FTIR study of zirconium tetra tert-butoxide dissociation process in correlation with ZrO₂ thin film growth deposited in low pressure plasma

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Abstract: Deposition of metal-organic thin films was obtained in MPP-DECR plasma using Zirconium Tetra tert-Butoxide (ZTB) as a precursor. To clarify the dissociation process of the precursor Fourier Transform Infrared Spectroscopy (FTIR) and Density Functional Theory (DFT) were employed for the examination of gas phase, while Scanning Electron Microscope (SEM) was used for thin film investigation.

Keywords: PECVD, ZTB, metal-organic thin films, dissociation process, FTIR, DFT

1. Introduction

Zirconium oxide thin films are of great scientific and technological interest. Their significance in both science and technology is due to their desirable physical and chemical properties. These properties include high thermal stability, low thermal conductivity, high melting point, chemical and corrosion resistance, large oxidation resistance and high hardness. They are used as thermal barrier coatings and oxygen gas sensors. High dielectric constant and wide band gap makes them eligible for use in microelectronic production. They are widely employed as optical coatings because of their high transparency and high refractive index. Biocompatibility makes zirconium oxides of interest for biomedical and prosthetic use.

Zirconium oxide coatings have been synthesized using various techniques such as Chemical Vapour Deposition (CVD) and sol-gel processes. In this work coatings were obtained by Plasma Enhanced CVD (PECVD). Zirconium oxide thin films were deposited using Zirconium Tetra tert-Butoxide (ZTB, C₁₆H₃₆O₄Zr) as a precursor.

Plasma phase reactions resulting in the appearance of different reactive species depend on the process parameters and affect composition and characteristics of deposited thin films. From the demand to achieve desired thin film characteristics arises the need for complete gas phase characterization, understanding the dissociation process and finally connecting the latter with thin film growth.

Fig. 1. Schematic diagram of the experimental setup.
2. Experimental procedure

Deposition of thin films was achieved using microwave multipolar plasma (MMP) excited by distributed electron cyclotron resonance (DECR). MPP-DECR source allows generating very low-pressure plasma, of the order of millitorr, and is capable of producing plasma of high electron density (ne ≈ 10^{11} cm\(^{-3}\)) [1]. The metal-organic coatings were obtained in a main chamber of the reactor which consists of a stainless steel cylinder of 25 cm in inner diameter and 30 cm in height. The chamber is connected by an airlock to a transfer chamber. The pumping is assured by a group consisting of a rotary vane pump and a turbomolecular pump as well as a cold trap. The gaseous precursors are injected and checked by series of mass flow meters (MKS). There is also a setup allowing injection of low vapour pressure precursors, as ZTB. The reactor is equipped with 8 internal antennas (injecting the microwave energy at 2.45 GHz) with regard to 8 external samarium-cobalt magnets distributed around the metallic cylinder composing the enclosure. A Sairem microwave generator, coupled with an impedance matching, allows injecting up to 800 watts. Metal-organic thin films were deposited on Si (100) substrates. During the deposition the total pressure was maintained at 1 mTorr.

Vibrational spectra were obtained using FTIR absorption spectroscopy of the plasma phase achieved in a multipass cell previously described [2]. The pressure was not fixed, yet it varied from 2 to 4 mTorr. Density functional theory (DFT) was used in order to support the analysis of experimental data and therefore help getting a clear image of the precursor dissociation process [3]. DFT calculations were performed with the purpose of obtaining IR spectra of precursor and fragment molecules and relevant bond energies. The calculations include optimization of the geometries of molecules and computation of Gibbs free enthalpies (at 298K) of the associated reactions. Regarding the computational details, B3LYP hybrid exchange-correlation functional with the 6-311++g (3df, 3pd) basis set was used. For open shell systems the unrestricted method (UB3LYP) was employed. All calculations were performed using the Gaussian09 package [4].

3. Results and analysis

Thin films deposited from ZTB/O\(_2\) plasma at different amounts of oxygen present in the gas mixture show significant structural differences. Figure 2 presents cross sectional SEM images of thin films deposited from 50% ZTB/50% O\(_2\) plasma (Fig. 2a) and 10% ZTB/90% O\(_2\) plasma (Fig. 2b). Thin films obtained from plasma at amounts of oxygen smaller than 80% are homogenous, while those obtained at 80% of O\(_2\) and higher show columnar structure. The diameter of the columns is of the order of tens of nanometers. Columns are perpendicular to the surface of the substrate. Columnar growth of zirconium oxide thin films deposited by PECVD has already been reported, but its appearance has not been explained nor correlated with plasma phase composition [5,6].

Figure 3 presents FTIR spectra of ZTB/O\(_2\) plasma phase obtained at different amounts of oxygen in the gas mixture. Most of the peaks are present with more or less equal intensities in all the spectra shown (spectra of 70%ZTB/30%O\(_2\), 50%ZTB/50%O\(_2\), 20%ZTB/80%O\(_2\) and 10%ZTB/90%O\(_2\) plasma). Yet some peaks show substantial differences in size between ZTB/O\(_2\) with <80% of O\(_2\) spectra and ZTB/O\(_2\) with ≥80% of O\(_2\) spectra. Peaks that significantly differ in intensities are labelled in figure 4. Those peaks and their assignations are listed in table 1. In 20%ZTB/80%O\(_2\) plasma, the 667 cm\(^{-1}\) peak (L9) characteristic for CO\(_2\) considerably increases. Also, a decrease in amount of hydrocarbons is detected. It is best visible for 729 cm\(^{-1}\) peak (L6) which corresponds to C\(_2\)H\(_4\).
Fig. 4. FTIR spectra of ZTB/O₂ plasma obtained at 30% and 80% of O₂ in the mixture (P = 125W; p = 2 – 4 mTorr).

4. Discussion

It is logical to conclude that there is a strong connection between the plasma phase composition and thin film structural growth. FTIR measurements show a clear difference in composition between plasma that derives deposition of homogenous thin films and the one that results in deposition of films with columnar structure. For plasmas with 80% and higher amounts of O₂ introduced in the gas chamber, a significant increase in amount of carbon oxides in the plasma can be observed, especially of CO₂ (Fig. 4, peak L6). At the same time a substantial decrease in ethylene (C₉H₄) takes effect (Fig. 4, peak L9). This is expected when considering the increase in oxygen in the gas mixture, but there still remains the question of explaining why the drastic change in plasma composition and film structure happens for 20% ZTB/80% O₂ mixture. Further study of plasma phase and thin film composition is needed.

Columnar growth was also reported in the case of thin film deposition using titanium isopropoxide (TTIP) as a precursor [7,8]. It has been shown that a small addition of hexamethyldisiloxane (HMDSO) (RHMDSO ≥ 0.5%) to TTIP/O₂ plasma causes disappearance of columnar structure [9]. Deposited films are very dense and homogenous. ZTB (C₁₆H₃₆O₄Zr) and TTIP (C₁₂H₂₈O₄Ti) have a similar structure. They are both composed of a central transition metal atom (zirconium and titanium for ZTB and TTIP, respectively). Central atom is surrounded with four oxygen atoms and each oxygen is bonded to three hydrocarbon chains (C₄H₉ for ZTB and C₃H₇ for TTIP). This suggests that adding a small amount of HMDSO to ZTB/O₂ plasma may result in removal of columnar growth and deposition of homogenous thin films. Thus, current work focuses on the use of ZTB/HMDSO/O₂ mixture. Also, a novel multipass optical system for FTIR spectroscopy (100 passes) will be used in future experiments. It will provide high sensitivity needed for further investigation of plasma phase and ZTB dissociation process.

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6. References
