Chapter 2

Single Source Precursors for Semiconducting Metal Oxide–Based Films

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ABSTRACT

Materials possessing interesting properties for current and future everyday products always have a valuable place in the scientific research. Accordingly, semiconductor materials are the foundation of modern electronics. In most of the applications, metal oxide based semiconductors are at present generally useful in the form of thin films. Metal–alkoxo complexes constitute a very important group of precursors for oxide materials. The most common chemical approaches are well described in the literature and the most relevant pathways will be summarized later in this chapter.

INTRODUCTION

Materials possessing interesting properties for current and future everyday products always have a valuable place in the scientific research. Accordingly, semiconductor materials are the foundation of modern electronics. There exists a large variety of semiconductor materials and they are classified according to their nature (inorganic or organic). In the case of inorganic semiconductors, two subclasses can be differentiated: elemental and compound semiconductors. Elemental inorganic semiconductors of group IV such as Silicon (Si) and Diamond are highly valuable due to their high stability and can be classified as excellent thermal conductor mediums.(Sze & Ng, 2006)

Among compound semiconductors, some interesting materials can be found based on combinations of elements such as Titanium dioxide, which is commonly used as pigment and photocatalyst and is classified in group II-VI, commonly named as group of the oxides.(Chen & Mao, 2007; Fujishima & Zhang, 2006) Another promising compound semiconductor of the same group is Zinc oxide (ZnO), which has
a wide variety of applications like UV-LEDs,(Look et al., 2002; Meyer et al., 2004) varistor,(Clarke, 1999) UV-photodetector material,(Monroy, Omnes, & Calle, 2003) or UV-blocker in sunscreens,(Carlos Lizandara-Pueyo et al., 2011) Bismuth oxide (Bi₂O₃) is also a semiconducting material possessing interesting properties as gas sensors(Devi, Manorama, & Rao, 1999) or as an effective UV light photocatalyst. (Heidong, Q. Wei, W. Xiaohong, D. Xianbo, & C. Long, 2007) It is also an important component of several ferroelectric(B. H. Park et al., 1999) multiferroic(Singh, Yang, C.G. Takoudis, & 2009) and superconducting oxide materials. (Michel et al., 1987) In most of the above-mentioned applications, metal oxide based semiconductors are generally used in the form of films. The most common chemistry-based methods to fabricate films are chemical vapor deposition (CVD) or sol-gel techniques. Both techniques usually employ metal-organic compounds of high purity in order to form films with the desired composition and high quality without high input of external energy. (Malik, Afzaal, & O’Brien, 2010)

One approach for the chemical vapor deposition of many metal oxides is to use two or more separate precursors that react individually on the growing film. This procedure makes it difficult to control film stoichiometry and usually high deposition temperatures are required. Also in some cases, toxic or pyrophoric materials are used in the production of the films. An alternative to these materials is to use Single-Source Precursors.(Malik et al., 2010)

The prime example of Single-Source Precursor for oxides was found more than 160 years ago. At that time it was observed that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions yielded a glass-like material, Silicon Dioxide.(Ebelmen, 1846) In the case of metal alkoxide precursors, the advantage to metal oxide materials is the same as in the case of TEOS and SiO₂, the precursors already have metal–oxygen bonds established. Thanks to that, their thermal decomposition can be performed at relatively low temperatures and maintains the metal–oxygen core. The metal oxides derived from alkoxide Single-Source Precursors are highly pure and have specific properties like high hardness, chemical and mechanical resistance, and high temperature stability.

Alkoxides M(OR)ₓ (M = metal cation of valence x; R = alkyl or aryl group) are formed by the replacement of the hydroxylic hydrogen of an alcohol (ROH) by a metal cation. It is also necessary to note that understanding the nature of alkoxide precursors (showing no analogy with, for example, the carbonyl compounds) and a good knowledge of the Inorganic Chemistry in general are very important in applying the new design and synthetic approaches.(L. John & Sobota, 2010)

The different coordination possibilities of the alkoxo ligands are represented in Figure 1. These possibilities are due to three unpaired electrons of the oxygen atom, which can be coordinated to the metal center in a terminal or bridging way. (Szafer, John, & Sobota, 2008)

Metal–alkoxo complexes constitute a very important group of precursors for oxide materials. There are a number of well-known applicable routes for the preparation of oxide materials using inorganic sources. The most common chemical approaches are well described in the literature and the most relevant pathways will be summarized later in this chapter. (Szafer et al., 2008)

**SINGLE SOURCE PRECURSORS**

The Single Source Precursors implies that all the elements (M-E) required in the film are incorporated into one compound (e.g. M = Ga and E = O for Ga₂O₃) bonded at the core of the molecule, with various other ligands attached to each of the elements, that behave as a precursor. The reaction pathway involves
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