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## Full Paper

**CVD of Metals Using Alcohols and Metal Acetylacetonates, Part II: Role of Solvent and Characterization of Metal Films Made by Pulsed Spray Evaporation CVD\*\***

By Peter Antony Premkumar, Naoufal Bahlawane,\* Günter Reiss, and Katharina Kohse-Höinghaus

Starting from their corresponding acetylacetonate complexes, nickel, copper, and cobalt thin films are deposited in a hydrogen-free atmosphere using CVD. The investigated pulsed spray evaporation (PSE) CVD process uses precursors dissolved in an organic solvent as the feedstock. This paper reports on the major role of the solvent for the growth of metal films. Alcohol solvents such as methanol, ethanol, and *n*-propanol enabled the growth of metallic films, while nonalcohol solvents such as tetrahydrofuran and *n*-butyl acrylate failed. Higher alcohols tend to result in higher growth rates; however, they present a limited solubility of the acetylacetonate complexes. Metal films grow, starting at 493 K, on glass and other substrates with no incubation time, and the obtained films, with thicknesses below 30 nm, present a smooth morphology. Phase analysis with X-ray diffraction (XRD) reveals the hexagonal polycrystalline structure of Ni and Co, and the cubic structure of Cu.

Keywords: Acetylacetonates, Alcohols, Metal films, Pulsed CVD, SEM, XRD

**1. Introduction**

Metal films and nanostructures are in demand for many technological applications. They are used to conduct electrical signals, as active materials in sensors and catalysis, as reflective and refractive coatings for optical elements, and as protective and decorative films for numerous purposes.<sup>[1–4]</sup> Although CVD is generally seen as a promising metallization method because of its numerous advantages, its widespread use is subject to some limitations with regard to the choice of the precursor molecule. Three classes of precursors have been widely used for the CVD of metals, including (1) inorganic precursors, mainly halides, (2) metal-organic (MO) precursors with the metal bound to elements such as O, N, and S, and (3) organometallic (OM) precursors which exhibit a metal-carbon bond.<sup>[5]</sup> The drawbacks of inorganic precursors include the possible generation of particles and corrosive by-products, as well as halide contamination in the deposited films. The latter two fa-

milies of precursors are preferred because of the wide range of metals that may be obtained. The formal valence state of the metal in the MO and OM precursor complexes influences the deposition result. The metal center in MO complexes and some OM complexes is bound in a high-valence state. Thus, the non-matched use of hydrogen-reduction is essential for the growth of metal films.<sup>[6–9]</sup> Very recently, however, metal films using MO complexes without adding hydrogen were demonstrated, but this was achieved with a plasma technology which uses highly energetic electrons for the scissoring of bonds which cannot normally be cleaved in thermal CVD.<sup>[10,11]</sup> In contrast, the metal center in OM precursors is mostly in its elemental oxidation state. However, OM precursors are typically toxic and highly sensitive to air, moisture, and temperature,<sup>[12,13]</sup> forcing their handling and deposition to be carried out in dry inert gases and glove boxes.<sup>[12]</sup> Furthermore, these precursors are usually costly, which can be a drawback for large-scale manufacturing. The other major disadvantage with OM precursors is the existence of a metal-carbon bond, which may lead to the formation of metal carbides rather than the metals.<sup>[5,14]</sup> Even though hydrogen is not needed to induce metal depositions, substantial carbon incorporation may be noted as a consequence of the ligand decomposition.<sup>[5]</sup> In these cases, better results were obtained in the presence of hydrogen which favors the proper cleavage of the metal-carbon bonds.<sup>[5,15,16]</sup> As far as metal carbonyls are concerned, their use is restricted by gas-phase reactions<sup>[12,17]</sup> and is limited to elements which do not allow surface dissociation of CO.<sup>[5]</sup> Otherwise, films are contaminated with metal carbides, metal oxides, and graphitic carbon.<sup>[5]</sup>

[\*] Dr. N. Bahlawane, Dr. P. Antony Premkumar,  
Prof. K. Kohse-Höinghaus  
Physikalische Chemie I, Fakultät für Chemie, Universität Bielefeld  
Universitätsstr. 25, 33615 Bielefeld (Germany)  
E-mail: naoufal@pc1.uni-bielefeld.de

Prof. Dr. G. Reiss  
Fakultät für Physik, Universität Bielefeld  
Universitätsstr. 25, 33615 Bielefeld (Germany)

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Considering the important role of molecular hydrogen in the deposition of metal by CVD, and the need for safety requirements and handling equipment associated with its use, it is worthwhile finding a suitable substitute for  $H_2$ -reduction for the more stable, less toxic, and less costly high-valence MO complexes to yield metal films.

Alcohols, in the context of being a potential substitute for hazardous hydrogen, have been used in spray pyrolysis at temperatures above 873 K to generate metal particles of Ni and Cu.<sup>[18–20]</sup> Alcohols decompose at these temperatures and produce carbon monoxide and hydrogen which supports the formation of metal particles. Ethanol was also used with polyvinylpyrrolidone to produce Ag, Au, Pd, and Cu nanoparticles by the liquid-phase reduction of their corresponding salts under reflux conditions.<sup>[21]</sup> Procedures exploiting alcohols solely as reducing agents for thin film production by CVD have not been reported to date. An intriguing feature of previous work, however, is the claim that using alcohols as solvents leads to increased growth rates of Cu films from  $Cu(hfac)_2$  ( $hfac$  = hexafluoroacetylacetonate) by enhancing the rate of mass transport and intrinsic reaction kinetics.<sup>[22]</sup> Zheng et al.<sup>[23]</sup> have proposed that alcohols can serve as co-reactants to supply the H atoms needed for the reduction of  $Cu(hfac)_2$  during plasma-assisted CVD. Very recently, a novel two-step method has been proposed,<sup>[24]</sup> comprising the deposition of an oxide layer in the first step, followed by its reduction, leading to the formation of Cu films. In this work, an ethanol/water mixture was used as an additive for the former, and ethanol for the latter, step. The formed  $Cu/CuO_2$  in the oxidation step is thought to induce catalytic dehydrogenation of ethanol, producing hydrogen radicals that then reduce  $Cu_2O$  to copper.

The present paper is the second in a series which discusses a novel strategy for metal film production with the exclusive use of alcohols as reducing agents and metal acetylacetonates as the precursors.<sup>[25,26]</sup> The first part, devoted to the successful demonstration of Ni, Cu, and Co films in PSECVD,<sup>[26]</sup> has presented the optimization of the process itself as a function of delivery and deposition parameters. Here, the use of cost-effective, metal-organic complexes like acetylacetonates, while avoiding hydrogen addition, makes the technology simple, inexpensive, poses less severe safety constraints, and enables the recycling of the reducing agent. The present paper will address the importance of alcohols for the growth of metal films in conjunction with their morphological and microstructural characterization.

## 2. Results and Discussion

### 2.1. Influence of Solvents on the Growth of Metal Films

This investigation was performed to explore the reducing ability of alcohols in comparison to non-alcoholic solvents. Depositions were carried via PSECVD using the process parameters defined in the optimization study, viz, a pulse

width of 25 ms, a pulsing frequency of 1 Hz, 5 mM concentration of precursor feedstock, 45 mbar deposition pressure, and 1 slm of nitrogen carrier gas.<sup>[26]</sup> Figure 1 represents the temperature-dependent growth rate of Ni films on glass using ethanol or *n*-butyl acrylate as solvents. These results show clearly that nickel films grow only when ethanol was used as the solvent, and that no appreciable growth occurs with *n*-butyl acrylate. Although not presented here, results showed that other non-alcoholic solvents, such as tetrahydrofuran (THF), were unsuccessful since no nickel film was grown.

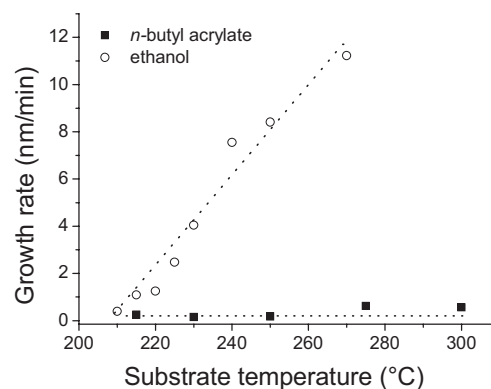


Fig.1. Effect of solvents on the growth rate of Ni films at various substrate temperatures.

Evidence for the formation of Ni films only in connection with the reducing ability of ethanol was obtained from further investigations which attempted to deposit Ni films by alternated delivery of  $Ni(acac)_3/n$ -butyl acrylate feedstock and pure ethanol. The growth of Ni films under these conditions confirms the fact that ethanol plays a major role in the growth of nickel thin films. These results are in agreement with those of Maruyama and Tago<sup>[6]</sup> who observed that nickel films do not form in an inert atmosphere from nickel acetylacetonate.

The effect of the solvent was also investigated for the growth of Cu films as a function of the temperature, and has been reported elsewhere.<sup>[25]</sup> The growth rate of Cu films using methanol increases linearly with temperature, whereas no films were grown with THF as the solvent in the temperature range 590–690 K. Films obtained using methanol usually exhibited the typical red color of copper, while a non-homogenous green thin condensate was observed with THF. This is a direct demonstration of the reducing ability of alcohols, here methanol, in copper film formation. Substitution of methanol with a longer-chain alcohol such as ethanol leads to a slight enhancement in the growth rate, at 673 K, to reach  $1.2 \text{ nm min}^{-1}$  instead of  $1 \text{ nm min}^{-1}$  for methanol. However, the solubility of  $Cu(acac)_3$  in ethanol is relatively low. The precursor recrystallizes upon prolonged use, which leads to the blockage of the spray nozzle and limits its usefulness to low precursor concentrations in the feedstock. Hence, methanol,

in which  $\text{Cu}(\text{acac})_2$  dissolves freely, was chosen as the solvent and reducing agent for further investigations. No difference was observed concerning appearance and microstructure of the deposited copper films using either of the alcoholic solvents.

Figure 2 shows the growth kinetics of cobalt using THF and various alcoholic solvents at a substrate temperature of 600 K. These experiments again confirm the reducing ability of alcohols. The resulting thickness of Co films increases linearly with time using methanol, ethanol, and *n*-propanol solvents, whereas no growth was observed with THF. The

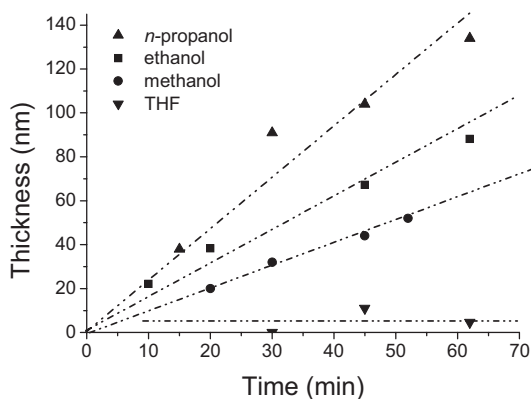


Fig. 2. Influence of solvents on the growth kinetics of Co films at a substrate temperature of 600 K.

growth of cobalt was also shown to occur without incubation time for all investigated alcohol solvents. Furthermore, it was noticed that the growth rate increased with the length of the alkyl chain of the selected alcohol molecule. Even though the growth rate is lower than for *n*-propanol, ethanol was preferred because of safety and availability considerations. The growth of metallic cobalt films from  $\text{Co}(\text{acac})_2$  was enabled by the reducing ability of alcohols, bearing in mind that other researchers have reported that Co metal film deposition using high-valence, metal-organic complexes like  $\text{Co}(\text{acac})_2$  and its derivatives is only possible in the presence of hydrogen.<sup>[7,8,27]</sup>

The positive effect of alcohols on the growth of Ni, Co, and Cu can be attributed either to their reaction with the precursor at the deposition temperature, or to their catalytic decomposition on the surface of the formed metallic layer. This decomposition is expected to form CO/CO<sub>2</sub> in addition to surface hydrogen which might facilitate the decomposition of the precursor. Further surface-based analyses should be performed to elucidate the role of alcohols in the growth of metals.

## 2.2. Structural Analysis of Metal Films

The structure characterization did not reveal any noticeable differences between films deposited using different alcohol solvents, so only results corresponding to the most

promising solvents are presented here. Figure 3 shows the typical XRD pattern of the obtained Ni and Cu films on glass, and Co films on SiC substrates. In spite of several substrates being used for the deposition, including stainless steel, silicon, and silicon carbide, glass was usually chosen for the analysis because of its amorphous nature. In the case of Co films, background peaks due to the SiC substrate were subtracted for clarity. The diffraction peaks cor-

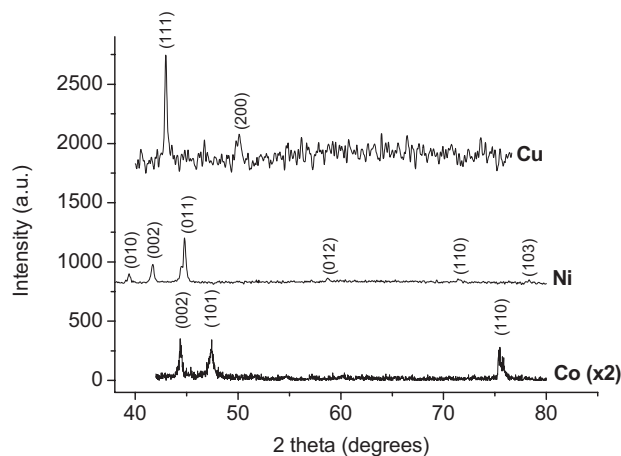


Fig. 3. XRD patterns of the obtained metal films. Co: 800 nm and Ni: 135 nm, using ethanol precursor solutions, and Cu: 65 nm using a methanol precursor solution.

responding to (010), (002), (011), (012), (110), and (103) of the hexagonal polycrystalline structure [PDF. No. 45-1027] were identified for the grown nickel films. No reflections due to oxide or carbide could be identified, and the mean crystallite size was calculated to be 60 nm from widths of the (010) and (002) peaks using the Scherrer equation.

The diffraction peaks in the Cu films correspond to polycrystalline cubic structure [PDF. No. 04-0836] with a crystallite size of 75 nm. The performed diffraction analysis excludes the presence of crystalline CuO and Cu<sub>2</sub>O phases. Comparing the relative peak intensities with those of the polycrystalline reference reveals the occurrence of a preferred (111) orientation in the deposited films. As this preferred orientation is known to prevent electro-migration of the metal layer, the Cu films deposited with the present technique may have the potential to deter failures caused by electro-migration.<sup>[24]</sup> The synthesis of phase-pure Cu films as demonstrated here, with no signatures from oxide or carbide, using exclusively alcohols as reducing agents in the PSECD process is the first of its kind. In a previous study, Lee et al.<sup>[28]</sup> proposed a mechanism for a two-step method for Cu film production from  $\text{Cu}(\text{hfac})_2 \cdot x\text{H}_2\text{O}$ , and reported that, with the addition of pure ethanol, the Cu<sub>2</sub>O+Cu film was not reduced to Cu film.

The XRD analysis of deposited Co films reveals its hexagonal structure [PDF. No. 05-0727] without signatures from oxides and carbides. The average crystallite size calculated from the (002), (101), and (110) reflections was found



to be 45 nm. The identification of the phase-pure hexagonal close packed (hcp) structure for Co, in the present case, is striking since using the same precursor by nebulized spray pyrolysis, a mixture of face-centered cubic (fcc) and hcp phases was observed at a temperature similar to that adopted for the present investigations.<sup>[29]</sup> It is worth mentioning here that such a difference in phases formed for Co can arise from the choice of different substrates, from the presence of seeding layer, observed grain sizes, and thickness of the Co films, as well as from difference in deposition temperature.<sup>[1]</sup>

### 2.3. Microstructural Analysis of Metal Films

Figure 4 shows surface scanning electron microscope (SEM) images of deposited nickel and copper films of different thicknesses on glass. All films exhibited similar morphologies. Films with lower thicknesses (Fig. 4a and c)

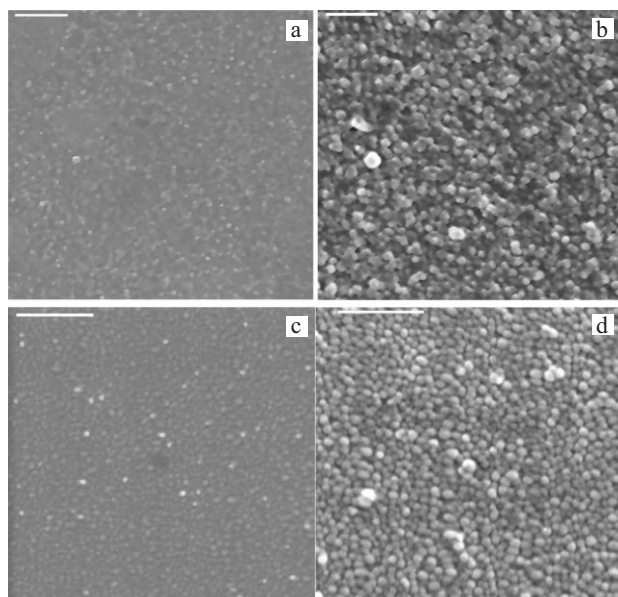


Fig. 4. SEM images of Ni and Cu films on glass with various thicknesses. a) 32 nm and b) 60 nm thick Ni films; c) 30 nm and d) 60 nm thick Cu films. (Scale bars = 1  $\mu$ m).

were smooth and continuous, while relatively larger grains were observed for thick films (Fig. 4b and d). The morphology of all films was identical throughout the film area, and was uniform without any apparent cracks. The smooth, continuous, and uniform grain size morphology demonstrated herein for Ni and Cu films of thicknesses near or below 30 nm can be of interest for magnetic and electrical applications.

The morphology of Co films deposited on SiC is given in Figure 5. Figure 5a and b show 35 nm and 800 nm thick Co films, respectively, using ethanol as the reducing agent. The change of grain morphology with thickness is clearly ob-

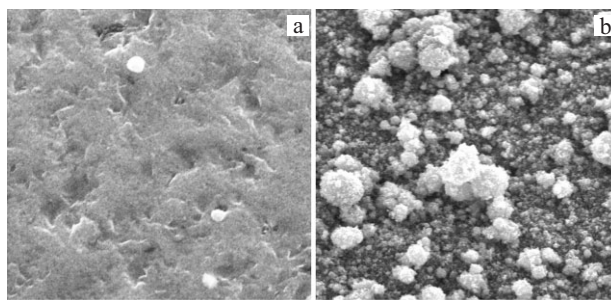


Fig. 5. Surface morphology of cobalt films deposited at 600 K on silicon carbide substrates with a thickness of a) 35 nm and b) 800 nm using an ethanol precursor solution. (Scale bars = 10  $\mu$ m).

served from the micrographs. The thinner films (Fig. 5a) are extremely smooth and resemble the morphology of the SiC substrate, while the thicker ones (Fig. 5b) are rough and form agglomerates of tiny crystallites.

The morphology of the metal films was found to have an impact on their electrical resistivity. Near bulk resistivity values were obtained for Ni and Cu films of 80 nm and 230 nm thickness, respectively, corresponding to their smoothness, whereas the observed resistivity of cobalt deviated from that of the bulk, due to the increased roughness and poorer connectivity. The relatively high resistivity of cobalt films was also observed despite the use of a supplementary flow of hydrogen to enhance the reduction.<sup>[26]</sup>

### 3. Conclusions

The growth of transition metal films employing exclusively alcohols as the reducing agents was developed using PSECVD. Investigations confirmed the growth of metal films using metal acetylacetonates with alcohols, but not when THF or *n*-butyl acrylate were used as solvents. XRD analysis revealed the presence of polycrystalline metal phases and excludes that of their corresponding oxides and carbides. The morphologies of Ni and Cu films on glass were found to be smooth and uniform whereas a rougher structure was observed for cobalt films deposited on silicon carbide. Smooth and shiny surfaces were obtained preferentially for films with thicknesses between 25 and 60 nm, which makes the process promising for nanoscale applications.

### 4. Experimental

The schematic set-up of the PSECVD apparatus for the growth of metal films, as well as the operational procedures to obtain them, has been described elsewhere [26]. Except for the investigations of the role that the solvents play in the growth of metal films at various temperatures, experiments were carried out for Ni, Co, and Cu films at a substrate temperature of 523, 600, and 673 K, respectively. XRD of the deposited films was carried out with an X'Pert pro MRD, Philips X-ray powder diffraction system using Cu K $\alpha$  radiation in  $\theta$ -2 $\theta$  geometry. The surface morphology of the films was ob-

served using a Philips XL-30 ESEM scanning microscope, while the film thickness was estimated gravimetrically.

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