Effect of Solvent on the Growth of Co and Co_2C Using Pulsed-Spray Evaporation Chemical Vapor Deposition

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Received July 22, 2007. Revised Manuscript Received October 2, 2007

Cobalt and cobalt carbide films were obtained using chemical vapor deposition (CVD) at low pressure in a hydrogen-free atmosphere at temperatures below 300 °C. Although the growth over bare glass was enabled, the use of a 5 nm nickel seed layer improves the morphology and eliminates the incubation time. The pulsed-spray evaporation using alcohol solutions of cobalt acetylacetonate as a liquid feedstock allows the growth of metallic cobalt or cobalt carbide, depending on the choice of the alcohol and of the deposition temperature. The growth of Co_2C was obtained, for the first time with CVD, using an ethanol precursor solution at temperatures in the range of 205–230 °C, whereas the deposition of high-quality metallic crystalline cobalt is attained with an *n*-propanol precursor solution at substrate temperatures above 250 °C. The obtained metallic films reach a near-bulk electrical resistivity for thicknesses above 300 nm.

Introduction

The electrical, magnetic, and catalytic properties of cobalt, cobalt carbide, and cobalt-based alloys make their application as thin films technologically important.[1–3] Among the variety of coating techniques, chemical vapor deposition (CVD) is considered as a promising method because of the relative ease of coating three-dimensional structures with a conformal layer.[4,5] Furthermore, CVD allows the growth of alloys with flexible variation of the composition.[6] While no attempt to grow Co_2C by CVD has been reported, most efforts to grow cobalt thin films by CVD involved $Co_2(CO)_8$ as the precursor[5,7–11] because it does not require hydrogen to form metallic films at temperatures below 100 °C. Nevertheless, this precursor is not convenient to handle because of its toxicity, air-sensitivity, and of thermal degradation in the gas phase, which affects the conformality of the growth on structured surfaces.[5]

Organometallic precursors with limited gas-phase decomposition have been employed.[10,12,13] These compounds allow deposition at high temperatures (300 °C) without gas-phase depletion and enable the growth of high-quality cobalt films. However, most of these precursors are still air-sensitive, and some require the use of hydrogen to form metallic coatings. Metal−organic compounds are more convenient to use, store, and handle, but very limited efforts have been devoted to their involvement for the growth of metallic cobalt films. Cobalt acetylacetonate[14–16] and cobalt acetate[17] allow the growth of metallic cobalt even at atmospheric pressure. Nevertheless, they require high partial pressure of molecular hydrogen to induce the reduction process, and the obtained films present a relatively high electrical resistivity, which indicates their contamination.

Our recent investigations show that alcohols can efficiently substitute hydrogen to induce the reduction of the metal−organic precursors of a variety of metals including nickel, cobalt, copper, silver, and iron.[18–22] In contrast to all other investigated metals, the growth of cobalt was noted to be highly

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10.1021/cm701957s CCC: $37.00

sensitive to the nature of the underlying substrate. Furthermore, the selection of alcohol shows a particularly complicated effect on the formed cobalt phases. The present investigation focuses on the possibility of enhancing the morphology, the growth rate, and the quality of metallic cobalt by an appropriate surface treatment prior to deposition and by an appropriate choice of the alcohol used to induce the reduction process.

Experiments and Methods

The growth of metallic films was performed in a cold-wall CVD reactor, which is equipped with pulsed-spray evaporation (PSE) as the precursor-delivery technique. A description of the experimental setup can be found elsewhere.[18,22] The metal(II) acetylacetonate complex was dissolved in alcohol to a concentration of 5 mM and used as the liquid feedstock, which was pulse-injected with a duration of 40 ms/cycle. The mean feeding rate of 3.7 mL/min was measured for a delivery frequency of 1 Hz, which is used in this study. An additional flow of nitrogen of 1 slm was used as the carrier gas. The growth of cobalt films was performed at 150 mbar, using linear alcohols to prepare the precursor solution.

The thickness of the deposited films was estimated gravimetrically with the assumption that the grown films are pure and possess the full density of the detected phase. The electrical resistivity of the obtained films was measured using a four-point probe, while scanning electron microscopy (SEM; Philips XL-30 ESEM), X-ray diffraction (XRD; Philips X'Pert pro MRD), and X-ray photoelectron spectroscopy (XPS; monochromated Al Kα radiation; Omicron-Nanotechnology) were used respectively to comment on the films morphology and to identify the existing crystalline phases and their composition.

Results and Discussion

1. Growth of Cobalt on Bare Glass. Our previous investigations of the growth of cobalt films by PSE-CVD show, in contrast to the growth of other metals, serious nucleation difficulties on bare glass.[18,19] Consequently, SiC was selected as the substrate to demonstrate the growth of metallic cobalt films in a hydrogen-free atmosphere using cobalt(II) acetylacetonate.[18,19] These films were grown at the substrate temperature of 325 °C in a vacuum (45 mbar).

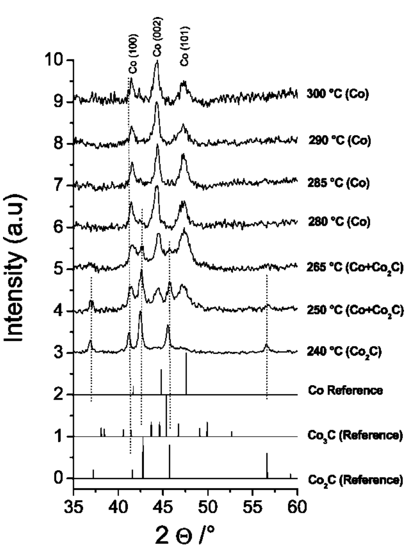

Figure 1. XRD patterns of grown films on bare glass using cobalt(II) acetylacetonate in ethanol (5 mM). The nominal thickness of the films was estimated at 80 nm. The reference spectra from JCPDS have the following powder diffraction file numbers: hcp Co, 05-0727; orthorhombic Co_2C, 05-0704; orthorhombic Co_3C, 26-0450. Diffractograms were normalized for a convenient comparison.

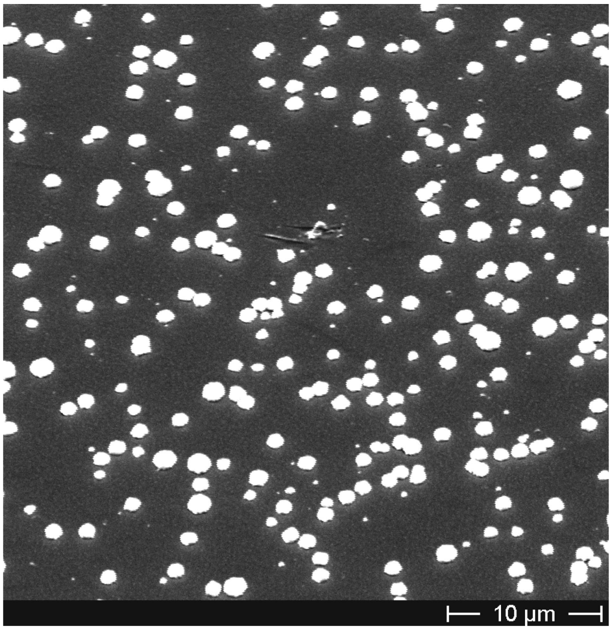

Figure 2. SEM micrograph of grown metallic cobalt on bare glass substrates at 300 °C.

A systematic investigation of the process parameters shows the possibility of growing cobalt-containing films on bare glass at temperatures above 240 °C, using an ethanol solution of cobalt(II) acetylacetonate. At low temperature (240 °C), the grown films present a single phase, Co_2C, as shown by XRD in Figure 1. This diffractogram indicates the presence of considerable lattice strain, which was calculated to be 0.25% using the Williamson−Hall analysis. Between 250 and 265 °C, a mixture of Co_2C and metallic cobalt was formed, while only metallic cobalt was detected above 265 °C. The metallic cobalt films exhibit a preferred (002) orientation and possess a high lattice strain, 0.62% calculated for films grown at 285 °C. It is worth mentioning here that, to the best of our knowledge, this is the first demonstration of the growth of cobalt carbide by CVD.

This investigation shows that metallic cobalt films can be grown on bare glass starting from a metal−organic precursor in ethanol without the addition of molecular hydrogen. Nevertheless, the grown films do not exhibit a metallic appearance. The morphology of these films, as shown by SEM in Figure 2, reveals an obvious nucleation limitation. The coverage of the surface is partial, and the film consists of disconnected micrometer-sized agglomerates. This is in agreement with the growth kinetics in Figure 3a, which shows the presence of an incubation time of ∼7 min. Therefore, physical nucleation hinders the two-dimensional growth of cobalt to a fully covering film. Similar difficulties

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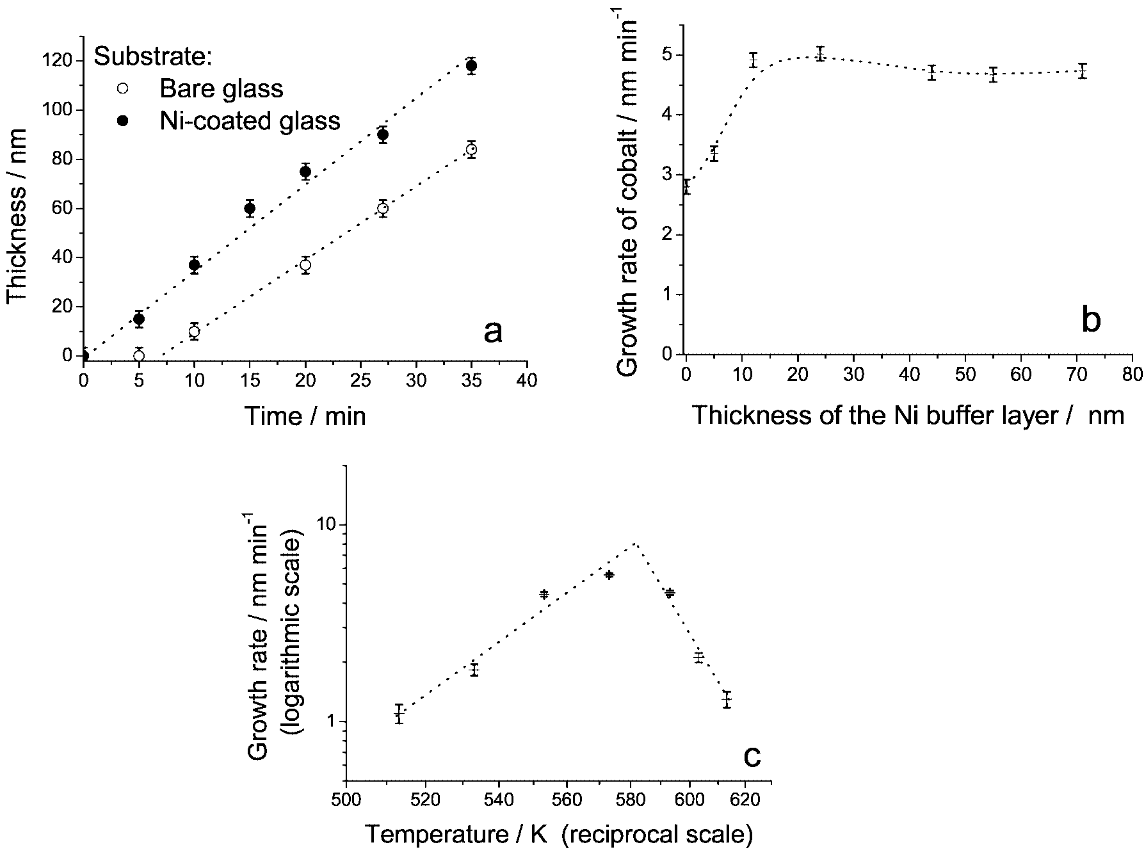

Figure 3. Growth kinetics of cobalt on nickel-coated glass (a) and the effect of the thickness of the nickel seed layer on the growth rate of cobalt (b) at a substrate temperature of 300 °C. (c) Arrhenius plot for the growth of a cobalt/cobalt carbide film on a 10 nm thick nickel buffer layer.

to deposit a good quality of cobalt films by CVD on glass and native oxide of silicon were reported by Paranjape et al.[23] These results demand, as a consequence, the use of surface treatment prior to deposition.

2. Assisted Nucleation and Growth. Unlike cobalt, nickel films grown under identical conditions are highly uniform and conduct electricity starting at a thickness of 7 nm, and a resistivity of 513 $\mu\Omega$ cm was measured for an 8 nm thick film. Nickel grows with a rate of 6 nm/min at 250 °C, starting from a 5 mM ethanol precursor solution. Therefore, a thin (5 nm) film of nickel, which requires a deposition time of 45 s, was grown on bare glass prior to the deposition of cobalt to serve as a seed layer.

The presence of a nickel seed layer suppresses the incubation time, as shown in the growth kinetics presented in Figure 3a, and it significantly improves the growth rate of cobalt, as shown in Figure 3b. In fact, the calculated growth rate, of 2.8 nm/min on bare glass, was improved to 3.4 nm/min because of the presence of a 5 nm nickel layer. As presented in Figure 3b, an increase of the thickness of the nickel seed layer to 10 nm further improved the growth rate of cobalt to 5 nm/min, which is nearly 2-fold faster than that on bare glass. Further, an increase of the thickness of the nickel layer above 10 nm has no effect on the growth rate of the cobalt overlayer, which is an indication that nickel totally covers the surface of glass starting at a thickness of 10 nm. Nickel films conduct electricity and present XRD patterns starting at a thickness of 7 nm, which is a disadvantage when investigating the structure and the electrical conductivity of the cobalt overlayer. Therefore, a nickel seed layer with a thickness of ~5 nm was routinely used to grow cobalt films.

The temperature effect on the growth of cobalt (Figure 3c) shows an Arrhenius behavior with a kinetically controlled growth between 240 and 300 °C. Within this range of temperature, the pressure has a negligible effect on the growth rate between 60 and 200 mbar. A further increase of the growth temperature above 300 °C leads to a decrease of the growth rate, indicating either thermodynamic or transport limitations. The deposition of cobalt was preferably investigated within the kinetically controlled growth regime.

The growth kinetics shown in Figure 3a indicates a suppression of the incubation time by the application of the nickel seed layer, and, consequently, the grown cobalt films exhibit a significantly improved morphology, as indicated in Figure 4. The overgrown cobalt has a morphology that is similar to that of the buffer layer and conducts electricity starting at a thickness of 30 nm. The XRD analysis shows, however, a complex dependence of the films crystalline structure on the type of the alcohol used and on the temperature.

3. Effect of the Alcohol on the Growth of Cobalt. Cobalt films were thus grown on a 5 nm nickel seed layer, to a thickness of 80 nm, at different temperatures and using

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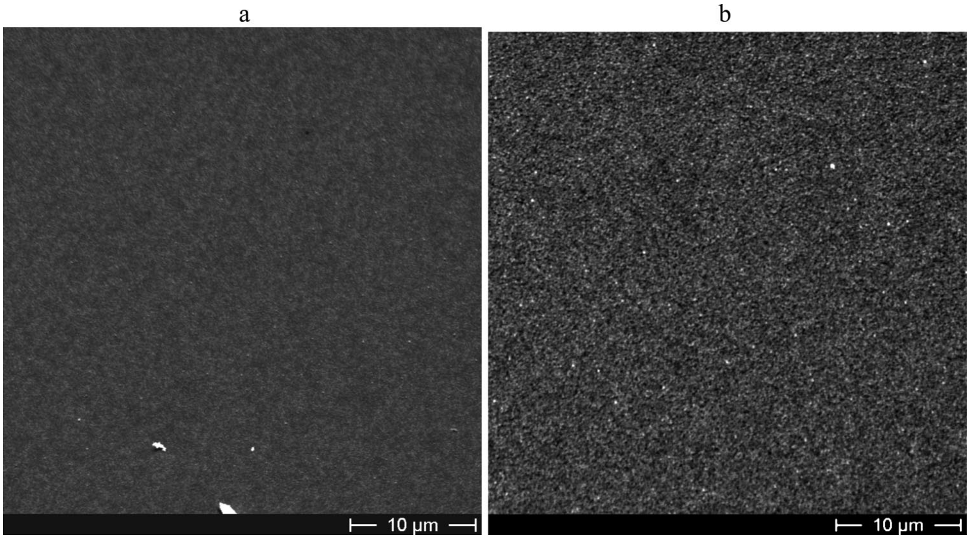

Figure 4. SEM micrograph of a 5 nm thick nickel seed layer (a) and an 80 nm thick cobalt layer grown on the nickel-coated glass.

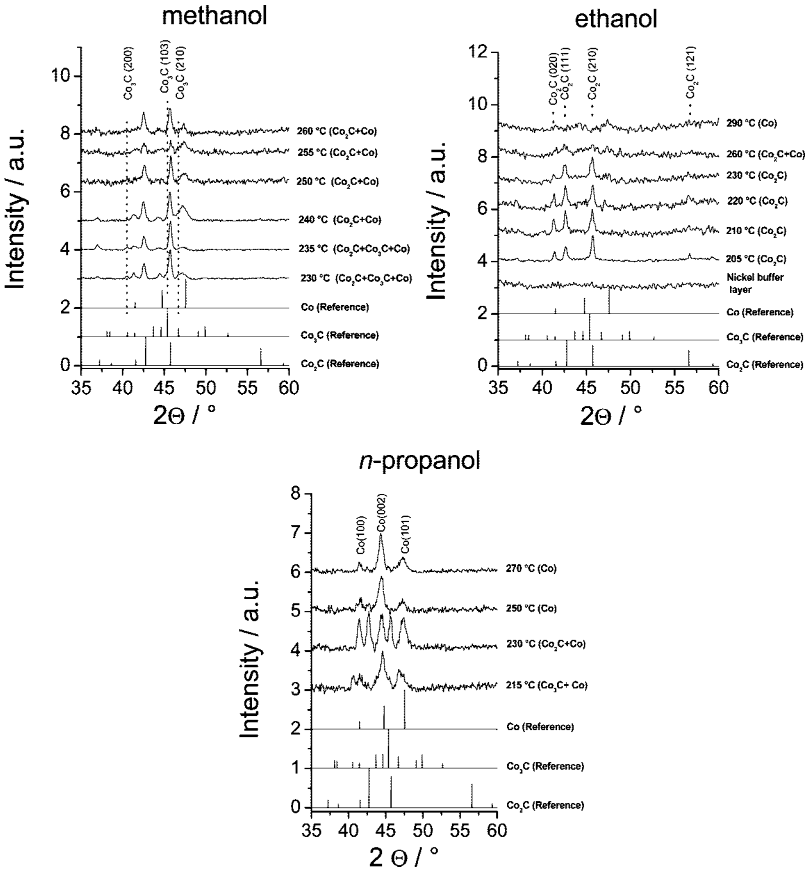

Figure 5. X-ray diffractograms of cobalt-containing films as grown from alcohol solutions of cobalt acetylacetonate at different temperatures.

different alcohols as solvents. The obtained films were subjected to XRD analyses, the results of which are depicted in Figure 5 showing significant differences already at first glance. The methanol precursor solution leads to the growth of films starting at a temperature of 230 °C, and Co$_2$C is the dominant crystalline phase in the entire investigated temperature range of 230–260 °C. This phase coexists with Co$_3$C in films grown at 230 and 235 °C and with crystalline cobalt at higher deposition temperatures.

The use of an ethanol precursor solution leads to the formation of films, starting at 205 °C, and the crystalline Co$_2$C is the only detected phase up to a growth temperature of 230 °C. The grown Co$_2$C films (205–230 °C) present negligible lattice strain when compared to the grown films on bare glass (Figure 1) and show a preferential (210) orientation. Weak diffraction peaks corresponding to metallic cobalt can be observed above 230 °C. The low XRD signal-to-noise ratio is attributed in this case to the poor crystallinity

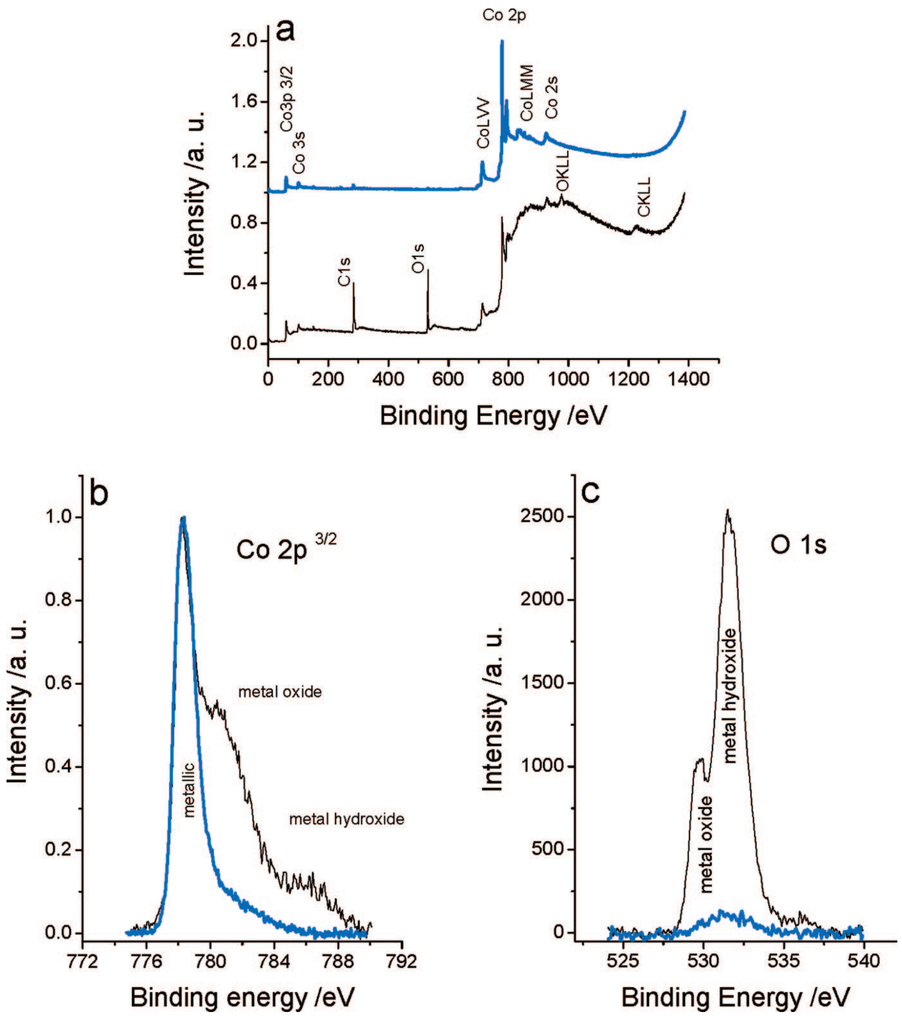

Figure 6. XPS analysis of metallic cobalt. Films with a thickness of 100 nm were grown using the *n*-propanol precursor solution at a substrate temperature of 250 °C: (a) overview spectrum; (b and c) highly resolved Co $2p^{3/2}$ and O 1s peaks, respectively. Thin lines correspond to the as-grown surface, and the blue thick lines represent the surface after argon ion sputtering.

of the film because all analyzed films have comparable thickness. A clear identification of the metallic cobalt layer by XRD was obtained for the grown film at 320 °C with a thickness of 800 nm over a SiC substrate.[19]

The use of *n*-propanol allows the formation of metallic crystalline cobalt, with a (002) preferred orientation, as the dominant phase in the entire investigated temperature range (215–270 °C). Weak signals from Co_3C were observed at 215 °C, while Co_2C was observed at 230 °C. Single-phase metallic cobalt was observed above 250 °C.

Beyond the general effect that alcohols have on the growth rate, which was demonstrated earlier for cobalt[19] and silver,[20] it is demonstrated here that the nature of formed crystalline phases of cobalt also can be influenced by the choice of the alcohol. Linear alcohols were investigated in this study, and it was noted that alcohols with longer alkyl chains favor the formation of the metallic crystalline phase, which correlates with their ability to dissociate and to deliver a proton to the surface during deposition.[24,25]

The nature of the underlying substrate was also observed to influence the nature of the obtained cobalt-containing phases. Comparing Figures 1 and 5 (ethanol) shows that the presence of a nickel seed layer shifts the formation of Co_2C to low temperatures (205–230 °C instead of 240–265 °C), whereas the obtained cobalt on bare glass shows better crystallinity. In situ surface and gas-phase analyses are underway to investigate the chemical affinity of different alcohols with cobalt precursors and with different surfaces including glass, cobalt, and nickel. This is expected to enable the proposition of deposition mechanisms for the metallic and carbide phases.

The obtained metallic films with a thickness of 100 nm, using an *n*-propanol precursor solution, were analyzed ex situ with XPS. The surface analysis of the as-grown films shows substantial carbon and oxygen contamination (Figure 6a). Sputtering the surface of the deposit for 7 min with argon ions (5 keV/20 μA and a pot diameter of ~20 mm) significantly reduces the amount of contamination. This result indicates that carbon and oxygen are present as surface contamination, which is typically observed with ex situ surface-sensitive analysis techniques.[5,12] The residual carbon after sputtering might be attributed to the presence of carbide in these conditions. The observation of the highly resolved Co $2p^{3/2}$ (Figure 6b) and O 1s (Figure 6c) peaks shows the presence of surface oxide and hydroxide that form upon

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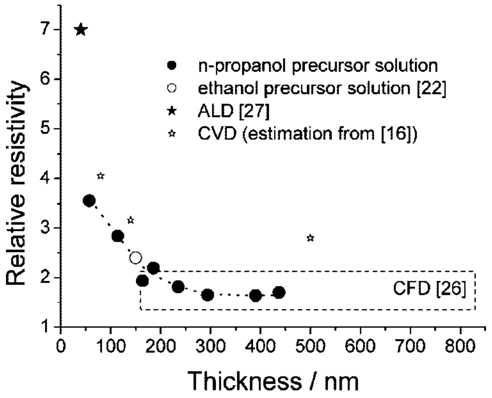

Figure 7. The electrical relative resistivity [resistivity of the films/bulk resistivity (6 $\mu\Omega$ cm)] of the as-grown cobalt films at 255 °C, using an *n*-propanol precursor solution of cobalt(II) acetylacetonate. Nickel-coated glass, which is used as the substrate in this study, does not conduct electricity. Some comparative literature data are plotted.

exposure of the as-grown cobalt film to air. The formed oxide and hydroxide layers can be removed by gentile argon ion sputtering.

4. Electrical Properties. The electrical resistance of the obtained cobalt over nickel-coated glass is presented in Figure 7 as a function of the film thickness. It is worth mentioning that nickel-coated glass, used as the substrate, does not present any measurable electrical conductivity. Cobalt films investigated here were grown at the substrate temperature of 255 °C using the *n*-propanol precursor solution. Thin films ($<$300 nm) exhibit an electrical resistivity that decreases with the thickness. This behavior can be attributed to the electron scattering at the grain boundaries, the density of which is minimized by the growth of large crystallites in thick films. The electrical resistivity saturates at a value that is 60% higher than that of the bulk, for a film thickness higher than 300 nm; this is due to the inherent surface oxidation of the films upon exposure to air after deposition, as shown in the XPS analysis in Figure 6.

The obtained performance, in terms of electrical conductivity, can be compared to the literature by considering different aspects. The choice of the alcohol solution has a nonsignificant effect on the electrical conductivity because a relative resistivity of 2.4 was measured for 150 nm thick cobalt obtained from an ethanol precursor solution at the substrate temperature of 325 °C, which is appropriate in this case for the deposition of metallic cobalt.[22] In contrast, the choice of the substrate influences significantly the electrical conductivity because relative resistivities exceeding 25 were measured for grown cobalt films with a thickness of 800 nm on SiC substrates without a seed layer.[18]

Maruyama[16] reported the growth of metallic films at substrate temperatures of 320–350 °C using cobalt(II) acetylacetonate as the precursor and hydrogen as the reducing agent. The obtained films exhibit relative resistivities ranging from 4 to 2.8 when the thickness is increased from 80 to 500 nm.[16] This shows that replacing molecular hydrogen with *n*-propanol not only reduces significantly the deposition temperature but also improves the electrical properties of the obtained films.

The PSE-CVD, which is used here with an alcohol precursor solution can be compared to other processes such as chemical fluid deposition (CFD)[26] and atomic layer deposition (ALD).[27] In fact, the CFD process, using a CoCp$_2$ and hydrogen mixture, at a substrate temperature of 285–320 °C and a pressure of 220–260 bar, allows the deposition of a cobalt film with a very similar relative resistivity of 2.14–1.4 for thicknesses ranging from 160 to 830 nm,[26] whereas the ALD, using bis(*N*,*N*′, diisopropylacetamidinato)cobalt(II) and hydrogen at substrate temperatures of 260–350 °C, allows the attainment of a relative resistivity of 7 with a film thickness of 40 nm.[27] Despite its simplicity, the PSE-CVD allows the growth of similar or improved quality of the cobalt films without using hydrogen reduction at a significantly lower temperature.

Conclusions

In this study, PSE-CVD has been used to grow metallic cobalt and cobalt carbide in a hydrogen-free atmosphere starting from cobalt acetylacetonate. The use of a nickel seed layer increases the growth rate, lowers the deposition temperature, and influences the nature and crystallinity of the obtained films. The effect of the solvent on the nature of the grown material has been investigated.

(1) A methanol precursor solution allows the growth of a film where the dominant crystalline phase is Co$_2$C in the entire investigated temperature range.

(2) An ethanol precursor solution allows the growth of Co$_2$C as a single phase at 205–230 °C and a poorly crystalline metallic cobalt above 290 °C.

(3) An *n*-propanol precursor solution allows the growth of a mixture of cobalt carbide and metallic cobalt below 250 °C, while crystalline metallic cobalt with near-bulk electrical resistivity was obtained above 250 °C.

Acknowledgment. One of the authors (P.A.P.) acknowledges a Fellowship of the Alexander von Humboldt (AvH) Foundation for his postdoctoral stay in Germany. The authors are indebted to Prof. K. Kohse-Höinghaus for her helpful discussion.

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