Formation of Metal Oxides Thin Films: A Thermodynamic Analysis

HECTOR M. HDZ-GARCIA, ARTURO I. MARTINEZ
Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (Cinvestav-Saltillo), Carr. Saltillo-Monterrey Km. 13 C.P. 25900, Ramos Arizpe.
MEXICO
hghm70@hotmail.com , arturo.martinez@cinvestav.edu.mx

Abstract: - An exhaustive thermodynamic analysis for the chemical reactions involved in preparation of different metal oxide films is considered in this work. The metal oxides studied in this paper are different classical transparent conducting metal oxides. The thermodynamic analysis realized in this work will facilitate the selection more adequate precursor for the preparation of metal oxide thin films.

Key-Words: - Transparent conducting thin films, chemical vapor deposition, spray pyrolysis

1 Introduction
Metal oxide thin films are used in many applications including solar energy devices, catalytic and photocatalytic processes, light emitting devices, fuel cells, etc [1-4]. These metal oxide films are prepared by a great variety of methods such as sputtering, pulsed laser deposition, chemical vapor deposition (CVD) [2], sol-gel [3] and spray pyrolysis (SPy) [4]. The last three methods are considered as chemical, because one or a series of chemical reaction have to take place in order to prepare an oxide thin film. A lot of different precursors have been used for the preparation of metal oxide thin films through the chemical methods. However, in the literature there is a lack of a thermodynamic analysis for the selection of an adequate precursor for obtaining a desired metal oxide film.

In this work, an exhaustive thermodynamic analysis for the chemical reactions involved in preparation of different metal oxide films is carried out. The metal oxides considered through this paper are different transparent conducting metal oxides; it is because of both their great variety of applications, and the importance of the chemical methods in their preparation.

2 Problem Formulation
In order to form a metal oxide thin film, the chemical methods such as CVD and SPy are based on the thermal decomposition of a metal precursor. The following equation can describe the formation of a metal oxide thin film starting from its precursor (\(MA_x\)):

\[ MA_x + H_2O \rightarrow MO_y + xHA_{(g)} \]  (1)

Where \(M\) is a metal, and \(A\) is an anion. In order to select an adequate precursor, a thermodynamic analysis can be conducted using a software package such as HSC 6.12 by Autokumpu. The probability of the metal oxide formation starting from different precursors could be expressed in terms of the reaction constant \((K)\). At equilibrium, when \(K\) is much larger than 1, the concentration of products is far greater than the reactants. Also, the enthalpy \((\Delta H^\circ)\) can be calculated through this package; if a positive enthalpy value is found, the reaction is endothermic. Typical formation reactions of metal oxide thin films are endothermic, because a certain amount of energy (temperature) is required for the formation of the film.

3 Results and discussion
For the synthesis of tin oxide films, some precursors have been selected in the literature [1-4]. For our calculations, the \(SnCl_4\), \(Sn(NO_3)_4\) have been considered in the reaction like (1). For the formation of \(SnO_2\), when tin (II) chloride is selected the oxygen should be as a reactant, because a change of oxidation state from (II) to (IV) is exhibited; the reaction is as follows:

\[ 0.5O_2(g) + SnCl_2 + H_2O(l) \rightarrow SnO_2 + 2HCl(g) \]  \(2\)

For reactions where the oxidation state does not change, the reaction is like equation (1); for example:

\[ SnCl_2(g) + 2H_2O(g) \rightarrow SnO_2 + 4HCl(g) \]  \(3\)

Figure 1 shows the \(\log(K)\) vs temperature (\(T\)) behavior. When \(SnCl_2\) is considered, \(SnO_2\) can only be obtained at temperatures higher than 510 °C. It is important when temperature sensitive substrates are
considered for the preparation of \( \text{SnO}_2 \) films. It has been reported that tin oxide films from the stannous precursor exhibit poor optoelectronic properties; comparable properties can only be reached when high \( \text{HCl} \) is added to the starting solution \([5]\). For \( \text{SnCl}_4 \) and \( \text{Sn(NO}_3)_2 \) precursors, the formation of \( \text{SnO}_2 \) is feasible at \( T \) higher than 100 and 170\(^\circ\)C, respectively. In contrast, the formation of \( \text{SnO}_2 \) from \( \text{Sn(CH}_3\text{COO})_4 \) can be obtained at low temperature, in this case the formation of tin oxide from \( \text{Sn(CH}_3\text{COO})_4 \) can be formulated by two steps; first, the formation of \( \text{Sn(OH)}_4 \), and its subsequent decomposition to \( \text{SnO}_2 \), it can be proposed as follows:

\[
\text{Sn(CH}_3\text{COO})_4 \rightarrow \text{Sn(OH)}_4 + 2\text{C}_2\text{H}_4\text{O}_2 + \text{CO}_2(g) \quad (4)
\]

\[
\text{Sn(OH)}_4 \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O}(g) \quad (5)
\]

Figure 1. Log (\( K \)) vs temperature for different tin precursors.

Starting from tin nitrate (reaction 6), the \( \text{SnO}_2 \) can be formed the temperatures higher than 200 \( ^\circ\)C. In figure 1, it can be observed that log (\( K \)) for tin nitrate growth faster than other precursors (see, Figure 1).

\[
\text{Sn(NO}_3)_2(\text{ia}) + 2\text{H}_2\text{O}(l) \rightarrow \text{SnO}_2 + 4\text{HNO}_3(g) \quad (6)
\]

All the reactions for the formation of tin oxide considered in this work are endothermic, see figure 2. It can be observed that the most endothermic reaction is expected when the tin nitrate is considered; the formation of tin oxide from this precursor can be not adequate because a lot of energy is necessary to growth the thin film.

For the formation of other metal oxide thin films were also considered as is described below. The precursor are \( \text{InCl}_3 \), \( \text{NiCl}_2 \), \( \text{Zn(NO}_3)_2 \), and \( \text{ZnCl}_2 \). The proposed reactions are as following:

\[
2\text{InCl}_3 + 3\text{H}_2\text{O}(l) \rightarrow \text{In}_2\text{O}_3 + 6\text{HCl}(g) \quad (7)
\]

\[
\text{NiCl}_2 + \text{H}_2\text{O}(l) \rightarrow \text{NiO} + 2\text{HCl}(g) \quad (8)
\]

\[
\text{ZnCl}_2 + \text{H}_2\text{O}(l) \rightarrow \text{ZnO} + 2\text{HCl}(g) \quad (9)
\]

\[
\text{Zn(NO}_3)_2 + \text{H}_2\text{O}(l) \rightarrow \text{ZnO} + 2\text{HNO}_3(g) \quad (10)
\]

Figure 2. Enthalpy vs temperature for different tin precursors.

Figure 3 shows that \( \text{ZnO} \) from \( \text{ZnCl}_2 \) can be formed at temperatures higher than 450 \( ^\circ\)C; the constant of reaction is lower than the reaction from \( \text{Zn(NO}_3)_2 \). From these results, this precursor can not be recommended for the synthesis of zinc oxide; this conclusion is similar to experimental results found by other researchers \([6]\). From the temperature point of view, the \( \text{NiCl}_2 \) is an adequate precursor for the

Figure 3. Log (\( K \)) vs temperature for different precursors.
formation of nickel oxide films, because of the films can be obtained at temperatures as low as 230 °C, see figure 3. For the formation of indium oxide films, an adequate precursor can be the \( \text{InCl}_3 \), despite the formation of the oxide can be plausible at temperatures higher than 330 °C, it avoids the use of temperature sensitive substrates, if indium oxide or indium doped tin oxide is expected to deposit on flexible substrates. The selection of other precursors can be more adequate, such as organometallic compounds as in the case of tin oxide described above.

As is shown in the figure 4, all the proposed reactions are endothermic. Chloride precursors show a decrease of the enthalpy of reaction when the temperature is increased; in contrast, when nitrate salts are used an inverse behavior is observed.

![Figure 4. Enthalpy vs temperature for different precursors.](image)

4 Conclusion
The thermodynamic analysis realized in this work facilitates the selection more adequate precursor for the preparation of metal oxide thin films. A more extended thermodynamic analysis is in developing, it will consider more precursors and side reactions that could affect the growth of thin films. Additionally, more complex systems as binary-binary, ternary and quaternary oxides will be considered for this kind of analysis in future works.

Acknowledgements
This work is supported by a kind Conacyt project.

References: