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Fabrication of layered nanostructures by successive electron beam induced deposition with two precursors: protective capping of metallic iron structures

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Abstract
We report on the stepwise generation of layered nanostructures via electron beam induced deposition (EBID) using organometallic precursor molecules in ultra-high vacuum (UHV). In a first step a metallic iron line structure was produced using iron pentacarbonyl; in a second step this nanostructure was then locally capped with a 2–3 nm thin titanium oxide-containing film fabricated from titanium tetraisopropoxide. The chemical composition of the deposited layers was analyzed by spatially resolved Auger electron spectroscopy. With spatially resolved x-ray absorption spectroscopy at the Fe L\textsubscript{3} edge, it was demonstrated that the thin capping layer prevents the iron structure from oxidation upon exposure to air.

(Some figures may appear in color only in the online journal)

1. Introduction
The controlled fabrication of nanostructures with arbitrary shapes and defined chemical composition is still one of the main challenges in nanoscience and nanotechnology. One promising approach is electron beam induced deposition (EBID), which is a mask-less, direct-write technique for the generation of nanostructures with arbitrary shapes at predefined positions on a surface \cite{1–4}. In EBID, adsorbed precursor molecules are decomposed into volatile and non-volatile fragments by the bombardment of electrons. Ideally, the volatile components and unexposed, intact precursor molecules desorb from the surface and are pumped off the vacuum chamber while the non-volatile fragments stay on the surface and locally form the intended deposit. A highly focused electron beam from a scanning electron microscope (SEM) or transmission electron microscope (TEM) allows for the fabrication of structures on the nanometer
scale on the surface of solids and even below 1 nm on ultra-thin samples [5]. A schematic representation of the EBID process is outlined in figures 1(a)–(c). By choosing suitable precursor molecules, deposits can be generated consisting of either metals [5–12], metal oxides [6, 13–16] or carbonaceous species [17]. In the last decade, various applications have been developed which are, e.g., reviewed in an article by Utke et al. [2]. The applications range from the fabrication of functionalized tips for scanning probe microscopy, conducting wires, electron sources, micro-Hall devices, nano-optic patterns, photonic crystals and diodes to the fabrication of seeds for the growth of carbon nanotubes. Moreover, EBID was recently established as the state-of-the-art mask repair tool in the semiconductor industry [18, 19].

Until recently, the vast majority of EBID experiments were performed in high vacuum (HV) instruments at pressures in the range of $10^{-6}$ mbar. Using organometallic precursors, typically rather low metal contents between 15 and 60% are observed in the resulting films [6, 7, 9–12], with carbon and oxygen as the main contaminants. Carbon originates from the decomposition of either organic ligands of the precursor or hydrocarbons from the residual gas of the HV chamber. By using a ‘surface science’ approach to EBID, i.e., performing the experiments under ultra-high vacuum (UHV) conditions at pressures in the range of $\sim 10^{-10}$ mbar on well-defined samples, we were recently able to demonstrate that these high contamination levels can be overcome [20–22].

With iron pentacarbonyl (Fe(CO)$_5$) we succeeded in fabricating extremely clean iron nanostructures: on Si(100) and SiO$_2$(300 nm)/Si(100) samples the Fe content was higher than 95% [20, 22], and on the catalytically active Rh(110) surface a purity of at least 88% was obtained [21]. In these studies, catalytic effects were found to contribute to the deposition of iron. In particular, the autocatalytic decomposition of Fe(CO)$_5$ on pre-deposited iron was observed already at room temperature. As a consequence, the EBID structures continue to grow after electron irradiation as long as the precursor gas is supplied (see figures 1(d)–(f)).

The metal alkoxide precursor titanium tetraisopropoxide (Ti(O’Pr)$_4$, TTIP) is a promising candidate to produce titanium oxide nanostructures. While TTIP is a well-known precursor in chemical vapor deposition (CVD) for the direct generation of titanium dioxide films [23, 24] and particles [25, 26], the use of it in EBID is rare [13–15]. Hoffmann et al demonstrated the fabrication of high refractive index materials for photonic bandgap structures [13] and Mitchell and Hu reported on the generation of $\mu$m-scaled, titanium and oxygen-containing area deposits on gallium arsenide [14, 15]. In a previous study we found that with TTIP, even when applied under UHV conditions, the deposits contained significant amounts of carbon, besides the targeted materials titanium and oxygen [16]. The carbon contamination was traced back to the carbon-containing precursor itself. In order to enable the localized fabrication of very clean titanium oxide nanocrystals, we developed a two-step post-treatment process after EBID with TTIP (see [16]).

Recently, Bernau et al presented the possibility of tailoring the chemical composition of deposits by simultaneously dosing CO$_2$(CO)$_5$ and hydrocarbons from the residual gas, and by using certain electron irradiation strategies [27]. Herein, we expand the EBID technique, which usually applies only one precursor, to the successive usage of two different, dedicated precursors to locally engineer laterally well-defined layered nanostructures. In particular, we demonstrate the local capping of iron nanostructures with an ultra-thin titanium oxide layer. A schematic drawing of the process is given in figure 2. The idea is that the capping layer protects the underlying metallic structure from oxidation, even under ambient conditions. This would be highly desirable, since after fabrication in UHV a sample transfer with exposure to ambient conditions is often inevitable. Thereby, oxygen and water can lead to oxidation of the nanostructures, which can hamper or destroy their targeted magnetic or electronic functionalities. In addition, the presence of hydrocarbons and carbon-containing molecules (CO, CO$_2$) can result in surface contamination. Our results show that the local EBID capping approach indeed works and presents a way to effectively prevent surface oxidation.

The idea of capping structures with protective layers, in order to improve their stability, to avoid oxidation, contamination and permeation, and to extend their lifetime in applications, is also widely spread in other fields of science. One example is extreme ultra-violet lithography (EUVL) [28–31] where so-called ‘multilayer mirrors’, consisting of 40–60 repeats of a double layer of typically Mo (2.8 nm) and Si (4.2 nm), are protected by a top-most capping layer [29]. Initially having started with ruthenium as one of the first capping layer materials [30, 31], recently Bajt et al found rhodium, titanita (TiO$_2$) and zirconia (ZrO$_2$) to be other promising candidates [29]. From a more general point of view,
Figure 2. Schematic sketch of local capping of EBID structures. (a) Basic substrate material, in our case, e.g., SiO$_2$ (300 nm) on Si. (b) Iron nanostructure deposited on the sample by EBID with Fe(CO)$_5$. (c) Titanium oxide capped iron nanostructure by EBID with TTIP.

by combining the deposition of conducting, semiconducting and insulating materials on the nanoscale the assembly of functional components in nanoelectronic applications might be feasible.

2. Experimental details

The EBID experiments were performed in a UHV instrument (Multiscanlab, Omicron Nanotechnology) with a base pressure of $<2 \times 10^{-10}$ mbar. A UHV-compatible electron column (Leo Gemini) and a hemispherical electron energy analyzer enable SEM and spatially resolved Auger electron spectroscopy (AES) with lateral resolutions better than 3 nm and 10 nm, respectively. For EBID the electron beam ($U_B = 15$ kV, $I_B = 400$ pA) was controlled via the SEM software (SmartSEM, Zeiss) and waveform generators (Hewlett-Packard, model: HP 33120A). Fe(CO)$_5$ (Acros Organics, purity 99.5%) and TTIP (Alfa Aesar, purity 99.995% metals basis; storage device heated to 413 K) were dosed through a 3 mm nozzle at a distance of 12 mm to the sample surface. The gas flow was controlled via the background pressure in the chamber and was adjusted to $3 \times 10^{-7}$ mbar (uncorrected) for all experiments. Based on simulations with the software GIS Simulator (version 1.5) [32] we estimated the local pressure on the sample surface to be $\approx 9 \times 10^{-6}$ mbar for the experiments with Fe(CO)$_5$ and $\approx 8 \times 10^{-6}$ mbar with TTIP. This corresponds to a factor of $\approx 30$ for Fe(CO)$_5$ and $\approx 27$ for TTIP compared to the adjusted background pressure of $3 \times 10^{-7}$ mbar.

The experiments were performed on two different samples. Sample I was an industrial 300 nm SiO$_2$ on Si(100) sample (CrysTec GmbH, thermal oxide, p-type, $\rho = 1\text{–}20$ $\Omega$ cm), which was freed from its organic protective coating (Ilmar P4) by sonicating it in acetone, isopropanol and distilled water for $5\text{ min}$, respectively. Sample II was a GaAs/AlAs multilayer mirror with a layer of Co ($\approx 1.5$ nm) and a capping layer of Al$_2$O$_3$ ($\approx 1$ nm). This special sample setup was also used for x-ray standing wave photoemission [33, 34]. We note that the underlying layers did not influence the x-ray absorption measurements, which were solely aimed at investigating the Fe structures. Neither substrate was further cleaned or annealed after it was introduced into UHV and before fabrication of the Fe lines.

The characterization via SEM and AES was performed in situ in the timeframe of days after the EBID experiments. All SEM images were acquired with the software SmartSEM (Zeiss) and are depicted with minor brightness and contrast adjustments in order to enhance visibility. The gray scale line profile (figure 3(d)) was taken and processed via the software WSXM [35]. For chemical characterization, spatially resolved Auger electron spectroscopy was performed using a beam energy of 15 keV and a beam current of 3 nA, with the sample tilted to $\approx 25^\circ$. The spectra were recorded using the software EIS/ISEM (Omicron) and processed via Igor Pro (WaveMetrics). We used a modified scan strategy, in which a defined small area (‘scan window’) is repeatedly scanned instead of irradiating one spot on the surface. This scan strategy has two advantages: first, it allows tracking of the position from which the spectroscopic information originates in situ; second, the electron irradiation (i.e. the total charge) is distributed over the whole ‘scan window’, which lowers the local electron dose. Thus, electron induced effects like electron stimulated desorption (ESD) or electron beam induced heating (EBIH) are reduced. In this work, the ‘scan window’ had a size of $200 \times 200$ nm$^2$; only for spectrum number ii (taken on a narrow iron line before the capping experiment (see figure 3(f))) it was set to $18 \times 18$ nm$^2$.

The characterization of the EBID deposits via atomic force microscopy (AFM) was carried out with an easyScan DFM system (Nanosurf AG, Switzerland) at ambient conditions in the dynamic force mode (vibration amplitude set to 50–60% of the free, undamped amplitude). The instrument is equipped with a ‘large scan head’ providing a maximum XY scan range of 110 $\mu$m, a maximum Z range of 22 $\mu$m and scan step resolutions of 1.7 nm in XY and 0.34 nm in Z direction. Silicon cantilevers (type PPP-NCLR-50) were used with a resonance frequency range from 146 to 236 kHz and a force constant range from 21 to 98 N m$^{-1}$.

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The capping layer thickness was determined by the modified straight-line approximation model using equations 2, 13 and 15 of Cumpson and Seah [36]. The relevant substrate intensities (peak areas) of the Si KLL Auger signal at 1605 eV and the Fe LMM Auger signal at 645 eV were determined via linear background subtraction. As reference intensity ($I_{B}^*$ in equation 2 of [36]) the Si signal of the silicon oxide surface (before the EBID experiments) and the Fe signal acquired on a thick, large EBID line deposit (with complete substrate signal damping) were deduced. The inelastic mean free path in the deposited capping layer ($\lambda_{\text{target}}^A (E_B)$ in equation 2 of [36]) was approximated with the attenuation length in a material with the same chemical composition, i.e., $\approx 13$ at.%;
carbon, \(\approx 31\) at.\% titanium and \(\approx 56\) at.\% oxygen as estimated from AES analysis. Using equations 13 and 15 of [36] and calculating with an averaged atomic mass per mol (25.4 g), an averaged density for titanium dioxide (from rutile, brookite and anatase, \(\rho \approx 4070\) kg m\(^{-3}\)) and an averaged atomic number (\(Z = 12.1\)), attenuation lengths of \(\approx 2.5\) nm at 1605 eV (for Si Auger electrons) and \(\approx 1.2\) nm at 645 eV (for Fe Auger electrons) were deduced.

Spatially resolved x-ray absorption spectroscopy and photoelectron emission microscopy (X-PEEM) on sample II were carried out using the Elmitec PEEM, permanently installed at the microfocus undulator beamline UE49-PGM at the synchrotron radiation facility BESSY II (Helmholtz-Zentrum Berlin). The x-rays impinge on the surface at grazing incidence and photoelectrons are collected normal to the sample surface. The PEEM image shown was taken using the secondary electron yield, which then also permits derivation of spatially resolved x-ray absorption spectra by scanning the photon energy over the Fe L-edge region. For more details on the experimental setup see [37].

3. Results and discussion

In figure 3 the results of a capping experiment performed on sample I are presented. In the first EBID experiment a 45 \(\mu\)m long iron line was deposited using Fe(CO)\(_5\), with a line dose of \(1.9 \mu\)C cm\(^{-1}\) (56 s total exposure time, 70,000 sweeps, 300 \(\mu\)s active line duration, 500 \(\mu\)s waiting time per line). After the EBID step the precursor gas was dosed for an additional 2 h and 30 min so that the line could grow autocatalytically (compare figures 1(d)–(f)). Figure 3(a) shows an SEM image of the Fe line, illustrating its continuous character, and figure 3(b) shows a higher magnification, demonstrating its polycrystalline structure. The width of the line is \(83 \pm 5\) nm and the height is 17–24 nm, as determined...
from \textit{ex situ} AFM measurements. The small particles in the area surrounding the line are iron clusters grown as a consequence of the backscattered electron (BSE) proximity effect in EBID [9, 18, 38]. In this effect, multiply scattered primary electrons can eventually exit the surface again away from the original point of irradiation, resulting in electron induced decomposition of adsorbed precursor molecules.

In the second EBID step, TTIP was used to fabricate a thin capping layer on top of the iron line. For this capping process a rectangular area (32.0 \(\mu m \times 2.5 \mu m\)) was irradiated with an area dose of 0.67 C cm\(^{-2}\) and a total exposure time of 30 min (10'000 frames, 134 ms active frame duration, 46 ms waiting time per frame). The result of this experiment is depicted in figure 3(c), showing the previously fabricated iron line in the center, appearing still bright in SEM, and the covering titanium oxide layer, appearing dark. To illustrate the borders of the capping layer a ‘gray scale line profile’ was extracted and is shown in figure 3(d). It shows good agreement between the width of the irradiated area (2.5 \(\mu m\)) and the obtained deposit width (\(\approx 2.7 \mu m\)). Figure 3(e) depicts an SEM overview image, which shows the whole capping area covering the lower part of the iron line including the large halo around the Fe line starting point. This feature (bright circular area deposit in the lower part of figure 3(e)) is due to a waiting time of the electron beam after each sweep, which leads to the circular deposit at this position due to proximity effects [9, 18, 38]. The same applies to the capping area. Here, the electron beam dwells in the top right corner after each frame, which results in a large deposit, visible as a white spot and its circular surrounding in the upper part of figure 3(e).

The chemical composition of the surface and of the EBID deposits was studied by AES (see figure 3(f)). The red spectrum (i) was acquired on sample I before the EBID experiments. The C KLL signal at 267 eV shows a minor carbon contamination, which can be attributed to residues of the initial protective coating. The large peaks at 484 and 504 eV are due to the substrate oxygen KLL signals. On an iron line fabricated with similar parameters to the one depicted in figures 3(a) and (b) the blue spectrum (ii) was measured before the capping experiment. This line had a diameter of 103 \(\pm 4 \mu m\) (determined by SEM) and a height of 26–33 nm (determined by AFM). The AE spectrum is clearly dominated by the Fe LMM Auger signals at 588, 595, 645 and 700 eV. In addition, it shows a small carbon signal, clearly visible oxygen substrate signals at 485 and 505 eV and a silicon substrate signal at 1605 eV (not depicted). Considering the thickness of \(\approx 30 \text{ nm}\) of the iron line structure the signals of the underlying substrate should be completely damped. Therefore, the corresponding carbon, oxygen and silicon signals probably derive from substrate Auger electrons in close lateral proximity to the original line excited by backscattered high energy electrons [39–41].

The capping layer was characterized by Auger spectra acquired at two different positions. One was taken from an area covering the silicon oxide substrate surface (iii; see green dot marker in figure 3(e)), the other one on an area covering the halo of the iron line starting point (iv; see green star-shaped marker). Both spectra in figure 3(f) (iii and iv) are dominated by the titanium LMM (381 and 418 eV) and oxygen KLL (491 and 511 eV) signals along with a small carbon contamination. The dominating Ti and O signals verify the effective deposition of titanium and oxygen with the precursor TTIP. Note that both oxygen signals in these spectra appear at 6–7 eV higher kinetic energy than the corresponding SiO\(_x\) substrate signals, which indicates the different chemical nature of the oxygen in the capping layer. A comparison of the spectra (iii and iv) with spectra measured on a TiO\(_2\)(110) single crystal shows a very similar appearance. In particular, the shape of the Ti LMV peak indicates oxidation states of +III and +IV in the capping layer, i.e., the presence of titanium oxide species. Furthermore, both spectra (iii and iv) show damped Auger signals of the material below the capping layer, i.e., a silicon signal for spectrum iii (not depicted) and three iron signals for spectrum iv. This allows us to estimate the layer thickness of the capping layer by the modified straight-line approximation model [36] (for details see section 2).

The estimated thicknesses of the capping layer covering the iron structure and the one covering the SiO\(_x\) substrate were 2.4 \(\pm 0.3\) and 3.2 \(\pm 0.3\) nm, respectively. The different thicknesses can be explained by the substrate dependence of the adsorption and diffusion properties of TTIP. AFM measurements performed on the capped line depicted in figure 3 yield a thickness of 2–3 nm, in good agreement with the estimation based on the Auger data. Thus, we demonstrated that we are able to produce a line structure and cover it with a continuous capping layer consisting of titanium, oxygen and carbon in a two-step EBID process using two different precursors.

To study whether the capping layer indeed protects the nanostructures against oxidation upon exposure to air the following experiment was performed on sample II. Again, iron lines were fabricated via EBID with Fe(CO)\(_5\) and one of them was capped with a thin titanium oxide layer by EBID with TTIP, using identical parameters to those on sample I. For the chemical analysis with X-PEEM iron lines were deposited on sample II with an increased width of between 1 and 2 \(\mu m\); local AES revealed a high purity of 87 \(\pm 3\%\) iron, with 9 \(\pm 3\%\) carbon and 4 \(\pm 3\%\) oxygen. After the capping step, the sample was exposed to ambient conditions for three days before it was introduced to the X-PEEM chamber.

The PEEM image in figure 4(a) shows three different contrasts. The black parts at the lower left and the upper right stem from the alumina substrate. The gray regions are due to the titanium oxide capping layer and the light gray regions are related to the buried iron line. The wider line in the lower part of the image is due to the fact that here also the starting point of the writing process of the iron line is imaged, which is broadened due to the larger applied electron dose. In figure 4(b) spatially resolved x-ray absorption spectra at the Fe L\(_3\) edge of a capped and an uncapped iron line on sample II are depicted. The spectrum of the capped line structure shows the typical line shape of metallic iron at the L\(_3\) edge, strongly suggesting a pure and unoxidized iron structure under the titanium oxide capping layer [42]. The spectrum of the uncapped iron line structure, on the other hand, shows an altered peak shape. The main peak is shifted toward higher photon energies (by \(\approx 1.2\) eV) and only a shoulder
resides at the peak position of the metallic iron line, which is typical for the formation of iron oxide [42]. This oxide formation is indeed expected for the uncoated iron deposits after exposure to air. While the peak shape is comparable to that of Fe$_3$O$_4$ [42], contributions from other Fe oxidation states cannot be ruled out from the observed line shape. In summary, the analysis of the x-ray absorption spectra, with the characteristic metallic and oxidic line shapes for the capped and uncapped regions, respectively, clearly demonstrates that the concept of the capping procedure was indeed effective, since oxidation of the capped iron structure was prevented.

4. Conclusions

We have demonstrated the fabrication of layered nanostructures by electron beam induced deposition (EBID) in ultra-high vacuum (UHV). EBID was performed in two successive steps using two different precursors. In the presented example, iron nanostructures, deposited in the first EBID experiment, were locally capped with an ≈2–3 nm thin titanium oxide layer. By local x-ray absorption spectroscopy at the Fe L$_3$ edge after exposure of the sample to air we could demonstrate that the thin titanium oxide capping layer effectively prevented oxidation of the metallic iron structure. The stepwise application of two precursors in EBID represents an important expansion to previous works in the field and opens up a novel pathway to tailor the fabrication of nanostructures. From a more general point of view, by combining the deposition of conducting, semiconducting and insulating materials on the nanoscale the assembly of functional components in nanoelectronic applications might be feasible.

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