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Small, Minimally Invasive, Direct: Electrons Induce Local Reactions of Adsorbed Functional Molecules on the Nanoscale

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Finely focused electron beams in scanning electron microscopes are routinely used to visualize small nanometer-sized objects. But add chemistry and they can do much more on the nanometer scale! When functional gas molecules are injected into an electron microscope chamber held at a pressure of 10^{-6} mbar or lower, they form adsorbed layers on many substrates. Focused electron beams can interact with these molecular layers, triggering surface reactions that can be used to etch or deposit, or to induce intermolecular reactions between the adsorbed molecules. All of these focused electron beam induced processes (FEBIP) can be performed on almost any kind of substrate. Pioneering work was performed by Matsui, Kunz, and Koops and their co-workers in the 1980s[1] (see also recent reviews[2]). Through the positioning of the electron beam, surface layers can be removed, deposited, or polymerized at nanometer-scale precision with almost any desired three-dimensional (3D) shape (see Figure 1). Definition, placement, and fabrication of the structures are achieved in a single-step process.

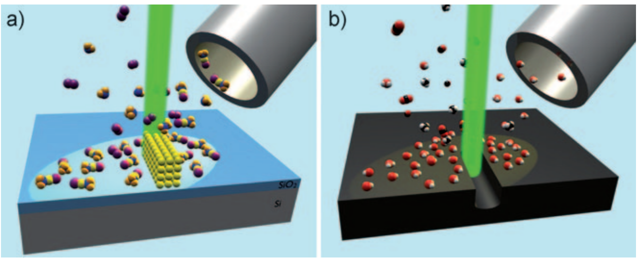

Figure 1. Gas-assisted focused electron beam induced deposition (a, FEBID) and etching (b, FEBIE) in three dimensions using functional molecules injected into the electron microscope. a) Electron-impact dissociation of physisorbed $AuClPF_3$ adsorbates leaves a pure gold deposit while the nonirradiated adsorbates and the volatile dissociation products PF_3 and Cl_2 are removed through the vacuum system. b) Electron-impact dissociation of adsorbed H_2O giving highly reactive species which locally etch carbon by forming volatile products like methane or carbon oxides.

The continuously supplied molecules form a more or less complete monolayer of adsorbed molecules according to the balance of adsorption and desorption, and the molecules are dissociated only upon electron impact. The reaction area is confined to the nanometer-scale primary electron beam (with ≥ 1 keV energy) and the closely emitted secondary electrons (with eV energy) that are created by inelastic collisions of primary electrons with the substrate electrons. In a continuously supplied molecule flux, deposition or etching proceeds co-axially within the beam. A stationary electron beam can either deposit a high-aspect-ratio cylindrical pillar or etch a circular channel, depending on the chemistry involved. When the beam is moved, many different structures can be directly "written"—dot/hole arrays, planar nanowires, pads, and trenches, and freestanding 3D pillars and walls—all extremely useful elements in nanoelectronics, nanomechanics, nanophotonics, and nano(bio)sensors (Figure 2). In contrast, a continuous flow of molecules is not needed when molecules chemisorb onto the surface. Chemisorbed self-assembled monolayers can be cross-linked by electrons, resulting in a polymerized mechanically stable coating that can be removed from the substrate as a free-standing nanomembrane.[3]

The beauty of the broadly applicable FEBIP nanofabrication scheme is that it is minimally invasive: The chemical reaction is confined to the dimensions of the incident focused electron beam and the adsorbate layer.

In the choice of molecules for FEBIP several criteria must be met: 1) high volatility—vapor pressure of around $>10^{-3}$ mbar, 2) little spontaneous thermal desorption to assure good surface coverage, 3) a reasonable electron-impact dissociation cross section, and 4) ideally nontoxic, noncorrosive properties.

Molecules used for local etching of semiconductors, metals, metal oxides, metal nitrides, and polymers are H_2O (see Figure 2c), O_2, H_2, halogens, XeF_2, NOCl, and mixtures thereof.[4] The surface must be etched by the electron-impact dissociation products rather than by the adsorbed molecules themselves. For local deposition, metal halogens (WF_6,

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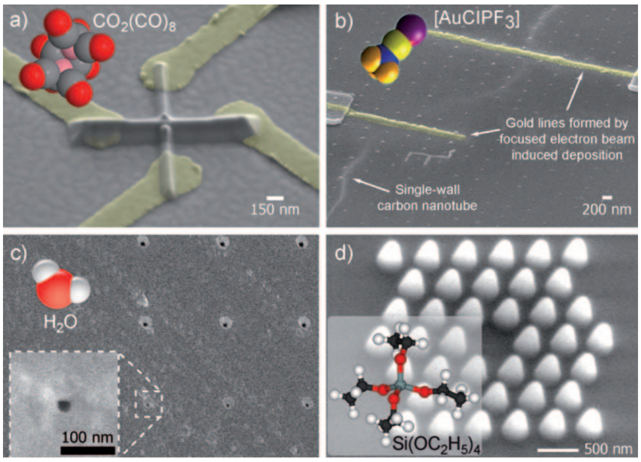

Figure 2. Nanostructures obtained by FEBIP with various molecules. a) Cobalt–carbon nanocomposite from $Co_2(CO)_8$ for sensitive magnetic Hall sensors. b) Pure granular gold deposited from $AuClPF_3$ for nanoelectric contacts. c) An array of holes in a carbon membrane etched with water. d) Dielectric, amorphous array of SiO_xC_y dots deposited from $Si(OC_2H_5)_4$ for photonic crystals.

WCl_6), metal carbonyls (see Figure 2a), orthosilicates (see Figure 2d), (fluorinated) metal acetylacetonates ($Cu(O_2C_5HF_6)_2$), metal cyclopentadienyls ([$Fe(C_5H_5)_2$]), and alkyl metal derivatives ([$(CH_3)_2Au(O_2C_5HF_6)$], [$(CH_3)_3Pt(C_5H_4)(CH_3)$]) are frequently used.

Ideally, the electron impact dissociates the adsorbate such that the nonvolatile metal remains on the substrate while the intact volatile ligands are removed through the vacuum system. However, the electronic excitation of the adsorbate can also dissociate intraligand bonds rather than the metal–ligand bond alone. This can result in co-deposition of nonvolatile, nonmetallic reaction products. Additionally, water and hydrocarbons that constitute the residual gases in the high vacuum (ca. 10^{-6} mbar) of the electron microscope still impinge on the surface at a rate of roughly one monolayer per second and can result in the unwanted co-deposition of carbon, oxygen, and hydrogen. Thus the resulting metal deposit is dispersed as nanocrystals in a carbonaceous matrix, with a metal content typically as low as 10–30 atom %. It is the major aim of current fundamental FEBIP research to increase this metal content, and the problem of carbonaceous co-deposition has been addressed by chemical and physical approaches.

The chemist's approach is to synthesize carbon-free molecules to avoid the co-deposition from the molecule itself. This functions very well for [$AuClPF_3$] (see Figures 1a and 2b), where a pure metal deposit (> 95 atom %) was obtained under high-vacuum conditions.[5] However, similar experiments with [$Ni(PF_3)_4$], [$Pt(PF_3)_4$], [$Rh_2Cl_2(PF_3)_4$], and [$Ir_2Cl_2(PF_3)_4$] generated relatively large phosphorus co-deposits. But why discard the wealth of organometallic chemistry if a second gas molecule could be co-injected and reacted to volatile carbon compounds upon electron irradiation as in Figures 1b and 2c? The balance of carbon co-deposition and etching would control the final metal-to-carbon ratio in the deposit. Studies showed that the concept has potential: Oxygen co-injection with organometallic molecules like $Si(OC_2H_5)_4$, $Si(OCH_3)_4$, $Si(CH_3)_4$, $Si(NCO)_4$ was shown to result in the deposition of pure, UV-transparent SiO_2.[6] H_2O, O_2, and XeF_2 etch carbon efficiently but also readily oxidize or fluorinate metals under electron impact. This is sometimes unwanted. Further studies will be needed to verify whether these two chemical concepts can really yield pure material for a large variety of metals and compounds.

The physicist's approach is to use ultrahigh-vacuum (UHV) electron microscopes. At a pressure of 10^{-10} mbar the impingement rates of residual water and hydrocarbons are less than 0.3 monolayers per hour—four orders of magnitude less than in conventional electron microscopes! Not surprisingly, the hydride Si_2H_6 and halide WF_6 gave the purest deposits under these UHV conditions.[7] However, also a carbon-containing molecule, $Fe(CO)_5$, resulted in pure iron deposits (better than 95 atom %)![8]

At this point the chemist's and physicist's approaches merge to one question: Why do [$AuClPF_3$] and $Fe(CO)_5$ molecules result in pure metal deposits upon electron irradiation? Or, in other words, why do the ligands desorb in intact form? Why were they not dissociated as well by electron impact to leave nonvolatile phosphorus or carbon as a deposit? It seems that a specific effect known as autocatalysis can explain these observations. The dissociation of metal–ligand bonds is autocatalytic if the reaction product, the clean deposited metal, is itself the catalyst for that dissociation. As a consequence, the continuously supplied adsorbate molecules can be dissociated to pure metal without electron irradiation. Indeed, such a process is known to occur near room temperature for both molecules. Now, when the ligand–metal bonds are dissociated by autocatalysis, the ligands could desorb before being further dissociated by electron impact to form a co-deposit. Evidently, the metal content of the initial stage of electron-impact deposition will determine how dominant autocatalysis can become for the entire deposition process and the purity of the final deposit.

In their article in *Angewandte Chemie* Issue 27, Marbach et al.[9] go one step further and exploit autocatalysis as a nanoxerography technique by separating electron exposure from molecule injection. The focused electron beam assumes the role of an "invisible" ink pencil which writes a pattern onto a 300 nm SiO_2 layer on silicon substrate under UHV conditions. After electron exposure, the molecule $Fe(CO)_5$ is injected and dissociates on the pre-irradiated surface. Further autocatalytic iron growth renders the "ink" pattern visible.

So far nano-xerography has been used to align nanoparticles from liquid or gas phases through the electrostatic fields caused by the implanted electrical charges. The novelty pursued in Marbach's group is that volatile molecules were supplied, which adsorb all over the substrate but selectively dissociate to pure metal only at irradiated areas while at the nonirradiated surface the molecules remain intact and finally desorb. They fabricated compact, small-width line structures of pure iron thus demonstrating a new means of nanoprototyping of pure materials. It is also a further proof that pure material can be deposited from molecules containing nonvolatile elements in their ligands.

Presently, the nature of the initial dissociation of molecules on the pre-irradiated surface still remains unclear. Is this “activation” a result of electrostatics or dangling SiO_x bonds? Understanding the mechanism would also indicate whether this approach with separate irradiation and autocatalysis steps can be extended to other surfaces or vacuum conditions. Although this work identifies autocatalysis to be an important mechanism for the deposition of pure material by electron impact, there might be a limit to the variety of molecules that can be used for this approach. Also with respect to the long process time it might then be interesting to search for the “golden mean” between autocatalysis and electron-impact dissociation: The fundamental issue to be solved is to tune the timescale of successive electron impacts and impinging molecules to the timescale of desorption of intact ligands.

What lies ahead? We have seen that physics and chemistry lead to a deeper understanding of the mechanisms that play a pivotal role in the electron-impact dissociation of adsorbates and the purity of materials deposited. Co-injection, novel functional molecules, characteristic timescales, and defined vacuum conditions—these concepts will finally lead in the near future to optimum electron-impact reactions resulting in materials with controlled purity deposited at the nanometer scale. Furthermore, FEBIP offers, when combined with co-injection of two gases, an outstanding possibility to disperse metal nanocrystals with controlled amount and size distribution in dielectric matrices (for example silicon dioxide or carbon polymers); composites with properties superior to those of the pure material, or laterally confined multilayer structures, like stacked nanowires, with tailored physical properties can be envisioned. In conclusion, local electron-induced reactions (and also similar local ion-induced reactions) in adsorbates could very soon evolve to a veritable platform (also in combination with focused ion beams) for flexible, minimally invasive, and direct nano-prototyping with respect to material, shape, and substrates—without exorbitant investments in clean-rooms; throughput issues are already being addressed by successful developments of multiple-beam systems.

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