Surface & Coatings Technology xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

High vacuum chemical vapour deposition of oxides: A review of technique development and precursor selection

Yury Kuzminykh [a,b,*], Ali Dabirian [b], Michael Reinke [a,b], Patrik Hoffmann [a,b]

[a] *Laboratory for Advanced Materials Processing, Empa, Swiss Federal Laboratories for Materials Science and Technology, Feuerwerkerstr. 39, 3602 Thun, Switzerland*
[b] *Laboratory for Photonic Materials and Characterization, Ecole Polytechnique Fédérale de Lausanne, EPFL, Station 17, 1015 Lausanne, Switzerland*

ARTICLE INFO

Available online xxxx

Keywords:
High vacuum chemical vapour deposition
Precursor delivery
Precursor efficiency
Oxides
Thin films

ABSTRACT

Thin films of oxide materials are widely used for various types of applications. The selection of an appropriate deposition method depends on the aimed material and application. We review here a high vacuum chemical vapour deposition (HV-CVD) method, which can be considered as a hybrid technique between classical low pressure chemical vapour deposition (LP-CVD) and molecular beam epitaxy (MBE). The principal features of HV-CVD are summarized and its main differences from other techniques analysed. The evolution of the design of precursor delivery systems from simple pressure reduction to a multiple effusion sources system has enabled the versatility of the HV-CVD method. Full wafer scale deposition, application of controlled precursor flux gradients and, based on it, combinatorial process optimisation are three main features of this development. In this contribution a comprehensive overview of oxide materials, which have been deposited by HV-CVD, and types of precursors reported in the literature is presented and analysed. Mostly metal-alkoxides, metal-β-diketonates and metal-alkyls have been utilized in HV-CVD processes. In our laboratory the following oxide materials have been deposited on full wafer substrates in HV-CVD reactors using alkoxide precursors or derivatives: TiO_2, TiO_2-SiO_2, Al_2O_3, Nb_2O_5, Nb_2O_5-HfO_2, $LiNbO_3$.

The deposition chemistry and the efficiency of the process vary strongly depending on the precursor type. Due to the reduced/absent intermolecular collision events in the gas phase in HV-CVD as compared to LP-CVD, substantial differences in the physics and chemistry of the deposition processes are observed. Efficient precursor decomposition with more than 95% efficiency and deposition rates up to 500 nm/h have been observed for certain alkoxide precursors, whereas the presence of strong oxidizers (O_3 or O_2 plasma) seems to be indispensable in order to obtain an oxide deposit using β-diketonate precursors. Here, slower deposition rates in the order of tens of nm/h are achieved. The main concern of the applicability of the technique for new oxide materials is the availability of precursors satisfying the requirements for easy precursor delivery, chemical stability in the delivery system, and efficiency of the absorption and decomposition on the substrate in high vacuum.

1. Introduction

Thin films of oxide materials are used in a very wide range of applications: from chemical and mechanical protection or surface functionalisation to functional layers in electronic or photonic devices. We will mostly refer here to applications of oxide films in electronic, photonics and integrated optics domains, where oxides can be used in various functions: as electrical insulator materials [1], gate oxide [2], transparent conductors [3], piezo-electric materials [4], optical waveguides [5], electro-optical material in modulators [6,7], laser active medium [8], wide-band gap semiconductor [9], etc. The demand of these applications has driven and still drives the development and optimisation of a wide variety of thin film deposition techniques: physical vapour deposition methods (MBE, sputtering, evaporation), chemical vapour methods (variations of CVD, ALD) sol–gel, liquid phase epitaxy.

Especially demanding are the applications, where high quality functional oxide films with relatively high thicknesses are required. These include among others materials for electro-optic or laser active medium applications, piezo-electric materials and wide band-gap semiconductors. The requirements imposed on the thin film deposition techniques are often challenging, such as highly crystalline and textured or epitaxial films, low density of scattering and absorption centres (both for photons or for electrons) to guarantee functional properties and provide a low loss medium. In order to enable industrial applications, the thin film deposition technique of choice, additionally to the required oxide film properties, needs to provide sufficiently high growth rates and scalability to full wafer scale.

---

[*] Corresponding author at: Laboratory for Advanced Materials Processing, Empa, Swiss Federal Laboratories for Materials Science and Technology, Feuerwerkerstr. 39, 3602 Thun, Switzerland.
E-mail address: yury.kuzminykh@empa.ch (Y. Kuzminykh).

0257-8972/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.surfcoat.2013.06.059

Please cite this article as: Y. Kuzminykh, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.06.059

In the present contribution we review the high vacuum chemical vapour deposition (HV-CVD) technique, which represents a promising candidate to satisfy the discussed requirements for a range of oxide materials. Several variation of naming for the technique exist: chemical beam epitaxy (CBE), chemical beam deposition (CBD), metal organic molecular beam epitaxy (MO-MBE), gas source MBE, (ultra) high vacuum chemical vapour deposition ((U)HV-CVD). The different names are used in the literature depending on the background of the development (e.g. MBE or CVD derived), nature of properties of the film and reactor design. In this contribution we will concentrate on the nature and features of the process itself and will refer to all of the above mentioned with the term high vacuum chemical vapour deposition (HV-CVD).

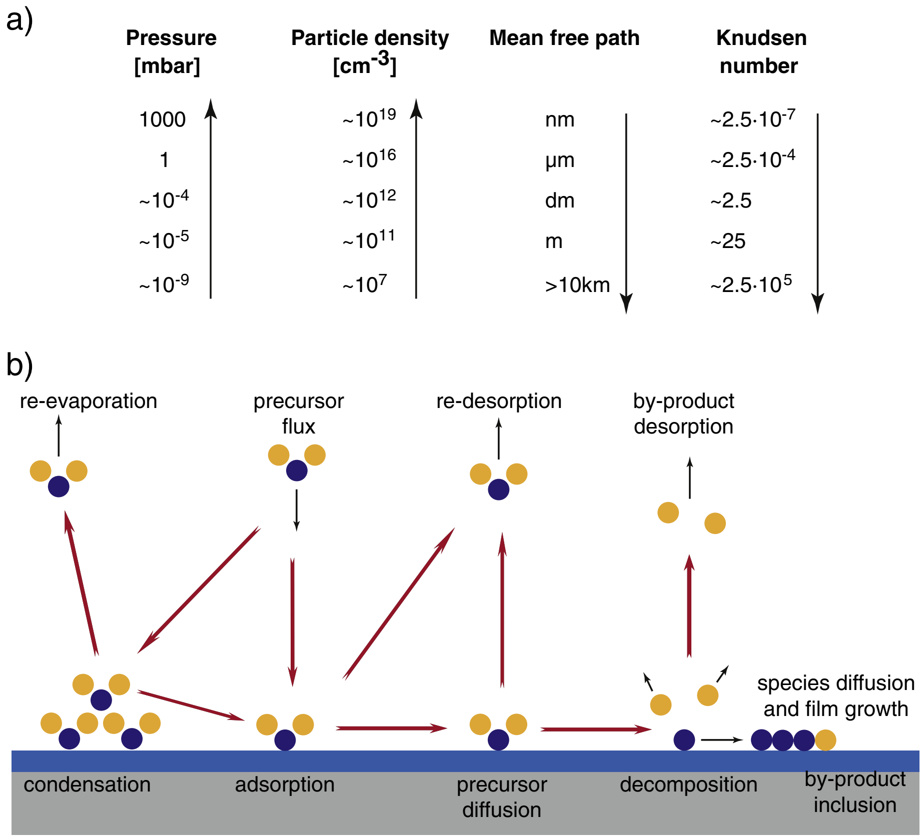
2. High vacuum chemical vapour deposition

2.1. Process

High vacuum chemical vapour deposition (HV-CVD) is a chemical process based on the decomposition of metal organic precursor(s) on the substrate surface in high vacuum conditions, which results in formation and deposition of a desired material. In contrast to the LP-CVD process, high vacuum should be understood as conditions, at which mean free path of the molecules is in the order of magnitude or larger than typical deposition reactor dimensions. Fig. 1a presents the estimation of the mean free path and Knudsen numbers for the range of pressures. Transition from low pressure CVD to high vacuum CVD regime for a typical reactor of size in the decimetre scale occurs at a processing pressure around 10^{-4} mbar. The fact that the process takes place in high vacuum conditions imposes certain principal differences as compared to classical metal organic LP-CVD processes.

In the Fig. 1b we illustrate individual sub processes taking place during the HV-CVD process. The precursor molecules undergo no (or very limited) interactions (i.e. collisions) in the gas phase before reaching the substrate. Therefore in HV-CVD, pre-heating, pre-decomposition of a precursor molecule before its interaction with the substrate surface is negligible. Also negligible in HV-CVD is spontaneous gas phase nucleation and particle formation in the gas phase. In HV-CVD the precursor molecules leave the effusion source and subsequently reach the substrate to physisorb on the substrate surface. Instantaneous desorption might occur at very high substrate surface temperatures. At high impinging rates, condensation (multi-layer coverage) is also possible with increasing probability by decreasing the substrate temperature. Precursor molecules diffuse on the substrate surface, until they partially or completely decompose and go into a stronger bound chemisorbed state. Typically the precursor decomposition process is thermally activated by heating the substrate, but additional chemical activation by oxidizing agents is often used for the deposition of oxides. In competition to the decomposition the re-desorption process takes place as well. Once a molecule detaches from the substrate surface, it typically has very low probability to contribute to the process a second time, due to the absence of gas phase collisions. All desorbed precursor molecular flights end on a cold trapping surface or in the pumping system.

Thus, in HV-CVD all relevant chemical reactions of the precursor molecules and reactive partners take place only on the substrate surface ensuring the single adsorption event of each molecule. This characteristic of the HV-CVD process determines the chemistry and efficiency of precursor decomposition, which may substantially differ from a MO-CVD process. HV-CVD oxide deposition differences as compared to CVD or MBE have been first underlined by Bade et al.



a)

Pressure [mbar]	Particle density [cm^{-3}]	Mean free path	Knudsen number
1000	~10^{19}	nm	~$2.5 \cdot 10^{-7}$
1	~10^{16}	μm	~$2.5 \cdot 10^{-4}$
~10^{-4}	~10^{12}	dm	~2.5
~10^{-5}	~10^{11}	m	~25
~10^{-9}	~10^{7}	>10km	~$2.5 \cdot 10^{5}$

Fig. 1. (a) Relation between chamber pressure, mean-free path and Knudsen number for a reactor with characteristic dimensions of L = 30 cm. Knudsen numbers larger than unity indicate conditions enabling molecular flow regime. (b) Schematic illustration of the individual sub-processes, which are taking place during HV-CVD process.

Please cite this article as: Y. Kuzminykh, et al., Surf. Coat. Technol. (2013), http://dx.doi.org/10.1016/j.surfcoat.2013.06.059