Final Report on ÖAD-Project SI 06 2016: Biocompatible nanostructured tetragonal zirconium oxide thin films with alternative stabilization dopants

1. Project Overview

Within this joint project between the Vienna University of Technology, Institute of Solid State Physics (IFP) and the Jozef Stefan Institute Ljubljana (JSI) the possibility to develop an alternative method for the synthesis of tetragonal zirconium oxide thin films was investigated. The Austrian group at the Vienna University of Technology (TUW) made use of its experience in deposition of metal thin films by physical vapour deposition techniques while the Slovenian group performed plasma oxidation of doped Zr for the synthesis of nanostructured metal oxide coatings. Within a masters thesis the Austrian group developed methods for the deposition of alloys containing zirconium, copper and aluminium and prepared numerous samples of different concentration of said metals in the thin film. These samples were transferred to Ljubljana and subjected to a treatment in inductively coupled high power RF oxygen plasma. After treatment the samples were investigated at JSI and TUW by dynamic AES, SEM, AFM and XRD. In general, within the whole project 11 mutual visits of the participating partners were executed. The names and affiliations of the visiting persons, the dates of the visits and their topics are given in Table 1 (see next page):

Name(s) of visitors	Date and place of visit	Topic
Dr. Miran Mozetic (JSI)	17.02.-20.02.2016 TUW	Planning of detailed project schedule, lab visit at TUW, evaluation of facilities at TUW, planning of first experiments.
Dr. Miran Mozetic (JSI)	29.03.-01.04.2016 TUW	Introduction of master student Christian Nöbauer, discussion about project goals, outline of master thesis.
Dr. Miran Mozetic (JSI)	05.07.-09.07.2016 TUW	Evaluation of progress in sample preparation by Mr. Nöbauer, discussion of preliminary results on untreated samples.
Mr. Christian Nöbauer (TUW)	22.05-26.05 2016 JSI	Plasma treatment of samples manufactured at TUW at JSI. Investigation of the elemental distribution in the treated coatings by AES and XRD.
Dr. Miran Mozetic (JSI)	05.07.-09.07.2016 TUW	Discussion of results of plasma treatment at JSI, planning of further experiments.
Mr. Christian Nöbauer, Dr. Christoph Eisenmenger-Sittner (TUW)	20.10-22.10 2016 JSI	Transfer of new samples with well defined composition gradients to JSI. Plasma treatment of samples. Planning of characterization schedule at JSI.
Dr. Miran Mozetic (JSI)	02.11.-05.11.2016 TUW	Transfer of plasma treated samples to TUW, Discussion of results of plasma treatment at JSI, planning of further characterization tasks and experiments at TUW.
Dr. Miran Mozetic (JSI)	26.04.-30.04.2017 TUW	Discussion of cumulative report on plasma treated ZrAl and ZrCu samples. Draft of master thesis Christian Nöbauer. Setting final parameters for last batch of samples.
Mr. Christian Nöbauer, Dr. Christoph Eisenmenger-Sittner (TUW)	14.05-17.05. 2017 JSI	Transfer of last batch of samples with well defined composition gradients to JSI. Plasma treatment of samples. Characterization of samples at JSI. Discussion of final draft master thesis Christian Nöbauer. Transfer of treated samples for XRD measurement at TUW.
Mr. Christian Nöbauer (TUW)	03.05-04.05. 2017 JSI	Transfer of XRD characterized samples to JSI. AES characterization at JSI. Compilation of results.
Dr. Janez Kovac (JSI)	17.12-20.12. 2017 TUW	Discussion of cumulative results of sample characterization by AES, XRD, SEM and AFM. Discussion of project results and draft of final report.

Table 1.: Overview on mutual visits during the project

2. Aims of the project

The possibility to stabilize the tetragonal phase of ZrO_2 by doping Zr with abundantly available elements like Al and Cu should be investigated. To form the oxide films a two step process was chosen. First Zr and the dopant material should be deposited by magnetron sputtering in a special geometry at TU Vienna. This geometry allows for the production of concentration gradients of the dopant material on one sample in the range from 5 – 15 at%. The second step should consist in plasma oxidizing the films at the Jozef Stefan Institute in Ljubljana. Then the films should be characterized at both institutions by AES, XRD, SEM and AFM, with a focus on AES at JSI and XRD at TUW. Apart from checking if tetragonal ZrO_2 was formed, special attention was also given to the possibility that plasma oxidation would form nanostructures in the doped coatings which could have influence on their bio-compatibility.

3. Project Results

3.1. Initial Project Schedule

The total project duration was scheduled for 24 months. 6 journeys per year for each partner were planned. Roughly a regular meeting schedule could be kept (see table 1), although the total number of trips was less than anticipated. Nonetheless, within the given time several tasks could be completed and a basis for further collaboration could be formed. In addition, by using electronic means of communication, preparatory work before the visits and refinements after the visits could easily be performed in the intermediate periods.

3.2. Modification of the Deposition Equipment

In order to allow for the deposition of Zr films containing a compositional gradient of dopant materials a sputter deposition plant at TUW was equipped with two magnetron sputter sources mounted perpendicular to each other. The first source was located opposite the substrate and contained the Zr target, while the second one contained the dopant material (see Fig.1a). On the substrate holder a small wall was mounted, which blocked part of the particle beam from the dopant material (see Fig. 1b).

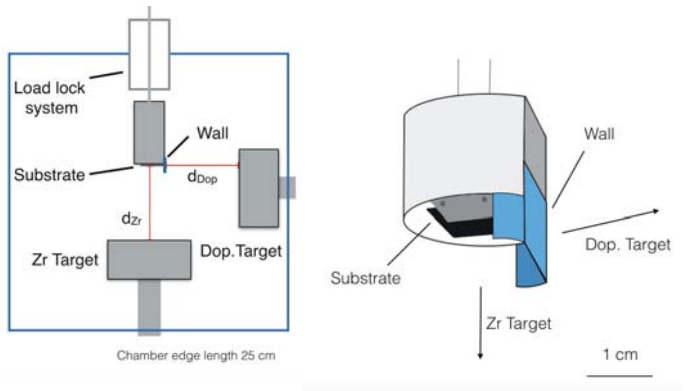

Fig. 1.: Schematic of the experimental setup for the production of Zr coatings containing dopant gradients.
(a) relative locations of Zr target, dopant target and substrate; d_{Zr}: distance Zr target/substrate; d_{Dop}: distance dopant target/substrate.
(b) partial shielding of the substrate from the dopant vapour by a small shielding wall.

This setup allowed for producing dopant gradients from5 to 15 at% dopant material in the Zr matrix, as it is shown in Fig. 2.

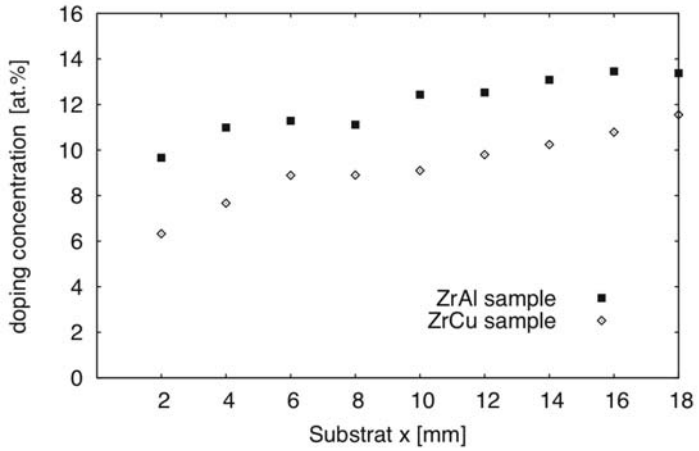

Fig. 2.: Atomic concentration of the dopant materials Cu and Al in the Zr matrix.

With this setup several samples were deposited to investigate the possibility to stabilize tetragonal Zirconia by doping with Al and Cu.

3.3. Plasma treatment

After growth the samples were treated with oxygen plasma created by an electrodeless inductively coupled radio frequency discharge at the JSI in Ljublajna. The RF power absorbed by plasma was adjusted to 600 W. The power density was therefore about 5 W/cm^3. Such a high power density allowed for sustaining a stable plasma in the H mode. The treatment time was 5 s. Such a short treatment time (which is not common for plasma

oxidation) was chosen because of the very high specific power when the plasma is in the H-mode. This high power allowed for rapid formation of the oxide film. The plasma oxidized films were investigated at JSI by dynamic Auger Electron Spectroscopy and by X-Ray diffraction at TUW. The results of these measurements were discussed in several mutual meetings, see table1.

3.4. Evaluation of Plasma Oxidation by Dynamic AES

Fig. 3 shows depth resolved AES scans for plasma treated coatings with Al (Fig. 3a) and Cu (Fig. 3b) doping.

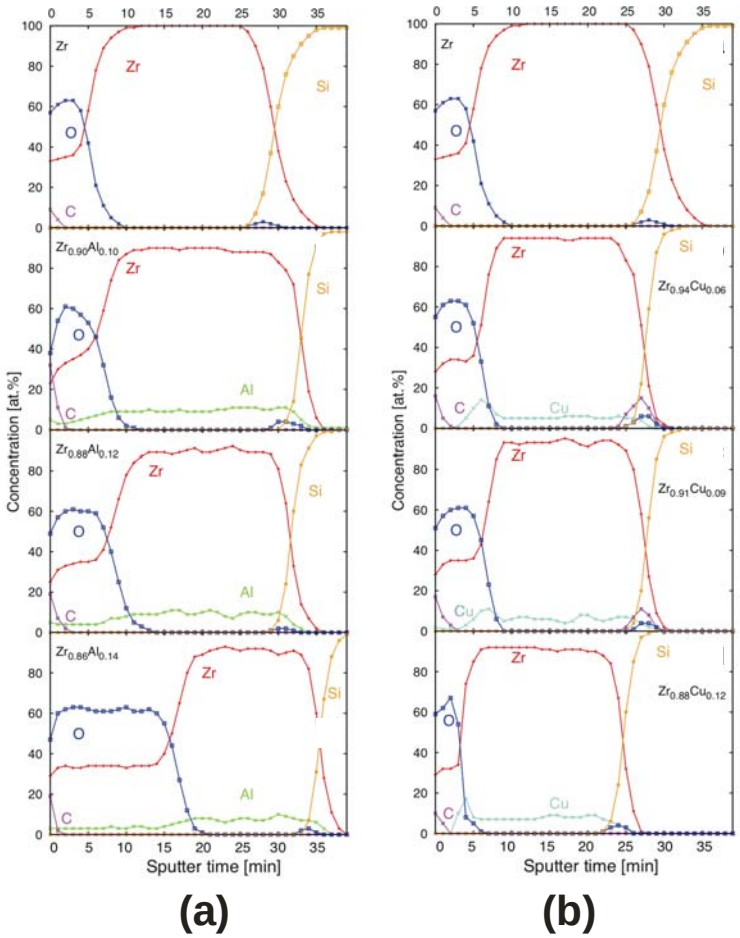

Fig. 3.: AES depth scans of plasma oxidized (a) Al doped Zr-coatings and (b) Cu doped Zr-coatings. Indices of the dopant material give the concentration of dopant in at% in the as deposited coatings

As Fig. 3 shows, the plasma oxidation worked well for both material systems. Oxygen penetrates a significant portion of the film (dark blue curve). Al or Cu signals are diminished in the oxidized region, but for Cu a local concentration maximum can be

observed at the interface between the oxidized and the unoxidized region, a phenomenon which is absent for Al doping. This local enrichment of Cu has consequences on the formation of crystalline ZrO_2, which was investigated by XRD at TUW.

3.5. Evaluation of Plasma Oxidation by XRD

Fig. 4 shows XRD diffractograms of Al doped (Fig. 4a) and Cu doped (Fig.4b) Zr coatings after plasma oxidation.

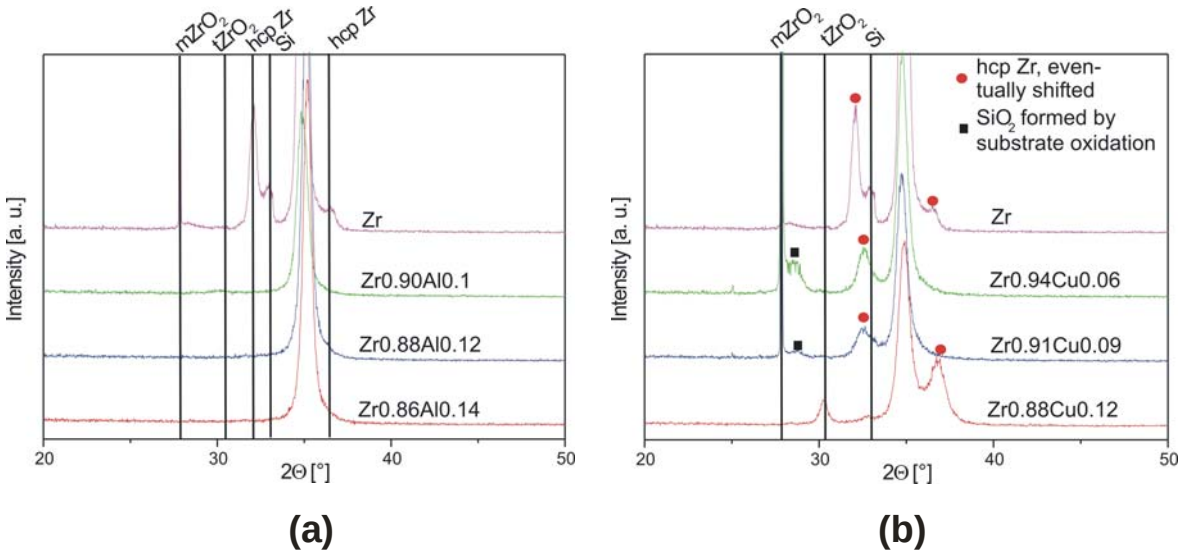

Fig. 4.: XRD diffractograms of plasma oxidized (a) Al doped Zr-coatings and (b) Cu doped Zr-coatings. Numbers right to the dopant material give the concentration of dopant in at% in the as deposited coatings; $mZrO_2$: monoclinic Zirconia, $tZrO_2$: tetragonal Zirconia, hcp Zr: hexagonally close packed metallic Zirconium

While for Al doped coatings no formation of crystalline oxides is observed (see Fig. 4a), for Cu doped coatings, at Cu concentrations up to 9 at% a clear signal for monoclinic ZrO_2 ($mZrO_2$) and for 12 at% a peak for tetragonal ZrO_2 ($tZrO_2$) is observed, while the signal for $mZrO_2$ vanishes completely. This behaviour, in association with the distinct enrichment of Cu at the interface between oxidized and unoxidized portions of the coating suggest that (i) Cu is a candidate dopant for the formation of $tZrO_2$ at room temperature and (ii) the enrichment of dopant at the oxidized/unoxidized interface may be necessary for crystalline oxide formation in general and for $tZrO_2$ stabilization in particular. Also peaks for metallic Zr (hcp Zr) are still visible, indicating that parts of the coating are still unoxidized.

4. Project Summary

Within the Project "Biocompatible nanostructured tetragonal zirconium oxide thin films with alternative stabilization dopants" it could be shown that

- it is possible to produce samples which contain a spatially variable content of dopant material by a simple modification of the deposition plant, thus allowing for the possibility to obtain differently doped materials on one sample.
- plasma oxidation of doped Zr is an extremely fast and efficient way (treatment time in the range of seconds) to transform Zr metal into its oxides. The resulting oxide coatings may be amorphous or crystalline, depending on the dopant material.
- a local maximum of dopant at the interface between oxidized and unoxidized portions of the material seems to be indicative for crystalline oxide formation.
- the stabilization of the tetragonal Zirconia phase is possible by doping Zr with approx. 12 (or more) at% Cu.

The formation of distinct nanostructures by plasma treatment, which may influence the biocompatibility of the oxide materials, was not observed. It has, however, to be said that within the project only a small parameter set in respect to dopant concentration, deposition parameters and duration of plasma oxidation was investigated, so that a more extensive parameter study, which may be subject of further collaboration, may yield results in this respect. Finally, the project also resulted in a master thesis [1] and in the submission of a joint paper to the journal "Surface and Coatings Technology" [2].

REFERENCES

[1] C. Nöbauer
Herstellung von Aluminium- und Kupfergradienten in gesputterten Zirkoniumschichten zur Stabilisierung von tetragonalem Zirkoniumdioxid
Master Thesis, Vienna University of Technology, 2017

[2] C. Eisenmenger-Sittner, C. Nöbauer, M. Mozetic, J. Kovač, and R. Zaplotnik
Stabilisation of tetragonal ZrO_2 by oxygen plasma treatment of sputtered ZrCu and ZrAl thin films
Submitted to Surface and Coatings Technology, under review.

Wien, 20.03.2018 Ao. Univ. Prof. Dr. Christoph Eisenmenger-Sittner

Institut
für
Festkörperphysik
der Technischen Universität
A-1040 Wien, Wiedner Hauptstr. 8-10