Nanometer-Thick Dielectric Films Deposited by Electron Cyclotron Resonance (ECR) Plasma-Enhanced CVD System

Matthew J. Smith, Material Science and Engineering, Johns Hopkins University
Center for Nanoscale Systems at Harvard University, 9 Oxford St, Cambridge, MA
MJSmith@jhu.edu
Ling Xie, lxie@deas.harvard.edu
Erli Chen, CNS at Harvard University

Abstract

Depositing ultra-thin high quality dielectric films to be compatible with nanoscale devices is a challenge. The aims of this study are: (i) to investigate the deposition of nanometer thick silicon nitride films using ECR-PECVD; and (ii) to characterize these films. X-ray photoelectron spectroscopy (XPS) was used for film composition analysis and spectroscopic ellipsometry for thickness and refractive index measurements. The results show a strong relationship between the refraction index and compositions for the films with a thickness of 50 nm. Important trends are also identified concerning index of refraction and deposition time for ultra-thin films. Mathematical formulae that use XPS peak intensity ratios to estimate the thickness of ultra-thin films are modified for ultra-thin silicon nitride films. The preliminary results show that the thickness of these silicon nitride films can be estimated using XPS peak intensity ratios.

Introduction

The purpose of this project is to further our understanding of silicon nitride films fabricated using ECR-PECVD. We are interested in depositing ultra-thin (less than 10 nm) silicon nitride films using ECR-PECVD because this process allows for very low deposition temperatures, below 150°C. In this project, we studied the effects of SiH_4 flow rates on the composition of films with a thickness of 50 nm; the variation of index of refraction with deposition time; and the estimation of the thickness of ultra-thin silicon nitride films using XPS.

Experiment

The composition of nitride films formed by ECR-PECVD is controlled by several factors, primarily the gas flow rate into the chamber. For silicon nitride deposition, SiH_4 and N_2 react and produce silicon nitride (Si_3N_4) and hydrogen gas. The nitrogen to silicon concentration ratio was measured using X-ray photoelectron spectroscopy, and then analyzed. For a stoichiometric nitride film, the concentration ratio of N/Si should be 1.33 (4 nitrogen for every 3 silicon) and the refractive index should be about 2.0, which can be measured using the spectroscopic ellipsometer (SE). The index of refraction was also analyzed vs. deposition time for thick and ultra-thin films. The Si substrates used for ultra-thin depositions were etched in HF solution to minimize native silicon oxide. The data collected using the ellipsometer was fitted to a 2-layer model to account for the native oxide present at the interface between substrates and films. Several oxide thicknesses were tested with the model, and the model with the lowest MSE was chosen for each series of films.

The ultra-thin films, ranging from 3–8 nm in thickness, are thin enough that photon electrons from the silicon substrate can escape through the thin film and appear as a Si-Si signal on the XPS measurements. The thinner the film, the larger the number of photon electrons that can escape from the substrate, and thus a larger Si-Si peak appears at 98.9 eV, separate from the Si-N peak at 102.0 eV. We explored using the area ratio of these peaks to calculate the thickness of the film. This was done previously for silicon oxide thin films [3], but has not been applied to silicon nitride films.

Results and Discussion

The XPS and SE measurements of the films deposited with different flow rates showed that the films deposited at higher silane flow rates (above 55–60 sccm) are silicon rich and have an index above 2.0, while those deposited at lower flow rates are indeed nitrogen rich and have an index below 2.0. Our data agrees with the accepted index-composition ratio correlation (Figure 1); a film with a N/Si ratio of 1.33 should have an index of 2.0.

When evaluating the index of refraction change with deposition time, we found that the thicker films had a constant index of refraction when the deposition time was varied from 400 to 600 seconds. However, the index of refraction of ultra-thin films, with variable deposition time from 10 to 60 s, did not remain constant with deposition time as shown in Figure 2. This implies that a unique combination of deposition time and flow rate is required to obtain a particular thickness and index of refraction when depositing ultra-thin Si_3N_4 films with ECR-PECVD.

When using XPS data to estimate ultra-thin film thickness, the inelastic-mean-free-path and the silicon concentration ratio of the film to the silicon substrate per unit volume, had to be approximated. We found that our best approximations for these constants could not get reasonable values for estimated film thickness. A scaling constant was introduced into the equation and this technique was able to return thicknesses that paralleled those determined by our best spectroscopic ellipsometry models. Figure 3 shows the simulation as well as the Ellipsometer results.

Future Work

In the future, we hope to refine the process of using XPS to measure silicon nitride film thicknesses of less than 10 nm. An alternate method of knowing film thickness is necessary, so that we have more accurate data to model our formulae after.

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References

Xie L., Deng J., Shepard S., Tsakirgis J., and Chen E., "Low-Temperature Deposition of High-Quality, Nanometer-Thick Silicon Nitride Film in Electron Cyclotron Resonance (ECR) Plasma-Enhanced CVD System", presented at Nanotech 2005, Anaheim CA, May 2005.

Flewitt A.J., Dyson A.P., Robertson J., and Milne W.I., "Low Temperature growth of silicon nitride by electron cyclotron resonance plasma enhanced chemical vapour deposition," *Thin Solid Films* **383** (2001),, 172–177.

Xie L., Zhao Y., White M.H., "Interfacial oxide determination and chemical/electrical structures of $HfO_2/SiO_x/Si$ gate dielectrics," *Solid-State Electronics* **48** (2004), 2071–2077.

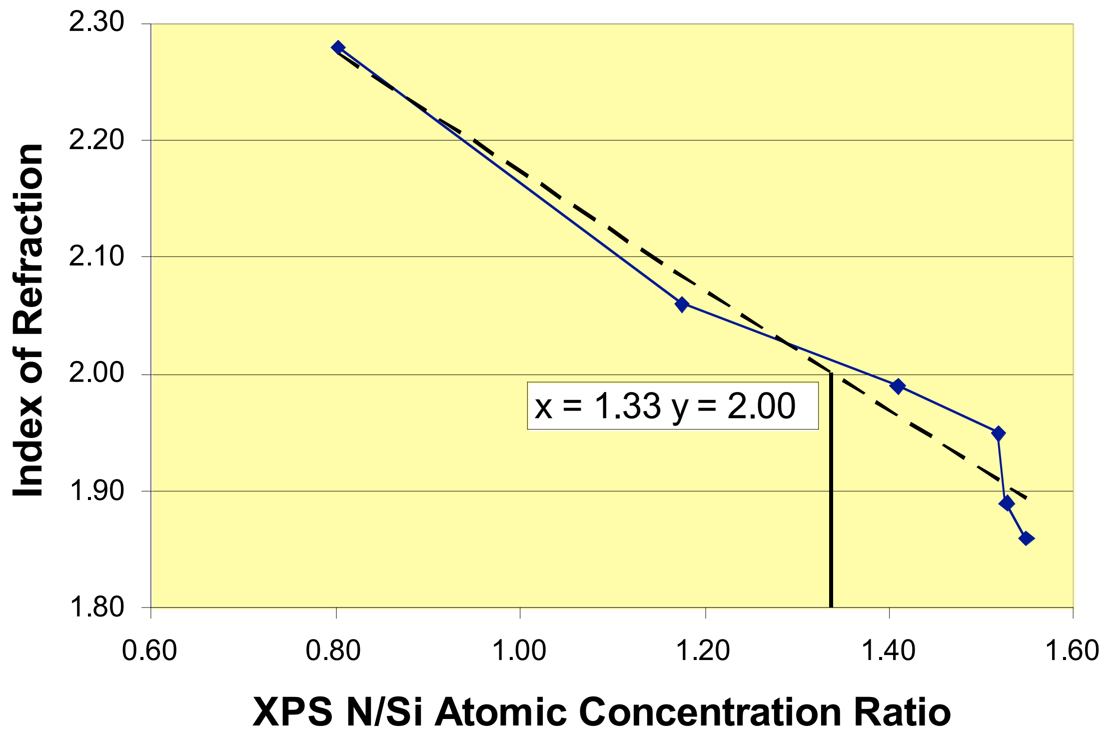

Figure 1: A stoichiometric silicon nitride film has an index of refraction of 2.

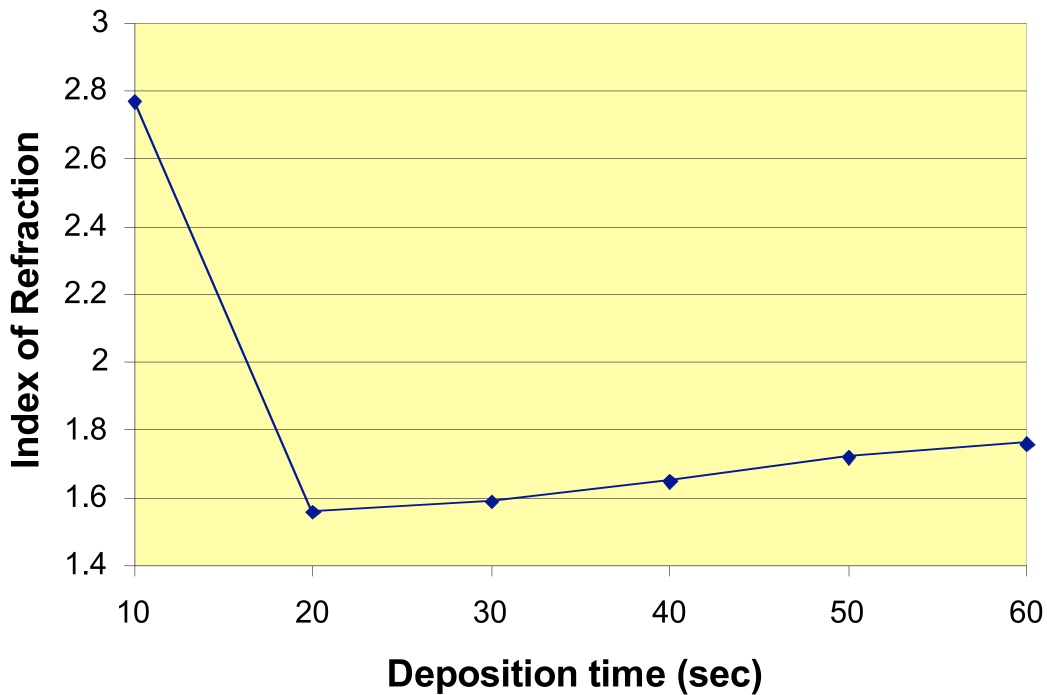

Figure 2: Unlike in thicker films, ultra thin silicon nitride films have an index of refraction that varies with thickness.

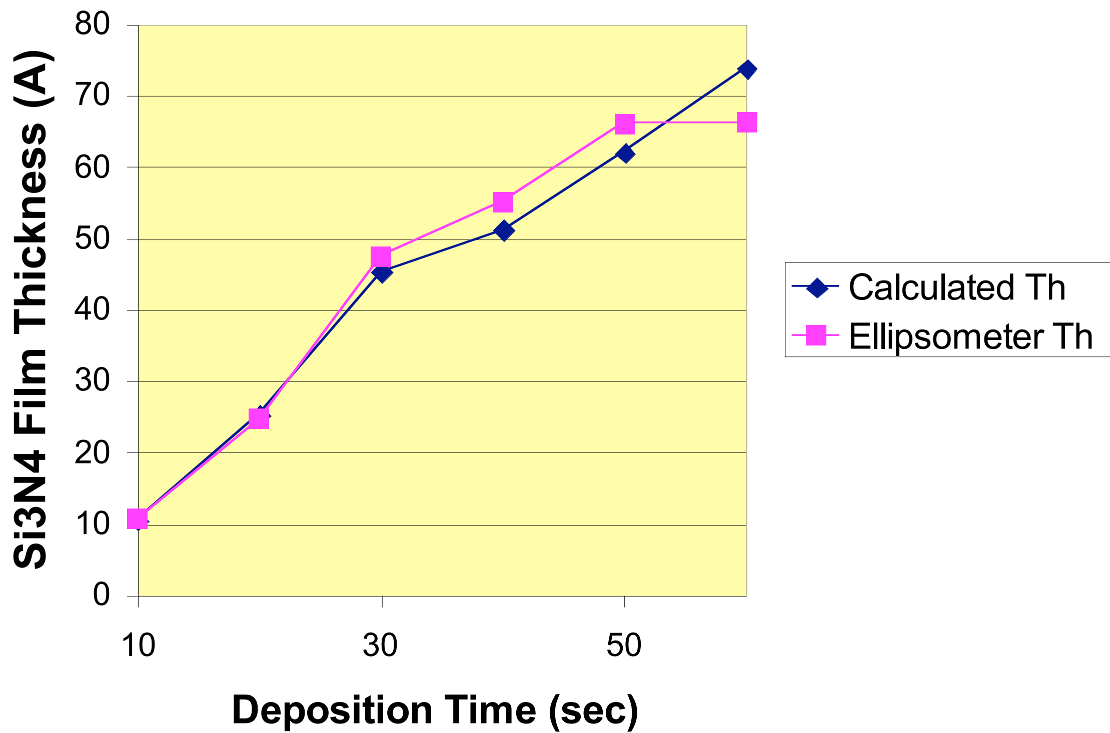

Figure 3: After introducing a scaling constant, the XPS data can be used to predict thicknesses that parallel the thicknesses measured using ellipsometry.