HTML ABSTRACT + LINKS

Optical Properties of Jet-Vapor-Deposited TiAlO and HfAlO Determined by Vacuum Utraviolet Spectroscopic Ellipsometry

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Abstract. In this report we use vacuum ultraviolet spectroscopic ellipsometry (VUV-SE) to determine the optical as well as structural properties of high-k metal oxides, in particular, of hafnium aluminates and titanium aluminates grown by jet-vapor deposition. In our opinion, the adapted approach employed in this study can be applied in most other high-k dielectric thin films which are of great interest in developing a new material replacement for the SiO_2 gate dielectric in CMOS and other IC devices. Specifically, VUV spectroscopic ellipsometry measurements were performed on a commercial ellipsometer with spectral range from 1.0 eV (1240 nm) to 8.7 eV (143 nm). The Generalized Tauc-Lorentz (GTL) dispersion was used to determine the dielectric functions of these films. An ellipsometric model consisting of two layers of different film densities was found to be in excellent agreement with the experimental data. For the TiAlO films, only one film was needed in the model to fit the data. The optical bandgaps are seen to increase, while the relative film densities decrease, with increasing Al in the films. In addition, the optical dielectric functions shift to higher energy and decrease in magnitude as the films become more insulating. As a result, the Al appears to be mixed at the atomic level instead of forming a phase separation between HfO_2 and Al_2O_3. For TiAlO, we observed similar results except that the fundamental optical bandgap was not strongly affected by the amount of Al incorporated in the films. In our opinion, the adapted approach employed in this study can be applied in most other high-k dielectric thin films which are of great interest in developing a new material replacement for SiO_2 in CMOS and other IC devices

INTRODUCTION

High-k dielectric thin films have been the subject of strong focus in the last few years in the IC industry and academic research communities as a potential replacement for the traditional SiO_2 gate dielectric in CMOS devices. [1] One of the most commonly used techniques to determine the thickness of these films has been that of ellipsometry.[2] However, for new high-k dielectric materials, the methodology for thickness and optical property measurement has not been established. It is mainly due to the rather complicated and varying structures which are strongly dependent on process conditions. In this report, we attempt to address and improve the methodology of the ellipsometric application to this class of materials by investigating, in particular, metal oxides of hafnium aluminates and titanium aluminates. Furthermore, since high-k thin films generally have bandgaps in the ultraviolet wavelength region, the application of ellipsometry technique with the wavelength extended to the vacuum ultraviolet spectral region is advantageous. More insight into the film properties and qualities can be ascertained when optical information is measured well above their optical bandgaps.

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EXPERIMENT AND DATA ANALYSES

Two sets of samples were investigated in this study. The first set consisted of five HfAlO samples (HfAlO-0, HfAlO-25, HfAlO-50, HfAlO-75, and HfAlO-100) and the second set of three TiAlO samples (TiAlO-15, TiAlO-30, and TiAlO-50). These films were deposited by Jet-Vapor-deposition (JVD) [3] at room temperature on HF-last Si substrates. The Hf vapor and Al vapor were generated by dc sputtering in separate nozzles. The metal vapors and O_2 were injected from the source nozzles by supersonic Ar jets. The nominal thickness of the HfAlO films are ≈80 nm and ≈30 nm, respectively. No post deposition annealing was performed for the ellipsometry measurements. The Al atom percentages in the HfAlO films (Al%=N_{Al} / [N_{Al}+ N_{Hf}]) were measured by X-ray photoelectron spectroscopy (XPS) and are listed in Table 1. The TiAlO films were made by a similar process.

Vacuum Ultra-Violet Spectroscopic Ellipsometry (VUV-SE) measurements were performed on a commercial ellipsometer (VUV-VASE VU302, J.A. Woollam Co., Inc.*) with the spectral range from 1.0 eV (1240 nm) to 8.7 eV (143 nm). The symbols in Fig. 1 show the ellipsometric Δ and Ψ experimental data for the HfAlO set. The objective in the data analyses is to determine the film thicknesses and the complex pseudo-dielectric functions, $\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle$, of these films.

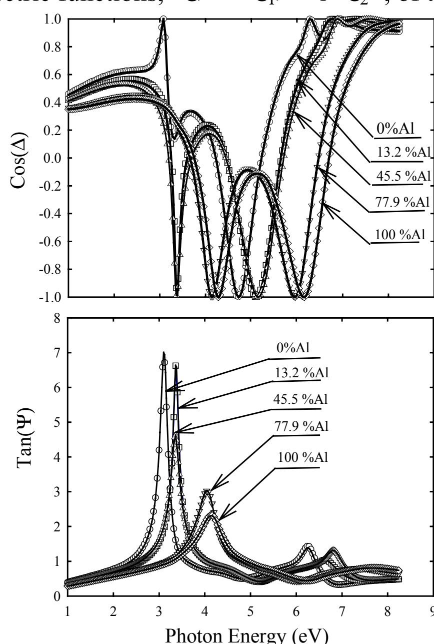

FIGURE 1. Comparison of the modeled (solid lines) with the experimental (symbols) data for HfAlO samples.

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

For spectroscopic ellipsometry, when the dielectric functions ($\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$) are known for the films and the substrate, a simple calculation provides the film thickness values. For the films in this investigation, the dielectric functions varied with the Al contents and are not known in advance. Furthermore, the nonuniform film density complicates much of the data modeling procedures. A single film on the silicon substrate was first used in the model to fit the data. The dielectric function of the films was assumed to follow the wavelength dependency described by the Generalized Tauc-Lorentz (GTL) or Tauc-Lorentz (TL) dispersion.[4]

$$\varepsilon_{2,n}(E)=\begin{cases}\dfrac{AE_0CE}{(E^2-E_0^2)^2+C^2E^2}\cdot\dfrac{(E-E_g)^n}{E_0^{n-2}E^2}, & (E>E_g),\\ \dfrac{AE_0CE}{(E^2-E_0^2)^2+C^2E^2}\cdot\dfrac{(E+E_g)^n}{E_0^{n-2}E^2}, & (E<-E_g),\\ 0, & (|E|\le E_g),\end{cases}$$

$$\varepsilon_1(E)=\varepsilon_\infty+\frac{2}{\pi}P\int_0^\infty\frac{\xi\varepsilon_2(\xi)}{\xi^2-E^2}d\xi$$

where n is 1, 2, 3, or 4, and A, E_g, E_o, and C are positive fitting parameters in units of energy. When n equals 2, GTL becomes TL as a special case. It should be mentioned that the relation between ε_1 and ε_2 satisfies the Kramers-Kronig requirement. With this single film model, the residuals (discrepancies between the experimental and modeled data) from the least-squares fitting produced a very unsatisfactory fit. However, when a model consisting of two layers of different film densities was employed, we were able to reproduce very well the experimental data as clearly shown in Fig. 1 by the solid lines for all five HfAlO samples. The layer thicknesses and the relative densities obtained by this fitting procedure are compiled in Table I. The pseudo-dielectric functions (solid lines) resulting from the fitting are displayed in Fig. 2 along with the data inversions (open circles) for comparison. In the inversion method, $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$ were obtained by fitting the experimental ellipsometric Δ and Ψ data, point by point, at each wavelength. In this procedure, the layer thicknesses and densities are the fixed values determined by the fitting of the two-layer model. The GTL dispersion is observed to match the inversions, $\langle\varepsilon_1\rangle$ and $\langle\varepsilon_2\rangle$, clearly. Thus, the dispersive GTL dielectric functions appear to be appropriate for modeling the optical properties of HfAlO and TiAlO films. Furthermore, the two-layer model is a proper representation for the optical responses of this particular set of HfAlO.

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RESULTS AND DISCUSSION

The experimentally determined dielectric function of HfO_2 without Al (sample HfAlO-0) clearly displays two distinct characteristics of a broader peak at ≈ 7.0 eV and a shoulder peak at ≈ 5.7 eV. The latter peak was similarly detected for HfO_2 prepared by reactive dc magnetron sputtering and annealed at high temperatures.[5] As the Al concentration increases to 50 %, the dielectric functions shift to the higher energy region and decrease in their magnitudes as the films become more insulating. The fact that the peak shifts to higher energy indicates that Al is mixed at an atomic level instead of forming a phase separation between HfO_2 and Al_2O_3. Phase separation would have caused the peak in HfO_2 to remain at the same critical transition energy (7.5 eV peak of HfO_2 sample). When the Al concentration reaches beyond 50 %, the dielectric function becomes broader without shoulders,

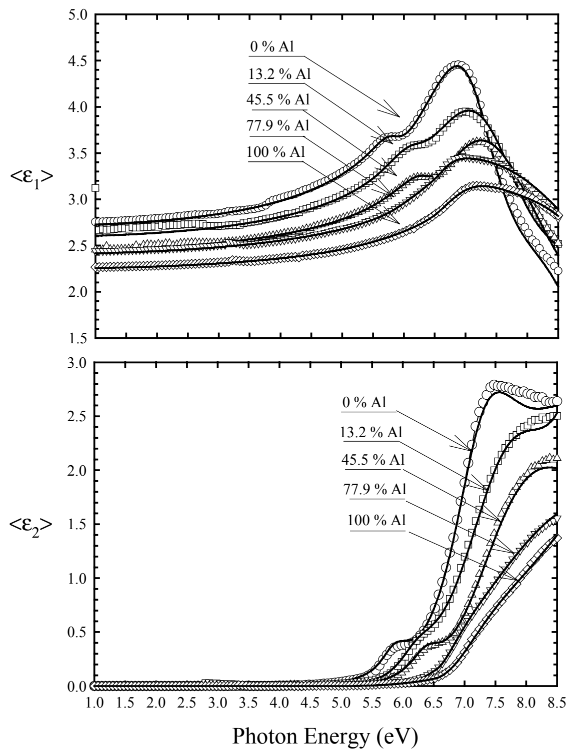

FIGURE 2. Comparison between the pseudo-dielectric functions obtained by the inversion (circles) and Generalized Tauc-Lorentz dispersion (solid lines) for the HfAlO set.

thus indicating that the films are becoming Al_2O_3-like.

Another quantity of great interest is the bandgap of these films. To estimate the bandgap values, we employed the traditional Tauc plots [6] of $(\alpha E)^{1/2}$ versus photon energy E, where $\alpha = 4\pi k/\lambda$ is the absorption coefficient, k the extinct coefficient (which can be calculated from $<\varepsilon_1>$ and $<\varepsilon_2>$), and λ is the light wavelength. Near the band edge of amorphous materials, Tauc-plots display a linear relation with E, and therefore, the bandgap can be extracted by extrapolating $(\alpha E)^{1/2}$ to zero. From the plots in Fig. 3, the bandgap was estimated to be about 5.08 eV for HfO_2, 5.28 eV for 13.2 % Al , 5.45 eV for 45.5 % Al, 6.05 eV for 77.9 % Al, and 6.25 eV for Al_2O_3. As shown in Table I, the relative densities of the two layers of the HlAlO films increase with increasing Al concentration. Thus, it is possible that, as deposited and without post annealing, the films are more porous with more Al. In our data analysis, the two distinct layers of different densities used in fitting the ellipsometric data should be perceived as a simplified structure because the density of the film is not necessarily uniform. Such two separate and distinctive layers are not expected when considering the film deposition process where there was no changing of the deposition parameters during film fabrications. Therefore, the two-layer film structure is considered as an optical approximation to the non-uniformity of densities in the films.

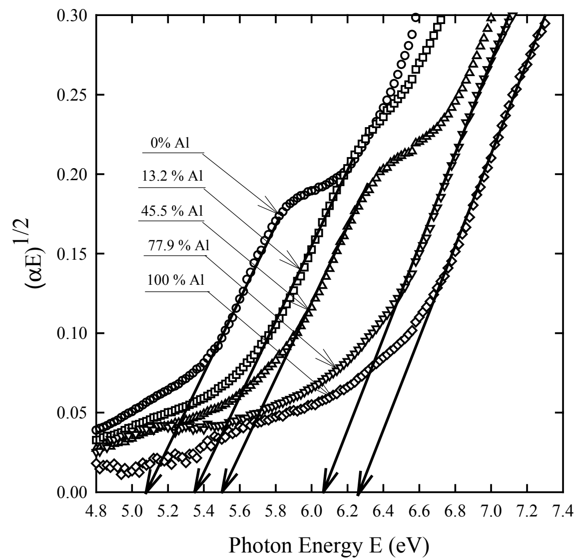

FIGURE 3. Tauc-plots for determining the optical bandgaps (see text) for the HfAlO set.

The same modeling procedure was applied for the analysis of TiAlO films. However, in this case, one layer was sufficient to yield a good fit with the data. This suggests that these films are fairly uniform throughout. As a result, the film thickesses for samples TiAlO-15, TiAlO-30, and TiAlO-50 are 324.0 ± 0.5 Å, 328.0 ± 0.4 Å, and 316.0 ± 0.7 Å, respectively. The dielectric functions derived from the fitting are shown in Fig. 4. Similar to the effects of Al in HfAlO samples, the dielectric functions of TiAlO shift to higher energies with increasing Al. Also the shape of the peaks in the range from 4.6 eV to 5.0 eV becomes broader as the Al concentration increases. In addition, a small shoulder peak is also discernible in the range of 3.0 eV and 4.0 eV.

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Compared with HfAlO, in addition to the peak at ≈ 4.5 eV, the narrower bandgap TiAlO samples exhibit a second broad peak at 7.5 eV as another optical characteristic. Furthermore, the thinner TiAlO samples are optically more uniform as demonstrated by the comparable fitting using a simple single film. It is also noticed that the bandgap values are essentially uneffected by the amount of Al concentration in the films. On the other hand, the higher interband transions at 4.5 eV and 8 eV slightly shift to higher energy with more Al in the films.

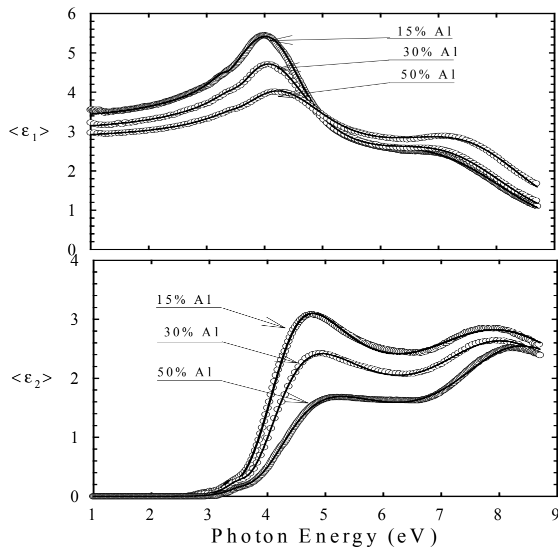

FIGURE 4. Comparison between the inversion (circles) and TL (solid lines) dielectric functions of the TifAlO set.

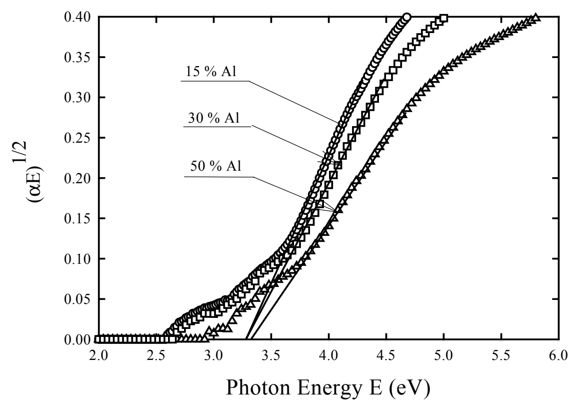

FIGURE 5. Tauc-plots for determining the optical bandgaps (see text) for the TiAlO set.

CONCLUSIONS

High-k dielectric thin films have been the subject of intense focus in the IC industry as well as academic research laboratories. The purpose behind the search is the need for the replacement of the traditional SiO2 gate oxide. Ellipsometry is one of the main metrology techniques routinely being used to ascertain the film quality and to monitor and control the film growth. For these relatively new and ever changing materials, it is important to establish a reliable methodology in the data analysis that could be used to achieve accurately the film thickness and optical property. In this study, we have demonstrated that a combination of VUV-SE measurement and the use of a correct optical dispersion enabled us to accurately determine film thickness, dielectric function (hence, the optical bandgap), and the structural qualities (i.e. density and uniformity). In our opinion, the adapted approach shown here can be applied in most other high-k dielectric thin films which are of great interest in developing a new material replacement for SiO_2 gate dielectric in CMOS and other IC devices.

Specifically, the analysis of the VUV-SE data shows that relatively thick JVD HfAlO films are inhomogeneous in density, but thinner TiAlO films have a better uniformity. Furthermore, using the generalized Tauc-Lorentz dispersion for the dielectric functions, we were able to determine the dielectric functions of the films and their optical bandgaps. The optical bandgaps are seen to increase, while the relative film densities decrease, with increasing Al. In addition, we observed that the dielectric functions shift to higher energy and decrease in magnitude for higher Al concentrations in the films. As a result, the Al appears to be mixed at the atomic level instead of undergoing a phase separation between HfO_2 and Al_2O_3. For TiAlO, similar results are seen, except that the fundamental optical bandgap was not strongly affected by the amount of Al incorporated in the films.

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TABLE 1: The thickness and relative densities of the two layers of the HfAlO films.

	HfAlO-00 (0 % Al)	HfAlO-25 (13.2 % Al)	HfAlO-50 (45.5 % Al)	HfAlO-75 (77.9 % Al)	HflAlO-100 (100 % Al)
Bottom Layer	446 ± 13 Å	386 ± 11 Å	395 ± 6 Å	284 ± 11 Å	345 ± 6 Å
Top Layer	354 ± 11 Å 20 % less dense	366 ± 10 Å 24 % less dense	403 ± 6 Å 24 % less dense	402 ± 9 Å 36 % less dense	346 ± 5 Å 37 % less dense

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