved greatly to produce molecules with unprecedented optical, magnetic, and electrical properties. Interestingly, many nature-produced molecules, such as DNA and porphyrins, are endowed with exotic electrical, magnetic, and optical properties that can make molecules dream device elements for future spin-based logic and memory devices. However, molecules' fate as a spintronics device element depends on which metal electrodes it will be tied to and how robust the physical gap among metal electrodes is to which molecule will interact in logic and memory device. The quest to make molecule-based devices is >70 years old. A mass fabrication method of molecular spintronics devices (MSDs) is indispensable to make this dream a reality. However, since the conceptualization of molecular devices in early 1970, no device fabrication approach has provided answers to critical device fabrication challenges. The most critical challenge is the lack of a commercially viable device fabrication approach to connect a vast range of ferromagnetic, antiferromagnetic, semiconducting, and different electrodes to molecules. A successful MSD fabrication approach must be easily configurable to allow the utilization of various types of molecules and magnetic electrodes to foster the development of a wide range of molecular spintronics devices. The author, Pawan Tyagi, has been researching tunnel junction-based molecular devices for 18 years and has established a tunnel junction-based molecular spintronics device route as a potential solution[3]. His prior contribution has shown unprecedented observations such as room temperature current suppression[4-7], spin photovoltaic effect[8], and several transient multiple orders of magnitude switchability [4, 9]. He has also contributed to the development of a Monte Carlo simulation program specifically to understand magnetic tunnel junction (MTJ) based MSD, widely referred to as MTJMSD[6, 7, 10-12]. However, the past approach has many limitations: (1) the physical spacer thickness between two metal electrodes must be smaller than the target molecule length, (2) roughness of the bottom electrode lead to inferior quality insulator, (c) deposition of the insulator along the vertical edges is challenging to cover uniformly, etc. [3]. He has come up with a new MSD device fabrication method to address these challenges and general molecular device field-related challenges that have been haunting the field for a long time. His new approach is patented as the method of utilizing robust and mass-producible grooved bottom electrode enabled magnetic tunnel junction based molecular spintronics device as P. Tyagi, "Trenched Bottom Electrode and Liftoff based Molecular Devices (TBELMD). U.S. Patent Application No. 16/102,732.," 2020. This paper discusses the details of the new method.

#### 2 TBELMD INVENTION DETAILS

### 2.1 Limitations of Prior MTJMSD Structure

A magnetic tunnel junction (MTJ) can be transformed into molecular spintronics device by covalently a ttaching molecular channels along the tunnel junction edge [3]. All

the prior work to date focuses on making insulator thickness less than the magnitude of molecule length. For the tunnel junction-based molecular devices, each molecule must have tethers to provide the required length. Tethers must have a thiol (-S) like chemical group to attach molecules to the metal leads or conductors. Suppose the target molecule length is 3.5 nm (Fig. 1a). In that case, a tunnel junction can have a 3 nm insulator thickness (Fig. 1b) to attach the end of the molecular channels to the top and bottom ferromagnetic (FM) electrodes (Fig. 1c). However, thick insulators and long molecules will demand high operational electric power. High power requirements may lead to Joule heating that can damage the molecular device channels. High heat can also lead to classic heating issues seen with the current technology. Short molecules are required to avoid heating issues. Utilizing short to long molecules also provides an ability to control the wave function overlap between molecule core and metal electrodes. However, utilization of short molecules necessitates a much thinner insulator. Thin insulators may be extremely difficult to produce over a large area and with long life. To integrate (Fig. 1d) a short molecule of ~1.5 nm length, we need a magnetic tunnel junction with  $\sim 1$  nm insulator thickness (Fig. 1e). Short molecules can bridge a cross the ~ 1 nm insulator with defects [6] to transform a MTJ into a molecular spin device (Fig. 1f).

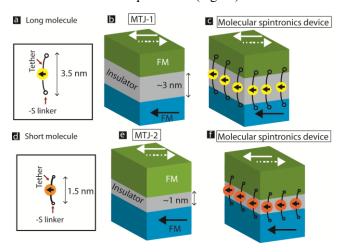


Figure 1: Bridging (a) 3.5 nm long molecule a long the exposed sides of prefabricated MTJ (b) will need 3 nm insulator, smaller than molecule length, for successful MTJ conversion to (c) MSD. (d) Reducing molecule length to  $\sim 1.5$  nm will demand a robust (e) MTJ fabrication with  $\sim 1$  nm insulator to convert MTJ into (f) MSD.

The challenge in using a  $\sim 1$  nm tunnel barrier is extreme. It is highly challenging to produce an atomic ally smooth and uniform thickness insulator [6]. A thin tunnel barrier is highly likely to have pinholes or pathways for the hot electrons leading to high background current. High background current will mask the effect of molecules. Moreover, mechanical stresses generated during fabrication and utilization will easily damage a thin tunnel barrier. The

invention disclosed the solution to address the issues associated with utilizing ~ 1 nm scale molecules

# 2.2 General Structure of TBELMD

A tunnel junction-based molecular spintronics device design method, where the length of a molecular device channel can be smaller than the combined thickness of the insulating barriers in the planar area of the trench on a conducting strip, is invented. Figure 2 shows the top view and cross-sectional view of the invention. The top view of the cross junction of the top and bottom conducting strip is shown in Figure 2a. At least one of the conducting strips will be made up of magnetic material. Molecular channels are bridged between two conducting strips along the black region to transform a magnetic tunnel junction into a molecular spintronics device. Figure 2b shows the key feature of this invention by the cross-section side view along the top conducting strip. The bottom conducting strip possesses a trench, due to which this method is named a trenched bottom electrode-based molecular device (TBELMD).

This arrangement enables the molecular device channels to dominate the charge and spin transport via the insulating spacer. This arrangement also ensures the physical gap between two conducting strips or interconnects is extremely robust and mass-producible with widely available low-cost microfabrication resources. This invention relies on creating a trench in the conducting strip, then filling the trench with insulating material to a pre-determined height, and depositing a second conducting strip on the top. A lowtemperature photolithography process is employed to control the (i) dimensions of the planar trench region on the first metal strip (also referred to as the bottom electrode), (ii) insulating spacers in the trench, and (iii) the top conductor. This invention utilizes molecular device channels with at least two thiols like anchoring groups. With the help of thiol functional groups, molecular device channels are chemically bonded to the top and bottom conductors along the tunnel junction's edges. Along the tunnel junction edges, the maximum gap between the top and bottom conductor is set by the planar width of the insulator-1 and the height of the insulator-2 above the top surface of the bottom electrode (Fig. 2). This maximum gap along the edges is smaller than the molecule channel length. However, the physical gap between top and bottom conductors in the planar area is governed by the total combined thickness of insulator-1 and insulator-2. The molecule length will be much smaller than the physical spacer between two conductors in the planar area. This invention is different than all the prior works where the physical gap between the top and bottom conductor in the planar area of tunnel junction must be less than or equal to the molecule channel length [13]. The top and bottom conductor will be made up of magnetic materials to serve as source and drain of spin for the molecular spintronics devices. All the processing steps will occur at <90°C or in

an inert environment to a void undesired oxidation of the magnetic conductors [14].

At least one insulator will be accommodated in it. The thickness and width of the insulator-1, the thickness of the insulator-2, and the depth of the trench can be adjusted to accommodate very small molecules. Yet leakage current via the insulator-1 and insulator-2 will be extremely low to enable molecules' to dictate the charge and spin transport via them. As a key attribute combine thickness of insulator-1 and insulator-2 can be significantly more than that of the target molecule length. A thick insulator in the planar area reduces the adverse impact of defects on the molecular spintronics device performance and long-term stability.

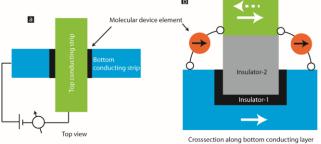


Figure 2: (a) Top view and (b) cross-sectional view of trenched bottom electrode-based molecular device.

## 2.3 TBELMD Fabrication Steps

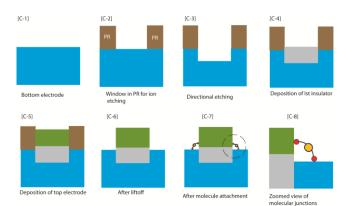


Figure 3 shows different steps involved in making trenched bottom electrode-based molecular device.

Figure 3 shows one of the several schemes disclosed in the patent. Scheme C is for the fabrication of trenched bottom electrode-based molecular devices for the cases when the bottom electrode cannot be oxidized to produce insulator-1 (Fig. 2b). For example, the bottom electrode is made up of gold and platinum-like inert metals (Fig. 3a). For this case (C-1) step deposits 1st metal strip on an insulating substrate, (C-2) step do photolithography to produce a window in the photoresist for creating a trench in the 1st strip or bottom electrode on the strip, (C-3) step remove desired thickness of the bottom electrode, a mount of material removed will be determined based on the type of molecular device elements, (C-4) step deposit in sulator in such a manner that insulator thickness is more than the

trench depth. (C-5) step Deposit top conducting metal electrode on the insulator, (C-6) step involve liftoff of photoresist to produce tunnel junction with the exposed side edges. (C-7) step bridge the molecules of interest between two metal electrodes along the two exposed edges of the tunnel junctions. (C-8) panel shows the zoomed-in view of the area where the molecule connects between two metal electrodes. The minimum separation between two electrodes is governed by the thickness of the insulator popping out of the trench.

# 3 UNIQUE ADVANTAGES

This paper disclosed the core concept of TBELMD that produces a number of unique advantages listed below.

- 1. Creation of a trench in the bottom electrode allows the creation of a robust insulating spacer. The thickness of the insulator in the planar junction area is significantly more than the magnitude of the length of molecular device channels. Due to this unique advantage, the electrical and spin transport via the insulator will be exponentially smaller than the charge and spin transport via the molecular channels.
- 2. Process of trench creation will clean the bottom electrode surface to a llow the high-quality insulator growth. This invention utilizes an ion etching step for the creation of a trench in the bottom electrode. This ion etching step brings two additional advantages (a) ion etching can remove the foreign impurities, and (b) it makes the bottom electrode surface atomically smooth to allow the growth of a high-quality insulator. None of the prior approaches attempted such a step to condition the bottom electrode.
- 3. A single photoresist cavity is utilized for three processes to make disclosed molecular spintronics device approach fast and economical. This approach utilizes a cavity in the photoresist to define the lateral dimensions of the trench area, insulating spacer, and the top electrode.
- 4. This invention utilizes the same cavity in a photoresist sheet as a means to cheaply control the lateral dimensions of the ion etched trench, insulating barrier, and the top conducting electrode. With the photoresist process's current capability, the device's lateral dimensions can be easily around ~50 nm, leading to the dense packing of the molecular electronics devices.
- 5. The liftoff approach ensures that the oxidation-sensitive magnetic electrode remains in the pristine stage until the time of the molecule attachment step. The top electrode edges touching the vertical wall of the photoresist cavity can remain in their nascent state until the time of liftoff. The molecule attachment process right after the liftoff can produce a very high probability of establishing metal electrode-molecular device element bonding.
- 6. The trenched bottom electrode and lift of f-based molecular spintronics device fabrication method enable the utilization of multilayer hard and soft ferromagnetic electrodes. Subsequently, top and bottom electrodes with a wide variety of anisotropy and magnetic attributes can bond

with molecular device elements. Each permutation and combination of magnetic electrodes and molecules will produce novel forms of molecular spintronics devices. The functioning of these devices can be far superior to that of the existing magneto resistance devices [15]. The molecular spintronics devices can switch among many resistance states due to the maneuverability of the magnetic moment direction of the molecules and the two ferromagnetic electrodes [2].

- 7. This invention enables the utilization of very interesting and capable molecules like single molecular magnets that can exhibit a transition between multiple spin states. This invention enables the connection of such molecules that can change their spin states as a function of magnetic field or light radiation with a variety of ferromagnetic electrodes. Changing the spin state of the molecular spin device element and recording its impact on the transport properties will lead to novel forms of logic and memory devices.
- 8. This invention enables the utilization of smaller molecular device elements. Smaller molecules can be extremely effective in coupling the wave functions of the two metal electrodes. The ability to control the wave function overlap via molecular device channels can lead to novel forms of magnetic metamaterials that have unprecedented attributes.
- 9. This invention recommends the utilization of Ni and Nickel alloy for the top region of the bottom electrode and bottom regions of the top electrode. By this approach, the thiol-functional group of the molecular device element will make a bond with the Ni and nickel alloys. The stability of NI-thiol bonds is more than the Ni-O bonds, and due to this reason, Ni-S bonds will be air-stable[14]. The molecular spintronics devices will be a ir-stable.
- 10. The proposed device design is compatible with the cross pattern architecture for the arrangement of functional logic and memory devices. The prior patent on cross junction pattern delineates the method of utilizing molecular spintronics devices from the logic devices.
- 11. This invention is also compatible with magnetic random access memory (MRAM) type memory device architecture. Hence, the present invention will be directly usable for developing molecular spintronics-based memory.

### 4 ACKNOWLEDGEMENTS

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