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Nanostructuring of iron thin films by high flux low energy helium plasma

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ABSTRACT

High flux, low energy He plasma exposure is proven to nanostructure iron thin films over their entire thickness to a highly open structure with large surface area. From a large set of plasma exposure parameters, the ion flux, the surface temperature, and the plasma exposure time are found to be the most relevant parameters to process mechanically stable, nanostructured Fe thin films on brittle glass substrates. The nanostructure stays stable during oxidation. Different surface morphologies are found, depending on the location where the plasma plume interacts with the thin film. This method paves the way to a new direction in top down nanostructuring of thin films, which can be adopted for many functional materials in diverse applications that require a high ratio of active to projected surface area.

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1. Introduction

Catalytic and electrochemical reactions take place at the surface of materials. For many applications, such as sensors, fuel cells, electrolyser, water splitting cells, it is of paramount importance to create materials with large surface area and high amount of open porosity to enable more reactions to take place and increase performance. Thin films are often used in these applications due to the necessity for miniaturization and reduction of materials costs.

Thin films with large surface area are commonly produced by wet chemical deposition methods, such as spraying or sol gel processing [1], or through microfabrication [2]. Wet chemical deposited thin films often suffer from homogeneity issues, necessitating rather thick film thicknesses (>100 nm) to ensure continuous films with large surface area. Microfabrication is time and cost intensive. In addition, the fabricated nanostructures are mostly not percolating, but are shaped in nanowires, which is not always favored for functional applications due to connectivity reasons.

In the field of controlled fusion, the formation of nanofuzz on tungsten reactor wall components was recently described [3–10]. Nanofuzz in this context is the formation of highly structured, large surface area material formed on the walls of a fusion reactor due to high flux, low energy Helium (He) plasma exposure. Surfaces with 90% porosity were reported in [11] for plasma exposed tungsten. Such porous surfaces are attractive for catalytic and electrochemical applications. It was recently found that nanofuzz can be formed at bulk tungsten discs during high temperature, high flux, low energy He plasma exposure. After oxidation, the evolved WO_3 was used for water splitting [12]. A five times higher photocurrent of plasma exposed samples was found compared to non-exposed samples. Hence, it was proven that these plasma exposed surfaces do not only have a large surface area, but are also catalytically active. Kajita et al. also studied the morphology development during plasma exposure for possible water splitting application using Fe and Ta bulk pellets recently [13]. For water splitting and many other energy applications, however, thin films and not bulk material are used as electrodes due to costs, materials scarcity, and integration reasons. Hence, it is important to know whether high flux, low energy He plasma nanostructuring can be transferred to thin film surfaces and to structuring over the entire thickness of the thin film. The main challenges here are delamination of the thin film from the substrate, cracking of the substrate, chemical interdiffusion caused by the high temperatures used during the plasma treatment, and thermal gradients between the plasma exposed surface and the mounting.

In the literature, plasma treatment is reported for diverse purposes, such as cleaning of surfaces [14–16], activation of interfaces [17,18], etching [19–21], and creation of oxygen vacancies [22]. Such plasma treatments are usually carried out with oxygen, hydrogen, or argon plasmas and use ion fluxes between 10^{18} m^{-2} s^{-1} to 10^{20} m^{-2} s^{-1}. In this paper, we use a plasma with high ion flux of around 10^{23} m^{-2} s^{-1} [3–5,23] in order to fabricate nanostructures. The basic principle for nanostructuring with high ion flux plasma relies on He trapping into the material. Enrichment of the He in the structure leads to He bubbles which burst and lead to nanostructure formation [24].

We will prove in this paper that thin films can be nanostructured by high flux, low energy He plasma even on brittle and fragile substrates, such as glass. This will open up a new window for top down nanostructuring of thin films and the fabrication of large surface area

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films. The method can be adopted to many applications. In this paper, we will mainly focus on the nanostructuring of iron thin films on glass substrates as a proof of concept of nanostructuring of thin films and because it is a promising material to study the oxygen evolution reaction in water splitting devices due to its abundance, stability, and low costs [25–28].

2. Experimental details

2.1. Thin film deposition

All Fe thin films were deposited by DC magnetron sputtering from a 2 in., metallic target on glass substrates (1 mm thick) with a F: SnO_2 (FTO) conducting layer. Substrates from manufacturers MTI (USA), Solems (F), and Solaronix (CH) were used. A sputtering tool from Kurt J. Lesker was used with a base pressure $<10^{-8}$ mbar and a target-substrate distance of 95 mm. All depositions were carried out at room temperature, at an Ar pressure of 1 Pa, and a power of 100 W. Different thicknesses were deposited with deposition times between 88 s and 881 s. Deposition times of 881 s resulted in a Fe film thickness of about 274 nm as shown by SEM in Fig. 1 and confirmed by atomic force microscopy step measurement.

2.2. High flux, low energy He plasma exposure

High flux low energy (20 eV) He plasma treatment was carried out in the Pilot PSI plasma set-up at DIFFER [23]. The magnetic field was 0.2 T and the bias voltage was set to −20 V. It was found in earlier studies that irradiating metals with ions having energy above the physical sputtering threshold resulted in considerable sputtering effect and, thus, reduction of thin film material during the plasma exposure [29,30]. Source currents between 40 A and 100 A and He gas flow rates between 2.5 slm and 4.8 slm were used. This resulted in ion fluxes between $0.07 * 10^{22}$ m^{-2} s^{-1} and $1.4 * 10^{23}$ m^{-2} s^{-1} and surface temperatures between 150 °C and 780 °C. The surface temperature was measured by infrared camera and pyrometer. The plasma exposure times were between 2 min and 50 min.

2.3. Annealing and characterization

All Fe samples were annealed at 645 °C for 10 min in air with a ramping rate of 5 °C/min in order to guarantee crystallization and oxidation of the Fe thin film while avoiding damage to the glass substrate. The morphologies of the thin films were characterized in top view and in cross section using a Field Emission Scanning Electron Microscope (SEM) (Zeiss Sigma, Germany). The porosity was estimated with the data analysis software Gwyddion [31].

3. Results and discussion

In order to find a suitable parameter space for plasma nanostructuring of thin films on glass substrates, the plasma exposure parameters were first varied on a large scale. It was found that source currents higher than 50 A resulted in sample breaking. This was related to local overheating of the substrate and consequent cracking due to the brittleness of the glass. At temperatures higher than 650 °C, glass substrates begin to soften and become rippled. Also, Sn diffusion from the FTO becomes relevant at higher temperature [32,33]. This means that much milder plasma conditions (lower temperature, lower source current) have to be chosen for plasma exposure of thin films on FTO-glass substrates compared to earlier high flux, low energy He plasma exposures of bulk materials [3–5].

In the following, we discuss Fe thin films on FTO-glass substrates and focus only on samples without mechanical damage, such as cracking or rippling. This means that we are restricting the plasma exposure parameters as discussed above. The plasma exposure parameters of these films are summarized in Table 1. It was found that all thin films adhere well to the substrate after plasma exposure. No delamination of the thin films from the substrates was detected.

3.1. Optical imprint

The as-deposited thin films are dark greyish and metallic shiny as typical for metallic thin films of several hundred nanometers on glass (Fig. 2a). After plasma exposure, the films are still metallic greyish and a circular mark – here termed *optical imprint* - is found that indicates where the surface was attacked by the plasma (Fig. 2b). A rough assessment of the impact of the plasma exposure on the thin films can be done by evaluating this optical imprint. It consists of concentric circles related to the Gaussian shape of the plasma plume over the exposed area. After annealing and oxidation at high temperature, the imprint becomes more clearly visible related to the color change from grey to orange. An example of a strong optical imprint (after high temperature oxidation and sample breaking for cross section characterization) is shown in Fig. 2c. The arrows and letters indicate locations that are later investigated in more detail.

The main parameters influencing the optical imprint were found to be the ion flux, the surface temperature, and the exposure time. Thin film thickness and the substrate manufacturer are not impacting the optical imprint. In general, three regions of optical imprint were identified and are illustrated together with all samples from Table 1 in Fig. 3: small optical imprint was found in the yellow region where two of the three main parameters are low. Medium imprint was found for samples where two of the plasma parameters were elevated, e.g. ion flux and temperature (ID 5) or temperature and exposure time (ID 8). The strongest optical imprint was observed in the red region with all three plasma exposure parameters being high, i.e. high ion flux, high temperature, and longest exposure time (ID 6).

3.2. Microstructure

In order to validate and quantify the observations of the optical imprints, top view SEM images were taken. Fig. 4 shows an as-deposited (Fig. 4a), an annealed (Fig. 4b), and several plasma exposed Fe thin films (Fig. 4c–f) for comparison; the images of the plasma exposed thin films were always taken in the middle of the imprint. The as-

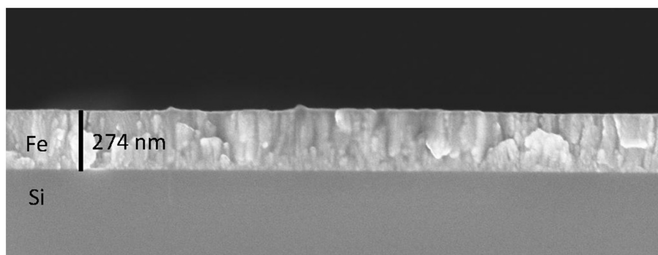

Fig. 1. Scanning electron microscopy image cross section of an as-deposited Fe thin film on Si (deposition time 881 s).

Table 1
Summary of plasma exposed Fe thin films processed without mechanical damage.

Sample ID	Fe sputter time [s]	Ion flux [10^{23} m^{-1} s^{-1}]	Surface temperature [°C]	Exposure time [min]
1	88	0.53	340	20
2	88	0.53	500	20
3	220	0.53	380	20
4	220	0.53	550	20
5	881	1.41	650	20
6	881	1.06	650	50
7	881	0.18	570	2
8	881	0.071	650	40

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