

Examination for the Advancement to Candidacy  
Original Research Proposal

**A *pseudo* Three-Terminal Molecular Device**

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## ABSTRACT

Recent advances in molecular device studies have shown that molecular-scale electronics is a promising successor to silicon based microelectronics. However, a three-terminal device, which is ultimately desired for many applications, has not been realized experimentally because of the difficulties in creating three terminals at extremely short length scale. In this proposal, we will describe a *pseudo* three-terminal device which uses a tunable laser as the third terminal and suggest one possible way of gating in molecular devices. The main part of this device is a nanoscale *metal/mixed self-assembled monolayer/metal* heterostructure. The self-assembled monolayer (SAM) consists of a mixture of molecules which have the same skeletal structure but different substituents. The skeletal structure has a  $\pi$ -electron system and contains a photo-active center. The photo-active center can undergo reversible isomerization upon photo-adsorption, thus changing the conductivity of the molecule (ideally, the two isomers correspond to ON and OFF states respectively). The number of molecules that are switched on or off determines the conductivity of the whole device. Adding different substituents shifts the UV absorption band ( $\lambda_{\text{max}}$ ) to slightly different values. We will choose a mixture of these molecules, which cover different, but slightly overlapped, absorption bands. This will allow different components to be switched on or off sequentially when swept by a tunable laser. By controlling the range of the laser sweep, we can switch on or off different numbers of molecules, and thus control the overall conductivity of the heterostructure. In this manner, it is possible to experimentally realize a *pseudo* three-terminal molecular device, in which the input of the third terminal controls the output of the other two terminals.

## Background and Significance

In the last few decades, there have been advances in solid-state and silicon based microelectronic technologies. The number of transistors that can be fabricated on a silicon integrated circuit, and therefore the computing power of such a circuit, has doubled every 18 to 24 months for over 4 decades. However, as the size of transistors shrinks down to  $\sim 0.1$  micron, phenomena such as stray signals on the chip, the need to dissipate the heat, and difficulties of fabrication will increase dramatically and probably at last halt the progress. Forced migration to new forms of electronics is expected to come about within one or two decades [1]. Until recently, none of the technologies proposed have shown enough promise as successors to solid state microelectronics.

Within the past few years, however, some revolutionary advances were achieved that may radically change the future of computing. Recent advances were in molecular scale electronics, a field emerging around the premise that it is possible to build individual molecules that can perform functions identical or analogous to those of the transistors, diodes, conductors and other key components of today's microelectronics. It has been shown that individual molecules can conduct and switch electric current and store informations. For example, a rudimentary molecular version of an AND gate was produced to perform a basic logic operation [2]. With well over a million molecules apiece, the switches are far larger than would be desirable, and they could be switched only once before becoming inoperable. Nevertheless, their assembly into a logic gate was of fundamental significance. Reed *et al.* reported a different class of molecules that contained a nitroamine redox center and could act as a reversible switch when subjected to certain voltages [3]. To produce the switch, they inserted regions into molecules that trapped electrons, but only when the molecules were subjected

to certain voltages. Molecules that could retain, rather than trap, electrons and could work as a memory element were also reported by the same group [1,4].

Various molecular species, organic or organometallic, can be used for molecular electronic applications. In general, desirable properties include stability, synthetic flexibility, solubility, rigidity, self-assembly, functionality and control of conductivity. The molecule of interest usually contains a  $\pi$ -electron system to guarantee the conductivity, and end groups which allow the attachment to electrodes. Self-assembly is a phenomenon in which atoms, molecules or groups of molecules arrange themselves spontaneously into regular patterns and even relatively complex systems without intervention from outside. The study and use of self-assembly techniques in molecular device has advanced the ability of constructing and testing useful molecular circuits which will consist of a vast number of devices (see Ref. [18,19] for overviews on SAMs). Molecules of benzene-1,4-dithiol were self-assembled onto two facing gold electrodes of a mechanically controllable break junction to form a statically stable Gold-Sulfur-aryl-Sulfur-Gold (Au-S-aryl-S-Ar) system, allowing for direct observation of charge transport through the molecules [5]. It was the first time that conductance of a single molecule was measured. Another fabrication technique that adapted traditional microelectronic fabrication techniques was reported in Ref. [6]. Nanostructures that have a metal top contact, a self-assemble monolayer, and a metal bottom contact can be fabricated with good control over the device area and contact stability. This technique can be easily adapted to other molecular wire systems. The same technique was used to create and demonstrate a molecular electronic device with a large ON-OFF ratio and negative differential resistance (NRD) [3]. Semiclassical as well as *ab initio* theoretical models were also proposed. Some of them can essentially reproduce the experimental results and

provide directions for further studies [8,9,11–16].

Although the advances are encouraging, the remaining challenges are enormous. So far the devices that were demonstrated had only two terminals. Realistically, to construct complex logic circuits requires devices that have more than two terminals, in which, for example, current between two is controlled by a third (the gate). Some molecules with three specially designed branches attachable to gold electrodes were proposed as candidates for molecular transistors [24]. First principle calculations using density-functional theory (DFT) have shown the possibility of gating using a third capacitive terminal [10]. However, due to the extreme technical difficulties of realizing three terminals at a molecular scale, three-terminal molecular devices have not been experimentally studied. While creating a real three-terminal molecular device may be still far beyond the capability of known technologies [1], it is proposed here that a *pseudo* three-terminal device can be realized using techniques that are already available. As shown in Fig. 1, the proposed device contains a *mixed* SAM that is photoactive. It employs a tunable laser as an external gate, thus avoiding three terminals within extremely short distance. The size of this device will be larger and response speed may be slower than desirable. However, the device is proposed mainly to experimentally study one possible way of gating in molecular devices, while experimental testing of any previously proposed three-terminal molecular device is still intangible [24].

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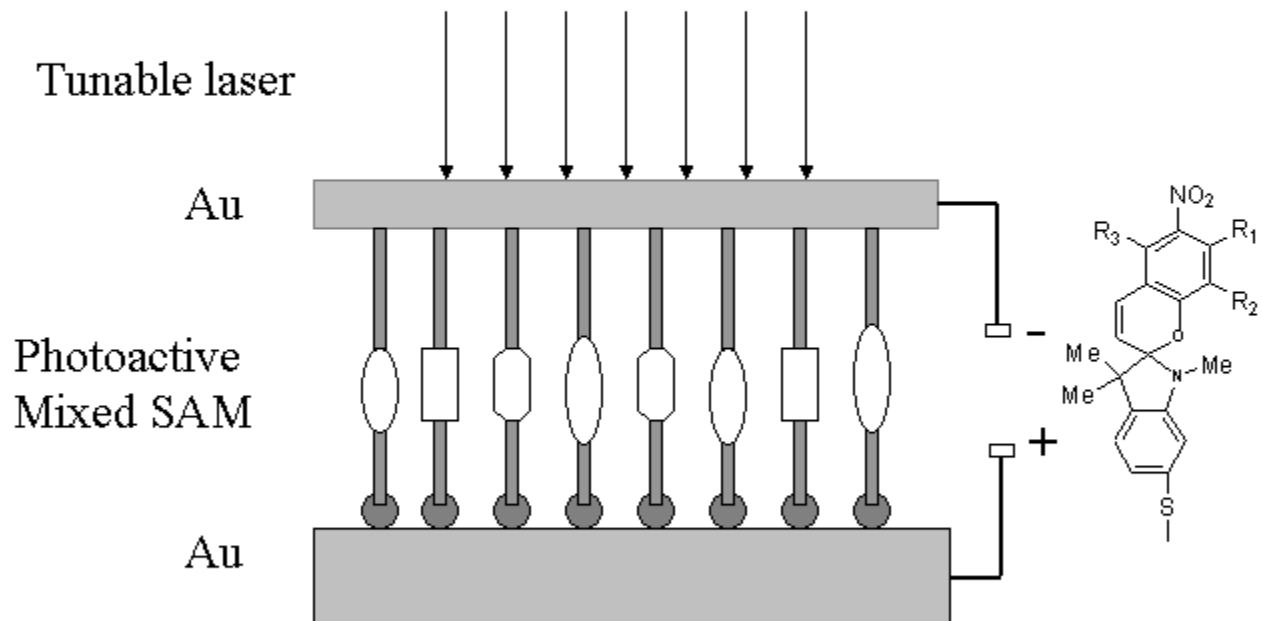


FIG. 1. Schematic drawing of the proposed device. The photoactive mixed SAM contains molecules shown on the right handside.  $R_1$ ,  $R_2$ , and  $R_3$  are different for different components so that the UV adsorption bands ( $\lambda_{\max}$ ) are slightly different (illustrated by using different shapes for the photoactive centers in the drawing).



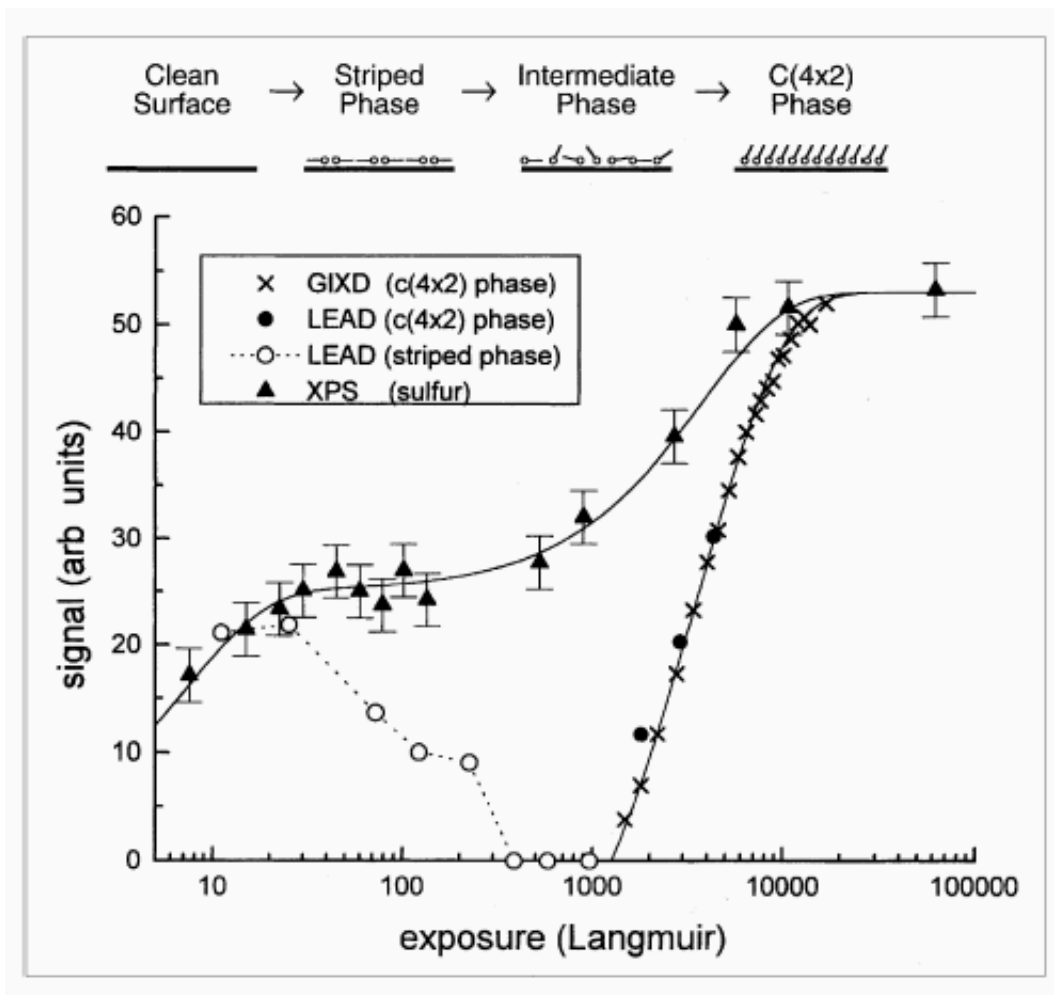


FIG. 2. The vapor-phase deposition of decanethiol on Au 111 is shown through X-ray photoelectron microscopy (XPS), low-energy atom diffraction (LEAD) and grazing-incidence X-ray diffraction (GIXD) at 25°C. The XPS data reflect changes both in the thiol coverage and in the attenuation through the hydrocarbon layer (when the hydrocarbon chain stands up in the intermediate and C(4×2) phases). The GIXD and LEAD data show the integrated intensity of diffraction peaks corresponding to the striped or C(4×2) phase. The resulting structural evolution is shown schematically at the top. This figure is adapted from [27].

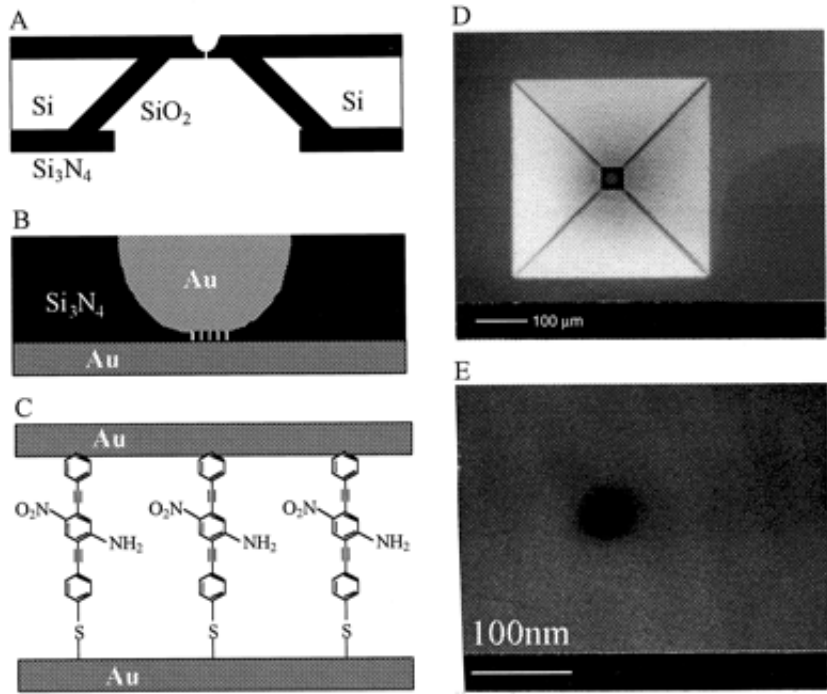


FIG. 3. Schematics of device fabrication. (A) Cross section of a silicon wafer with a nanopore etched through a suspended silicon nitride membrane. (B) Au-SAM-Au junction in the pore area. (C) Blowup of (B) with 1c sandwiched in the junction. (D) Scanning electron micrograph (SEM) of pyramid Si structure after unisotropic Si etching [that is, the bottom view of (A)]. (E) SEM of an etched nanopore through the silicon nitride membrane (adapted from reference [3]).

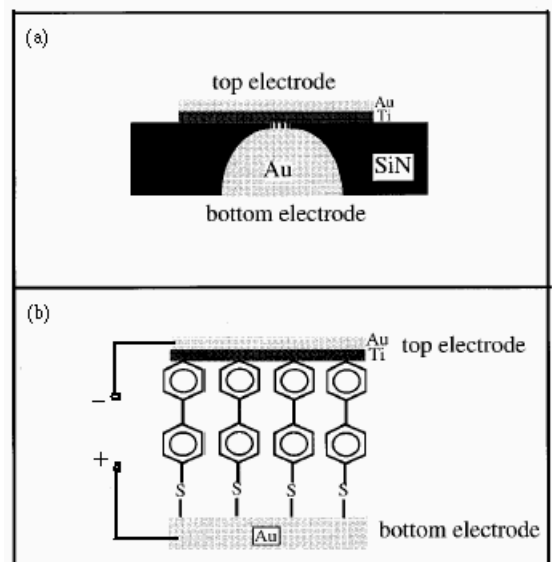
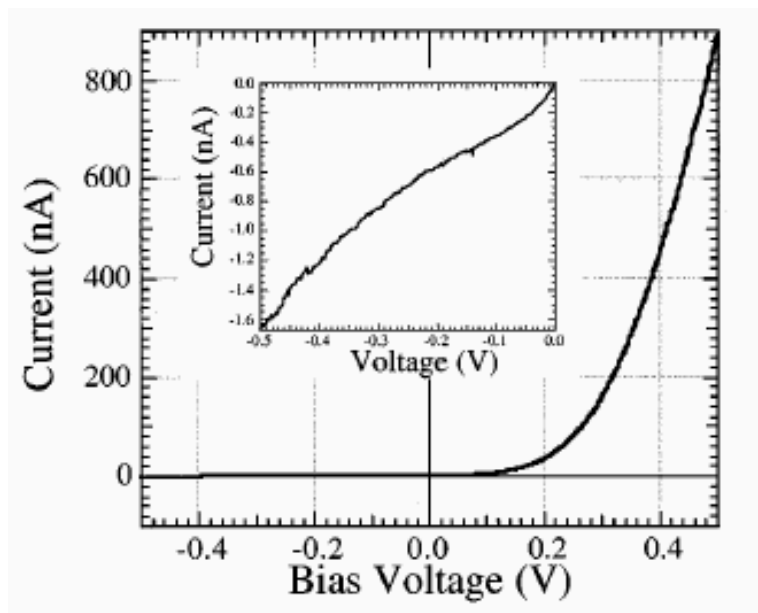


FIG. 4. *I-V* characteristics at room temperature of the molecular device shown on the right panels [6]. The inset is the magnified view of the negative bias part. (adapted from reference [6])

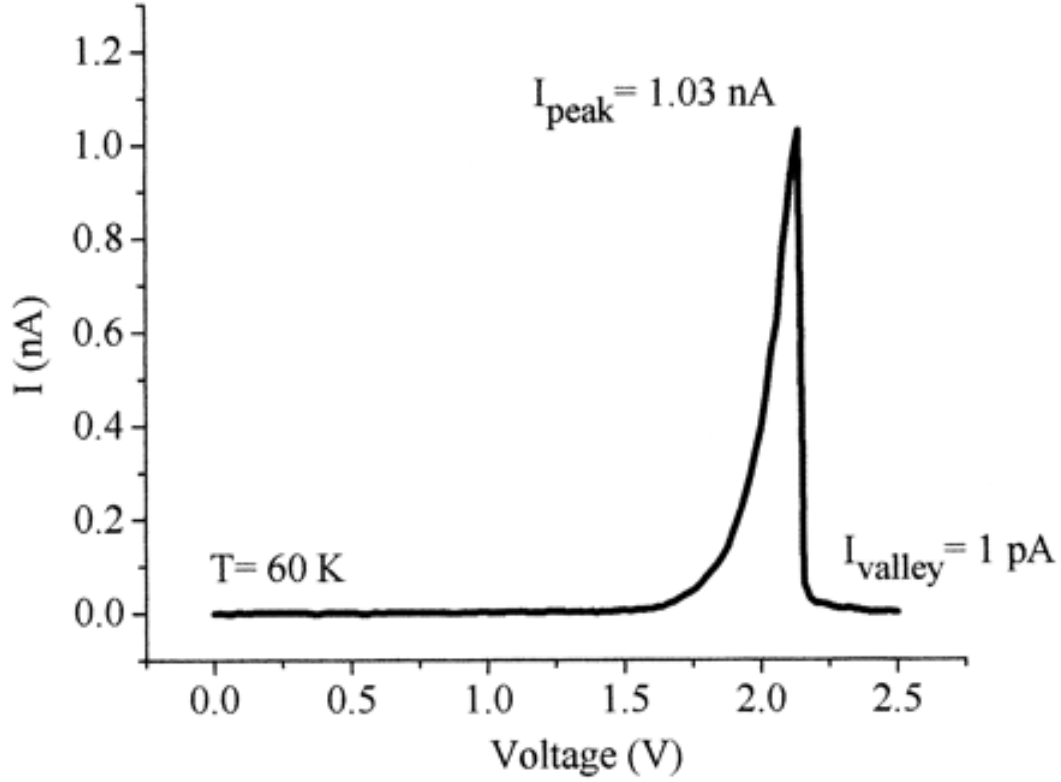


FIG. 5. *I-V* characteristics of the Au-SAM-Au device at 60 K. The peak current density is about  $50 \text{ A/cm}^2$ , the NDR is about  $-400 \mu\text{ohm}\cdot\text{cm}^2$ , and the peak to valley ratio is 1030:1. This figure is adapted from Reference [3] to show that even though sulfur atom breaks the conjugated  $\pi$  electron system, the conductance of ON and OFF states can still be significantly different.