Thin Solid Films 594 (2015) 101–108

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Influence of magnetron sputtering deposition conditions and thermal treatment on properties of platinum thin films for positive electrode–electrolyte–negative electrode structure

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ARTICLE INFO

*Article history:*
Received 3 October 2014
Received in revised form 7 October 2015
Accepted 7 October 2015
Available online 14 October 2015

*Keywords:*
PEN structure
Porosity
Platinum
Argon Gas Working Pressure
Magnetron Sputtering
Residual Stress Analysis
Titanium
Adhesive Layer

ABSTRACT

In the present research, microstructure, porosity, stresses and resistivity of thin platinum electrodes (thickness of 200 nm) deposited on titanium/silicon oxide/silicon and yttria stabilized zirconia (YSZ) substrates (the positive electrode–electrolyte–negative electrode (PEN) structure) were studied. Platinum films were formed at different working pressure of argon gas in the chamber during magnetron sputter-deposition process and following thermal treatment. Crystalline structure of the platinum (Pt) electrodes was analyzed using grazing incidence X-ray diffraction. Lattice parameter and residual stresses of the platinum thin films were defined using $\sin^2\psi$ method. Morphology of electrodes was investigated using atomic force microscopy. Scanning electron microscopy was used to study surface morphology of the platinum thin films and microstructural properties of the PEN structure. Electrical properties of the platinum films were evaluated using the four-point probe method. Typical time intervals and substrate temperature ranges were defined to produce stable porous Pt electrodes that are applicable in the PEN structure (Pt-YSZ-Pt). It was found that lower Ar gas working pressure during magnetron sputtering results in denser and smoother platinum films. Correspondingly, higher Ar gas pressure allows the production of porous platinum thin films without any thermal treatment. Morphological changes of the Pt thin films were analyzed in the temperature region (500–800 °C) that is typical of operation of micro solid oxide fuel cells.

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## 1. Introduction

Power for portable electronic devices is usually supplied by rechargeable batteries [1–3]. Recently, considerable attention has been focused on solid oxide fuel cells (SOFC) due to their potential for providing clean and reliable electric power [4]. The desire for alternative small-scale energy supplies (miniaturized fuel cells), from which more energy is expected than from batteries, now is of substantial interest.

Miniaturization of the solid oxide fuel cell size to micron range brings the microscale devices — μ-SOFC that are considered to be one of the most effective approaches increasing the volumetric power density [5]. Basic configuration of μ-SOFC membrane is composed of three active layers: two porous electrodes (anode and cathode), which are separated by a dense oxygen-ion conducting electrolyte [2,6,7]. This trilayer structure is often referred to as a positive electrode–electrolyte–negative electrode (PEN) element [3]. The thermal and mechanical stability, chemical compatibility during preparation and operation, reliability and electrochemical performance of microfabricated μ-SOFC membranes are scale-dependent properties, therefore, the structural design and behavior of all components, especially at high temperatures, of the electrochemically active membrane must be configured carefully [4,6,8].

Platinum with low electrical resistivity, stable structure at the substrate interface, catalytic behavior and appropriate porosity is one of the most widely used catalysts in the fuel cells. Recently, researchers have shown an increased interest in sputtered platinum, as potential electrode for micro-solid oxide fuel cells [1].

Various methods of deposition for the formation of platinum thin films have actively been investigated in terms of low loading control via vacuum technology. Magnetron sputtering is one of the physical vapor deposition methods distinguished by precise control of Pt loading, significantly uniform dispersion and high through-put [7,9].

Several reports [9–12] proved that the argon pressure during the magnetron sputtering process as well as further thermal treatment can influence the surface morphology and electrical properties of platinum films. For example, Ikwhang Chang et al. [10] reported the electrochemical surface area dependency on the thicknesses and porosity of Pt thin film anodes. The porosity and roughness of Pt thin film were controlled by the Ar pressure during the sputter deposition process. The surface roughness of sputtered Pt deposited at various pressures showed two separate areas: dense (0.67–5.33 Pa) and porous (8–16 Pa) films. The authors argued that relatively porous Pt films (sputtered at 8–16 Pa)

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http://dx.doi.org/10.1016/j.tsf.2015.10.016
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showed significantly larger exchange current densities by 4–5 orders of magnitude relative to the dense film.

One of the main disadvantages of this method is poor adhesion of the layers on typical dielectrics such as silicon dioxide and silicon nitride, which are most frequently used in μ-SOFC microfabrication processes as a sacrificial layer. Pt easily reacts with silicon and forms platinum silicide at relatively low temperatures (200–450 °C) [13]. Therefore, an intermediate titanium (Ti), tantalum (Ta), zirconium (Zr) or chromium (Cr) protective layers between the Pt film and the substrate are often used to improve adhesion and to prevent formation of silicides [14].

Determination and control of residual stress in the Pt thin films is important for producing mechanically stable PEN structure, because manufacturing processes are the most common causes of residual stress [15]. The stress could be caused by the localized yielding of the material or by certain surface treatments (like annealing at high temperatures) [16]. Despite their importance, residual stresses are difficult to foresee. There are only a few studies on the stress evaluation of Pt thin films [14,17–19].

On the other hand, with the development and miniaturization of components of micro-SOFC devices, the state of surfaces at operating conditions of these components becomes more and more important.

In the current research, we have investigated electrical properties, morphology and residual stress of the Pt layers versus technological conditions with the aim to contribute to the understanding of the role of thermal treatment of Pt electrodes deposited on typical surfaces used in the technology of micro solid oxide fuel cells ($SiO_2$, Ti/$SiO_2$, yttria stabilized zirconia). Microstructure, roughness parameters, resistivity, porosity and microstrain of platinum electrodes as well as PEN structures were varied using different argon gas pressure in the chamber during platinum magnetron sputter-deposition process and following thermal treatment.

## 2. Experimental technique

### 2.1. Surface preparation

The RCA-1 cleaning [20] for 60 min was used for the preparation of the thermal silicon oxide ($SiO_2$) substrates. The RCA cleaning was followed by ion–plasma processing, where the substrates were exposed to $O_2$ RF plasma in the camera of the device Plasma-600-T at 133 Pa pressure (RF = 13.56 MHz, P = 0.3 W/cm$^2$, t = 7 min).

### 2.2. Thin film preparation and processing

Pt electrodes with thickness of 200 nm were deposited on $SiO_2$ substrates by direct current (DC) magnetron sputtering source ("Kurt J. Lesker" company) which was integrated in a "Leybold Heraeus-A-700-QE" device vacuum system. A turbomolecular pump was used to evacuate the main chamber to a base pressure of $2 \times 10^{-4}$ Pa. Argon (purity 99.996%) was used as a sputtering gas. Argon pressure in the chamber during deposition was varied systematically as follows: 4.9 Pa, 0.13 Pa, 0.6 Pa, and 0.065 Pa, further in the text: first (1$^{st}$), second (2$^{nd}$), third (3$^{rd}$) and fourth (4$^{th}$) sample series, respectively. Thin titanium layer (~20 nm) as an adhesion layer was magnetron sputtering deposited on silicon dioxide before the formation of Pt electrodes. The Pt target (purity 99.99%) with a diameter of 5.08 cm was placed at a distance of 16 cm from the substrate and tilted at 30° angle with respect to the substrate. The substrate holder was rotated during the deposition process in order to obtain homogeneous distribution of the film thickness. Silicon oxide/silicon substrate was heated up to 150 °C temperature during Pt electrode deposition process. The magnetron voltage was 510 V, and current was 0.4 A. The growth rate was determined by a quartz microbalance sensor.

Yttria stabilized zirconia (YSZ) electrolyte (thickness of 600 nm) was deposited using the electron beam (e-beam) evaporation technique. As a source material for e-beam evaporation of electrolyte, the commercial yttria stabilized zirconia ceramic powders containing 8 mol.% of $Y_2O_3$ (8YSZ, Tosoh, ball-shaped granules with 45 μm in diameter) was used. The powder was pressed into pellets of 10 mm in diameter and annealed at 1000 °C temperature in air. The evaporation of the YSZ electrolyte was performed at the pressure of 0.7 Pa, and the e-gun power was 10 kW. During the evaporation process, the temperature of the substrate was kept constant at around 200 °C and the thickness of the thin film was controlled by a quartz microbalance sensor. The evaporation rate of 8YSZ was ~0.6 nm/s.

The thermal treatment of the Pt thin films on $SiO_2$ (including titanium adhesive sublayer) was performed in a furnace from 600 to 800 °C for 15 min. Additionally Pt/Ti thin films were annealed at 800 °C for 4 h. The final Pt/YSZ/Pt/Ti/$SiO_2$/Si structures (PEN structures) were thermally treated in the furnace at 600 °C for 15 min.

### 2.3. Characterization techniques

Characterization of the Pt/Ti thin films was carried out using grazing incidence X-ray diffractometry (XRD) with incident angle of 1.5° using $CuK_\alpha$ radiation of wavelength 1.5418 Å. It was performed in a Discover D8 diffractometer (Bruker, Germany). The XRD data were collected at accelerating voltage 40 kV and electric current 40 mA. The samples were positioned using a centric Eulerian cradle sample stage. A collimator of the size of 1 mm was used to focus the X-ray beam for the stress measurements. The $\sin^2\psi$ method [21] was used to evaluate the residual stress. This method is based on the measurement of the shift of a diffraction peak position measured for different Euler angles. In our work, the strain was measured using (331) reflecting plane and was defined for the six values of the $\psi$ angle, that varied from 0° to 50.77°. The software Bruker DiffracEVA V3.0 and database PDF-4 were used for characterization of the microstructures.

Scanning electron microscopy (SEM) images were obtained using E-line Multi-application Nanoengineering Workstation (Raith) without special sample preparation. The porosity of platinum thin films was estimated using ImageJ image processing technique with the addition of Pore analysis program.

Atomic force microscopy (AFM) experiments were carried out in air at room temperature using an atomic force microscope NT-206 (Microtestmachines Co.) and SPM-data processing software SurfaceXplorer. V-shaped silicon cantilever (spring constant of 3 N/m, tip curvature radius 10.0 nm, cone angle 20°) operating in a contact image mode with 12 μm × 12 μm field of view was used. Surface morphology was evaluated in terms of AFM surface topography images, roughness parameters: root mean square roughness ($R_q$), skewness ($R_{sk}$) and kurtosis ($R_{ku}$). The definition of these parameters can be found elsewhere [22].

Atomic composition on the surfaces of as-deposited and annealed Pt/Ti thin films was studied using X-ray photoelectron spectroscopy (XPS). For the surface analysis the Thermo Scientific ESCALAB 250Xi spectrometer with a monochromatized $AlK_\alpha$ radiation ($h\nu$ = 1486.6 eV) was used. Base pressure in the analytical chamber during spectra acquisition was better than $2 \times 10^{-7}$ Pa. X-ray spot size for the spectra acquisitions was 0.3 mm. The 40 eV pass energy was used for the spectra acquisition. Energy scale of the system was calibrated according to Au 4f7/2, Ag 3d5/2 and Cu 2p3/2 peaks position. Calculations of atomic concentration were performed using original ESCALAB 250Xi Avantage software. Thin films were analyzed without surface cleaning procedure.

Resistivity of the Pt/Ti thin films was measured using the four-probe point method. The four-probe point was placed in contact with the surface of the Pt/Ti film and a fixed current of 11 mA was applied across the outer two probes. The distance between the adjacent probes was 2 mm. The voltage drop was measured across the two inner probes. Five sets of measurements were made for each thin film. The average value of

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