

XPS chemical state analysis of sputter depth profiling measurements for annealed TiAl-SiO₂ and TiAl-W layer stacks

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Funding information

Bundesministerium für Bildung und Forschung,
Grant/Award Number: 03IPT610Y; German
Federal Ministry of Education and Research,
Grant/Award Number: InnoProfile-Transfer
03IPT610Y

For the application of surface acoustic wave sensors at high temperatures, both a high-temperature stable piezoelectric substrate and a suitable metallization for the electrodes are needed. Our current attempt is to use TiAl thin films as metallization because this material is also known to be high temperature stable. In this study, Ti/Al multilayers and Ti-Al alloy layers were prepared in combination with an SiO₂ cover layer or a W barrier layer at the interface to the substrate (thermally oxidized Si or Ca₃TaGa₃Si₂O₁₄) as an oxidation protection. To form the high-temperature stable γ -TiAl phase and to test the thermal stability of the layer systems, thermal treatments were done in vacuum at several temperatures. We used X-ray photoelectron spectroscopy (XPS) sputter depth-profiling to investigate the film composition and oxidation behavior. In this paper, we demonstrate how the semiautomatic peak fitting can help to extract beside the elemental information also the chemical information from the measured depth profiles.

KEYWORDS

CTGS, depth-profiling, peak fit, SAW, surface acoustic wave, TiAl, XPS

1 | INTRODUCTION

High-temperature sensors based on the surface acoustic wave (SAW) principle are of high interest for automatization and process control in many fields. One general demand for such devices is to find material systems for the metallization which are compatible with the complex piezoelectric substrates and withstand the high application temperatures. One approach we discussed earlier is the use of Ru-Al layers and appropriate barrier systems.¹⁻⁴ Currently, we concentrate on the Ti-Al⁵⁻⁷ system known from aerospace applications. The next challenge is to find barrier layers for the protection of the metallization from both oxidation with the surrounding atmosphere and chemical reaction with the substrate at the high temperatures.

Sputter depth profiling investigations with electron spectroscopic methods are an effective tool to investigate material changes in such layer structures. In a previous study,⁷ we dealt with Auger electron and X-ray photoelectron spectroscopy measurements (AES, XPS) to

analyze the Ti-Al system with AlN barriers, also already using peak fit during XPS depth profiling to separate the Ti and N signal. The main conclusion was that the AlN barriers were stable up to 600 °C (high vacuum); however, a partial preferential oxidation of Al was already observed.

In this paper, we study two film systems: A Ti/Al multilayer system with SiO₂ cover layer on thermally oxidized Si substrates and a Ti-Al alloy film with a W barrier layer between the film and the Ca₃TaGa₃Si₂O₁₄ (CTGS) substrate by XPS and sputter depth profiling. Keeping the possible influence of an ion beam damage in mind, from analyzing the characteristic peak shape changes the phase stability or degradation of the film was followed. A detailed discussion of the high temperature behavior of the Ti-Al thin film system is presented in a separate paper,⁶ which includes also a large series of Auger electron depth profiles for different annealing procedures.

In contrast to this, the main focus of the present paper is to demonstrate the possibilities of the peak shape analysis for the Ti-Al

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material system under investigation by peak fitting of spectra series from XPS depth profiling, because this methodology is not used regularly. Such studies mostly are focused on the investigation of damages from the ion sputtering effects.^{8,9} In this context, also the reduced damaging of material by use of alternative ion sources (C₆₀, Ar-cluster) is in focus.^{9,10} Another attempt for chemical shift identification in spectral series from XPS depth profiling would be the use of multivariate methods like factor analysis applied by us earlier.^{11–13}

2 | EXPERIMENTAL

All depositions were done in a multichamber vacuum coating tool from Creavac GmbH. The substrates were mounted on a holder and moved with an automatic handling system between the process chambers for the Ti/Al and barrier layer deposition without vacuum interruption. The base pressure of the deposition process chamber was $\sim 2.0 \times 10^{-6}$ mbar. The Ti/Al multilayers were prepared by DC magnetron sputtering from elemental targets with an individual layer thickness of 10 nm and a total thickness of 200 nm ($[\text{Ti}_{10\text{nm}}\text{Al}_{10\text{nm}}] \times 10$) on thermally oxidized Si substrates. The Ti and Al layers were deposited at room temperature by means of a sputtering source (Lesker, type Torus 4 HV) with DC power supply (Huettinger trump, type MP-2) at a pressure of 1.8×10^{-3} mbar (gas: 8 sccm Ar).

The SiO₂ barrier layers were prepared by magnetron sputtering from a SiO₂ target at a substrate temperature of 180 °C (pressure 4.2×10^{-3} mbar; gas: 30 sccm Ar and 4.5 sccm O₂).

For the series on the CTGS substrates, initially a 20 nm W buffer layer was deposited by magnetron sputtering at a substrate temperature of 400 °C (pressure 2.3×10^{-3} mbar; gas: 30 sccm Ar). An Ti-Al alloy layer with a thickness of 180 nm was deposited by electron beam evaporation of Ti in combination with thermal resistance evaporation for Al with quartz-microbalance regulation at room temperature in high vacuum (more details on the deposition setup are documented in Lattner et al.⁵).

The samples were annealed under high vacuum for 10 h at up to 800 °C. The heating rate was 6.5 K min^{-1} .

The XPS investigations were performed with a PHI 5600 CI (Physical Electronics) system using nonmonochromatic Mg-K α X-rays (400 W) for excitation. The spectra were recorded with a hemispherical electron analyzer working at a pass energy of 29 eV. For depth profiling Ar⁺ ions with an energy of 3.5 keV scanned over an area of $2 \text{ mm} \times 2 \text{ mm}$ were used. The effective sputtering rates were 3.3 nm/min measured at a SiO₂ reference sample. The measuring area was about 800 μm in diameter. For the layer analysis the C1s, O1s, Al2p, Ti2p, Si2p, and W4f XP peaks were used. For the measurements at the CTGS substrates in addition a low energy electron source was used to try to minimize the extreme surface charging of the piezoelectric CTGS material.

For the concentration quantification the method of relative sensitivity factors was applied using standard single element sensitivity

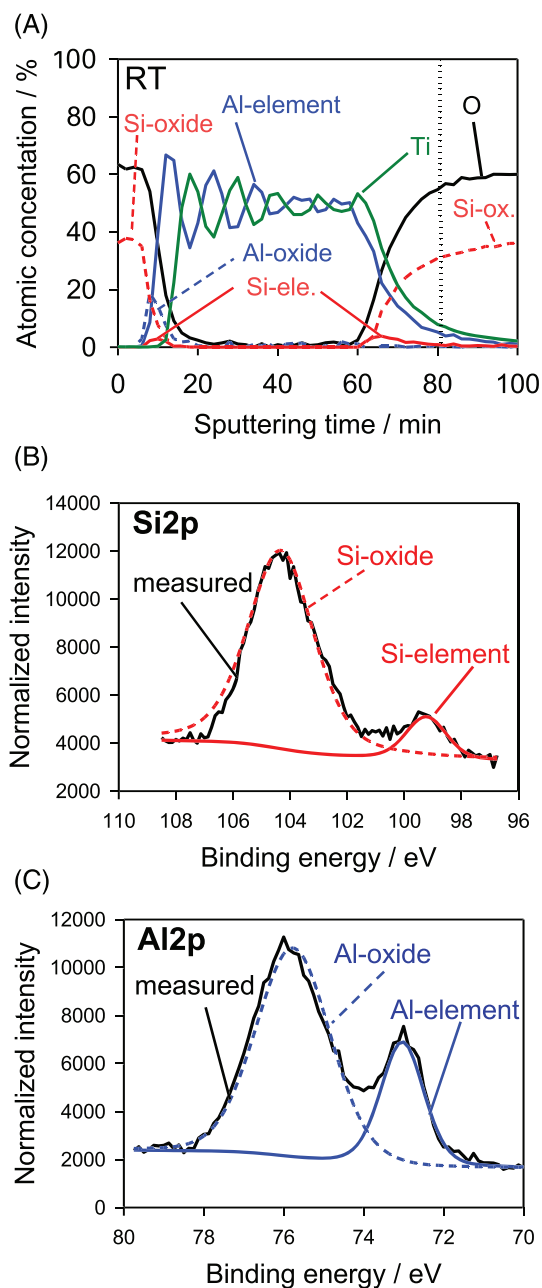


FIGURE 1 XPS depth profile results (A) from peak fits for Al and Si for a SiO₂/Ti/Al-multilayer/SiO₂ sample after preparation. From (B) the Si2p- and (C) Al2p-spectra at the interface SiO₂/Al-layer region (after 10 min of sputtering), one can recognize the interface reactions: a reduction of Si and oxidation of Al. The solid and broken lines in (B) and (C) correspond to the elemental and oxide part of Si and Al determined by peak fit

factors from the PHI-Multipak software.¹⁴ The effective peak areas (Shirley background subtraction) were used for determining the element intensities. Considering furthermore a possible demixing of the multicomponent material at the surfaces by the ion bombardment (preferential sputtering), it becomes clear that only comparative measurements between different samples states can be expected. An exact determination of the stoichiometry would need reliable standard samples for the layer materials.

For the semiautomatic peak fit of the spectra from the depth profile measurements, also the PHI-Multipak software¹⁴ was used. The peak fits were done after the background subtraction (Shirley type) by using the Gauss-Lorentz-peak shape. As discussed later using the example of the results shown in Figure 1 individual constraints for the peak shape/position were defined so that the fitting of the whole depth profile data was then possible without further efforts.

3 | RESULTS AND DISCUSSION

3.1 | Ti/Al-multilayers with SiO₂ barrier

Figure 1 shows the result of the XPS depth profiling measurement of an as-prepared multilayer film with an SiO₂ cover layer on a thermally oxidized Si substrate. The general sequence of the films is clearly visible in Figure 1A. The measurement of the Ti/Al layer stack is distorted with increasing depth due to the influence of the limited crater size in comparison with the XPS measurement area.

Looking at the measured spectra (Figure 1B,C) of the interface region (after 10 min of sputtering) between the top SiO₂ layer and the first Al-layer in both the Si2p and Al2p spectral windows elemental and oxide species are observed. That means that already during the preparation a reaction between both layers occur: The Al is partially oxidized and the Si oxide is partially reduced. It should be mentioned here that this finding is no sputter-induced effect by the ion beam—both Si and Al oxides are well known as stable oxides which are not influenced by the ion beam.¹⁵ The reduction of SiO₂ in contact with Al was observed also by other authors (e.g., Dadabhai et al.¹⁶ and references therein). Using the chemical information for the peak fit of the spectra during the depth profile, one can observe this formation of elemental Si on both top and bottom interfaces. For the semiautomatic peak fit, the peak positions and the full-width-half-maximum of the Al and Si species were determined for selected spectra from the depth profile, where the signal-to-noise ratio of the measured data allows a reliable calculation—as in Figure 1C for Al2p. These values then were fixed for the fit procedure, which leads to low a scattering in the data for the regions in the depth profile with no well-defined spectra.

At the bottom interface between the bottommost Ti layer and the SiO₂ of the substrate, no Ti oxidation was observed despite the presence of elemental Si. It is known that Ti is able to reduce SiO₂, the residual O is then solved within the Ti layer.

In Figure 2, the results of the XPS depth profile of the annealed samples are shown. After the annealing at 600 °C (Figure 2A), a further oxidation of Al is visible at the interface between the SiO₂ cover layer and the TiAl. In addition, oxidized Al is measured at the interface to the SiO₂ substrate. In both cases, the presence of Al oxide is connected with a reduction of oxidized Si. The SiO₂ cover layer is still intact; the Ti/Al multilayers are completely intermixed. Ti is present in the whole layer only in elemental form, no oxidation of Ti occurred.

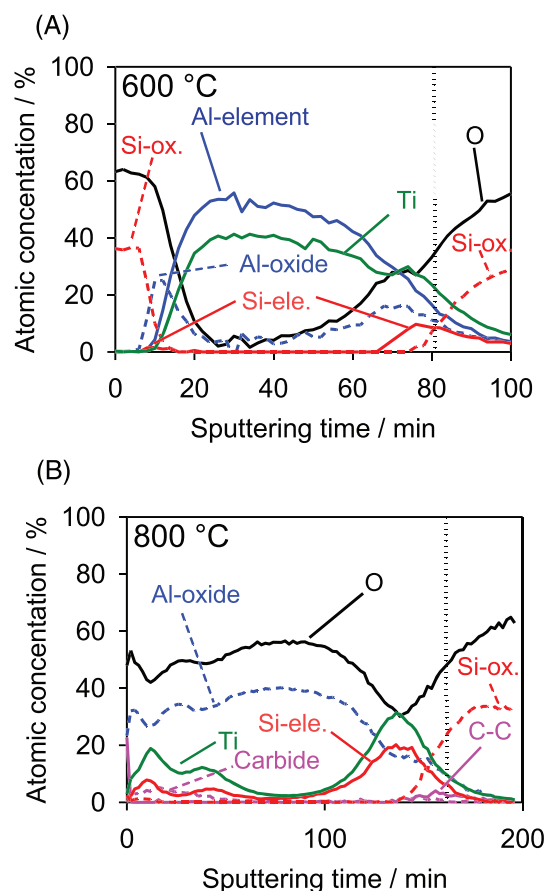


FIGURE 2 XPS depth profile results for the SiO₂/TiAl/SiO₂ sample with Ti/Al multilayers with peak fit results for Al, Si, and C after annealing at (A) 600 °C and at (B) 800 °C under HV. (A) Elemental Ti and Al are present in the whole layer; Al-oxidation occurs at the top and bottom. (B) Al is completely oxidized; the residual Ti (not oxidized) exists as Ti silicide

After the annealing at 800 °C (Figure 2B), the SiO₂ cover layer is destroyed and Al is completely oxidized and this Al oxide is present across the whole layer. The Ti spectra reveal that the peaks are nearly in elemental position (not shown here). The identical intensity vs. time course of the elemental Ti and the elemental Si signal points to a Ti silicide formation at both former Si-rich regions: the outer surface and the interface to SiO₂ substrate. In addition, residual carbon leads to carbide formation in the surface region. The formation of Ti₅Si₃ is confirmed by further X-ray diffraction and cross-section transmission electron microscopic (TEM) measurements.⁶

3.2 | Ti-Al-alloy layers with W barrier

Because of the superposition of the Ti3p (33 eV) with the W4f (32/34 eV) spectral peak for this kind of samples already the simple element versus depth analysis is disturbed. Using the standard quantification routine would result in the calculation of 5 at% of W in the Ti-Al layer already in the as-prepared sample. This artifact can be eliminated by using the peak fit procedure with a fixed Ti3p peak shape

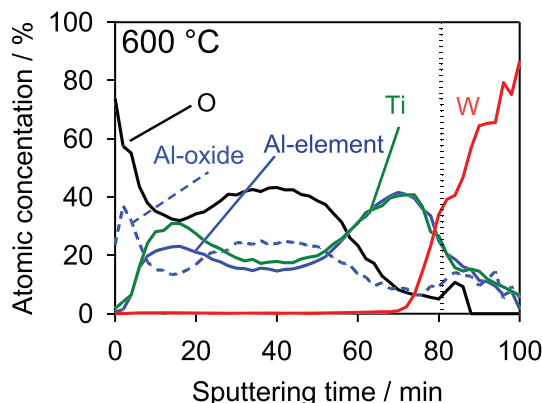


FIGURE 3 XPS depth profile results for the Al-Ti alloy layer on a CTGS substrate with W barrier layer and peak fit results for Al after annealing at 600 °C in HV. A 20-nm thick Al oxide layer is formed on top of the film and a partial oxidation of Al across the whole layer thickness takes place. Nevertheless, a high amount of residual elemental Al-Ti is found

which is defined, as described above for the Al/Si chemical states, from well-defined spectra in the region of the Ti-Al mixed layer.

After deposition the depth profile (not shown here) points to a Ti-Al layer with some fluctuations of the composition originating from the regulation of co-evaporation, a completely closed W barrier layer and only a thin Al oxide layer on top of the Ti-Al layer.

During annealing an oxidation takes place mainly from the surface. Figure 3 shows a depth profile for a sample annealed at 600 °C in HV. At the surface an Al oxide layer of 20 nm thickness is formed (thickness determined in TEM). In the former Ti-Al mixed layer Ti and Al are present in the non-oxidized state; however, almost across the whole layer in addition a high amount of Al oxide is observed. There is no interdiffusion of W into the Ti-Al layer. Due to the strong charging at the interface to the CTGS substrate and resulting peak shifts only a signal in the W4f measuring window was still detected (Figure 3—W increase, no O from the CTGS oxide) by a charging-induced artificial overlay of W with a Ta peak. Thus, also no stable measurement was possible in the underlying CTGS substrate itself. After annealing at 800 °C (not shown here) the film is completely oxidized; both Al- and Ti-oxides are found.

4 | SUMMARY

It is demonstrated that XPS sputter depth profiling measurements in combination with semiautomatic peak fits are a powerful tool to study chemical reactions in layer structures and to help to overcome distortions by peak overlap in multielement samples. In this work, the semiautomatic peak fitting was applied in the first part to separate the oxidized and elemental state of Al and Si and with this to determine the respective content in the sample. In the second example it was used to distinguish between W and Ti. The analyses reveal that in the Ti-Al system studied for an application as a high-temperature metallization in SAW devices the preferential oxidation of Al is the main

damaging effect. Ti is initially not taking part in the oxidation. Furthermore, it was not possible to investigate the interface between the W layer and the insulating CTGS substrate due to the extremely strong and instable charging which makes measurements in general very challenging.

ACKNOWLEDGEMENT

The work was supported by German Federal Ministry of Education and Research under grant InnoProfile-Transfer O3IPT610Y.

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How to cite this article: Oswald S, Lattner E, Seifert M. XPS chemical state analysis of sputter depth profiling measurements for annealed TiAl-SiO₂ and TiAl-W layer stacks. *Surf Interface Anal.* 2020;52:924-928. <https://doi.org/10.1002/sia.6820>