Abstract

This project represents a detailed research on the decomposition efficiency of titanium (IV) isopropoxide (TTIP) precursor in high vacuum chemical vapor deposition of TiO₂. The set-up for combinatorial depositions enabled to investigate film growth process as a function of two parameters: substrate temperature and precursor impinging rate. A two dimensional map representing dependence of decomposition efficiency on these parameters was constructed. Obtained results enable existing image of precursor behavior for this system [1]. A new trend in film growth is observed: precursor decomposition efficiency increases with increasing flux for the temperatures higher than 330°C. We propose a hypothesis attributing this effect to precursor autocatalysis. Furthermore, activation energies for precursor reaction and desorption were extracted from collected experimental data.

Motivation

- investigation of growth kinetics of TiO₂ thin films deposited at different substrate temperatures and precursor fluxes; 
- establishing decomposition efficiency.

Results

Precursor decomposition efficiency

The main parameter of interest for this project is precursor decomposition efficiency which is quantified by titanium incorporation coefficient:

\[ k_{\text{Ti}} = \frac{N_{\text{Ti}}}{n} \]

- \( k_{\text{Ti}} \) is the number of incorporated Ti atoms per unit volume.
- \( n \) is the refractive index of film determined by spectroscopic ellipsometry.
- \( N_{\text{Ti}} \) is the total number of incorporated Ti atoms per unit of film surface calculated as

\[ N_{\text{Ti}} = \frac{N_{\text{inc}}}{h} \]

- \( h \) is the film thickness measured with SEM.

1. Quantitative Energy-dispersive X-ray spectroscopy

EDX spectra were collected, processed and total number of incorporated Ti atoms per unit of film surface was determined.

Two approaches were used to determine \( k_{\text{Ti}} \):

1. Method based on Lorentz-Lorenz law

According to Lorentz-Lorenz law number of incorporated Ti atoms per unit volume:

\[ N_{\text{Ti}} = \frac{n^2 - 1}{n^2 + 2} \times \frac{\text{TiO}_2}{m} \]

where:

- \( n \) is the refractive index of film;
- \( m \) is the mass of TiO₂.

2. Method based on refractive index measurement

Deposition efficiency is calculated as:

\[ N_{\text{inc}} = \frac{N_{\text{Ti}}}{h} \]

Method

High vacuum chemical vapor deposition (HV-CVD) is a technique where film is synthesized through decomposition of metal-organic precursors on a substrate in high vacuum conditions [2]. High vacuum implies that mean free path of precursor molecules is significantly higher than dimensions of a reactor. Consequently, molecules do not interact with each other in the gas phase.

Desired distribution of precursor flux along the substrate is achieved through tuning the arrangement of effusion sources by closing one or several openings of prechamber ring.

HV-CVD reactor

+ molecular flow regime;
- controlled precursor flux gradient;
- high growth rates;
- scalability to full wafer scale;
- availability of suitable precursors

Titanium incorporation coefficient calculated from two methods

\[ k_{\text{Ti}} = \frac{N_{\text{Ti}}}{N_{\text{inc}}} \]

where:

- \( N_{\text{Ti}} \) is the total number of incorporated Ti atoms per unit of film surface;
- \( N_{\text{inc}} \) is the total number of incorporated Ti atoms per unit of film surface calculated as

\[ N_{\text{inc}} = \frac{N_{\text{Ti}}}{h} \]

- \( h \) is the film thickness measured with SEM.

Kinetic parameters of film growth process

Model describing film growth process was developed and fitted to experimental data. Activation energies for precursor reaction (\( E_r \)) and desorption (\( E_d \)) together with pre-exponential (\( A_r \), \( A_d \)) factors were extracted.

<table>
<thead>
<tr>
<th>( E_r ) (kJ/mol)</th>
<th>( E_d ) (kJ/mol)</th>
<th>( A_r ) (cm²)</th>
<th>( A_d ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>87</td>
<td>0.36</td>
<td>6.5 × 10²</td>
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</table>

Conclusion

- Successful study on the decomposition efficiency of TTIP precursor in HV-CVD of TiO₂ was done;
- The effect of precursor autocatalysis on decomposition efficiency was established;
- Reliability of obtained results was confirmed with two methods based on different experimental techniques;
- Fitting of model to experimental results yielded kinetic parameters of film growth process.

References: