



Thermal stability of platinum, palladium and silver films on yttrium-stabilised zirconia

Gesa Beck^{a,*}, Christoph Bachmann^b, Rita Bretzler^c, Ralf Kmeth^a

^a Chair of Resource Strategy, Institute of Physics, University Augsburg, Universitätsstrasse 1a, 86159 Augsburg, Germany

^b Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

^c Research Institute Precious Metals & Metals Chemistry, Katharinenstrasse 17, 73525 Schwaebisch Gmünd, Germany

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ABSTRACT

Platinum, palladium and silver films with different microstructures have been prepared on differently orientated yttrium-stabilised zirconia (YSZ) substrates by pulsed laser deposition and then annealed at temperatures between 200 °C and 850 °C. Thereby, an influence of the type of metal, of the microstructure of the as-prepared film and of the orientation of the substrate on the annealing behaviour could be determined. The following annealing effects were observed for platinum, palladium and silver films: i) sharpening of the film boundary, ii) smoothing of the film surfaces, iii) sharpening of the texture [thereby: reduction of the fraction of small angle and twin grain boundaries], iv) grain growth and accordingly reduction of the fraction of grains as well as v) grooving at grain boundaries, vi) void formation at the metal|YSZ-interface, vii) hole formation within the films and viii) reduction of the fraction of droplets. In the case of palladium films also ix) oxidation [between 300 °C ≤ T < 750 °C] and stronger de-wetting phenomena than for platinum [with x) waving of the film and xi) island formation at T ≥ 750 °C] have been found. Silver films are not oxidised, but show stronger de-wetting phenomena than platinum and palladium, with xi) island formation and xii) evaporation of the silver at T ≥ 550 °C. Interestingly, silver films on (111) orientated YSZ are thermally much more stable than silver films on the other orientated substrates up to 750 °C. The annealing effects were described by interface, grain boundary and surface energy minimization.

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1. Introduction

The precious metals platinum, palladium and silver have several outstanding properties: good thermal and electrical conductivities, good catalytic activity for several reactions, corrosion resistance, relative high melting points and good solubility for hydrogen and oxygen [1]. Therefore, these metals are very important technology metals, used for example in electronics and catalysts. Due to the increased markets for these technologies, the demand of these metals and their prices have greatly increased in the last 30 years [2]. Since these metals have also very limited sources and are mined in only a few countries they are rated as critical [3,4]. Accordingly, there are research activities to reduce the demand of these metals by substitution or more efficient use in their applications or to introduce effective recycling methods and systems [5–7].

The substitution of these metals is difficult because of their special properties, but the properties of the three metals are similar and their criticality decreases in the sequence: platinum–palladium–silver. Therefore, in some applications of platinum it had been substituted by palladium or silver. One example of this is the use of palladium instead

of platinum or as an additive to reduce the proportion of platinum in automobile catalysts. However, palladium is not a good substitute for platinum, since it is similarly critical and the prices increased drastically with the increased demand in automobile catalysts [2]. From the economic point of view (criticality and price) the use of silver should be preferred to platinum or palladium, but its catalytic activity is less and its melting point is lower ($T_{m, Pt} = 1768$ °C, $T_{m, Pd} = 1555$ °C, $T_{m, Ag} = 962$ °C). Therefore, silver could not be active enough for a particular reaction or it might de-wet in applications, which work at higher temperatures.

In the here presented work we focus on the usages of the three metals in the solid state electrode metal|YSZ (YSZ: yttria-stabilised zirconia). YSZ is zirconia stabilised with yttria in the fcc fluorite-type structure (fully stabilised YSZ has 8 mol% yttria). It has outstanding electrical, mechanical, thermal and optical properties, e.g. high thermal and mechanical stability [8–10]. Therefore it has many applications, e.g. as diamond imitation. At temperatures above 400 °C a unique property of YSZ is the high oxygen ion conductivity due to oxygen vacancies (incorporated by Y^{3+} cations substituting Zr^{4+} cations) with negligible electron conductivity. Therefore it is used as a solid electrolyte model system to study the fundamental aspects of solid ion conductors. Moreover, the metal|YSZ electrode is already used in applications like electrocatalysts, oxygen sensors or in solid oxide fuel cells. Thereby, platinum is

* Corresponding author. Tel.: +49 821 598 3570; fax: +49 821 598 3002.
E-mail address: gesa.beck@physik.uni-augsburg.de (G. Beck).

(besides nickel in solid oxide fuel cells) the metal, which is used mainly in these electrodes, because of its high catalytic activity for several reactions and its thermal stability (working temperature of the electrode is mainly $\geq 750^\circ\text{C}$), but in a few cases palladium or silver show similar or even better properties (e.g. silver can be used for the catalytic oxidation of toluene or in intermediate temperature solid oxide fuel cells) [11–15]. However, for the substitution of platinum by palladium or silver in applications of the platinum|YSZ-electrode the palladium and silver films have to be at least thermally stable at the working temperature of the electrode. For an assessment of the thermal stability, platinum, palladium and silver films on YSZ were annealed in the temperature range between 200°C and 850°C in the here presented study. Thereby metal films with different microstructures were used to investigate if the particular microstructure also has an influence on the thermal stability.

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 [5–7,11–20]. Most of the prepared films are polycrystalline with diverse defects. In earlier papers we described the preparation of well-defined platinum and palladium films on (111) and (100) orientated YSZ single crystals by pulsed laser deposition (PLD) [16–18]. These films have only a few defects with small defect concentrations, some of them are even nearly single crystalline. PLD is a deposition technique where a pulsed laser beam is focused on a very small area of the target and each laser pulse is applied for a very short time period (between 1 ns and 100 ns). Accordingly, an extremely high power density (up to 10^{20} W/cm^2 , whereas sputtering has only approximately 30 W/cm^2 and electron beam evaporation approximately 10^4 W/cm^2)

is applied, which evaporates a small portion of the target material within the vacuum in the chamber and forms a plasma with very high kinetic energy of the ions [21]. Due to the short pulses the deposition rate of this technique is very low compared to other deposition methods. We assume that these factors – high kinetic energy combined with low deposition rate – are the reason for the formation of such well-defined platinum and palladium films, since the film forming atoms, which are adsorbed on the substrate, have enough energy and enough time to form the energetically favoured structure and heal out defects (especially at high substrate temperatures).

Accordingly, to obtain well-defined silver, palladium and platinum films for our annealing experiments we deposited silver, palladium and platinum on (111), (110), (100) and (311) orientated as well as on polycrystalline YSZ substrates by PLD. In the case of platinum we also used two different deposition temperatures.

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 (MaTeck GmbH, Germany). All YSZ substrates were end-polished by a polisher with Al_2O_3 -nanoparticles of 20 nm diameter. This results in a mean roughness $\langle\text{Ra}\rangle$ 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 ($\lambda = 248\text{ nm}$) with a pulse duration of 10 ns, a repetition rate of 6 Hz and a pulse energy of 450 mJ

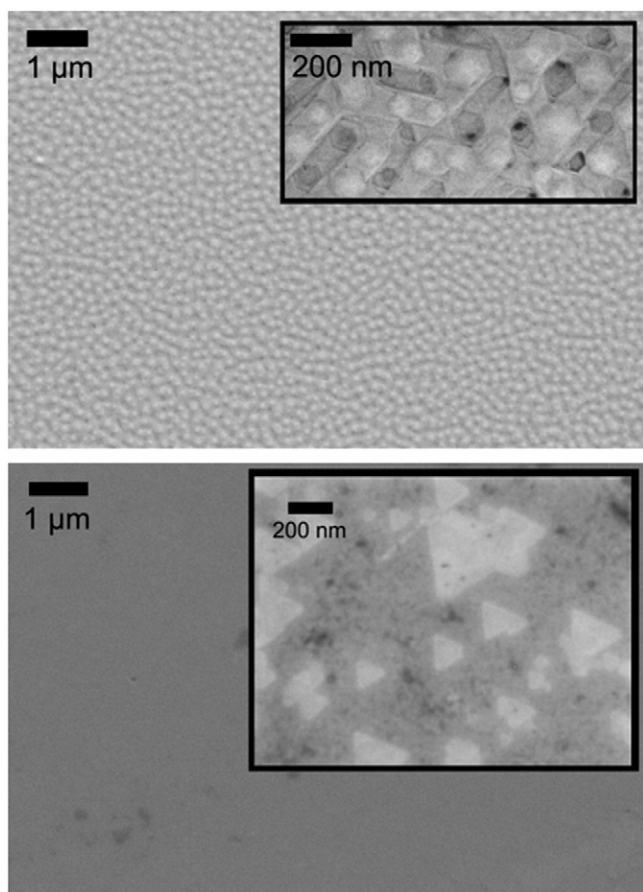


Fig. 1. SEM images of a (111) orientated, nearly single crystalline platinum film on (111) YSZ prepared at 400°C (top) and annealed at 750°C for 48 h (bottom). The smoothing of the film is clearly visible.

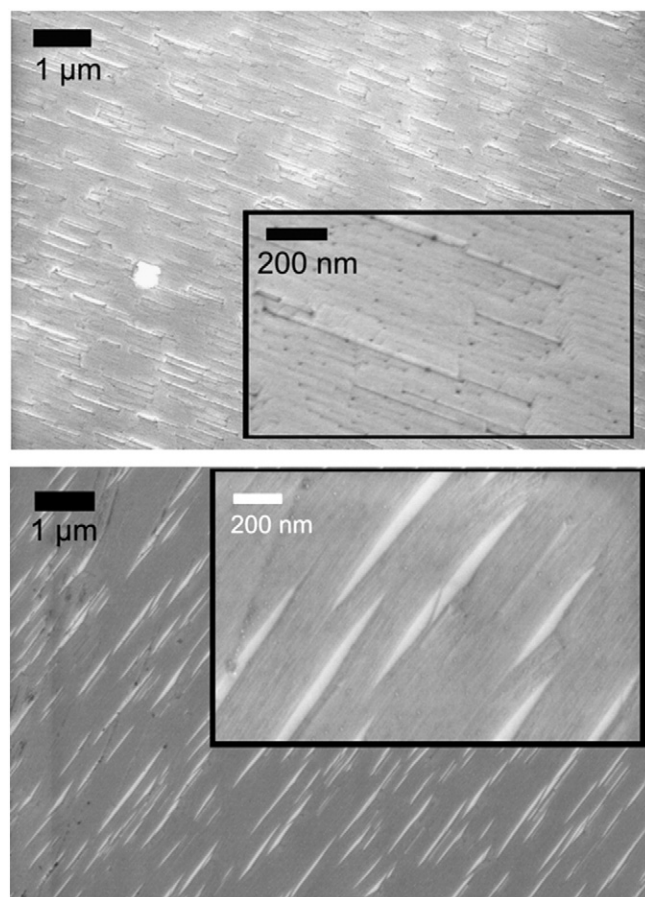


Fig. 2. SEM images of a (311) orientated, nearly single crystalline platinum film on (311) YSZ prepared at 400°C (top) and annealed at 750°C for 48 h (bottom). The smoothing of the film and the sharpening of the edges at the surface are clearly visible.

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