1. Title of the Project

Assembling Structures at Nanoscale by Utilizing the Photochemical Reactivity of Ferroelectric Domains

2. Applicant

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4. Abstract

Ferroelectric materials have been extensively studied because of their unique properties like the coupling of the electrical polarization with or their giant dielectric constant. Besides, in 2001, photochemical reactivity of ferroelectric surfaces was shown to be linked to the polarization orientation underneath [1]. In the last decade, photochemical investigation on ferroelectric crystals drew considerable attention and was used to assemble structures at the nanoscale using the adsorption selectivity between the different oriented domains. Reduction of metals was reported on up domains whereas it is less prominent on down domains. This is explained by the change in the electronic structure of the ferroelectric with polarization orientation. However, our preliminary results have shown opposite behavior of the adsorption selectivity on multiferroic $BiFeO_3$ thin films and imply that there is more to discover in the physics lying behind the selective deposition on ferroelectric crystals. Given the potential of multiferroic crystals for applications, investigation on surface properties of ferroelectrics and multiferroics will give valuable insight to the field. In this project, we propose to study the reduction of various metals, particularly Ag on $BiFeO_3$ thin films prepared by Pulsed Laser Deposition.

5. Duration of the Project

4 years, starting from September 2011.

6. Personnel

6.1 Senior Scientist

Name	Task in the Project	Time
Prof. Dr. Beatriz Noheda	Supervision	20%

6.2 Junior Scientists and Technicians

Name	Task in the Project	Time
Alim Solmaz	Experiments and Analysis	90%
Jacob Baas	Technical Support	10%
Henk Bonder	Technical Support	10%

7. Cost Estimates

7.1 Personnel Positions

One ‘onderzoeker in opleiding’ position for four years.

7.2 Running Budget

15 k€/year for conferences, summer schools and maintenance.

7.3 Equipment

No additional budget is required for equipments.

7.4 Budget Summery (in k€)

The expenses are summarized in the table below.

		2011	2012	2013	2014	2015	Total
Position	PhD Student	15	50	50	50	35	200
	Postdocs	-	-	-	-	-	-
	Technicians	-	-	-	-	-	-
	Guests	-	-	-	-	-	-
Costs	Personnel	15	50	50	50	35	200
	Running Budget	5	15	15	15	10	60
	Equipment	-	-	-	-	-	-
Total							**260**

8. Research Program

8.1 Introduction

Ferroelectrics are fascinating materials due to their strong electromechanical coupling and high dielectric properties. Since the discovery of the Rochelle salt in 1920 by Valasek [2], ferroelectrics have been utilized in many applications such as sensors, transducers and actuators etc. In one form or another, ferroelectric materials have become ubiquitous to today's society. Besides commercial applications, in the last decade, ferroelectrics have drawn attention due to their photoelectric and photochemical properties.

Indeed, ferroelectrics were among the first materials that were shown to have photochemical properties. This effect was first realized by blistering or discoloring of paints that contain TiO_2 particles upon exposure to sunlight. In 1938, it was showed that TiO_2 is photoactive [3] and this paved the way to investigate the photochemical properties in ferroelectrics. $BaTiO_3$ was also proven to be photoactive around that time. However it remained untouched for many years until Giocondi and Rohrer [1] studied the surface photochemical properties of $BaTiO_3$ and found out the relation between the polarization direction and the variation of the band bending, thus, photochemical activity. Due to technological developments, synthesis and manufacturing of devices at micro and nano scale has become the focus of very intense study in recent years. Many interesting and significant approaches have been offered and applied. Among them, scanning probe based nanolithography techniques and microcontact printing are nowadays very common method of patterning self assembled monolayers and enabled nanoscopic resolution. There are numerous ways of controlling and manipulating molecules at the nanoscale to produce devices by utilizing the magnetic, electric or mechanic driven forces.

Assembling dissimilar molecular and nanostructural elements into complex functional structures is a very powerful driving force to design new functionalities and build up new ways of producing nanostructures. One of the most novel techniques to achieve this is named Ferroelectric Nanolithography and was proposed in 2002 by Kalinin et al. [4] upon the discovery of the relation between the polarization direction and the electronic structure of the ferroelectric materials. The main idea lying behind the technique is to access the polarization direction to control the band bending at the surface of the ferroelectric. Hence electron hole pairs generated by irradiation of UV light separate due to the electric field created by the band bending at the surface; depending on its direction either electrons or holes are driven to the surface. These electrons or holes can be used to perform reduction or oxidation at the surface with high spatial selection. This is the basis of the photochemical selectivity at the ferroelectric surfaces and in this way assembling of nanostructures at predefined locations can be achieved.

Development of ferroelectric nanolithography is, briefly mentioning, a combination of two phenomenon. First is the atomic polarization and the local domain structure are controlled in ferroelectric thin film through patterning by Piezoresponse Force Microscopy (PFM) or by using electron beam system. Second, the photo reduction or oxidation takes place at the surface to assembly the nanostructures selectively. This is particularly interesting with the reduction of metals at ferroelectric surfaces since it could provide a very efficient way of electroding ferroelectric capacitors at the nanoscale. One of the biggest advantages of ferroelectric nanolithography is the resolution that can be achieved. It was shown that by using PFM, 10-20 nm size domains could be written on a ferroelectric thin film [5]. If the relation between the polarization and the photochemical selectivity can be well understood, it could open the way to optimize this process and achieve higher performance electronic or opto-electronic devices.

Considering the application point of view, Ferroelectric RAM or FeRAM is a type of random access memory built similarly to a dynamic random access memory with a ferroelectric thin film layer instead of a dielectric one. Since ferroelectric thin films possess a remnant polarization upon removal of applied field, having a ferroelectric thin film layer in a device gives rise to non-volatility characteristics so wanted in memory applications. FeRAMs bring to the field advantages of lower power consumption, faster writing performance and much longer life of write-erase process whereas the disadvantages ascribe with lower storage density compared to Flash devices, storage capacity limitations and higher cost. Even though early applications of FeRAMs in real life have been introduced by Samsung cell phones and Play Station II, there is still a big room for enhancement in the storage density. At this step, ferroelectric nanolithography can be a very crucial technique to realize the dream of higher capacity FeRAMs. More precisely, 1Tbit/in^2 storage capacity can be reached by having 25x25nm^2 size data bits. Hence ferroelectric nanolithography is a promising technique.

Upon demonstration of selective deposition of silver on polycrystalline $BaTiO_3$ ferroelectric up domains [1], quite intense study on the relation between the polarization direction and the surface photoactivity had begun. Utilizing the phenomenon, Kalinin et al. studied the Ferroelectric Lithography mostly on single/polycrystalline $BaTiO_3$ and $PbZr_{0.3}Ti_{0.7}O_3$ (PZT) thin films [4,6] where the reduction of silver and other metals occurs on the up domains and oxidation of anions on down domains, if possible ever. In 2007, Dunn et al. [7] reported the growth of silver both on up and down

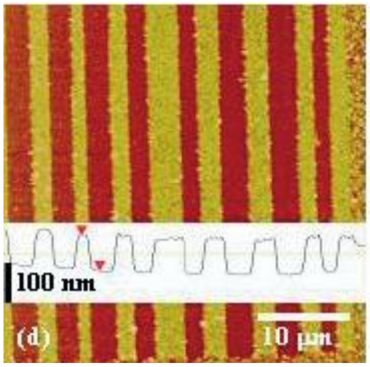

Figure 1 Ag deposition on PZT thin films. Retrieved from [6]

domains of (100) oriented PZT thin films which brought modifications to the theory by taking the influence of orientation and composition of thin film on space charge region into account. In the recent years, the materials under focus slightly shifted from $BaTiO_3$ and PZT to $LiNbO_3$ and organic ferroelectrics. Variety in the details of the results for $LiNbO_3$ was published [8,9] and it is attributed to the fact that surface reactivity is not only determined by the polarization but also by the defect concentration and adsorbed charges. Besides to oxide studies, Bonnell et al. [10] worked on PVDF organic ferroelectric and managed to get selective deposition and, indeed, focused on the origin of photoconductivity. On the other hand, Zhang et al. [11] worked on the variation of surface photochemical reactivity of organic ferroelectrics with polarization orientation and reported a change in the deposition behavior of organic molecules.

Assembling nanostructures by selective deposition of metals on ferroelectric surfaces still keeps drawing attention and very lately, another way of patterning the ferroelectric domains was showed. Shen et al. [12] demonstrated that embossing the PZT thin film creates a certain pattern which facilitates the selective deposition.

One of the most intriguing oxides is $BiFeO_3$ which is a multiferroic and attracted much attention due to the potential use in memory devices. The interplay between its electric and magnetic properties has been studied passionately and is still under investigation. However it is not the least exciting physical phenomenon observed in BFO. Optical investigations demonstrated that it shows photovoltaic effect near to visible light edge due to the lower band gap energy compared to other oxides. Upon demonstration of the photovoltaic effect in BFO [13], as expected, Schultz et al.[14] have recently reported the selective reduction of Ag on polycrystalline BFO films.

Ferroelectric lithography has attracted much attention since it was introduced and is seen as one of the promising techniques to assemble structures and devices at the nanoscale.

8.2 Theoretical Background

In a ferroelectric material, regions with same polarization orientation are named domains and the boundaries between them are called domain walls. Regions with polarization towards the surface along out-of-plane direction are up domains and those with opposite direction are down domains. It is also possible to have domains with polarization parallel to the sample surface and they are named in-plane domains. Domain walls between up and down domains are 180° walls and those between out-of-plane and in-plane domains are 90° walls as depicted in Figure 2. The polarization is created due to the displacement of the ions in the unit cell and causes to excess of certain type of charges at the surface which is named surface bound charges or polarization charges. The formation of both 90° and 180° domain walls are responsible to minimize the depolarization field which arises due to the need for compensation of the polarization charges. Moreover formation of 90° domain walls can release the elastic energy stored in the crystal and they will form if the elastic boundary conditions permit it.

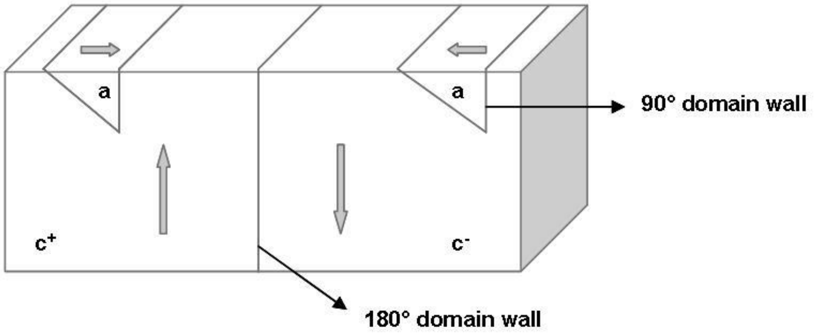

Figure 2 Representation of domain walls in ferroelectrics

In the last decade, Piezeresponse Force Microscopy (PFM) has become an important tool in order to detect the piezoelectric properties at the nanoscale. The technique uses an Atomic Force Microscope with a metallic tip and works in the contact regime. Applied AC bias, either to the tip or to the sample causes the sample to response elastically which is detected by the deflection in the tip. The phase of the response shed light on the polarization direction and the amplitude image gives information about the magnitude of the piezoelectric response even though the quantitative interpretation is quite difficult, but possible in some cases. In addition to the detection of piezoelectric properties, by applying a large enough DC bias in the system (above the sample's coercive voltage), it is possible to switch the polarization direction and, hence, to write well defined domain patterns on ferroelectric samples.

As mentioned in the introduction, Ferroelectric Lithography utilizes the reactivity difference between the up and down domains at the surface of a ferroelectric material. This stems from the change in the electronic structure in the vicinity of the surface due to the polarization orientation. Polarization results in the formation of surface bound charges which need to be compensated to minimize the energy. It can happen internally by migration of the defects and by the band bending at the surface and externally by surface adsorbents. The interplay between the internal and external mechanisms ultimately determines the electronic band structure. On up domains, polarization brings positive surface bound charges which can be fully or partially screened by downward band bending which enhances the number of negative free charge carriers. On the other hand, down oriented polarization causes upward band bending at the surface. Photochemical activity is triggered by the illumination of UV light with energy higher than the band gap of the exposed material. This generates electron-hole pairs in the bulk of the crystal which are separated away by the electric field created inside the ferroelectric. On the up domains, electrons are driven towards the surface whereas holes are driven away from the surface. On the contrary, for down domains, electrons experience a barrier at the surface that requires electrons to possess higher energy to surmount. In brief, electrons are favored at the surface of up domains and holes on the down domains. This results in the selective deposition of certain type of ions on certain domains when immersed in aqueous solution under UV light illumination. This mechanism was proposed by Kalinin et al. [4] and is depicted in Figure 3.

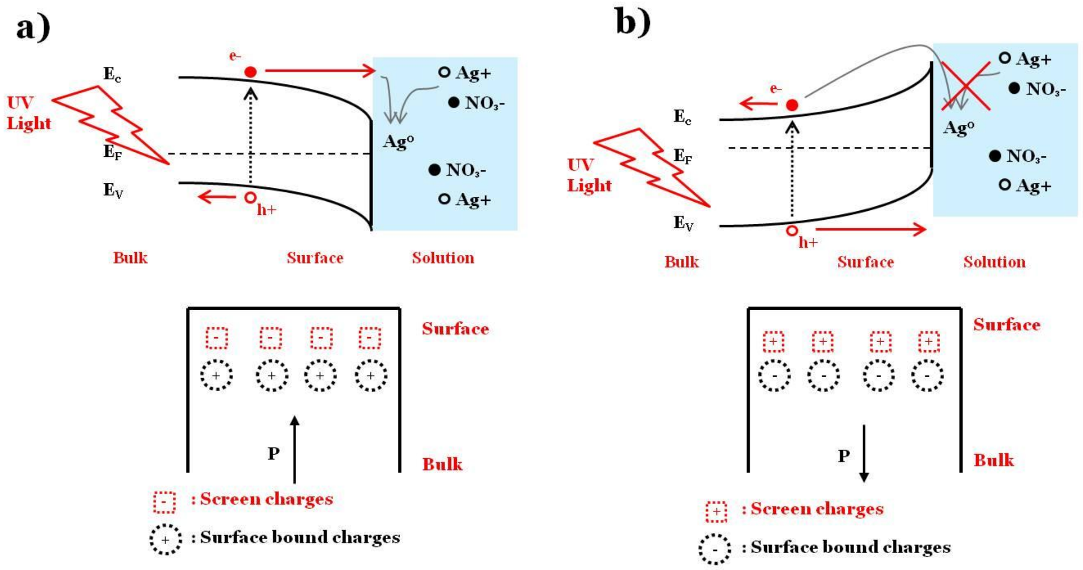

Figure 3 Reduction mechanism of Ag ions on ferroelectric surface with (a) up and (b) down oriented polarization as proposed by Kalinin et al.

8.3 Goal of the Proposal

In the proposed PhD project, we would like to study the physics lying behind the Ferroelectric Lithography technique on single crystalline ferroelectric thin films. Preliminary results on the reduction of Ag on $BiFeO_3$, in the scope of my master thesis project, showed that silver cations selectively attach to the down domains instead of up domains, contrary to the mechanism proposed in the literature. Interpretation of the results shows that it is not only the polarization determining the surface reactivity but also the interplay of defect states, orientation of the thin film, composition of the material and surface adsorbents. Our preliminary surface potential measurements have demonstrated that surface adsorbents play an important role in the behavior of the sample surface and that maybe different than the expected according to the polarization direction underneath.

Most of the studies regarding the Ferroelectric Lithography were done on the single/poly crystal bulk materials or sol-gel prepared thin films which usually contain grain boundaries and have relatively rough surfaces. In our group, we have the ability to produce atomically flat single crystalline thin films by Pulsed Laser Deposition (PLD) so that we can eliminate the topography factors on the electronic structure. In addition, changing the growth condition of the thin films gives control on the defect concentration in the films. Thus we can more precisely find out the relation between the surface adsorbents, defect density and polarization direction and figure out their overall influence on the surface reactivity.

Understanding the surface properties of BFO is of large importance due to its potential use in the applications. Nowadays, many studies are investigating the relation between the ferroelectricity and ferromagnetism. Outcome of this project will be very valuable on the interpretation of the surface dependent measurements.

The project will also cover the ferroelectric thin films which already have a regular domain pattern as grown. Even without writing a pattern on the surface, useful structures at the nanoscale, whose size might be determined by the growth conditions, can be manufactured. In the host group knowledge is available about how the domain size changes with thickness in the $PbTiO_3$ thin films on $DyScO_3$ substrates. This film/substrate combination possess interesting characteristic of a near zero mismatch at the growth temperature. This allows a defect free material to be grown (no dislocations) and thus a much more controlled domain structure. The project is intended to study this system as well.

In the further steps of the project, we will consider addressing the deposition of DNA molecules on predefined locations, regarding the fact that DNA is a negatively charged molecule and UV irradiation does not harm the structure. This will be in collaboration with the research group of Prof. Dr. Andreas Herrman at Zernike Institute for Advanced Materials.

8.4 Plan of Work

Intended plan of the work is summarized in the table below. Deviations from the plan might occur due to the problems encountered or interesting findings might open different directions.

Time (year)	**Activity**
1st	Learning the PLD technique and optimizing the process to grow thin films.
2nd	Discovering the influential parameters on $BiFeO_3$ samples.
3rd	Investigating the ferroelectric nanolithography technique to $PbTiO_3/DyScO_3$ system and figure out the achievable smallest size.
4th	Applying the method to the DNA and organic systems and thesis writing.

9. Infrastructure

This project is going to be carried out in the Solid State Materials for Electronics Group at Zernike Institute. For the manufacturing and the analysis of the samples, Pulsed Laser Deposition and Atomic Force Microscopy with Piezoresponse mode are available in the group laboratories. In case of need for cleanroom, we have an access to the Nanolab Groningen cleanroom at the institute. Moreover, the group has the knowledge of producing many ferroelectric thin films by PLD with different properties and has the capacity to characterize the electrical and magnetic properties with ample equipments such as PPMS, MPMS, and cryogenic probe systems.

10. Application perspective in industry, other disciplines or society

Ferroelectric materials are extensively used in the industry for many different applications. Nowadays, multiferroic materials are considered as one of the most promising materials to be used in the memory device applications due to the possible coupling between the electrical and magnetic properties. Even though this project do not aim to give a direct output for an industrial application, the knowledge about the surface properties that is going to be gained during the project will be enormously valuable for both academic and industrial use. On the other hand, assembling at the nanoscale is very hot topic in the science field and controlling the domain size even up to 10nm will allow to build up structures at such small scale. As mentioned before, there are a few studies combining the technique with organic systems and our project will pave a way to attract attention of the scientists within our institute as well as the world wide into ferroelectric lithography.

11. References

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