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Epitaxial and non-epitaxial platinum, palladium and silver films on yttrium-stabilised zirconia

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HIGHLIGHTS

- Pt, Pd and Ag films are prepared on differently orientated YSZ.
- Substrate orientation and deposition temperature influences the microstructure.
- Pt forms epitaxial and polycrystalline films.
- Pd and Ag form polycrystalline films, sometimes with epitaxial grown grains.
- The formed microstructures are described by energy minimization.

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ABSTRACT

Platinum, palladium and silver films have been prepared on differently orientated YSZ (yttrium-stabilised zirconia) substrates by PLD (pulsed laser deposition). The deposition temperatures for platinum were 200 °C and 400 °C, whereas palladium and silver were deposited only at 200 °C. The microstructure of the films depends on the particular metal, on the orientation of the substrate and on the deposition temperature. Platinum – deposited at 400 °C – forms single crystalline, epitaxial (111), (311) and (110) orientated as well as (111) orientated polycrystalline films. Platinum, palladium and silver – deposited at 200 °C – always form (111) orientated and polycrystalline films, in some cases also with a fraction of epitaxial grown grains. The formed microstructures were discussed on the basis of interface and surface energy minimization and structure zone models.

1. Introduction

Platinum, palladium and silver have several outstanding properties: good thermal and electrical conductivities, corrosion resistant, good catalytic activities, absorption of high fractions of hydrogen and oxygen and at least platinum and palladium have high melting points [1]. Therefore these metals are used in many of the today's key technologies (e.g. catalysts, electronics in computers or mobile phones), thereby platinum and palladium are mainly used in automobile and chemical catalysts, whereas silver is mainly used in electronics [2–4]. Due to the increased markets for these technologies the demand for these metals and their prices have greatly increased [2] and because of very limited sources these metals are rated as critical (the criticality decreases in the sequence: platinum–palladium–silver) [4–6]. Accordingly, there are research activities to reduce the economic risk. Three ways are possible: effective recycling methods, substitution, or more efficient use. A substitution of these metals in their applications would be desirable, but because of their notable properties this is difficult and recycling rates of consumer products are in general small [7–9]. Therefore, these metals should at least be used efficiently.

A more efficient use of a material means the reduction of the amount of the material in an application, but still providing the same function of the application. In turn that means the use of the material with a suitable and efficient microstructure, i.e. a functional form. Accordingly, a precondition of an efficient use is a detailed understanding of the behaviour of the material in its applications under consideration of the microstructure. In the here presented work we focus on the usages of the three metals in the solid state electrodes Pt|YSZ, Pd|YSZ and Ag|YSZ (YSZ: yttrium-

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stabilised zirconia), since these electrodes are applied in today's and future technologies (as electro-catalysts, oxygen sensors and solid oxide fuel cells). In addition, there are hints that the microstructure has here a very important influence on the function of these electrodes [10–14].

In the literature the preparation of platinum, palladium and silver films on YSZ by paste deposition, wet impregnation, sputtering, electron beam evaporation, thermal evaporation and pulsed laser deposition is described [10–24]. Most of the prepared films are polycrystalline with diverse defects. In earlier papers we described the preparation of well-defined (111) orientated platinum films on (111) and (100) orientated YSZ single crystals by pulsed laser deposition (PLD) [19,20]: The platinum films on (111) YSZ are epitaxial single crystalline, the films on (100) YSZ are polycrystalline, but with only four possible arrangements of the crystals on the substrate. Subsequently, we prepared platinum and palladium films with only 30° and twin grain boundaries [12]. Similar polycrystalline platinum films on (100) YSZ have been prepared by Hesse et al. and Opitz and Fleig via sputtering as well as by Gsell et al., by Trassin et al. and Gaukler et al. via PLD [21–24]. The single crystalline epitaxial films have not been reproduced by other authors up to now.

On the basis of our former results, we deposited in the here presented work platinum, palladium and silver on differently orientated YSZ substrates (i.e. (111), (110), (100) and (311) orientated as well as on polycrystalline YSZ) by PLD. Due to this we could investigate the influence of the substrate orientation on the metal microstructure. Thereby one focus was the question, if we can prepare not only (111), but also (110), (100) and (311) orientated epitaxial metal films by this method. For this we investigated the texture and the morphology of the films in detail. On the basis of these investigations we could determine the orientation of the films, the orientation relation to the substrate, grain sizes and grain boundary angles. These are important parameters to conclude on the crystallinity and the epitaxy of the films. Beside differently orientated substrates, we used different deposition temperatures in the case of platinum to investigate also the influence of this temperature. The choose of different metals – with similar properties, but different melting points – allowed us also to discuss the influence of the metal melting point on the resulting metal films crystallinity and epitaxy.

2. Experimental

2.1. Preparation of the metal films

As substrates, we used commercial (111), (110), (100) and (311) orientated YSZ single crystals as well as polycrystalline YSZ. All YSZ substrates were end-polished by a polisher with Al_2O_3-nanoparticles of 20 nm diameter. This results in a mean roughness < Ra> of 20 nm in the case of the single crystalline substrates and of 70 nm in the case of the polycrystalline substrate, determined by a laser perthometer (Mahr, Perthometer Concept).

For the pulsed laser deposition a KrF laser ($\lambda = 248$ nm) with a repetition rate of 6 Hz and a pulse energy of 450 mJ was used. The deposition was performed in argon ($p = 2$ Pa, purity 99.95%) as the background gas. The cylindrical and polished platinum, palladium or silver target (purity 99.95%) was placed at a distance of 4.5 cm to the substrate. Films with a thickness of about 500 nm were prepared with a mean growth rate of about 1 μm/h. The substrate temperature was approximately 400 °C or 200 °C in the case of platinum and 200 °C in the case of palladium and silver. We did not deposited palladium and silver at 400 °C since pre-experiments showed problems with oxidation of palladium and de-wetting of silver at this temperature.

2.2. Characterisation of the microstructure

The morphologies of the films were investigated by SEM (scanning electron microscope: Zeiss, Supra 55 VP and FEI/Philips XL30 FEG ESEM). For texture investigations we performed X-ray pole figure measurements and EBSD (electron backscatter diffraction; additional equipment for the SEM microscope of Crystal, Oxfords Instruments). The pole figures were measured with a D5000 S diffractometer equipped with an Eulerian cradle. We used Cu-K_α radiation, a nickel filter, an X-ray lense and an aperture that was round in shape (2 mm) within the primary beam as well as Soller slits within the secondary beam. The detector was a proportional counter. The (111), (110), (100) and (311) pole figures of the metal films were measured and the (111) pole figure of the particular substrate was measured through the metal films. From the EBSD investigations we determined the grain boundary maps and grain boundary distributions.

An important difference between the pole figure measurements and the EBSD investigations for texture analysis is the size of the investigated area. In the case of the XRD measurements with the used 2 mm aperture, an area of about 4 mm in diameter (the absolute size depends on the tilt angle) was irradiated and therefore investigated. In the EBSD measurements we investigated only an area of about 30 μm × 30 μm. Even though we always did three or four EBSD measurements at different areas of the samples, the statistic of the XRD measurements is much better. In contrast, we also get local information from the EBSD measurements.

3. Results

3.1. Platinum films prepared at 400 °C

The microstructures of the platinum films prepared at 400 °C on differently orientated YSZ substrates are all very different and depend on the particular substrate. Fig. 1a to e show the SEM images of all as-prepared platinum films, Fig. 2 show the pole figures of a platinum film and its substrate and Fig. 3a and b show selected results of the texture investigations. On the basis of the SEM and the texture investigations, it can be concluded that the following microstructures have been prepared:

On (111), (311) and (110) orientated YSZ the platinum films grow epitaxial and only a small fraction of twin grains (approx. 200 nm size with 60° grain boundaries) can be found (Figs. 2 and 3a). The epitaxial growth with no tilt or rotation of the platinum film on the substrate can be seen exemplary in Fig. 2, since here the single crystal reflections of the platinum film are at the same positions (phi and chi) as those of the substrate. The twins (here: contact twins) can be seen in extra reflections within the pole figures (e.g. three reflections at 70.5° in Fig. 2) and as grains within the grain boundary maps (e.g. white lines within Fig. 3a). Therefore, these films can be referred to as nearly single crystalline. The SEM images show substructures within these nearly single crystalline films (Fig. 1a–c, Table 1). The shapes of these substructures depend strongly on the orientation of the film. The substructure within the (111) orientated platinum films looks like pyramidal heads (sizes approx. 100 nm). The (311) and (110) orientated platinum films have edges at the surfaces. These elongated substructures are approx. 50 nm wide in the case of the (311) orientated film and approx. 100 nm wide in the case of the (110) orientated film, whereas in both films they are approx. 500 nm long.

On (100) YSZ the as-deposited platinum film is (111) orientated, but have a large number of 60° grain boundaries (= twins, white lines) and also 30° grain boundaries (dark-grey lines) (Fig. 3b). Also the pole figure reveals these different types of grain boundaries, showing 12 reflexes at 70.5° (this angle was determined from the 2-