Nanofabrication of Integrated Circuits using Conventional Top-down and Single Molecule Bottom-up Approaches

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Abstract – Nanofabrication can be done using two methods: top-down and bottom-up. In this paper the different methods are compared for the fabrication of integrated circuits. Conventional silicon integrated circuits are made by photolithography, a top-down method. Dimensions of 30 nm can be reached at the moment, and with a lot of research this can be brought down to 8 nm in 2020. These structures are all essentially 2D. An alternative method to fabricate integrated circuits is to use a bottom-up approach. The electronic elements considered in this paper are single molecule switches because of their small size. They can for example be switched by light or hysteresis. One bottom-up approach considered is self-assembly, which is a process that makes use of reversible interactions to form the desired ordered structure. The advantages are the small size and the possibility to build 3D structures to provide more space. While integrated circuits from single molecules are not yet made by self-assembly, there are promising developments in that field. Another bottom-up approach is to use nanorobots that can assemble anything. There is a lot of debate in the scientific community if nanorobots are possible. There is a sound physical basis, but there are no examples to prove it. However, less advanced robots could aid in the bottom-up self-assembly of integrated circuits. Another approach is to use a hybrid of bottom-up and top-down methods which can take advantages from both approaches. In the end it is expected that self-assembled bottom-up integrated circuits are the best choice in the long term, but the hybrid approach may prove important to bridge the gap.

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1. Introduction

1.1 Feynman's Talk

It was the Nobel Prize winner Richard Feynman who first talked about the field of nanofabrication in his 1959 lecture "*There's Plenty of Room at the Bottom*". He was the first to talk about doing things at the small, atomic scale. A few examples he talked about were writing all the books in a volume as large as a particle of dust, building very small computers or synthesizing any molecule *physically*.

The implications and applications of these small scale objects will be endless: a backup of any library at a size of a normal air mail letter, much faster computers that can calculate almost anything, surgery by those small objects or just for scientific fun.

It was not yet possible during those times to build those small scale objects due to two main problems: the inability to make objects and the inability to characterize such small scale objects. His solution was that the electron microscope had to be improved one hundred times to be able to characterize the small scale objects. He also thought of two ways to fabricate them: reverse the electron or light microscope, so it is possible to write things instead of only observing. The other solution was to get small scale "robots" to build other small scale objects.[1]

1.2 Nanofabrication

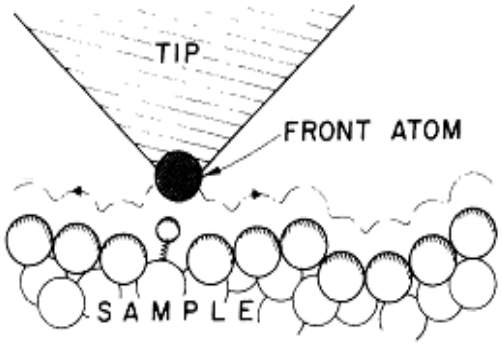

***Fig 1**: Working principle of STM or AFM. There is a sharp tip which has an interaction with the sample. The interaction is either a tunneling current (STM) or a force (AFM). The tip is scanned over the surface and the profile of the surface is known by the change in interactions.[7]*

Richard Feynman was the first to talk about the field of *Nanotechnology*, but it was not until 1986 that the field really started by Eric Drexler[2] who was the first to use that word.

This paper covers a subset of nanotechnology, namely *Nanofabrication*: *Fabricating functional objects/devices with nanometer dimensions by design.* Functional means that the object or device is useful (it can do something) and that it is possible to detect what it does in the macroscopic world.[3]

Research has nowadays made several things possible that Feynman talked about. Computers are much faster and they revolutionized our world; entire libraries are being put on the internet[4] and the detection of nano-objects and individual atoms is possible with electron microscopes with a resolution of 0.5 Å[5]. The invention of the Scanning Tunneling Microscope (STM)[6] and the Atomic Force Microscope (AFM)[7] (**Fig 1**) have also made characterization at the atomic scale possible. Creating nano-objects is possible with, for example, photolithography (**Fig 2**)[8] or STM (**Fig 3**)[6].

The methods to create nano-object described above are the so-called *top-down* approaches to do nanofabrication. When working top-down, a method to create macroscopic objects is taken and this method is modified to be able to make smaller and smaller objects.

Another approach to do nanofabrication is the

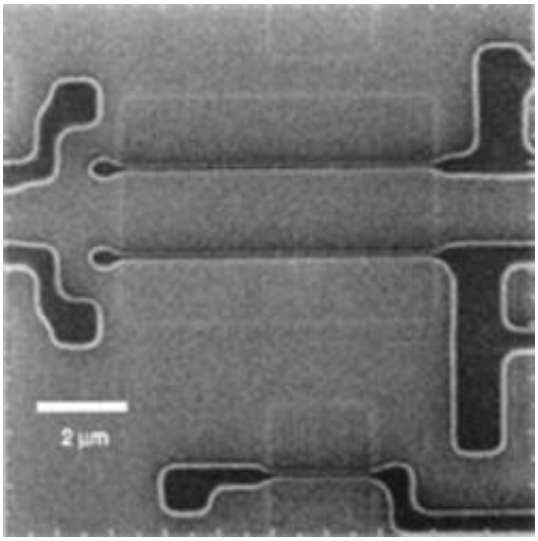

***Fig 2**: Nano-object created by photolithography; chip created by light with a wavelength of 248 nm.[8]*

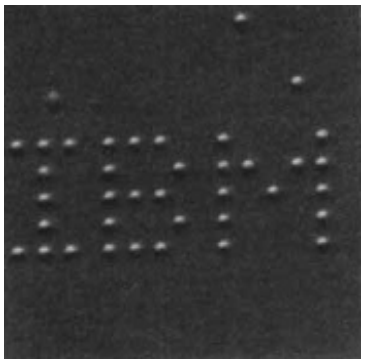

***Fig 3**: Fabrication of nano-objects by STM: the letters IBM are written with Xenon atoms on a Nickel surface, each letter 50 Å large.[6]*

bottom-up approach: nano-objects are made by other nano-objects. The robots Feynman talked about are an example of bottom-up nanofabrication.

1.3 Drexler-Smalley Debate

Eric Drexler was the first to give technical details of the those robots: in a book published in 1986 he described a system of molecular assemblers that can build nearly anything in a bottom-up fashion. It has several components: A central computer to provide intelligence to control the assembly process; an instruction architecture containing the information (comparable to the role DNA has in the cell); a construction robot with an arm to carry out the assembly and instruction transmission to transfer the information to the robots. All components are simple and small, at nanoscale lengths. Drexler laid the foundations for this system, describing and proving all the physics required for such a system. However, it does not give a detailed design of all the components and of the molecular basis underlying the system. And up to now nobody has realised such a system.[2]

A famous debate between Eric Drexler and Rick Smalley was published in Chemical & Engineering News about the system suggested by Drexler in 2003. Smalley believes such systems are not possible, mainly due to the fact that the robot arm will have "sticky fingers": an atom or a group of atoms picked up by the arm have a tendency to remain stuck, so it is impossible to just pick up atoms and place them somewhere else. The other criticism is the fact that such systems have never been shown to work, or they lack functionality, like biological systems that only work in water.[9]

Drexler argues that such a sticky finger is of no concern, since reactive groups of atoms are used for the assembling process and together with positional control they will provide the desired outcome. If one assembling process doesn't work, other conditions should be chosen to ensure it does work.[9]

A few examples of positional control are found in literature where the sticky fingers don't pose a problem. It is possible to move individual atoms by an STM tip[6], as shown in **Fig 3**, and individual hydrogen atoms can be moved[10,11]. Life is also a perfect example of assembling small molecules.

Things have been done in the literature given above that Smalley thought would be impossible. So there doesn't seem to be a physical, fundamental reason why the Drexler robots can't work, but it will require much more research to make his universal assembler. There hasn't been a system that even comes close to such performances.

1.4 Top-down vs Bottom-up

There has been a lot of progress in the field of nanofabrication using the top-down approach, and nanostructures with dimensions down to 30 nm are being produced at the moment with relatively cheap, industrial processes[12]. With expensive laboratory equipment it is possible to reach 10 nm[13,14]. It is very difficult to push the dimensions down even more, to the 1-10nm range, and a lot of research is required for that[3]. Another problem with the top-down approach is that it gives essentially 2D structures, while 3D structures offer much more space and flexibility[15].

However, the alternative, the bottom-up approach, has a hard time to match the current performances of the top-down approach. It is very hard to build large objects using bottom-up principles. There is a gap between the dimensions that can be reached by top-down and bottom-up nanofabrication, and more research is needed to be able to close that gap.[16]

There are several ways to imagine to do bottom-up nanofabrication. One of the methods

is the robots that Drexler described. Making use of the full concepts described by Drexler will be way too difficult to make any progress in the near future. To use the concepts, one should try to build a highly simplified version of the Drexler robot system as a starting point for research.

Nevertheless, the most obvious and promising candidate to do bottom-up nanofabrication is to make use of self-assembly. In that process the forces at the nanoscale are used to get nanoparticles to organise themselfes in a desired structure.[3,17]

1.5 Challenges for Nanofabrication

Why should people even care about nanofabrication? There are several challenges in the scientific community and ultimately in the real world where nanofabrication can be of great help.

Just a small selection of the challenges: Feynmans's nano-objects capable of surgery[1]; smaller CD's[18,19]; drug delivery[20,21]; nano-motors[22,23]; hydrogen storage[3] or molecular electronics[3].

For most of those challenges, the progress in the top-down approach is getting less and less, while new projects have started from molecular principles, where the bottom-up approach should ultimately lead to new functional objects or devices.

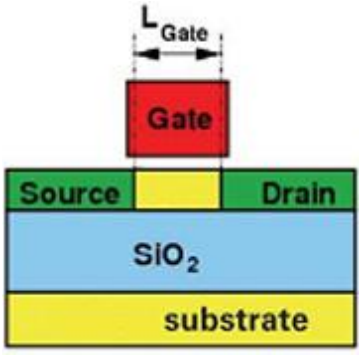

***Fig 4**: Typical design of a conventional transistor made from semiconducting silicon. Doping in this semiconductor gives the special features to the transistor. The transistor has three connections: source, drain and gate. A signal is applied to the source and received from the drain, while another (small) signal can be applied to the gate to influence what happens to the signal received from the drain.[26]*

This paper will be limited to the nanofabrication of electronics, with the integrated circuit as a goal. The top-down approach is getting to the limit of what is possible and more progress could be made by making use of bottom-up nanofabrication of molecular electronics.

In **Section 2** the top-down approach to electronics is reviewed with questions like what the current progress in that field is and what can be expected in the future. In **Section 3** the current progress in molecular electronics is reviewed. In **Section 4** there will be looked at the principles of self-assembly. In **Section 5** there will be taken a look at the bottom-up nanofabrication of molecular electronics. In the last section there will be a conclusion on the question if it is possible to make use of the bottom-up approach to build an integrated circuit and in what directions research should go to make it possible.

2. Top-down Approach to Electronics

2.1 Integrated Circuit

An integrated circuit is a structure that is densely packed with transistors and the connections to the transistors. Integrated circuits are the basis for all modern electronics,

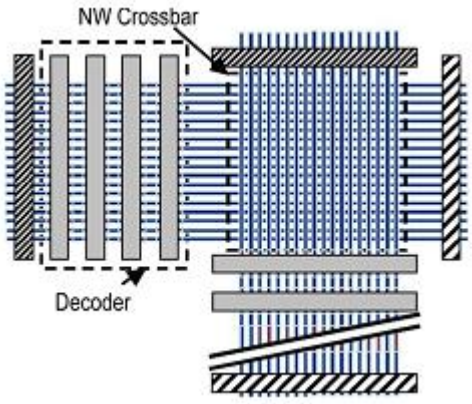

***Fig 5**: Crossbar array-based design. The decoder can transform signal produced by the outside world into the addressment for one specific transistor.[27]*

which are important for many different applications: from digital watches to computers to Moon-landing rockets.

Silicon transistors are the main components in integrated circuits. A typical design of a transistor is shown in **Fig 4**. A transistor has two functions in an integrated circuit. The first is the transformation of small voltages into large currents and that is important is almost every logic circuit[24]. The second function is a switch. A voltage applied to the gate (see **Fig 4**) can control the resistance between the source and the drain, so the transistor can have states of high or low resistance, which is actually the basic principle of a switch.[25]

One of the simplest ways to connect the transistors in the integrated circuit with the outer world, is to make use of a crossbar array-based design as shown in **Fig 5**. It consists of an array of wires placed in two orthogonal directions, with a transistor at every crosspoint. One specific transistor can be used by addressing two specific wires placed orthogonally. The decoder can transform a (binary) signal produced by the outside world into an addressment of one specific transistor. Only a few connections to the outside world are required to use the whole integrated circuit.[27]

Moore's law states that the density of transistors on an integrated circuit doubles every two years, and due to this law the transistors have become smaller and smaller.[28]

With the conventional transistors and techniques there will be problems when the transistors reach sizes smaller than about 22 nm. One of the problems is increased power dissipation. Due to the lower dimensions, the insulating layer between the gate and the device becomes smaller, so there will be a leakage current due to tunneling.[29,30] Another problem is less device control. The parasitic resistance and capacitance will become of the same order as the device resistrance and capacitance and that will mean the parasitics will domine how the device works.[26]

2.2 Photolithography

Integrated circuits are conventionally made by photolithography. The setup commonly used for photolithography is shown in **Fig 6**. Laser light comes in, it is treated by the illuminator, sent through a photomask that contains the final pattern and it is projected onto a wafer which has been treated with a photoresist. The exposed parts of the photoresist are etched away in the developing process.[31] An example of a photoresist is a polymer with an inhibitor, a molecule that prevents its dissolution. The inhibitor is destroyed by illumination with light. When the photoresist is being developed, it is etched by using a weak solvent to dissolve the exposed parts only.[32]

The resolution of photolithography depends on several parameters (see **Equation 1**): λ, the wavelength of the light used; k, a constant of the system and NA, the Numerical Aperature, which is a measure for the amount of light that can be captured. NA is equal to n sin θ, where n is the refractive index of the material in contact with the photoresist and θ is the angle of the light (see **Fig 6**).[31]

$$Resolution = \frac{k\,\lambda}{NA} \qquad (1)$$

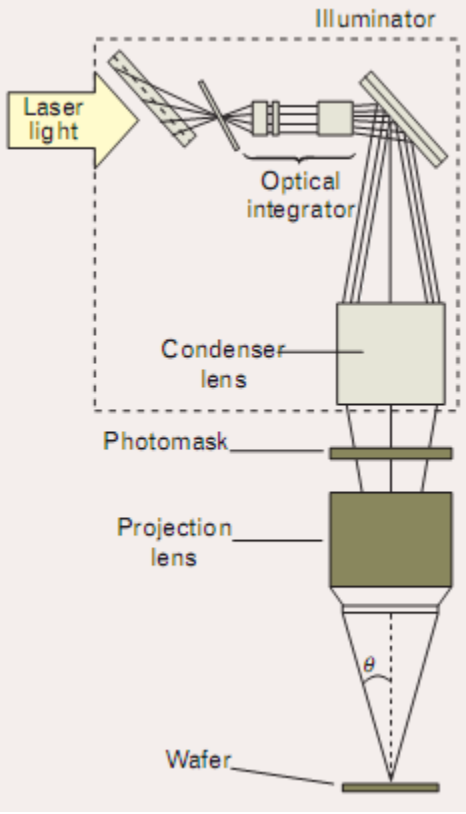

***Fig 6**: Typical setup used for photolithography. Laser light comes in, is treated by illuminator, is passed through the photomask that contains the final pattern, and is projected onto the wafer.[31]*

The first method to increase the resolution is to decrease the wavelength of the laser used. Currently the best performance is seen at a wavelength of 248 nm[8]. Decreasing the wavelength poses a few problems that need to be solved before the smaller wavelengths can be used. One of the problems is that there is no photoresist working at lower wavelengths that has the same performance as the photoresist at 248 nm[8]. Another issue is that the optics that have to be used at the smaller wavelengths give more difficulties[31]. A new system working on 157 nm needs optical elements of (expensive) high quality CaF_2 and no suitable photoresist has been found yet. With more research, these lower wavelengths will probably start working.[31]

Extreme UV is also a candidate to decrease the wavelength drastically with wavelenths of 11-13 nm. The problems with these wavelengths are the absorption of the UV in air, the need for extremely precise control (0.1-0.2 nm control) of the optical elements to get good control of the light[33] and a new suitable photoresist[8].

Another way to increase the resolution is to increase the Numerical Aperature. It is determined by the angle (which is commonly easily optimized) and by the refractive index of the material next to the photoresist. That refractive index can be increased by using immersion lithography: the photoresist is immersed in a liquid with a high refractive index.[34]

At the moment the photolithographic advances have pushed down the resolution to 30 nm. There are several very promising methods under development to improve the resolution by decreasing the wavelength used or by immersion. With the overwelming amount of solutions to increase the resolution to around 10 nm, it is not expected that photolithography will be a main problem to create smaller transistors.[8,12]

2.3 Developments in Top-down Integrated Circuits

Conventional integrated circuits have reached dimensions of 30 nm now and with the conventional transistors the limit is about 22 nm and it is expected that this size will be reached in a few years. The International Technology Roadmap for Semiconductors expects the transistors to reach dimensions of 8 nm in 2020.[12] New ways to keep the transistors working at the smaller scale need to be developed and the progress in photolithography needs to continue like it is promising to do. That makes this statement challenging, but it is not undoable.

There are many examples in literature to improve or replace the silicon transistor by other materials or methods, like the use of group III-V compounds[29] and the single electron transistor[55]. I will explain the last example further.

The single electron transistor is an extremely small transistor (~1 nm size) where the principle of operation is built on a single electron. This electron sits on an island between the source and drain, and the current flow between the source and drain is influenced by the electron on the island (by the principle called the Coulomb blockade). This electron can be influenced by the gate voltage. This technique seems to offer an enormous reduction in size of the transistors. However, there are currently two very large problems: the island where the electron sits needs to be of subnanometer size, and randomly fluctuating background charge have a huge impact on the device. So the single electron transistor isn't expected to be operating very soon, if ever.[35]

Concluded, conventional integrated circuits have obeyed Moore's law for a long time. There are many developments in the field, like the improved photolithography to make the integrated circuits, the continuous scaling of conventional silicon transistors to make them even smaller and improvements to them to make them function better and at a smaller scale. However, it is not expected that the top-down field will go much below the 8 nm range soon, as new developments like the single electron transistor are highly doubtful.

3. Single Molecule Electronics

Radical new methods to build electronics are being developed to replace the conventional silicon transistors. Molecular systems based on single molecules seem to be a good candidate with their much smaller size of just a few

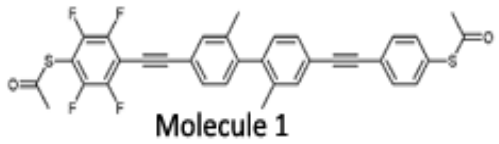

***Fig 7**: A rectifying molecule. The left part is electron poor, the right part is electron rich and both parts are separated by an internal twist of the structure.[24]*

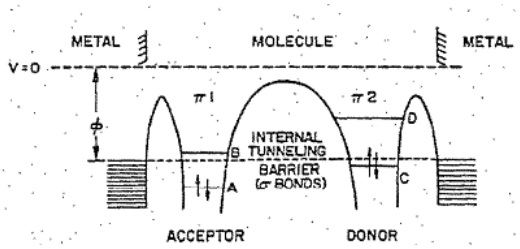

***Fig 8**: Energy versus the distance in the device. The electrons in the metal have the energy of the metal fermi level. The unoccupied pi level in the acceptor is just a little above the fermi level, and the unoccupied pi level of the donor is high in energy compared to the acceptor pi level. All energy levels are separated by barriers and the electrons have to tunnel through them.[36]*

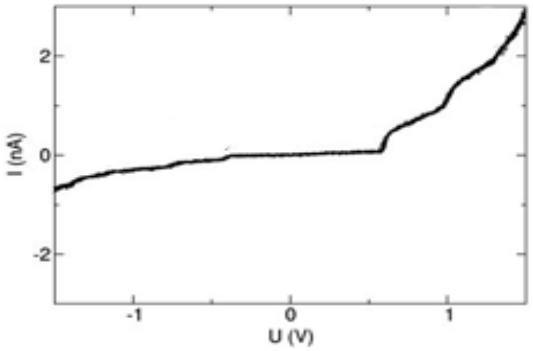

***Fig 9**: I-V curve of **Molecule 1**. This shows that the current is allowed to pass only in one direction, since there is a very small current at negative voltages and a larger current at positive voltages.[40]*

nanometer. Most research focuses on molecules with only two electrodes which means they don't have the full functionalities that a transistor has. Due to that these molecules can't form a true integrated circuit, but they can give a good proof of principle. Examples of those molecules are rectifying molecules, light-driven switches, hysteresis-driven switches and electrochemically-driven switches.[24]

3.1 Molecular Rectifier

Rectifiers are used to discriminate electric currents to pass only in one direction. They are important components for electronics. Conventionally they are a p-n junction in silicon.[36] It is a good proof of principle that molecules can be used in electronics when a molecule is capable of rectification. With those molecules it is possible to make logical circuits.[37]

A molecular rectifier is composed of an electron rich part and an electron poor part which have to be separated. The molecule needs to consist of two separate molecular energy levels at the two parts for the device to work.[36]

There are many molecules that can give rectifying properties[36,38,39] and one of the molecules (**Molecule 1**) is shown in **Fig 7**[24].

The device energetics are shown in **Fig 8**. A small voltage is required for electrons to go from the left to the right (in the drawing) and a large voltage is required for electrons to go from the right to the left, and this principle means that it is a rectifier.[36]

The I-V curves of the rectifier is shown in **Fig 9**. It can be seen from the graph that the current can only pass in one direction, which resembles the way a rectifier works.[40]

Molecule 1 was immobilized between the two electrodes of a Mechanically Controlled Break-junction (MCB)[24]. The setup of an MCB is shown in **Fig 10**. A structure of two areas with a thin bridge is made by photolithography in gold. This structure is put on the setup and the setscrew breaks the thin bridge very carefully. The gap that is formed between the two parts of the thin bridge is controlled with sub-Ångström precision. Space can be left for a single molecule to span this gap using this precision.[41]

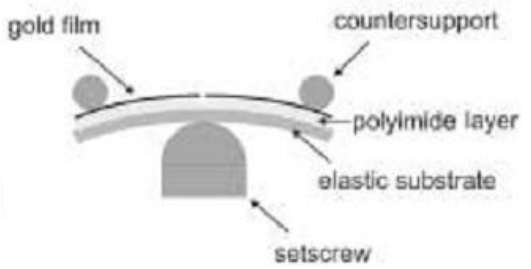

***Fig 10**: Setup of Mechinically Controlled Break-junction (MCB). A gold film is deposited on a polymeric layer which is deposited on an elastic substrate. This gold film has two large areas with a thin bridge in between. This bridge is broken in a controlled way by the setscrew while the countersupports keep the gold film in place.*[41]

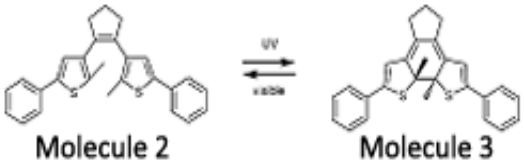

***Fig 11**: Molecules used in single molecule switch driven by light. It is a dithienylethene that can be switched between an open (**Molecule 2**) and closed (**Molecule 3**) form. In the closed form, there is a pi-conjugated path between the two ends of the molecules, which means the molecule conducts. In the open form, this conjugation is broken and the molecule is an insulator.*[24]

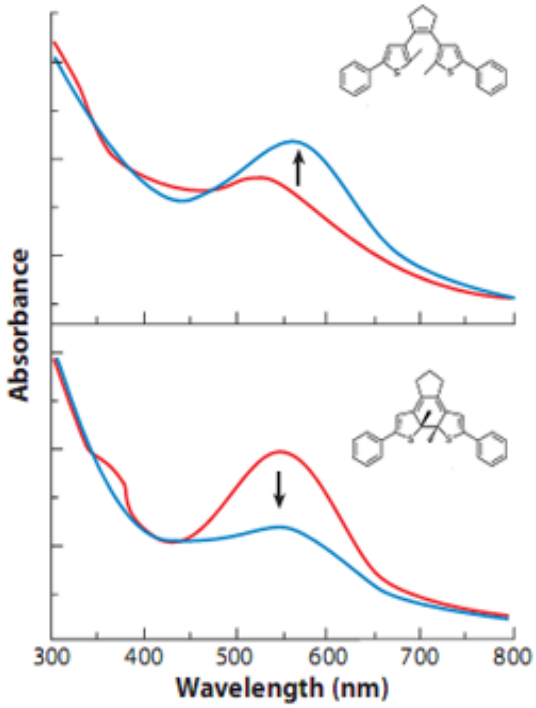

***Fig 12**: In the upper graph the absorbance spectrum of **Molecule 2** is given before (red line) and after (blue line) irradiation of UV light. In the lower graph the absorbance is given of **Molecule 3** before (red line) and after (blue line) irradiation of visible light. The spectrum of **Molecule 2** after irradiation (upper graph, blue line) is approximately equal to the spectrum of **Molecule 3** before irradiation (lower graph, red line), and the other way around. This gives a good clue that it is possible to switch between the two states of the molecule using UV and visible light.*[45]

This technique can provide analysis and connection to the macroscopic world of a single molecule. But this method is not suited for an integrated circuit as the dimensions of the total device (single molecule plus MCB) are much bigger than conventional integrated circuits and connecting many single molecules in one device is not possible.[41]

3.2 Light-driven Molecular Switch

A single molecule can act as a switch if it has two stable states that can be switched on request. One way to switch between two stable states is light. Light is an attractive medium to use to switch between the states, as it can be easily addressed with short response times.[24] There are many molecules that can perform switching driven by light, like a photoisomerization of a betaine or a cyclophanediene group linked to a porphyrin[42], photo-induced linear motion of a rotaxane[43], photoinduced conformation change in self-assembled monolayer[44] or photoisomerization of **Molecule 2 and 3** (**Fig 11**)[24].

Using UV or visible light it is possible to switch between the two molecules. In **Fig 12** the absorbance spectra of the molecule in different states are given. These graphs give a good clue that it is possible to switch between the two states of the molecule.[45]

The switching behavior of the single molecule switch can be read out using cyclic voltammetry, shown in **Fig 13**. The closed state (**Molecule 3**) shows a redox wave around 0.45 V and the open sate (**Molecule 2**) doesn't show that. That can be used to identify the open or closed states. So the single molecule switch can be read using this characterization method.[45,46]

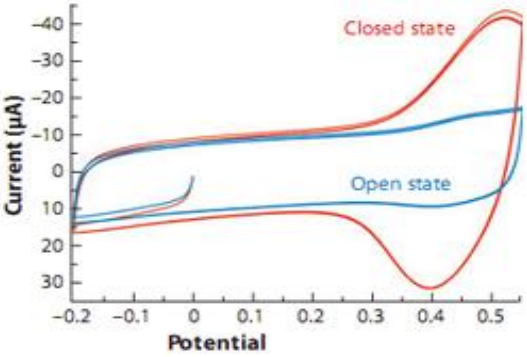

***Fig 13**: Cyclic voltammetry of **Molecule 2** (open state) and **Molecule 3** (closed state). A reversible redox wave is observed for the closed state, while this is not observed for the open state.*[45,46]

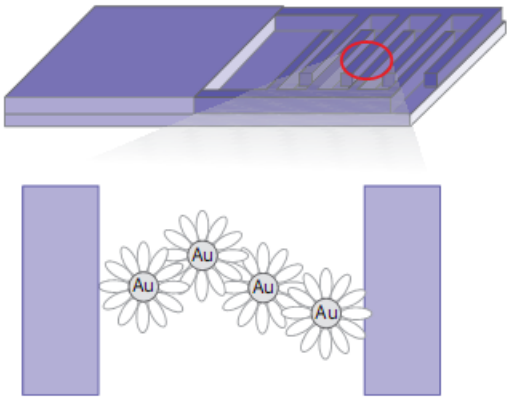

***Fig 14**: A device to use the switching abilities of the molecule. There is a path between the two electrodes consisting of gold nanoparticles with the molecules coordinated to it.*[47]

It is possible to make switching units out of the molecules as shown in **Fig 14**. A path between the electrodes is made by a bridge of gold nanoparticles with the molecules linked to the gold by a thiol-spacer. This device has shown switching between a conducting and an insulating state, even though the switching time is 10 hours.[47]

This light-driven single molecule switch is very unlikely to be used in integrated circuits. The most important reason is the fundamental problem that light is used as a switching agent. The resolution that can be reached with light is not good enough to get much improvement over conventional silicon based systems. However, they are a good proof of principle that molecules can be used as switching agents in electronics.[24]

3.3 Hysteresis-driven Molecular Switch

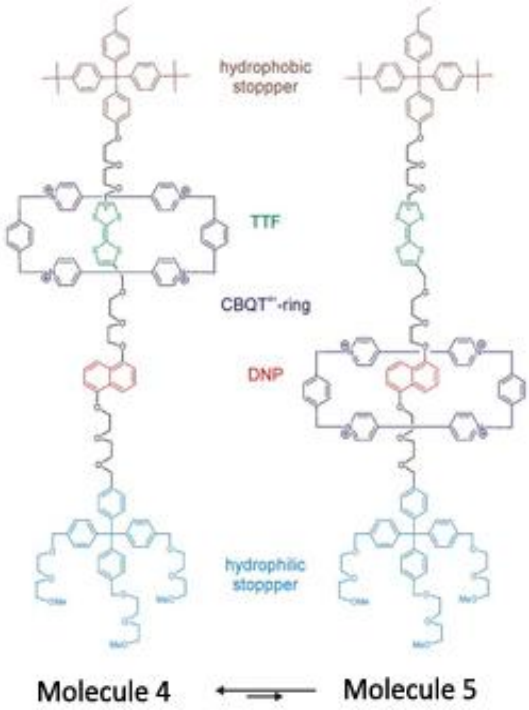

***Fig 15**: A rotaxane interlocked in a linear molecule with stoppers at the ends to prevent the rotaxane from coming off. **Molecule 4** (the low-conductance state) is slightly more stable than **Molecule 5** (the high-conductance state).*[24]

Making use of hysteresis is another agent that can be used to switch single molecules. Hysteresis is the behavior of a system to show a delayed reaction to an applied force. There are several systems that show this characteristic behavior with some of them being an OPE rod comprising a bipyridyldinitro central unit[24], spin crossover in inorganic complexes[48] and a rotaxane molecule interlocked with several types of linear molecule. One of those systems is shown in **Fig 15** where **Molecule 4 and 5** are displayed. This molecule has two (meta-)stable states with the rotaxane at the TTF or DNP positions where the voltage determines that position. An applied voltage gives a temporal electrochemical charging of the TTF unit, and this pushes the rotaxane away to the DNP position as the molecule becomes more stable when the rotaxane is at that position. An

oppositely applied voltage has the opposite effect. The conformational change, the movement of the rotaxane to the other position, has hysteresis.[24]

The hysteresis is shown in **Fig 16**. The applied voltage versus the current through the switch is plotted, and by the black line it can be seen that a writing voltage of approximately 2/-2 V is required to switch the molecule into the other state.[49] So this hysteresis effect can be used for switching: voltages of 1/-1 V can be used to read the switch and voltages of more than 2/-2 V can be used to write the switch into the other state.[50]

As shown in **Fig 17** a Langmuir-Blodgett film was made of these molecules with a crossbar architecture of electrodes. Individual or a group of molecules can be addressed In this device at the crosspoints of the electrodes.[49]

This hysteresis-driven single molecule switch has good potential to make it into integrated circuits since there are no fundamental problems.

3.4 Three-electrode Single Molecules

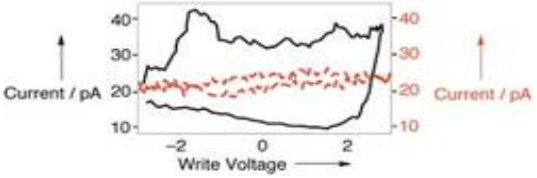

***Fig 16**: The voltage versus the current. A clear hysteresis loop can be seen (black line), where voltages of 2/-2 V are used to change the state of the molecule. The red dots are the performances of the control molecules that shouldn't and don't give hysteresis.[49]*

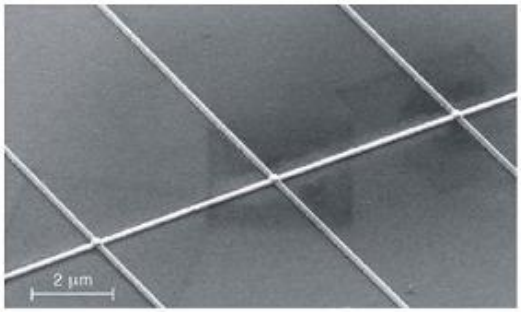

***Fig 17**: SEM image of a crossbar architecture of electrodes with a Langmuir-Blodgett film of the molecules in between. There are about 5000 molecules at every crosspoint. The dimensions are this large to give proof of concept easier.[49]*

Even though most research is focused on two electrode molecules, there are some methods under development with three electrodes connected to the molecule in some way, which means that a transistor can be built from a single molecule. Examples of those include electrostatic trapping of two gold particles connected by a short organic molecule[51,52], electric field control over the magnetic properties of an Fe_4 complex[53] and several methods where a single molecule is connected to two electrodes and a third electrode influences the conducting properties electrostatically [51,54,55].

One of those examples is shown in **Fig 18**. An MCB holds the molecule, and another gold electrode serves as the gate contact. The conducting properties of the molecule change by applying a voltage to the gate contact. The results for this device are shown in **Fig 19**, where the voltage over versus the current through the molecule is shown at several gate

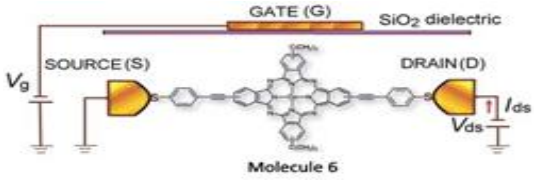

***Fig 18**: The molecular transistor and the electrodes. An MCB holds the molecule and another electrode serves as the gate. There is an insulating dielectric layer of SiO_2 between the gate and the molecule to prevent conduction.[55]*

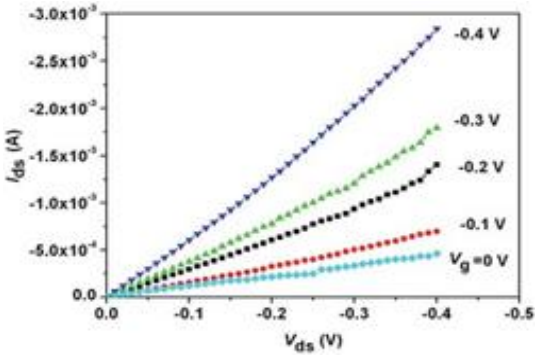

***Fig 19**: The voltage versus the current through the molecule/over the source and drain contacts for several gate voltages. At low voltages there is hardly any conduction and by increasing the gate voltage, the molecule becomes more conducting.[55]*

voltages. This shows that the molecule indeed shows the properties common for a transistor.[55]

4. Self-assembly

As stated in the introduction, self-assembly is the most obvious and promising candidate for nanofabrication using a bottom-up approach. Self-assembly is a process where pre-existing components become ordered in a designed way using reversible interactions.[15] The various aspects of self-assembly are now explored in more detail.

Fig 20 shows the different classifications of self-assembly. The major classification is between static and dynamic self-assembly. In dynamic self-assembly, a constant energy dissipation is required to keep the system in the self-assembled state. Living systems are a good example. This type of self-assembly is very complex to build and not desired in integrated circuits because of energy waste, so it will not be considered here any further. Static self-assembly means that the final structure that is made doesn't change (under those conditions); it doesn't mean that nothing happens. The structure is continuously being assembled and deassembled because of the reversible interactions.[3]

The next classification of self-assembly is in co-assembly, hierarchical self-assembly and directed self-assembly. Co-assembly is the process that several different components can only form the desired ordered structure together. Hierarchical self-assembly is the process where self-assembly is going on over several length scales. The components form an ordered structure, those ordered structures assemble into a larger ordered structured, etc. Life is a good example of it, with for example molecules ordered in a cell and cells ordered in a body. Generally, different interactions play a role in the different length scales and the hierarchical self-assembly can be tuned with those interactions. The last class is directed self-assembly. Here external forces are used to direct the self-assembling process into the desired structure. In this class, both top-down (the directions) and bottom-up (the self-assembly) aspects are used. The distinction between the classes are not set and combinations of several classes can be used to create the desired structures.[3]

The second important aspect about self-assembly are the interactions. Due to the

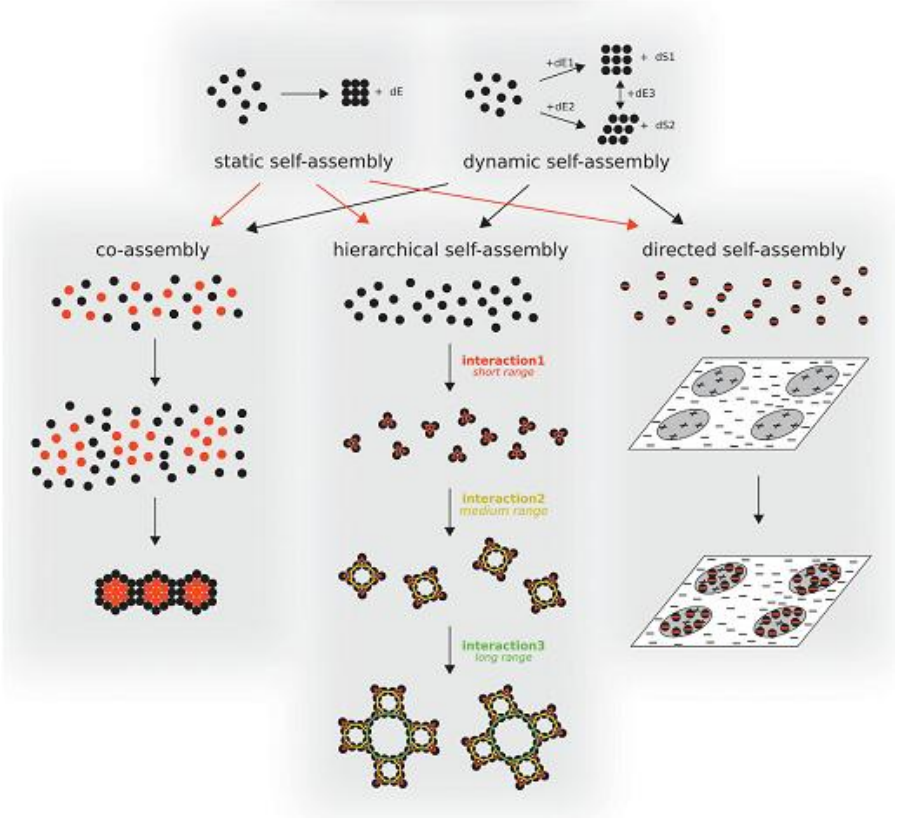

***Fig 20**: Different types of self-assembly. There are two classifications in self-assembly: the classes of static self-assembly and dynamic self-assembly, and the classes of co-assembly, hierarchical self-assembly and directed self-assembly.[3]*

reversible interactions, the stable self-assembled state must be a thermodynamic minimum of the system. This means that the Gibbs free energy must be minimal (**Equation 2**). The Gibbs free energy can by minimized by the enthalpy or the entropy. There are systems that assemble entropy-driven, like the ordering of liquid crystals[56]. But since entropy is associated with disorder while order is created in a self-assembly procees, most systems are driven by a decrease in enthalpy.[57]

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

The interactions that have an influence on the enthalpy are forces. At the nano-scale, the important forces to be considered are Coulombic forces, molecular forces, like Vanderwaals forces and hydrogen bonding, and magnetic forces. All the forces have associated length scales where their effect has the greatest impact.[15,17]

The very specific Coulombic forces arise from the attractive or repulsive nature of charges. Many degrees of freedom can be used to design a system: the sign of the charge, the position of the charge, choice of solvent and choice of the counterion.[17] The typical length scales range from 1 nm to 1 µm and the interaction is pretty strong.[58]

There are many types of molecular forces, all of them short-range (1-10nm)[58]. They include attractive hydrogen bonding, attractive or repulsive dipolar interactions and repulsive steric hindring. These interactions are rather specific and very orientation dependent so they can be used to design very specific systems.[17]

Another important molecular force is the Vanderwaals force. It is a force due to electromagnetic fluctuations in molecules and it arises between any two molecules and it is orientation dependent. It is rather indiscriminative so it is usually used to assemble just any component in an ordered close packed structure.[17] The typical length scales are 1-10 nm and the interaction is rather weak.[58]

Magnetic forces are rather uncommon in self-assembly, since magnetism is rare in molecules, the force is rather weak and the interaction is long-range (10-100 nm). However, this does give good opportunities to use for higher order hierarchical self-assembly.[17]

With the almost endless possibilities of self-assembly it is possible to design very specific systems. However, the many possibilities are also its major drawback: it is very hard to guess how the self-assembled system will look and theoretical studies hardly give clues. There are a few rules of thumb to keep in mind when designing systems. The system should be able to be disturbed so the system can find a thermodynamic minimum by the reversible interactions. Furthermore, specificity and directionality will give very special types of order that can be predicted rather easily. And the last one is that the use of one dominant interaction will give simple structures, while using many equally dominant interactions will likely give an unpredictable mess.[58]

5. Bottom-up Nanofabrication of Integrated Circuits

In this section the nanofabrication of integrated circuits using a bottom-up approach is treated. Conventional top-down methods are expected to reach at most 8 nm dimensions as shown in **Section 2**, while **Section 3** shows that single molecule switches have dimensions of only a few nanometers, so they have the potential to give much smaller integrated circuits. Furthermore, top-down methods can only create 2D structures while a bottom-up approach is not limited by 2D and can use the space that 3D structures offer.

A radical new method is required to be able to fabricate the single molecules in a functional way. Top-down approaches fail to fabricate the molecules at such length scales and a bottom-up strategy must be used. Three possible ways will be shown to fabricate integrated circuits from single molecule switches: self-assembly, a hybrid of top-down approaches and self-assembly and nanofabrication using small robots.

5.1 Nanofabrication using Self-assembly

One possible way to build integrated circuits from single molecule switches is to use the principle of self-assembly. Reversible interactions are used to design an ordered system. To build an integrated circuit on these principles is difficult, since absolute control is

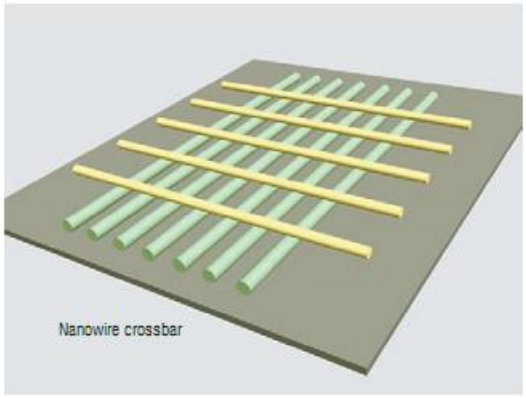

***Fig 21**: Connecting wires from the single molecule switches to the world can be done using two arrays of wires made from carbon nanotubes placed orthogonally, with the switches at the crosspoints of the wires.*[37]

required over all the length scales. Packing the individual molecules is not hard to do and is done routinuously by chemists, but connecting the individual molecules to the macroscopic world and being able to address them is very hard. The role of defects is not to be underestimated because self-assembly inevitably means that defects are created[3,16].

The most simple method to wire elements to the macroscopic world is the method shown in **Fig 5**, with two arrays of wires placed orthogonally. In **Fig 5** these wires were made with a top-down approach, but recent research has shown that they can also be made using self-assembly (**Fig 21**). These wires made from carbon nanotubes are 10 nm thick which is considerably larger than the molecules that are used for the single molecule switches so the minimum theoretical dimensions are not reached. But it is still possible to build an integrated circuit using self-assembly only in this way which gives a good proof of principle.[37]

The problem of defects that are built into self-assembled systems can be solved by using a nanoscale application-specific architecture, which slightly changes the orthogonal wires method to be able to handle some defects. One of the methods how that is done is to build redundancy into the system.[29]

Using hierarchical co-assembly, one could think of a speculative system where the theoretical minimal dimensions are reached. One designes short-range interactions (like ionic interactions or hydrogen bonds) so that the switches and small wiring elements assemble together. With longer-ranged interactions (like vanderwaals or magnetic interactions), the wiring elements all get the same orientation (an asymmetric switch is taken to get the wires orthogonally) and then they are connected (can for example be done using another molecule or polymerization). Due to the reversibility of the interactions, a thermodynamic minimum will be found without too many defects.

It has already been shown that small logical circuits can be made using self-assembly. In this study 10-30 nm silicon and GaN single crystals self-assembled from solution into logical circuits including wiring.[59] These are not yet the scales and the components that are required for self-assembly of molecules, but this study shows that logical circuits can be built using self-assembly. Logical circuits are not yet integrated circuits as they contain only a few elements, but it is a step in the right direction.

The molecules described in **Section 3.3**, the hysteresis-driven single molecule switches, have shown to work as a logic circuit[50], without the self-assembling aspect. Now the only thing that is required to build a logical circuit is a combination of the self-assembling properties of the former study and the molecules of the latter. Due to the fact that molecules can be tweaked very easily, such a self-assembling process shouldn't be too hard.

All these methods have only shown 2D architectures. The real advantage of using self-assembly is the possibility to build 3D architectures, even though it is much more difficult.[15]

There have been a few developments towards 3D architectures. A formation of 3D Bi_2S_3 ultrathin nanofibrils of tunable thickness and porosity has been reported, made from a self-assembling process called chemospinning.[3] These structures can be the start of new research to find applications in the field of electronics.

It is possible to think of other highly speculative methods to use 3D structures for integrated circuits. One of them is that a long polymeric wire is bonded to the single molecule switch that is conducting through the chain but insulating to other chains, which could be done by adding an insulating small molecule that self-assembles around the polymer to screen it. These chains could end at a small decoder as

discussed in **Section 2.1** and shown in **Fig 5**, and many of such decoders can be connected to another decoder, to build a piramidal structure of decoders because it is not possible to connect all cables to one single decoder. If the decoder can be made at the same small scale as the molecules, such a system could exploit the small scales of the molecules and the space that a 3D structure gives.

There are many ways to design an integrated circuit using self-assembly as a tool and it just comes down to the creativity of the researcher to think of new systems.

5.2 Nanofabrication using Top-down plus Self-assembly

Another approach to do nanofabrication is to make use of both the top-down and the bottom-up approaches, to create a hybrid approach. The most common one is to do directed self-assembly, where self-assembly uses internal interactions between the components and external interactions with a structure that is made by a top-down method.[16]

For integrated circuits these hybrid methods can give an improvement over the conventional silicon devices. The advantage is that this method is more versatile and it can build devices smaller than 8 nm by combining the photolithographic limit of about 10 nm with bottom-up methods that can build structures in the photolithograpic patterns.[14]

The most easy way to think of an example to use this method is to use photolithography to create patterns and to use self-assembly to fill the patterns with useful components, and to use several layers to create a useful device. It is for example possible to fabricate wiring with conducting molecules, then dots with single molecule switches and then again wiring.

There are many experiments where structures are made using hybrid approaches, like the method displayed in **Fig 17** (molecules self-assembled; wires made by photolithography)[49], lithographically controlled wetting[60], nanogap formation by lithographically patterned nanowire electrodeposition[13], inserting block-copolymers into photolithographic structures[61] and nanogap fabrication by electron beam lithography and self-assembly[14].

The nanogap fabrication by electron beam lithography is shown in **Fig 22**. The electrodes in the device are made using electron beam lithography and then a 2nm thick self-assembled monolayer of molecules is grown on them. This layer serves as a nanoscale gap (nanogap) between the electrodes. Subsequently another electrode can be fabricated lithographically. The advantage of this approach is that a molecular layer of only 2nm is grown between the electrodes which is a much better than the conventional top-down approaches.[14]

The hybrid approach to integrated circuits has the potential to give low-cost manufacturing and reduced variability (compared to pure bottom-up approaches), which makes the design much easier. This easier design and the ability to combine it with methods that have made substantial progress in development, like photolithography, makes that this hybrid approach has a good chance to make it into functional devices.

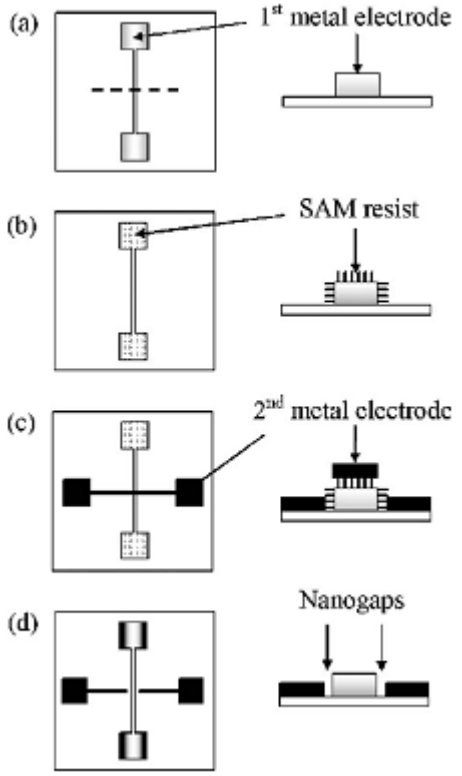

***Fig 22**: Device formation for nanogap fabrication by electron beam lithography. The first electrode is fabricated lithographically and a 2 nm thick self-assembled monolayer is grown on top of that electrode. This layer serves as a gap between the first and the second electrode.[14]*

5.3 Nanofabrication using Robots

Another way to do nanofabrication using a bottom-up approach is to make use of the robots that have been described by Drexler in **Section 1.3**. In the literature very few references to such robots are made and many authors even think nano-robots are not possible[15], which was also the basis of the Drexler-Smalley debate[9]. There are no examples in literature which can come close to Drexler universal assembler systems, and even worse, the scientific community already has difficulties to use the much simpler self-assembly to build large functional devices. Due to the fact that examples are rare, and not the fact that they are fundamentally impossible, it seems unlikely that such systems will be made in the near or little further future. But it should also be said that the lack of interest of the scientific community in these systems also slow the development.

The fact that a universal assembler won't be possible soon doesn't mean that robot systems can't give any useful results. It should be possible to use small robots to help building nanoscale objects. There are many ways to think of a robot: from a large complicated molecule that picks up groups of atoms and places it somewhere else with exactly knowing what it is doing, to a small molecule that uses self-assembly to bind another molecule and due to the interaction of both, deposit it at the desired place. Proteins are a perfect example that robots can carry out such tasks, with pretty good efficiency.

One could for example modify the example of hierarchical co-assembly thought of in **Section 5.1**. There are many self-assembling processes going on there and it could be possible to replace one of those with a robot-assisted step to improve the process. One could design a robot that helps to connect the wires with all wires being connected in the same orientation. It is also possible to think of another example where the robots act as a template and the structure builds on the robot. When the structure is finished, the robots disentangles and moves to another position to make the structure larger.

The tasks these robots perform resembles the task of a catalyst – they improve a certain process without being consumed. This is a field of chemistry that is used routiniously so the development of the robots could greatly benefit from the knowledge that has already been gained in that field. Building it up from this principe, it is possible to improve the robots and add more complexity, which could ultimately result in the universal assembler.

6. Conclusion and Outlook

The topic of this paper is in general about nanofabrication using several methods, and in partical about nanofabrication of integrated circuits to use in electronics. Moore's law has been followed for many years and the end is not yet found, but new technologies are constantly needed to fulfill Moore's law.

Using a top-down approach to integrated circuits with conventional silicon devices, the dimensions are expected to be 8nm in 2020, but that will be faced with many problems that need to be solved.

A bottom-up approach can give smaller structures, especially when single molecule switches are used because they have dimensions of only a few nanometers. But the most important improvement of a bottom-up approach is the ability to use 3D structures instead of 2D structures so much more space can be used.

The most promising developments are in the area of self-assembly. There are many developments going on in this field and many promising results are obtained. It is possible to speculate about many new ways to build integrated circuits using self-assembly. Speculative structures often don't work, but that's why there should be a lot of research in the field, so one of the many speculations could give a working structure. The only real limiting factor is the creativity of the researchers. To quote another group of researchers (G.A. Ozin et al.): "Based on results from our laboratory as well as others around the world the future seems bright for nanofabrication by self-assembly."[3]

A development that is the subject of many debates in the scientific community[9] is that of the universal assembler using robots, described by Drexler. While there are no fundamental problems, their complexity means that they are not expected to work in the near or slightly

further future. But this approach should not be abandonned completely as it would be a huge missed chance if this is never developed. One should start with small robots to build simple systems, and once more knowledge is gained, more complex systems can be built using robots.

It is also possible to use a hybrid approach to nanofabrication: using both top-down and bottom-up. This is a less promising but easier approach to nanofabrication than a pure bottom-up one, while it does give benefits over pure top-down approaches. This method can be a good bridge to make the gap from conventional systems to a radical new system smaller.

What is the way to go to make smaller and better integrated circuits? The conventional top-down approaches haven't reached the theoretical limit yet, so they will keep dominating the industry for the coming years. But the new technologies should be developed already, especially since it takes about 30 years to implement a radical new technology[26]. The current research for the new technologies have only given proof of certain concepts, and more research is required before integrated circuits are built on these principles. Of the new technologies, self-assembly has the greatest potential of all, but the hybrid approach can prove very valuable to bridge the gap.

Now the path is laid out for integrated circuits by nanofabrication, what is expected from nanofabrication in general? It has been proven in this paper that there are many ways to do nanofabrication, using top-down and bottom-up principles and that important problems in society can be solved by it. But electronics is not the only problem for society, there are many other problems that can be solved by it, like nanodiagnostics and treatment in medical science, hydrogen storage, solar cells, batteries and nanomotors[3,62]. Seeing the overwhelming amount of methods to do nanofabrication for integrated circuits, it should also be possible to do it for these problems.

Nanofabrication is not just one of the many fields of science; as shown in this paper it requires knowledge of many different fields. Input is needed from all those disciplines; all need to contribute and communicate in order to make progress. That is a lesson for anyone who wants to make progress in this field.[62]

I want to conclude with another quote from G.A. Ozin et al.: "Vision is the imagining of where we are heading; hype is the delusion of where we already are."[62] Only time can tell if nanofabrication is a vision or a hype, but by the look of it, it is a vision.

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