Oxygen CCP global model for investigate the influence of plasma power on PEALD TiO_2 thin film properties

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Abstract: In this study, we use a global model to investigate the oxygen plasma cycle of PEALD of TiO_2 thin films. The reactor geometry is an asymmetric capacitive coupled (CCP) radio frequency discharge and it was investigated the effect of discharge power in the range of 10-500 W, for a working pressure of 1.0 mbar, on plasma parameters: neutral and ion species densities. These are typical conditions for PEALD process. The global model assumes that the discharge contains several species such as O_2^+, O^-, electrons, ground state O_2 and O atoms, and $O_2(a^1\Delta g)$ metastable. In parallel we have investigated the growing of TiO_2 thin films onto Si(100) by PEALD using TTIP and oxygen plasma. Oxygen plasma power was varied from 50-200 W for a fixed temperature of 250ºC and the as-deposited TiO_2 thin films were investigated regarding its structure and morphology. From global model results, it was possible to infer the main species that can achieves the substrate and correlate the as-deposited TiO_2 thin film analyses in order to explain the effect of discharge power in film crystallinity and morphology.

1. Introduction

The motivation for this work is the lack of studies of titanium dioxide (TiO_2) by Plasma-Enhanced Atomic Layer Deposition (PEALD) using titanium (IV) isopropoxide (TTIP) as precursor and the effect of oxygen plasma power in TiO_2 film properties. As it known, the plasma power dictates the ion and reactive species flux to substrate, so it is important to understand its influence in as-deposited film morphology and crystallinity.

TiO_2 is a semiconductor with two mineral forms more common: anatase and rutile [1]. Due this, TiO_2 is a versatile material with a unique combination of properties. It may be used in a variety of areas such as optical coatings for antireflection, high dielectric constant film for electronic capacitor, photo-sensitive layers for solar cell, and photo-catalysts for decomposition of organic pollutants [1, 2]. However, for formation of crystalline TiO_2 phases is necessary to achieve an activation energy. This can be supplied by heating and/or by plasma energetic species.

In this study, we use a global model (volume averaged) to investigate the oxygen plasma cycle of PEALD of TiO_2 thin films in order to explain as-deposited film properties such as structure and morphology.

2. Experimental and global model

The films were deposited in a Beneq TFS 200 ALD reactor operating in capacitively coupled 13.56 MHz plasma mode. The reactor was operated in remote plasma configuration meaning that a grid acting as a bottom electrode separated plasma from the substrates (Fig. 1a). The grid allows bringing the plasma close to the substrate, yet keeping it remote in a sense that ion bombardment of substrates is relatively low and thus little damage is caused to the growing film. The spacing between the grid and the substrate was 1.0 cm. The top electrode is a showerhead electrode which enables uniform distribution of the reactive plasma gas. The spacing between the top electrode and the grid was 3.0 cm. In the present studies the depositions were carried out with plasma power ranging from 50 to 200 W.

Pieces from a 350 µm thick Czochralski Si wafer (p-type, 4 Ω.cm, (100)-orientation) were used as substrates. Here, were used the following ALD cycle time steps for deposition of the films: 0.25–2–2–2 s, i.e. the TTIP pulse of 0.25 s, the first purge of 2 s, O_2 plasma pulse of 2 s and the second purge of 2 s. Nitrogen (N_2) of 99.999% purity was used as purge gas. The vapor of TTIP was led into the reactor from an external reservoirs kept with liquid TTIP (Sigma-Aldrich 97.0% purity) at temperature of 75°C. Oxygen gas (99.999% purity) was inserted through plasma chamber. During the deposition the gas pressure in reactor chamber was maintained around 1.0 mbar through the insertion of 250 sccm of N_2 in reaction chamber.

The structural and morphological TiO_2 films properties were measured by grazing incidence x-ray diffraction (GIXRD) and by atomic force microscopy (AFM), respectively.

(a) (b)

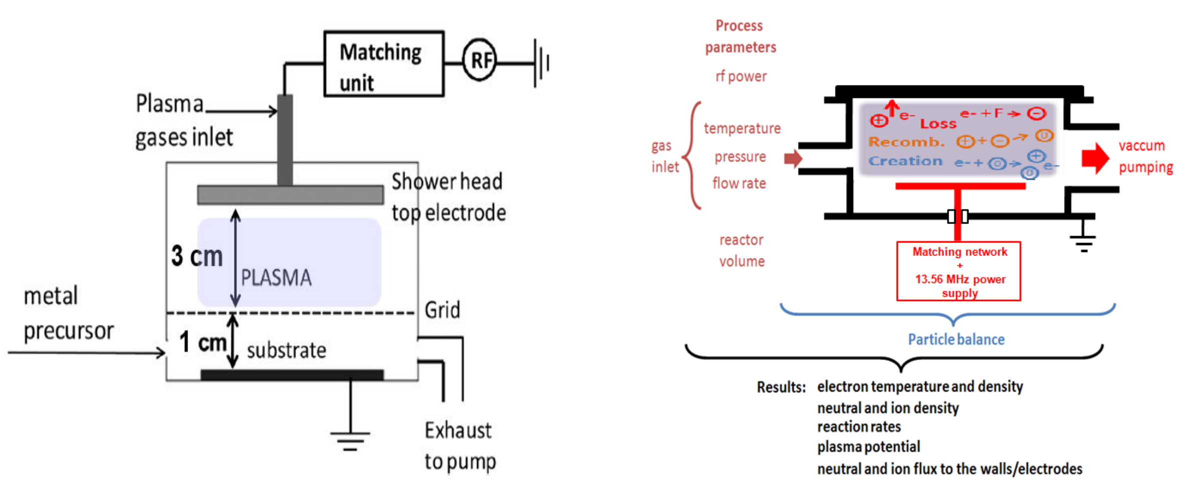

Figure 1. (a) Schematics presenting the remote PEALD configuration of the Beneq TFS 200 ALD reactor. Picture is modified from ref. 1. (b) Schematic diagram of the global model. The set of reactions considered in the model are based from ref. [3].

A global model was formulated for the analysis of O_2 CCP plasma generated in a cylindrical chamber of radius R = 0.12 m and length L = 0.03 m (Fig. 1). The model governing equations are derived from mass and energy conservation arguments and may be expressed as a set of nonlinear ordinary differential equations described in details in ref. [3, 4]. Figure 2 illustrate the schematic diagram of global model, basically were inputted process parameters such as gas temperature, pressure, flow rate, and discharge power, for obtain plasma parameters such as electron temperature and density, neutral and ion densities/flux, etc. In this work it was assumed that the discharge contains the following plasma/gas species: O_2^+, O^-, electrons, O_2 and O ground state, and $O_2(a^1\Delta g)$ metastable. Moreover, the model developed considers the main chemical reactions occurring in O_2 plasma: momentum transfer, vibrational, ionization, dissociation, electron attachment/loss, recombination between charged and neutral species in the gas phase and the reactor walls [3, 5].

4. Results and discussion

Figure 2 illustrate the GIXRD spectra of TiO_2 thin films deposited at plasma power of 70 and 150 W at process temperature of 250ºC. It is possible to see from Fig. 2 that pure anatase phase can be obtained on Si substrate for plasma power of 70 W. When the plasma power was increased to 150 W, there was a degradation of anatase peaks where only the main peak, A(101), was observed.

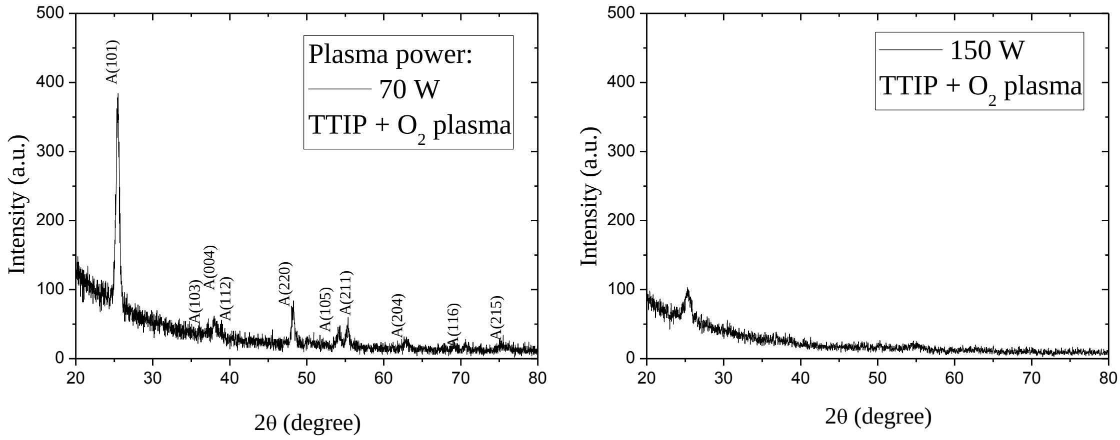

Figure 2. GIXRD spectra of atomic layer deposited TiO_2 thin films on Si(100) for plasma powers of 70 and 150 W. Where A represents the anatase phases of TiO_2.

Figure 3 presents the AFM images of the samples presented in Fig. 2. The film deposited at 70 W has a RMS surface roughness of order of 5.0 nm, while for 150 W was measured a value of 3.6 nm. The higher surface roughness is in agreement with film crystallinity as stated in other works from literature [6, 7].

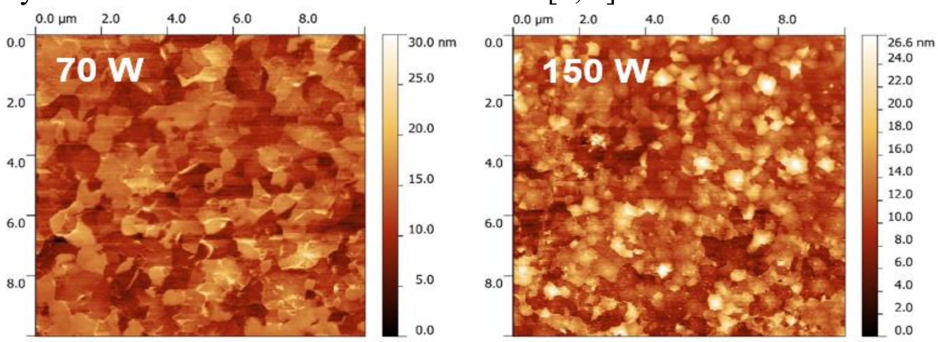

Figure 3. Atomic force microscopy (AFM) images of TiO_2 ALD films at the indicated oxygen CCP discharge power.

In order to explain the decrease of TiO_2 film crystallinity for PEALD process, in Fig. 4 are presented the densities of the main plasma/gas phase species that can reach the substrate surface during O_2 plasma cycle. As can be seen, for the investigated experimental conditions, the density of O_2^+ and neutral species tends to increase almost linearly with plasma power. This increase in plasma species densities and the low crystallinity obtained for 150 W is not common and let us to conclude that the deposition process of TiO_2 by TTIP metal precursor and O_2 plasma ligant cycles have the contribution of an additional phenomenon during material growth process after TTIP cycle caused by O_2 plasma: the etching process of TTIP molecule monolayer. This explain the lower surface roughness and, consequently, the low crystallinity.

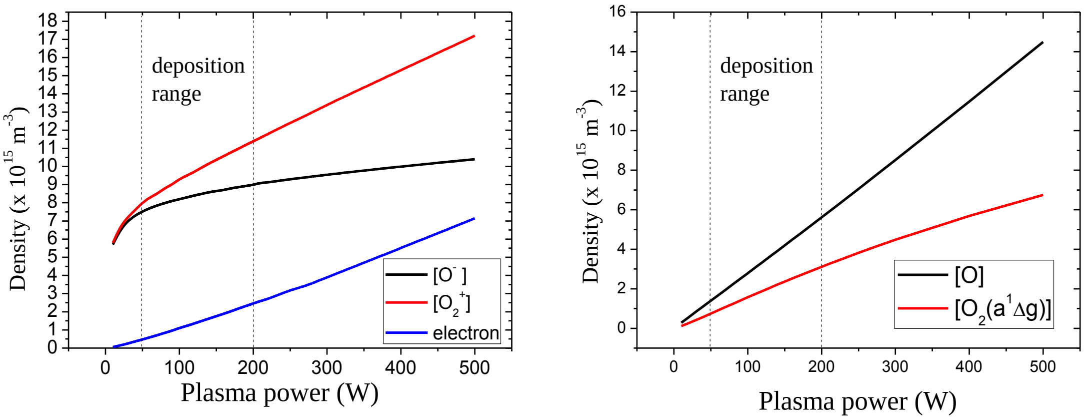

Figure 4. (a) Charged species densities and (b) neutral species densities as a function of plasma power for O_2 CCP cycle during Plasma Enhanced Atomic Layer Deposition of TiO_2 thin film.

5. Conclusion

The effect of power was investigated for plasma enhanced atomic layer deposition technique when is considered the deposition of TiO_2 thin film. It was chosen the TTIP due to its low aggressiveness in comparison with other metal precursors such as $TiCl_4$. The process temperature was fixed at 250ºC. It was observed a drastic decrease in the film crystallinity as well as its surface roughness with increase of plasma power. The analysis of plasma by global model presents an increase of radical species such as atomic oxygen, metastable, and positive ions, consequently causing an etching phenomena of TTIP molecule monlayer by these species for higher plasma power. Moreover, it is possible to infer from simulation that the plasma electronegativity for the ALD condition are of order of 1–15, where for higher plasma electronegativity the TiO_2 film is more crystalline. Next steps is confirm these results with experimental ion energy analysis during PEALD process.

6. Acknowledgements

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7. References

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