Observation of Optical Properties of Neodymium Oxide with Spectroscopic Ellipsometry

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The annealing dependence of the optical properties of Nd_2O_3 films deposited by atomic layer deposition has been investigated by variable-angle spectroscopic ellipsometry (VASE). Based on VASE measurements, it is found that the refractive index and high-frequency dielectric constant decrease with increasing annealing temperature. The optical bandgap energy extracted using the Cody method varies from 4.13 eV for the as-grown state to 4.78 eV for the film annealed at 900°C. Moreover, three proposed physical models with corresponding optical models are applied to fit the experimental data to understand the possible structural change of the films with annealing temperature. Fitting results indicate that the interfacial interaction between the substrate and the film bulk occurs during the postdeposition annealing procedure and the surface properties of the Nd_2O_3 films are improved after annealing at 900°C. It is shown that the extracted VASE parameters well represented the characteristics of $\text{Nd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ stacks with different annealing temperatures.

Key words: High- k , Nd_2O_3 , atomic layer deposition, spectroscopic ellipsometry

INTRODUCTION

The downscaling of metal–oxide–semiconductor field-effect transistors (MOSFETs) requires the development of high- k dielectrics, as silicon-dioxide-based gate dielectrics approach their fundamental physical limits. Recently, the rare-earth sesquioxide Nd_2O_3 , as one of the promising candidates, has become attractive because of its high dielectric constant ($k = 10$ to 15),^{1–4} wide bandgap ($E_g \approx 5.8$ eV),^{5,6} and good lattice matching and thermodynamic stability in contact with silicon substrate.⁶ It also has good insulating properties and an appropriate band offset (over 1 eV) with Si for microelectronic applications.^{6–8}

Variable-angle spectroscopic ellipsometry (VASE) is an efficient, noncontact tool to probe the optical properties of a sample.^{9–13} It allows the determination

of a material's optical functions, refractive index n , extinction coefficient k , and thickness for multilayer films in a nondestructive manner. In the semiconductor industry, VASE has been used to characterize a variety of different materials such as HfO_2 ,^{14,15} ZrO_2 ,^{9,16} Ta_2O_5 ,⁹ and indium tin oxide (ITO) thin films.¹⁷

Although several studies have focused on the electrical and compositional properties of Nd_2O_3 films deposited by atomic layer deposition (ALD),^{1,4,8} the optical properties of $\text{Nd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ stacks have not been investigated systematically. In this work, VASE was used to investigate the dependence of the optical properties of the dielectric films on the postdeposition annealing temperature. The variations of refractive index, extinction coefficient, and high-frequency dielectric constant with annealing temperature are presented. Bandgap energies of all the samples are extracted. Besides, the behavior of Nd_2O_3 on annealing is investigated using proposed single-, double-, and triple-layer physical models.

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EXPERIMENTAL PROCEDURES

Film depositions were performed in a commercial R-SERIES-150 ALD reactor. Nd_2O_3 films were grown on *p*-type silicon (100) substrates with resistivity of 8 Ω cm to 12 Ω cm. Before the deposition, the wafers were cleaned with a standard Radio Corporation of America (RCA) method.¹⁸ Native oxide on silicon was not removed before deposition. Volatile $\text{Nd}(\text{thd})_3$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) and ozone were used as precursors. Nitrogen was used as carrier and purge gas. The Nd_2O_3 films were deposited at reduced pressure of 10 mbar to 12 mbar at temperature of 320°C. Five hundred growth cycles were carried out with fixed precursor pulse length of 1 s and 1.5 s for $\text{Nd}(\text{thd})_3$ and O_3 , respectively. Selected Nd_2O_3 samples were annealed at 700°C and 900°C for 5 min in N_2 ambient atmosphere. All measurements were performed with a J.A. Woollam VASE ellipsometer at room temperature. Selected as-grown and annealed samples with nominal thickness of 18 nm were characterized at wavelength from 190 nm to 1200 nm. To improve accuracy and provide cross-check modeling, optical data were obtained at light incident angles of 55°, 65°, and 75°.

RESULTS AND DISCUSSION

Determination of Refractive Index (n) and Extinction Coefficient (k)

To determine the refractive index (n) and extinction coefficient (k), the film thickness should be determined first. For all selected samples, a three-layer model (Si substrate/native SiO_2 layer/ Nd_2O_3 layer) was used to extract corresponding optical parameters. The obtained VASE data were modeled using optical models for SiO_2 and Si layers provided by J.A. Woollam, Inc., and a Cauchy model was applied for the Nd_2O_3 layer in a nonabsorbing region of 1 eV to 3 eV in this case. The thickness of the Nd_2O_3 layer was variable, while the optical properties of the layer and thickness of the underlying Si and SiO_2 were constant. The fixed thicknesses of the underlying Si substrate and SiO_2 layers were determined from measurements of the Si/ SiO_2 stacks before deposition. The obtained thicknesses were 17.347 nm, 17.980 nm, and 15.623 nm for the as-grown sample and samples annealed at 700°C and 900°C, respectively, with mean square error (MSE)¹⁹ of less than 2.163 nm as presented in Table I.

With the fixed film thickness, the refractive index (n) and extinction coefficient (k) were obtained by applying a pointwise fitting procedure over the entire spectral range, as shown in Fig. 1.

The refractive index was 1.862 at wavelength of 620 nm (2 eV) for the as-grown sample. This value is slightly lower than the value of 2.1 reported in literature.²⁰ In particular, it was observed that the refractive index followed a normal dispersion behavior with photon energy, increasing as the photon energy increased. Furthermore, a decrease in film refractive index was obvious with increasing annealing temperature. A similar trend has been observed for $\text{Er}_2\text{O}_3/\text{Si}$ ^{21,22} and HfO_2/Si ²³ annealed in N_2 ambient. However, the opposite trend was reported for $\text{Y}_2\text{O}_3/\text{Si}$ and ZrO_2/Si ²⁴ annealed in air ambient, and HfO_2/Si ²⁵ annealed in oxygen ambient. In particular, the film annealed at 900°C exhibited the lowest refractive index, being attributed to a decrease in the packing density with higher crystallinity and incorporation of silicon into the film with increasing annealing temperature. It is known that Si atoms can easily diffuse from the substrate into the films to form Nd silicate or more silicon oxide components at the interfacial layer with increasing annealing temperature.²⁶ Film density is expected to decrease due to the contribution of the lower film density of 2.37 g/cm³ for SiO_2 . Moreover, the film morphology may evolve from an amorphous configuration to polycrystalline at lower annealing temperature (700°C), and eventually to a more crystalline configuration at higher annealing temperature (900°C).²⁷ Due to the lower packing density with higher crystallinity,^{28,29} the decrease in refractive index is expected. This trend was also observed for Er_2O_3 ²¹ films after high-temperature heat treatment.

Figure 1 also shows the extinction coefficient data for the three samples. It was observed that the transparent regime ($k = 0$) is evident at lower energies. On the other hand, an extinction onset at 5.34 eV corresponding to absorption across the bandgap of the film was found for the sample annealed at 900°C. However, the data recorded from the as-grown film and the film annealed at 700°C showed a pronounced feature at lower energy, with a shoulder at 4.7 eV followed by a rapid rise above 5.0 eV. This rapid rise is associated with absorption due to optical transitions through the bandgap, while the former features are attributed to interfacial defect states below the band edge.^{30–32} The

Table I. Dispersion parameters of Nd_2O_3 films with different annealing temperatures

Sample	Thickness (nm)	S_0 (m ⁻²)	λ_0 (nm)	ϵ_∞	E_0 (eV)	E_0/S_0
As grown	17.347	0.106×10^{15}	147	3.29	8.434	7.939×10^{-14}
700°C	17.980	0.108×10^{15}	146	3.30	8.492	7.852×10^{-14}
900°C	15.623	0.113×10^{15}	140	3.23	8.856	7.806×10^{-14}

Fig. 1. Refractive index (n) and extinction coefficient (k) for all selected samples.

absence of subband defect states in the sample annealed at 900°C indicates that the high temperature greatly reduced film defects. These trends are in agreement with the trends reported for HfO₂ deposited by ALD.^{30,33}

Refractive Index Dispersion Analysis

The resultant data on the refractive index can be analyzed to obtain the high-frequency dielectric constant (ϵ_∞), average oscillator wavelength (λ_0), and oscillator strength (S_0) for the films by applying the following simple classical dispersion relation:^{34–37}

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - \lambda_0^2 / \lambda^2}, \quad (1)$$

$$S_0 = \frac{(n_0^2 - 1) \lambda_0^2}{\lambda_0^2}, \quad (2)$$

where λ_0 is the average oscillator position, S_0 is the average oscillator strength, and n_0 is the refractive index at infinite wavelength λ_0 (the average interband oscillator wavelength). The plots of $1/(n^2 - 1)$ versus $1/\lambda^2$ give straight lines with different slopes, and can be fit well by the classical single electronic oscillator dispersion formula, as shown in Fig. 2. The parameters S_0 and λ_0 can be deduced from the slope ($-1/S_0$) of the resulting straight line and the infinite-wavelength intercept ($1/S_0 \lambda_0^2$), respectively. The refractive index dispersion parameter (E/S_0) and the high-frequency dielectric constant ($\epsilon_\infty = n_0^2$), which depend on the characteristics of the various interband transitions, can also be determined, as presented in Table I.

Fig. 2. Plots of $1/(n^2 - 1)$ versus $1/\lambda^2$ for Nd₂O₃ films treated at different annealing temperatures.

From Table I, it can be noted that the high-frequency dielectric constant decreases with increasing annealing temperature, originating from the decrease in the refractive index of the films. The average interband oscillator energy can be given by $E_0 = hc/\lambda_0$, where h is Planck's constant and c is the velocity of light. The estimated E_0 values increase with the annealing temperature. Furthermore, the evaluated E_0/S_0 values are of the same order as those obtained for HfO_xN_y films.³⁵

Optical Bandgap Determination

To determine the bandgap values of the as-grown and annealed Nd₂O₃ films, Cody plots³⁸ of $(\alpha n/E)^{1/2}$ versus photon energy E were employed, where the absorption coefficient α is defined as $\alpha = 4\pi k/\lambda$, λ is the light wavelength, and k is the extinction coefficient.

From Fig. 3, the bandgap of the as-grown film is measured to be about 4.13 eV. After annealing at 700°C and 900°C, the bandgap E_g increases from 4.6 eV to 4.78 eV. The bandgap energy obtained for the as-grown sample is smaller than the reported value of 5.8 eV found from the O 1s energy loss spectrum.⁵ The variation appears to relate to the methods of deposition, film thickness, and experimental techniques used to obtain the bandgap energy. Furthermore, bandgap increase is observed with annealing temperature growth. It is believed that the presence of defects and disorder in the film would produce localized states in the band structure and contribute to the low value of the energy gap. Meanwhile, the annihilation of oxygen vacancies and disorder in the annealed film would result in decreased density of localized states in the band and increase of the bandgap.^{35,39} Additionally, crystalline oxides may have larger bandgap.⁴⁰ Similar

Fig. 3. Curves of $(\alpha n/E)^{1/2}$ versus photon energy E .

results were reported for Hf silicate⁴¹ and Er oxide²¹ on silicon substrates.

Physical Models

To understand the effects of annealing on the physical and optical properties of the $\text{Nd}_2\text{O}_3/\text{SiO}_2/\text{Si}$ gate stacks, three physical models were considered to describe the Nd_2O_3 films. First, a single homogeneous layer model (M1) was assumed, as shown in Fig. 4a, and a Cody–Lorentz (C–L) oscillator model¹⁹ was applied to describe the Nd_2O_3 layer. The second proposed model (M2) consisted of a double-layer film with dense Nd_2O_3 layer and surface roughness layer (SRL), as shown in Fig. 4b. The C–L model and srough model [a shorthand for the 50% effective medium approximation (EMA) mixture of Nd_2O_3 and void optical constants] were used for simultaneous fitting in this case. Considering the possible interaction at the interface between the Nd_2O_3 and SiO_2 layer, the third proposal (M3) included a heterogeneous mixture layer of Nd_2O_3 and SiO_2 material (Fig. 4c). The mixture was modeled using the Bruggeman effective medium approximation (BEMA) for the estimation of the component fraction.

The three proposed physical models were fit against the experimental data curves. The results obtained using the models for the as-grown films and those annealed at 700°C and 900°C are presented in Tables II, III, and IV, respectively.

The MSE can be used to quantify the quality of the match between the experimental and modeled data. The smaller the MSE value, the more accurate the film structure prediction. It can be seen from Table II that the MSE values decrease as more complicated physical models are applied, indicating that M3 may provide the most probable physical structure of the as-grown film. Similar variation trends are also observed for the annealed samples in Tables III and IV. Comparison of the MSE values

Fig. 4. Schematic representation of the proposed (a) single- (M1), (b) double- (M2), and (c) triple-layer models (M3) for the SE modeling procedure.

suggests that M3 may provide the most probable physical structure for all three samples.

Furthermore, it is noticed that the fractional content of Nd_2O_3 in the BEMA layer was -0.34 for the as-grown sample, except when applying model M3. This result further validates the hypothesis that interfacial interaction between Nd_2O_3 and SiO_2 barely occurs during the film deposition. However, a fractional content of Nd_2O_3 of 0.048 was found for the sample annealed at 700°C, suggesting interfacial reaction between SiO_2 and Nd_2O_3 . Further increase of the annealing temperature to 900°C resulted in a lower value of the fractional content of Nd_2O_3 of 0.026 . The decreased Nd_2O_3 fraction indicates less Nd oxide component in the interfacial layer between the silicon substrate and the bulk Nd_2O_3 layer. This trend can be understood because more silicon atoms may diffuse from the substrate into the films with increasing annealing temperature, and Nd silicate component with higher silicon oxide component at the interfacial layer may be formed when annealing at 900°C.^{8,26}

The analysis of the MSE and the fractional content of Nd_2O_3 in the BEMA layer indicates that the most suitable physical model for the as-grown sample is M2. For the annealed samples, model M3 provides the most accurate description of the film structure.

Moreover, the thickness of the surface roughness layer is presented in Tables I, III, and IV. The fitting results in the framework of model M2 are used to obtain the variation of the thickness of the SRL depending on the annealing temperature. It can be seen that the SRL thickness decreased from 0.437 nm to 0.425 nm after annealing at 700°C and to 0.119 nm after annealing at 900°C. It is evident that higher-temperature annealing at 900°C significantly improved the film surface properties.

Table II. Results from VASE analysis of Nd₂O₃ films (as grown)

Physical Model	Sublayers	Fitting Model	Thickness (nm)	MSE	Nd ₂ O ₃ Fraction
M1	Nd ₂ O ₃	C-L	17.523	3.137	—
M2	SRL	Srough	0.437	3.106	—
M3	Nd ₂ O ₃	C-L	17.421	2.902	-0.34
	SRL	Srough	0.811		
	Nd ₂ O ₃	C-L	16.802		
	SiO ₂ + Nd ₂ O ₃	BEMA	1.895		

Table III. Results from VASE analysis of Nd₂O₃ films (annealed at 700°C)

Physical Model	Sublayers	Fitting Model	Thickness (nm)	MSE	Nd ₂ O ₃ Fraction
M1	Nd ₂ O ₃	C-L	18.012	2.704	—
M2	Srough	Srough	0.425	2.685	—
M3	Nd ₂ O ₃	C-L	17.878	2.653	0.048
	Srough	Srough	0.418		
	Nd ₂ O ₃	C-L	17.516		
	SiO ₂ + Nd ₂ O ₃	BEMA	1.597		

Table IV. Results from VASE analysis of Nd₂O₃ films (annealed at 900°C)

Physical Model	Sublayers	Fitting Model	Thickness (nm)	MSE	Nd ₂ O ₃ Fraction
M1	Nd ₂ O ₃	C-L	15.658	4.718	—
M2	Srough	Srough	0.119	4.688	—
M3	Nd ₂ O ₃	C-L	15.556	4.653	0.026
	Srough	Srough	0.095		
	Nd ₂ O ₃	C-L	15.452		
	SiO ₂ + Nd ₂ O ₃	BEMA	1.633		

Similar results have been obtained by other groups^{3,42} using atomic force microscopy (AFM).

CONCLUSIONS

VASE was used to evaluate the optical properties of high-*k* dielectric Nd₂O₃/SiO₂/Si stacks as a function of annealing temperature. It was found that the refractive index (*n*) decreases with increasing annealing temperature due to the decrease in packing density with higher crystallinity and silicon incorporation into the film. Analysis of extinction coefficient data showed that subband states, related to defects in the film, were significantly reduced after annealing at 900°C. Moreover, the high-frequency dielectric constant decreased with increase in annealing temperature, originating from the decrease in the refractive index of the film. The optical bandgap extracted using the Cody method varied from 4.13 eV for the as-grown film to 4.78 eV for the film annealed at 900°C. Besides, the behavior of Nd₂O₃ was investigated using different reflection models. Analysis of the MSE and the fractional content of Nd₂O₃ in the BEMA layer

indicated that the M2 physical model is the most suitable for the as-grown sample. For the annealed samples, while M2 provides reasonable fitting results, M3 may provide the most accurate description of the film structure. Furthermore, the thickness of the SRL decreases with increase of the annealing temperature, suggesting that annealing at a higher temperature of 900°C significantly improves the surface properties of the film. Thus, the VASE technique has been proven to be an efficient way to characterize the samples without film destruction.

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