

Single source MOCVD precursors for $RNiO_3$ ($R = \text{rare earth metal}$) thin film deposition

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New volatile heterobimetallic complexes $[Ni(\text{acacen})R(\text{pta})_3]$ ($R = \text{La, Nd, Sm}$) were tested for $RNiO_3$ thin film deposition by MOCVD. The precursors have been prepared from two individual metal complexes. $Ni(\text{acacen})$ behaves as double faced bidentate oxygen donor Lewis Bases and react with Lewis Acids – $R(\text{piv})_3$, forming stable heteronuclear complexes. The prepared precursors congruently sublime in the temperature range 200–220 °C (figure 1).

The oxide films were deposited by single source metal-organic chemical vapour deposition (MOCVD). The experimental setup, equipped with band flash evaporator and hot wall vertical reactor (stagnation flow type), is described elsewhere (1). Single crystal (001)-oriented substrates with perovskite related structure were used: $SrTiO_3$ for La-Ni-O films; $LaAlO_3$ and $CaGdAlO_4$ for Nd and Sm containing films. Following deposition conditions were used: $P_{\text{total}} = 13 \text{ mbar}$, $P_{O_2} = 6.5 \text{ mbar}$, evaporation temperature 250 °C. 5 different deposition temperatures in the range 700 – 900 °C were tested for La-Ni-O films growth, while Nd and Sm containing films were deposited only at 750 and 850 °C. After the deposition the films were oxidized at $P_{O_2} = 1 \text{ bar}$ at deposition temperature for 20 min (the films grown at the temperature higher than 800 °C were oxidized at 800 °C).

XRD patterns and the composition determined by EDX of the films grown from $[Ni(\text{acacen})La(\text{pta})_3]$ at different temperatures are given in the figure 2. As could be seen the films deposited at 700 and 750 °C consist of NiO and LaOF. The perovskite phase $LaNiO_3$ forms in the films grown at 800 – 900 °C. The amount of perovskite increases with increasing of the deposition temperature while the amount of LaOF diminishes. The elemental composition of the films grown at 750–900 °C is almost constant and equals $La/Ni \sim 0.65$. It differs very much from the desired ratio 1:1. The difference could be explained by the decomposition of the bimetallic precursor in the gas phase. In spite of congruent sublimation of bimetallic compound and its possible existence in the gas phase as single molecule at intermediate temperature (200 – 400 °C) it is very likely that the bimetallic compound decomposes in the hot reactor zone before reaching the substrate surface. The obtained $LaNiO_3$ films have typical for this material transport properties. The peculiarities of the phase and elemental composition of the films containing Nd and Sm were similar to the films La-Ni-O.

As we found out the main disadvantages of these new single source precursors are fluorine contamination at low deposition temperatures and the dissociation into parent individual complexes during transport to substrate.

REFERENCES

1. M.A. Novozhilov, A.R. Kaul, O.Yu. Gorbenko, I.E. Graboy, G. Wahl, U. Krause, J. Phys. IV, **9**, Pr8-629 (1999).

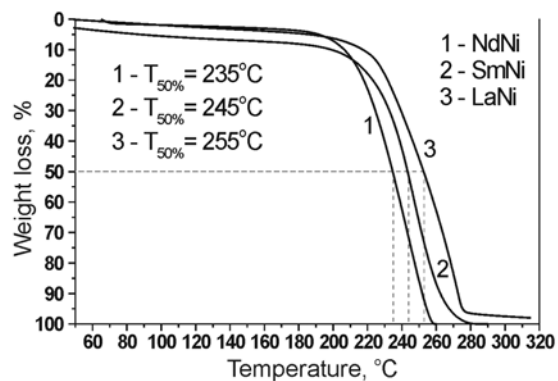


Figure 1. TG curves under vacuum (0.01 mbar) for heterobimetallic complexes $[Ni(\text{acacen})R(\text{pta})_3]$.

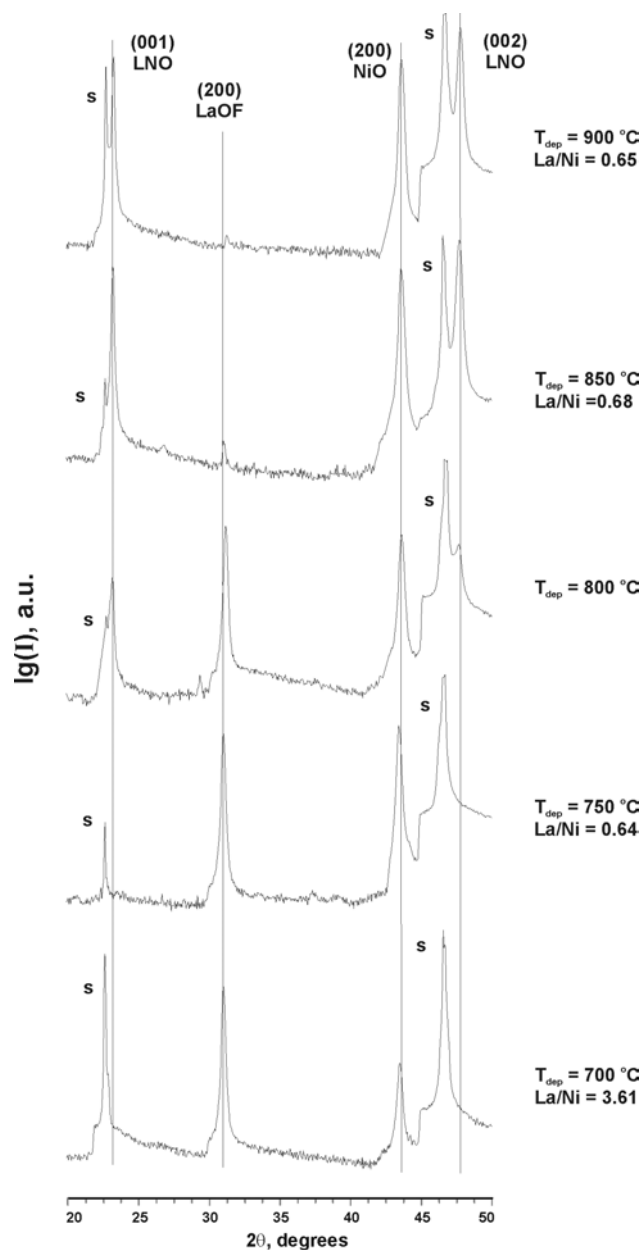


Figure 2. XRD patterns ($CuK\alpha$ radiation) of the films grown from $[Ni(\text{acacen})La(\text{pta})_3]$ at different temperatures. s – reflections of the substrate ($SrTiO_3$), LNO – $LaNiO_3$. The composition of the films La/Ni is determined by EDX.