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Stabilization of tetragonal ZrO_2 by oxygen plasma treatment of sputtered ZrCu and ZrAl thin films

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ABSTRACT

The stabilization of tetragonal zirconium dioxide (zirconia) by doping at room temperature has already been carried out with dopant materials like Y or Mg. Also alternative dopants like Al and Cu have been investigated using reactive sputtering processes at elevated temperatures with oxygen as a reactive gas. In the present work we investigate if stabilization is possible by dopants like Al and Cu which are added by means of non-reactive sputtering in a dual cathode magnetron sputtering device. Because it is expected that the stabilization depends on the dopant concentration, the Zr coatings were produced with a dopant gradient. So it was possible to investigate many different compositions with only few samples. This dopant gradient could be produced with a modification of the substrate holder in the sputtering chamber where a small wall partially shadows the vapor beam of the dopant. After production of the metallic ZrAl and ZrCu samples, first their chemical composition was determined by energy dispersive X-ray spectroscopy in a scanning electron microscope. Then they were treated with oxygen plasma. Depth profiles were recorded by Auger electron spectroscopy to investigate the progress of the oxidation. For crystallographic analysis X-ray diffraction was used. The surface morphology was measured with an atomic force microscope.

The results show that the stabilization worked successfully with Cu while for Al no formation of the tetragonal phase was observed and the films remained essentially amorphous. The results show that oxygen plasma treatment is a viable and fast way to transform doped metallic Zr films into tetragonal Zirconia.

1. Introduction

Zirconium dioxide (ZrO_2) is a material which is applied in many technical fields, like in high performance mechanics because of its hardness [1], protective coatings, thermal barrier coatings [2], oxygen sensors, solid oxide fuel cells [3] or catalysis [4,5]. There are three modifications of ZrO_2. At room temperature the monoclinic crystal structure, above 1170 °C the tetragonal and above 2370 °C the cubic crystal structure is thermodynamically stable. The tetragonal phase, however, can be stabilized at lower temperatures by the addition of doping materials like Y or Mg, and also doping with two or more materials is a common method [6–8]. By means of reactive deposition processes like DC- or pulsed DC magnetron sputtering the formation of tetragonal Zirconia (t-ZrO_2) could be achieved at deposition temperatures as low as 300 °C by doping with Al or Cu [9–14]. The reactive process, however, triggers the formation of the oxides of the dopant materials during deposition, so that the stabilization of the tetragonal phase is likely to be related to the incorporation of dopant oxides.

Within this work a different route for the stabilization of t-ZrO_2 shall be pursued. First, purely metallic films consisting of doped metallic Zr shall be deposited by conventional non-reactive DC magnetron sputtering, making use of the higher stability and higher deposition rates of this process. In a second step, Zirconioa shall be formed by a plasma treatment process, which supplies reactive oxygen thus presumably making the oxidation process happen at a considerably higher reaction speed and at lower temperatures.

The aim of this work is to stabilize tetragonal ZrO_2 in thin coatings by plasma treatment at temperatures as close to room temperature as possible. Especially low cost and easily obtainable dopants of, like aluminium or copper, shall be considered. If the stabilization with these elements is successful, the doping concentration necessary for t-ZrO_2 stabilization shall be determined. Doped Zr films will first be produced by magnetron sputtering, and in a second step the oxidation of the as deposited films will be performed by plasma oxidation.

There are several ways for the stabilization of tetragonal Zirconia which range from the supply of elastic energy, via solid solution stabilization, grain size manipulation, oxygen over- or under stochiometry or doping [15–17]. Considering the process of stabilization by the

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oxidation of doped coatings the prevalent mechanism is selective oxidation which is based on the model of Cabrera and Mott described in the review paper [18] and tested for several material combinations e.g. in [19,20]. Surface treatment and the treatment of metal alloys treatment by oxygen plasma is e.g. discussed in [21,22]. In the case of oxygen plasma treatment of ZrAl or ZrCu coatings (major component: Zr), the oxygen atoms penetrate the coating and form bonds with Zr which is the major component. Thermodynamically, metallic Al and Cu are not soluble in the oxidized Zr and should be expelled out of the oxide layer into deeper areas of the coating, which the oxygen did not yet reach. Therefore there will be a certain depth dependent concentration of Al or Cu, which is important for the stabilization of tetragonal ZrO_2, The dopant concentration is low in the oxide layer, may increase at the interface between the oxidized and not-oxidized region and then tends towards the concentration value as given before the plasma treatment [23–26]. A dopant concentration increase at the interface between oxidized and non-oxidized portions of the film is very important for the stabilization of the tetragonal ZrO_2. After the oxidation of the upper layers of the coating, the oxygen tries to penetrate deeper, but the mentioned increase acts as oxygen barrier. Now super saturated oxygen remains before the barrier and leads to the creation of tetragonal ZrO_2 [27]. Considering the formation enthalpies for the oxides of the involved materials (Al_2O_3: $\Delta H = -1675$ kJ/mol, Cu_2O: $\Delta H = -171$ kJ/mol, ZrO_2: $\Delta H = -1097$ kJ/mol [28]) which govern the oxidation behavior of the respective metals in an alloy [18] it becomes evident that this mechanism will be valid for Cu, since its oxide is harder to form, but Al will transform to Alumina easier and may therefore be trapped in the Zirconia matrix without forming the maximum in dopant concentration which acts as oxygen barrier.

The process of selective oxidation and the process of building the oxygen barrier depend on the concentration of the dopant material. An easy method to vary the composition is the production of a dopant gradient in the Zr coatings along the extension of the substrate. This can be realized by placing a small wall between the substrate and the dopant target, which partially blocks the dopant vapor beam, as described in detail later-on.

The present work is basically divided into two steps. Firstly thin doped Zr coatings are produced and investigated by various analytical methods. The layers are deposited in a magnetron sputtering device with two sources, and the mentioned modification of the substrate holder. Subsequently, these samples are treated with oxygen plasma to create ZrO_2 and then examined for the presence of the tetragonal zirconium dioxide.

2. Experimental

The ZrAl and ZrCu films were deposited on Si(001)-wafers by a dual-cathode magnetron sputtering device (Fig. 1). The Zr target with a diameter of 5 cm was located on the bottom of a cubic vacuum chamber, opposite to the substrate which led to a constant zirconium vapor beam which basically impinges perpendicularly to the substrate surface. A second target, also with a diameter of 5 cm was mounted 90° relative to the Zr target at the side wall of the chamber. This target is made of the dopant material and will be called "dopant target" further on. The substrate, $20 \times 20\,mm^2$ surface area, is mounted on a heatable substrate holder which can be inserted into the sputter chamber via a load lock system which is located on the upper wall of the vacuum chamber, see Fig. 1. Located between the dopant target and the substrate is a small wall, which is mounted on the substrate holder (Fig. 2). Due to this special modification of the substrate holder it was possible to produce a gradient of the dopant in the zirconium coating by partially blocking the dopant vapor beam from the substrate. The base pressure of the sputter chamber was $p_O = 1{\cdot}10^{-6}$ mbar. The working gas pressure ($p_W = 7{\cdot}10^{-3}$ mbar) was achieved by introducing argon, which was used as a sputtering gas, into the vacuum chamber. The distance of the targets from the substrate center was approximately $d_{Zr} = 63$ mm for Zr and $d_{Dop} = 27$ mm for the dopant target. The mean free path of the sputtered atoms at the given working gas pressure is in the cm range [29], so that scattering events may occur also after the shielding wall. Therefore, the dopant concentration, displayed in Fig. 3 for Al and for Cu is not exactly zero right behind the wall. The coating thickness was about 320–350 nm for all coatings and was measured with a Taylor-Hobson Surtronic 3+ Profilometer. The substrate temperature could freely be chosen between room temperature and 400 °C.

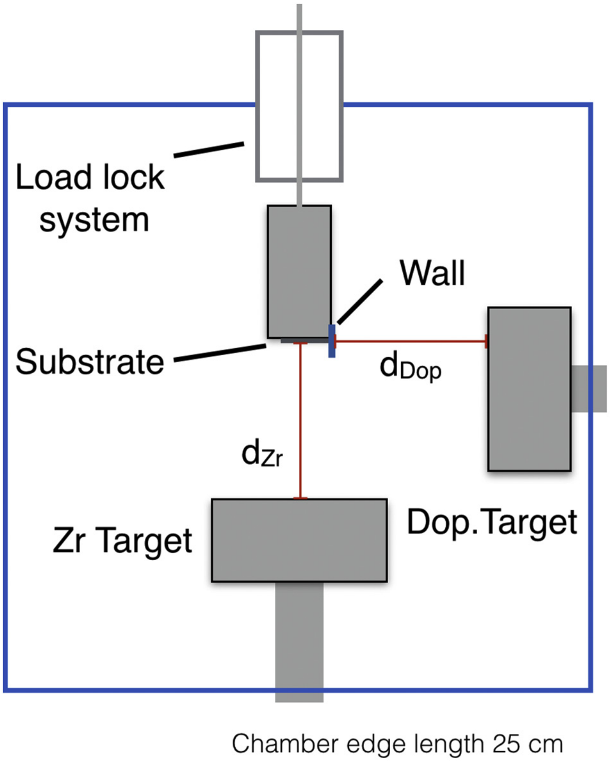

Fig. 1. Sketch of the sputter chamber geometry. Distance Zr-Target to substrate, $d_{Zr} = 63$ mm, distance of dopant target to edge of the substrate, $d_{Dop} = 27$ mm.

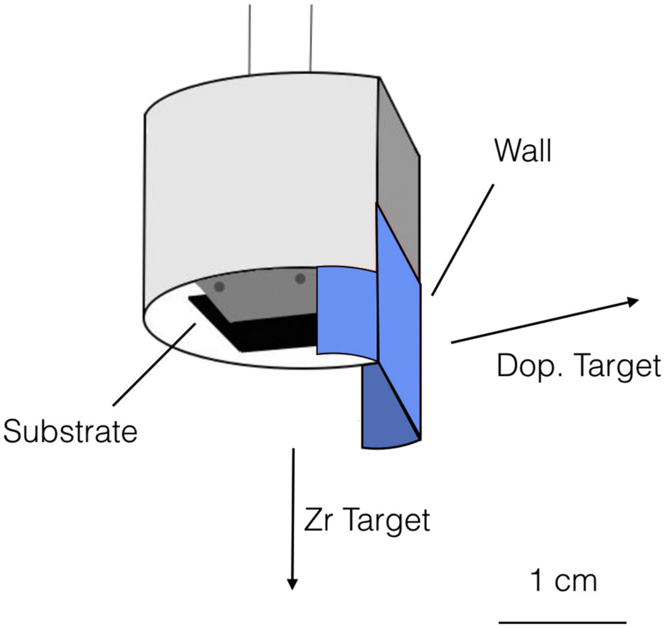

Fig. 2. Schematic image of the modification of the substrate holder by a small shield (called "wall") which partially blocks the vapor beam emerging from the dopant target.