Characterization of ZrO$_2$ and (ZrO$_2$)$_X$(Al$_2$O$_3$)$_{1-X}$ thin films on Si substrates: effect of the Al$_2$O$_3$ component

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Abstract. ZrO$_2$ and (ZrO$_2$)$_X$(Al$_2$O$_3$)$_{1-X}$ films were deposited by the sol-gel technique on Si substrates. The effect of the Al$_2$O$_3$ additive on the film surface morphology was studied by atomic force microscopy (AFM). The mixed oxide films showed a smoother morphology and lower values of the root-mean-square (RMS) roughness compared to ZrO$_2$. Further, FTIR spectra indicated that ZrO$_2$ underwent crystallization. The electrical measurements of the MIS structure revealed that the presence of Al$_2$O$_3$ and the amorphization affects its dielectric properties. The MIS structure with (ZrO$_2$)$_X$(Al$_2$O$_3$)$_{1-X}$ showed a lower fixed charge ($\approx 6 \times 10^{10}$ cm$^{-2}$) and an interface state density in the middle of the band gap of $6 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$). The dielectric constant measured was 22, with the leakage current density decreasing to $2 \times 10^{-8}$ A cm$^{-2}$ at $1 \times 10^6$ V cm$^{-1}$.

1. Introduction

A large number of dielectrics have a higher permittivity than SiO$_2$, some of them possessing a low leakage current, a high thermal stability and good interface properties comparable to the Si/SiO$_2$ interface. Binary metal oxides such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$ and HfO$_2$ are being intensively studied as they are predicted to be thermodynamically stable on Si and have a reasonably large band gap and, consequently, a good barrier height for electrons and holes in the semiconductor. Amorphous films are recommended for numerous applications due to their improved dielectric properties. To stabilize the amorphous phase of ZrO$_2$, SiO$_2$, and Al$_2$O$_3$ can be added to form a pseudobinary alloy [1]. It has been reported that sputtered (ZrO$_2$)$_X$(Al$_2$O$_3$)$_{1-X}$ [2] and co-evaporated (Zr$_{0.6}$Al$_{0.4}$)O$_{1.8}$ films [3] showed increased stability of the amorphous phase. Recently, films of pseudobinary alloys as (Al$_2$O$_3$)$_X$(TiO$_2$)$_{1-X}$ and (ZrO$_2$)$_X$(Al$_2$O$_3$)$_{1-X}$ obtained on Si by chemical solution deposition (CSD) have been studied in view of different possible applications [4]. We synthesized mixed oxide films by the sol-gel technique because of the several advantages it offers, such as low processing temperature, homogeneity and cost effectiveness. Unlike other deposition technologies, the sol-gel process does not require high-vacuum equipment; the films prepared have been used as functional materials in optical, microelectronic, and opto-electronic applications [5].

We report that the addition of Al$_2$O$_3$ changes the properties of the dielectric films, such as degree of crystallinity, roughness, thermal stability on Si, and the films’ dielectric properties as well.
2. Experimental

Zirconium (IV) propoxide was used as a Zr precursor to form the ZrO$_2$ films. A more detailed description can be found in [6]. For the aluminum component, AlCl$_3$ anhydrous dissolved in absolute ethanol was used. The Zr/Al molar ratio was 1:1.5. The thin films were deposited by spin coating at 8000 rpm. Firing was carried out at 350 °C/30 min to pyrolyze the organic components; this was followed by a high-temperature annealing at 750°C/60 min in N$_2$. This deposition method requires individual processing; under the same conditions (sol density and spinning rate), the same thickness is reproduced. In the single-layer deposition procedure, the layer thickness was around 30 nm for ZrO$_2$ and 50 nm for (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$. After repeating the deposition, the thicknesses were 60 nm for ZrO$_2$ and 102 nm for the mixed system. ZrO$_2$ and (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ layers were deposited on 3” p-type polished Si with resistivity of 5-7 Ω cm.

The films’ thickness and refractive index were measured by a He-Ne laser ellipsometer at 632.8 nm; the results are presented in table 1. The thickness uniformity across the wafer was 2 – 5 %.

Table 1. Refractive index and thickness of ZrO$_2$ and (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ layers annealed at 750 °C as estimated from the ellipsometric data.

| Layer type                     | Refractive index | Thickness [nm] |
|--------------------------------|------------------|----------------|
| (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ | 1.68             | 50 – 100       |
| ZrO$_2$                        | 1.88             | 30 – 60        |

The FTIR measurements were performed in the spectral region 350 – 1600 cm$^{-1}$ by an IRPrestige-21Shimadzu FTIR Spectrophotometer in view of studying the chemical bonding configuration. The XRD measurements were performed on a SIEMENS D500 diffractometer in a Bragg-Brentano geometry with secondary graphite monochromator and CuK$\alpha$ radiation.

3. Results and discussions

A typical top-view AFM image showing the surface morphology of the ZrO$_2$ films (60-nm thick) is presented in figure 1. Using these images, the root-mean-square (RMS) roughness and average roughness were estimated. The microstructure observed of the sol-gel film is dense and fine grained. The average roughness values vary from 0.9 nm to 0.8 nm for different wafer areas. The RMS values are in the range 1.18 nm to 1.16 nm. Figure 2 shows an AFM micrograph of a (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ film. The surface is smooth and uniform. The RMS values vary from 0.17 to 0.21 nm, while the average roughness ranges from 0.16 nm and 0.14 nm. The values for the mixed system are lower by about a factor of ten compared with those of ZrO$_2$, suggesting a very high degree of smoothness.

Figure 1. AFM micrograph of ZrO$_2$ films deposited on Si, annealed at 750°C.

Figure 2. AFM image of (Al$_2$O$_3$)$_x$(ZrO$_2$)$_{1-x}$ layers deposited on Si, annealed at 750°C.
These values are close to the reported RMS of ALD PrxAl1-xO3 [7]. The higher values for the ZrO2 layers can be due to their polycrystalline structure [8]. The same tendency has been previously observed by SEM investigation [6] for thicker films. The ZrO2 films show a columnar structure and a rougher surface compared to the mixed films, the latter revealing a much smoother surface with a small-grain structure. Both microscopic methods demonstrate that adding Al2O3 results in smoother and amorphous-like films.

The ZrO2 and mixed (ZrO2)x(Al2O3)1-x films were studied by FTIR spectroscopy to characterize the chemical bonding and molecules vibrations; the measured spectra are presented in figure 3. The ZrO2 film’s FTIR spectrum exhibits an intense band at 408.9 cm⁻¹ and two weaker bands at 391.6 cm⁻¹ and 435.9 cm⁻¹. The IR lines at 408.9 and 572.9 cm⁻¹ can be assigned to Zr-O bond vibrations in monoclinic ZrO2 [9].

The absorption bands at 609.5 and 686.7 are connected to the Zr-O stretching mode. The absorption peak at 648.1 cm⁻¹ may be due to the stretching vibrations of tetragonal ZrO2. The intense line at 1068.6 cm⁻¹ is due either to Si-O bonds of silicon dioxide or to the zirconyl bonds (Zr=O) [10]. Some overlapping of these two bands might exist. The spectrum of (ZrO2)x(Al2O3)1-x presents some new additional bands, while the other bands are slightly shifted with respect to those of ZrO2. The weak broad band at 522.7 cm⁻¹ has been reported to be related with crystalline ZrO2. The absorption band at 648.1 cm⁻¹ can be related to tetragonal ZrO2. The presence of the Al2O3 component is manifested by a broad absorption band centred at 823.6 cm⁻¹, which can be assigned to the stretching vibrations of Al-O bonds [11].

We also recorded XRD spectra of ZrO2 and (ZrO2)x(Al2O3)1-x layers annealed at 750 °C for 1 hour (not shown here) [6]. The spectra revealed that ZrO2 is well crystallized, exhibiting four XRD peaks of the tetragonal crystal phase (JPCDS card 50-1089) and two diffraction features due to monoclinic ZrO2 [6]. The XRD spectrum of (ZrO2)x(Al2O3)1-x layer is without characteristic features, indicating that the film’s structure is amorphous, despite of the high-temperature treatment [6].

Based on the FTIR analysis, one can conclude that ZrO2 film undergoes crystallization. The spectra of the (ZrO2)x(Al2O3)1-x layers exhibit new absorption bands, which suggests a low degree of crystallization of the ZrO2 component in the mixed system. This confirms the results from the microscope studies, namely, that the addition of Al2O3 induces amorphization of the film structure.

The dielectric properties of the layers were studied using an upper contact of Al dots, thus forming a MIS (metal-insulator-semiconductor) structure. The layers were deposited on chemically-cleaned Si surfaces, where the thickness of native SiO2 did not exceed 1 nm. Figure 4 presents C-V curves of ZrO2 and (ZrO2)x(Al2O3)1-x layers at 1 MHz with Al dots and a contact area of 2.5×10⁻³ cm². The ZrO2 film showed a positive fixed charge with a density of 5.42×10¹¹ cm⁻². The fixed charge density of the (ZrO2)x(Al2O3)1-x film was smaller: 6.46×10¹⁰ cm⁻², which is due to the Al2O3 content.
The frequency dependence of the dielectric constant $k$ was measured in a parallel circuit mode by an LCR HP 4274A device (see table 2). The dielectric constant was determined from the capacitance in strong accumulation and the physical film thickness. The estimated $k$ for ZrO$_2$ films was smaller than that reported by other authors ($k = 27$) [12], which can be due to the presence of a monoclinic phase that has a lower permittivity thus decreasing the overall permittivity [12].

Moreover, the dielectric constants of the (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ films were smaller (10 - 17.2) due to the Al$_2$O$_3$ additive. The sol-gel Al$_2$O$_3$ films annealed at 750 °C possessed a dielectric constant of 7.4 (1 MHz) [13].

The quasistatic pulse method ($CV$ map 92B) was used to study the dielectric/Si interface. This technique allows one to avoid the dielectric loss and the error in the phase-angle capacitance measurement. The results for the dielectric constant $k$ and the density of the interface states, $D_{it}$, in the middle of the band gap are summarized in table 3. In [14], the effective dielectric constant $k$ of (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ was determined to be $k = 22.1$. This is a proof of the thermal stability of the layer on a Si substrate after a high-temperature treatment.

### Table 2. Dielectric constant $k$ for ZrO$_2$ and (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ films at different frequencies.

| Oxide type          | 1 MHz   | 100 kHz  | 10 kHz   | 4 kHz    | 1 kHz    |
|---------------------|---------|----------|----------|----------|----------|
| (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ | 10.7    | 12.2     | 14.5     | 15.5     | 17.2     |
| ZrO$_2$             | 11.5    | 15.3     | 20.2     | 21.8     | 23.9     |

The values of $D_{it}$ registered for the pseudobinary alloy (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ are considerably smaller than those of the ZrO$_2$ layer, which can be connected with the influence of the Al$_2$O$_3$ component and the amorphization of the layer.

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### Table 3. Dielectric constant $k$ and interface state density in midband gap, as measured by the quasistatic pulse technique.

| Oxide type          | Dielectric constant $k$ (QS method) | $D_{it}$ interface state density in midband gap (cm$^{-2}$ eV$^{-1}$) |
|---------------------|-------------------------------------|---------------------------------------------------------------------|
| (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ | 22.3                                | 6.00×10$^{11}$                                                       |
| ZrO$_2$             | 24.1                                | 1.45×10$^{12}$                                                       |

Figure 5 illustrates the corresponding leakage current ($J$-$E$) characteristics of MIS structures with (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ and ZrO$_2$ layers, where $J$ is the current density and $E$, the electric field.

The $C$-$V$ measurements of the MIS structures with a (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ film showed that the addition of aluminum oxide leads to a very small decrease of the dielectric constant. At high electric fields, the leakage currents of the pseudobinary layers are lower by several orders of magnitude compared to those of pure ZrO$_2$. One can presume that the ZrO$_2$ films have higher leakage currents caused by grain boundaries, which serve as leakage paths. The composite system (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ possesses an amorphous structure, which decreases the possibilities for a similar type of leakage. The other possibility is to assume that the presence of the Al$_2$O$_3$ component changes the conductivity as a result.
of the larger equivalent band gap of the pseudobinary dielectric film. It is known that two transport mechanisms are important for the leakage in dielectrics: Schottky effect and Poole-Frenkel emission. They result from the lowering of the Coulomb potential barrier by a high electric field. The Schottky effect is associated with the barrier at the interface metal electrode-insulator and therefore, the current is electrode-limited. The Poole-Frenkel emission is related to barriers of the traps in the bulk of the material. It should be expected that the larger equivalent band gap of \((\text{ZrO}_2)_{x}(\text{Al}_2\text{O}_3)_{1-x}\) layer will lead to a decrease in the dielectric conductivity. This has been observed experimentally for \((\text{ZrO}_2)_{x}(\text{SiO}_2)_{1-x}\) films [15].

4. Conclusions
Thin films of ZrO\(_2\) and \((\text{ZrO}_2)_{x}(\text{Al}_2\text{O}_3)_{1-x}\) were deposited by similar sol-gel technological procedures on Si wafers. The surface and electrical characteristics of the layers was thus improved as the presence of \(\text{Al}_2\text{O}_3\) leads to amorphization of the ZrO\(_2\) structure and to a smoother surface. This results in lowering the refractive index and the leakage current, while maintaining a rather high value of the dielectric constant. The system – \((\text{ZrO}_2)_{x}(\text{Al}_2\text{O}_3)_{1-x}\) films on silicon – shows a good thermodynamic stability at high-temperature annealing (750 °C for 60 minutes), as no degradation was observed of the electrical properties. The results are encouraging and determine the pseudobinary alloy films \((\text{ZrO}_2)_{x}(\text{Al}_2\text{O}_3)_{1-x}\) as a promising material with good dielectric properties.

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