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Nickel Thin Films Grown by MOCVD Using Ni(dm_g)₂ as Precursor

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Abstract: The aim of this study was (i) to investigate alternatives to the very toxic Ni(CO)₄, (ii) optimization of the parameters for Ni film growth, and (iii) characterization of the film morphology. The thermal behaviour of the precursors bis(dimethylglyoximato)Ni(II), [Ni(dm_g)₂], bis(2,2,6,6-tetramethyl-3,5-heptandionato)Ni(II), [Ni(thd)₂], N,N'-ethylenebis(2,4-pentandion-iminoato)Ni(II), [Ni(enacac)], and bis(2-amino-pent-2-en-4-onato)Ni(II), [Ni(apo)₂] were investigated in a model reactor. Furthermore, the evaporation rates of these compounds were determined. Metallic nickel films were obtained using Ni(dm_g)₂ as precursor. The deposition was carried out in a horizontal quartz reactor at reduced pressure in a hydrogen/helium atmosphere. The films were analysed by profilometry, X-ray diffraction, atomic force microscopy (AFM), four-point resistivity measurements and electron spectroscopy for chemical analysis (ESCA). Comparison of the AFM and ESCA data with the electrical resistances resulted in a two layer film model.

1. INTRODUCTION

Nickel and nickel alloys are currently being investigated in several research fields due to their promising properties. Ni is known to be an excellent catalyst for many processes. The catalytical formation of highly oriented graphite on nickel was recently investigated by TEM[1]. In the fabrication of III-V semiconductor devices nickel gallides and aluminides could play an important role in the future. These intermetallic compounds are thermodynamically stable with respect to the III-V semiconductors preventing chemical reactions at the metal/semiconductor interface[2, 3]. Lanthanide-Ni systems have been studied for many years for their hydrogen storage capability. They can store and release hydrogen reversibly when cycled electrochemically or under hydrogen pressurization[4-6].

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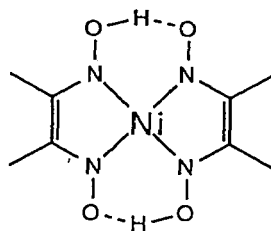
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Thin metallic films of high purity can be prepared by Metal-Organic Chemical Vapor Deposition (MOCVD). The advantages of MOCVD are conformal step coverage, high throughput and low-cost. In the case of Ni only a few reports exist. The deposition of Ni using $\text{Ni}(\text{CO})_4$ was first discovered by Mond over a hundred years ago[7]. The high toxicity of $\text{Ni}(\text{CO})_4$ is the major disadvantage of this precursor[8]. Alternative precursors are the cyclopentadienides of Ni, $\text{Ni}(\text{Cp})_2$ and its methyl derivative $\text{Ni}(\text{MeCp})_2$ [2, 9, 10].

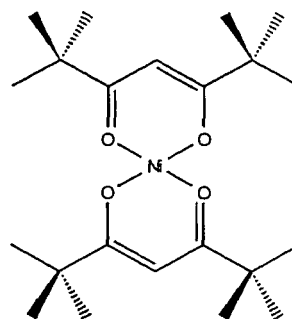
In this work, we report growth experiments of nickel films using bis(dimethylglyoximate)Ni(II), $\text{Ni}(\text{dmg})_2$, in a horizontal MOCVD reactor. Furthermore, we present the evaporation rates of $\text{Ni}(\text{dmg})_2$, bis(2,2,6,6-tetramethyl-3,5-heptandionato)Ni(II), $\text{Ni}(\text{thd})_2$, N,N'-ethylenebis(2,4-pentandion-iminoato)Ni(II), $\text{Ni}(\text{enacac})$, and bis(2-amino-pent-2-en-4-onato)Ni(II), $\text{Ni}(\text{apo})_2$. These precursors were also used in a model reactor to investigate the influence of the nickel film on the decomposition process[11].

Structures of the precursors:

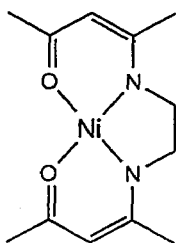
Ni(dmg)₂:



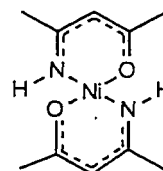
Ni(thd)₂:



Ni(enacac):



Ni(apo)₂:



2. EXPERIMENTAL

The horizontal hot-wall quartz reactor used was described earlier[12]. The precursor $\text{Ni}(\text{dmg})_2$ was synthesized according to *Gmelins Handbuch der Anorganischen Chemie*[13]. $\text{Ni}(\text{thd})_2$, $\text{Ni}(\text{enacac})$, and $\text{Ni}(\text{apo})_2$ were prepared following literature procedures[14, 15].

The precursors were investigated in a model reactor shown in Figure 1. The compounds were evaporated (temperatures: Ni(dmg)₂ = 240°C, Ni(thd)₂ = 150°C, and Ni(enacac) = 170°C) and transported to the reactor (p = 20mbar) by the helium carrier gas (flow = 20ml/min). The temperature in the reactor was increased stepwise and at a certain temperature, T₁, signals of the decomposition products could be observed in the mass spectrometer. The temperature was further increased to about 100°C above T₁ and then decreased. A second temperature, T₂, was obtained during cooling where no signals were observed in the MS.

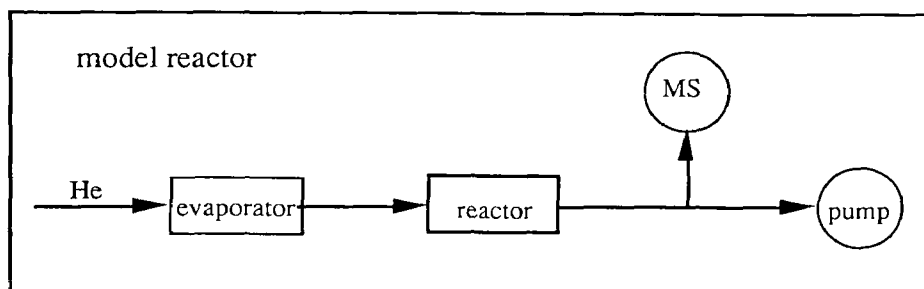


Figure 1: Model Reactor for the Investigation of the Thermal Properties of the Precursors (He Atmosphere).

The experimental conditions of the film growth using Ni(dmg)₂ in the MOCVD apparatus are summarized in Table 1. The evaporation rate was determined by weight loss of the ceramic boat in the system. The films were investigated by profilometry, X-ray diffraction (XRD), atomic force microscopy (AFM), four-point resistivity measurements and electron spectroscopy for chemical analysis (ESCA).

Table 1: Experimental Conditions used for the Deposition of Ni films using Ni(dmg)₂ as Precursor.

substrate	quartz, Si(100)
carrier gas; gas flow	helium; 66 sccm
reaction gas; gas flow	hydrogen; 66 sccm
pressure	20 ± 2 mbar
evaporation temperature	220-250°C
substrate temperature	300 -690°C
time	15 - 60min

3. RESULTS AND DISCUSSION

3.1. Investigations in the model reactor

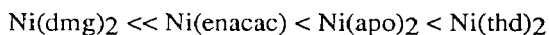
All compounds showed a similar behaviour in the model reactor. The film prepared during deposition influenced the decomposition of the Ni precursor. The decomposition temperatures T₂ were lower than T₁:

	T ₁ (heating)	T ₂ (cooling)
Ni(dmg) ₂ :	540°C	420°C
Ni(thd) ₂ :	430°C	370°C
Ni(enacac):	640°C	620°C

We explain these results with a catalytic effect of the solid film material. This effect may also cause problems in the reproducibility of the film growth experiments (see discussion below!).

3.2. Evaporation rates

In Figure 2 it can be seen that the precursors have different volatilities:



Ni(dmg)_2 has a chelate structure with polar O-H-O groups. These groups are probably responsible for its low volatility. The "closed" structure in the case of Ni(thd)_2 , formed by the big nonpolar *tert.*-butyl groups, leads to a much better volatility. Ni(enacac) and Ni(apo)_2 have similar structures. They belong to the β -keto-iminoate where O and N are coordinated to the metal center. However, their volatilities are slightly lower compared to the volatility of Ni(thd)_2 . Obviously, the replacement of O by N leads to this result which was also observed in Cu complexes[16].

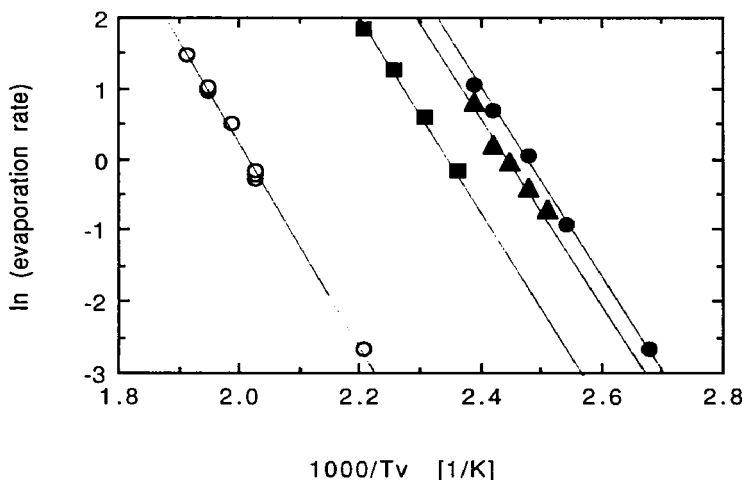


Figure 2: Arrhenius Plot of the Evaporation Rates of Ni(dmg)_2 (open circles), Ni(thd)_2 (filled circles), Ni(enacac) (filled squares), and Ni(apo)_2 (filled triangles).

3.3. Results of film growth experiments

It was impossible to get good results from the precursors Ni(thd)_2 , Ni(enacac) , and Ni(apo)_2 using the following conditions:

precursor	T_v	T_s
Ni(thd)_2	140°C	300 - 570°C
Ni(enacac)	150 - 180°C	500 - 635°C
Ni(apo)_2	125 - 145°C	500 - 600°C

The films were black, amorphous and nonconducting.

Ni(dmg)_2 resulted in mirror-like, conducting films. The deposition time, the evaporation temperature, T_v , and the substrate temperature, T_s , were systematically varied to obtain the best deposition parameters.

T_V was varied between 220 - 250°C ($T_S = 450^\circ\text{C}$) leading to an exponential increase in the film thickness. However, at a temperature of 250°C the precursor was partially decomposed in the vessel. A decrease in the evaporation rate was observed at higher deposition times (Figure 3a). The colour of the precursor changed during the experiment indicating a thermally induced reaction. It was not possible to decrease the evaporation temperature below 240°C due to the low volatility of $\text{Ni}(\text{dmg})_2$. Although, we obtained a high decomposition temperature of 540°C in the model reactor (He) the atmosphere is different in the film growth apparatus (He and H_2). Unfortunately, no further data are available at the moment from Thermogravimetric Analysis.

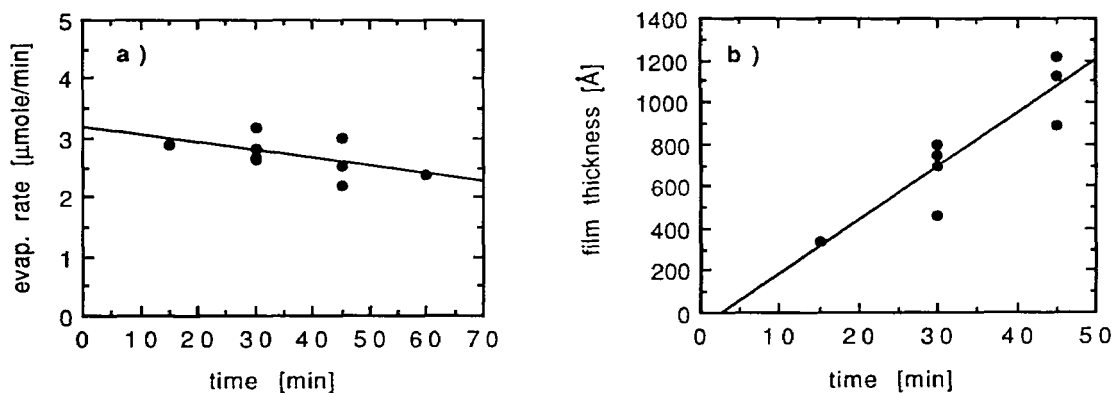


Figure 3: Evaporation Rate (a) and Film Thickness (b) as a Function of the Deposition Time; $T_V = 240^\circ\text{C}$.

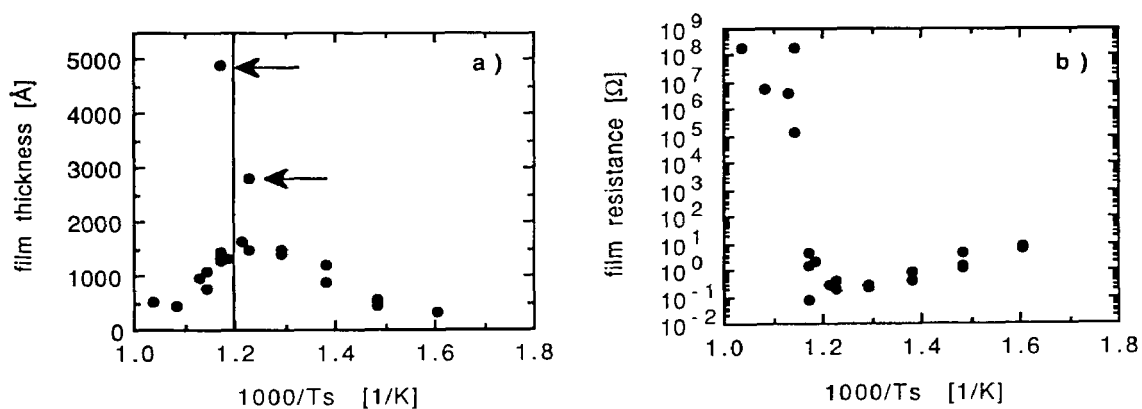


Figure 4: Influence of the Substrate Temperature on the Film Thickness (a) and Film Resistance (b); Deposition Time = 45min, $T_V = 240^\circ\text{C}$.

In Figure 3b), it can be seen that the deposition starts after about 3min. This delay is caused by the experimental procedure. The precursor vessel was placed into the preheated reactor. Then the reactor was

closed and the gas flows and pressure were adjusted. Most likely, the heating up of the precursor is the cause for the delay in the deposition.

In Figure 4a) two regimes can be distinguished. An increase in the growth at low temperatures can be explained by the kinetic control of the surface reaction. At higher temperatures no diffusion controlled region was observed. The growth decreased after a maximum at about 550°C (marked in Figure 4a) with a vertical line). Side reactions on the hot reactor wall are dominating in this temperature region. Therefore the precursor concentration at the substrate was decreased leading to a lower growth rate. Some experiments exhibited nonreproducible results (marked in Figure 4a) by arrows). The films were much thicker compared to other films in this temperature region. Our investigations in the model reactor resulted in the proposal of a catalytic effect which may be the reason for these findings.

The film resistance was determined by four-point resistivity measurements. In the kinetic controlled part of the film growth the resistance decreased with increasing film thickness. The minimum of the values are found at about 550°C, similar to the maximum film thickness (see Figure 4a). The films grown at higher temperatures showed rather bad resistances which may be explained by incorporation of C, O, or N from the ligand.

The structure of the films was investigated by X-ray diffraction. The X-ray diffraction patterns exhibited sharp diffraction peaks, characteristic for polycrystalline Ni. A slight preferential orientation in the [111] direction was observed. The random ratio of [111]/[200] is 2.38 whereas we obtained ratios in the range of 6 - 7.

AFM of the films showed that the surface consists of grains with a diameter of 1000Å in V 26, 1000 - 2000Å in V 23, 4000 - 6000Å in V 40, and 2000 - 4000Å in V 27.

. From the AFM measurements we obtained the surface roughness, R_a , and Z_{avg} (average of all measured Z values where Z is the measured height perpendicular to the surface) of four films prepared at different substrate temperatures (see Table 2).

Table 2: Results of AFM Measurements of Ni Films (growth conditions: time = 45min; $T_V = 240^\circ\text{C}$; AFM conditions: surface area = $2 \times 2 \mu\text{m}^2$; film thickness d was measured by Profilometry).

film no. (T_S [$^\circ\text{C}$])	R [Ω]	d [\AA]	R_a [\AA]	Z_{avg} [\AA]	d - Z_{avg} [\AA]
V 26 (350)	7	325 ± 150	40	140	185
V 23 (450)	0.43	885 ± 100	150	490	395
V 40 (610)	3.7×10^6	955 ± 50	210	820	135
V 27 (580)	0.081	4910 ± 300	700	1900	3010

Assuming three-dimensional clusters in the beginning of the film growth and a low mobility of Ni adatoms on the surface the clusters are growing to macroscopic grains independent of each other. The grains grow together at a certain point, however, the rough surface created during the first steps of film growth is not flattened during the growth process. With this simple model the surface roughness should increase with increasing film thickness. The AFM measurements resulted in these findings (see Table 2).

Films of experiment V 26 and V 40 have similar film thicknesses, however, T_S is higher in V 40. In V 40, Z_{avg} is about 820Å and in the range of the film thickness. The high electrical resistance of this film can be

explained by a columnar growth of badly connected grains. In V 23 the grains must have stronger connections resulting in a good conductivity. In V 26 the film was grown at a T_s of 350°C . In this case the low electrical resistance is mainly caused by the low film thickness of 325\AA . The film V 27 exhibited the best electrical resistance and, therefore, the film must consist of well connected grains with low grain-boundary resistances. Unfortunately, the good result ($d = 4910\text{\AA}$ and $R = 0.081\Omega!$) of this experiment could not be verified. Films grown in this temperature region usually have thicknesses below 1000\AA (see V 40).

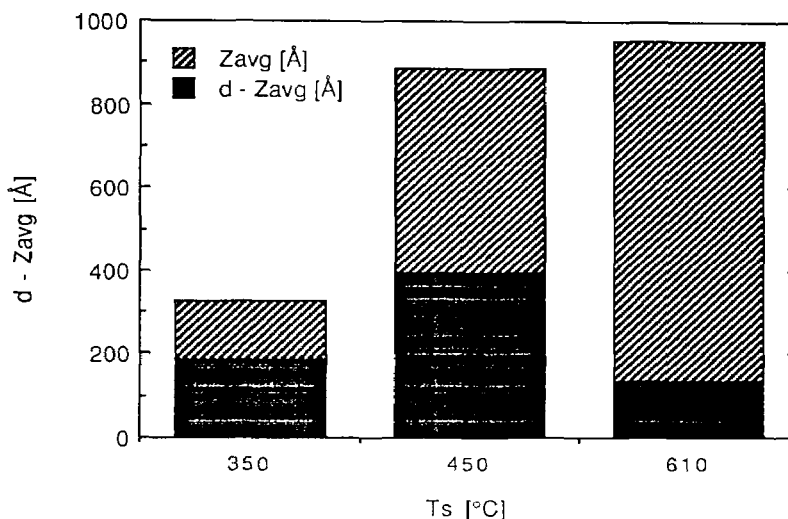


Figure 5: AFM Results of Ni Films. Two Layer Model of Films grown at different Substrate Temperatures.

Similar to recent results obtained in Cu film growth[17] we propose a two layer film structure of the Ni films prepared in this study. The films consist of a relatively compact "bulk film" and a porous overlayer. These two layers are represented in Figure 5 by $d - Z_{avg}$ and Z_{avg} , respectively. Higher substrate temperatures lead to thicker porous layers. It is known that higher temperatures favour the "dewetting phenomena" observed in the growth of metals on insulators[17].

The samples investigated by AFM were also investigated by ESCA. This analysis showed that the films consisted of pure Ni. The impurities (O, N, and C) were in the range of 1% (detection limit of ESCA!). However, the interpretation of the depth profiling was difficult because no clear interface to the substrate could be observed. This can be explained by a porous structure. Therefore, the bad electrical properties in some Ni films were mainly caused by the film morphology rather than incorporation of ligand atoms.

4. CONCLUSION

It was shown that $\text{Ni}(\text{dmg})_2$ is a suitable precursor for the growth of nickel thin films by MOCVD. The films were metallic and mirror-like. The growth depends on the evaporation and substrate temperature. The films consisted of grains with a grain size of $2000 - 5000\text{\AA}$. The impurities were found to be in the range of

1% and the electrical properties were governed by the film morphology. The film structure can be described with a two layer model: a relatively compact "bulk film" and a porous overlayer.

The thermal stability of the precursor was analyzed in a model reactor under an atmosphere of helium. The decomposition products were analyzed in-situ by a mass spectrometer. The temperature at which decomposition could be observed was higher in the non-coated reactor indicating a catalytic influence of the deposited film on the decomposition of the Ni precursor.

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