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XPS characterization of thin ZrO_2 and $(ZrO_2)_x(Al_2O_3)_{1-x}$ films deposited on silicon

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The study deals with thin films of zirconia (ZrO_2) and $(ZrO_2)_X(Al_2O_3)_{1-X}$, deposited on silicon substrates, using the chemical solution deposition method. The thin films were obtained by spin coating, followed by firing at 350°C/30 min and high temperature annealing at 750°C/60 min. Both compositional and chemical bonding data were obtained from X-ray Photoelectron Spectroscopy (XPS). XPS analysis shows the presence of carbon impurities only on the film surface. XPS spectra of a pure ZrO_2 film revealed $Zr3d_{5/2}$ and O1s peaks, characteristic of fully oxidized Zr atoms. A negligible amount of Si atoms was detected in the surface region. The deposition of $(ZrO_2)_X(Al_2O_3)_{1-X}$ films led to the formation of a pseudobinary alloy. The XPS spectra showed a $Zr3d_{5/2}$ peak at 183.5 eV and an Al 2p peak at 74.4 eV, attributed to photoemission from the ZrO_2 and Al_2O_3, respectively. An increased amount of Si atoms in the $(ZrO_2)_X(Al_2O_3)_{1-X}$ layers was observed in comparison to the ZrO_2 film.

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1. Introduction

As one of the most reliable high-k dielectrics, ZrO_2 has been intensively studied among many other candidates. A suitable large band gap (5.8 eV), a high dielectric constant of 24 and good thermal stability with Si are its distinctive advantages as a promising material [1]. In addition, zirconium oxide is reported to be thermodynamically stable on a Si substrate [2].

Mixed metal oxides, formed by adding a third element to a metal oxide, have been considered as alternative dielectric candidates for improved material properties [3]. Their electrical and optical properties can be tailored by adjusting the composition and structure. Aluminium oxide films are extensively investigated as electrical insulating materials, as well as good passivation layers [4].

It has been recently reported that thin films of ZrO_2 and $(ZrO_2)_X(Al_2O_3)_{1-X}$, deposited on silicon substrates show good electrical properties [5]. The layers were obtained using the chemical solution deposition (CSD) method. The effect of adding aluminium oxide to other metal oxides, such as ZrO_2, is the formation of amorphous dielectric films, which are thermodynamically stable on silicon and have good dielectric properties.

This work presents results from the XPS analysis of ZrO_2 and $(ZrO_2)_X(Al_2O_3)_{1-X}$ thin films, deposited on Si wafers. The aim of the investigations was to prove that the chemical solution deposition method can produce thin films with the required chemical composition and stoichiometry. The influence of Al_2O_3 on the properties of the mixed oxide system, as well as its effect on the silicon substrate, has been investigated.

2. Experimental

Zirconium (IV) propoxide (Fluka) was used as a precursor to form the ZrO_2 films. A more detailed description can be found in [5]. For the aluminium component, anhydrous (Merck) $AlCl_3$ dissolved in absolute ethanol was used. The Zr/Al molar ratio was 1:1.5. The thin films were deposited by spin coating at 8,000 rmp for 30 s.

The samples were dried at 80 °C for 30 min, to obtain a xerogel film and to remove residual solvents. Firing was carried out at 350 °C/30 min to pyrolize the organic components, and it was followed by high temperature annealing at 750 °C for 60 min in air. The layers of both zirconia and the compound system $(ZrO_2)_x(Al_2O_3)_{1-x}$ were deposited on p-type Si wafers. The Si was CZ, with <100> orientation and resistivity 5-7 Ω.cm.

The deposition method required individual processing of the wafers. Under the same deposition conditions (sol solution density and spinning rate), the same thickness was produced. For a single layer deposition procedure, the layer thickness was 31 nm for pure ZrO_2 and 50 nm for $(ZrO_2)_x(Al_2O_3)_{1-x}$. After repeating the deposition, the film thickness was 60 nm for ZrO_2 and for the mixed system 102 nm. Previous studies revealed a thickness uniformity of 2–5% along the wafer.

The XPS studies were performed in a VG Escalab II system, using AlK_α radiation with an energy of 1486.6 eV. The chamber pressure was 10^{-7} Pa. The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with an energy of 285.0 eV. The accuracy of the BE measured was ± 0.2 eV.

The photoelectron spectra were quantified using the peak areas and Scofield`s photoionization cross-sections. The depth profiles were obtained with an Ar^+ ion gun operated at 3 keV (45^0 incidence angle, 16.0 μA cm^{-2} ion current density).

3. Results and discussions

The XPS studies give information about the composition and chemical state of the deposited oxide films. Table 1 presents the results for the chemical compositions of ZrO_2 and $(ZrO_2)_X(Al_2O_3)_{1-X}$ thin films, derived from the XPS analysis.

Table 1. Chemical compositions of ZrO_2 and $(ZrO_2)_X(Al_2O_3)_{1-X}$ films, derived from XPS data.

Material	d [nm]	Composition [at.%]			
		Zr	Al	O	Si
ZrO_2	31	35.6	-	62.9	1.4
ZrO_2-Al_2O_3	50	10.8	24.9	56.7	7.6

The presence of carbon (C1s peak at 285.0 eV with a shoulder at ~ 289.0 eV) was registered only on the film surfaces (Fig. 1 a, b). This monolayer coverage of the organic species is considered as the background level for a wafer exposed to the atmosphere for an extended period of time. The adventitious surface carbon was quickly removed by Ar sputtering. The performed depth profile revealed that the C1s peak disappeared after Ar sputtering for 1 min. This was observed for pure zirconium oxide as well as for the mixed oxide films.

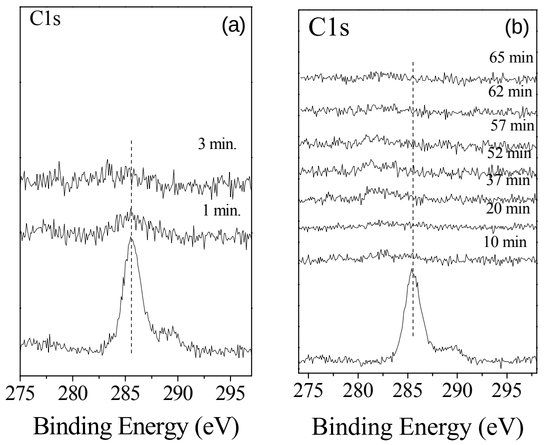

Fig. 1. XPS C1s spectra of a) ZrO_2 film and b) $(ZrO_2)_x(Al_2O_3)_{1-x}$ layers.

The Zr3d, O1s and Si2p spectra of a ZrO_2 layer are shown in Fig. 2. The Zr3d spectrum shows a characteristic doublet structure with maxima at 183.0 and 185.7 eV, corresponding to $Zr3d_{5/2}$ and $Zr3d_{3/2}$, respectively. These values represent the fully oxidized zirconium (Zr^{4+}) state [7-9]. No peak at 178.4 eV corresponding to Si-Zr bonding was observed, suggesting a lack of silicide formation [10].

The O1s peak at 531.0 eV corresponds to oxygen coordinated with zirconium atoms. The observed shoulder of the O1s peak at 532.5 eV was attributed to a C-O bond in the carboxyl species, adsorbed on the surface. After Ar sputtering for 1 min, the carbon peak disappeared. The position of the O1s peak at 531.0 eV did not change during Ar sputtering. Usually, when there is a formation of Zr-O-Si bonding, the binding energy of the O1s peak is located between the values characteristic for ZrO_2 (531.0 eV) and SiO_2 (533.0 eV) [6].

In the surface region of the film, a negligible amount of Si atoms was detected (0.8 to 1.4 at. %), and its concentration decreased with the film depth. The Si2p spectrum of the film surface shows a peak at 103.2 eV, the position of which shifts to a lower binding energy of 102.5 eV in the bulk of the film. The binding energy values in this range (102.5- 103.2 eV) are typical of SiO_2 oxide.

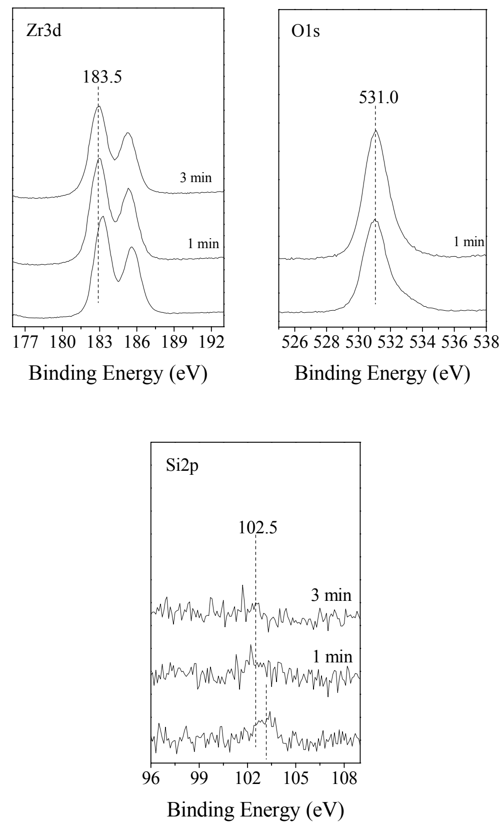

Fig. 2. XPS Zr3d, O1s and Si2p spectra of a ZrO_2 layer.

An XPS analysis was carried out for the mixed oxide system, and the estimated elemental contents are presented in Table 1. These data for the chemical composition of the films are in agreement with the results from a previous RBS study [5]. The calculated XPS intensity ratio Al/Zr of 2:1 (from Table 1) suggests that the ratio of both phases Al_2O_3: ZrO_2 in the mixed system is 1:1 or x = 0.5 in the compound formula.

In Fig. 3, the depth profiles of Al, Zr, O and Si elements in the $(ZrO_2)_x(Al_2O_3)_{1-x}$ film are shown. The mean sputtering rate was 0.7 nm/min. The stoichiometric $(ZrO_2)_x(Al_2O_3)_{1-x}$ alloy detected at the surface was preserved up to the interfacial transition region.

The XPS spectra show a $Zr3d_{5/2}$ peak at 183.5 eV and an Al 2p peak at 74.4 eV, attributed to photoemission from the ZrO_2 and Al_2O_3, respectively. It must be pointed out that these peaks have been retained up to the Si substrate (see Fig. 4). Approaching the interface region of the oxide film/Si, a weak Zr3d peak appears at 178 eV, which can be assigned to Zr-Si bonds.

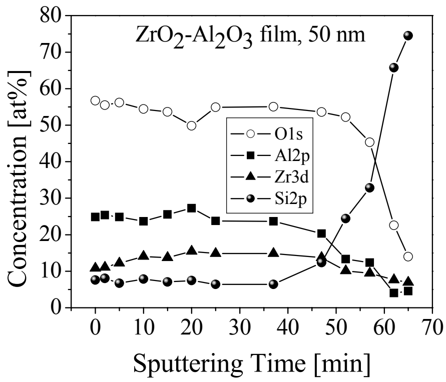

Fig. 3. XPS depth profile of Al, Zr, O and Si elements in $(ZrO_2)_x(Al_2O_3)_{1-x}$ film.

An increased amount of Si atoms in the surface layer was observed. The Si concentration was around 6-7% and remained unchanged within the bulk of the film.

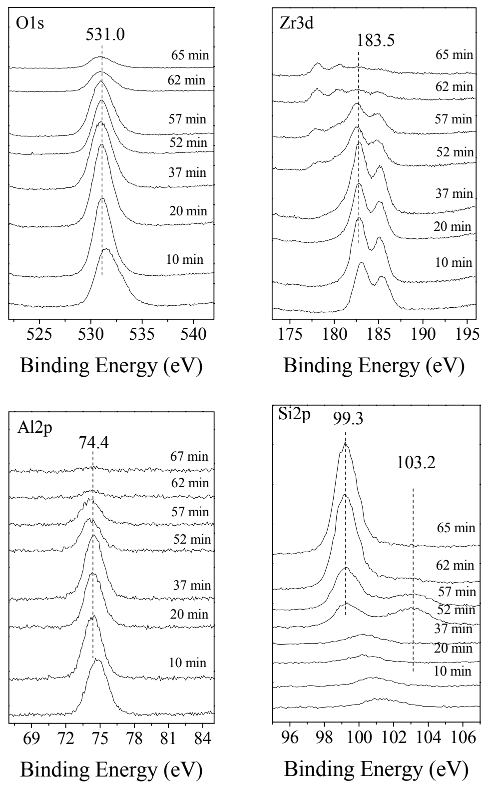

Fig. 4. XPS O1s, Zr3d, Al2p and Si2p spectra of $(ZrO_2)_x(Al_2O_3)_{1-x}$ film.

The Si2p peak was located at 101 eV, which binding energy corresponded to the formation of either sub-stochiometric silicon oxides or silicate bonds (Si-O-Zr).

After Ar^+ sputtering for 52 min, the interface region of oxide film/Si was approached and the Si2p peak showed a chemical shift to 103.2 eV due to the formation of Si-O bonds. Further ion sputtering up to 60 minutes resulted in the appearance of a Si2p signal from the bulk Si, with a binding energy at 99.3 eV [12].

The presence of an interfacial SiO_2 layer is attributed to the native oxide layer. Oxygen diffusion and its reaction with the Si substrate during the high temperature annealing is less probable. It is worth mentioning that no interfacial layer of pure SiO_2 has been detected. It can be suggested that near to the silicon surface, a non-stoichiometric alloy of SiO_2, Al_2O_3 and ZrO_2 **is** formed.

Two reactions are supposed to occur at the Si surface[11]:

$$Si + SiO_2 \rightarrow SiO$$
$$6\ SiO + ZrO_2 \rightarrow ZrSi_2 + 4\ SiO_2$$

Si atoms react with SiO_2 in the interface, forming the SiO species. Once the SiO comes into contact with the ZrO_2, a second reaction takes place yielding $ZrSi_2$ and more SiO_2.

There is another possible reaction path that could occur if the Si comes into direct contact with the ZrO_2 layer, i.e.

$$4Si + ZrO_2 \rightarrow ZrSi_2 + 2\ SiO$$

Probably, what we observed was the decomposition of ZrO_2 and the formation of Zr-Si bonds in the interfacial layer during high temperature annealing.

4. Conclusions

ZrO_2 and $(ZrO_2)_x(Al_2O_3)_{1-x}$ thin layers on Si substrates were investigated by the XPS method. The results showed that the chemical solution deposition method produces stoichiometric layers of ZrO_2. The amount of Si was negligible and the registered Si2p photoelectron peak corresponded to the Si-O bond. The mixed system of ZrO_2 and Al_2O_3 in a ratio of 1:1 was detected for the layers of $(ZrO_2)_x(Al_2O_3)_{1-x}$. The silicon concentration was about 7 at. % on the surface and within the bulk of the film. The Si2p peak was located at 100.4 eV, which indicates the presence of silicon suboxides or silicate bonds. Near to the Si substrate, the bond Zr-Si was registered. XPS analysis showed that a non-stoichiometric alloy of SiO_2, Al_2O_3 and ZrO_2 was probably formed in the interfacial region. Decomposition of the native oxide on the Si substrate, after the layer deposition process, was observed.

The study revealed that by chemical solution deposition, stoichiometric layers of ZrO_2 and $(ZrO_2)_x(Al_2O_3)_{1-x}$, which are thermally stable on Si substrates after the annealing at 750 ^oC, can be obtained.

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