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Estimate of dielectric density using spectroscopic ellipsometry

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ABSTRACT

The optical dielectric functions for hafnium oxide and hafnium silicate films were extracted from spectroscopic ellipsometry measurements and the density then calculated using a previously proposed method. The values obtained were then compared to those obtained using X-ray reflectometry. The optical dielectric functions for gadolinium oxide films deposited under various conditions were also extracted from spectroscopic ellipsometry measurements. It was found using medium energy ion scattering that gadolinium oxide films deposited using $Gd[N(SiCH_3)_2]_3$ and H_2O as precursors, contained significant levels of silicon and the silicon concentration was directly proportional to the wafer deposition temperature. This effect was also observed in the density measurements extracted from spectroscopic ellipsometry data.

1. Introduction

The density of a dielectric film compared to its ideal value, is an important indicator of film quality and hence possible electrical performance. Accurate values for the density of materials are also required for many analytical techniques. We have previously proposed a new technique for using spectroscopic ellipsometry (SE) to extract density of a thin dielectric film [1]. SE can be carried out quickly and non-destructively both in- and ex-situ without the need for time-consuming or destructive sample preparation techniques as in other methods such as the use of Rutherford backscattering spectroscopy and transmission electron microscopy [2] or X-ray reflectometry (XRR) [3]. This technique could therefore become important for both the rapid screening of prototype layers of possible high-k dielectric replacements and also for the analysis of the quality of dielectric layers during device production. In this paper we have employed both SE and XRR to extract density in order to compare the two techniques and also to assess errors and limitations related to the new technique.

2. Sample preparation

Hafnium oxide and hafnium silicate, $(HfO_2)_x(SiO_2)_{1-x}$, thin films ($x = 0.3$, 0.5 and 0.7), nominally 4 nm thick, were deposited using metal organic vapour deposition (MOCVD) on p-type silicon wafers. Prior to this a SiO_2 chemical oxide of ~1 nm nominal thickness was grown on the Si substrate. The gadolinium oxide, Gd_2O_3, films were deposited on n-type silicon wafers using atomic layer deposition (ALD) with $Gd[N(SiCH_3)_2]_3$ and H_2O as precursors. The wafer temperature was varied between 175 and 275 °C and the number of cycles varied between 75 and 300.

3. Sample measurements and data analysis methodology

SE measurements were performed on the hafnium based films using a J.A. Woollam VUV-VASE ellipsometer over a spectral range of 140–1700 nm at multiple angles of incidence (70–75° in 1° steps). The thickness and optical constants of the chemical oxide were extracted from measurement of a chemical oxide film grown identically to those used in the experimental samples. The thickness of the layers was extracted in the near infra-red (NIR) spectral range using a Cauchy layer representation for the high-k layer. The optical constants were extracted using a four term, general oscillator layer in the model. The extracted refractive indices from SE analysis can be seen in Fig. 1.

The XRR measurements were carried out on the hafnium based samples using a wavelength of 1.451 Å with the incidence angle varied through a range of 300–15000 s with a step-size of 50 s. The experimental data was modelled using a four layer representation comprising of a silicon substrate, a silicon dioxide interfacial layer and two high-k layers representing a dense high-k layer and a less dense high-k overlayer.

For the Gd_2O_3 films, ellipsometry measurements were performed on a J.A. Woollam M2000UI VASE ellipsometer over a spectral range of 240–1700 nm and an angle range of 65–80° in

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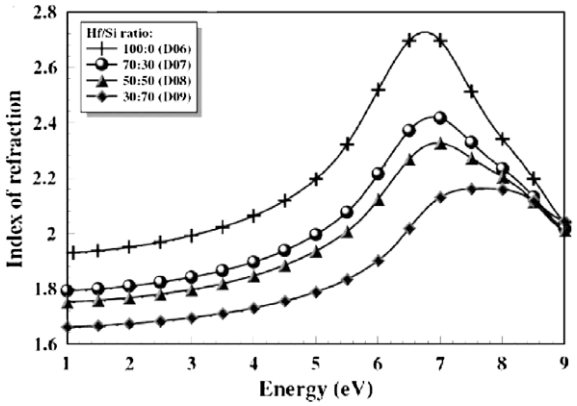

Fig. 1. Extracted index of refraction for $(HfO_2)_x(SiO_2)_{1-x}$ films of various composition (x = 0.3, 0.5, 0.7 and 1.0).

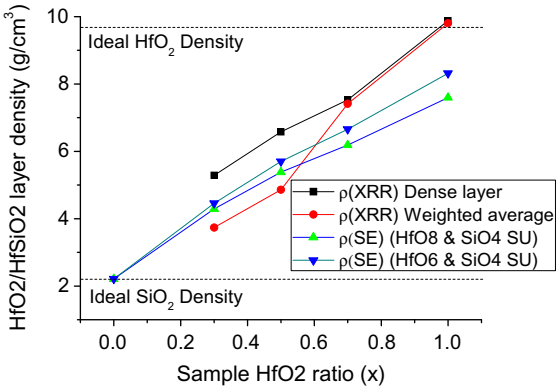

Fig. 2. Extracted density of $(HfO_2)_x(SiO_2)_{1-x}$ films from SE for a film comprised of only HfO_6 or HfO_8 SU and the dense layer density and the averaged density extracted using XRR.

5° steps. A 1 nm SiO_2 interfacial layer was assumed and a Cauchy layer with Urbach absorbtion was used to model the Gd_2O_3 layer and to extract the optical constants of the layer. All spectroscopic ellipsometry data fitting was carried out using the J.A. Woollam WVASE32 software.

Medium energy ion scattering was carried out at the STFC Daresbury facility, as described in [6]. A 200 keV He^+ beam was used. Samples were aligned to the beam along the $[\bar{1}\,\bar{1}\,1]$ channel direction and data was recorded along the [1 1 1] blocking direction yielding a scattering angle of 70.5°.

4. Density extraction theory

The density extraction technique is based upon the simple Clausius–Mossiti relationship between the refractive index (n) and density (ρ) given by Eq. (1) below where α_e is the electronic polarizability, V_m is the molecular volume, M is the molar mass and N_A is Avogadro's constant.

$$\frac{n^2-1}{n^2+2}=\left(\frac{4\pi}{3V_m}\right)\alpha_e=4.19\left(\frac{\alpha_e}{V_m}\right)=4.19\left(\frac{N_A\rho}{M}\right)\alpha_e \quad (1)$$

The refractive index is taken from the lowest measured frequency in the extracted optical constants and the polarizability is taken from published values. The full description of the analysis can be seen in [1].

5. Results – hafnium oxide and hafnium silicates

Hafnium oxide can exhibit two possible structural units (SU), namely HfO_6 and HfO_8. The complexity of the morphology increases in the case of hafnium silicates which also contains the structural unit SiO_4. Using the technique explained in [1], the density was calculated for the two cases of pure HfO_6 or HfO_8 structural units, using the theoretical polarizabilities calculated by Riganese [4]; results are given in Fig. 2, which also shows the results of the density measured using XRR. The density values for bulk HfO_2 and SiO_2 are also plotted on Fig. 2 as a reference. The best fit model for the experimental XRR results are obtained by considering the hafnium silicate as two layers, namely a dense high-k layer and an overlayer of density between 10 and 20% less than the dense layer. To allow comparison of the results from the XRR analysis and the single high-k layer density extracted using ellipsometry, the density measured using XRR was converted to an average value using Eq. (2) below, where ρ_{OL} and ρ_{DL} are the densities of the dense layer and the overlayer and t_{OL} and t_{DL} are the thicknesses of the dense layer and overlayer, respectively.

$$\rho_{average}=(\rho_{OL}\tau_{OL}+\rho_{DL}\tau_{DL})/(t_{OL}+t_{DL}) \quad (2)$$

The density extracted using SE was then at most, 15% lower than the density extracted using XRR. A possible source of error for the XRR results is the surface roughness of the films as the density values extracted for the porous overlayer for samples containing the highest proportion of SiO_2 dropped to below half that of bulk silicon dioxide. This suggests some limitations of the 4-layer model for the hafnium silicate layers at least for the case of hafnium oxide molecular fraction (x) less than 0.5.

6. Results – gadolinium oxide

Deposition at lower temperatures produced films with the highest optical permittivity. Using the polarizability value for Gd_2O_3 – taken from Medenbach et al. [5] – the densities of the Gd_2O_3 films was calculated. The density of a Gd_2O_3 film decreased as wafer deposition temperature was increased as shown in Fig. 3. The observed decrease in film density is expected to be due to a combination of two effects both related to an increased silicon uptake in the gadolinium oxide film with increasing deposition temperature. The first effect is a change of physical density which is caused by the variations in maximum packing density due to a change in the composition of the film. The second effect is not due to a physical change in density but rather is due to a change in the average polarizability of the high-k films. This is because

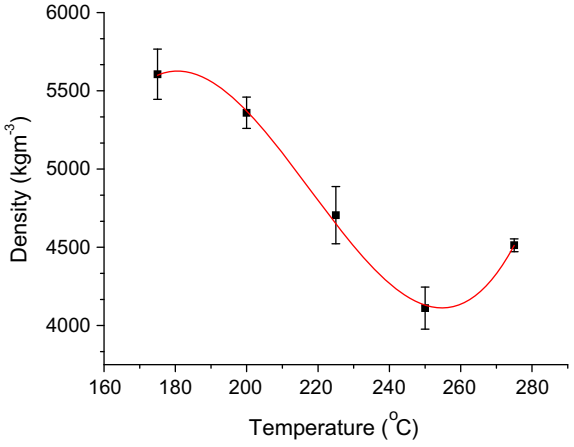

Fig. 3. Extracted density of ALD Gd_2O_3 films for varying wafer deposition temperature (100 cycles).

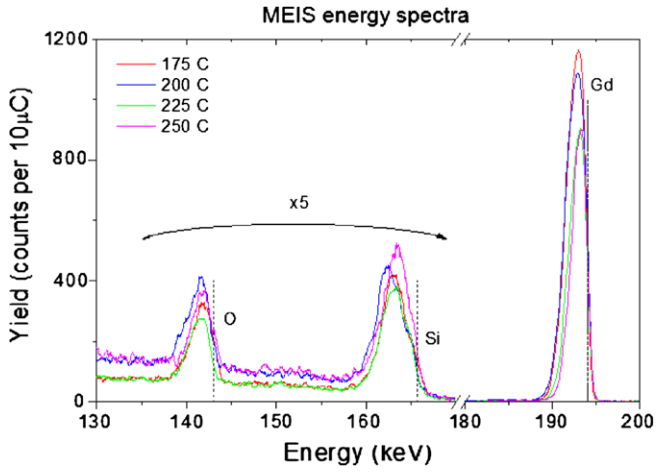

Fig. 4. MEIS energy spectra for Gd_2O_3 films deposited at various wafer deposition temperatures.

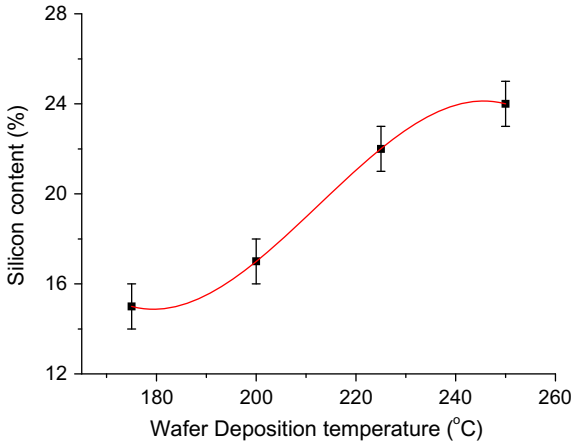

Fig. 5. Plot showing the extracted silicon concentration for Gd_2O_3 films deposited at different wafer deposition temperatures.

the average polarizability of a material is highly dependent on the structural units and these will change with composition of a given film.

MEIS was performed on the high-k layers deposited at temperatures between 175 and 250 °C and the energy spectra are shown in Fig. 4. The presence of silicon is apparent within the films, as is expected when using this precursor. In fact, the Si is introduced deliberately to improve the thermal stability of the film. The energy spectra were converted to a depth profile and the silicon content of the films was extracted. These values were then plotted against the wafer deposition temperature. The increase in silicon content within the Gd_2O_3 layer clearly increases with wafer deposition temperature as shown in Fig. 5. Fig. 6 shows that increasing the number of ALD cycles produce films of greater density, as

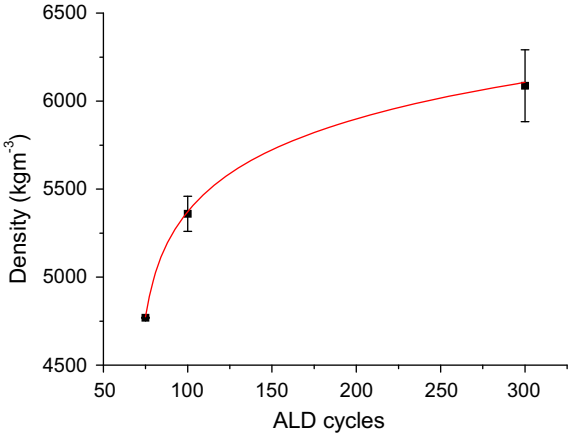

Fig. 6. Extracted density of ALD Gd_2O_3 films for an increasing number of ALD cycles at a fixed wafer deposition temperature of 200 °C.

expected because increasing the number of deposition cycles will produce a thicker film with closer physical properties to those of bulk material. It becomes apparent from the study, that there is a need to better understand the chemistry of gadolinium oxide films containing significant levels of silicon so as to allow better modelling of the structural units and in turn, obtain more accurate values of polarizability.

7. Conclusions

We have developed further, a method for extracting the density of dielectric films using spectro-ellipsometry. In this paper we have reported a comparison with a density extraction technique using XRR. It is apparent from the study that further improvements to the accuracy of this technique will require better understanding of the chemistry occurring within the high-k dielectric materials. The accuracy of the density extraction technique using SE results could also be improved by further study into the use of structural units within the films, given that structural units are used to describe a crystalline structure and our films are thought to be amorphous.

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