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**ENERGY SENSORS AND ABSORBERS BASED ON NANOSCALE MAGNETIC TUNNEL
JUNCTION METAMATERIALS**

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ABSTRACT

This paper explores nanoscale energy sensors and absorber metamaterials that can be used in various applications, such as solar cells and infrared detectors. It is possible to gain highly efficient and adjustable energy absorption, creating absorber metamaterials at the nanoscale that enhance the performance of solar cells. These metamaterials are based on molecular spintronics devices (MSD) and magnetic tunnel junctions (MTJ). The pillar shaped MTJs are made of two ferromagnetic metals separated by an insulating barrier, such as aluminum oxide (AlOx). The manufacturing process includes photoresist spin coating on a silicon wafer, photolithography, thin film sputtering, and liftoff. Following fabrication, the top and bottom electrodes are covalently bonded by a single magnetic molecule (SMM) on the exposed side edges for strong magnetic coupling that changes the magnetic properties of both ferromagnetic metals. This study has considered different thin film deposition materials, configurations, and thicknesses. Magnetic field resonance and light reflectance measurements have been performed before and after molecule attachment to understand the molecule effect on the metamaterials' energy absorption behavior. The Ferromagnetic Resonance (FMR) test revealed that the devices shifted following molecule attachment in both acoustic and optical modes. Moreover, due to molecule attachment, there have been significant alterations in the MTJ's electromagnetic wave absorption characteristics with about 30% less reflectance. This metamaterial has various potential applications in aerospace, renewable energy, sensing, imaging, and communication. It is also a cheaper alternative to traditional solar cells and can inspire the development of smart metamaterials with selective absorption and tunable response.

KEYWORDS: Magnetic Tunnel Junctions; Molecular Electronics; Photovoltaic Cell; Light Absorber; Energy Sensors, Anti-reflective; Metamaterial, Renewable Energy.

1. INTRODUCTION

The energy crisis and increase in pollution has forced humanity to look for new energy sources in order to satisfy global energy necessities sustainably and cleanly. According to Harvard environmental research, traditional fossil fuel energy sources must be reduced and changed because they are responsible for 1 in 5 deaths [1]. PV solar panels have been improving for the last decades and are now one of the principal renewable energy sources. However, they still need to reach high efficiency; one of the reasons for this lack of efficiency is the reflection of the light when it arrives at the surface of the PV solar panel. Solar panels without anti-reflective protection are currently losing around 30% of the photons that reach the cell. To overcome such problems, new magnetic meta-materials are being used to create a new type of solar cell and anti-reflective nanoscale coats.

Metamaterials are innovative, artificial, and advanced engineered materials made in a specific order and scale to have special characteristics that cannot be found in nature[2]. Metamaterials are multi-disciplinary and have practical applications in different areas, such as electrical engineering, electromagnetics, solid-state physics, antenna engineering, optoelectronics, classical optics, microwave, materials science, semiconductor engineering, and nanoscience[3],[4]. Metamaterials (MMs) are synthetic materials whose properties are obtained from carefully made meta-atoms rather than their constituents' properties. The meta-atom is small in comparison

to the wavelength of light. Meta-materials are classified as the negative reflective index (NIMs), zero indexes, mechanical index, photonic index, chiral, hyperbolic, semiconductor MMs, quantum, and atomistic [5]–[7]. Magnetic metamaterials are materials with negative permeability in a specific frequency band. Smart magnetic is a future material with permeability and permittivity created by interpenetrating lattices that respond to magnetic and electric fields[8], [9].

The metamaterial built in this project is based on magnetic tunnel junction molecular spintronics devices (MTJMSD). Magnetic tunnel junctions (MTJs) are a novel type of thin film device that was successfully manufactured for the first time in the mid-1990[10]. In most simpler cases, MTJ is a tri-layer "sandwich" composed of two layers of magnetic material kept separate by an ultra-thin insulating film. If a voltage is given to the top and bottom of this structure, classical physics does not allow a current to pass, but if the insulating layer is sufficiently thin, electrons can flow across the barrier layer via quantum mechanical tunneling. An applied magnetic field can alter the relative orientation of the magnetizations of the two ferromagnetic layers, which determines the tunneling current in MTJs[7], [10], [11]. Regarding MTJ performance, integrating molecular channels between two ferromagnetic electrodes can have some unique benefits; it has been shown that after a molecular treatment, it produced strong magnetic coupling between two ferromagnetic films[11], [12]. This strong coupling changed the physical properties of magnetic layers[13]. This MTJMSD behaves like energy sensing and absorbing magnetic meta-material.

In this study, a magnetic tunnel junction molecular spintronics device is built using different combinations of materials and film thicknesses to investigate the possibility of having energy sensing and absorbing behavior. These metamaterials are made using materials that are already widely available, which makes them a great alternative to the traditional P-N junction solar cells with a new photovoltaic mechanism.

2. MATERIALS AND METHODS

Pillar structure nano design is used in this study with different metals, insulator, and metal nanolayers. We tried various configurations of thin film deposition materials and insulator thicknesses to check the light absorption behavior of devices. The materials used can be separated into two groups. First, a list of the metals which function as conductors includes Nickel (Ni), Nickel/Iron (Ni/Fe), Cobalt (Co), and Tantalum (Ta). Second, the nonconductor insulator used in different thicknesses is Aluminum Oxide (Al_2O_3). The layers are always in the nanoscale, and the thickness of the insulator is always the smallest layer. The base wafer where the MTJ is developed is a 199 nm silicon dioxide layer. The first step to fabricate this MTJMSD device is to use photolithography to create a cavity where the layers will be deposited in a given shape.

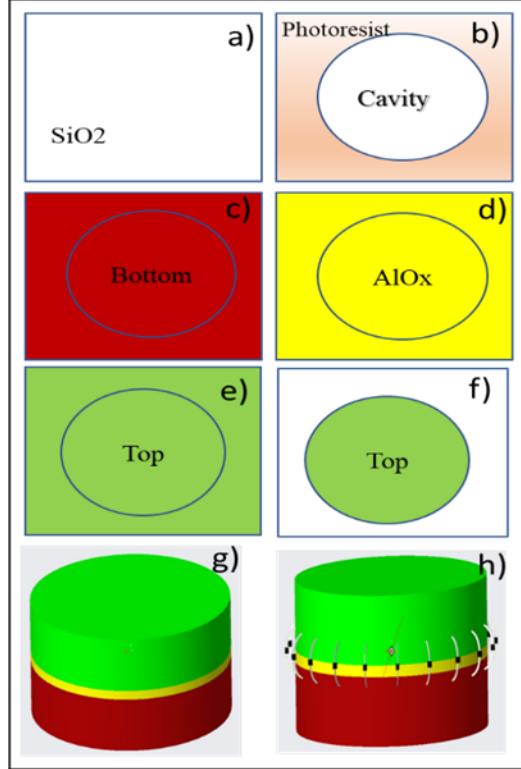


Figure 1 Fabrication process of MTJMSD a) silicon dioxide wafer, b) photolithography for the deposition pillars, c) bottom electrode deposition, d) AlOx insulator deposition, e) top electrode deposition, f) photoresist lift-off, g) 3D view of an MTJ with exposed side edge, h) 3D view of an MTJMSD, where the molecule is bridging the top and bottom electrode.

The photolithograph process starts with spin coating of photoresist on the sample. Then exposes the samples to a UV light while the samples are in contact with a pillar shaped photomask (Fig.1b). After exposure the samples will be submerged in a developer to get the shapes on the sample. The next step is the deposition of the nano layers using the sputtering machine. First, the bottom electrode, which is a mixture of the metals described above is deposited (Fig.1c), next the insulator is deposited (Fig.1d), finally a metal layer is placed in the structure as a top electrode (Fig.1e). When all the layers have been deposited and the MTJ structure has been formatted, lift-off of the photoresist leaves the tunnel junction with a pillar structure (Fig.1f and g). To finish the manufacturing process of our MTJMSD, the molecules are covalently bonded to both metals (Fig.1h). The molecule attachment process involves subjecting to the alternating ± 100 mV biasing between two metal electrodes with a time interval of 0.02 seconds for a period of 2 minutes.

The sample's ferromagnetic magnetic resonance (FMR) is measured using Electron Resonance Spectroscopy (ERS) Magneetech 5000. Because energy involved with microwave absorption in ultrathin films like our device is in the μK region, FMR is the technique of choice for investigating the

thermodynamic ground-state characteristics. Also, SEMICONSOFT is used to measure the light reflectance of samples. The thin film measuring systems in SEMICONSOFT measure the thickness, composition, and other aspects of thin films using a variety of methods, including spectroscopic ellipsometry and reflectometry. The measurement was performed in two phases, first before molecule attachment and then after attachment to see the effect of the molecular bridge on our samples.

3. RESULTS AND DISCUSSION

The first set of our samples is composed of Ta(1-2 nm)/Co(4-6 nm)/NiFe(1-2 nm)/Al₂O₃(2-3 nm)/NiFe (6-8 nm) as shown in Figure 2. In this experiment we have used two different wafers, one being the commonly used Silicon oxide (SiO₂) and the second one is glass. Silicon oxide wafers are extremely pure and have a very high degree of crystalline perfection, which is essential for the reliable operation of electronic devices, while glass is amorphous and lacks a well-defined crystal structure. Another significant distinction between silicon oxide wafers and glass is their optical characteristics. Because silicon oxide wafers are transparent to infrared light, they may be used to build optical components such as lenses and filters. In contrast, glass may be designed to be transparent to a larger range of wavelengths, including visible light. In this experiment, we deposited the same film stack to assess their light absorption behavior.

SiO₂ and glass-based samples have the same thin film stack as shown in the schematic below in Figure 2, the only difference being the base wafer used to deposit pillar structures. The FMR measurement is also displayed in Figure 3b and 3c before and after SMM molecule attachment to both samples. The FMR measurement reflects the magnetic properties of the ferromagnetic material alone. After the molecule is attached, the FMR measurement shows changes in the precession frequency or other characteristics, indicating that the molecule has affected the magnetic properties of the material.

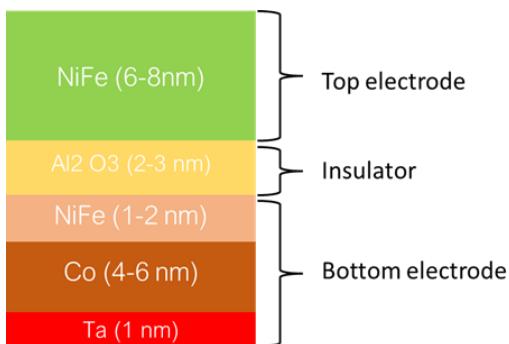


Figure 2 schematic of magnetic tunnel junction (MTJ) builds in experiment One, which contain a top ferromagnetic, insulator and bottom ferromagnetic layers.

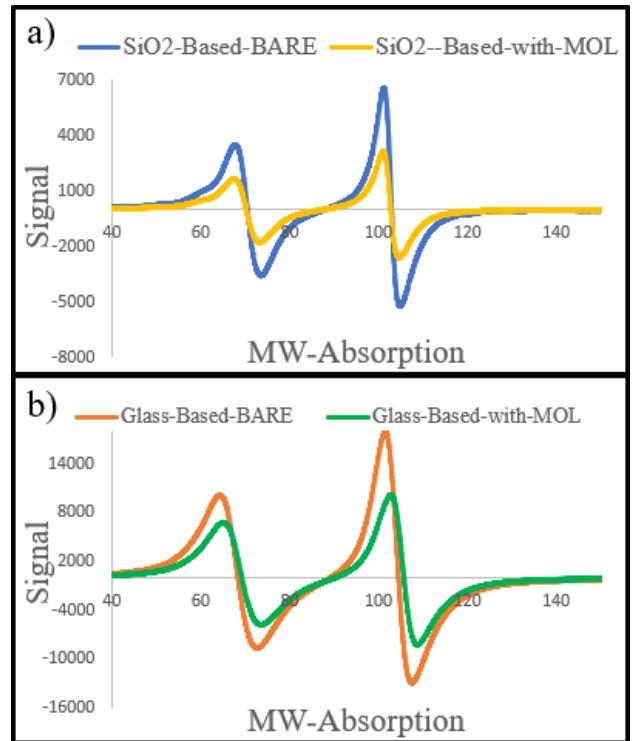


Figure 3 a) FMR spectra before and after SMM molecule attachment for SiO₂ based samples, Bare indicates the device before molecule attachment and with-SMM indicates the device after molecular attachment. b) FMR spectra before and after SMM molecule attachment for glass-based samples, Bare indicates the device before molecule attachment and with-SMM indicates the device after molecular attachment.

As can be seen in the graphs before and after molecule attachment graphs are somewhat different, after molecule attachment the FMR graph's amplitude has decreased, and it started to shift to the right. From these results we can see that the molecules started to show some effect on our device, however the effect is not quite strong to show dramatic change.

The reflectance measurement is shown for the devices that have 1nm insulator thickness is shown in Figure 4. By utilizing reflectance measurements, the light absorption of the surface of the device is evaluated. In comparison to undeposited silicon oxide, the multilayered device exhibits superior light absorption across a wide range of the visible light spectrum.

The observed oscillations in the reflectance graph may be attributed to the deposition of pillar structures, consisting of thousands of pillars spaced apart by a small area. As depicted in Figure 6a below, while silicon oxide displays high absorption around 400 nm wavelength, its reflectance is significantly high elsewhere. In contrast, our sample maintains constant absorption throughout the entire wavelength range even prior to molecular treatment. According to the graph, the light absorption of the device improves by 9.4% following molecule treatment compared to its pre-treatment level. In Figure 4b, the reflectance of the sample using glass as a wafer is shown. Due to the transparent nature of glass the one that does not have any

deposition has a lowest reflectance. However, when we compare our device before and after molecular treatment, there is about 42.83% better absorption of light after molecular treatment.

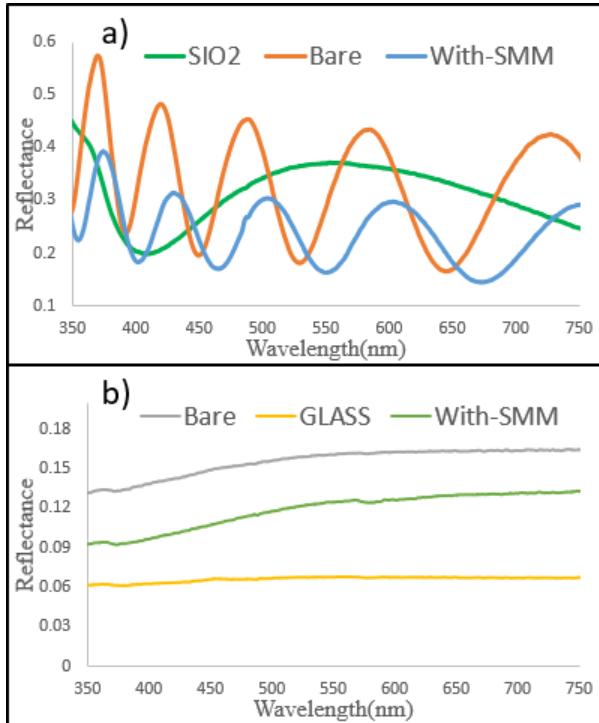


Figure 4 Reflectance measurement of sample 2, a) the results for a silicone oxide wafer, SiO_2 stands for a standard wafer without any thin film deposition, Bare stands for our thin film multilayer device before any molecular treatment, and With-SMM shows the results after molecule attachment. b) shows the results for a glass wafer, the reflectance of the amorphous glass without any thin film deposition is shown by the label of glass, Bare stands our device without any molecular treatment and With-SMM shows the results after molecule attachment.

Our second set of samples were composed of the thin film stuck $\text{Co}(4\text{-}6\text{ nm})/\text{NiFe}(2\text{-}4\text{ nm})/\text{Al}_2\text{O}_3(0.5\text{-}1.5\text{ nm})/\text{NiFe}(6\text{-}8\text{ nm})$ as it is shown in Figure 5.

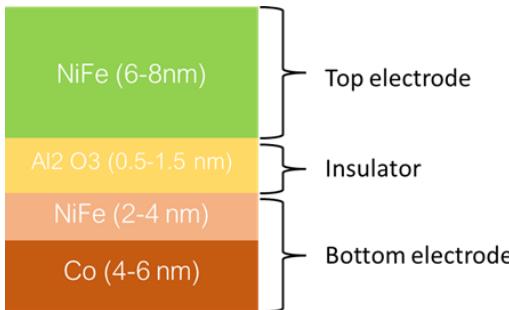


Figure 5 schematic of magnetic tunnel junction (MTJ) builds in experiment two, which contain a top ferromagnetic, insulator and bottom ferromagnetic layers.

The results of a magnetic resonance analysis of sample two that is obtained before and after molecule attachment is shown in Figure 6. The measurement is performed to assess if the molecule attachment has any effect on the magnetic resonance of the sample. Our sample showed two clear modes. The location of an optical mode relative to an acoustic mode in a material can provide important information about the magnetic interactions between the layers. If the optical mode is located at a higher frequency than the acoustic mode, it can indicate the presence of antiferromagnetic coupling between ferromagnetic layers. As seen in the graph, before any molecular treatment, the bear sample showed differences in pick initiation and amplitude. As a result of the attachment of molecules, when the Ferromagnetic Resonance (FMR) test was performed, it was discovered that the devices had shifted in both acoustic and optical modes.

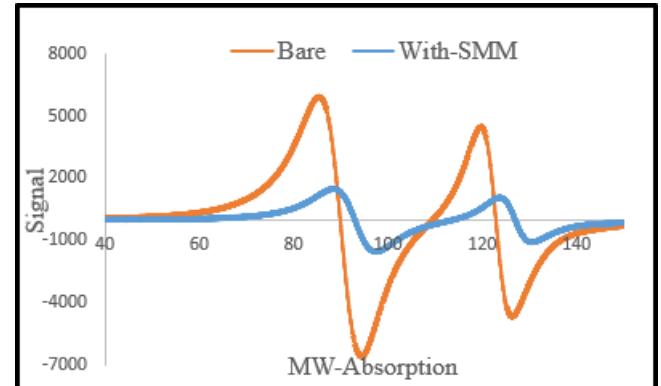


Figure 6 FMR spectra before and after Single magnetic molecule SMM molecule attachment, Bare indicates the device before molecule attachment and with-SMM indicates the device after molecular attachment.

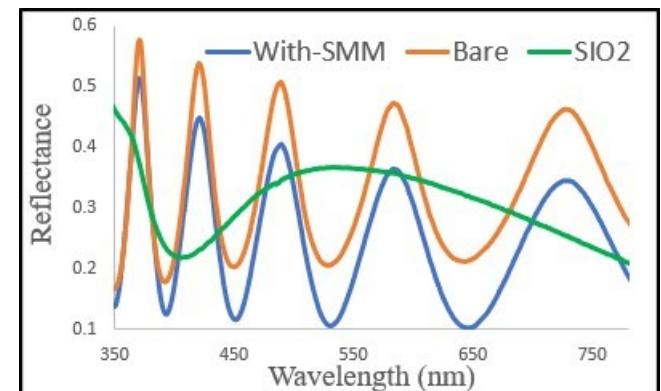


Figure 7 Reflectance measurement, SiO_2 stands for a standard wafer without any thin film deposition, Bare stands for our thin film multilayer device before any molecular treatment, and With-SMM shows the results after molecule attachment.

This change suggests that the presence of molecules has a major impact on the magnetic characteristics of the material. This is because molecules can interact with the material's magnetic moments, affecting their orientation and interactions with each other.

The reflectance measurement for sample set 2 is shown in figure 7, as discuss earlier SiO₂ has lower reflectance only around 400 nm wavelength which is not desirable absorption, however sample 2 even before attachment of molecular bridge has better absorption thought the whole visible light spectra. After molecular attachment the absorption increases by 48.79 % as shown in the graph. This suggests that the molecular bridge enhances the absorption properties of the sample.

4. CONCLUSION

In this paper, novel metamaterial energy sensors and absorbers were made based on pillar shaped MTJMDS. The device fabrication includes photolithography and thin film suppering. The result from the magnetic resonance measurement showed shaft on both acoustic and optical modes after molecule treatment indicating the influence of the molecule on the device. The results of reflectance measurements revealed that the device developed in this work has better absorption through the whole visible light spectrum. Also, the SMM effect on the light absorption was significant as it decreased the reflectance by more than 48.79%. These innovative materials have the potential to greatly enhance the efficiency of solar cells and other energy-harvesting devices, while also enabling new approaches to energy storage and conversion

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