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PHYSICAL CHARACTERIZATION OF ZrO_2 FILMS ON SILICON AFTER RAPID THERMAL ANNEAL

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In this investigation ZrO_2 samples were prepared by a dc magnetron reactive sputtering. The samples were annealed in a rapid thermal processing system at temperatures from 400 to 1050 °C in various gas ambients, including O_2, N_2, forming gas (H_2/Ar), wet H_2, and wet O_2. Spectroscopic ellipsometry (SE) was used to characterize the thickness, refractive index and microstructures of the as-deposited and annealed ZrO_2 films. The RTP annealing conditions have shown significant effects on the ZrO_2 film thickness and refractive index. Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS) depth profile and cross section TEM were also used to characterize the films in comparison with SE. The electrical characterization results of ultra-thin ZrO_2 were also presented.

INTRODUCTION

Because of high direct tunneling currents and reliability concerns, conventional thermal oxide (SiO_2) thinner than 15 Å cannot be used as the gate dielectric of CMOS devices [1]. This means that thermally grown SiO_2 or a silicon oxide/nitride composite layer with a relative lower dielectric constant must be replaced by physically thicker stacked dielectrics based on alternative insulators with dielectric constants greater than that of SiO_2. As an alternative to oxide/nitride systems, currently there is intense effort in the search for high-K metal oxides as a means to provide a substantially thicker (physical thickness) dielectric for reduced leakage and improved gate capacitance. Most high dielectric constant materials can be grouped into two general categories: (i) Materials that are not thermally stable with Si, such as TiO_2 (K=40-80), Ta_2O_5 (K=26), $SrTiO_3$ (K=150) [1,2]. A thin barrier layer is required to prevent reaction and interdiffusion at the interface; (ii) Materials that are stable with Si, such as ZrO_2 (K=25), HfO_2 (K=30), Al_2O_3 (K=11.6), Y_2O_3 (K=14), La_2O_3 (K=20.8), and Zr and Hf silicates (K=11) [3,4]. Key issues related to the development of the high K dielectric gate stack are: low equivalent oxide thickness (EOT), low leakage current, the interface layer between high K and Si, thermal stability and gate electrode compatibility.

ZrO_2 is among the most promising high K candidates. ZrO_2 has a dielectric constant of 20-25 and is thermodynamically stable in contact with silicon. In addition, ZrO_2 has a large energy band gap of 5.1 eV and a lattice mismatch with Si (100) of 2.1% [5].

The goal of this study is to better understand material properties and microstructural aspects of the films that occur in a ZrO_2 and Si system as a result of RTP anneals in various gas ambients. In this work we present an investigation of the influence of rapid thermal anneal on ZrO_2 thin films, their interfaces with Si substrates, and etch rates in HF solution. The ZrO_2 samples with thickness of about 150 Å were annealed at temperatures from 400 to 1050 ^{o}C in various gas ambients. Spectroscopic ellipsometry with a proper optical model was used to measure the optical properties and thickness of ZrO_2 films and their interfaces. RBS, TEM and XPS depth profile were used for analyzing the chemical composition of interfaces and determining the film thickness.

EXPERIMENTAL

For sample preparation, ZrO_2 films were deposited directly on p-type Si substrate using two-step dc magnetron-reactive sputtering from a pure Zr target. At the first step a very thin Zr layer was deposited in Ar ambient. The Zr layer works as an oxidation barrier during ZrO_2 deposition. Then a thicker ZrO_2 layer was deposited at a power of 3000 W in Ar+O_2 ambient. The thickness of ZrO_2 is about 150 Å. The ZrO_2 samples were annealed in a rapid thermal processing system at temperatures between 400 and 1050 ^{o}C in various gas ambients, including O_2, N_2, forming gas (H_2/Ar), wet H_2 (15% H_2O in H_2), and wet O_2 (15% H_2O in O_2). A Tencor UV-1250 spectroscopic ellipsometry (SE) with wavelengths from 250 to 750 nm was used to characterize the ZrO_2 films. The thickness and optical properties were calculated by using a proper optical model. RBS, XPS and cross section TEM were used for composition analysis and verifying the thickness measured from SE optical technique. The ultra-thin ZrO_2 films for electrical characterization were deposited by rapid thermal CVD with about 5 Å SiN interface and 40 Å ZrO_2.

RESULTS AND DISCUSSIONS

1. Spectroscopic Ellipsometry Analysis of ZrO_2 Films

Spectroscopic ellipsometry (SE) is a sensitive, non-destructive, and non-invasive optical technique that has been used extensively in Si processing technology both as an ex situ analytical tool, and as an in situ monitoring technique. Ψ and Δ are the measurables of ellipsometry that represent the change in amplitude and phase, respectively.

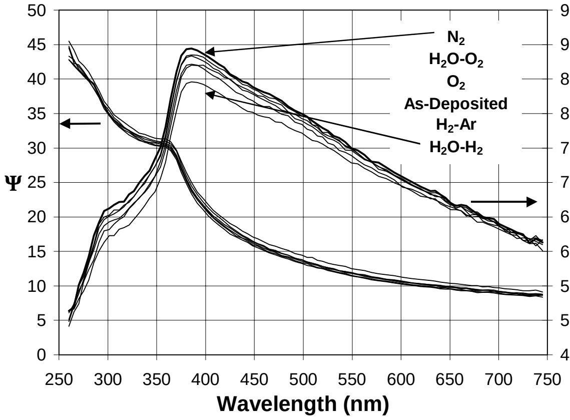


Figure 1. SE results of as-deposited ZrO_2 films and films annealed at 600 ^{o}C for 60 s in various gas ambients.

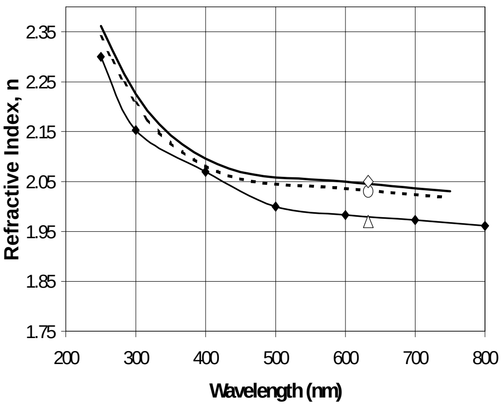


Figure 2. Refractive index of ZrO_2. solid line: sputtered at 3 kW; dashed line: sputtered at 2 kW; Δ and ◊ are PVD film before and after anneal from Ref. 3; o is CVD film from Ref. 8; dotted line: e-beam evaporated film from Ref. 9.

Previously we have used SE for analysis of complex multilayer film structures in plasma oxidation and rapid thermal chemical vapor deposition (RTCVD) [6,7]. Figure 1 shows typical SE results for as deposited ZrO_2 film and for films annealed at 600 ^oC in O_2, N_2, forming gas, wet O_2 and wet H_2. It is clear from the spectra that the Ψ values for most ambients are similar and the Δ values show significant difference at the wavelength of about 400 nm.

Table 1 Spectroscopic ellipsometry results using a BEMA one layer model

Sample Conditions		Thickness (Å)	Voids %	n at 633 nm	RMSE
As-deposited ZrO_2 (3KW sputter)		154.7	4.2511	2.046	0.7373
O_2	800 ^oC	142.6	5.9172	1.992	0.5619
N_2	800 ^oC	146.1	6.9994	1.958	0.5792
10%H_2 in Ar	800 ^oC	137.8	7.2229	1.951	0.8144
Wet O_2	800 ^oC	154.5	7.8261	1.934	0.6445
Wet H_2	800 ^oC	159.5	7.8812	1.933	0.6522

For ellipsometric modeling of inhomogeneous media, the Bruggeman effective medium approximation (BEMA) was used which assumes that for a mixed composition film, each component can be represented by its bulk dielectric function, and each component is large relative to the wavelength of the probing radiation. Thus, by using known optical properties in the BEMA, the ellipsometric data can be modeled to obtain the thickness and composition of the various annealed ZrO_2 films. The relative quality of the fit of ellipsometric data to particular model is reported as the root mean square error (RMSE). The RMSE can be used to compare fits to one model.

In order to interpret the measured SE data some realistic models were evaluated. The simplest model is of one layer with two components, ZrO_2 and voids. The typical results were shown in Table 1.

The refractive index of as-deposited films at wavelength from 250-750 nm was shown in Figure 2, comparing with other literatures [3,8,9]. For the as-deposited or low-temperature-annealed samples a single-layer model shows good fit for the calculated and experimental results indicating typical thickness of 156.7 Å and refractive index of 2.05 at 632.8 nm wavelength. However, a two layer model, with a topmost layer composed of ZrO_2 and voids, and with an interface layer composed of ZrO_2 and SiO_2 underneath always yielded the best fit for the samples annealed at higher temperature in terms of the lowest RMSE.

2. Characterization by RBS and XPS

The BEMA-fit models of SE data were independently checked by RBS and XPS depth profiles. Estimates of film composition and thickness can be made directly from the RBS analysis, as shown in Table 2.

RBS data show that the sputtered ZrO_2 film has typical ZrO_2 chemical structure for both as-deposited and annealed samples. The thickness of ZrO_2 film measured by RBS is 155 Å, in good agreement with the value of 156.7 Å from SE. A serious problem in high

K gate dielectric growth involves excess SiO_2 formed at the interface during growth or post-process. ZrO_2 shows very high rates of oxygen exchange when Zr (also Hf, Y, and La) oxide is exposed to O_2 at elevated temperature [8].

This behavior is expected based on the known high ionic conductivity of these materials. It has been thought that the metal oxide supplies oxygen (presumably atomic, not molecular) to an internal SiO_x/metal oxide interface, and the initial SiO_2 so formed is the rate limiting barrier in the film for further SiO_2 formation. Sputter XPS depth profile analysis was used to study the interface formation, as shown in Figure 3. It is clear that two layers were formed in the PVD ZrO_2 film after annealing at 700 ^oC. The top layer seems to be a ZrO_2 layer without any Si. The interface (or bottom layer) is more complicated. The concentrations of Zr and O gradually reduce to minimum at the Si surface. The concentration of Si increases from edge of top layer to 100% on Si surface. Since the interface is not thin and the chemical components are not uniform in whole interface area, SE using the two-layer model BEMA is only an approximate method to show the interface information.

Table 2 Comparison of RBS and SE

A. RBS Result					
Depth	O	Zr	Si	Hf	Ar
0-155 Å	67.0%	29.8%	2.0%	0.3%	0.9%
>155 Å			100%		
SE Result: 156.7 Å					

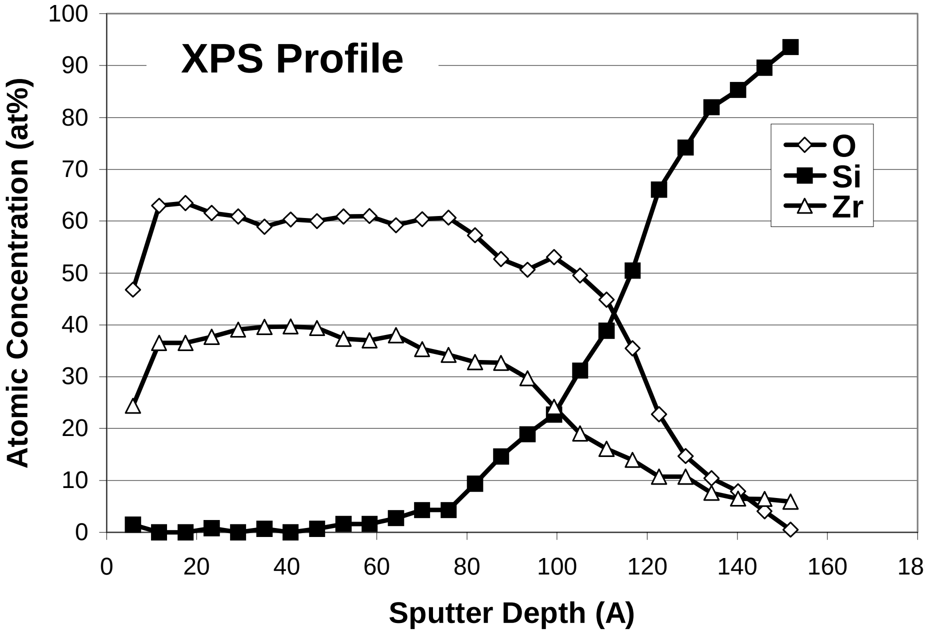


Figure 3. XPS depth profile of ZrO_2 sample annealed at 700 ^oC in O_2.

3. Characterization by cross section TEM

The cross section TEM has been used widely to measure the physical thickness of high K thin films and gives the dielectric constant when combined with the electrical data (CV). Since TEM analysis is complicated and expensive, it should be much easier if SE has the similar result with TEM. In order to compare SE with the cross-sectional TEM we prepared ZrO_2 samples which were annealed in N_2 at 700°C for 60 s. The samples were been measured by SE, then analyzed by TEM. The SE data were simulated by both one layer and two layer optical models. The one layer (ZrO_2 + Voids) model gives the thickness of 168.2 Å with the best-fit error of RMSE=0.4896. The two layer model has better best-fit of RMSE=0.3545, and gives the top layer (ZrO_2 + Voids) of 146.3 Å and interface (ZrO_2 + SiO_2) of 27.2 Å. Figure 4 shows the comparison of SE with the cross section TEM results. TEM gives the top and interface layers are 145 and 27 Å, respectively. The agreement between SE and TEM is good.

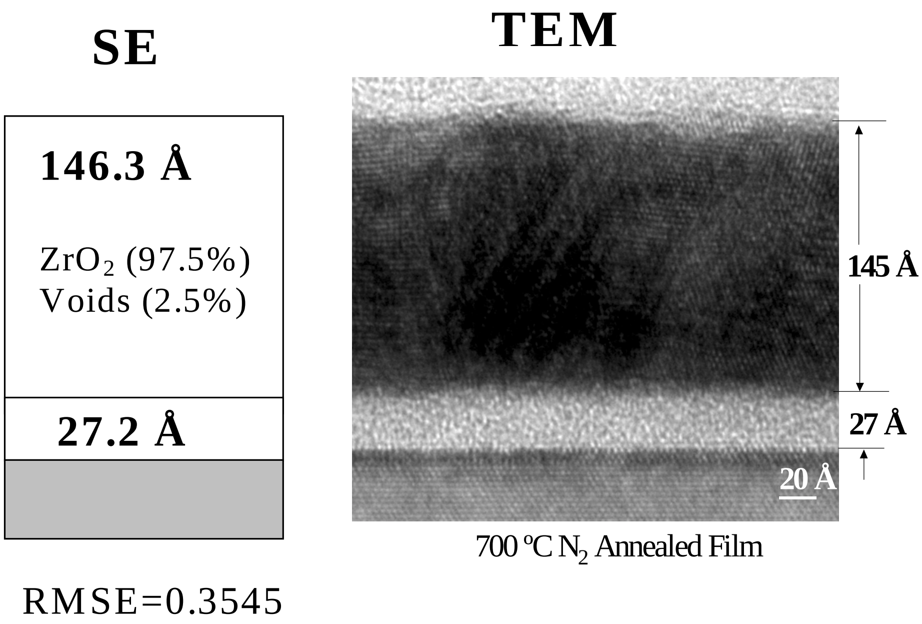
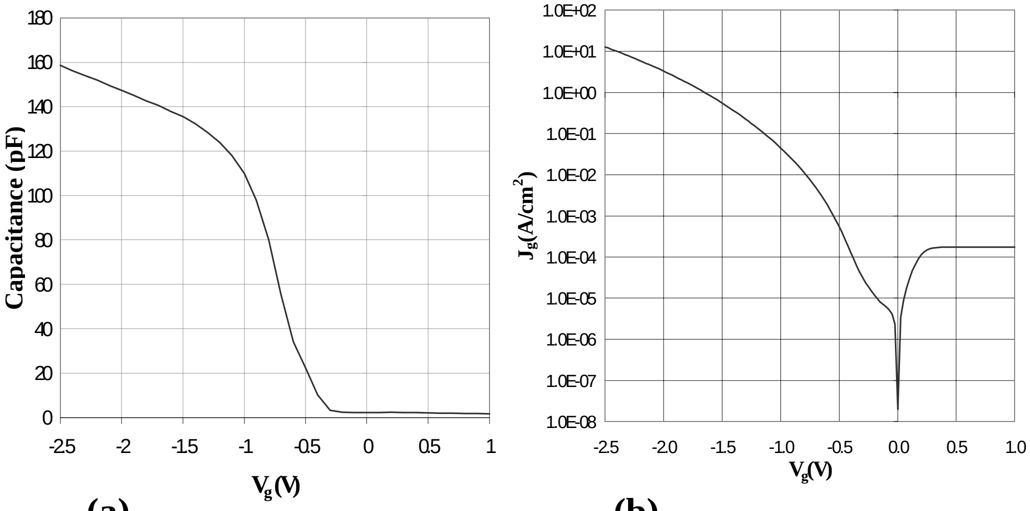


Figure 4. SE and cross-sectional TEM of ZrO_2 sample annealed at 700 °C in N_2.

4. Electrical Characterization

The capacitors used in RTP anneal study with the ZrO_2 gate stack were fabricated on p-type (100) epitaxial Si wafers. After definition of active pattern and pre-gate cleaning, an NH_3-based interface layer was grown at 700°C for 10 sec. The ZrO_2 thin film was deposited by rapid thermal CVD at 500 °C using zirconium tertiary-butoxide ($C_{16}H_{36}O_4Zr$) and O_2. The thicknesses of the interface nitride and ZrO_2 film were about 5 and 40 Å, respectively. The ZrO_2 samples were annealed in a rapid thermal processing system at temperatures of 800°C for 60 s in various gas ambients, including O_2, N_2, forming gas (H_2/Ar), wet H_2 (15% H_2O in H_2), and wet O_2 (15% H_2O in O_2). Some samples were annealed by spike RTP with 120 °C/s ramp rate and 2 sec steady state. The capacitor electrode was TaN of 1800-2000 Å thickness.

Figure 5 shows the typical C-V and J-V curves with an electrode area of $5x10^{-5}$ cm^2 for a ZrO_2 sample annealed in N_2 at 800°C by spike anneal. The equivalent SiO_2 thickness (EOT) values were calculated from the C-V curves. Figure 6 show EOT of ZrO_2 films annealed in various gas ambients at 800 and 1000°C for 60 s and 2 s (spike). The gas ambient effect on EOT in RTP post-deposition anneal is significant. The EOT for ZrO_2 film annealed in N_2 at 800°C for 60 s was 14 Å. When annealed in O_2 or wet-O_2, the EOT values increased to 31.4 and 36.7 Å respectively as a result of interfacial oxide growth. This is due to the fact that the high K thin films are poor diffusion barriers to oxygen. The lowest EOT in this comparison is 10.9 Å for the sample spike-annealed in N_2.



(a) **(b)**

Figure 5. (a) C-V and (b) I-V characteristics of SiN_x/ZrO_2 stacked dielectrics post-annealed in N_2 at 800°C for 2 s. The electrode is TaN.

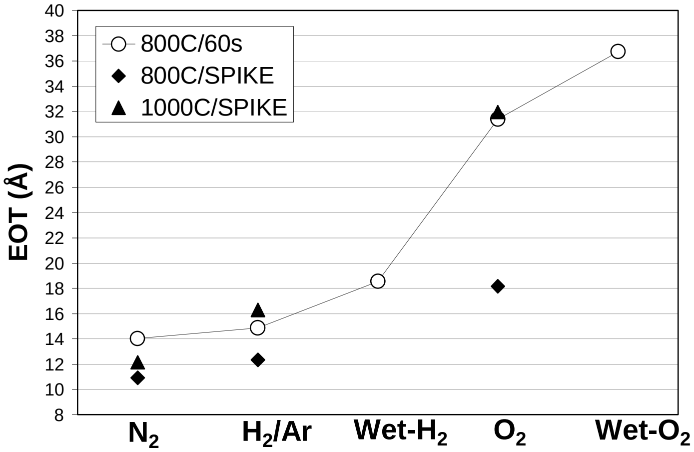


Figure 6. Dependence of EOT of ZrO_2 films on post-deposition anneal conditions.

The I-V characteristics (Figure 5 (b)) for the $TaN/ZrO_2/SiN/p\text{-}Si$ samples are also significantly dependent on the RTP anneal conditions. Figure 7 shows leakage current density values, measured at Vg =-1 V, as a function of EOT for various RTP anneal conditions. The samples annealed in N_2 show lowest leakage currents and EOT values. It is interesting to see the data on O_2 anneal effect in Figure 7. The leakage current of sample spike-annealed at 800°C is good. However, the leakage currents are much worse for the higher temperature and longer anneal time in O_2. This may be due to the O_2 diffusion time in the film layers. In comparison with SiO_2, a curve on leakage currents vs gate voltage of the standard SiO_2 gate was added in the same figure. A pure SiO_2 layer of the same electrical ~18 Å thickness has a leakage current density of approximately 1 A/cm2, nearly five order of magnitude higher leakage current that for an electrically equivalent ZrO_2 films.

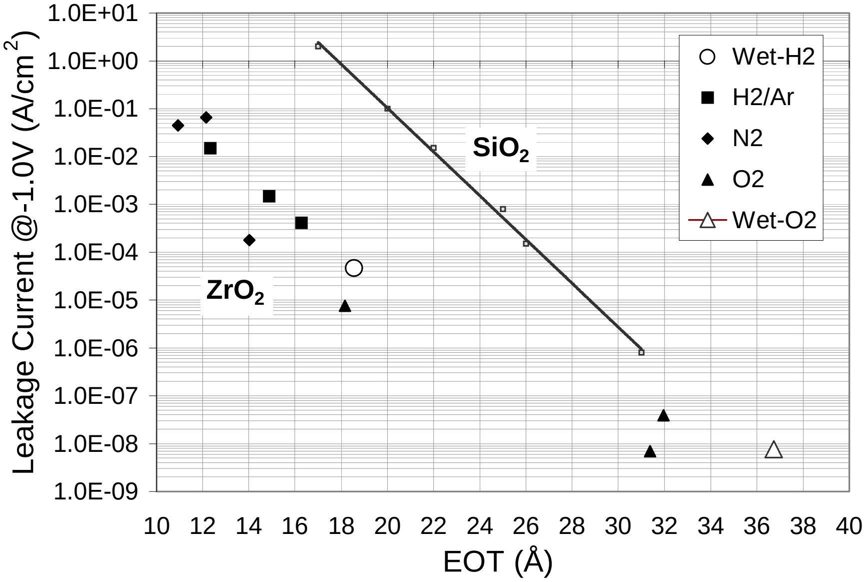


Figure 7 Leakage current density values at Vg=-1V versus EOT for $TaN/ZrO_2/SiN_x$/p-Si and standard SiO_2 gate.

CONCLUSION

A variety of RTP anneal conditions for ZrO_2 films on Si substrate have been evaluated, including annealing temperatures from 400 to 1050 °C and gas ambients of forming gas, N_2, O_2, wet O_2 and wet H_2. In this paper we have demonstrated that spectroscopic ellipsometry is a useful tool for ZrO_2 physical thickness measurement and evaluation of the interface. RBS, XPS depth profile and cross section TEM techniques have been used to verify the thickness measured from SE optical technique, indicating good agreement. The electrical characterization of ultra-thin ZrO_2 films show that the gas ambients in post-deposition anneal affect the EOT and leakage current significantly. The lowest EOT in this study is 10.9 Å. The leakage current of ZrO_2 is nearly five order of magnitude lower leakage current that for an electrically equivalent SiO_2 films.

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