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Stoichiometry of nickel oxide films prepared by atomic layer deposition**

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The versatility of the ligand cyclopentadienyl, $C_5H_5^-$ or Cp^- , has made the metallocenes Cp_nM (mostly $n = 2, 3$) an unusually general type of model compounds in coordination chemistry,^[1] a framework on which to elaborate various organometallic reagents and catalysts,^[2] and more recently, a well behaved class of precursor molecules in materials chemistry. Among the materials preparation techniques, atomic layer deposition (ALD) is no exception. In ALD, the “self-limiting” property of a surface reaction between two alternatively pulsed, thermally stable but mutually reactive gaseous precursor molecules allows for an accurate control of deposited film thickness and, perhaps more importantly, for the conformal coating of substrates with complex geometries.^[3] Metallocenes or their derivatives can be either hydrolyzed or oxidized in ALD mode (depending on their reactivity) to obtain various oxides MO or M_2O_3 , $M = Mg, Sr, Ba, Sc, Y, Zr, Fe, Ru, Co, Ni, Pt, Lu$.^[4–7] In the hydrolytic case the electropositive element retains its initial oxidation state n from the Cp_nM compound, whereas in an oxide obtained by oxidation of Cp_nM the oxidation state of M may be higher than n . In the case of the ALD reaction between nickelocene and ozone (O_3), the stoichiometry of the product material has not been investigated to date, under the assumption that nickel(II) oxide, NiO , should be formed.^[7,8] This assumption is credible in NiO films formed from a hydrolysis reaction,^[9] but much more questionable when the aggressive oxidant ozone is involved, especially since sub-stoichiometric oxides are well documented.^[10] Given the differences in physical and chemical properties between green NiO and the sub-stoichiometric black solids Ni_xO , $x < 1$, the stoichiometry of nickel oxide films deposited from the ALD reaction between nickelocene and ozone is worth an accurate investigation.

A film forms when a silicon wafer is heated to 230 °C and submitted to 1500 alternating exposures of nickelocene vapor (from the solid precursor heated to 110 °C) and ozone /

Fig. 1. X-ray reflectivity curve (synchrotron radiation, 11.5 keV) obtained after 1500 cycles of nickel oxide ALD: the film is 138 nm thick.

dioxygen mixture. An X-ray reflectivity curve recorded using synchrotron radiation (XRR, **Figure 1**) reveals a periodic oscillation stemming from a homogeneous single film of 138 nm thickness on the substrate. This value corresponds to a growth rate of 0.92 Å per cycle and is within the (wide) range reported earlier for ALD-grown nickel oxide.^[7] The XRR data attest the smoothness of the film, with an estimated root-mean-square roughness below 1 nm. A microscopic investigation indicates that despite the overall smoothness of the film, many pinholes are present (**Figure 2b**). This aspect is most likely related to a difficult nucleation of the film on the substrate.^[11] Structural information is obtained by diffraction of the X-ray beam in grazing incidence geometry (GIXRD, **Figure 2a**). The grazing incidence is used here to avoid all substrate diffractions, which are otherwise so prevalent that they obscure the peaks due to the film analyzed. Because the GIXRD signal originates from a thin layer (tens of nanometers), the diffractogram is noisy, but the quality is sufficient for phase assignment. Three peaks are observed, which can be assigned to the (111), (200) and (220) planes of cubic NiO . The unit cell size is evaluated to be 4.158(±0.005) Å from the peak positions, whereas the value of 4.1758 Å is accepted for the bulk material.^[12] The identity of the crystal, however, is in no means a proof of the stoichiometry. Indeed, elemental analysis of the Ni content in the film yields 77% and 76% (mass) at two different positions on the substrate, corresponding to the stoichiometry $Ni_{0.89}O$ and $Ni_{0.87}O$, respectively. This amounts to over 10% vacancies at the Ni sites in the solid, which may cause the contraction of the crystal unit cell observed by GIXRD.

The nickel-deficient nature of the film affects its magnetic properties. At room temperature, the sample gives rise to a diamagnetic signal (black squares of **Figure 3**), most of which is due to the substrate. This behavior is consistent with either a diamagnetic film or an antiferromagnetic out — the former case being often observed for bulk substoichiometric oxide,^[13] whereas NiO notoriously has the latter character. Upon annealing under argon, however, the material is transformed.^[10] Changes in morphology and magnetism start to be discernible at 500 °C, and after an hour-long annealing at 700 °C they are complete. The film continuity has been lost

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Fig. 2. Structural characterization of nickel oxide films as grown by atomic layer deposition (*a,b*) and after annealing at 700 °C under argon (*c,d*). The glancing-angle X-ray diffractograms (*a,d*) reveal the transformation from the structure of NiO to that of metallic Ni. The angle axes are scaled to the Cu K α wavelength; the main peaks of the corresponding bulk phases are indicated by dotted lines and labeled. The scanning electron micrographs (SEM) in top view (*b,c*) reveal the presence of pinholes in the deposited film, which becomes discontinuous upon annealing, with the formation of discrete clusters. Both micrographs are on the same scale.

irreversibly, clusters of various sizes have formed (Figure 2c). The material is thereby completely converted to metallic nickel, as shown by the GIXRD diffractogram (Figure 2d). The (111) and (200) peaks of cubic Ni appear and correspond exactly to the unit cell size of the bulk (measured: 3.520($\pm$ 0.005) Å).^[14] At this point, the film displays the strong ferromagnetic hysteretic behavior expected of elemental nickel (Figure 3, gray disks). The negative slope apparent at large absolute values of the applied field parallels that observed with the oxide sample. This confirms that it originates in the diamagnetic substrate.

The evolution of O₂ gas from the oxide upon thermal treatment in argon can be monitored. When a nickel oxide film is covered by an additional 50 nm thick amorphous Al₂O₃ layer (by ALD), a cross-section of the sample obtained upon 700 °C anneal under inert gas reveals two new layers in transmission electron microscopy (TEM, Figure 4a). The first is a void space between the nickel-containing layer and the substrate, as confirmed by an X-ray spectroscopic profiling

Fig. 3. Magnetic isotherms of the films recorded at 300 K. The nickel oxide deposited (black squares) shows a diamagnetic signal, which converts to a ferromagnetic hysteresis typical of metallic Ni upon annealing at 700 °C under argon (gray disks, dashed line).

Fig. 4. Demonstration of a loss of gas from the nickel oxide layer upon annealing underneath a thick Al₂O₃ sheath. (*a*) Transmission electron micrograph taken in cross-section after annealing at 700 °C: bubbles have appeared at the interface between nickel oxide and aluminium oxide and the nickel oxide film was separated from the substrate. (*b*) The identity of the layers is confirmed in a composition profile determined by energy-dispersive X-ray spectroscopy. The element carbon originates from the glue used to prepare the thin TEM sample: its presence signifies a void in the film stack. The discernible layers are (from left to right): silicon, silicon oxide, void, nickel and/or nickel oxide, aluminium oxide, void.

Fig. 5. Graphical summary of the stoichiometries demonstrated here on a compositional axis between the extremes 100% nickel (metal, left) and 100% oxygen (O_2 , right).

(EDX, **Figure 4b**). The second consists of what appears as bubbles at the interface with Al_2O_3 . We attribute both to the buildup of O_2 liberated from the substoichiometric material. After treatment to 800 °C, the stress induced by liberating molecular oxygen is released as microscopic film pieces have peeled off the underlying substrate.

Finally, the stoichiometry of the nickel oxide initially grown can be changed by treating the film at 700 °C without protecting layer under aerobic conditions. In this case, the partial pressure of O_2 suffices to maintain, and even increase, the O/Ni ratio in the solid. After cooling, the product contains 73% Ni by mass according to elemental analysis, which corresponds to $\text{Ni}_{0.74}\text{O}$.

Thus, the ALD reaction between nickelocene and ozone at 230 °C yields, in contrast to what has been assumed in the literature to date,^[7,8] a nickel-deficient oxide $\text{Ni}_{0.88}\text{O}$ that exhibits the crystal structure of NiO. Its stoichiometry can be adjusted by annealing (**Figure 5**). Under inert atmosphere, the solid converts to Ni metal at 700 °C with concomitant loss of gaseous oxygen. Its magnetic properties thereby switch from diamagnetism/antiferromagnetism to ferromagnetism. In aerobic conditions at 700 °C, the partial pressure of O_2 drives the oxidation of the deposited film further to the composition $\text{Ni}_{0.74}\text{O}$. These findings are of importance in the context of solid-state reactions between nickel oxide and the oxides of trivalent transition metal ions, which may yield spinel phases with interesting physical properties.^[15]

Experimental

Silicon (100) wafers (phosphorus-doped, 1-10 Ω cm) with native oxide layer were purchased from Si-Mat and used as substrates without further cleaning. Small amounts of nickelocene (99% from Strem, deep green powder) were transferred to a stainless steel bottle from Swagelok and heated to 110 °C for ALD. Ozone was obtained from dioxygen in a generator by OzoneLabs. Atomic layer deposition was performed in a home-made reactor that combines a low-vacuum system based on a rotary vane pump, a circular vacuum chamber with 2-inch sample stage heated to 230 °C, and pneumatic three-way valves supplied by Swagelok and controlled electronically. One ALD cycle consisted of 2 s Cp_2Ni pulse, 10 s exposure, 30 s purge, then 0.2 s O_3 pulse, 15 s exposure and 30 s purge. Annealing was carried out in an Ulvac-Riko oven model Mila 3000 working under 1 atm. Argon gas (99.998%) was purchased from Westfalen AG. Scanning electron microscopy was performed at a Zeiss Evo 50, transmission electron microscopy with a Philips CM20T at 200 kV, and EDX

linescans with a FEI TITAN 80-300 operated in the scanning transmission mode (STEM) at 300 kV. Magnetic measurements were taken on a SQUID magnetometer MPMS-XL from QuantumDesign. XRR and GIXRD data were collected at the E2 beamline of HASYLAB/DESY at the incoming photon energy of 11.5 keV. The GIXRD data were scaled on the angle axis for the energy difference between the synchrotron radiation and the usual Cu K α X-ray. Elemental analyses were obtained commercially from Mikroanalytisches Labor Kolbe (Mühlheim, Germany): films of several cm^2 were dissolved off of the substrate and analyzed.

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