Thickness dependence of the physical properties of atomic-layer deposited Al_2O_3

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Yael Etinger-Geller,[1] Ekaterina Zoubenko,[1] Maria Baskin,[2] Lior Kornblum,[2,3,a] and Boaz Pokroy[1,3,a]

AFFILIATIONS

[1]Department of Materials Science and Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel
[2]Andrew and Erna Viterbi Faculty of Electrical Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel
[3]Russell Berrie Nanotechnology Institute, Technion—Israel Institute of Technology, Haifa 32000, Israel

[a]Authors to whom correspondence should be addressed: bpokroy@technion.ac.il and liork@tx.technion.ac.il

ABSTRACT

Inspired by nature, we investigate the short-range order effect on the physical properties of amorphous materials. Amorphous Al_2O_3 thin films exhibit a higher proportion of their 4-coordinated Al sites close to the surface, causing variations in the average short-range order of the film. Below some thickness, the density of these films changes with size. In this work, we address the short-range order effect, through the thickness, on the electronic and optical properties of atomic layer deposited Al_2O_3 thin films. Both the refractive index and the permittivity were found to vary with size. The refractive index increased with thickness, and for thick films (~ 50 nm), it was comparable to that of bulk amorphous Al_2O_3. The permittivity values increased with thickness as well, but did not reach those of the bulk material. Our experimental design circumvents the unpredictable Al_2O_3–Si interface, allowing new insights into the permittivity–thickness relations. By combining this design with accurate thickness and density measurements, we systematically correlate the refractive index and permittivity with the density and short-range order. These results shed light on the size effects in thin amorphous oxides and may guide the design of electronic and optical components and devices.

I. INTRODUCTION

Due to increasing interest in amorphous materials,[1,2] it would be intriguing to expand the study on its structure and properties. Our previous studies[3,4] have found that size effects can alter the short-range ordering within amorphous Al_2O_3 thin films deposited by atomic layer deposition (ALD), where thinner films exhibited a higher proportion of their 4-coordinated Al (Al_4) sites in comparison to thicker ones; these sites are located, mostly, at the surface and occur due to surface reconstruction. It was also shown that the density of the films increases with size by more than 15%,[4] where the density is lower closer to the surface due to the multiple Al_4 sites.[4] Theoretically, it is also possible that an interfacial layer exists between the Al_2O_3 film and the substrate, which is of lower density and could also affect the overall structure and properties. However, our previous work has shown that the average density of the Al_2O_3 thin films is increased with the thickness;[4] hence, we conclude that this is negligible. Since several physical properties of a material are density-dependent,[5–9] we expect that technologically important electronic and optical properties would exhibit significant variations with thickness.

We test this hypothesis on films grown by ALD, which allows the fabrication of amorphous oxides with excellent quality, and precise and conformal morphology.[10–14] ALD-Al_2O_3 is one of the most common amorphous oxides in use in science and technology, owing to its large growth window and useful optical and electronic properties. As such, Al_2O_3 thin films are useful for antireflective coatings,[15,16] in particular, the quarter wavelength type used in optical sensors,[17] for MEMS applications,[18,19] and others.

The permittivity–thickness relations have already been investigated to some extent[20] when the considerable advantages of ALD in microelectronics were becoming widely recognized.[21,22] In this context, most of the studies from that time have investigated ALD films deposited directly on hydrofluoric-acid-terminated Si. This Si surface is reactive and it forms a surface oxide layer within minutes in air; the conditions inside an oxide ALD reactor further promote the oxidation of the Si surface, and uncontrollable variations in ambient exposure times before loading into the reactor, and ALD process conditions (including the number of pulses) can considerably affect this interface layer.[23] This interface layer of low quality

SiO$_x$ or SiO$_x$M$_y$ (with M being the ALD oxide cation) has lower permittivity than the ALD oxide, and it can vary in thickness and physical properties as a function of the ALD oxide thickness. This small capacitor-in-series has a significant effect on the total capacitance, and when ignored, it leads to a common misinterpretation of the dielectric constant. Moreover, the relative magnitude of this effect is larger for lower ALD oxide thickness. In addition, at low thicknesses, leakage currents can complicate the capacitance measurements, resulting in an additional potential source of errors.

Motivated by our interest in thickness–density relations and their potential effects on the physical properties, we focus on the electronic and optical properties of the technologically important ALD-Al$_2$O$_3$ system in this work. We overcome the above challenges by completely circumventing the uncontrollable interface layer between the ALD oxide and Si, by employing a high quality thermal SiO$_2$ layer below the Al$_2$O$_3$ films used for capacitance measurements. This approach provides a consistent substrate and eliminates the possible effects of an interface layer and leakage currents on the interpretation of the permittivity.[24] Demonstrating a new approach for tuning these properties is expected to contribute to the design and application of these materials in optical and electronic components and devices.

II. EXPERIMENTAL

The deposition of amorphous Al$_2$O$_3$ by ALD is a common practice and has been well studied.[11–13,25,26] Given its very wide ALD window, this procedure serves as an ALD model process, and the resulting thin films are of high quality, smooth, and pinhole free.[10–12] Al$_2$O$_3$ films were grown in a plasma-enhanced ALD reactor (PEALD, ALD R-200 Advanced, Picosun, Finland) at 200 °C using trimethylaluminum and water, as described elsewhere.[4] The substrates were rinsed in ethanol and dried in N$_2$ prior to loading into the reactor. The thicknesses of the films were determined by x-ray reflectivity (XRR, SmartLab, Rigaku, Japan) analysis and spectroscopic ellipsometry (VASE, Woollam, USA).

Optical characterization was conducted on films deposited on p-Si (100) wafers. Spectroscopic ellipsometry was performed in the wavelength range of 300–1000 nm at three different angles (65°, 70°, and 75°). An interfacial oxide layer was accounted for in the interpretation of the results.

Metal-oxide-semiconductor (MOS) capacitors were fabricated on n-type Si wafers (nominal resistivity of 5–10 Ω cm) with 7.3 nm of SiO$_2$ grown by dry thermal oxidation. ALD-Al$_2$O$_3$ films were deposited directly onto the SiO$_2$ layer. 50 nm thick Al pads were deposited using e-beam evaporation (Airco Temescal FC-1800) through a shadow mask, and 300 nm blanket Al was deposited for a back contact.

Capacitance–voltage (C–V) measurements were performed using an Agilent E4980A LCR meter (Agilent Technologies, USA), with the capacitance corrected for series resistance based on multifrequency analysis.[27]

In all samples, the SiO$_2$ layer was analyzed separately and taken into consideration within the model and calculations.

III. RESULTS

The optical properties of amorphous materials make these materials attractive for various applications in science and
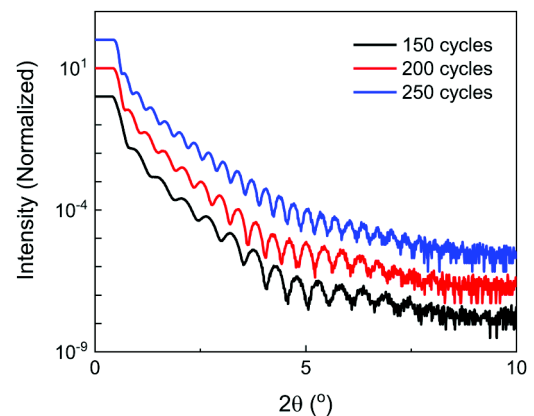

FIG. 1. XRR spectra of 3 samples that were investigated in this study. The number of cycles refers to the number of the ALD cycles that were performed.

technology.[2,28] The nature of the relationship between a material's density and its refractive index has prompted different theories, in all of which it is assumed that an increase in density should result in a higher refractive index. To study the refractive index of the Al$_2$O$_3$ layers, we used spectroscopic ellipsometry; thin Al$_2$O$_3$ films of various thicknesses ranging between 15 and 65 nm were deposited directly onto Si wafers and scanned with a spectroscopic ellipsometer. The results were fitted using the "WVAZE 32" software. In order to justify the use of spectroscopic ellipsometry in our analysis, we have compared the results that were achieved with this method with the XRR analyses that were performed on the same samples. Figure 1 presents the XRR spectra of 3 of our samples; it can be seen that the layers are extremely uniform and of low roughness. The thicknesses of the samples were calculated from the periodicity of the spectra,[29] and the results are summarized and compared with the values achieved with spectroscopic ellipsometry in Table I. It can be concluded that the values are in good agreement, which confirms our ellipsometry model.

In Fig. 2, a High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) image of a cross section of a 600-cycle Al$_2$O$_3$ film is presented; here, the uniformity and high quality of the film can be observed. The measured thickness for this sample was 63.7 ± 0.2 nm, which is in good agreement with the ellipsometry and XRR data.

TABLE I. Comparison between thickness values that were achieved using different methods.

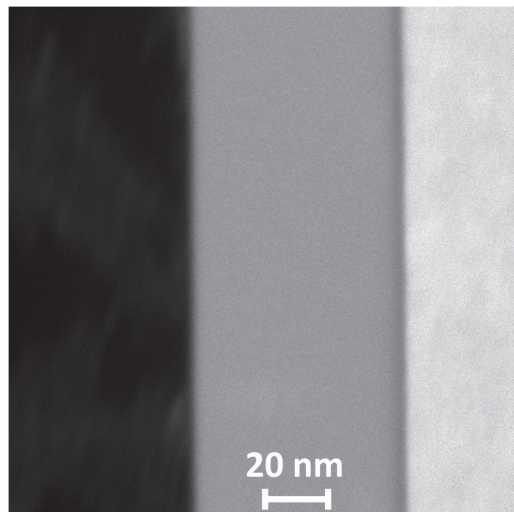| Number of deposition cycles	Thickness by ellipsometry (nm)	Thickness by XRR (nm)
150	16.8	16.5 ± 0.9
200	22.1	21.9 ± 1.1
250	27.2	26.8 ± 1.2
300	32.5	33.7 ± 1.4
600	63.8	64.6 ± 1.7

FIG. 2. HAADF-STEM image of a 600 cycles Al_2O_3 film (cross section).

The changes in the refractive index with different Al_2O_3 thicknesses can be seen in Fig. 3.

The figure shows that as the thickness increases, so does the refractive index. This result coincides with previous findings indicating that density increases with thickness, since a change in density should result in a corresponding change in the refractive index.

Since the value of the refractive index does not change significantly (<1%) at wavelengths higher than 600 nm, it can be considered to be constant above that level. The selected value of refractive index was at a wavelength of 635 nm (comparable with results from other studies, achieved with a single-wavelength ellipsometer, at a wavelength of 632.8 nm). In Fig. 3(b), the relationship between refractive index and thickness is plotted; As shown, for thicknesses below 40 nm, the refractive index gradually increases until it reaches a constant value of ~1.63. This value is close to values reported for amorphous aluminum oxide in previous studies.[25,30,31] This relationship is reminiscent of the relationship, reported in the past,[4] between

the refractive index and the thickness. Thus, as expected from both the theoretical and previous findings, the refractive index increases with density.

Another important parameter that is theoretically affected by the density is the dielectric constant (k). This parameter was studied using MOS capacitors with varying thicknesses of Al_2O_3. C–V analysis at 1 MHz was employed to determine the dielectric constant [Fig. 4(a)], accounting for the bottom 7.3 nm SiO_2 layer, which was uniform across samples.

The C–V curves [Fig. 4(a)] exhibit well-behaved characteristics[32] that indicate negligible (and uniform) contribution of interface states. The maximum value of each curve (accumulation, in positive voltages) was used to obtain the capacitance of the oxides.

A summary of the resulting dielectric constants [Fig. 4(b)] reveals that the dielectric constant increases with increasing thickness until it reaches a value of ~8.3. This value is higher than the values of ~7 reported for Al_2O_3 grown directly on Si.[20] However, the value of ~8.3 is lower than the dielectric constant of some crystalline Al_2O_3 phases.[33] It is also known that crystallinity increases its value.[34] It can be seen that the dielectric constant at 24.5 nm is slightly lower than that of the 19.1 nm thick sample; however, the difference between the two values is within experimental uncertainty. Since the density also increases with thickness and, according to these results, thicker films exhibited higher dielectric constants, these findings agree with our prediction. Therefore, the thickness can be used, in some cases, as a tuning parameter for the dielectric constant.

IV. DISCUSSION

A. Dependence of the refractive index on thickness

The refractive index of a thin Al_2O_3 film was found to vary with thickness, with higher thicknesses yielding higher refractive indexes. For thick films, the accepted refractive index is similar to that of bulk amorphous Al_2O_3 (~1.63), but the values obtained for thin films in the present study were lower, indicating that by changing the thin film's thickness, it is possible to manipulate this optical property according to a specific requirement.

In our previous study, we examined the relationship between the density of an amorphous Al_2O_3 film and its critical angle (θ_c).[4] According to Snell's law, the ratio between the refractive indexes (n) and the refraction angles (θ) when a ray passes from one medium to
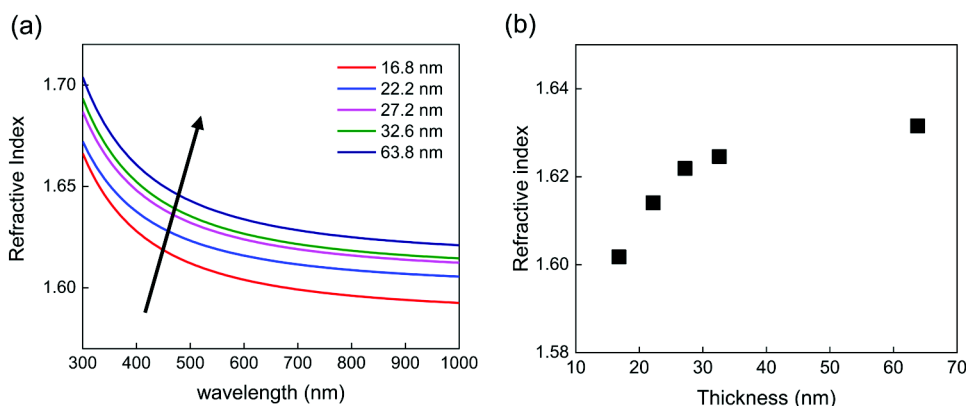

FIG. 3. (a) Changes in refractive index with thickness of the ALD-Al_2O_3 amorphous thin films. (b) Dependence of refractive index on thickness of the amorphous Al_2O_3 layer.
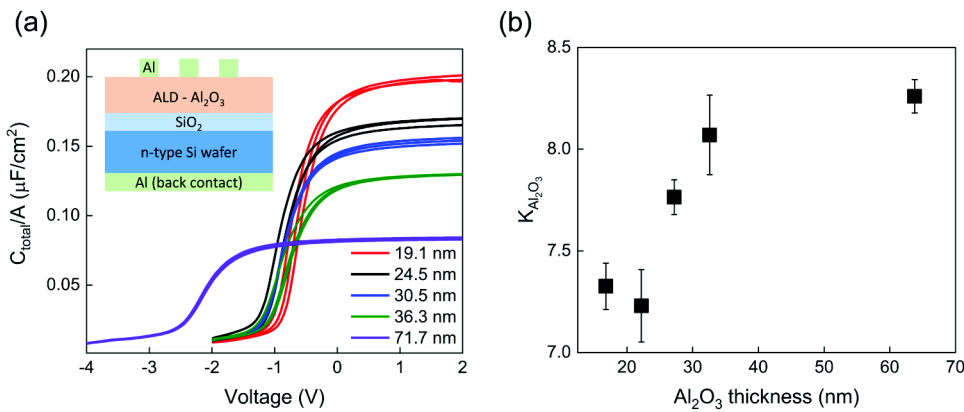
FIG. 4. (a) C–V curves achieved for the different capacitors, with different thicknesses of Al_2O_3 layer, normalized to the measured contact area measured at 1 MHz; inset: Schematic description of the MOS capacitors used to determine the dielectric constants of Al_2O_3 films. (b) Dependence of the dielectric constant on thickness of the Al_2O_3 layer.

another is defined by Eq. (1),[35]

$$\frac{n_1}{n_2} = \frac{\sin(\theta_2)}{\sin(\theta_1)}. \tag{1}$$

In our case, assuming that the x-ray passes from air ($n_1 = 1$) to our layer and that total reflection occurs ($\theta_2 = 90°$), the relationship between the critical angle and the refractive index of the layer would be

$$n = \sin(\theta_C). \tag{2}$$

This relationship can be plotted (Fig. 5), since the critical angle for total reflection can be found by XRR, as reported previously.[4,36]

Good linearity is observed between the two values, with $R^2 = 0.99$. The proportionality factor is 1.15, which is close to 1, the theoretical factor, supporting the high correlation between the measured parameters.

Another parameter that changes with thickness, as previously shown, is the density. The general relationship between the density (ρ) and the refractive index (n), according to Anderson and Schreiber, which takes into consideration an overlapping field for the near-neighbor interaction is as follows:[7]
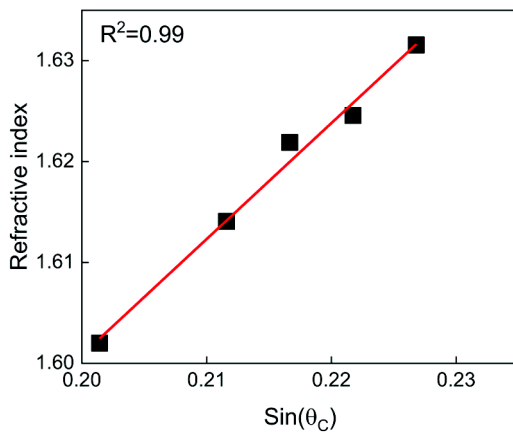
$$\frac{n^2 - 1}{[4\pi + b(n^2 - 1)]\rho} = \frac{\alpha}{M} \equiv R, \tag{3}$$

where b is the electronic overlap parameter, which is unique to each material and can be found via the extrapolation of n-ρ data, M is the molecular weight, and α is the polarizability, which is the ability to form a dipole. It is also possible to rewrite Eq. (3) as follows:

$$\frac{4\pi}{n^2 - 1} = \frac{1}{R} \cdot \frac{1}{\rho} - b. \tag{4}$$

Our previous findings, which concern the relationship between thickness and density,[4] enable us to plot Eq. (4) as shown in Fig. 6.

Since the amorphous Al_2O_3 ALD films exhibit similar structural features to those of γ-Al_2O_3,[3,4] the theoretical parameters for γ-Al_2O_3[37,38] have been added to the figure. These values can be seen to show good linearity, with $R^2 = 0.97$, further validating the correlation between the density (owing to thickness variations) and the refractive index in amorphous ALD thin films of Al_2O_3. By
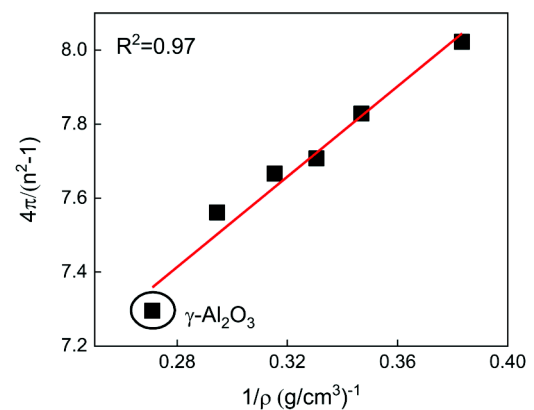

FIG. 5. Relationship between the critical angle (measured by XRR) and the refractive index (measured by ellipsometry).

FIG. 6. Dependence of the refractive index on density, according to Anderson and Schreiber.
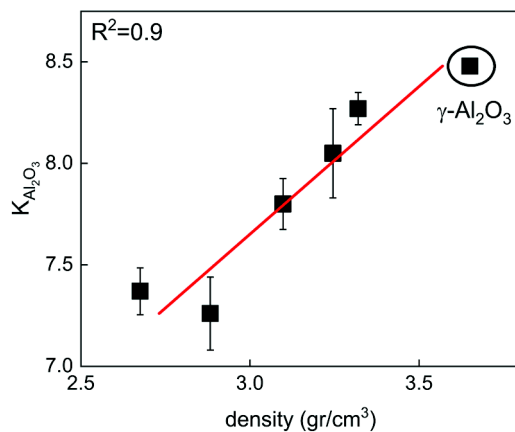
FIG. 7. Dependence of dielectric constant on density.

subjecting the results to linear regression, it is possible to extract that $b = -5.7 \pm 0.2$ and $R = 0.16 \pm 0.02$.

B. Dependence of the dielectric constant on thickness

According to our present results, it is clear that the dielectric constant increases with the thickness of the amorphous film. It was previously shown that density also changes with thickness,[4] implying that the dielectric constant changes due to density variations. The values obtained in our experiments are similar to the values achieved in other studies.[20,25,34]

Many studies have been carried out on various materials, in which the change in dielectric constant was studied as a function of density, and it was found that higher density yields higher dielectric constant.[6,39,40] The relationship between the density and the dielectric constant is plotted in Fig. 7. Theoretical values for crystalline γ-Al_2O_3 were added as well.[41]

It can be seen that the values align well, indicating a clear correlation between the density and the dielectric constant. This is an important finding, as it can open a variety of new possibilities for amorphous dielectric materials.

In addition, flatband voltages (V_{FB}) appear to vary with thickness [Fig. 4(b)], which indicates that some charges are present in the stack, as is usually the case. A detailed analysis of the flatband voltage vs effective oxide thickness was performed.[32,42] By approximating these charges to a sheet near the Si surface, we obtain $Q_F \approx + 1.2 \times 10^{12}$ cm^{-2} charges. These are typical values for fixed charges caused by the e-beam deposition of the gate metal, as was previously shown for similar Al contacts.[43]

V. SUMMARY AND CONCLUSIONS

Amorphous ALD-Al_2O_3 films are commonly used and are of significant interest for various applications. Previous studies showed that the short-range order close to the surface in these films differs from that in the bulk amorphous Al_2O_3; hence, the average short-range order in thinner films differs from that in thicker ones. These variations were previously found to affect the density of the films,

pointing to a potential for tuning density-dependent properties. It is shown here that the refractive index and the dielectric constant of ALD-Al_2O_3 films change with size, owing to variations in film density: thinner films, which have a lower density, exhibit lower refractive indices and dielectric constants than those of the higher density, thicker films. This finding implies the possibility of tuning these properties solely by size. This effect is not expected to be limited Al_2O_3 and should manifest in other amorphous systems, where it might further emerge at different thicknesses.

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