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I Introduction

Various applications of metal nanostructures such as advanced scanning probes, ^{1,2} photolithography masks, ² and Hall sensors^{3,4} require fabrication of nanoscale objects with well-defined composition and orientation. One promising technique for producing such structures is focused electron beam induced deposition (FEBID), in which a focused electron beam impinges onto a

Electron induced surface reactions of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$, a potential heterobimetallic precursor for focused electron beam induced deposition (FEBID)⁺

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Electron-induced surface reactions of $(\eta^5-C_5H_5)$ Fe(CO)₂Mn(CO)₅ were explored *in situ* under ultra-high vacuum conditions using X-ray photoelectron spectroscopy and mass spectrometry. The initial step involves electron-stimulated decomposition of adsorbed $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ molecules, accompanied by the desorption of an average of five CO ligands. A comparison with recent gas phase studies suggests that this precursor decomposition step occurs by a dissociative ionization (DI) process. Further electron irradiation decomposes the residual CO groups and (η^5 -C₅H₅, Cp) ligand, in the absence of any ligand desorption. The decomposition of CO ligands leads to Mn oxidation, while electron stimulated Cp decomposition causes all of the associated carbon atoms to be retained in the deposit. The lack of any Fe oxidation is ascribed to either the presence of a protective carbonaceous matrix around the Fe atoms created by the decomposition of the Cp ligand, or to desorption of both CO ligands bound to Fe in the initial decomposition step. The selective oxidation of Mn in the absence of any Fe oxidation suggests that the fate of metal atoms in mixed-metal precursors for focused electron beam induced deposition (FEBID) will be sensitive to the nature and number of ligands in the immediate coordination sphere. In related studies, the composition of deposits created from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ under steady state deposition conditions, representative of those used to create nanostructures in electron microscopes, were measured and found to be qualitatively consistent with predictions from the UHV surface science studies.

> surface that is continuously exposed to a gas stream of organometallic precursor molecules in a vacuum environment.^{5–8} Physisorbed precursor molecules are decomposed by electrons resulting in formation of volatile fragments, which desorb into the gas phase, and non-volatile fragments, which form the deposit.

> FEBID enjoys a number of advantages as a nanofabrication strategy. For example, when compared to other nanoscale deposition techniques such as extreme ultraviolet lithography (EUVL), electron beam lithography (EBL) and focused ion beam induced deposition (FIBID), FEBID produces the smallest reported features (0.7 nm diameter nanodots) without damaging the substrate.^{9–13} In contrast to EBL and EUVL, FEBID does not require a resist layer or etching step for nanostructure fabrication and geometrically well-defined two- and three-dimensional metallic nanostructures can be obtained by manipulation of the electron beam.^{14–16} For these reasons, FEBID has been successfully utilized to fabricate nanostructures for a variety of advanced nanoscale applications including repair of gate contacts, photolithography and EUVL masks,^{2,17–20} selective functionalization of customized nanostructures,²¹ and fabrication and modification

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 $[\]dagger$ Electronic supplementary information (ESI) available: Fig. S1 shows the effect of X-ray irradiation alone on a nanoscale thick film of $(\eta^5\text{-}C_5H_5)\text{Fe}(CO)_2\text{Mn}(CO)_5$ as measured by XPS; Fig. S2 shows the effect of a partial pressure of water on $(\eta^5\text{-}C_5H_5)\text{Fe}(CO)_2\text{Mn}(CO)_5$ films in the presence and absence of electron irradiation. See DOI: 10.1039/c7cp07994j

of nanodevices such as ultra-small Hall sensors $^{\rm 3,4}$ and nanologic devices. $^{\rm 22}$

Although FEBID is a promising deposition technique for fabricating self-supporting nanostructures, there are still technical challenges that limit its larger scale use as a nanofabrication tool. One of the most critical problems with FEBID of metallic nanostructures is low metal content resulting from unacceptable levels of contamination (especially carbon and oxygen impurities) derived principally from ligands in the precursor.^{6,7} For many applications, these impurities will interfere with device performances due to suboptimal conductive and magnetic properties of the deposited material.⁶ To increase metal content in FEBID nanostructures, tailored precursors whose designs are based on an understanding of mechanistic processes are required.²³

Gaining mechanistic details from in situ FEBID studies under the steady state deposition conditions that prevail during device fabrication in electron microscopes is challenging due to simultaneous occurrence of precursor adsorption/desorption, electron-stimulated dissociation of the precursors and desorption of volatile products. In addition, residual gas molecules such as water and hydrocarbons in the vacuum chambers may affect the results. To address these challenges, ultrahigh vacuum (UHV) surface science studies have recently been used to study electron interactions with adsorbed FEBID precursors.²³⁻³¹ Our approach to these UHV experiments is to adsorb a thin precursor film (1 to 2 monolayers) onto cold (typically \approx 150 K), chemically inert substrates and then expose the film to varying doses of 500 eV electrons. X-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS) are used to monitor surface and gas phase species simultaneously.^{27,29} The combination of a fixed initial coverage of precursor molecules and low background pressure simplifies analysis of the results, allowing elucidation of the sequence of elementary bond breaking steps and reactions relevant to FEBID. Furthermore, although the primary electron energy (500 eV) is lower than that used in FEBID (typically > 5 keV),^{6,7} the secondary electron energy distribution is very similar.32,33

Our previous UHV surface science studies are consistent with two distinct mechanistic steps during electron irradiation of organometallic compounds.^{23,26,28-30,34,35} First, precursor dissociation occurs as a result of interactions of the secondary electrons generated by the primary beam with the substrate. This step is typically accompanied by desorption of some of the ligands, leading to a surface-bound intermediate. Further electron irradiation decomposes the remaining ligands; this is the principal cause of the contamination observed in FEBID. For example, in the case of the FEBID precursor Pt(PF₃)₄, electronstimulated reactions initially led to the desorption of one of the PF₃ ligands, forming a surface bound Pt(PF₃)₃ intermediate.²⁶ Subsequent electron-stimulated reactions, however, decompose the remaining three PF₃ ligands, causing desorption of fluoride anions and the formation of a Pt deposit contaminated with phosphorus.26

Nanostructures containing a single metal have been fabricated by FEBID from various precursors such as WF_6 ,³⁶ MeCpPtMe₃,³⁷ Me₂Au(tfac),³⁸ Me₂Au(acac),³⁹ Co₂(CO)₈,^{40,41} and Fe(CO)₅.⁴²

By using a mixture of different precursors including Fe(CO)₅/ MeCpPtMe₃ (Fe-Pt),⁴³ MeCpPtMe₃/Co₂(CO)₈ (Pt-Co)⁴⁴ and MeCpPtMe₃/Si(SiH₃)₄ (Pt-Si)⁴⁵ FEBID has been extended to produce mixed (alloy) metallic nanostructures with tunable magnetic and conductive properties.⁴⁴ However, variation in gas phase transport and electron-stimulated reactivity between different precursors make it challenging to precisely control the deposit's stoichiometry. Therefore, heterobimetallic single-source precursors have recently been considered as an alternative approach to produce deposits with well-defined metal ratios. Most noticeably, Porrati et al. fabricated CoFe alloy nanobars using HFeCo3(CO)12 as a heteronuclear precursor.⁴⁶ HFeCo₃(CO)₁₂ shows promise as a FEBID precursor as it resulted in metallic nanostructures with high metal content (80%) and a stoichiometric Co:Fe metal ratio (3:1) that matches the precursor. The success of this precursor has provided the impetus for more fundamental gas phase and surface science studies of HFeCo₃(CO)₁₂ as well as a related precursor, H₂FeRu₃(CO)₁₃.⁴⁷⁻⁴⁹

Here we report on the electron-stimulated surface reactions of the heterobimetallic precursor (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅. A central goal was to investigate susceptibility of CO groups to desorption and decomposition and how differences in the local coordination sphere of each metal and the fate of the CO ligands translated into differences in the fate of the two metal (Fe and Mn) atoms. In addition to surface science studies of thin precursor films, the chemical composition of electron beam induced deposits created from (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ under steady state deposition comparable to those used in FEBID were obtained. Data from these surface science and electron beam deposition studies have also been compared to a recent study on the low energy (<100 eV) electron interactions with gas phase (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ molecules.⁵⁰

II Experimental

 $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}Mn(CO)_{5}$ was synthesized by reacting Na[Mn(CO)_{5}] (generated *in situ* by adding Na to Mn₂(CO)₁₀) with $(\eta^{5}-C_{5}H_{5})$ -Fe(CO)₂I using modified literature procedures.^{50–53}

Electron-induced surface reactions and deposition of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$

The electron-induced reactions of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ were studied in an UHV system equipped with XPS and MS. To complement these studies, deposits were created from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ in a scanning Auger Spectrometer (PHI 610). Base pressure in both systems was less than 5×10^{-9} Torr. Further instrumentation details including analytical and experimental capabilities are provided in previous publications.^{26,27,54,55}

(1) Electron-induced surface reactions

In these experiments, the effects of electron irradiation on nanometer scale thin films of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ were probed by XPS and MS.

Thin film preparation. $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ was added to a glass finger, which was attached to a UHV compatible leak

valve in a N₂ glove box. The leak valve was subsequently coupled to the XPS/MS chamber. Nanometer scale films were produced by heating the precursor to 35 °C and introducing the vapor into the UHV chamber where it was adsorbed onto a cooled substrate. For the majority of these experiments, the substrate was a Au foil attached to a UHV compatible manipulator and cooled by liquid nitrogen to 150 ± 5 K. Signal attenuation of the substrate Au(4f) XPS photoelectrons was measured to determine film thickness.^{56–58} Because there was a spectral overlap between the $Au(4p_{1/2})$ and Mn(2p) peaks⁵⁹ a more limited set of experiments was performed on an amorphous carbon (a:C) substrate generated by Ar⁺ bombardment of HOPG. This also allowed us to demonstrate that the effect of electron irradiation was substrate independent. For experiments on a:C, the substrate temperature was 193 \pm 5 K to minimize the adsorption of residual water in the UHV chamber. Au and a:C substrates were sputtered with Ar⁺ ions to regenerate fresh surfaces between experiments, as verified by XPS measurements.

Electron source. A flood gun (Specs FG 15/40) was used to irradiate adsorbed $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}Mn(CO)_{5}$ molecules with 500 eV electrons. This electron energy is the sum of the electron energy from the flood gun (480 eV) and a positive bias (+20 V) applied to the sample. This positive bias helps to ensure an accurate target current reading by preventing the escape of most of the low energy secondary electrons generated during by electron beam irradiation of the sample by the higher energy (500 eV) primary beam. The target current was maintained at 5 μ A and the electron flux is reported in terms of electron dose (e⁻ cm⁻²; 1 × 10¹⁷ e⁻ cm⁻² = 1.6 mC cm⁻²). Further electron source details can be found in previous publications.^{27,28,31}

X-ray photoelectron spectroscopy (XPS). XPS data were obtained using a step size of 0.125 eV and pass energy of 22 eV and were deconvoluted with commercial software (CASA XPS). Binding energies measured for the films deposited on Au and a:C substrates were calibrated to the Au($4f_{7/2}$) peak at 84.0 eV and C(1s) peak at 284.6 eV, respectively.^{59,60}

Mass spectrometry (MS). Gas phase species generated during electron irradiation were identified using a quadrupole mass spectrometer (Balzers Prisma, 0–200 amu). Additionally, MS was used to monitor the purity of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ during thermal desorption from the substrate.

(2) Deposits created from $(\eta^5$ -C₅H₅)Fe(CO)₂Mn(CO)₅ by electron irradiation

In these experiments, deposits were created in the Auger system from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ under steady state conditions more typically used in FEBID. The chemical compositions of these deposits were obtained using AES (*in situ*) and EDS (*ex situ*).

Deposit formation. $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ was heated to 35 °C and dosed onto a Ru-capped Si/Mo multi-layer mirror substrate through a leak valve, coupled with a directional doser. While dosing $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ at a constant chamber pressure (~2 × 10⁻⁷ Torr), the substrate was irradiated by the electron beam (3 kV) and maintained at ambient temperature (~21 °C), while substrate target current varied from 0.33 to 0.53 µA.

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Deposits were analyzed using Auger spectroscopy (*in situ*), followed by SEM/EDS (*ex situ*).

Scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) analysis. Deposits formed in the Auger spectrometer were characterized *ex situ* by a cold-cathode field emission scanning electron microscope (FE SEM JEOL 6700F) with a 1.0 nm resolution at 15 kV equipped with an energy dispersive X-ray analyzer (EDAX Genesis 4000 X-ray analysis system, with detector resolution of 129 eV) for imaging and compositional analysis. SEM imaging and EDS analysis were performed with an accelerating voltage of 10 kV and a probe current of 10 μ A.

III Results

Fig. 1 shows the evolution of the C(1s), O(1s), Fe(2p) and Mn(2p) XPS transitions for $\sim 0.5\text{--}3.0$ nm thick films of ($\eta^5\text{-}C_5H_5\text{)-}$ Fe(CO)₂Mn(CO)₅ adsorbed onto a Au substrate at 150 K and subjected to increasing doses of 500 eV incident energy electrons. To ensure that observed changes were dominated by the effects of electron (rather than X-ray) irradiation, control experiments were performed to compare the effects of X-ray and electron irradiation on $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ films (ESI,† Fig. S1). Analysis of these control studies revealed that X-ray irradiation produced similar effects to electron beam irradiation supporting the idea that secondary electrons generated by the interaction of the primary beam with the substrate are responsible for the surface reactions involved in this study and in FEBID in general. A comparison of the C(1s) and O(1s) regions in ESI,† Fig. S1 and Fig. 1 reveals that an X-ray exposure of 18 minutes is comparable to an electron dose of $\approx 1.5 \times 10^{15} \text{ e}^{-1} \text{ cm}^{-2}$. Since the acquisition of a single set of C(1s), O(1s), Fe(2p), Mn(2p) and Au(4f) regions (Au(4f) data not shown) required ≈ 27 minutes we can estimate that each set of XPS scans shown in Fig. 1 corresponds to an electron dose of $\approx 2.7 \text{ e}^- \text{ cm}^{-2}$.

To minimize the effect of X-ray irradiation, XPS spectra of the pristine adsorbed compound were not taken. In the absence of initial XPS spectra of the adsorbed compound, it was necessary to normalize the XPS intensities and calculated areas so values could be compared between different days, due to slight differences in the initial film thicknesses and instrument response. This data normalization was made possible by the observation that for electron doses in excess of $\approx 5.6 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$, the C(1s) area remained unchanged. Consequently, in each experiment, the film was exposed at some point to an electron dose of $\approx 5.6 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$ and the measured C(1s) area was used as reference for normalization of all other measured XPS transitions on that particular day.

Prior to electron irradiation, the XPS data in Fig. 1 of the "as deposited" film (electron exposure = 0) support the idea that the $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ is molecularly adsorbed onto a Au substrate at 150 K; the experimentally determined Mn : Fe ratio is very close to 1:1 and the O:C ratio in the film prior to electron irradiation is 0.58:1, comparable to the expected value derived from the stoichiometry of the $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ precursor. Moreover, the C(1s) region demonstrates the presence



Fig. 1 Evolution of the (a) C(1s), (b) O(1s), (c) Fe(2p) and (d) Mn(2p) XPS regions for ~ 0.5–3.0 nm thick films of (η^5 - C_5H_5) $Fe(CO)_2Mn(CO)_5$ adsorbed onto a Au substrate at 150 K and subjected to increasingly greater doses of electron irradiation. The C(1s) region is fit to show contributions from carbonyl (CO) and Cp/graphitic carbon.

of both carbonyl (CO) and cyclopentadienyl (η^5 -C₅H₅ or Cp) species. Thus, based on literature values, peaks centered at 287.6 eV and 285.2 eV in the C(1s) region are assigned as carbon atoms in the <u>CO</u> and η^5 -C₅H₅ ligands, respectively.^{59,61} Similarly, in the O(1s) region, a sharp peak centered at 534.5 eV is characteristic of adsorbed CO species, while a second peak at higher binding energy at 541.2 eV is consistent with a CO O(1s) π - π^* shake-up feature.^{62,63} XPS data show no evidence of adsorbed water in the O(1s) region (peak at \approx 532.3 eV) or of metal oxide formation in the Fe(2p) or Mn(2p) regions.^{64,65}

As a consequence of electron exposure, Fig. 1 shows there is a significant decrease in the intensity of the carbonyl C(1s) signal. In fact, for electron doses $\geq 1.2 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$, the C(1s) carbonyl peak (<u>C</u>O) has essentially disappeared. During electron irradiation, the C(1s) peak at ~284.5 eV increases slightly in intensity, although this is a minor change compared to the decreases in intensity observed for the C(1s) <u>C</u>O peak. Analysis of the total C(1s) area reveals that after an electron dose of $\approx 2.0 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$, the coverage of carbon atoms has decreased by approximately 42%, although little to no change in the C(1s) area was observed thereafter.

Fig. 1 also shows that the spectral features in the O(1s) region decrease significantly in intensity as a result of electron exposure. Thus, for electron doses $\geq 1.2 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$ the smaller shake-up feature becomes indistinguishable. The principal peak in the O(1s) region is observed to downshift in binding energy from 534.5 eV to approximately 533.4 eV. As the electron dose increases, the loss of O(1s) intensity associated with the CQ

peak is accompanied by a gradual increase in intensity of a new, broader, lower binding energy-feature centered at 531.5 eV which ultimately becomes the dominant feature in the O(1s) region.

In the Fe(2p) region, an Fe(2p_{1/2}/2p_{3/2}) doublet is observed with peaks centered at 721.6 eV and 709.5, respectively.^{59,65} During electron irradiation, the Fe(2p_{1/2}/2p_{3/2}) peak positions remain relatively unchanged; even for large electron doses, there are no significant changes or shifts in the Fe(2p) profile or discernible changes in the spectral intensity. The Mn(2p) region is initially characterized by a doublet ascribed to $Mn(2p_{1/2}/2p_{3/2})$ peaks centered at 653.0 eV and 642.2 eV.⁶⁵ In contrast to the behavior observed for the Fe(2p) peaks, however, electron irradiation broadens the Mn(2p) peaks and shifts them to lower binding energies, particularly for electron doses $\geq 1.2 \times 10^{16} e^- cm^{-2}$. However, the presence of overlap in the Mn(2p) region from a Au(4p_{1/2}) peak centered at 643 eV means that this interpretation remains somewhat qualitative.

Based on XPS analysis of the O(1s) and C(1s) peak areas, Fig. 2 shows how electron irradiation changes (a) the fractional coverage of adsorbed oxygen atoms and (b) the oxygen-to-carbon ratio (O/C) in (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ films as a consequence of electron irradiation. Both the fractional coverage of O atoms and the O/C ratio exhibit a similar dependence on electron dose, decreasing rapidly during the initial stage of electron irradiation (<1.2 × 10¹⁶ e⁻ cm⁻²), but remaining constant for larger electron doses. The data shown in Fig. 2(a) and (b) can be well-fit by a first order exponential decay process that leads to a non-zero baseline ($y = a + be^{-x}$; x = electron dose); the solid lines



Fig. 2 Change in (a) fractional coverage of adsorbed O atoms and (b) O/C ratio, for $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ films as a function of electron dose. Both data sets have been fit by a first order exponential decay function with a non-zero baseline ($y = a + be^{-x}$; x = electron dose). In (b) the horizontal dashed lines represent the change in O/C ratio that would be expected for the loss of 3 CO ligands, 4 CO ligands *etc.*

in Fig. 2(a) and (b) represent the best fit lines. Analysis of these fits indicates that the fractional coverage of O atoms decreases by approximately 70% of its initial value, while the O/C ratio decreases from an initial value of $\approx 0.58:1$ to a value of $\approx 0.24:1$.

To gain better insight into the changes in the Mn(2p) region and to determine if our data was influenced by the substrate, we adsorbed $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ onto an amorphous carbon (a:C) substrate and exposed this film to electrons. Results of these experiments, shown in Fig. 3 reveal that there were no significant differences in the evolution of the O(1s) or Fe(2p)profiles upon electron irradiation of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ films adsorbed on a:C as compared to the Au substrate. Detailed analysis of the C(1s) region is complicated by the overlap of the a:C substrate peak with that of the carbon atoms in the Cp ring. However, Fig. 3 shows that upon adsorption of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$, a shoulder at 288.2 eV appears due to the carbon atoms in the CO groups, and this peak disappears as a result of electron irradiation consistent with the behavior observed in Fig. 1. The Mn(2p) region is initially composed of a $Mn(2p_{1/2}/2p_{3/2})$ doublet with peaks centered at 653.0 eV and 642.5 eV, respectively, also consistent with the data shown in Fig. 1. As the film is exposed to electron irradiation, the Mn(2p) envelope remains relatively unchanged for electron doses $< \approx 3 \times 10^{15} \text{ e}^{-1} \text{ cm}^{-2}$; however, for larger electron doses it broadens and shifts to higher binding energies, indicative of Mn oxidation, again consistent with the observations on the Au substrate (Fig. 1). It should be noted that in both Fig. 1 and 3, the partial oxidation of Mn atoms that accompanies larger electron doses causes the less intense $Mn(2p_{1/2})$ transition to become indistinguishable from the background signal above a certain electron dose. However, when $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ films are electron irradiated in



Fig. 3 Evolution of the (a) C(1s), (b) O(1s), (c) Fe(2p) and (d) Mn(2p) XPS regions of $\sim 0.5-3.0$ nm thick ($\eta^{5}-C_{5}H_{5}$)Fe(CO)₂Mn(CO)₅ films adsorbed onto an amorphous carbon (a:C) substrate at 190 K, as a function of increasing electron dose.



Fig. 4 Mass spectra (0–80 amu) of gas phase species produced when; (a) a 3.0 nm thick film of adsorbed (η^{5} -C₅H₅)Fe(CO)₂Mn(CO)₅ molecules thermally desorbs from the Au substrate and, (b) a 0.5 nm thick film of (η^{5} -C₅H₅)Fe(CO)₂Mn(CO)₅ molecules adsorbed onto an Au substrate at 150 K was exposed to an electron dose of 1.1 × 10¹⁷ e⁻ cm⁻². In both (a) and (b) mass spectra were normalized to the CO peak (*m*/*z* = 28) for comparison.

the presence of a partial pressure of water (Fig. 6) all of the Mn atoms ultimately become heavily oxidized. As a result, the $Mn(2p_{1/2})$ peak becomes more distinct again due to the more homogeneous chemical environment of the Mn atoms, showing that the peak at $\approx 653.0~\text{eV}$ is indeed associated with the $Mn(2p_{1/2})$ transition.

Fig. 4 shows mass spectra (MS) of the gas phase species detected when $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ molecules thermally desorb from a Au substrate as it warms to room temperature (Fig. 4a) and is exposed to 500 eV electrons (Fig. 4b). In Fig. 4a, the MS is dominated by peaks associated with CO (m/z = 28, m/z = 12, m/z = 16), Fe (m/z = 56), Mn (m/z = 55), residual H₂O (m/z = 18) and other fragments such as C₃H_n (n = 2-5), C₄H_n (n = 2-5) and C₅H_n (n = 2-5) associated with the Cp ring.^{66,67} In contrast, when adsorbed ($\eta^5-C_5H_5$)Fe(CO)₂Mn(CO)₅ is irradiated (Fig. 4b) the only significant MS peaks detected are those associated with CO (m/z = 28, 16, and 12), along with much smaller contributions from H₂O (m/z = 18) and a peak at m/z = 14.

Fig. 5 shows the normalized kinetics of electron-stimulated CO (m/z = 12; C⁺ is used as a "clean" ion to monitor CO, as opposed to m/z = 28 which can also contain contributions from nitrogen and residual hydrocarbons in the vacuum chamber) desorption from (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ films adsorbed onto a Au substrate at 150 K, plotted as a function of electron dose (target current × time) cm⁻². The rate of CO evolution is seen to be greatest at the onset of electron irradiation and decreases with increasing electron dose, with the majority of CO desorption occurring for electron doses ($\approx 3 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$.

Fig. 6 shows the O(1s), Mn(2p) and Fe(2p) XPS regions for ~0.5–3.0 nm thick films of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ adsorbed onto an a:C substrate and exposed to electrons in the presence of a measurable partial pressure of H₂O molecules in the UHV chamber (as determined by residual gas analysis). In contrast to its behavior in the absence of H₂O, the Fe(2p) profile broadens towards lower binding energies for electron doses in excess of



Fig. 5 Kinetics of CO (m/z = 12 amu) desorption from a (η^5 -C₅H₅)Fe-(CO)₂Mn(CO)₅ film adsorbed onto a Au substrate at 150 K and irradiated with 500 eV electrons at a target current of 5 μ A, plotted as a function of electron dose (target current \times time).



Fig. 6 Evolution of (a) O(1s), (b) Mn(2p) and (c) Fe(2p) XPS regions for a 0.5 nm thick film of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ adsorbed onto an a:C substrate at 190 K and exposed to electron irradiation in the presence of a measurable partial pressure of water.

 $4.7 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$, indicative of iron oxidation.⁵⁹ In the O(1s) XPS region, electron irradiation initially (electron dose = $4.7 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$) produces a decrease in peak intensity and a downshift in peak position (from 535.0 eV to 532.5 eV). However, for electron doses > $4.7 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$ the peak intensity in the O(1s) region increases with electron dose, although the peak position remains largely unchanged. In the absence of electron irradiation no iron oxidation was observed even in the presence of a partial pressure of water (see Fig. S2, ESI†).

Fig. 7a shows the Auger spectrum obtained from a $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ deposit created in the AES system. Following deposition, Fe (47, 598, 651, and 703 eV), Mn (542, 589, and 636 eV), C (272 eV) and O (510 eV) are observed. The deposit contains a significant amount of organic contamination with a C:O ratio of $\approx 4:1$. A detailed analysis of the Fe and Mn content is complicated by the close proximity and overlap



Fig. 7 (a) AES and (b) SEM image of a deposit created from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ under steady state deposition conditions (see text for details). (c) EDS and (d)–(g) elemental maps of O, C, Mn and Fe, respectively obtained for the same deposit.

between the principal Mn and Fe peaks, although the principal peaks have similar heights and exhibit similar peak sensitivities, suggesting a Mn : Fe ratio close to unity. Fig. 7b shows a SEM image of the $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ deposit which illustrates that deposition is localized within the area of electron beam irradiation. EDS analysis shown in Fig. 7c indicates that the deposit is composed of Fe (18%), Mn (18%), C (51%), and O (13%). EDS elemental maps of O K, C K, Mn K, and Fe L X-rays (Fig. 7d–g) show that the various elements are also co-localized and distributed uniformly within the deposit.

IV Discussion

Results from the XPS and MS studies (Fig. 1–5) indicate that during the initial period of electron irradiation (electron doses $<1.2 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$; 0.19 mC cm⁻²), changes in composition and bonding within the (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ film reflect CO desorption. The clearest evidence of CO desorption is provided by mass spectrometry (Fig. 4), although CO desorption is also apparent in the XPS data; in the O(1s) region by loss of intensity and disappearance of the CQ (and π - π^* shake-up) peaks, and in the C(1s) region by a significant decrease in intensity of the <u>CO</u> peak (Fig. 1–3). Fig. 2(a) indicates that during this period of electron irradiation the O(1s) intensity decreases by 70% as a result of CO desorption. Based on the stoichiometry of the parent molecule, this corresponds to an average loss of ~4.9 CO molecules from each adsorbed (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ molecule. The extent of CO loss can also be estimated by measuring the decrease in the O/C ratio; Fig. 2(b) shows that this analysis predicts a loss of ~5.6 CO ligands. Considered collectively results from these two analyses suggest an average loss of approximately 5 CO ligands from each molecule during electron-stimulated decomposition. No fragments indicative of loss of the η^5 -C₅H₅ (Cp) ligand (Fig. 4) were detected by mass spectrometry, and the C(1s) peak associated with the Cp carbon atoms remained relatively unchanged (Fig. 1) under electron irradiation. Similarly, there is relatively little change in the Fe(2p) and Mn(2p) regions during the earliest stages of the reaction.

This initial step of the reaction, in which the precursor undergoes electron-stimulated decomposition, is shown in Fig. 8 and can be described in its most general form as:

$$\begin{split} (\eta^{5}\text{-}C_{5}H_{5})\text{Fe}(\text{CO})_{2}\text{Mn}(\text{CO})_{5(ads)} + e^{-} \rightarrow (\eta^{5}\text{-}C_{5}H_{5})\text{Fe}\text{Mn}(\text{CO})_{2(ads)} \\ &+ 5\text{CO}_{(g)}\uparrow \end{split}$$

where the chemical formula of the adsorbed product reflects the presence but not the binding sites of the remaining CO ligands.



Fig. 8 Electron-stimulated CO desorption from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ (stage 1); electron-stimulated decomposition of the $\eta^5-C_5H_5$ (Cp ring) and the residual CO groups that do not desorb during the initial deposition process (stage 2).

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The $(\eta^5-C_5H_5)$ FeMn(CO)_{2(ads)} species can be considered to be a partially decarbonylated intermediate which contains those CO ligands that do not desorb when the precursor decomposes. In the UHV surface science studies, precursor dissociation occurs under the influence of a constant flux of electrons and in a pseudo precursor limited regime, since there is no supply of precursor molecules during electron irradiation. Under these conditions the rate of CO loss as the precursor decomposes should follow first order kinetics as a function of the electron dose. Indeed, the initial loss of oxygen from the film, using the data in Fig. 2(a), can be well fit to a first order exponential decay process, yielding a rate constant of $1.0 \times 10^{-16} e^{-10} cm^{2}$. This value corresponds to the total reaction cross-section⁶⁸ for HFeCo₃(CO)₁₂ molecules adsorbed on gold and exposed to 500 eV electrons (σ ((η^{5} -C₅H₅)Fe(CO)₂Mn(CO)₅)_{500eV} = 1.0 × 10⁻¹⁶ e⁻ cm²). This value is comparable to the total reaction cross-sections previously measured for MeCpPtMe₃ (σ (MeCpPtMe₃)_{500eV} = $2.2 \times 10^{-16} \text{ e}^{-10} \text{ cm}^{-16}$ cm²),⁶⁶ a common FEBID precursor^{69,70} and for HFeCo₃(CO)₁₂ (σ (HFeCo₃(CO)₁₂)_{500eV} = 1.1 × 10⁻¹⁶ e⁻ cm²), a heteronuclear bimetallic FEBID precursor, both studied on Au substrates. In the present study, a comparison of Fig. 1 and 3 reveals that oxygen loss from the film is complete by $\approx 1 \times$ $10^{16} e^{-} cm^{2}$ on both Au and a:C, indicating a similar reaction cross section on both substrates.

Table 1 shows the principal charged fragments detected from a recent study on low-energy (<100 eV) electron interactions with gas phase (n⁵-C₅H₅)Fe(CO)₂Mn(CO)₅.⁵⁰ This study is of direct relevance to the present investigation as it is widely agreed that the initial step in FEBID involves electronstimulated decomposition of the precursor by the low energy (<100 eV) secondary electrons generated by the interaction of the primary beam with the substrate.³⁷ In the surface science studies adsorbed (n⁵-C₅H₅)Fe(CO)₂Mn(CO)₅ molecules are irradiated by 500 eV incident energy electrons and are simultaneously exposed to a range of low energy secondary electron energies produced by the substrate, analogous to the situation in FEBID.^{32,33} In contrast, the energy of the low energy electrons can be carefully controlled and systematically varied over the relevant energy range (<100 eV) in the gas phase experiments. This allows the effect of different electron-stimulated processes, with the exception of neutral dissociation channels⁷¹ to be studied independently. Thus, gas phase results can be compared with surface science data to help identify the most likely mechanism responsible for

precursor decomposition. In this context, the surface science results shown in Fig. 1 and 2 point towards extensive CO desorption (5 CO ligands/(η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ molecule) but retention of the Cp ligand during electron-stimulated decomposition of adsorbed (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ molecules.

For secondary electrons with energies <10 eV, precursor dissociation occurs predominantly as a result of dissociative electron attachment (DEA) ($(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5 + e^- \rightarrow$ $[(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5]^- \rightarrow \text{decomposition}).^{72-74}$ Table 1 reveals that DEA of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ under single collision conditions produces predominantly $[Mn(CO)_5]^-$ and $[(\eta^5-C_5H_5)FeMn(CO)_6]^-$, whose production would liberate one or two CO ligands at most. As the secondary electron energy increases above 10 eV, dissociative ionization (DI) becomes the dominant decomposition process $((\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5 +$ $e^{-} \rightarrow [(\eta^{5}\text{-}C_{5}H_{5})\text{Fe}(\text{CO})_{2}\text{Mn}(\text{CO})_{5}]^{+} \rightarrow \text{decomposition}).^{73-75}$ Much more extensive CO dissociation accompanies DI with principal fragments including species such as $[(\eta^5-C_5H_5)FeMn (CO)_2$ ⁺ and $[(\eta^5 - C_5 H_5)FeMn(CO)]^+$ and insignificant Cp loss. Statistical analysis of the average number of CO ligands lost per dissociation event indicates that 0.6-1 CO ligands will be lost per molecule in DEA, while from 3-6 CO ligands are lost per molecule in DI. Consequently, in FEBID the initial electroninduced decomposition of (n⁵-C₅H₅)Fe(CO)₂Mn(CO)₅ molecules appears to be driven by DI rather than DEA. A similar conclusion was reached for another CO-containing organometallic complex, $(\eta^3-C_3H_5)Ru(CO)_3Br$ in FEBID.⁷⁶

Table 1 also highlights the fact that electron-stimulated decomposition is a statistical process. Thus, after initial electroninduced dissociation of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ the adsorbed layer will be composed of a mixture of partially decarbonylated species such as $(\eta^5-C_5H_5)$ FeMn(CO), $(\eta^5-C_5H_5)$ FeMn(CO)₂, etc., yielding a film with an average stoichiometry of $(\eta^5-C_5H_5)$ -FeMn(CO)₂ as shown in Fig. 8. XPS data alone, however, does not enable us to identify to which metal atom(s) the residual CO ligands are bonded. No measureable changes in the Fe or Mn coverage were observed by XPS as a result of electronstimulated decomposition, indicating that if any Fe-Mn bond cleavage accompanies precursor decomposition (as is suggested by Table 1), none of the resultant metal-containing fragments desorb. Thus, we would expect the Fe:Mn stoichiometry in deposits created by FEBID to reflect the 1:1 stoichiometry in the precursor.

Table 1 Comparison of the principal charged fragments produced when gas phase (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ is irradiated by electrons with (left hand side) <10 eV energy and, (right hand side) 20 eV. Adapted from ref. 50

Incident electron energy <10 eV		Incident electron energy 20 eV	
Fragment	Rel. intensity (CPS)	Fragment	Rel. intensity (CPS)
$[Mn(CO_5)]^-$	1	$[(n^{5}-C_{5}H_{5})Fe]^{+}$	1
$[(\eta^5 - C_5 H_5)]$ FeMn(CO) ₆] ⁻	$7.4 imes 10^{-1}$	$[(\eta^5 - C_5 H_5)Fe(CO)_2]^+$	$9.3 imes10^{-1}$
$[(\eta^5 - C_5 H_5)FeMn(CO)_3]^-$	$4.0 imes10^{-2}$	$[(\eta^5 - C_5 H_5)FeMn(CO)2]^+$	$7.9 imes10^{-1}$
$\left[\left(\eta^{5}-C_{5}H_{5}\right)FeMn(CO)_{2}\right]^{-}$	$1.5 imes10^{-2}$	$[(\eta^5 - C_5 H_5)FeMn(CO)]^{+}$	$7.7 imes10^{-1}$
$\left[\left(\eta^{5}-C_{5}H_{5}\right)FeMn\left(CO\right)_{5}\right]^{-}$	$1.5 imes10^{-2}$	Mn ⁺	$4.0 imes10^{-1}$
$[(\eta^5 - C_5 H_5)FeMn(CO)_4]^-$	$3.0 imes10^{-3}$	$\left[\left(\eta^{5}-C_{5}H_{5}\right)FeMn(CO)_{7}\right]^{+}$	$3.9 imes10^{-1}$
Average CO loss (lower bound)	0.6	Average CO loss (lower bound)	3.0
Average CO loss (upper bound)	2.0	Average CO loss (upper bound)	6.0

For electron doses $\geq 1.2 \times 10^{16} \text{ e}^{-} \text{ cm}^{-2}$ (0.19 mC cm⁻²) analysis of Fig. 2 demonstrates that there are no further changes in the chemical composition of the film as measured by the oxygen atom coverage and the O/C ratio, both which remain constant. Similarly, Fig. 5 shows that the extent of CO desorption is minimal for electron doses $> \sim 3 \times 10^{16} \text{ e}^{-} \text{ cm}^{-2}$. However, these larger electron doses do produce measurable changes in the bonding within the film. In the C(1s) region these changes include a continued decrease in the intensity of the CO peak at 287.6 eV accompanied by a slight increase in intensity in the C(1s) peak at 285.2 eV. In the O(1s) region the peak position decreases to 532.1 eV. These changes in the C(1s) and O(1s) envelopes are indicative of electron-stimulated decomposition of those CO ligands in the partially decarbonylated intermediates, forming graphitic carbon and reactive oxygen species (ROS), thus:

$$(CO)_{(ads)} + e^- \rightarrow ROS + C_{(ads)}$$

Indeed, the most obvious evidence of CO ligand decomposition for electron doses $\geq 1.2 \times 10^{16} \text{ e}^{-} \text{ cm}^{-2}$ occurs in the Mn(2p) region (see Fig. 1 and 3) where the peak broadens significantly while decreasing in average binding energy, both indications of Mn oxidation.⁷⁷ This is consistent with Mn oxidation by the ROS (Reactive Oxygen Species) generated in the electron-stimulated decomposition of CO ligands:

$Mn + ROS \rightarrow Mn_xO_{y(ads)}$

Formation of manganese oxides also accounts for the decrease in binding energy of the O(1s) peak observed for electron doses $\geq 1.2 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$ in Fig. 1 and 3.⁷⁷ In principle, Mn oxidation could also occur from reactions involving residual water in the UHV chamber. However, if this were the case, we would reasonably expect evidence of iron oxidation and a measureable increase in the O(1s) signal intensity, neither of which are observed experimentally (see Fig. 2). It should be noted that Fig. 1 reveals that some Mn oxidation has already taken place for electron doses $< 1.2 \times 10^{16} \text{ e}^- \text{ cm}^{-2}$. This can be ascribed to the onset of electron-stimulated CO decomposition within some of the partially decarbonylated intermediates before all of the $(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}Mn(CO)_{5(ads)}$ molecules have decomposed, implying both processes proceed at similar rates. This onset of electron-stimulated CO decomposition is responsible for the increase in the C(1s) peak intensity at 284.5 eV observed during the initial stages of the reaction (Fig. 1).

The η^5 -C₅H₅ group has been observed previously to be unable to generate volatile products during electron-stimulated decomposition of organometallic precursors.³⁴ This persistence of the Cp carbons in FEBID deposits has been ascribed to its multidentate bonding to the metal center.^{78,79} Although the fate of the hydrogen atoms in the Cp ring cannot be directly ascertained in the current study due to the presence of residual hydrogen in the chamber, previous studies have shown that hydrogen is lost from organic molecules adsorbed on surfaces as a result of electron-stimulated C–H bond cleavage.^{80–83} Thus, we can infer that the fate of the Cp ligands is; η^5 -C₅H₅ (ads) + $e^- \rightarrow 5C_{(ads)} + H_{2(g)}$. This argument is supported in the present study by the persistence of the C(1s) peak located at 285.2 eV throughout the course of electron irradiation (see Fig. 1) and the absence of any desorbing Cp fragments (Fig. 4).

In sharp contrast to the fate of the Mn atoms, electronstimulated reactions of adsorbed (n⁵-C₅H₅)Fe(CO)₂Mn(CO)₅ molecules do not produce any measureable change in the Fe(2p) region throughout the entire course of electron irradiation (Fig. 1 and 3), suggesting an absence of iron oxidation. This suggests that in the present study Fe atoms are "protected" from oxidation by ROS generated when the residual CO groups decompose. One possibility is that Fe atoms become encased in the carbonaceous matrix formed as the η^5 -C₅H₅ ligand decomposes. Alternatively, if CO groups in the partially decarbonylated intermediates are attached exclusively to the Mn atoms, then CO ligand decomposition could lead exclusively to Mn oxidation. Regardless, the markedly different fate of the Fe and Mn atoms (illustrated in Fig. 8) supports the idea that the fate of metal atoms in heterobimetallic FEBID precursors is critically dependent upon the nature, number and reactivity of those ligands in the immediate coordination sphere. This assertion is also supported by related studies of another iron-containing bimetallic precursor, HFeCo₃(CO)₁₂, where iron oxidation in the absence of any Co oxidation was observed.48

The behavior of Cp and CO ligands in $(\eta^5-C_5H_5)Fe(CO)_2$ -Mn(CO)₅ during electron irradiation is analogous to previous UHV surface science studies of other organometallic precursors. For example, multiple CO ligands desorbed during the electroninduced reactions of adsorbed (n³-C₃H₅)Ru(CO)₃Br,³⁴ W(CO)₆,³⁰ Co(CO)₃NO²⁹ and *cis*-Pt(CO)₂Cl₂ molecules,³⁵ while all of the carbon atoms in Cp (η_5 -C₅H₅) and allyl (η^3 -C₃H₅) ligands were retained in the deposit during the electron-stimulated decomposition of MeCpPtMe₃ and $(\eta^3$ -C₃H₅)Ru(CO)₃Br, respectively.⁵⁴ In FEBID, where the highest metal content in the deposit is invariably the goal, the inclusion of polyhapto unsaturated hydrocarbon ligands (e.g. η^3 -C₃H₅ or η^5 -C₅H₅) should therefore be avoided. Moreover, results from the present study support the general reactivity trends observed in previous studies, in which those CO groups that do not desorb during the initial precursor decomposition step undergo subsequent electronstimulated decomposition to produce graphitic carbon and ROS that oxidize metal atoms.^{29,30} The number of CO groups that can desorb before the onset of CO induced decomposition is, however, precursor dependent.^{29,30}

Our UHV surface science results indicate that partially decarbonylated intermediates will initially be produced in FEBID using (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅. In FEBID, the substrate temperature is at or around room temperature while our UHV surface science studies are performed at significantly lower temperatures (~150 K). These low temperatures mean that potential thermal reactions of intermediate species produced during the FEBID process will not be observed in our UHV surface science studies. To provide a "bridge" between FEBID and UHV surface science conditions, we performed a limited number of experiments where (η^5 -C₅H₅)Fe(CO)₂Mn(CO)₅ films adsorbed at ~150 K were initially exposed to an electron dose, which was sufficient to decompose the majority of the parent

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molecules into the partially decarbonylated intermediates. These irradiated films were analyzed by XPS, annealed to room temperature and then reanalyzed by XPS. These studies (data not shown) revealed that annealing did not produce any measureable changes to the O(1s) region. Consequently, during FEBID CO groups which do not desorb during the electron stimulated decomposition of the precursor should remain. Under these conditions the fate of these residual CO groups will likely be determined by the effects of additional electron exposure which they will experience during FEBID, leading to ligand (CO) induced decomposition. The sequence of reaction steps described in Fig. 8 therefore likely describes the fate of the precursor in both the UHV surface science and FEBID processes.

To evaluate the performance of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ under FEBID like conditions, deposits were fabricated under steady state deposition conditions in an Auger system. The deposits contain Fe, Mn, C and O, all of which are co-localized and distributed uniformly within the deposit (Fig. 7). The Fe: Mn metal ratio as determined by EDS and AES is close to 1:1, consistent with the lack of any measurable change in the integrated intensities within the Fe(2p) or Mn(2p) regions observed in the UHV surface science experiments. This heterobimetallic FEBID precursor therefore provides stoichiometric control over the deposit's metal content, which is essential to control the magnetic and conductive properties of alloy nanostructures.⁴⁶ The C:O ratio in the deposit is significantly higher than that of the precursor, consistent with extensive CO desorption during deposition. However, the presence of >50%carbon as measured by EDS, principally due to the retention of all carbon atoms in the η^5 -C₅H₅ ligand, means that (η^5 -C₅H₅)- $Fe(CO)_2Mn(CO)_5$ is unlikely to be a viable FEBID precursor.

In typical FEBID experiments, deposition is often performed in a significant partial pressure of water.⁵⁻⁸ In our UHV experiments when adsorbed $(\eta^5 - C_5 H_5) Fe(CO)_2 Mn(CO)_5$ were electron irradiated in the presence of residual H2O (Fig. 6), Fe atoms did eventually become oxidized. However, in the absence of electron irradiation, the presence of H2O did not induce iron oxidation (Fig. S2, ESI[†]). This is consistent with Fe oxidation involving ROS generated by the electron-stimulated decomposition of transiently adsorbed water molecules. In FEBID, the fate of metal atoms will therefore be determined not only by the ligands, but also by the nature and relative partial pressure of gas phase molecules present in the chamber during deposition. However, although ROS have a negative effect on the metal content for this precursor, ROS can also remove carbon contamination and leave behind pure metal deposits when the precursors contain noble metals such as Pt and Au.84,85

V Conclusions

Surface science studies have shown that adsorbed (η^5 -C₅H₅)Fe-(CO)₂Mn(CO)₅ molecules undergo electron-stimulated reactions in two sequential steps. In the first step, a dissociative ionization process decomposes the molecular precursor into a partially decarbonylated intermediate; a process which is accompanied by loss/desorption of an average of 5 CO ligands per molecule. Further electron irradiation decomposes the remaining CO ligands and the cyclopentadienyl (η^5 -C₅H₅) ligand to produce graphitic carbon and reactive oxygen species which selectively oxidize the Mn atoms. The absence of Fe oxidation suggests that, during FEBID, the fate of metal atoms in bimetallic precursors is intimately dependent upon electron-stimulated reactions of those ligands in the immediate coordination sphere. In a typical FEBID process, however, deposition occurs in the presence of a partial pressure of water vapor and our results show that electronstimulated reactions of surface bound water can oxidize the Fe atoms produced as a result of $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ decomposition. Deposits created from $(\eta^5-C_5H_5)Fe(CO)_2Mn(CO)_5$ exhibited a stoichiometric Fe:Mn metal ratio (1:1) that matches the composition of the heterobimetallic precursor, illustrating the ability to use heterobimetallic precursors to precisely control the metallic composition of FEBID nanostructures.

Conflicts of interest

There are no conflicts to declare.

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