Electronic Structure and Optical Quality of Nanocrystalline \( \text{Y}_2\text{O}_3 \) Film Surfaces and Interfaces on Silicon

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ABSTRACT: Nanocrystalline yttrium oxide (\( \text{Y}_2\text{O}_3 \)) thin films were made by sputter deposition onto silicon (100) substrates keeping the deposition temperature fixed at 300 °C. The surface/interface chemistry, \( \text{Y}–\text{O} \) bonding, and optical constants of the \( \text{Y}_2\text{O}_3 \) film surface and \( \text{Y}_2\text{O}_3–\text{Si} \) interface were evaluated by the combined use of X-ray photoelectron spectroscopy (XPS), depth-profiling, and spectroscopic ellipsometry (SE). XPS analyses indicate the binding energies (BEs) of the Y 3d doublet; i.e., the Y 3p\(_{3/2}\) and Y 3d\(_{3/2}\) peaks are located at 117.0 and 119.1 eV, respectively, characterizing yttrium in its highest chemical oxidation state (\( \text{Y}^{3+} \)) in the grown films. The optical model is constructed based on the XPS depth profiles, which indicate that the \( \text{Y}_2\text{O}_3//\text{Si} \) heterostructure can be represented with \( \text{Y}_2\text{O}_3–\text{Si}_x\text{O}_y \) interfacial compound—Si substrate. Such a model accounts for the experimentally determined ellipsometry functions and accurately produces the dispersive index of refraction \( n(\lambda) \) of \( \text{Y}_2\text{O}_3 \) and \( \text{Y}_x\text{Si}_y\text{O}_z \). The \( n(\lambda) \) of \( \text{Y}_2\text{O}_3 \) and \( \text{Y}_x\text{Si}_y\text{O}_z \) follows Cauchy’s dispersion relation, while the \( \text{Y}_x\text{Si}_y\text{O}_z \) formation accounts for degradation of optical quality.

I. INTRODUCTION

Oxide dielectrics have been the subject of numerous investigations for many years due to their possible device integration in a wide range of technologies involving electronics, electro-optics, optoelectronics, and magneto-electronics.1–5 Yttrium oxide (\( \text{Y}_2\text{O}_3 \)), a stable oxide of yttrium metal, has received significant attention in recent years in view of its possible integration into a wide range of scientific and technological applications.6–12 \( \text{Y}_2\text{O}_3 \) films exhibit excellent electronic properties such as transparency over a broad spectral range (0.2–8 \( \mu \)m), high dielectric constant (~14–18), high refractive index (~2), large band gap (~5.8 eV), low absorption (from near-UV to IR), and superior electrical breakdown strength (~3 MV/cm).1,3–11,13–15 These properties make \( \text{Y}_2\text{O}_3 \) films interesting for various electrical and optical devices.16–22 Yttrium oxides were proposed as hosts for rare-earth elements, and efficient thin film phosphors were prepared.23–29 The interface layer formation, however, was detected for several compounds, and structural and chemical parameters of the interface were dependent on the deposition conditions. Therefore, controlled growth and manipulation of microstructure, particularly at the nanoscale dimensions, has important implications for the design and applications of \( \text{Y}_2\text{O}_3 \) films.

Yttrium oxide is a c-type rare-earth oxide.30 The c-type structure of \( \text{Y}_2\text{O}_3 \) is stable up to 2325 °C in the air. The c-type structure is a modified fluorite-type cubic structure with one-fourth of the anion sites vacant and regularly arranged. The structural stability coupled with mechanical properties also make \( \text{Y}_2\text{O}_3 \) an interesting material for other applications. Specifically, \( \text{Y}_2\text{O}_3 \) has been in use in the development of functional ceramics for solid oxide fuel cells, nuclear engineering, high-temperature protective coatings, and metal-reinforced composites for high strength structural components.31–35

A wide variety of physical and chemical deposition techniques have been employed to fabricate \( \text{Y}_2\text{O}_3 \) films. However, in both physical and chemical deposition methods, the ultramicrostructure in terms of the chemical valence state of

Received: March 23, 2014
Revised: May 15, 2014
Published: May 30, 2014
Yttrium oxide (Y$_2$O$_3$) thin films were deposited onto silicon (Si) (100) wafer substrates by radio frequency (RF) (13.56 MHz) reactive magnetron sputtering. All the substrates were thoroughly cleaned using the RCA (Radio Corporation of America) procedure. The cleaning procedure has three major steps. (1) Removal of insoluble organic contaminants using 5:1:1 H$_2$O/H$_2$O$_2$/HCl solution. (2) Removal of ionic and heavy metal contaminants using 6:1:1 H$_2$O/H$_2$O$_2$/HCl solution. (3) Removal of native oxide by buffered oxide etching solution. At the stage, a Kikkuchi pattern was recorded commonly from Si substrates by RHEED measurements. Finally, the substrates were dried with nitrogen before introducing them into the vacuum chamber. After this, the substrates were transferred to a magnetron sputtering chamber through the laboratory air because we do not have an isolated substrate transport system. The vacuum chamber was initially evacuated to a base pressure of $\sim 10^{-6}$ Torr. An yttrium (Y) target (Plasmaterials Inc.) of 2” diameter and 99.95% purity was employed for reactive sputtering. The Y-target was placed on a 2-in. sputter gun, which is placed at the distance of 8 cm from the substrate. A sputtering power of 40 W was initially applied to the target while introducing high purity argon (Ar) into the chamber to ignite the plasma. Once the plasma was ignited the power was increased to 100 W, and oxygen (O$_2$) was released into the chamber for reactive deposition. The flow of the Ar and O$_2$ and their ratio were controlled using MKS mass flow controllers. Before each deposition, the Y-target was presputtered for 10 min using Ar alone with the shutter above the gun closed. The deposition was made keeping the substrate temperature ($T_s$) at 300 °C, which was found to be optimum to produce nanocristalline Y$_2$O$_3$ films as reported elsewhere.\textsuperscript{11,15,20}

## II. EXPERIMENTS

### A. Fabrication

Yttrium oxide (Y$_2$O$_3$) thin films were deposited onto silicon (Si) (100) wafer substrates by radio frequency (RF) (13.56 MHz) reactive magnetron sputtering. All the substrates were thoroughly cleaned using the RCA (Radio Corporation of America) procedure.\textsuperscript{36–38} Briefly, the RCA cleaning procedure removes organic, alkali ions, and heavy metal contaminants present on the surface of the substrate. The cleaning procedure has three major steps. (1) Removal of insoluble organic contaminants using 5:1:1 H$_2$O/H$_2$O$_2$/NH$_4$OH solution. (2) Removal of ionic and heavy metal atomic components using a solution of 6:1:1 H$_2$O/H$_2$O$_2$/HCl solution. (3) Removal of native oxide by buffered oxide etching solution. At the stage, a Kikkuchi pattern was recorded commonly from Si substrates by RHEED measurements. Finally, the substrates were dried with nitrogen before introducing them into the vacuum chamber. After this, the substrates were transferred to a magnetron sputtering chamber through the laboratory air because we do not have an isolated substrate transport system. The vacuum chamber was initially evacuated to a base pressure of $\sim 10^{-6}$ Torr. An yttrium (Y) target (Plasmaterials Inc.) of 2” diameter and 99.95% purity was employed for reactive sputtering. The Y-target was placed on a 2-in. sputter gun, which is placed at the distance of 8 cm from the substrate. A sputtering power of 40 W was initially applied to the target while introducing high purity argon (Ar) into the chamber to ignite the plasma. Once the plasma was ignited the power was increased to 100 W, and oxygen (O$_2$) was released into the chamber for reactive deposition. The flow of the Ar and O$_2$ and their ratio were controlled using MKS mass flow controllers. Before each deposition, the Y-target was presputtered for 10 min using Ar alone with the shutter above the gun closed. The deposition was made keeping the substrate temperature ($T_s$) at 300 °C, which was found to be optimum to produce nanocristalline Y$_2$O$_3$ films as reported elsewhere.\textsuperscript{11,15,20}

### B. Characterization

#### X-ray Photoelectron Spectroscopy (XPS)

Electronic properties of the Y$_2$O$_3$/Si system were characterized by X-ray photoelectron spectroscopy. Depth profiling of Y$_2$O$_3$ films on Si was performed with the standard procedure, which is a combination of Ar$^+$ ion sputtering/bombardment followed by XPS data acquisition and analysis.\textsuperscript{39–41} The XPS valence-band and core-level spectra of Y$_2$O$_3$ were measured using the ultrahigh vacuum (UHV) Analysis-System assembled by SPECS (Germany). The system is equipped with a PHOIBOS 150 hemispherical analyzer and X-ray monochromator FOCUS-500. The Al K$_\alpha$ irradiation ($h\nu = 1486.74$ eV, 200 W) was used as a source of photoelectron excitation. The survey spectrum was recorded at the analyzer pass energy of 50 eV and the narrow spectral regions at 10 eV. The atomic concentration ratios of elements on the sample surface were calculated from the integral photoelectron peak intensities and known atomic sensitivity factors (ASFs).\textsuperscript{42} The energy of Ar$^+$ ions for depth profiling, the current density, and the angle of sputter erosion were 1.05 keV, 4–5 $\mu$A/cm$^2$, and 45°, respectively. The depth profiling rate under these conditions was estimated as $\sim 0.3$ nm/min in reference to the Al$_2$O$_3$/Si model film system.

#### Reflection High-Energy Electron Diffraction (RHEED)

The surface crystallography of Y$_2$O$_3$ film was investigated using reflection high-energy electron diffraction (RHEED) measurements. The electron diffraction imaging was performed using a 50 keV electron beam in the EF-Z4-5 (Carl Zeiss, Germany) setup.

#### Spectroscopic Ellipsometry (SE)

The dispersive refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ were determined by means of spectroscopic ellipsometry (SE). Ellipsometric angles $\Psi$ and $\Delta$ were measured as a function of $\lambda$ in the spectral range of $\lambda \sim 250–1030$ nm using an ELLIPS-1771 SA ellipsometer.\textsuperscript{35} The instrumental spectral resolution was 2 nm, and the recording time of the spectrum did not exceed 20 s. The SE measurements were produced at three angles of incidence of light beam on the sample of 50°, 60°, and 70°. The four-zone measurement method was used with subsequent averaging over all the four zones.\textsuperscript{44–46}

## III. RESULTS AND DISCUSSION

The RHEED pattern of Y$_2$O$_3$ films grown at 300 °C is shown in Figure 1. The formation of a well-defined ring structure indicative of Y$_2$O$_3$ film of polycrystalline nature is evident from the RHEED pattern shown in Figure 1. The observed electron diffraction pattern matches the cubic-Y$_2$O$_3$ (JCPDS 43-613).\textsuperscript{47} The detailed XRD data and RHEED analysis of Y$_2$O$_3$ films as a
function of variable \( T_s \) were reported elsewhere.\(^{20,22} \) Briefly, the XRD and RHEED analyses indicate that the \( \text{Y}_2\text{O}_3 \) films grown at 25–100 °C were amorphous (\( \alpha \)-\( \text{Y}_2\text{O}_3 \)) in nature. The onset of crystallization with a (222) peak in XRD patterns corresponding to the cubic phase (\( \beta \)-\( \text{Y}_2\text{O}_3 \)) began to appear for the \( \text{Y}_2\text{O}_3 \) samples grown at \( T_s = 200 \) °C. The peak intensity increases with the increasing \( T_s \), indicating an increase in the average grain size with the increasing \( T_s \). The present RHEED data confirm the crystalline nature of the \( \text{Y}_2\text{O}_3 \) films grown on Si(100) substrates.

To obtain the surface and interface chemistry and accurately determine the optical constants, the \( \text{Y}_2\text{O}_3 \) film was sputtered all along the depth of the film until the signature of the Si substrate, while the surface/interface chemical composition was probed with XPS. The survey photoemission spectrum recorded from the initial surface is shown in Figure S1 (Supporting Information). Besides constituent element core levels and Auger lines related to \( \text{Y}_2\text{O}_3 \) oxide, the C 1s core level and C KVV Auger line were detected and attributed to adventitious hydrocarbons adsorbed from the air.

The detailed photoemission peaks of Y 3d, Si 2p, and O 1s levels are shown in Figures 2–4. All the spectra are shown as a function of sputtering time of the \( \text{Y}_2\text{O}_3/\text{Si} \) heterostructure.

The integrated sputtering (etching) time is as indicated in the XPS curves in Figures 2–4. The initial time setting (\( t = 0 \)) corresponds to most of the film top surface (as-grown). When the top surface contaminated layer was sputtered by ion bombardment, in the film bulk, the binding energy (BE) position of the Y 3d doublet (Y 3d\(_{5/2}\) and Y 3d\(_{3/2}\)) and O 1s line occurred at 157.0, 159.1, and 529.2 eV, respectively (Figures 2 and 4). The BE values can be compared to those earlier reported for the \( \text{Y}_2\text{O}_3 \) oxide. However, an observation of available electronic parameters of this functional oxide reveals a drastic scattering of BE values in the literature.
accumulated set of BE values of Y 3d<sub>5/2</sub> and O 1s lines in Y<sub>2</sub>O<sub>3</sub>, together with BE difference ∆BE<sub>Y</sub> = BE (O 1s) − BE (Y 3d<sub>5/2</sub>), is shown in Table 1. As found for many chemical classes of oxides, the BE difference parameters are insensitive to surface charging effects and BE scale calibration methods, and they are particularly suitable for the comparative analysis of XPS results measured by different spectrometers. In Table 1, the scattering of BE (Y 3d<sub>5/2</sub>) and BE (O 1s) values is as high as 3.0 and 2.9 eV which is evidently above any physically conditioned range. Comparatively, the scattering range of ∆BE<sub>Y</sub> is as low as 1.7 eV. Moreover, this scattering can be further decreased by simple selection. The highest and lowest ∆BE<sub>Y</sub> values appeared from refs 49 and 51, and this indicates an inexact energy scale calibration. If we exclude the results, the scattering range of ∆BE<sub>Y</sub> becomes as narrow as 0.7 eV. The value obtained in the present study is in good agreement with stoichiometric Y<sub>2</sub>O<sub>3</sub> and characterizes the yttrium ions in their highest oxidation state (Y<sup>3+</sup>). The calculated atomic concentrations are shown as a function of depth in Figure 5. As is evident from Figures 2–4, over the range of t = 3–60 min, the composition of the film bulk is stable and well related to stoichiometric Y<sub>2</sub>O<sub>3</sub>. The change in chemical composition is evident at t > 60 min, where the signals of yttrium and oxygen decrease while the silicon signal increases. The evolution of the Si signal and concentration as a function of time/depth can be clearly seen in Figures 2, 3, and 5. The most interesting feature is that, at t > 80 min, the Si 2p (BE ∼ 99.3 eV) and Si 2s (BE ∼ 150.4 eV) lines appear due to the presence of elemental Si<sup>0</sup>. Furthermore, the BE value of the Si 2p line remains constant up to the substrate. Simultaneously, at t = 80–90 min, the small intensity signal at 102.8 eV is recorded in the Si 2p core-level spectra shown in Figure 3. This line, in accordance with the energy difference ∼ −3.5 eV, in reference to the Si 2p (BE ∼ 99.3 eV) line from Si<sup>0</sup>, should be attributed to Si<sup>4+</sup> states. As for Y 3d<sub>5/2</sub> and O 1s levels, at t > 80 min, the lines shift to higher energies. The O 1s band can be subdivided into two components at ∼530.4 eV and ∼532 eV. The low-energy component indicates the value of ∆BE<sub>Y</sub> = BE (O 1s) − BE (Y 3d<sub>5/2</sub>) = 372.2 eV, which can be attributed to the Y−O−Si bonding. The higher-energy component in the O 1s band may be related to interfacial carbonate species because the increased C 1s line intensity is found at t = 80–90 min. All film components disappeared at t = 140 min, which relates to a film thickness of ∼42 nm.

Y<sub>2</sub>O<sub>3</sub>/Si film optical constants were primarily probed by spectroscopic ellipsometry (SE), which measures the relative changes in the amplitude and phase of the linearly polarized monochromatic incident light upon the oblique reflection from the sample surface. Ellipsometric parameters Ψ and Δ are related to the complex Fresnel reflection coefficients by the equation

$$I_g = \frac{R_p}{R_s}$$

(1)

where R<sub>p</sub> and R<sub>s</sub> are the coefficients for p- and s-polarized light waves. To calculate the dependencies of refractive index n(λ) and extinction coefficient k(λ) on optical wavelength λ, the experimental data were processed using the multilayer model. Over the whole spectral range, the spectral dependences of polarization angles were fitted for m points of the spectrum by minimization of the error function

$$\sigma^2 = \frac{1}{m} \sum_{i=1}^{m} [(\Delta_{\text{expt}} - \Delta_{\text{calc}})^2 + (\Psi_{\text{expt}} - \Psi_{\text{calc}})^2]$$

(2)

Extracting meaningful physical information from ellipsometry requires the construction of an optical model of the sample which generally has a number of distinct layers with individual optical dispersions. Interfaces between these layers are optical boundaries at which light is refracted and reflected according to the Fresnel relations. In the present case, to determine the dispersive optical constants accurately, the optical model of the Y<sub>2</sub>O<sub>3</sub>/Si system is constructed based on the XPS depth profiling results. The model contains the Y<sub>2</sub>O<sub>3</sub> top layer, multicomponent multilayer system, and the Si substrate. The optical model is schematically shown in Figure 6, while the layer composition is summarized in Table 2. The thickness and chemical composition of each layer are basically derived from XPS data with the following key points taken into consideration. As seen from Figure 5, at t < 60 min the film is completely formed by pure Y<sub>2</sub>O<sub>3</sub> oxide with the thickness of ∼18 nm. Between the Y<sub>2</sub>O<sub>3</sub> layer and Si substrate, the bulk of the interface film is modeled as a set of six sublayers with a different composition. The thickness of each sublayer between the Y<sub>2</sub>O<sub>3</sub> film and Si substrate was directly estimated from the XPS sputtering rate. The atomic composition of each layer is taken as the averaged value of boundary XPS measurements. Principally, the whole system is represented as the (Y<sub>2</sub>O<sub>3</sub>...
The experimental and calculated $\Psi(\lambda)$, $\Delta(\lambda)$ curves obtained for the Y$_2$O$_3$/Si multilayered system are shown in Figure 7.

Dispersive optical constants of Si and Y$_2$O$_3$ were taken from refs 66 and 67, respectively. The inverse ellipsometric problem was solved for compound Y$_x$Si$_y$O$_z$, with a fixed composition to generate the $n(\lambda)$ function. It was supposed that the $n(\lambda)$ function of Y$_x$Si$_y$O$_z$ falls between the $n(\lambda)$ functions of SiO$_2$ and Y$_2$O$_3$. The $n(\lambda)$ functions of Y$_2$O$_3$ and Y$_x$Si$_y$O$_z$ were approximated by Cauchy’s polynomials

$$n(\lambda) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}$$

For the calculations of the multilayer system, the Bruggeman effective medium model was used

$$\sum_i \left( \frac{\varepsilon_i - \varepsilon_{\text{eff}}}{\varepsilon_i - 2\varepsilon_{\text{eff}}} \right) = 0$$

where $f_i$ and $\varepsilon_i$ are the part and dielectric permittivity of the $i$-component and $\varepsilon_{\text{eff}}$ is the effective dielectric permittivity of the medium. The calculation results are shown in Figures 7 and 8.

The best correlation between the experimental and calculated $\Psi(\lambda)$, $\Delta(\lambda)$ curves (1) in Figure 7 is achieved at the best optical dispersion of Y$_x$Si$_y$O$_z$ interfacial oxide, as represented by curve (2) in Figure 8. The drastic difference, however, is evident between experimental points and $\Psi(\lambda)$, $\Delta(\lambda)$ curves (2) in Figure 7 calculated using the model of single homogeneous transparent layer. The refractive index dispersion calculated in the framework of a single homogeneous transparent layer is shown by curve (3) in Figure 8. Thus, the simple reflection model of a single homogeneous layer is principally not applicable for the adequate description of the real Y$_2$O$_3$/Si layered system. The refractive index dispersion in Y$_x$Si$_y$O$_z$ obtained in the framework of the multilayer reflection model is defined by Cauchy’s polynomial (3) with parameters $a = 1.749$, $b = 6.76 \times 10^3$, and $c = -8.3 \times 10^7$. The refractive index of oxide Y$_x$Si$_y$O$_z$ is noticeably lower than that of Y$_2$O$_3$ over the spectral range observed. For comparison, the $n(\lambda)$-curve (3) calculated using the single homogeneous transparent layer model (Figure 8) indicates very low refractive index values, but a little higher than those of pure SiO$_2$.

The significance of our present approach and model can be understood as follows. Several optical models were tested for the Y$_2$O$_3$/Si layered system in the literature. The multilayer stack of (surface roughened Y$_2$O$_3$ layer)—(Y$_2$O$_3$ bulk layer)—(SiO$_2$ interface layer)—(Si substrate) was proposed in ref 54. However, a very strange refractive index dispersion has been found for the Y$_2$O$_3$ oxide formed by Y$_2$O$_3$ target sputtering in the (Ar + O$_2$) mixture. The dispersion is very strong over the
spectral range of 200–500 nm and is practically absent at longer wavelengths. The results are not at all in correlation with the available dispersion properties of the Y₂O₃ bulk. In addition, the refractive index of Y₂O₃ films was found to decrease with (Ar + O₂) pressure increase and under better oxidative conditions. The SE method was applied for the determination of optical parameters of oxide films prepared by Y₂O₃ sputtering in ref 69. For the film formed at 700 °C, the refractive index dispersion was found to be close to that of Y₂O₃ bulk. However, the optical model used for SE calculations was not reported in detail.  

In the present study, the appearance of silicon in the Si⁰ state in the interface layer is detected by XPS depth profilometry. This material is available free of charge via the Internet at http:// pubs.acs.org.

IV. CONCLUSIONS

The depth profiling of the Y₂O₃/Si layer system produced by Ar⁺ ion bombardment and XPS measurements yields detailed information on the chemical composition and thickness needed for the construction of an adequate optical model of the reflecton system. This optical model was applied for the calculations of dispersive optical parameters of the interfacial Y₆Si₄O₁₃ oxide formed at the substrate temperature of 300 °C. Now, the results can be used as a basis for accurate SE determination of the Y₂O₃/Si layer thickness and interface control. Furthermore, the formation of a Y₆Si₄O₁₃ + Si composite is found by core level photoemission spectroscopy. As it is supposed, the silicon nanocrystals are generated by chemical reaction of yttrium and the SiO₂ layer on the substrate surface resulted in silicon reduction up to the Si⁰ state. This new effect may be of general significance for high-k dielectrics based on Y and rare-earth elements because of similar chemical properties. It is expected that these observations and model made for Y₂O₃/Si films may be applicable to a large class of similar layered systems, such as rare-earth oxide films grown on Si, SiGe, and Ge substrates.

ASSOCIATED CONTENT

Supporting Information

Survey XPS spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Authors at University of Texas at El Paso acknowledge with pleasure the support from NSF; NSF-PREM grant # DMR-1205302. This study is partly supported by the Ministry of Education and Science of the Russian Federation.

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