I-SEEC2011

Determination of Optical and Physical Properties of ZrO₂ Films by Spectroscopic Ellipsometry

R. Yusohᵃ, M. Horprathumᵇ, P. Eiamchaiᵇ, P. Chindaudomᵇ, K. Aiempanakitᵃ*  
ᵃDepartment of Physics, Faculty of Science and Technology, Thammasat University, Pathumthani, 12121, Thailand  
bOptical Thin-Film Laboratory, National Electronics and Computer Technology Center, Pathumthani, 12120, Thailand

Elsevier use only: Received 30 September 2011; Revised 10 November 2011; Accepted 25 November 2011.

Abstract

Film characterization based on spectroscopic ellipsometry (SE) is desirable in order to understand physical and optical characteristics of films. In this work, ZrO₂ films were deposited on Si substrates by d.c. reactive magnetron sputtering with deposition times from 4 to 7 hr. The film thickness determined by SE technique was compared to field emission scanning electron microscopy (FE-SEM) results. From SE modelling process, the double-layer physical model and the Tauc-Lorentz for two oscillator dispersion models offered the best result. The refractive index at photon energy of 2.25 eV of the film was decreased from 2.14 to 2.08 with time of 4 to 7 hr, respectively. The optical band gap of films was found to be in the range of 5.25-5.3 eV. Finally, the film thickness was determined by SE technique which the result showed the thickness values of all films closely to the film thickness measured by FE-SEM technique.

© 2010 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of I-SEEC2011

Open access under CC BY-NC-ND license.

Keywords: ZrO₂ films; d.c. reactive magnetron sputtering; spectroscopic ellipsometry

1. Introduction

ZrO₂ film is one of the most well studied transition-metal oxides in optical field. Because of the excellently optical properties of ZrO₂ films such as high refractive index, large optical band gap, low optical loss and high transparency in the visible and near-infrared region.

For optical application, transparency and homogeneity of thin films on the substrate are very important, while the characterization of ZrO₂ film by spectroscopic ellipsometry (SE) is a powerful

* Corresponding author. Tel.: +66 2 5644440; fax: +66 2 5644448.  
E-mail address: akamon@tu.ac.th.
technique to investigate the optical response of materials [1]. Therefore, this study focuses on the
determination of optical and physical properties of ZrO₂ films by SE with different films thickness.

2. Experimental details

2.1 Film preparation

ZrO₂ thin films were deposited on silicon wafer by d.c. magnetron sputtering from a zirconium target.
Before sputtering process, the vacuum chamber was initially evacuated to 7.5×10⁻⁷ Torr by a turbo
molecular pump coupled with a rotary pump. During sputtering process, the pressure was kept at 3×10⁻³
Torr by pressure control gate value. The high purity (99.99%) of both Ar and O₂ gases flow rate of 30 and
20 sccm, respectively, were introduced in vacuum chamber with controlling by mass flow controller. A
sputtering power was kept at 200 W and a deposition times were in the range from 4 to 7 hr.

2.2 Film characterization

The physical structure and optical dispersions of the films were examined by J.A. Woollam variable-
angle spectroscopic ellipsometry (VASE) on the films deposited on the silicon wafers. The measurements
were conducted in the range of 0.75-6.0 eV at 70° incident angle. The film thickness was determined by
FE-SEM technique to compare with the VASE result.

2.3 Data analysis

In general, the film thickness and optical constants can be computed from physically possible models
and compared to experimental data. Once the appropriate physical film model is achieved, a variety of
optical dispersion oscillators are available for curve-fitting.

The VASE ellipsometer generally measures the phases (Δ) and the amplitude (ψ) of the reflected
light components of p-wave and s-wave. Base on the fundamental equation of ellipsometry:

\[ \rho = \frac{R_p}{R_s} = \frac{E_{sp}}{E_{sp}} / \frac{E_{sp}}{E_{sp}} = \tan \psi \tan \Delta \]

where Δ is the phase difference that develops between the s-and p-wave components after reflection. The
quantity tan ψ is related to the amplitude ratio.

The proposed physical model corresponding to each film sample is associated with appropriate
generalized oscillators for the optical dispersions, which are the Cauchy and Tauc-Lorentz dispersion. The
generated data for the proposed physical model, utilizing all generalized oscillator, are to be curve-fitted
with the experimental data. The goal is to minimize a common mean square error function in order to
represent good matches between experimentally measured data and theoretical calculation.

2.3.1 Physical modeling

A physical model is constructed in order to describe physically possible ZrO₂ films. The films,
assumed to be ideally homogeneous, are first described by a single-layer model (SLM) (Fig. 1a). The
second proposal is a double-layer model (DLM) with a dense ZrO₂ layer and a surface roughness (Fig.
1b), based on the island film formation. Generally, inhomogeneity is considered for the island film growth which optically represented a mixture of dense material and void.

These proposed physical models are curve-fitted in comparison with experimental data in association with the Cauchy dispersion in the rage of 0.75-3 eV. As seen in Fig. 2. The double layer model offer the best curve-fits in most of photon energy range.

\[ n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}, \ldots, k = 0 \]  

where $A_n, B_n$ and $C_n$ are the Cauchy parameters. This optical model is generally suitable to describe optical constants in visible and infrared regions. Therefore, it is a model of choice for insulators and dielectrics.
The Tauc Lorentz oscillator is introduced in an attempt to describe the optical constants for semiconductor, by using a classical spring-mass system for dipole oscillation of atom and combining the Tauc band edge with the classical Lorentz broadening function

\[
\varepsilon_{2}(E) = \begin{cases} 
\frac{AE_0 C \left(E-E_g\right)^2}{(E-E_0^2)^2 + C^2 E^2} & , E > E_g \\
0 & , E \leq E_g 
\end{cases},
\]

(3)

where \( A \) is the amplitude, \( E_0 \) is the peak transition energy, \( C \) is the broadening constant and \( E_g \) is the band gap.

Fig. 3 illustrates the generated and experimental data, measured at 70\(^\circ\) incident angle in the range of 0.75-6 eV for the three optical models. It is observed that the Tauc-Lorentz with two oscillator optical model offers the best curve-fits for all ellipsometry data.

![Fig. 3. Illustration of generated and experimental data curve-fitted with three optical models by fitting on \( \psi \) and on \( \Delta \) at 70\(^\circ\) incident angle. The representation was taken from generated data utilizing the double layer model.](image)

### 2.3.3 Optical band gap

For ZrO\(_2\) thin films, the relation between the optical gap, the optical absorption coefficient and the incident photon energy is given by

\[
(h\nu)^{1/2} = A(h\nu - E_g) 
\]

(4)
The indirect optical band gap energy can now be calculated for $\alpha = 0$ where the linear part of the curve intercepts the x-axis just above the fundamental absorption threshold.

3. Results and discussion

Based on the film characterization by VASE, the all sample films are represented by a double layer model with only a dense ZrO$_2$ layer and a surface roughness, due to the island film growth by sputtering deposition which generally promotes inhomogeneity. Fig. 4 shows the refractive index calculated from the extracted best-fit parameters of the model for the ZrO$_2$ films. It can be seen that with increase of the deposition time, the refractive index shows a decrease trend. The most probable reason for this is the low packing density for the film and films possibly have not been continuous, many void still exist in the films, many defect due to lose arrangement. The refractive index of ZrO$_2$ films at 2.25 photon energy was found to 2.13-2.05, similar the refractive index of ZrO$_2$ films deposited by sputtering and greater than that seen for evaporation and sol-gel method [2-4]. The thickness of films was found to increase with increasing the deposition times from 4 to 7 hr (Table 1).

![Fig. 4. Variation of refractive index as a function of photon energy](image)

The variation of extinction coefficient $k$ as a function of energy is depicted in Fig. 5. It can be seen that the absorption edges shifted toward the higher energy side and showed no obvious change with increasing the deposition times.
Fig. 5. Variation of extinction coefficient as a function of photon energy

From Fig. 6 an example of the plot of $(ahv)^{1/2}$ versus photon energy of the films at deposition time of 4 hr. The energy band gap of all films was found to be 5.30-5.25 eV. The energy band gap in this present is closely to the theoretical value of 5.4 eV for bulk monoclinic zirconia and previous report [5-6].

Fig. 6. Illustration of the plot of $(ahv)^{1/2}$ versus photon energy of the films at deposition time of 4 hr

The FE-SEM results were shown in Fig. 7 to confirm the actual film thickness obtained from SE. Table 1 represents comparable thickness of films at deposition time from 4 to 7 hr by SE and FE-SEM techniques. It was found that the film thickness from the SE technique corresponded with the FE-SEM technique.

Fig. 7. Cross section FE-SEM image of films at deposition time of 4 hr
4. Conclusions

The ZrO$_2$ films were deposited on Si wafer substrates by dc reactive magnetron sputtering with different deposition times from 4 to 7 hr. The SE modelling process with double-layer physical model and using the Tauc-Lorentz for two oscillator dispersion models offered the best results. The refractive index of ZrO$_2$ films at photon energy of 2.25 eV decreased from 2.14 to 2.08 while the film thickness increased from 440 to 795 nm with increasing the deposition times from 4 to 7 hr, respectively. The optical band gap of films was found to be in the range of 5.25-5.3 eV.

Acknowledgements

The authors would like to thank the Nation Electronics and Computer Technology Center (NECTEC) for providing the experimental facilities.

References


