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Metal/Self-Assembled Monolayer/Metal Junctions for Magnetoelectronic Applications.

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ABSTRACT

Metal/organic self-assembled monolayer/metal junctions were investigated for junction areas 10^{-2} to 10^{2} μm^2. Several types and thickness of monolayers are investigated, and magnetic electrodes were made. Electroless deposition was used to make the top metal without disrupting the organic film. This deposition is activated with Pd clusters obtained by evaporation or by chemical reduction of a Pd-based catalyst. This method allows us to obtain a high yield of junctions that are not electrically shorted and are mechanically and electrically stable over a wide temperature range. Low-temperatures investigations reveal strong non-linearity in the IV curves and an increase of resistance with decreasing temperature. Zero bias anomalies observed at low temperatures are attributed to a Coulomb blockade associated with the Pd clusters.

INTRODUCTION

Metal-Insulator-Metal (MIM) tunnel junctions are of great interest for applications as magnetic sensors and memory devices. If both metals are ferromagnetic, the tunnel resistance of the system depends on the relative magnetic orientations of the two magnetic layers [1]. The magnitude of this effect (typically reaching 40%) depends on the properties of the insulator. The main desirable properties are the possibility to make very thin barriers (smaller than 1 nm), with atomically sharp interfaces. To date, the vast majority of tunnel magnetic junctions have been constructed using Al_2O_3 barriers. We intend to examine the possibility to use organic films as an alternative to Al_2O_3 in MIM structures.

It is well-documented that a variety organic thiols can be used to construct self assembled monolayers (SAM) on metallic surfaces [2]. However, significant synthetic difficulties are encountered when trying to deposit a top metallic electrode without disrupting the organic substructure. Evaporated and sputtered metal layers are often not stable on organic thiol monolayers [3]. High diffusibility of thiols [4], as well as low structural stability of evaporated/sputtered films, usually destroys the MIM structure.

We have successfully used electroless deposition (ELD) to plate ferromagnetic metal films on top of self-assembled organic tunnel barriers. Such metal films can show better structural stability than their evaporated or sputtered counterparts [5]. Mechanical and thermal damage to the organic layers is avoided. We can also tailor the distal end of alkanethiols with functional groups capable of activating ELD growth. This method is known as selective ELD [6].

We report here the preparation and characterization of two types of MIM junctions (Figure.1). The first, which was pattern using lithographic techniques, has a planar cross geometry with junction areas ranging from 10 to100 μm^2. The second type of junction was prepared by electrodeposition in a template to produce columnar MIM structures with 30 to 400 nm diameters. These geometries enable us to investigate junctions with areas spanning several orders of magnitude. The junctions with smallest cross-sectional area are particularly attractive for minimizing the probability of pinholes.

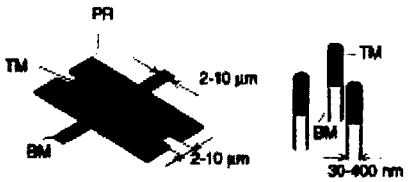

Figure 1. Schematics of the samples geometries for the planner junction (left) and nanowires (right). Thiol layer was deposited on bottom metal electrode (BM) from solution. Top metal electrode (TP) was obtained by electroless deposition. Photoresist mask (PR) was used in planar junction to limit the area.

SAMPLE PREPARATION

Planar MIM junction

Optical lithography was used to pattern lines down to a 2 µm width on silicon wafers coated with SiO(300nm)/Ti(10nm)/Au(100nm). Ni and Co top layers were then obtained by thermal deposition. An opening of a few µm was patterned using a second layer of photoresist. Depositions of alkanethiols were made in a Braun Labmaster 130 inert atmosphere box. The coating solutions were comprised of ca. 0.1 M alkanethiol (ethanethiol, pentanethiol, hexanethiol or dodecanethiol) dissolved in ethyl alcohol. All alkanethiols (Aldrich) were used as purchased. Ni and Co bottom metal layers were electrochemically cleaned to remove native oxides prior to SAM deposition. Some of the samples where subsequently heat-treated at 60-100 C for 1-24 hours. Top layers of Cu and Ni were made by ELD method. The ELD plating process was catalyzed by a Pd seed layer of 3 - 5 Å thickness. The seed layer was obtained by slow evaporation in a vacuum chamber. Cu films were made using a bath composition found in the literature [7]. Ni films were made using an electroless hypophosphate bath [5].

Nanowires in nonoporous membranes.

We used polycarbonate nanoporous membranes (Watman corp.) with a thickness of 10 μm and nominal cylindrical pore diameters of 30, 100 and 400 nm. One side of the membrane was sputtered with gold, which served as working electrode. Growth of cylindrical wires of diameters slightly larger than the nominal pore diameter value was reported in the literature for a variety of materials [8]. Bottom Ni half-wires were plated from a classic Watt's bath by adjusting the deposition time to grow the wire approximately half way through the membrane. The membranes were then dried and transferred to an inert atmosphere box where they were electrochemically cleaned. A SAM was prepared from 2-mercaptoethylamine or 4-aminothiophenol. Both molecules have $-NH_2$ tail groups that are used to generate the Pd catalyst. (Synthetic details for the Pd catalyst can be found in [9]). Samples were exposed for 1 hour to the Pd catalyst solution, which was made by dissolving 10 mg Na_2PdCl_4 and 1.75 g of NaCl in 50 ml of H_2O, and then adjusting the solution to pH=1 with 37% HCl. Ni top electrodes were obtained by ELD deposition using the method described above for planar junctions. The deposition process was terminated when metal islands were visually detected on the membrane surface.

RESULTS AND DISCUSSION

Samples were investigated in a temperature range of 1.5 K – 300 K and under applied magnetic fields up to 10 T. Four point connections were made to perform AC and DC electrical measurements. Weak adhesion between the SAM and the top electrode was generally found on planar samples, indicating a lack of chemical bonding to the top electrode. The resistance values of the junctions varied over several orders of magnitude without any direct correlation with junction area or molecular length. We found a lower probability of electrical shorts for heat-treated SAMs, which indicates that this process leads to a highly ordered and more densely packed tunnel barriers. This conclusion in consistent with that found in a recent report concerning electrochemical characterization of SAMs [10].

Junctions with resistances ranging from tens of kOhm to several MOhm were investigated. Most samples showed good temperature stability, and were capable of sustaining several temperature sweeps between room temperature and a few Kelvin. We observed a slow variation of the resistance as a function of temperature between 300 K and 20 – 50 K. A much larger increase was observed upon lowering the temperature below 20 K. Such behavior is related to a large bias dependence of the differential resistance, spanning several orders of magnitude (Figure 2). These observations can be attributed to a Coulomb blockade caused by the Pd particles incorporated in the organic layers. If a particle is separated by a total capacitance C from the electrodes, the charging energy necessary to add one electron on the particle (i.e., $e^2/2C$) hinders the electron flow if the charging energy is significantly larger than the thermal energy [11]. From the temperature dependence of the resistance, a charging energy of several meV can be deduced, corresponding to the bias values at which the resistance of the sample diminishes significantly.

Some samples demonstrated complicated dependence of the resistance on bias. Asymmetrical shoulders and hysteresis on these shoulders (Fig. 3a) were observed. Since the width of R(Bias) curve is proportional to 1/C, where C is capacitance of particle, the appearance of shoulders can be explained by a significant parallel current channel through smaller particles. In this case hysteresis may reflect metastability of particle positions. Switching instabilities

(Figure 3b) and long term relaxation after applying a magnetic field (not shown) were observed for these samples as well. Again, instabilities were attributed to mechanical variability of Pd clusters trapped inside the organic film. The nanowire junctions showed properties similar to those of larger areas, which confirms the assertion that the electrons flow though a limited area.

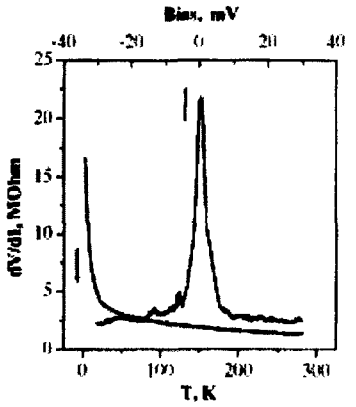

Figure 2. Zero bias differential resistance as a function of temperature (bottom scale) and as a function of voltage bias at 1.6 K (upper scale) for Ni-ethanethiol-Ni planar junction.

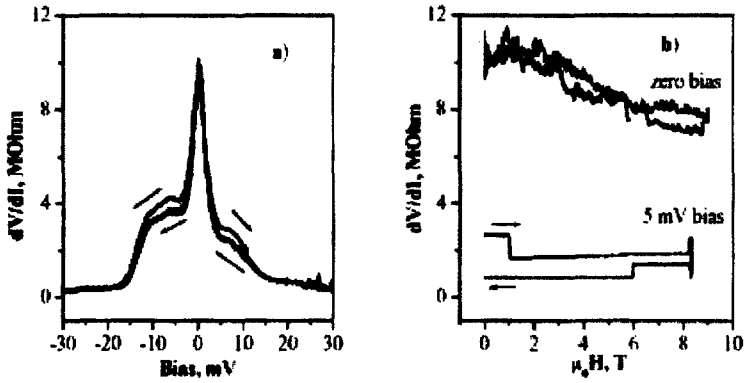

Figure 3. (a):Differential resistance of Au-dodecanothiol-Ni tunnel junction at 1.6 K as a function of applied bias. The hystereis in the IV curves disappears after several voltage weeps, stabilizing the lower curve. (b)Magnetic field dependence for two voltage bias.

CONCLUSION

A variety of MIM structures were investigated, with area values varied from 10^{-2} μm^2 to more than 10^2 μm^2. We observe a systematic blocking of the current at small bias, which we interpret in terms of a Coulomb blockade associated with Pd clusters. Synthetic routes that do not rely on a Pd seed layer need to be found to avoid blockade effects. Alternatively, the use of lighter elements for seed clusters, or the use of magnetic seeds, will provide interesting systems for which the effect of Coulomb blockade on spin-dependent transport properties in tunnel junctions may be studied. Theoretical predictions [12,13] , as well as preliminary experiments [14], indicate that magnetoresistance can be enhanced in the Coulomb blockade regime.

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