XPS characterization of thin \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) films deposited on silicon

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Abstract. The study deals with thin films of a pseudobinary alloy \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) (PBA), deposited on silicon substrates using the chemical solution deposition (CSD) method. The thin films were obtained by spin coating followed by thermal treatment at 750°C. Both compositional and chemical bonding data were obtained by X-ray photoelectron spectroscopy (XPS). The depth analysis reveals that the stoichiometric \((\text{Al}_2\text{O}_3)\) and \((\text{TiO}_2)\) ingredients detected at the surface are preserved up to the interfacial transition region with Si wafer. The analysis shows the presence of carbon impurities on the film surface only. The Si penetration and the interface PBA dielectric/Si is investigated and discussed. The interface with the Si substrate is studied with the purpose of explaining the electrical properties of the \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}/\text{Si}\) structure.

1. Introduction
TiO\(_2\) is the subject of intensive research, especially regarding its applications in solar cells, chemical sensors, photoelectrochemical cells, photocatalysis and electronic devices. This interest was provoked by the needs of developing new dielectric materials with high dielectric constants which could replace the thermally grown silicon dioxide in a new generation of metal-oxide-semiconductor (MOS) transistor and dynamic random access memory (DRAMs) [1]. TiO\(_2\) is an attractive dielectric as it possesses high permittivity, \(k=80-100\), depending on the crystal structure and the deposition method. On the other hand, TiO\(_2\) is not thermally stable when in direct contact with silicon; a buffer layer between TiO\(_2\) and Si is necessary to prevent an interface reaction during high-temperature treatment [2]. An innovative idea in this respect is to use a system of two metal oxides.

The aim of the present work is to investigate \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) films obtained by chemical solution deposition (CSD) on Si wafers. The surface and depth analysis of TiO\(_2\) and \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) films were performed by XPS focused on the dielectric / Si interface.

2. Experimental
The chemical solution deposition method offers the possibility of preparing \((\text{Al}_2\text{O}_3)_x(\text{TiO}_2)_{1-x}\) thin films from a homogenous solution containing both metal precursors. \(\text{Ti(OEt)}_4\) (titanium ethoxide from Fluka) was used as titanium precursor. Acetylacetone was used as a peptizing agent. Anhydrous AlCl\(_3\)
(Merck) dissolved in absolute ethanol was used for the aluminum component. Both sols were mixed in a molar ratio Ti/Al =1:1.5. More details regarding the sol preparation can be found in reference [3].

The thin films were deposited on Si wafers by spin-coating at 8000 rpm for 30 s. The (Al₂O₃)ₓ(TiO₂)₁₋ₓ (PBA) layers were formed after a low temperature annealing at 350°C for 30 min to remove all organics components and high temperature annealing at 750°C in air for 60 min. The thickness of the pure TiO₂ film was 18 nm, and that of (Al₂O₃)ₓ(TiO₂)₁₋ₓ film, 70 nm.

The XPS studies were performed on a VG Escalab II system using AlKα radiation with energy of 1486.6 eV. The binding energies (BE) were determined utilizing the C1s line (from adventitious carbon) as a reference with 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° incidence angle, 16.0 µA cm⁻² ion current density).

3. Results and discussions
The XPS studies provide information concerning the composition and chemical states of the elements in the deposited oxide films. The XPS spectra of various elements of the two structures, TiO₂/Si and (Al₂O₃)ₓ(TiO₂)₁₋ₓ/Si, are shown in figures 1 and 2.

**Figure 1.** Ti 2p, O 1s and Si 2p photoelectron spectra of a TiO₂ film.

**Figure 2.** Al2p, Ti 2p, O 1s and Si 2p photoelectron spectra of an (Al₂O₃)ₓ(TiO₂)₁₋ₓ film.

The O 1s spectrum of pure TiO₂ film on the surface shows a maximum at the binding energy of 530.3 eV with a clear shoulder at 532.9 eV. The 530.3 eV value is attributed to titanium oxide [4] and
the higher energy is considered as a sign for SiO$_x$ or silicate (Ti-Si-O bonding) formation [5]. This is in agreement with the Si 2p spectrum, where two distinctive peaks are detected at 99.48 and 103.25 eV. The peak at 99.5 eV corresponds to bulk silicon, while the 103.2 eV peak is a contribution from the silicon oxidation state [5, 6].

The Si 2p photoelectron spectrum shows Si 2p peaks at 459.1 eV and 464.8 eV. The peak position observed at 459.1 eV with the doublet separation between the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of $\sim$5.7 eV and the strong satellite shifted by 14 eV from the main peak are characteristic of TiO$_2$. The binding energy at 464.8 eV corresponds to Ti 2p$_{1/2}$, indicating the TiO$_2$ form, too. Some authors [7] associate the XPS peak at 459 eV with possible Ti–Si bonds formation. For Si atoms, which diffuse to the layer surface after high temperature annealing, the following reaction is thermodynamically favorable:

$$1 \text{ TiO}_2 + 3\text{Si} \rightarrow 1 \text{TiSi}_2 + 1 \text{SiO}_2.$$ 

This reaction can explain the presence of Si – O bonds on the film surface, which is not observed in the case of (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ films that have been subjected to the same high temperature treatment.

The XPS analysis of the (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ film reveals some differences compared to pure TiO$_2$. The Si 2p spectra consist of one peak at 99.3 eV on the film surface corresponding to Si$^0$. The O 1s peak at 531.00 eV is broad due to contribution of both Al$_2$O$_3$ and TiO$_2$. The Al 2p spectrum shows a peak at 74.4 eV assigned to Al$_2$O$_3$. It was found that the Al chemical state does not change into the depth of the film, implying no Al compounds different from Al$_2$O$_3$ are formed at the interface.

The presence of carbon (C 1s peak at 285.0 eV with a shoulder at $\sim$ 289.0 eV) was registered only on the film surfaces. This monolayer coverage of 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 depth profile performed revealed that the C 1s peak disappeared after Ar sputtering and this was observed for pure titanium oxide as well as for the mixed oxide films.

Figure 3 presents the Si 2p, Ti 2p and O 1s spectra obtained at the interface between TiO$_2$ and (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ and Si substrate. In the case of the TiO$_2$ film, the XPS spectrum shows a Ti2p...
doublet with peaks at 453.0 eV and 458.7 eV that can be attributed to TiSi$_2$ [5]. The Ti2p$_{3/2}$ and Ti2p$_{1/2}$ peaks show also shoulders at 457 and 463.2 eV, respectively assigned to Ti suboxides.

The pseudobinary system (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ exhibits a Ti2p$_{3/2}$ peak at 453.2 eV attributed to metallic Ti, while the peak at 459 eV corresponds to titanium oxide. The O 1s spectrum of the Ti oxide layer reveals a peak at 530.3 eV, due to TiO$_2$, but as it is seen, the peak shape is broad, probably due to the presence of Ti suboxides. For the PBA layer, the O 1s peak shifts to the higher binding energy at 531 eV due to the presence of Al-O bonds.

The Si 2p spectrum near the interface is also illustrated in figure 3. There is only one peak due to emission from the Si substrate; no interfacial SiO$_2$ layer exists. The native silicon oxide film on Si substrate has been changed to TiO$_2$ during the high temperature annealing at 750 °C in oxygen ambient. This takes place according to the reaction, as proposed in ref. [6]:

\[
\text{SiO}_2 + \text{Ti} \rightarrow \text{TiO}_2 + \text{Si}.
\]

These XPS results differ from our previous study on similar chemically prepared films of (ZrO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ [8]; we assume that a nonstoichiometric alloy of SiO$_x$, Al$_2$O$_3$ and ZrO$_2$ can be formed in the interfacial region. A decomposition of the native oxide on the Si substrate after the layer deposition process is observed.

4. Conclusion

TiO$_2$ and (Al$_2$O$_3$)$_x$(TiO$_2$)$_{1-x}$ thin films on a Si substrate were investigated by XPS. For TiO$_2$ films, Si atoms were registered on the surface, which are bonded in SiO$_2$. In the case of PBA layers, no presence of SiO$_2$ and SiO$_x$ into film structure was detected. The registered peak of Si 2p at the binding energies of 99.2 eV can be related to the Si$^0$ or to the presence of Ti-Si bonds.

XPS analysis near the dielectric/Si interface shows that a nonstoichiometric alloy of TiSi$_2$, Al$_2$O$_3$ and TiO$_2$ can be formed in the interfacial region. A decomposition of the native oxide on the Si substrate after the layer deposition process is observed.

Acknowledgments

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