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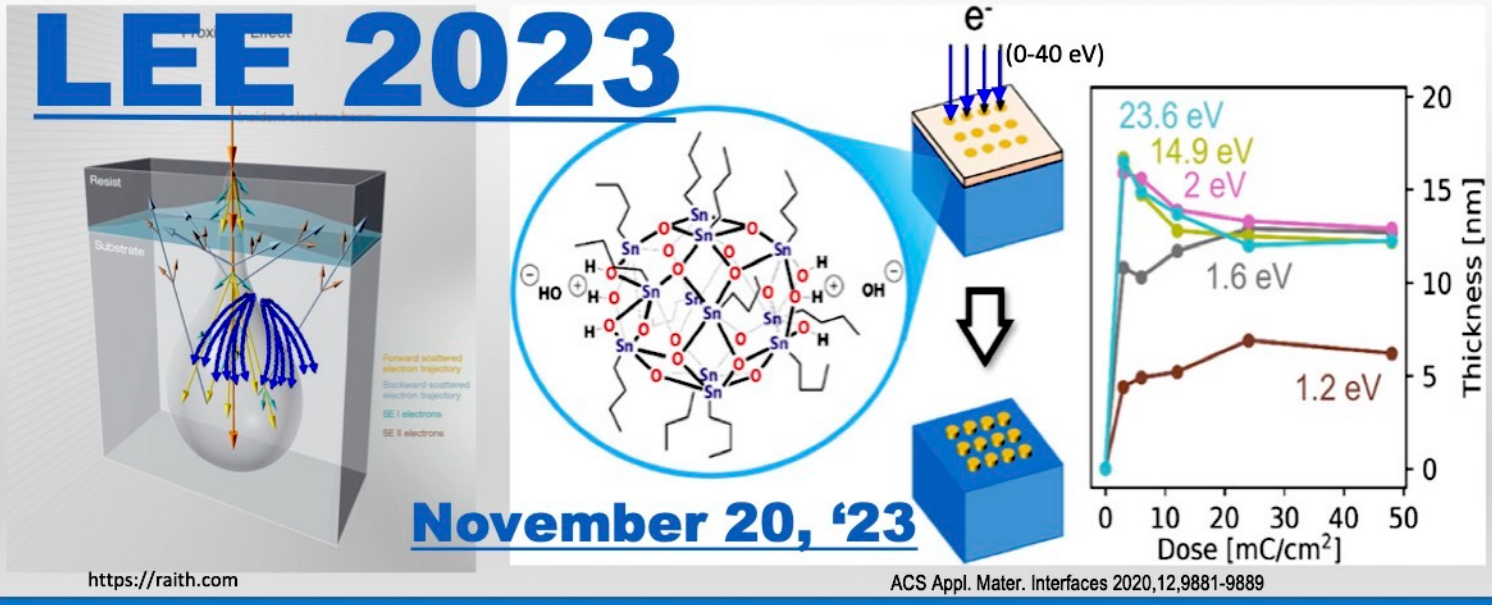

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A brain storming meeting on relevance of Low-Energy Electrons in nanolithography, electron-microscopy and adjacent fields

CNR Istituto di Struttura della Materia

Organized in cooperation with Tor Vergata University by *Stefano Iacobucci & Giovanni Stefani* (ISM-CNR)

TOR VERGATA UNIVERSITÀ DEGLI STUDI DI ROMA

Book of Abstracts

List of Speakers

ROBERTO FALLICA	IMEC (Belgium)		
ODDUR INGOLFSSON	Iceland University (Iceland)	*PETRA SWIDEREK*	Bremen University (Germany)
CHRISTOPHE INGUIMBERT	ONERA (France)	*STEFANO TURCHINI*	CNR-ISM (Roma)
CORNELIS W. HAGEN	Delft University (NL)	*CLAUDIO VERONA*	Tor Vergata University (Roma)
ANDREA NOTARGIACOMO	CNR-IFN (Roma)	*JOHN S. VILLARUBIA*	NIST (US)
SYLVIE RANGAN	Rutgers University (US)	*WOLFGANG WERNER*	Technical University Vienna (Austria)

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Mean free path of electrons in EUV photoresist in the kinetic energy range 20-450 eV

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Abstract

The mean free path (MFP) of electrons is technologically relevant in many applications of lithography. In particular, electrons of kinetic energy below 92 eV are generated during EUV lithography and can travel considerable distance in the photoresist before thermalization. This effect is recognized as the main cause of "resist blur" and resolution loss[(1)]. Moreover, in scanning electron microscopy, secondary and backscattered electrons of energy ≤ 500 eV are emitted from and travel through photoresists films[(2)], causing imaging artifacts that have to be corrected by computational metrology[(3)]. Similarly, the probing depth of photoemission techniques (UPS/XPS) is strongly variable due to the energy-dependent emission of photoelectrons. All these applications rely on the knowledge of MFP. Models exist[(4)] and predict a "universal MFP curve" for elemental solids[(5)] at high kinetic energy (> 1keV); but these models fail at lower kinetic energy, especially in the solid state.

In this study, we measured the MFP of electrons of kinetic energy 20–450 eV in a positive-tone polymer photoresist (PHS+tBMA) with and without PAG (triphenylsulfonium) and quencher (trioctylamine) using energy-dependent photoemission spectroscopy of Si *2p* core levels at CNR-IOM beamline BEAR at Elettra synchrotron (Trieste, Italy)[(6),(7)]. Photoresist damage from the beam was minimized using a one-point-per-exposure acquisition strategy. At EUV energy and below, the MFP ranged between 0.85 nm and 2.5 nm, regardless of PAG/quencher content. At energy above EUV, the MFP increased up to 4 ± 2 nm. Results are discussed and compared with previous studies[(5),(8),(9)].

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Nebula, a simulation tool for electron beam imaging and lithography

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Abstract

In Delft we develop instrumentation and methods for electron imaging and electron lithography. To interpret images and to understand the fundamentals of resist-based lithography one has to understand the physics of electron-matter interaction. To that end, we spent over a decade to develop a Monte Carlo simulator for the interaction of electrons and matter, based on the best possible physics models. It is our intention to simulate properties, such as electron yields, energy distributions, angular distributions, etc., which are as close as possible to experimental measurements, without the need for scaling factors. I will briefly discuss the physics models in the simulator, and present some simulation results in comparison to experimental results. I will also show the sensitivity of the simulation results to certain model parameters, such as the inelastic mean free path and the phonon mean free path. Then I will show one example of how we use our simulator to compare the line edge roughness (LER), as determined from critical dimension SEM's, with the actual sidewall roughness (SWR). It turns out that the LER is heavily biased with respect to the true SWR.
I will also list what is missing in our simulations, part of which will be addressed in a large recently funded program called 'Foundations for electron beam metrology & inspection'. The motivation for this program, in collaboration with industry, and the program description will be briefly touched upon.

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Secondary electron induced secondary and tertiary reactions in FEBID Case studies on $(CH_3)AuP(CH_3)_3$ and $[(CH_3)_2AuCl]_2$ and $CF_3AuCNC(CH_3)_3$

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Abstract

Significant effort has been made in the last decade to design precursor molecules that enable high purity deposits in focused electron beam induced deposition (FEBID). This is not a simple task as inelastically scattered and secondary electrons, produced through interaction of the primary beam with the substrate and the forming deposits, play a significant role in the fragmentation process. Hence, the electrons responsible for the decomposition have a wide energy distribution and may cause dissociation by as different processes as dissociative electron attachment (DEA), dissociative ionization (DI), and neutral and dipolar dissociation through electron excitation (ND and DD, respectively). [1] It is thus important to understand the underlying processes and their extent, and how these influence the deposits, to eventually be able to design high performance precursors.

Here we take a step in this direction and study three different gold precursors with different ligand structures, i.e., $(CH_3)AuP(CH_3)_3$[2], $CF_3AuCNC(CH_3)_3$[3] and $[(CH_3)_2AuCl]_2$[4]. DEA and DI of these precursors is studied in the gas phase under single collision conditions and the appearance energies are determined for individual channels. These are compared to quantum chemical threshold calculations for the m/z ratios observed to aid the assignment of the ions and the neutral counterparts formed in these processes and FEBID depositions are made under UHV to explore how the elementary processes observed in the gas phase are reflected in the composition of the deposits. In this context, the deposition experiments allow for electron-dose-dependent studies of the elemental composition of the deposit while gas phase studies, using controllable, quasi mono-energetic electron beams under single collision conditions, provide information on the electron energy dependence and extent of the individual fragmentation processes.

In the current presentation, the observed fragmentation reactions of the selected gold precursors are discussed in relation to the underlying reactions and potential implications for their suitability as FEBID precursors. Though there are correlations between the gas phase reactions observed, and the composition of the deposits from the respective precursors, it is evident that the initial electron-induced fragmentation reactions are not directly reflected in the deposit's compositions. Rather, we expect these to determine the initial composition of immobilized fragments, while the final composition of the deposit is determined by electron-induced secondary and tertiary reactions caused by further irradiation after immobilization.

Importantly, the consideration of the role of electron induced secondary and tertiary reactions changes the parameter space that needs to be considered in the rational design of FEBID precursors and has consequences for the deposition strategies applied. Specifically, potential precursors need to be designed in such a way that the immobilized fragments from the initial electron-induced dissociation processes are still susceptible to further electron-induced fragmentation, leading to desorption of the respective secondary ligand fragments.

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Secondary Electron Emission in DIELECTRICS Experimental and modelling challenges

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Abstract

The electron emission under the impact of electrons plays a crucial role in various applications. It is both fundamental to the formation of images in scanning electron microscopy and the amplification of the signal (MCP), but also an undesirable phenomenon in many cases, such as satellite charging and discharging, as well as multipactor effects, among others. The characterization and modeling of electron emission remain challenging, especially at very low energies and for dielectric materials. The aim of our contribution is to provide an overview of the development of our measurement and modeling techniques for electron emission and to outline their current limitations. We will conclude by discussing our future directions on the subject.

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Low-energy electrons-assisted deposition from precursors using focused-ion and electron beams for device fabrication

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Abstract

The formation of solid C:Pt structures from gaseous precursors can be induced in vacuum using a deposition process mediated by low energy electrons. C:Pt nanostructures of controlled shape and thickness can be fabricated by using focused electron or ion beams which produce spatially-localized low-energy secondary-electrons in the interaction with the substrate.
The morphology of C:Pt features will be described as well as the capabilities of such kind of structures to act as nanoelectrodes for application in electronic micro devices and as hard masks in reactive ion etching process for micro/nanofabrication.

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Photon- and electron-induced chemistry of resist materials: electronic structure, secondary electron yields and chemical transformations

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Abstract

The ever-decreasing critical dimensions required for future photolithography in the semiconductor industry have imposed significant demands on candidate resist materials, including efficient chemical transformation, absence of phase segregation or limitation of stochastic effects. Satisfying these demands will require a fundamental understanding of all the steps involved during the photon- and electron-induced resist chemical transformation process.

Using a combination of x-ray and UV photoemission spectroscopies, electron energy loss spectroscopy, and ab-initio computational techniques, we have studied the electronic properties of two chemically amplified resist materials as well as their individual components (two polymers and two photoacid generators). Phase segregation is observed, and molecular modeling can be used to understand the pathway for chemical transformation of the resist upon irradiation.

Using a similar approach, the chemical transformation of polymethyl methacrylate films has been characterized and correlated with changes in secondary electron yield and film work function.

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Electron-induced chemistry in Bremen: From fundamentals to astrochemistry and nanofabrication

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Abstract

Chemical reactions induced by electrons contribute to many processes in nature and technology. For instance, electron-molecule collisions are the driving force of plasma generation and play a central role in mass spectrometry. Electron irradiation is an established tool to modify the properties of polymeric materials. Also, low energy electrons released upon impact of ionizing radiation such as hard UV radiation or X-rays make a significant contribution to radiation damage. It is even argued nowadays that such processes can contribute to chemistry occurring in the upper atmosphere and also in space. Electron beams, on the other hand, are not only a common analytical tool in surface science. They drive chemical reactions that modify surfaces, provide them with specific functionalities, and enable state-of-the art nanofabrication technologies.

Our research is concerned with the fundamental chemistry that underlies these phenomena and processes. Specific focus lies on (i) electron-driven molecular synthesis both from a reaction mechanistic point of view and within the context of astrochemistry and (ii) on the electron-induced reactions inherent in nanofabrication by focused electron beam induced deposition (FEBID) and extreme ultraviolet lithography (EUVL). This contribution will provide an overview of our research.

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Low energy electron emission, injection, and charge riequilibrium from plasmonic nanostructures for catalysis applications

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Abstract

Plasmonics encompasses a wide range of phenomena such as nano-antenna electromagnetic hot spots generation, energy transport, electron injection via plasmon dephasing, surface enhanced Raman scattering and photoluminescence, photoconductivity enhancement [1]. Plasmonics is of utmost importance in the field of nanoscience with Localized Surface Plasmon Resonances (LSPRs) directly excited by the light. The tailoring of the plasmonic properties by materials properties and nanostructure shapes provided a wealth of new phenomenology in the last decades. The methods to estimate the efficiency of injecting electrons by light absorption are crucial for photodetectors, photovoltaics and photocatalysis applications.
CeO_2 is a versatile catalytic material with surface acid–base properties, with promising photocatalysis applications. Ultraviolet photoexcitation of CeO_2 leads to the population of 4f Ce, with the formation of oxygen vacancies.
In this communication the system composed by Ag plasmonic nanoparticles embedded in CeO_2 will be presented, enlightening the role of LSPR de-excitation in the injection of electrons from the metal nanoparticles to the Ce 4f levels and in the lifetime of positive charges generated by multiphoton photoemission.
In the first case a direct assessment of the electron injection by plasmon de-excitation was made by Free Electron Laser Ultrafast Transient Absorption in the soft X-ray range probing the population of the Ce $N_{4,5}$ edge [2]. A transient efficiency of about 8% was found.
The lifetime of photogenerated charge was probed by an ultrafast pump and probe photoemission experiment; the role of the plasmons in the photoemission process was clarified by a resonant and non-resonant experiment [3]. The charge riequilibrium time of the system after the resonant pump photoemission process was estimated to be about 300 ps, giving an indication of the overall efficiency in a steady-state process.

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Effect of secondary electrons emission in extreme-UV diamond detectors

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Abstract

Effect of secondary electrons emission on the detection of extreme-UV radiation by diamond detectors was investigated. Two different detector structures were compared: interdigitated contacts and a transverse Schottky diode configuration. Both detectors were measured in the extreme UV spectral region by using He-Ne gas discharge radiation sources and a toroidal grating vacuum monochromator. The contribution of the internal photocurrent and of the photoemission current were analysed and separately evaluated.

The results showed that secondary electron emission, which clearly depends on the experimental conditions (e.g., external electric field, pressure, etc.), is one of the most relevant processes affecting the spectral responsivity in the extreme UV. For interdigitated devices, extreme care must be taken in order to obtain an absolute value of their responsivity, while detectors in the transverse configuration can be shielded in such a way to avoid secondary electron current contribution and therefore provide a more correct and reliable response.

Title:

Problems with low-energy electrons in imaging and lithography

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ABSTRACT

Secondary electron (SE) images from a scanning electron microscope (SEM) are sensitive to surface topography, particularly for samples with steep features like those produced in electronics manufacturing. Metrology, for example assignment of dimensions to nanometer-scale features, requires knowledge of the contrast-producing interaction processes: SE generation, electron diffusion, boundary crossing, etc.[1] Interaction models in wide use agree on mean free paths at energies greater than about 200 eV but disagree by factors of 2 to 5 at energies below 50 eV,[2] unfortunately the very region relevant for SE signals. Since the value of the measurand is assigned by model-based inference from the measured signal, model errors are expected to produce measurement errors.

Dissociative electron attachment (DEA) by electrons with around 5 eV of energy is thought to play a role in exposure of resists.[3,4] These electrons likely originate as SE generated by beam electrons in an e-beam writer or by EUV photo-electrons in photo-lithography. Once generated, the SE slow down as they travel until they reach an energy low enough to render DEA events probable. Their distance from the point of generation represents "electronic blur." If our SE generation and slowing-down models were accurate to the relevant low energies, they might usefully account for such blur.

To validate our models or inform development of new ones, the most useful experimental information would be the differential scattering cross sections. These are difficult to measure directly for electrons with energies in the 10 eV to 50 eV range because mean free paths are in the single-digit nanometers.[5] Samples thick enough to have bulk-like scattering properties are also thick enough that emerging electrons undergo multiple scattering events. Instead of individual events, we could rely upon the composite outcome of multiple events: the yield and energy distribution of emerging electrons as functions of beam energy and angle of incidence. Existing data of this kind have large interlaboratory variation.[6] We are nearing completion of our own measurement apparatus, where we hope to be able to do such measurements with controlled surface cleanliness.

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Understanding low energy electron emission using coincidence spectroscopy

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Abstract

The contribution of coincidence spectroscopy to the understanding of low energy electron emission is reviewed, highlighting the possibility of coincidence spectroscopy to establish a causal relationship between scattering of primary electrons and the ejection of low energy electrons. The basic principle of the technique is briefly explained, i.e. the use of temporal correlation between detected particles to establish the full kinematics of a scattering process. The discussed examples where coincidence spectroscopy proved essential include (1) the fact that energy losses of primary electrons act as sources for secondary electrons; (2) the fact that multiple scattering can be viewed as a Markov-type process; (3) decay of surface and bulk plasmons and their role in secondary electron emission; (4) coherent vs non-coherent multiple plasmon excitation; (5) the role of the inner potential and the size of the SE-escape cone; (5) measurement of the electron affinity in insulators and (6) plasmon-induced symmetry breaking in graphite solving the riddle of the X-peak in graphite after 50 years.