1. Applicant

Bo Sun

2. Title of the project

Fundamental aspects of chemistry induced by low-energy electrons

3. Abstract

Extreme ultraviolet lithography (EUVL) is the most promising approach to fabricate faster and more powerful integrated circuits. EUVL uses EUV light to transfer patterns from a mask to a sensitive layer (a resist) on Si wafers. EUV light with a wavelength of 13.5 nm is ionizing. Low-energy secondary electrons, generated by EUV light react with the resist, after which the resist can be developed. Similarly, in electron beam lithography (EBL) the low-energy electrons are responsible for chemically changing the resist. To minimalize the feature size and optimize the resists used in EUV and EBL lithography, it is urgent to study how the low-energy electrons interact with resists.

I propose a detailed study of reactions of low-energy electrons with EUV and EBL resists, using *in situ* surface analysis and post-irradiation characterization. Together with density functional theory calculations of different dissociation pathways of selected resists, I shall obtain a fundamental understanding of how the low-energy electrons react with resist thin films. I shall also study other model compounds to provide insight on reactions of low-energy electrons with solids.

4. Keywords

Low energy electrons, extreme ultraviolet lithography, photoresist, electron-induced chemistry, density functional theory

5. Host group and institution

Supervisor: Prof. Dr. Petra Rudolf, Dr. Remco Havenith

Research groups: Surface and Thin films & Theoretical Chemistry

Zernike Institute for Advanced Materials

Program of the proposal

1. Introduction

The feature size of electronic circuits shrinks every year, roughly according to "Moore's Law". By the year 2020, the International Technology Roadmap for Semiconductors foresees that the half pitch of flash memory is miniaturized to 10 nm. Because of this small dimension, the standard lithography technique (using UV light) cannot meet the requirements for future chip manufacture. Among the predicted technologies that could be optimized for future use, extreme ultraviolet lithography (EUVL) is the most promising approach using extreme ultraviolet (EUV) light with a wavelength of 13.5 nm. The schematic drawing can be found below:

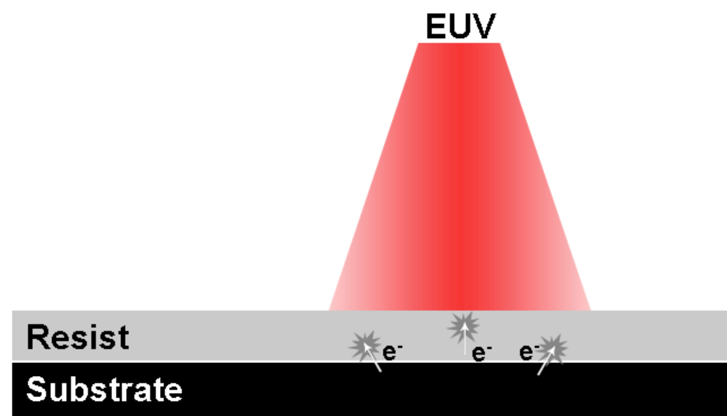

Fig.1 Schematic drawing of secondary electrons generated in EUV lithography

Generally in industrial lithography, a resist (a photo-sensitive layer) is used to transfer patterns from a mask onto a Si wafer. While UV light exposes the resist through photon-induced chemistry, EUV light is ionizing. This involves a paradigm shift in the technology and implies that a fundamentally different mechanism is now responsible for exposing the resist. The ionizing radiation releases secondary electrons from the substrate that react with the resist. It is these secondary electrons that initialize the chemistry, amongst others through a chemical process named dissociative electron attachment (DEA) [1]. It has been estimated that about four secondary electrons on average are generated by one EUV photon [2]. As Figure 2 shows, the inelastic mean free path of these low energy secondary electrons first decreases as the electron energy decreases because a slower electron has a longer interaction time with matter and therefore a higher probability of interacting, and then increases again below electron energy range about 15 eV because the number of available interaction channels decreases [3].

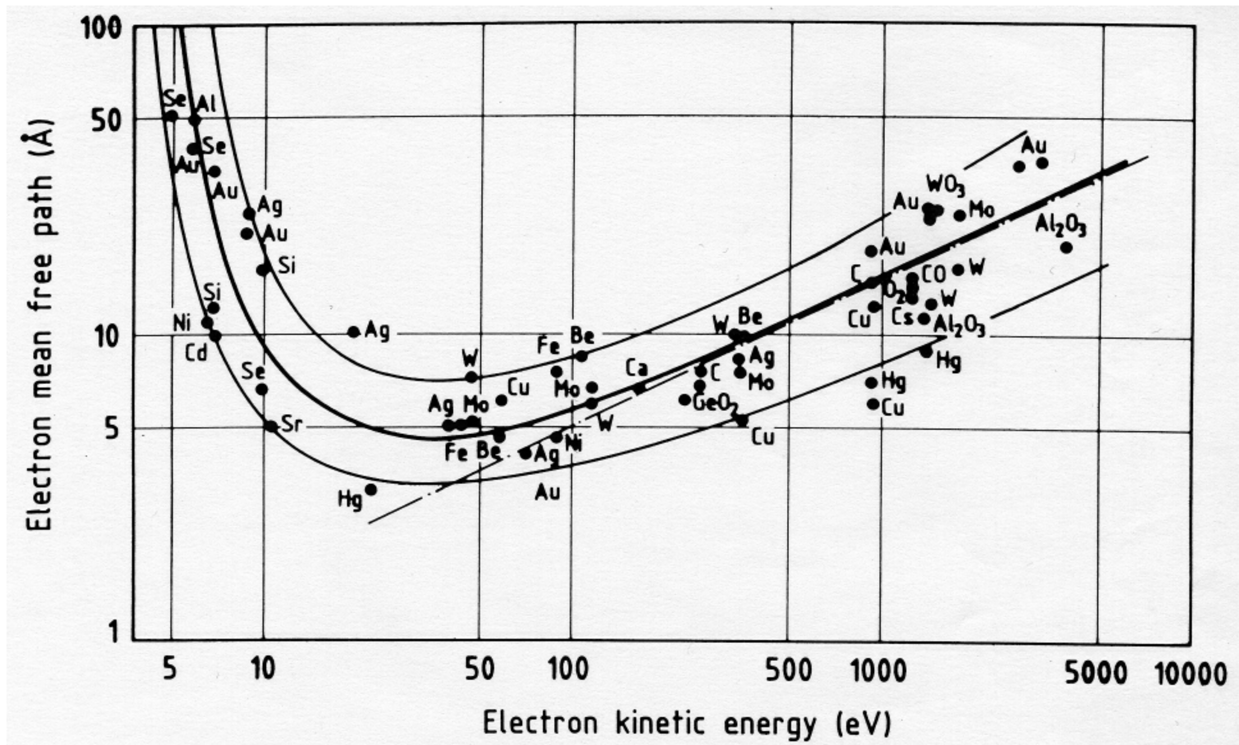

Fig. 2 Universal electron mean free path profile in different materials [3]

The inelastic mean free path of electrons with energies in the range of few to tens of eV is well above 3-5 nm [4], and this limits the ultimate resolution of EUV resists. To optimize the resist materials used in semiconductor lithography, a fundamental understanding of how the low energy electrons interact with resists has to be achieved.

PMMA, for instance, is a well-known resist for UV, electron or X-ray lithography. However, most of the studies on PMMA irradiation chemistry do not distinguish explicitly between the effects of high-energy primary irradiation and those of low-energy secondary electrons [5,6]. While it is known that low-energy electrons induce most of the chemistry, little is known about this chemistry proceeds. The only work that studies the effects of low-energy electron irradiation on PMMA thin films was reported by V. M. Bermudez [7]. The study is based on polarization-modulated infrared reflection absorption spectroscopy. The results suggest that low-energy electrons appear to damage PMMA in the same manner as more energetic forms of radiation, but the fundamental model of the underlying mechanism is still missing.

Secondary electrons also play an important role in focused electron beam induced deposition (FEBID), a direct-write technique that is used in the semiconductor industry for mask repair [8]. Similar to EUV lithography, the chemistry of the deposition is driven by the secondary electrons generated from the interaction between high-energy electrons with the substrate. Adsorbed precursor molecules can react with these low energy electrons, dissociate and form a residue (the

desired material) on the substrate. To optimize the quality of the deposit (the reaction product), new precursors need to be developed. To accomplish this goal, the role of the low energy electrons must be well examined.

It is surprising to note that, while companies such as ASML make massive investments in EUV technology, the studies on the boundary between physics and chemistry proposed here are outside their scope. The same is true for the suppliers of resist (such as BASF).

In summary, it is therefore very timely to study the effects of low-energy electrons on condensed matter and specifically on resists. Since in both industrial and scientific respects it is demanded that we understand the interaction better, the proposed project is of crucial importance.

2. Research questions and aims

The research questions I propose to address are:

1. Which process that dominates the reaction: dissociative electron attachment, dipolar dissociation or direct ionization?
2. Is there an energy threshold for electron-induced chemistry and (if so) what determines it?
3. How can we control the reaction towards specific directions?
4. Do general rules for electron-induced chemistry exist? If so, what are they?

To answer these questions, I propose to do the following research:

1. Irradiation and post-irradiation study by surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IRS), and mass spectrometry (MS) on existing photoresists and electron beam resists such as PMMA, simple photo acid generators, and selected compounds that will be determined later.
2. Density functional theory calculations at the molecular level on resist molecules or short chains.

Together, this will provide a full picture of the reactions, giving a detailed insight into the mechanisms.

3. Experimental Methods:

Ultra-high vacuum (UHV)

The surface analyses will be conducted under ultrahigh vacuum (UHV) conditions, where the chemical environment can be well controlled. Influences of unwanted reactions, such as oxidation, can be reduced or excluded.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a commonly used, powerful chemical analysis technique. XPS enables us to determine the binding energies of electrons, providing quantitative information on the chemical composition and the chemical environment of elements (oxidation state, binding to a more or less electronegative element). Changes in binding energies (called chemical shifts), peak areas and peak shapes as result of electron exposures will allow to determine the changes in molecular bindings, reaction rates, etc.

The existing setup is well suited for the demanded characterization. The setup is schematically represented in Figure 3.

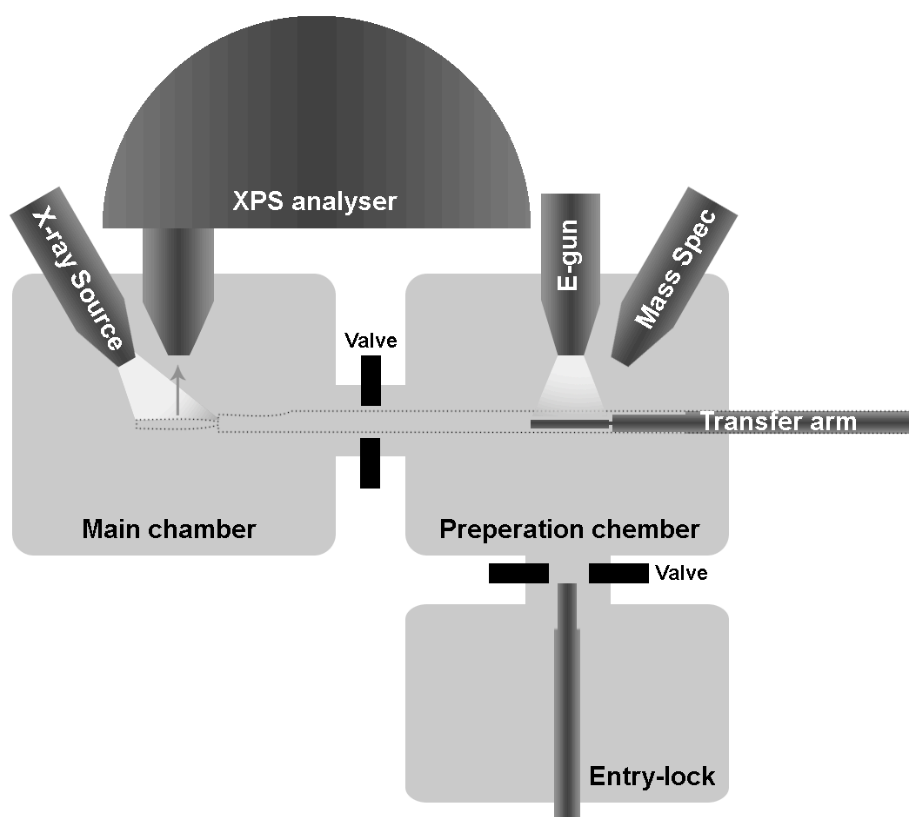

Fig. 3 Schematic drawing of the existing XPS setup: the sample can be introduced via the entry lock which is pumped down before introducing the sample in the preparation chamber; there the sample can be irradiated while measuring the desorbing molecular groups with the mass spectrometer without compromising the vacuum in the main chamber. The XPS spectrometer in the main chamber is used to collect spectra on the pristine and on the irradiated sample.

The reaction process can be followed in detail by repeating exposure and post-irradiation analysis. Quantitative information of reaction mechanism such as rate constant and qualitative information of reaction order are acquired by both XPS peak area analysis and mass spectrum in time trace. Figure 4

shows preliminary data from experiments with a common photoresist poly(methyl methacrylate) (PMMA).

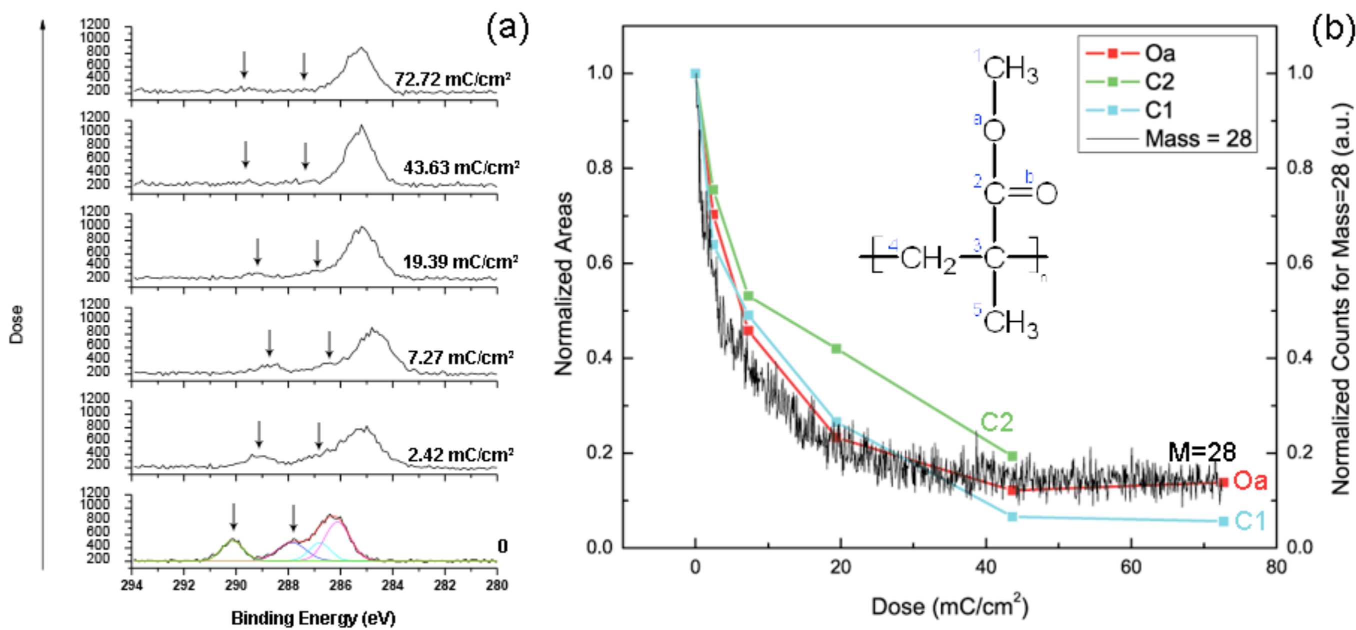

Fig. 4 Preliminary data of PMMA

Figure 4 shows XPS data of the C1s core level region collected on a PMMA thin film exposed to an increasing dose of 20 eV electrons. Chemistry changes are indicated in Figure 4b, where the evolution of the peak areas of the various components (carbon atoms labeled with 1-5 and oxygen atoms labeled with a, b) is plotted. These data can be used to calculate the rate constant. The XPS data show that two peaks at higher binding energy that correspond to carbon atoms in the O-containing groups of PMMA are disappearing. This suggests that the O-containing groups (binding energy around 290 eV and 288 eV) leave the surface, as indicated by the arrows in Fig. 4(a). This is confirmed by the data from the mass spectrometer. As shown by the black line in Fig. 4(b), a similar reaction rate is observed for the evolution of gas phase CO, strongly suggesting the two processes are linked.

Infrared Spectroscopy (IRS)

Infrared spectroscopy is a powerful technique for studying chemical changes in thin films. If a thin PMMA film is spin-coated onto an Au substrate, the reactions during electron irradiation can be followed *in situ* by reflection absorption infrared spectroscopy that posed no limitation on the vacuum conditions in the chamber. The experimental setup is shown in Figure 5a. The absorption peaks in the spectrum are characteristic of different modes of molecular vibrations as illustrated in Figure 5b for a sample where changes are induced not by e-bombardment but by annealing. Comparison of spectra before and during electron irradiation can provide detailed binding and structure changes in the resist, enabling us to analyze the mechanism.

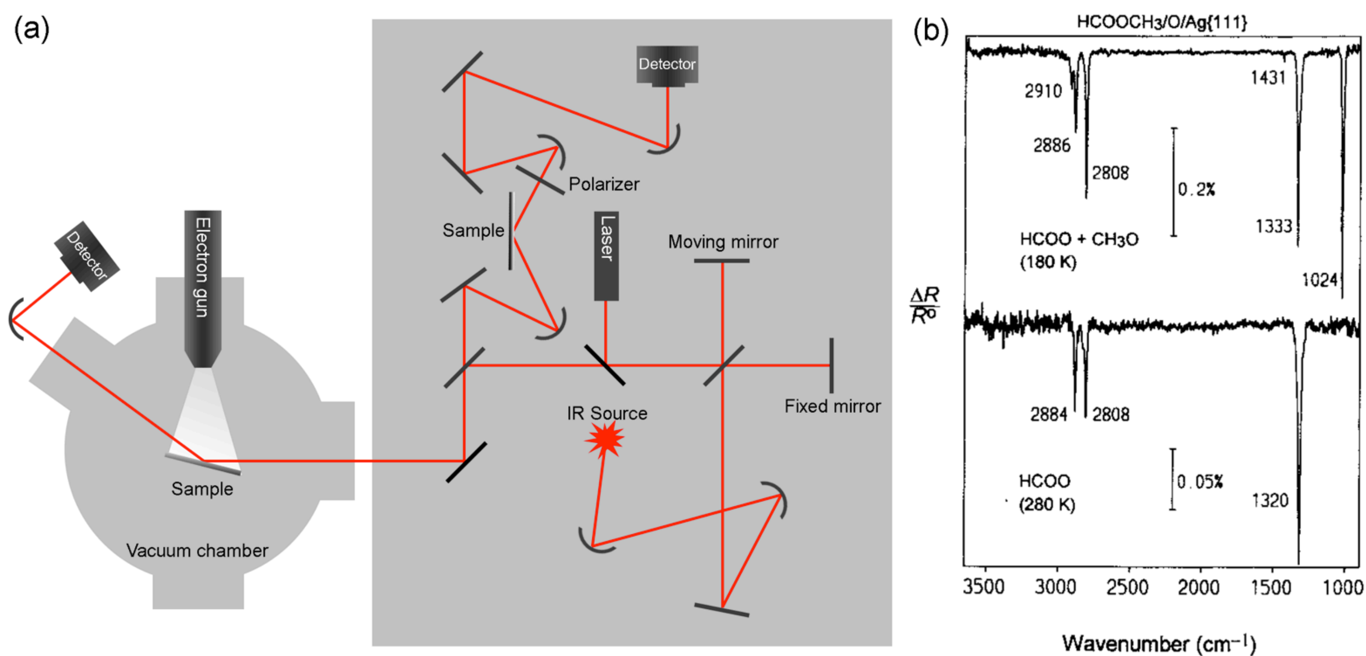

Fig. 5 (a) Schematic drawing of IR measurement setup. (b) Spectra changes in resist after annealing.

Mass Spectrometry (MS)

Mass spectrometry will be used to trace the evolution of gaseous reaction products during and after the exposure. Time traces of specific masses are used to calculate the reaction rates.

4. Theoretical calculations

Density functional theory (DFT) calculations can give us fundamental insights in how specific reactions evolve after a low-energy electron is absorbed into a molecular orbital. It is a quantum mechanical modeling method for electron structure investigation. While it is not new to combine theoretical calculations and experiments, only few DFT calculations have been performed on polymer resists and electron-induced reactions.

For instance, electron-induced fragmentation of a general molecule AB follows different pathways, including ionization, dipolar dissociation and dissociative attachments, as schematically indicated in Figure 6. The energies of the system along these pathways can be calculated using DFT, and from the results of DFT calculations we can determine what favors one pathway over the other, which is essential information for the development of novel, improved compounds and resists. Starting with monomers of the resists, proper boundary conditions can be chosen to accurately model the polymer system [9].

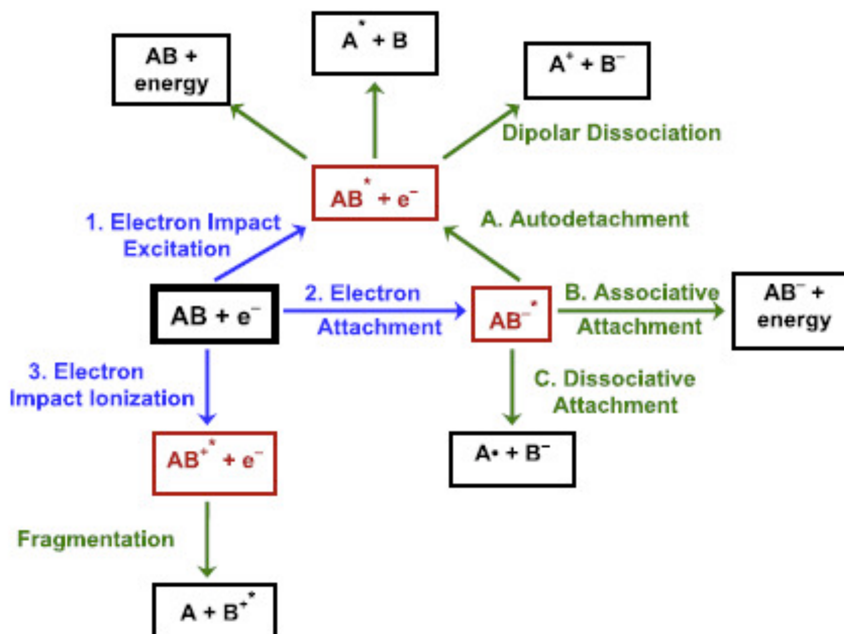

Fig. 6 Electron-induced dissociation pathways [10]

5. Timetable

	2014		2015				2016				2017				2018	
XPS, MS and IR study of MMA	x	x														
XPS, MS and IR study of PMMA		x	x													
Introduction into DFT calculations				x	x											
DFT calculation of MMA and PMMA					x	x	x									
Experiments & calculation photo-acid-generator							x	x	x	x						
Experiments & calculations on EBL resist										x	x	x	x			
Study other compounds*													x	x	x	
Summary project and write thesis															x	x

6. Work plan

2014: (1) Experimentally study PMMA and MMA using XPS, IR and MS. (2) Analyze data of PMMA and MMA. (3) Participate in the Ameland summer school and attend courses and colloquiums for PhDs.

2015: (1) Complete experimental works on PMMA and MMA and finish up data analysis. (2) Learn about DFT calculations at molecular level. (3) Start DFT calculations on PMMA and MMA. (4) Participate in Ameland summer school, attend courses and colloquiums for PhDs.

2016: (1) Complete DFT calculations on PMMA and MMA. (2) Write first manuscript on new findings of PMMA and MMA. (3) Conduct experiments and DFT calculations on photo-acid-generator. (4) Write second manuscript on new findings on photo-acid-generator. (5) Participate in Ameland summer school and attend courses and colloquiums for PhDs. (6) Attend (inter)national conferences.

2017: (1) Conduct experiments and do DFT calculations on an EBL resist. (2) Write third manuscript on new findings on EBL resist. (3) Select and study one or two compounds, especially when additional information is needed for project completion. (4) Participate in Ameland summer school and attend (inter)national conferences.

2018: (1) Summarize project findings. (2) Repeat some experiments or calculations if needed. (3) Write and defend PhD thesis. (4) Participate in conferences.

7. Facilities and supervision

Prof. Dr. Petra Rudolf has headed the Surfaces and Thin Films group of the Zernike Institute for Advanced Materials since 2003. For the past 20 years she has been active in different aspects of surface analysis, investigating the electronic structure with the help of direct and inverse photoemission and X-ray absorption spectroscopy; studying the vibrational properties of thin molecular films by infrared spectroscopy and the surface crystalline structure by low-energy electron diffraction, atomic force and scanning tunneling microscopy. She has published over 180 papers in peer-reviewed journals including Nature, Nature Materials, ACS Nano, JACS, Small and Physical Review Letters. She was awarded the 2007 EU Descartes Prize for research on molecular motors and elected in 2010 Fellow of the American Physical Society for her explorations of fullerenes, carbon nanotubes and graphene. So far 16 PhD students have successfully defended their dissertations under Prof. Rudolf's supervision and another 2 will do so in the coming year. She is therefore ideally qualified to carry out this project and to supervise the PhD student for whom financing is requested.

The Surfaces and Thin Films group at the Zernike Institute for Advanced Materials is perfectly equipped for all aspects of exploiting electron-induced chemistry and analyze the products as outlined in this proposal

References

1. T. Kozawa, Y. Yoshida, M. Uesaka, and S. Tagawa, Jpn. J. Appl. Phys. 31, 4301 (1992).
2. T. Kozawa, S. Tagawa, H. Oizumi, and I. Nishiyama: J. Vac. Sci. Technol. B 24 (2006) L27.
3. M. P. Seah, W.A. Dench, Surf. Interface Anal. 1, 2 (1979).
4. S. Tanuma, C.J. Powell and D.R. Penn, Surf. Interface Anal. 21, 165 (1994).
5. C. P. Ennis and R. I. Kaiser, Phys. Chem. Chem. Phys. 12, 14902 (2010).
6. T. Kozawa, S. Tagawa, Jpn. J. Appl. Phys. 49, 030001 (2010).
7. V. M. Bermudez, J. Vac. Sci. Technol. B 17, 2512 (1999).
8. T. Liang, E. Frendberg, B. Lieberman, A. Stivers, Advanced photolithographic mask repair using electron beams, J. Vac. Sci. Technol. B 23, 3101 (2005).
9. A. N. Rissanou and V. Harmandaris, J. Nanopart. Res. 15, 1589 (2013).
10. C.R. Arumainayagam, H. L. Lee, R.B. Nelson, D.R. Haines, R.P. Gunawardane, Surf. Sci. Rep. 65, 1 (2010).

Project statements

1. Starting date and project duration

   The proposed project starts at 1st September 2014. The duration of the project is 4 years.

2. Budget

		2014	2015	2016	2017	2018	Total
Position (year)	PhD	0.5	1	1	1	0.5	4
Costs (k€)	Travelling	1.25	2.5	2.5	2.5	1.25	10
	Consumables	5	10	10	10	5	40
Total cost except salary/fellowship (k€)		6.25	12.5	12.5	12.5	6.25	50

3. CV of the applicant

Sun Bo

Topmaster Nanoscience cohort 2012-2014

Zernike Institute of Materials Science

University of Groningen

sun@student.rug.nl

+31 6 34310502

EDUCATION

Materials Chemistry (BSc), Department of Materials Science and Engineering, Nanjing University. "Synthesis of Ag_{core}-Pt_{shell} nanowires and the bimetallic interface effects on their catalytic activity." Supervised by Prof. Shaochun Tang.

2012-now: Topmaster Nanoscience (MSc), Zernike Institute of Materials Science, University of Groningen.

RESEARCH EXPERIENCE

2008-2012: National Laboratory of Solid State Microstructures of China, Nanjing University.

Studies on synthesizing Ag nanowires, and Ag_{core}-Pt_{shell} bimetallic nanowires in different applications, as well as the bimetallic interface effects.

Supervised by Prof. Shaochun Tang, Prof. Xiangkang Meng

April-June 2013: Zernike Institute of Materials Science, University of Groningen.

Studies on electron transport dynamics in TiO_2 quantum dots sensitized solar cells using impedance spectroscopy.

Supervised by: Lai-hung Lai, Prof. Dr. Maria Antonietta Loi (Photophysics and opto-electronics group)

Sept 2013-now: Zernike Institute of Materials Science, University of Groningen.

A study of the role of low-energy electrons on the lithography resist PMMA.

Supervised by: Dr. Willem van Dorp (Materials Science group)

university of groningen / faculty of mathematics and natural sciences / zernike institute for advanced materials

Version 3 Dec. 2013

Declaration of hospitality and financial support for research costs

Appendix to the Proposal for a PhD research position
in the NWO Graduate Programme Advanced Materials, deadline 2 Feb. 2014

Name of the applicant: Bo Sun

Title of the proposal: Fundamental aspects of chemistry induced by low-energy electrons

---

By signing this document the staff member declares that she/he is willing to host and supervise the PhD research project that is mentioned above. In addition, the staff member declares that she/he has and makes available the materials, infrastructure and the funding that is needed for covering the research costs (the costs in addition to the salary of the PhD student some funding for travel and training), as described in the proposal.

The signing staff members must be affiliated with the Zernike Institute for Advanced Materials (including the associate members).

Signatures

Applicant (the student applying for the PhD grant)

Date: 01-02-2014 Name: Bo Sun Signature:

Daily PhD supervisor (only needed if applicable, in case of supervision by an assistant professor or UD/UHD without ius promovendi)

Date: Name: Signature:

1st Promotor (staff member with ius promovendi)

Date: 01-02-2014 Name: Petra Rudolf Signature: