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Nadhom, H., Lundin, D., Rouf, P., Pedersen, H., (2020), Chemical vapor deposition of metallic films using plasma electrons as reducing agents, *Journal of Vacuum Science & Technology. A. Vacuum, Surfaces, and Films*, 38(3), 033402. <https://doi.org/10.1116/1.5142850>

Original publication available at:

<https://doi.org/10.1116/1.5142850>

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Chemical vapor deposition of metallic films using plasma electrons as reducing agents

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Metallic thin films are key components in electronic devices and catalytic applications. Deposition of a conformal metallic thin film requires using volatile precursor molecules in a chemical vapor deposition (CVD) process. The metal centers in such molecules typically have a positive valence, meaning that reduction of the metal centers is required on the film surface. Powerful molecular reducing agents for electropositive metals are scarce and hampers the exploration of CVD of electropositive metals. We present a new CVD method for depositing metallic films where free electrons in a plasma discharge are utilized to reduce the metal centers of chemisorbed precursor molecules. We demonstrate this method by depositing Fe, Co and Ni from their corresponding metallocenes using electrons from an argon plasma as a reducing agent.

I. INTRODUCTION

Thin films of metals are important in several areas such as microelectronics and catalysis. Co and Ni can form CoSi₂ and NiSi contacts if deposited on Si contacts and subsequently annealed and magnetoresistive random access memories are formed from

thin layers of magnetic metals such as Fe, Co and Ni.¹ These applications often require a metallic film of uniform thickness to be deposited on a topographically complex surface, making line-of-sight deposition methods such as magnetron sputtering unsuitable. The method of choice is therefore often a form of chemical vapor deposition (CVD), which relies on chemical reactions with precursor molecules containing the atoms for the film material.² CVD precursors for metals typically comprise of metal centers with a positive valance. Deposition of a metal thin film requires reduction of the metal center after the precursor molecule, or its decomposition products, has chemisorbed. Reduction of chemisorbed surface moieties with positive metal centers is commonly realized by a second CVD precursor, i.e. a molecular reducing agent.¹ Recent research on volatile reducing agents with enough reducing power to reduce also electropositive metals including titanium³ and aluminum⁴ has allowed for highly conformal, thermal CVD processes of several metals. However, such molecular reducing agents are complicated to synthesize in high yields and are difficult to transfer to a large-scale CVD process.

Here, we present an alternative approach to CVD of metallic films where we use a positive bias to attract electrons from a plasma discharge to reduce the metal center in metal precursors adsorbed on a substrate surface. To our knowledge, this is the first time such a CVD approach has been reported. Electrons have earlier been used to control the surface chemistry in CVD. An example is a technique known as focused electron beam induced deposition (FEBID), or electron beam induced CVD (EBI-CVD), in which a stationary electron beam, typically with energy in the keV range, albeit there are examples of lower electron energies,⁵ typically undertaken in an electron microscope, is used to deposit patterns of metals on a moving substrate.^{6,7} It should be noted that EBI-

CVD does not use the electron beam for redox chemistry; instead the deposition mechanism for EBI-CVD is a very localized heating of the substrate by the electron beam to induce breakage of the metal-ligand bonds in precursors with zero valent metal centers. A recent development is electron enhanced atomic layer deposition (EEALD), which has been used to deposit GaN,⁸ BN,⁹ Si,¹⁰ and Co¹¹ at low temperatures (20–100 °C). EEALD utilizes low energy (50–100 eV) electrons and ultra-high vacuum conditions to stimulate ligand desorption from the film surface, creating highly reactive dangling bonds. In EEALD of Co, the zero valent Co precursor cobalt tricarbonyl nitrosyl is used,¹¹ and thus there is no redox chemistry involved in the deposition of Co films with EEALD. Although free electrons have been utilized in CVD, as described above, their potential to directly participate in reductive surface chemistry is still not explored.

In this work we demonstrate the proposed CVD approach by depositing iron, cobalt and nickel films from their corresponding metallocenes using electrons in a low energy hollow cathode argon plasma. We show that the electrical conductivity of the substrate and the polarity of the substrate bias plays a crucial role in depositing metallic films with this CVD approach. We also demonstrate how the proposed method differs from a conventional plasma-enhanced CVD (PECVD) process by experimentally differentiating between substrate reactions and plasma-volume reactions.

II. EXPERIMENTAL DETAILS

The CVD experiments were carried out in a custom-built 150 mm diameter stainless-steel vacuum chamber, schematically given in Fig. 1, with a base pressure of 6 Pa, obtained by an oil-sealed mechanical pump. Films were deposited from

bis(cyclopentadienyl)M(II) (MCp₂), where M = Fe, Co or Ni, 98 %, Sigma-Aldrich™, as metal precursors. A vacuum Schlenk line system (50 Pa) and a heated oil bath were used to determine the precursor sublimation temperatures required. The sublimation temperature for FeCp₂, CoCp₂ and NiCp₂ was determined to 70, 100 and 70 °C, respectively, at 50 Pa. CoCp₂ and NiCp₂ are air and moisture sensitive and were therefore handled in a glove box system filled with nitrogen gas. Powder of MCp₂ was placed in a stainless-steel evaporation chamber, mounted on the deposition system and purged with argon gas (50 sccm), while pumping on the deposition system for 2 h to remove the nitrogen gas in the bubbler. After purging, the evaporation chamber was heated using a heating jacket to sublime MCp₂. The vapor was carried to the deposition chamber through heated gas lines without using a carrier gas. The plasma was generated by flowing argon gas (28 sccm, 99.995 %) through a custom-built titanium hollow cathode (7 mm diameter, 53 mm long) mounted in the vacuum chamber lid. The hollow cathode plasma was ignited using a DC power supply delivering 50-150 W. Electronic mass flow controllers were used to control the argon flow to the hollow cathode and to the precursor evaporation chamber.

FIG. 1. Schematics of the experimental setup for CVD of metals using plasma electrons. Precursor vapor is introduced into a continually evacuated vacuum chamber (a) where a hollow cathode plasma jet extends from the ceiling. A substrate is placed upstream from the plasma on a positively biased substrate holder. A top view schematic drawing (b) of the substrate holder shows the position of the substrate and the precursor gas flow direction over the substrate.

Deposition was done on three different types of substrates: Si (100); 50 nm Ag sputtered on Si (100); and 300 nm thermally grown SiO₂ on Si (100). The Ag sputtered substrates were prepared by cleaning Si substrates in a 80 °C H₂O:H₂O₂:NH₃ 5:1:1 solution followed by a 80 °C H₂O:H₂O₂:HCl 6:1:1 solution, and etched using hydrofluoric acid (HF, 12 vol. %) prior to Ag sputtering. The Si (100) and the SiO₂ substrates were used as received, i.e. without cleaning and etching. All substrates were 1×1 cm².

A substrate holder made of stainless steel with the dimensions 65×42×1 mm was placed in the gas stream upstream from the plasma source with 6 cm (measured diagonally) to the orifice of the hollow cathode (Fig. 1). This configuration allows precursors to adsorb on the substrate without entering the plasma bulk to minimize plasma chemical decomposition of the metal precursors. This is supported by film deposition experiments where the substrate holder was placed directly under the hollow cathode which resulted in films consisting predominantly of carbon. Note that the plasma from the hollow cathode will be concentrated in the region between the cathode and the anode. Hollow cathode plasma densities typically reach 10¹⁹ - 10²⁰ m⁻³ in the vicinity of the hollow cathode,¹² but decrease significantly, typically to ~10¹⁶ m⁻³, as shown by spatial studies of the plasma density in similar highly dense discharges,¹³ outside the region close to the hollow cathode. Thus, the probability of dissociating any precursor gas existing in the volume outside the dense plasma region decreases significantly as the mean free path for such electron–

precursor gas collisions scales with the inverse of the electron (plasma) density. We believed this to be a result of plasma chemical decomposition of the metallocene precursors prior to adsorption to the substrate surface.

The substrate was electrically connected to the substrate holder using silver paint (Agar Scientific). A DC bias voltage in the range -40 V to $+80$ V, with respect to ground, was applied to the substrate holder via a DC voltage supply where one electrode was spot welded onto the backside of the substrate holder and the other electrode connected to ground. A part of the upper surface of the substrate holder (50×42) was masked with Kapton tape on the downstream side of the gas flow to ensure electron attraction mainly towards the upstream area where the substrate was placed. Since the conducting substrate holder extends around the substrate (Fig. 1), it can be regarded as an anode for the plasma when suitably biased.

Plasma electrons were attracted to, or repelled from, the substrate holder by applying positive, or negative, substrate bias voltage. When positive substrate bias voltage was applied, the plasma electrons were transferred from the substrate surface to ground. This led to a closed electric circuit with measured bias currents in the mA range, depending on the bias voltage and substrate material (see Section 3.1 for details). The current drawn through the substrate holder was measured using a current clamp (PeakTech 4350) connected to the substrate bias voltage cable outside the vacuum chamber. There was no intentional heating of the substrate. Limited heating of the substrate holder, caused by the electron current through the substrate, was noticed. The temperature of the substrate holder was measured using a type K thermocouple, spot welded to the backside of the substrate holder. Temperatures in the range 35 – 50 °C, depending on deposition time and substrate

bias, were measured immediately after film deposition. Film deposition was carried out by introducing the precursor into the evacuated deposition chamber and igniting a continuous plasma discharge. The depositions were done in a total pressure range of 53–60 Pa for 60 s.

X-ray photoelectron spectroscopy (XPS) was used to analyze elemental composition and chemical bonding in the deposited films using a Kratos AXIS Ultra DLD instrument with a monochromatic Al K α X-ray source in an analysis chamber with base pressure of 10⁻⁸ Pa. A charge neutralizer filament was used to compensate for the charge build-up effect. The conditions used for survey scans were as follows: energy range = 0–1200 eV, pass energy = 160 eV, step size = 0.1 eV and X-ray spot size = 2 mm in diameter. A binding energy range of 20–40 eV (depending on the examined peak) was used for high-resolution spectra with a pass energy of 20 eV. Argon (0.30 eV) was used as the sputtering source. XPS spectra were analyzed using CasaXPS software where the C 1s peak with a value of 285 eV was used for calibration in all spectra. Gaussian-Laurentius (GL) functions and Shirley background were used to fit all the experimental XPS data. Scanning electron microscopy (SEM) images for surface morphology characterisation were acquired using a LEO 1550 instrument with an acceleration energy of 3 kV. Film crystallinity was studied using θ – 2θ and Grazing Incidence X-ray Diffraction (GIXRD) in a PANalytical EMPYREAN MRD XRD with a Cu-anode X-ray tube and a 5-axis (x-y-z-v-u) sample stage. The same instrument was used in X-ray Reflectivity (XRR) mode to measure film thickness and density. XRR data fitting were carried out using the PANalytical X'Pert reflectivity software.

III. RESULTS AND DISCUSSION

A. Deposition process

The current-voltage (*IV*) characteristics for the positive substrate bias range was studied during a plasma discharge with the substrate holder acting as a flat probe, measuring the current drawn through the substrate. Fig. 2 shows an *IV*-curve for a 70 W Ar plasma with a flow of 56 sccm Ar at 53 Pa. The electron saturation current regime¹⁴ is found in the 10–80 V (DC) region. Our measurements show that 97 % of the plasma electrons are drawn through the substrate holder when a substrate bias of ≥ 10 V is applied.

FIG. 2. Current-voltage (*IV*) curve for a 70 W Ar plasma with a flow of 56 sccm Ar at 53 Pa. The red dashed line shows the plasma cathode current read out on the plasma power supply at different substrate biases and the solid black line shows the current drawn through the substrate holder at different substrate biases, which correspond to 97 % of the plasma cathode current when a substrate bias of ≥ 10 V is applied.

The film deposition process is found to be strongly dependent on the polarity of the substrate bias voltage applied to the substrate holder (Fig. 3). The atomic content of Fe, Co and Ni in the deposited films increases when changing the polarity of the substrate bias voltage from -40 to $+40$ V. By inserting a conductive surface in a DC plasma, it can become an anode – particularly when given a positive bias – which causes a positive column of plasma to extend out to that surface, where it forms a sheath. The large electron current drawn through the substrate holder is a strong indication of this phenomenon. Deposition with a positive bias polarity of $+40$ V, capable of attracting plasma electrons to the substrate holder, results in metallic contents of 74 at. % Fe, 43 at. % Co and 33 at. % Ni on silver substrates. In contrast, deposition experiments with negative bias polarity of -40 V, which repel plasma electrons from the substrate holder, present no detectable amounts of metal atoms by XPS on the silver substrate surface. This can possibly be explained by extensive etching by positive ions. As the substrate bias is only -40 V, the energy of the ion bombardment will be rather low, lower than what is needed for etching reactions (typically a few hundred eV), making ion bombardment less plausible.

Deposition with a grounded (0 V) substrate holder contains 34 at. % Fe, 28 at. % Co and 26 at. % Ni. From Fig. 2 it is seen that when the substrate bias is zero, the current measured through the sample holder is around 170 mA indicating that a small electron current is still drawn from the plasma. These results show that the deposition process functions only when plasma electrons can be attracted to the substrate surface. It could be argued that negative plasma ions may play a role in the deposition. To evaluate any such role, one could compare the influence of negative ions vs electrons by comparing their densities. For our type of regular cold plasma discharge with typical electron densities of

around 10^{18} - 10^{19} m^{-3} in the dense plasma region in the vicinity of the hollow cathode, one can expect negative ion densities that are about three to four orders of magnitude lower. One such example is described for oxygen-rich plasmas generating O^- ions, where the negative ion density is on the order of 10^{15} m^{-3} for similar plasma densities as in our case.¹⁵ We do not rule out negative ion formation, but we do not have any indication that negative ions would play a significant role in our discharges. Control experiments without plasma discharge, but with a positive substrate bias, show no detectable amounts of metal atoms.

FIG. 3. The effect of applied substrate bias on the film composition from XPS for films of (a) Fe, (b) Co and (c) Ni, all deposited on silver substrates. The plasma power was 70 W for Fe and Co deposition and 50 W for Ni deposition. Note the different scaling of the y-axes.

The film deposition process is also found to be depending on the plasma power. Fig. 4 shows XPS analyses of Fe, Co and Ni films deposited at +40 V substrate bias voltage with different plasma power. The results show that the optimal plasma power in the investigated range 0–150 W is 70 W for Fe (74 at. % Fe in the film) and Co (43 at. % Co in the film), and 50 W for Ni (33 at. % Ni in the film). The plasma power relates to the plasma density, i.e. the electron and ion density in the plasma. A higher plasma power generally leads to a higher density of electrons available for the surface reduction reactions.

We therefore speculate that the higher plasma power needed for deposition of Fe and Co, compared to Ni, reflects their lower standard reduction potentials.¹⁶

FIG. 4. The effect of plasma power on the film composition from XPS for films of (a) Fe, (b) Co and (c) Ni, all deposited on silver substrates at +40 V substrate bias voltage. Note the different scaling of the y-axes.

B. Film composition

The composition analysis by XPS of films deposited on silver and silicon substrates after sputter cleaning the surface, is given in Fig. 5. The substrate bias was +40 V. Deposition on electrically insulating silicon dioxide substrates yielded no detectable amount of metal atoms on the substrate surface, indicating that an electron current through the substrate is needed to grow metal films. It should be noted, however, that a significant bias current was still recorded also in the case of silicon dioxide substrates, in line with the results presented in Section 3.1. This is due to the substrate covering only a small fraction of the conductive substrate holder, as seen in the inset of Fig. 1. The substrate holder thus maintains the role as anode independent of substrate material used. Deposition of films onto conducting silver (conductivity $\kappa_{\text{Ag,bulk}} = 6.2 \times 10^7 \text{ S/m}$) result in films with 74 at. % Fe, 43 at. % Co and 33 at. % Ni. In contrast, deposition of films on semiconducting silicon (conductivity $\kappa_{\text{Si}} = 10^3 - 2 \times 10^3 \text{ S/m}$) result in films with 35 at. % Fe, 15 at. % Co and 12

at. % Ni. XRR measurements of films deposited on silver show that the films have thicknesses of 20, 10 and 16 nm for Fe, Co and Ni, respectively. These values correspond to a deposition rate of 20, 10 and 16 nm min⁻¹ for Fe, Co and Ni films, respectively. No film thickness could be obtained of films deposited on Si, indicating very thin films. These results indicate that the deposition process functions better, i.e. deposit higher amount of metal, on highly conducting substrates, less metal is deposited on poorly conducting substrates, while the deposition process is not functioning at all on insulating substrates. Nitrogen is found as an impurity in some films, likely due to the relatively low vacuum (53–60 Pa) used during deposition. A small amount of Ti, 1–7 at. %, is found in a few of the films. This is most likely due to sputtering of the titanium hollow cathode.

FIG. 5. Elemental composition from XPS after sputter cleaning of the film deposited on (a) silver and (b) silicon. The substrate bias was +40 V.

High resolution X-ray photoelectron spectroscopy of deposited Fe, Co and Ni films, after sputter cleaning the surface, are given in Fig. 6. The films were deposited on silver substrates with +40 V substrate bias voltage. The Fe, Co and Ni regions show peaks predominantly from the zero valent elements, indicating that the metal centers with a

formal +2 valence in the metallocene molecules were reduced to a zero valent metallic state and that metallic films were deposited. It can be noted that the 2p peaks of metallic Ni is seen already in the XPS spectrum of as deposited Ni film (Fig. S3). We attribute the absence of metallic XPS peaks in Fe and Co films to the lower reduction potential of these elements compared to Ni. Peaks positioned at 707.0 eV and 720.2 eV (Δ 13.2 eV) correspond to zero valent Fe 2p_{3/2} and Fe 2p_{1/2},^{17,18} respectively (Fig 6a). Peaks located at 778.5 eV and 793.5 eV (Δ 15.0 eV) correspond to zero valent Co 2p_{3/2} and Co 2p_{1/2},^{19,20} respectively (Fig. 6b). Peaks located at 852.9 eV and 870.2 eV (Δ 17.3 eV) correspond to zero valent Ni 2p_{3/2} and Ni 2p_{1/2},²¹ respectively (Fig. 6c).

FIG. 6. High resolution XPS spectra showing the metal regions after sputter cleaning the surface. Films deposited from (a) ferrocene, (b) cobaltocene and (c) nickelocene.

First-row transition metals have a high tendency to form an oxide, albeit decreasing with increasing standard reduction potential. Oxidation of the metal films is indicated by the high energy shoulders on the zero valent metal peaks (Fig. 6). This oxidation is believed to be caused by the post deposition exposure to air. As the deposition chamber has a base pressure in the medium vacuum range, exposure to oxygen during deposition, from trace amounts of O₂ and H₂O in the deposition chamber, is also a plausible source of oxidation. This is confirmed by high resolution XPS of the films before and after sputter cleaning the

surface (Figs. S1-S3). The O 1s region shows peaks at 529–530 eV, which correspond to M-O;²² 530.9–531.7 eV and 533 eV, which correspond to C-O and C=O,²³ respectively. The M-O peak intensity decreases for all deposited films after sputter cleaning, indicating that it is mainly the surface of the metal films that is oxidized during post deposition air exposure. We note that the amount of oxygen in films deposited on silicon decreases with increasing standard reduction potential of the metals, i.e. 23, 9 and 7 at. % for Fe, Co and Ni, respectively.

In contrast, the amount of carbon in the films increases with increasing standard reduction potential of the metals deposited on silver and silicon (Fig. 5); 8, 10 and 53 at. % for Fe, Co and Ni films, respectively, deposited on silver and 42, 73 and 76 at. % for Fe, Co and Ni films, respectively deposited on silicon. The solubility of carbon in Fe, Co and Ni is about 1 at. %²⁴ and the high resolution XPS analysis of the metal region (Fig. 6) show no signs of metal-carbon bonds. Hence, the origin of the C impurities is most likely Cp ligands from the metal precursors remaining on the film surface being incorporated in the film. XPS of the C 1s region shows predominantly C–C bonds with minor contributions from C–O bonds (Fig. S4). The trend for the carbon content is puzzling. It does not follow the reported binding strength of cyclopentadienyl ligands to the metal centre, where the binding enthalpy increases as $\text{NiCp}_2 < \text{FeCp}_2 < \text{CoCp}_2$.²⁵⁻²⁷ It can also be noticed that the level of carbon impurities far exceeds the amount of carbon reported in cobalt and nickel films deposited by thermal ALD using molecular reducing agents.^{28,29} It should be noted that these films were deposited using a metal precursor with two bidentate diazadienyl ligands forming metal–nitrogen bonds instead of metallocene precursors as in this study.

C. Film structure

SEM top-view images of Fe, Co and Ni films as-deposited on silver and silicon substrates (Fig. 7) show films with a grain morphology, suggesting an island growth mode. XRD in both θ - 2θ and Grazing Incidence geometries of films deposited on silver and silicon showed no peaks besides substrate peaks, indicating that the films are X-ray amorphous. Density measurements show that the films have densities of 3.5 g cm^{-3} for Fe film (compared to 7.87 g cm^{-3} for bulk Fe), 4.7 g cm^{-3} for Co film (compared to 8.86 g cm^{-3} for bulk Co) and 7 g cm^{-3} for Ni film (compared to 8.90 g cm^{-3} for bulk Ni).¹⁶ These measurements are associated with some uncertainty due to the roughness of the films, as seen in the top-view SEM micrographs (Fig. 7). The film thicknesses and densities for the films deposited on silicon could not be obtained due to surface roughness.

FIG. 7. SEM top-view images of Fe, Co and Ni films deposited on 50 nm Ag/etched Si (Top) and on Si (bottom) substrates. Note the different length scale on the images.

D. Deposition mechanism: surface versus plasma-volume reactions

Finally, we should critically examine the possible influence of PECVD effects to the here proposed method, which we claim is governed by redox chemistry on the substrate surface. The reason is that the plasma discharge extends towards the substrate region and may result in plasma-induced gas phase cracking of the precursor molecule, i.e., conventional PECVD, and possibly metal film deposition. To what degree does such mechanisms come into play in the present case? To answer this question, let us first focus on the results presented in Figs. 3 and 5, which show that the present CVD approach depends on

- 1) plasma electrons being attracted to the substrate surface, and
- 2) the ability for the attracted electrons to be conducted away from the substrate surface.

The first point is realized by applying a suitable bias to the substrate holder, which results in a significant electron substrate current (Fig. 2). Under such conditions, we suggest that the CVD process utilizes the electrons in surface chemical reactions to reduce the metal centers chemisorbed on the substrate surface. This is supported by the dependence of the deposition process on the substrate bias, where only bias conditions enabling an electron flux to the substrate surface result in films containing metals. A negative substrate bias, used in some experiments, repels plasma electrons from the substrate surface, preventing reduction reactions on the surface. Experiments with a negative substrate bias resulted in films with close to zero at. % metallic content.

The second point concerns the dependence on the electrical conductivity of the substrate surface, which in Section 3.2 was found to be a decisive factor for film growth

with more metal being deposited at higher substrate conductivity. Using insulating substrates, such as silicon dioxide yielded no detectable amount of metal atoms on the substrate surface, indicating that an electron current through the substrate is required to grow metal films. A key observation is that a significant bias current was still recorded going through the substrate holder, *i.e.*, the plasma always extended towards the substrate and could in principle enable plasma-induced volume reactions. However, in the absence of metal film growth using electrically insulating substrates (but conductive substrate holder), we believe that any such volume reactions, typical for PECVD, are of minor influence in the present setup. Note that this was not the case when the substrate holder was placed directly below the hollow cathode discharge, as described in Section 2. In addition, no films were deposited in control experiments without plasma, but with the substrate holder pre-heated by drawing a plasma current through it. This indicates that the deposition process is not thermally activated and is a further indication that plasma electrons are active in the deposition chemistry and that the deposition chemistry is surface-controlled.

Under present conditions, the film deposition method renders substantial amounts of carbon impurities. Unlike the above described metal film growth, this undesired contribution could be due to an unwanted PECVD effect, where a small part of the metallocene precursors are decomposed above the substrate by plasma-induced volume reactions, presumably dominated by electron-neutral collisions. Such reactions would contribute with reactive carbon fragments to the film deposition. It can be noted that film deposition experiments on insulating SiO₂ substrates rendered only minute amounts of carbon and no metals on the substrate, indicating that a PECVD effect could be present but

play only a minor role for the total film deposition on conducting substrates. We speculate that this can be mitigated by extending this CVD approach in a time-resolved, ALD-like fashion, where the plasma discharge and the supply of precursors are alternated. Such an approach should avoid decomposition of the metal precursors in the plasma.

IV. SUMMARY AND CONCLUSIONS

We have developed a new CVD method for metallic thin films where the free plasma electrons are utilized as reducing agents for positive metal centers in precursor molecules. We demonstrate this CVD method by depositing Fe, Co and Ni from their metallocenes. The deposited films are shown to contain metal atoms of mainly a zero valent state with carbon as the main impurity. As an electron current is drawn from the plasma to the substrate bias unit, the film deposition is highly dependent on the ability to pass the electron current through the substrate surface. The consequence is that the deposition process works better on electrically conducting substrates, manifested by lower impurity levels and higher metal deposition rates.

ACKNOWLEDGMENTS

Andreas Jamnig, Nikolaos Pliatsikas and Kostas Sarakinos are acknowledged for supplying the silver substrates and assisting with some of the XRD and XRR measurements together with Naureen Ghafoor. Fruitful discussions with Raymond Adomaitis and Nathan O'Brien are gratefully acknowledged. Financial support from the Swedish Research Council (VR) under contract 2015-03803 is gratefully acknowledged.

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PLEASE CITE THIS ARTICLE AS DOI: 10.1116/1.5142850

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Electrical connector

Substrate

Gas flow

Substrate holder

(a)

(b)

(c)

(a)

(b)

At. %

(c)

(a)

(b)

(b)

(c)

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PLEASE CITE THIS ARTICLE AS DOI: 10.1116/1.5142850

Supporting information to:

Chemical vapor deposition of metallic films using plasma electrons as reducing agents

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FIG. S1. High resolution XPS of Fe film deposited on silver before and after sputter cleaning the surface. The Fe 2p region (left spectra) shows peak at 711.2 eV which correspond to M–O. Upon sputtering, the M–O peak shifts towards lower binding energies, i.e. 707.0 eV which correspond to zero valent Fe.^{1,2} The shoulder in the sputtered spectra correspond to M–O peaks with lower intensities. Decreasing in intensities and shifting towards lower binding energies upon sputtering is an indicating that it is mainly the surface of the metal films that is oxidized during post deposition air exposure. The O 1s region (right spectra) shows peaks at 529–530 eV which correspond to M–O and 530.9–531.7 eV which correspond to C–O.^{3,4} The M–O peak intensity decreases after sputter cleaning, is another indication of surface oxidation upon post deposition air exposure.

FIG. S2. High resolution XPS of Co film deposited on silver before and after sputter cleaning the surface. The Co 2p region (left spectra) shows peak at 781.1 eV which correspond to M–O. Upon sputtering, the M–O peak shifts towards lower binding energies, i.e. 778.5 eV which correspond to zero valent Co.^{5,6} The small shoulder in the sputtered spectra correspond to M–O speaks with lower intensities. Decreasing in intensities and shifting towards lower binding energies upon sputtering is an indicating that it is mainly the surface of the metal films that is oxidized during post deposition air exposure. The O 1s region (right spectra) shows peaks at 529–530 eV which correspond to M–O and 530.9–531.7 eV which correspond to C–O.^{3,4} The M–O peak intensity decreases after sputter cleaning, is another indication of surface oxidation upon post deposition air exposure.

FIG. S3. High resolution XPS of Ni film deposited on silver before and after sputter cleaning the surface. The Ni 2p region (left spectra) shows peaks at 852.9 eV and 855.4 eV which correspond to zero valent Ni and Ni(OH)_2 , respectively. Upon sputtering, the intensity of the Ni peak increases significantly and Ni(OH)_2 peak shifts towards lower binding energy, i.e. 853.6 eV which correspond to M–O.⁷ This is an indicating that it is mainly the surface of the metal films that is oxidized during post deposition air exposure. The O 1s region (right spectra) shows peaks at 529–530 eV which correspond to M–O;³ 530.9–531.7 eV and 533 eV which correspond to C–O and C=O,⁴ respectively. The M–O peak intensity decreases after sputter cleaning, is another indication of surface oxidation upon post deposition air exposure.

FIG. S4. High resolution XPS of the C 1s region for: (a) Fe, (b) Co and (c) Ni films deposited on silver. The C 1s region shows peaks at 284–288.5 eV which correspond to C–C, C–O and C=O.^{8,9} The spectra show no sign of carbides in all films.

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