Three Terminal Self-Assembled Monolayer Based Electronic Devices

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3. Abstract

Two terminal electronic devices based on self-assembled monolayers (SAMs) are attractive currently due to a recent breakthrough that involved a novel technology for making contacts to molecules[1]. The aim of the current project is to exploit further the use of this novel technology to develop other SAM-based electronic devices, especially transistors, for purpose of generally accomplishing this devices as well as to gain more insight into molecular properties, which are manifested in these devices.

4. Duration of the Project

The project will start in July 2006 and will continue until July 2010 since this will be the applicant's time as a PhD student.

5. Personnel

The personnel working on this project are all part of the research group *Physics of Organic Semiconductors*, part of the research cluster *Molecular Electronics* of the *Materials Science Centre^{Plus}* :

Prof. Dr. Ir. P.W.M. Blom (Professor / Leader of the research group)
Dr. B. de Boer (Assistant Professor / Project Leader)
Ir. H.B. Akkerman (PhD Student)
A. J. Kronemeijer (Applicant / PhD Student)
J. Harkema (Technician)
F. van der Horst (Technician)

6. Cost Estimates

The funding is requested for the applicant, one PhD position. Furthermore, all specifically related needs such as wafers, lithography masks and chemicals will be acquired from this budget. The equipment needed for this project is already present in the laboratory of the research group or within the *Materials Science Centre*^{Plus} and no other support will be required for this project.

Budget summary of the funding requested

	2006	2007	2008	2009	2010	Total
PhD Students	1	1	1	1	1	
Postdocs	-	-	-	-	-	
Technicians	-	-	-	-	-	
Guests	-	-	-	-	-	
Personnel Costs	€ 21.500	€ 43.000	€ 43.000	€ 43.000	€ 21.500	€ 172.000
Running Budget	€ 7.500	€ 15.000	€ 15.000	€ 15.000	€ 7.500	€ 60.000
Equipment	-	-	-	-	-	-
Total	€ 29.000	€ 58.000	€ 58.000	€ 58.000	€ 29.000	**€ 232.000**

7. Research Programme

7.1. Introduction

In present day technology, the miniaturization of electronic devices faces a huge challenge since conventional silicon technology is reaching its limits. To ensure that Moore's law is obeyed, which states that the number of transistors on integrated circuits double every 18 months, other solutions have to be exploited. Since the theoretical study of Aviram and Ratner in 1974 predicting a single molecule functioning as a diode[2], the field of *Molecular Electronics* has received much attention. From that time scientist have been searching to develop methodologies and processing schemes for measurement templates to determine the electronic properties of single molecules or an ensemble of molecules, since molecules are advantageous in their size together with the diversity which can be obtained by chemical synthesis. Yet it has taken around two to three decades since the 1974's publication to develop the first experimental setups to measure the properties of molecules.

One of these methods is based on the development of scanning probe microscopy techniques. By using STM (scanning tunneling microscopy) or CP-AFM (conducting-probe atomic force microscopy) to contact molecules that are self-assembled on a conducting surface (e.g., gold), currents through these molecules can be measured by applying a potential between surface and tip[3]. A disadvantage of these techniques is that the contact area between tip and surface is unknown and thus the number of molecules contributing to the current. Furthermore, in STM an additional tunnel gap is created since the STM tip is hovering above the self-assembled monolayer (SAM).

Another method is to use an electrically or mechanically controlled break junction to separate two electrodes from each other in such a way that a gap of the size of a molecule is formed in between[4,5]. A problem with this technique is the reproducibility of one junction. In general, however, statistics can be done to determine the properties of the molecules used.

A very interesting other approach is defining junctions in so-called *via* holes or vertical interconnects[6]. In these holes, which are created by lithography, a self-assembled monolayer (SAM) is formed on the underlying substrate. Then by special, indirect evaporation of the metallic top contact, molecular junctions are formed with a pre-determined area. Direct evaporation of a metal top contact on the SAM is not possible since this results in penetration of the metal into the SAM resulting in shorts[7].

At the Materials Science Centre*Plus* of the University of Groningen, this concept of *via* holes is further exploited. A processing flow chart has been designed to make two-terminal devices with a SAM as active component[1]. All steps in the flow chart are conventional and industrially used processes such as spincoating and photolithography (Figure 1). The key step in this flow chart is spincoating the conducting polymer PEDOT:PSS on top of the SAM. The idea is that because the polymer molecules are long, they do not penetrate the SAM and form a layer on top of it. Furthermore, the hydrophilic PEDOT:PSS (a water-based suspension) will not penetrate the hydrophobic interior of the SAM during spincoating. Because of this extra layer, direct evaporation of the auxiliary top metal contact is possible, since now it will only penetrate to some extent into the polymer but leaving the SAM intact.

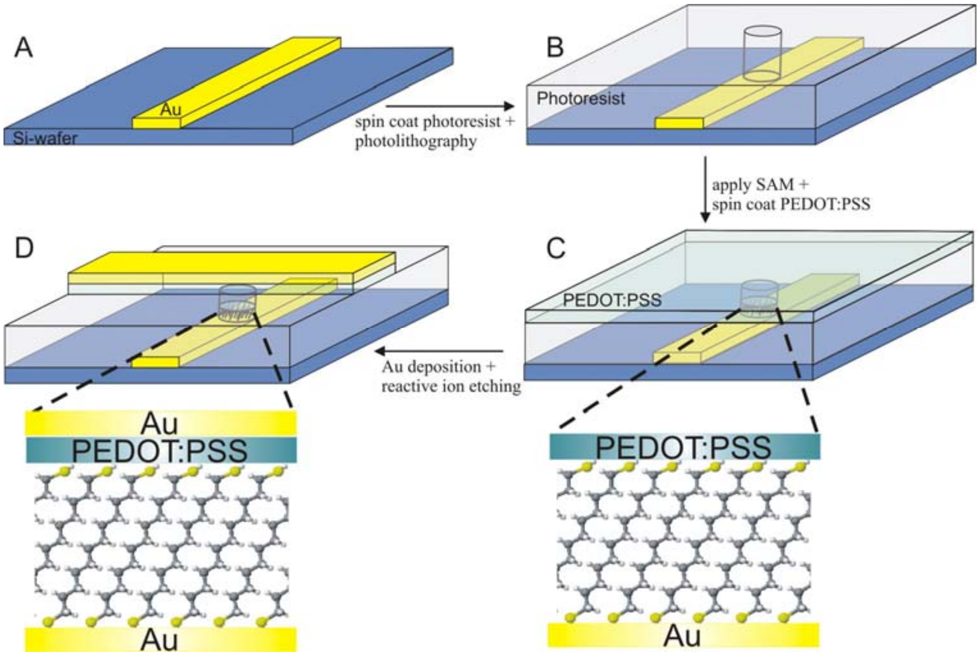

Figure 1: Processing flow chart for the two-terminal self-assembled monolayer devices.

The aim of this proposed project is to exploit further the utilization of this novel technology to develop other electronic devices, especially transistors or other three terminal devices such as a MIMIM (metal-insulator-metal-insulator-metal) device. The first step is to accomplish these devices with the molecules as basic component, and secondly to understand how the molecular properties are manifested in these devices to gain more insight in fundamental electronic properties of molecules for the use in electronics. Interesting topics are the relation between charge transport and molecular structure, properties of the metal-molecule interface and the response of molecules to an external applied field.

7.2. SAM-FETs

Transistors are the key components in integrated circuits. The basic concept is that the current between two contacts, the source and the drain, can be modulated by applying a potential to a third contact, the gate. In field-effect transistors (FETs), the gate is separated from a semiconductor by an insulator. Due to a voltage applied on the gate, charge carriers from the bulk semiconductor are accumulated at the interface between the semiconductor and the insulator making a 'channel', which is situated between source and drain. These charges at the interface contribute to the current from source to drain. As the voltage on the gate is raised, more carriers are accumulated in the channel and the conductance of the channel increases[8].

The key component in a FET is the material in the channel, in general the semiconductor. In a SAM-FET, the electronic channel should consist of molecules and the current through these molecules should be affected by a gate potential. The FET-geometry offers an good template for measuring several properties of the molecules. Furthermore, when a good processing scheme is developed to produce these devices, due to the compatibility of SAM formation, many different chemical structures can be measured making systematic studies possible. Some intriguing questions for the use of molecules instead of conventional semiconductors, however, have to be cleared up first.

When a monolayer of molecules is used as the channel, there is no bulk semiconducting region present. The result of this is that the accumulating charges should be provided by the source and/or the drain. This is already a large difference with conventional FETs and will influence the characteristics of the device.

An advantage of molecules in these systems is that a semiconducting and an insulating part can be both coupled in one molecule. In this way, the semiconducting channel and the insulator are directly aligned with each other since they are designed and synthesized to be incorporated in one molecule. Consequently, by incorporating the insulating dielectric layer into the semiconducting molecule, it is possible to tune (by chemical synthesis) the insulator thickness and to reduce its thickness down to the Ångstrom level.

This however raises other interesting questions, such as whether the molecular monolayer is able to manage the charge induced in the monolayer. Since the sizes of monolayers are in the order nanometers, the electric fields already become very large when applying small voltages. This means that quickly very many charges could be induced in the layer, which can possibly damage the device or cause breakdown of the device. Also the induced charges are confined, making the geometric structure and the electronic structure of the monolayer intimately related.

7.3. MIMIM Tunnel Transistors

Another device geometry for a three-terminal device is the Metal – Insulator – Metal – Insulator – Metal (MIMIM) tunnel transistor[8]. A band diagram of this transistor is shown in Figure 2. This transistor is an example of a "hot electron" device. The principle of this device is based on electron tunneling by applying a bias between the emitter and base (V_{EB})[9]. However, if the base is significantly thin, electrons can get through the base region without any scattering. Also because these electrons are "hot", which means they have excess of kinetic energy, these electrons can pass over the second barrier between base and collector. Low energy electrons in the base cannot contribute to the current between base and collector since they cannot surpass the insulating barrier in between. This means the current from base to collector, I_{BC}, is determined by the electrons coming from the emitter into the base, which is again determined by the bias applied between emitter and base (V_{EB}). Effectively, the current through the device is determined by voltage V_{EB}, which then acts as an on/off switch.

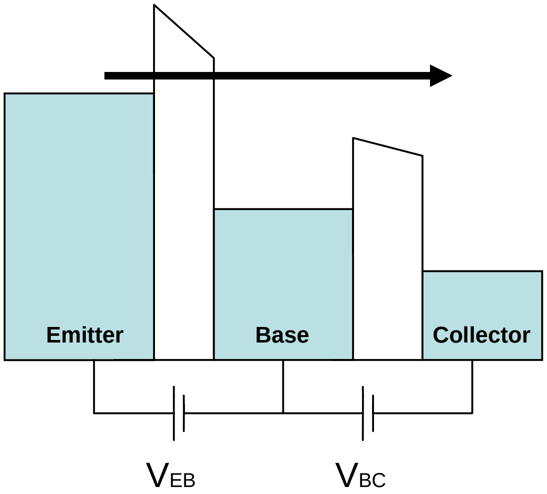

Figure 2: Band diagram of an MIMIM tunnel transistor. Emitter, base and collector metals are separated by insulating regions. The base metal should be thin such that electron can directly travel through this region without scattering.

MIMIM transistors are interesting because of the large on/off ratios and fast response times which can be obtained in these devices, making them very useful for electronic applications. Speed limitations arise from the base transversal time. Inherently in the construction of these devices with a very small base region and "hot electrons" (i.e. high velocity carriers), this transversal time is very small.

As for the construction of these devices without molecules, bottlenecks have been the need for two tunnel barriers with different heights in one devices and the very thin base electrode. Different barriers can be easily obtained by using different molecules. Furthermore, the devices are similar to the large-area junctions that were developed in Groningen,[1] since those devices are already MIM junctions. MIM devices with one contact of 10 nm thickness have been processed in Groningen, which should be thin enough to serve as base contact.

7.4. Project Outlook

As the two terminal large-area junctions are the basic, preceding devices from which eventually the SAM-FET should follow, the first part of the project will involve the use and further investigation of these junctions with various molecules to determine the conduction mechanisms involved in molecular electronics. As the key part of the processing of the two-terminal junction is the use of PEDOT:PSS, this will be the basis for processing other electronic devices. Furthermore the control of the SAM formation can be important for device performance. Investigations of the conditions for this formation in connection with the properties of the SAM will be performed, e.g., the grafting density, the orientation of the molecules with respect to the electrode and the thermal stability of the SAM.

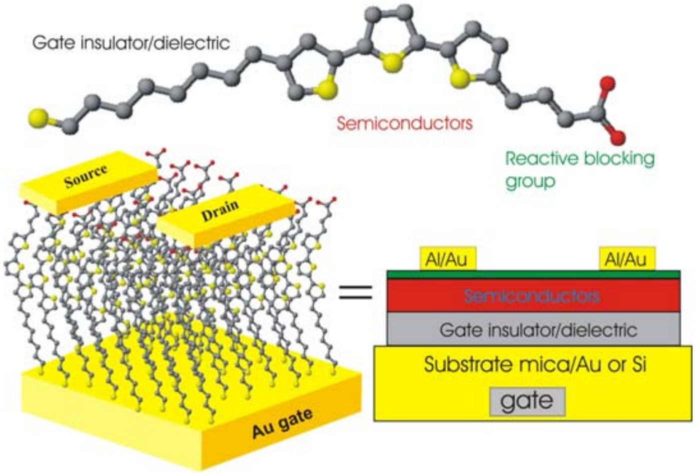

Figure 3: First proposed structure for a SAM-FET.

As for the 1st generation SAM-FETs, a processing scheme should be developed to fabricate these transistors. Several interesting geometries are proposed from which the in-plane SAM-FET is shown in Figure 3. In this construction, already a molecule is used with an insulating and a semiconducting moiety, an alkane part and a thiophene part, respectively. Also fullerene derivatives can be used as the semiconductor. By modifying the different functional parts of the molecules, information can be obtained about the structure - properties relationship for the performance of the transistor and possibly other devices.

As a first step, electrodes should be constructed which are compatible with SAM formation and are flat relatively to the dimensions of the device. Processes which can be utilized for this are (standard) lithography and lift-off techniques and possibly micro contact printing (μ-CP).

After the SAM is formed, the most important step for fabrication of this device is the positioning of the source and drain contacts on the SAM. Several processes have been proposed, e.g., low temperature evaporation of the contacts through a mask and incorporation of a metal blocking functional group in the molecule and spincoating / patterning PEDOT:PSS on top of the SAM, following the procedure of the large-area junctions. The route that is followed in this proposal is based on spincoating PEDOT:PSS as the source and drain electrode. This has proven to be successful in the two-terminal large-area junctions.[1]

The second proposed structure and its processing flow chart is shown in Figure 4. In this structure, the SAM channel is formed on the vertical side of a structured Au electrode. Current perpendicular through this SAM, parallel to the wafer, should be influenced by the silicon gate substrate. An advantage of this proposed structure is that the size of the channel can be tuned both in length, by changing the length of the molecule, and in width, by etching away more or less PEDOT:PSS. Also, all separate steps used in this flow chart are used in the fabrication of the large-area molecular junctions. One question that remains, is the general statement that the length of the channel should be around 10 times larger than the insulator thickness. This is completely reversed in this SAM-FET geometry. However, realisation of these devices is feasible on a relative short time scale to check the properties of these kind of devices.

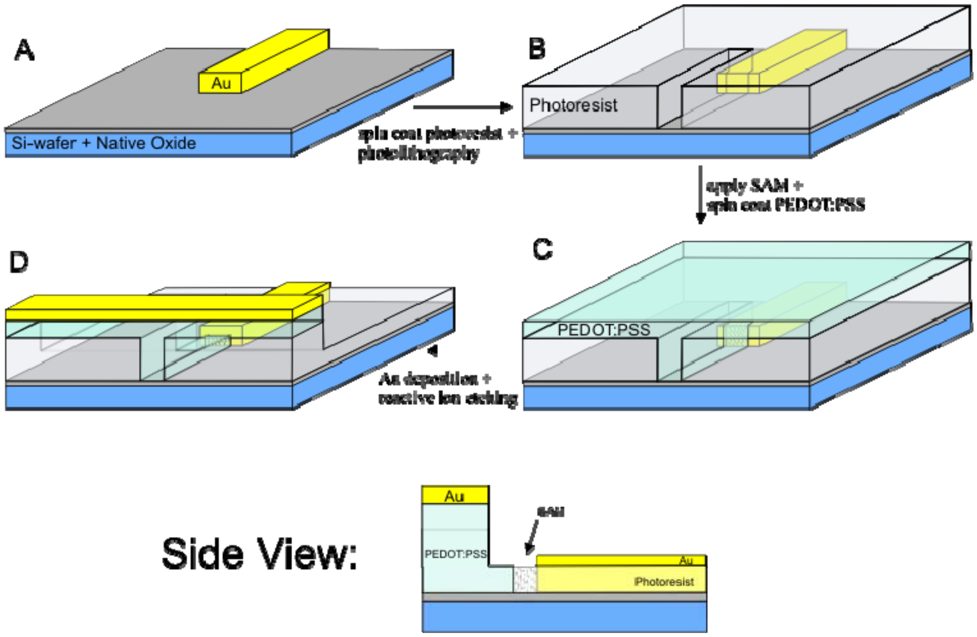

Figure 4: Second proposed geometry and processing flow chart for a SAM-FET. Note that the photoresist layer in the side view should be interpreted as a transparent layer.

As for the MIMIM devices, since in this geometry only insulating and metallic regions are needed, no big changes are needed from processing point of view. The devices made with the benchmark experiment exploiting the PEDOT:PSS are already MIM junctions[1]. The proposed flow chart for MIMIM devices is shown in Figure 5. The key step in the processing is the fabrication of the base or middle contact which should be thin enough for the tunnel transistor to work. One possible fabrication trick could be processing the large-area MIM junctions on a silicon wafer with very thin gold bottom contacts. Then by removing (etching) the silicon wafer, e.g., by a template stripping process[10], the whole processing could possibly be done on the back side of the first metal electrode, producing the desired MIMIM structure (see Figure 5). It may be needed to strengthen the devices by using a support on the top side to allow all processing steps on the back side. An advantage of this procedure is that the insulating regions in the MIMIM can be modified independently of each other by just applying different SAMs.

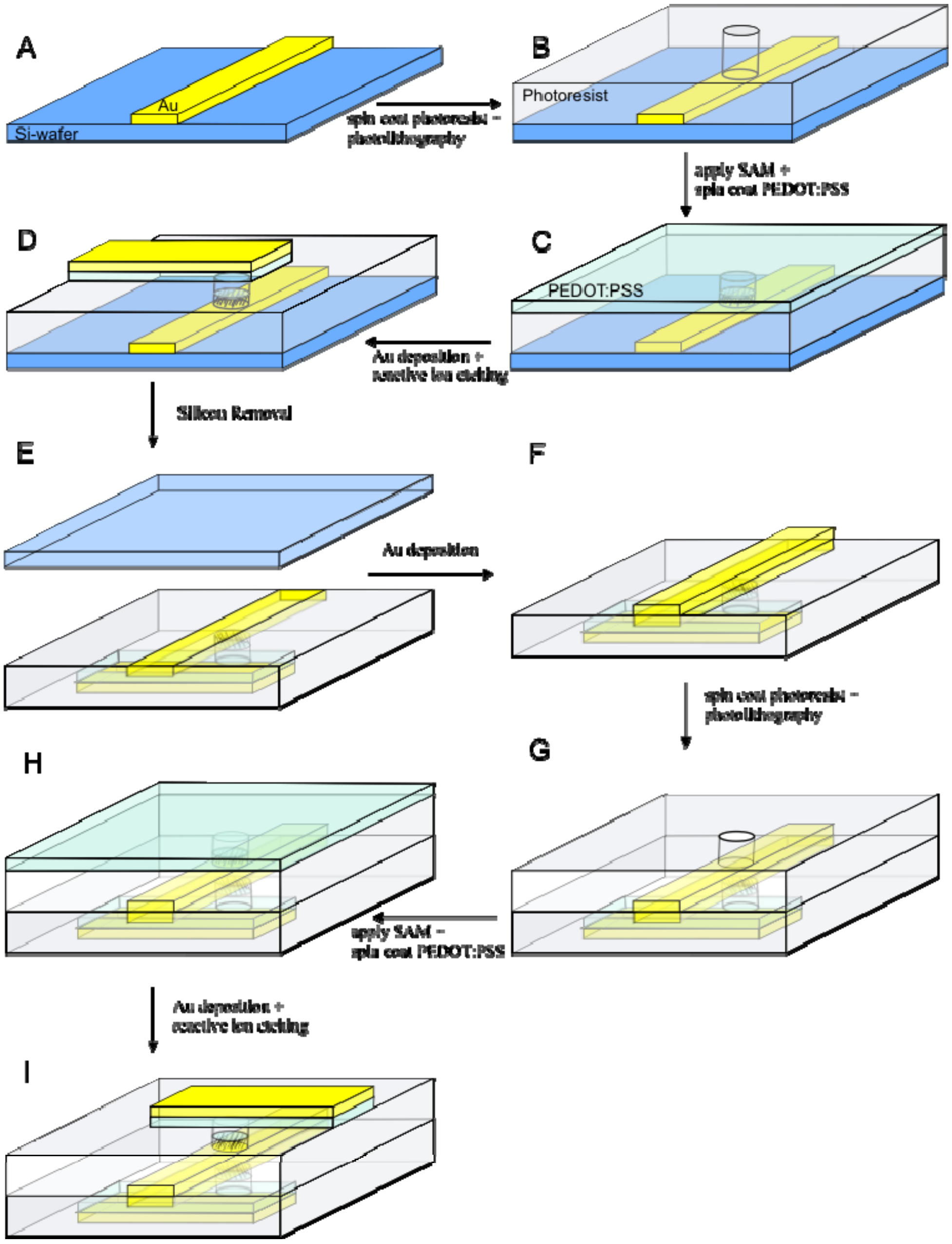

Figure 5: Processing scheme for a MIMIM transistor.

When operating transistors are produced, the devices will be characterized according to their on/off currents and gain. Also a scientific basis for the description of the transistors should be produced incorporating the injection, conduction, distribution and tunnelling of charges in the device.

8. Infrastructure

All research equipment needed for this project is present within the research group *Molecular Electronics: Physics of Organic Semiconductors* or the *Materials Science Centre^{Plus}*..

9. Application Perspective

The need for smaller electronic devices based on other technologies different from silicon technology becomes more and more important since this conventional silicon technology is reaching its limits. Electronic devices based on molecules are anticipated to ensure the miniaturization because of the size and the variety of functional molecules. Also chemical synthesis of specific functional molecules offers a great opportunity for fine tuning the properties of the molecules for specific applications. Many attempts to make molecular electronic devices make use of self-assembled monolayers, which are films of organic molecules just one molecule thick. When researchers tried previously to use these molecular films to create devices such as diodes, they found that the electrical properties vary widely, often with poor electrical contact between the molecules and the electrodes adjoining them.

Recently the joined research team from Groningen and Philips overcame this problem of creating a good contact with the metal electrodes by introducing two innovations. First, they deposit the self-assembled monolayer within a microscopic cylindrical pore that penetrates an insulating plastic film, exposing a gold electrode beneath. This protects the molecular film, which stays stable for months. And the researchers ensure a good contact with the top electrode by first covering the molecular film with a thin layer of an electrically conducting polymer, acting as a kind of soft cushion as well as blocking layer for any intruding metal filaments. These new finding will pave the way for novel device geometries as suggested in this proposal.

By putting effort in the physical manufacturing of molecular electronic devices and the characterization of these devices concerning their functioning, a leap forward can be made to eventually produce a new class of electronic devices based on molecules, followed by a new class of electronic equipment based on this new technology having fortunate properties such as small size, light weight and low energy consumption.

10. References

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