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Evaluation of niobium dimethylamino-ethoxide for chemical vapour deposition of niobium oxide thin films

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ABSTRACT

Chemical vapour deposition (CVD) processes depend on the availability of suitable precursors. Precursors that deliver a stable vapour pressure are favourable in classical CVD processes, as they ensure process reproducibility. In high vacuum CVD (HV-CVD) process vapour pressure stability of the precursor is of particular importance, since no carrier gas assisted transport can be used. The dimeric $Nb_2(OEt)_{10}$ does not fulfil this requirement since it partially dissociates upon heating. Dimethylamino functionalization of an ethoxy ligand of $Nb(OEt)_5$ acts as an octahedral field completing entity and leads to $Nb(OEt)_4(dmae)$. We show that $Nb(OEt)_4(dmae)$ evaporates as monomeric molecule and ensures a stable vapour pressure and, consequently, stable flow. A set of HV-CVD experiments were conducted using this precursor by projecting a graded molecular beam of the precursor onto the substrate at deposition temperatures from 320 °C to 650 °C. Film growth rates ranging from 8 $nm \cdot h^{-1}$ to values larger than 400 $nm \cdot h^{-1}$ can be obtained in this system illustrating the high level of control available over the film growth process. Classical CVD limiting conditions along with the recently reported adsorption–reaction limited conditions are observed and the chemical composition, and microstructural and optical properties of the films are related to the corresponding growth regime. $Nb(OEt)_4(dmae)$ provides a large process window of deposition temperatures and precursor fluxes over which carbon-free and polycrystalline niobium oxide films with growth rates proportional to precursor flux are obtained. This feature makes $Nb(OEt)_4(dmae)$ an attractive precursor for combinatorial CVD of niobium containing complex oxide films that are finding an increasing interest in photonics and photoelectrochemical water splitting applications. The adsorption–reaction limited conditions provide extremely small growth rates comparable to an atomic layer deposition (ALD) process indicating that HV-CVD has the potential to be an alternative to ALD for growth of ultrathin films on low aspect ratio substrates.

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1. Introduction

High vacuum chemical vapour deposition (HV-CVD) provides several interesting features involving addressable combinatorial experiments for fast optimization of thin films [1–12], controlled growth of nanowires in a vapour–liquid–solid (VLS) process [13–15], and selective area growth exploiting laser [16–18], ion [19], or electron [20] beam assisted depositions.

The HV-CVD of niobium oxide is of high importance because niobium oxide is the key constituent of complex compounds such as $LiNbO_3$, $Nb:TiO_2$, and $SrNbO_2N$. $LiNbO_3$ [21] is the most important material of photonics and optical communication where due to its nonlinear and electro-optics features it is used for data modulation [22] and generation of coherent light at wavelengths for which lasing materials do not exist [23,24]. Niobium-doped anatase ($Nb:TiO_2$) [25] is a compound that is attracting growing attention as an alternative transparent conducting oxide for applications in solar cells [26] and smart windows [27]. $SrNbO_2N$ is an oxynitride compound that is usually synthesized by annealing its respective oxide under partial pressure of ammonia. So far this material is one of a few materials that experimentally demonstrated photo-electrochemical splitting of water without the need of an external potential [28].

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In HV-CVD the precursor vapour effuses into the deposition chamber in high vacuum conditions. Carrier gas cannot be used as the system pressure must be kept low. Hence precursors that provide stable vapour pressure and flows upon heating are essential to achieve reproducible depositions. The dimeric niobium penta-ethoxide ($Nb_2(OEt)_{10}$) [29] is often used as a precursor for Nb_2O_5 CVD however it is not a suitable HV-CVD precursor because it partially dissociates upon heating even at temperatures as small as 100 °C [29].

Here we show that $Nb(OEt)_4(dmae)$ in which one ethoxy ligand is substituted by a dimethylamino-ethoxy (dmae: 2-dimethylaminoethanolate [$OCH_2CH_2NMe_2$]) ligand evaporates as monomeric species and exhibits a stable vapour flow with larger evaporation rates. The vapour pressure of $Nb(OEt)_4(dmae)$ was measured under high vacuum conditions for different evaporation temperatures. The HV-CVD experiments were performed with a graded molecular beam of the precursor being projected onto the substrate essentially simulating different precursor fluxes on different parts of the substrate surface. A set of experiments was carried out at various substrate temperatures and the resulting niobium oxide films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron (XPS), and spectroscopic ellipsometry measurements. Four characteristic CVD limiting conditions, i.e. adsorption–reaction [1], reaction, flux, and desorption limited conditions were identified in these experiments and the optical and structural properties of the films classified and assigned to the relevant regime. High optical quality polycrystalline niobium oxide thin films with chemical compositions close to stoichiometric Nb_2O_5 were obtained in flux and desorption limited conditions. The adsorption–reaction and reaction limited conditions led to films with carbon contamination and also with sub-bandgap optical losses. The growth rate and properties of the films can be adjusted over the large range (e.g. 8–400 nm/h growth rate in this work) while going through different deposition regimes by changing the deposition temperature and the precursor flux.

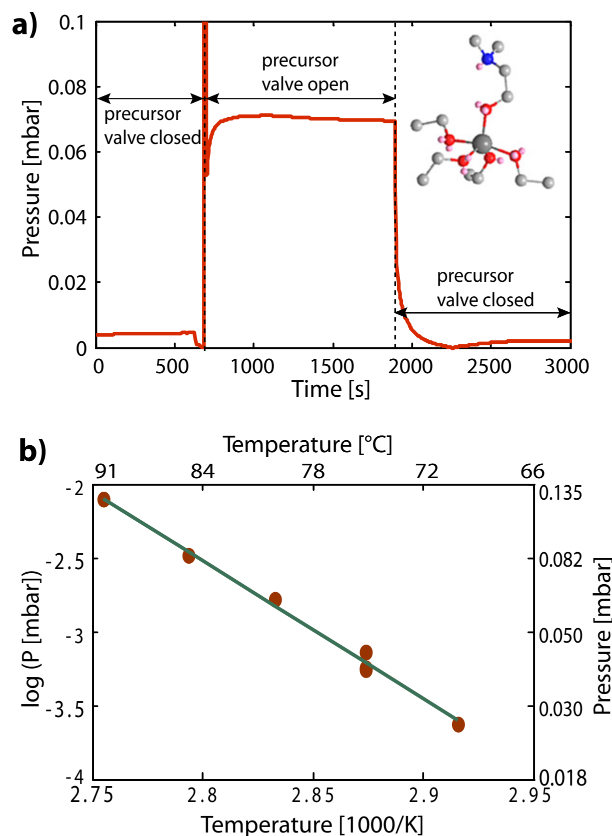

Fig. 1. (a) Temporal evolution of $Nb(OEt)_4(dmae)$ partial pressure inside the prechamber upon operation. The inset shows the molecular configuration of the precursor molecule. (b) Logarithmic plot of the $Nb(OEt)_4(dmae)$ partial pressure versus 1000/T [K^{-1}]. The experimental data are fitted with the Clausius–Clapeyron relation.

2. Experimental

2.1. Materials

$Nb(OEt)_5$ [CAS: 3236-82-6] and $Nb(OEt)_4(dmae)$ [research compound] were provided by SAFC Hitech. $Nb(OEt)_4(dmae)$, schematically depicted in the inset of Fig. 1a, was prepared from $Nb(OEt)_5$ and dimethylaminoethanol (Me_2NEtOH) [CAS: 100-37-8] and then purified on a 100 g batch size using various sublimation and distillation processes.

2.2. Deposition system

Thin film deposition and precursor vapour pressure measurement experiments were carried out in a Sibylla-150 (ABCD Technology) HV-CVD reactor [30]. In this system the deposition chamber was pumped by a two-stage system composed of a primary pump and a turbomolecular pump to achieve a background pressure of 5×10^{-6} hPa.

Precursors are continuously evaporated from temperature stabilized reservoirs into volumes called prechambers. The precursor vapour flow from separate prechambers into the high vacuum chamber was controlled using a reconfigurable array of Knudsen effusion sources [30]. In a certain configuration of Knudsen effusion sources the introduction of precursors vapours into the high vacuum chamber can be shaped such that the distribution of the precursor molecules on the substrate surface has a linear gradient distribution.

The partial pressure of precursor inside the prechamber was measured using a self-heated MKS 631B Baratron membrane pressure gauge. These precursor pressure values together with known arrangement of the effusion sources were used to calculate the spatial distribution of precursor molecules on the substrate surface [31]. To avoid undesirable contribution to the process, all molecules, either precursor molecules bouncing back from the substrate or reaction by-products are trapped on liquid nitrogen cooled panels installed inside the deposition reactor.

2.3. Analytical techniques

The (θ–2θ) X-ray diffraction (XRD) measurements were carried out on a D8 Discover Bruker AXS X-ray diffractometer with the Cu-$K_{\alpha1}$ line to identify the crystalline phase present inside the layer. Phase identification was carried out in Bruker AXS:EVA-XRD software linked with the ICDD (International Centre for Diffraction Data) database. ICDD PDF cards 01-075-2947 for monoclinic $Nb_{12}O_{29}$ and 01-071-0336 for orthorhombic Nb_2O_5 were used in this work.

X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AXSI Ultra with 100 meV steps. The measured XPS spectra were calibrated with carbon impurity peak C1s fixed at binding energy (B.E.) = 285.0 eV. Background removal and fitting procedure of the XPS spectra were carried out in CasaXPS software with components of Gaussian/Lorentzian product form. For observations of volume composition a few tens of nanometers of film were sputtered away from the sample surface with Ar^+ beam.

Scanning electron microscopy (SEM) observations were performed on a FEI XLF30 instrument using electron beam energies of 15 keV or 20 keV to achieve the resolution of 10 nm.

Spectroscopic ellipsometry measurements were conducted on a Sopra GES-5E instrument in microspot mode in which the samples were illuminated with a light beam whose projection on the sample surface was an ellipse with diameters of 300 μm and 100 μm under 75° from the normal direction to the film. Measurements were performed from 0.7 eV to 6.5 eV and then the measured data were fitted

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