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TEM and SEM studies of microstructural transformations of thin iron films during annealing

Wojciech Lisowski[a], Enrico G. Keim[b,*], Mark Smithers[b]

[a]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01-224 Warszawa, Poland*

[b]*MESA+ Research Institute, Central Materials Analysis Laboratory, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

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Abstract

High-temperature induced transformations of the bulk structure as well as the surface and bulk morphology of thin polycrystalline iron films have been investigated using a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The polycrystalline Fe films were evaporated onto a quartz substrate at 78 K under UHV conditions and then annealed in situ within a temperature range 330–1000 K. The morphology of both the surface and bulk Fe films have been observed ex situ after successive annealing steps of the Fe film using SEM and cross-sectional TEM analysis, respectively. An anisotropic polycrystalline bulk morphology accompanied by a fine-grained surface and the formation of microvoids was observed after heating the Fe film at 330 K. The iron films annealed at higher temperatures, exhibit large grain size surface morphology. Polycrystalline Fe film transformation occurred at an annealing temperature of 700–1000 K, resulting in the formation of a columnar microstructure of the bulk phase. The crystallites formed as a result of annealing at 1000 K revealed a monocrystalline structure characterised by low-index Fe bcc diffraction patterns.

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Keywords: Iron films; Annealing; Structure and morphology; Roughness; Scanning and transmission electron microscopy

1. Introduction

Thin iron layers deposited on certain substrates are known materials widely used in microelectronics and catalysis. Recently, such layers deposited onto monocrystals of various metals [1–4] and semiconductor substrates [5,6] have drawn significant attention because of their promising properties. Thin Fe films, evaporated on glass, appears to be a very useful material for in situ investigation of both single gas adsorption [7–13] and multi-gas interactions [14–16]. It is a common practice for these films to be deposited at liquid nitrogen or room temperature, and then heated to higher reaction temperature. This annealing procedure can change the structure of the film. However, in spite of the wide applications, experimental investigation of Fe film structure during such annealing treatment is relatively scarce [17]. In the present work, we try to partially fill this gap by investigating the morphology and structure of thin Fe films (50–100 nm) evaporated onto a quartz substrate at 78 K followed by annealing within the temperature range 330–1000 K. Both the surface and bulk morphology as well as the microstructure of distinguished regions of

* Corresponding author. Tel.: +31-53-4892563; fax: +31-84-8507351.
E-mail address: e.g.keim@tn.utwente.nl (E.G. Keim).

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the bulk films as a result of various annealing temperatures are analysed. For this purpose we use the combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Experimental

The preparation of iron films was performed in a glass UHV apparatus which has been described in detail elsewhere [18]. The thin Fe films were deposited each time onto clean, quartz substrate plates (10 mm × 10 mm in size and 1.5 mm thick), placed within a quartz cell maintained at 78 K, by evaporation of an Fe wire (0.1 mm diameter, Johnson Mathey, grade I) wound around a tungsten heater (0.35 mm in diameter). The pressure during the deposition was lower than 4×10^{-8} Pa. Mass-spectrometer analysis disclose nitrogen as a main component of the gas phase. After evaporation the films were annealed in situ, at a vacuum pressure lower than 10^{-6} Pa, by heating the outer wall of the quartz cell. All samples were preliminary warmed from 78 to 330 K in 15 min immediately after evaporation and then annealed at 330 K for 30 min. The separated samples were subsequently heated at 700 and 1000 K for 60 and 30 min, respectively. The procedure for annealing the Fe films up to 1000 K was performed in two ways. In the first procedure, the Fe film was heated for 30 min with a continuous increase in temperature from 330 to 1000 K. During the second procedure the Fe film was annealed successively at 700 and 1000 K for 60 and 30 min, respectively. The annealing temperature was carefully monitored using two Ni–Cr thermocouples fixed to the outer cell wall.

Morphological and structural examination of the iron films was performed ex situ in separate analytical systems. SEM (Hitachi S800) was carried out to study the Fe film surface morphology. TEM (Philips CM30 Twin (S)TEM), on the other hand, was used to obtain information regarding the internal structure of the Fe films. Microdiffraction analysis allowed the selected crystal phases in the Fe bulk films to be identified.

The TEM specimen preparation was similar to that described in [19]. The cross-section TEM specimens were prepared from two plates (3 mm × 6 mm in size) of the Fe/quartz sample. Fe films were glued together face to face in a sandwich structure using a thin layer of a two-component epoxy resin G1 (Gatan), and then cut in cross-sectional slices. The 500 μm thick cross-section slice was then abraded plane-parallel to about 200 μm thickness. Mechanical thinning was continued by dimpling (Gatan model 656 Dimple Grinder) this disk on both sites further down until the centre part had reached a thickness of about 20 μm. Finally, the sample was thinned to electron transparency by using the Gatan model 691 precision ion polishing system (PIPS), with an etching angle as low as $\pm 3^{\circ}$ for both ion guns (on top- and bottom-side sputtering, respectively) and an accelerating voltage of 5 kV.

3. Results

3.1. SEM analysis of Fe film surface morphology

Fig. 1 shows SEM images of Fe film surfaces after annealing at 330 K (a), 700 K (b) and 1000 K (c) and (d), respectively.

The Fe films warmed up to 330 K reveal a fine-grained (10–30 nm) surface morphology (Fig. 1(a)). Irregular microvoids, 10–20 nm across, appear as a result of evaporation and a low-temperature annealing procedure.

A distinct transformation in the surface morphology has been observed after annealing the Fe film at 700 K for 60 min (Fig. 1(b)). A granular structure with a grain size of 30–90 nm appears and the microvoids at the grain boundaries of the Fe film surface seem to disappear.

Aggregation of small Fe particles (30–90 nm) into large heterogeneous grains (∼400 nm) can be observed after fast heating the Fe film from 330 to 1000 K (Fig. 1(c)). Small grains covering the large ones are easily distinguishable, indicating an intermediate state in the larger grain formation. The large-grained particles formation is limited by the heating conditions applied. Annealing at 1000 K, preceded by 1 h heating at 700 K, causes the surface Fe grains to become more homogeneous and distinctly shaped, reaching a size of 100–800 nm (Fig. 1(d)).

3.2. Cross-sectional TEM analysis of the Fe films

In order to obtain information on the annealing-induced microstructural transformation of the Fe

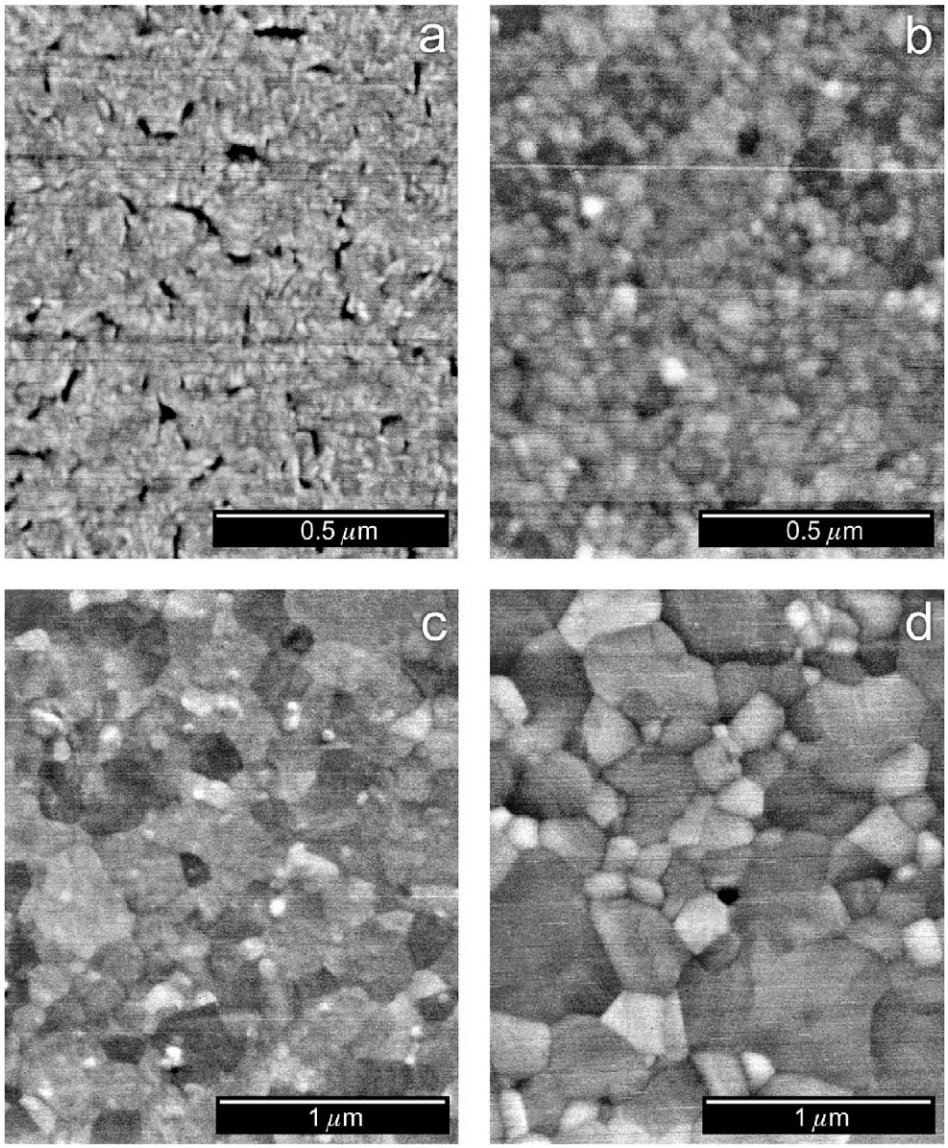

Fig. 1. SEM images of the Fe film surface as a result of vacuum annealing at 330 K (a), 700 K (b) and 1000 K (c) and (d). Image (c) shows the Fe film surface after continuous heating from 330 to 1000 K in 30 min. Image (d) shows the Fe film surface after annealing stepwise at 700 and 1000 K for 60 and 30 min, respectively. The thickness of the films was 108 ± 4 nm (a), 54 ± 2 nm (b) and 57 ± 2 nm (c) and (d).

films, TEM measurements on cross-sectional Fe/quartz samples were carried out. Four types of Fe films were analysed, which were prepared after successive steps in the annealing procedure. Fig. 2 shows the cross-sectional TEM images of these films.

Fig. 2(a) shows a TEM image of an Fe film in cross-section, obtained after warming the Fe film up to 330 K. It reveals a polycrystalline structure with fine crystallites forming a randomly distributed structure. Annealing at 700 K leads to transformation of the polycrystalline Fe film into much better aligned columnar microcrystalline bulk structure (Fig. 2(b)). The width of the crystalline columns (30–100 nm) shows a good agreement with the surface grain size

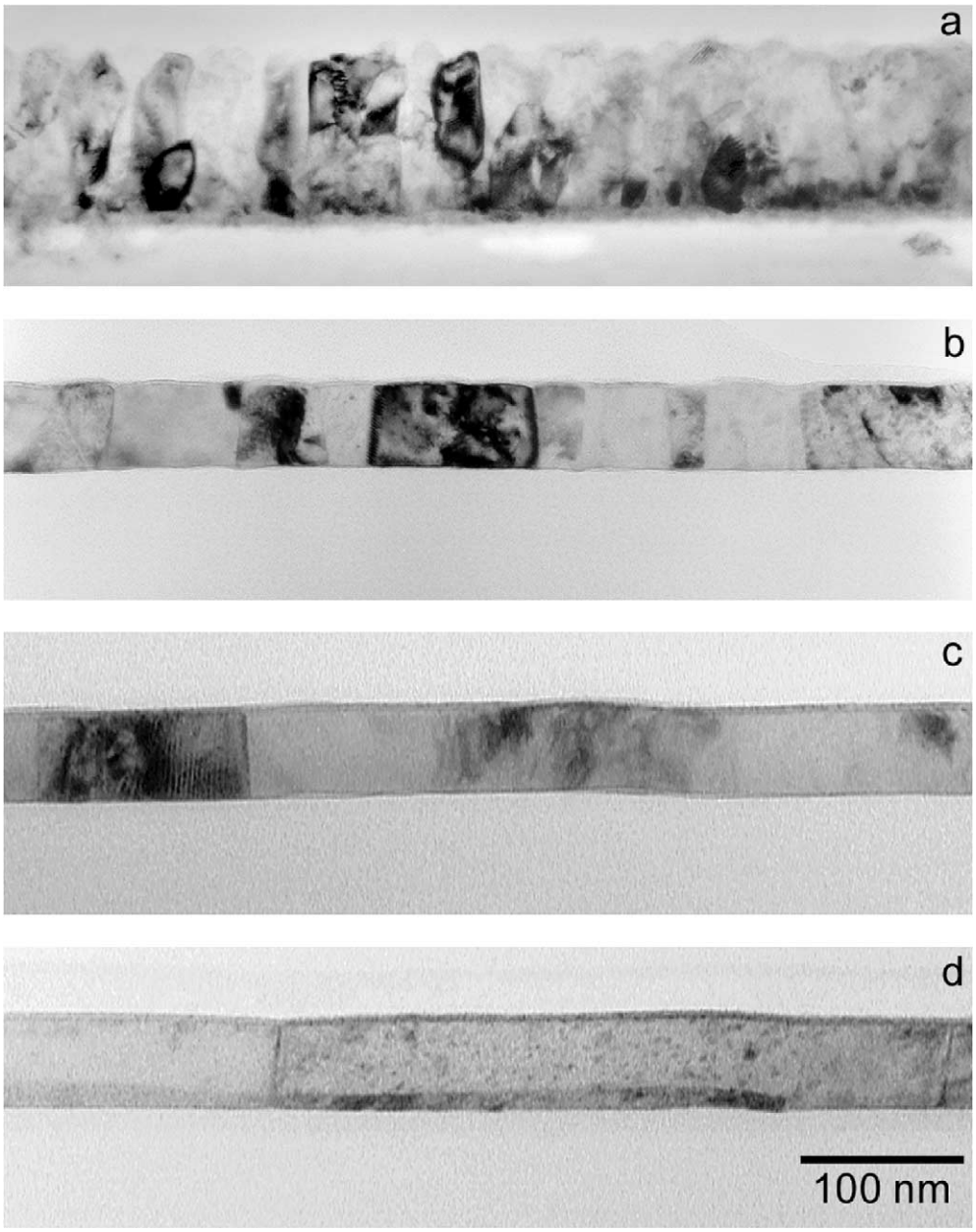

Fig. 2. Cross-sectional TEM images of Fe films: (a) after annealing at 330 K for 30 min; (b) after annealing at 700 K for 60 min; (c) after continuous heating from 330 to 1000 K during 30 min; (d) after annealing successively at 700 and 1000 K for 60 and 30 min, respectively. The thickness of the films was 108 ± 4 nm (a), 54 ± 2 nm (b) and 57 ± 2 nm (c) and (d).

observed by SEM (Fig. 1(b)). Annealing at 1000 K causes the crystalline columns to become broader, reaching values of the order of 100–800 nm (Fig. 2(c) and (d)).

TEM images of the cross-sectional Fe/quartz samples clearly disclose how surface roughness is influenced by an increase in the annealing temperature. The relatively rough surface of the Fe film warmed at

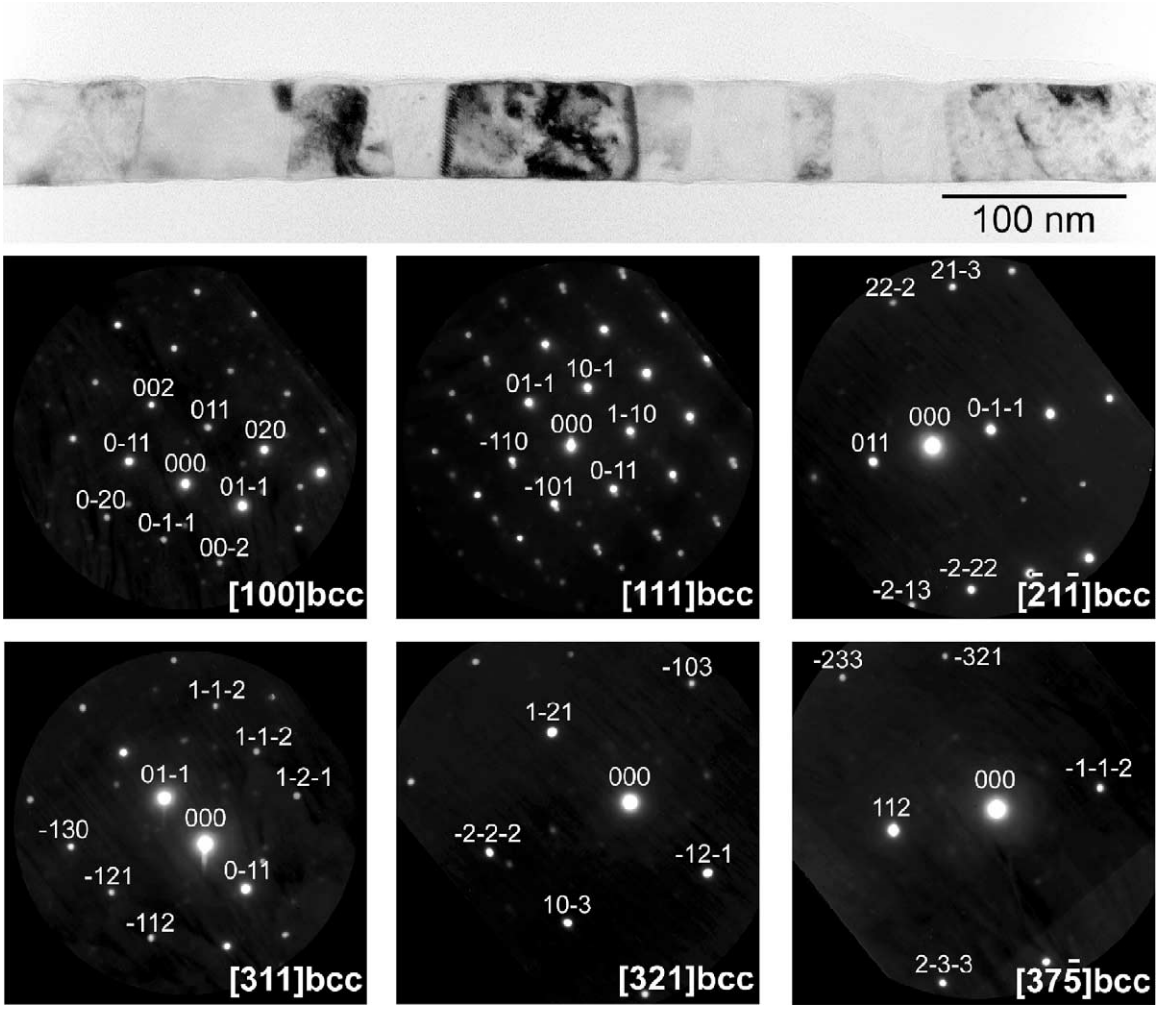

Fig. 3. Electron diffraction patterns of distinguishable areas in the cross-section of the Fe film (top image). The Fe film was annealed in vacuum at 700 K for 60 min.

330 K (Fig. 2(a)) becomes smooth after heating at 700 and 1000 K (Fig. 2(b) and (c), respectively).

In order to obtain information on the structure of the crystal phases as observed within the Fe films, as well as their orientation after various annealing procedures, TEM microdiffraction analyses were carried out.

The electron diffraction patterns, taken from a cross-section plane of the Fe film annealed at 700 K, are shown in Fig. 3. The existence of Fe grain families with different orientations, showing both low- and high-index Fe bcc diffraction patterns, (1 0 0), (1 1 1), $(\bar{2}\,1\,\bar{1})$, (3 1 1) and (3 2 1), can be seen in this figure. The unique high-index diffraction pattern, i.e. $(3\,7\,\bar{5})$ was also observed.

Fig. 4 shows that vacuum annealing performed at 1000 K leads to a reduction in the high-index Fe bcc diffraction patterns. Low-index planes were observed mainly in selected areas of the broad columnar structure of the Fe film, indicating a monocrystalline structure of well separated Fe grains. A small number of Fe grains characterised by higher index Fe bcc diffraction patterns (e.g. (3 1 0)) have also been disclosed (Fig. 4). However, all analysed crystallites, forming the columnar structure of Fe film as a result

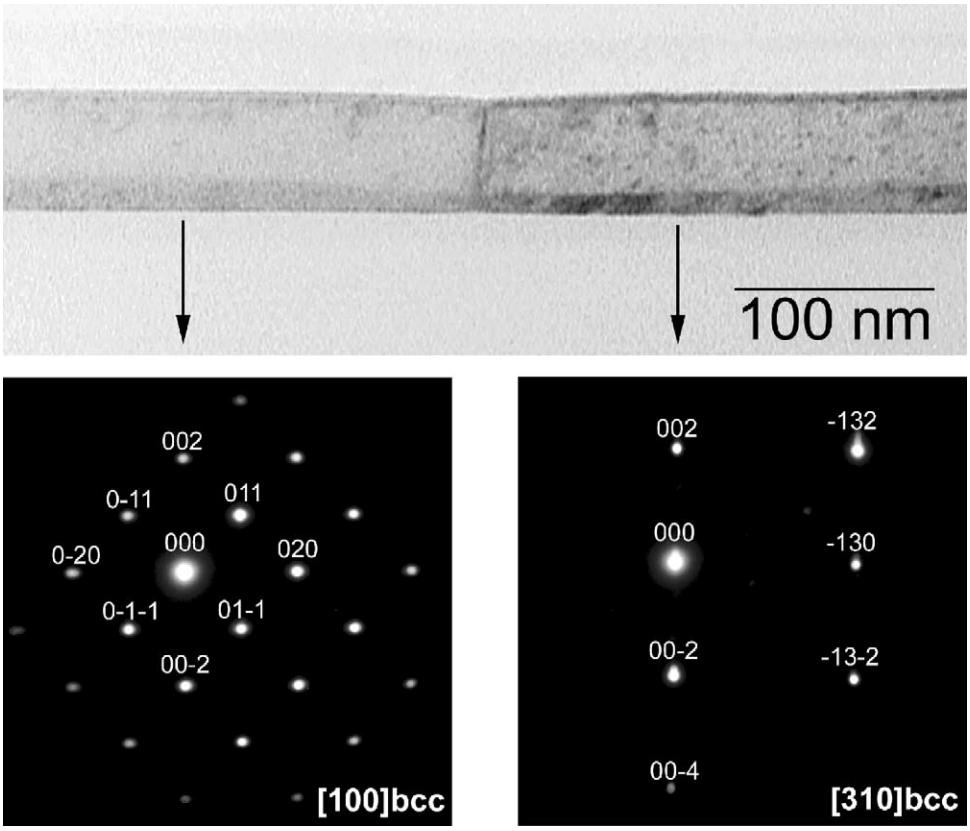

Fig. 4. Electron diffraction patterns of distinguishable areas (marked by arrows) in the cross-section of Fe film (top image). The Fe film was annealed in vacuum in two steps at 700 and 1000 K for 60 and 30 min, respectively.

of annealing at 1000 K, were well oriented in the (0 0 1) direction (Fig. 4). The Fe film heated from 330 to 1000 K in 30 min, produces grains with a slightly distorted (0 0 1) orientation, relative to the normal surface, in addition to well oriented Fe crystallites (Fig. 5).

4. Discussion

In the present work we present the behaviour of the Fe films evaporated at 78 K and then annealed at different temperatures up to 1000 K. In order to compare our observations with other results it is convenient to use a temperature ratio, $\tau = T/T_M$ [17], where T is the substrate temperature and T_M the melting point of evaporated metal ($T_M = 1808$ K for Fe [17] is taken for calculation of τ in this work). It was stated that the behaviour of all metals is similar at the same value of τ [17].

The Fe film evaporated from a hot source onto a quartz substrate maintained at 78 K give rise to a configuration that is far from thermodynamic equilibrium. An annealing treatment therefore plays a dominant role in establishing a reproducible structure of the Fe film used finally as a reagent in chemical reactions. Because the morphological and structural examinations of Fe films were available only ex situ in separate systems at 300 K, all films were warmed in situ in the preparation cell up to 330 K in order to make this step of annealing reproducible for all analysed films. This temperature is too low to anneal the film to a considerable degree. However, analysing the film roughness behaviour when increasing the temperature from 78 to 330 K, and taking into account the τ value (0.18) at a final annealing temperature (330 K), we can

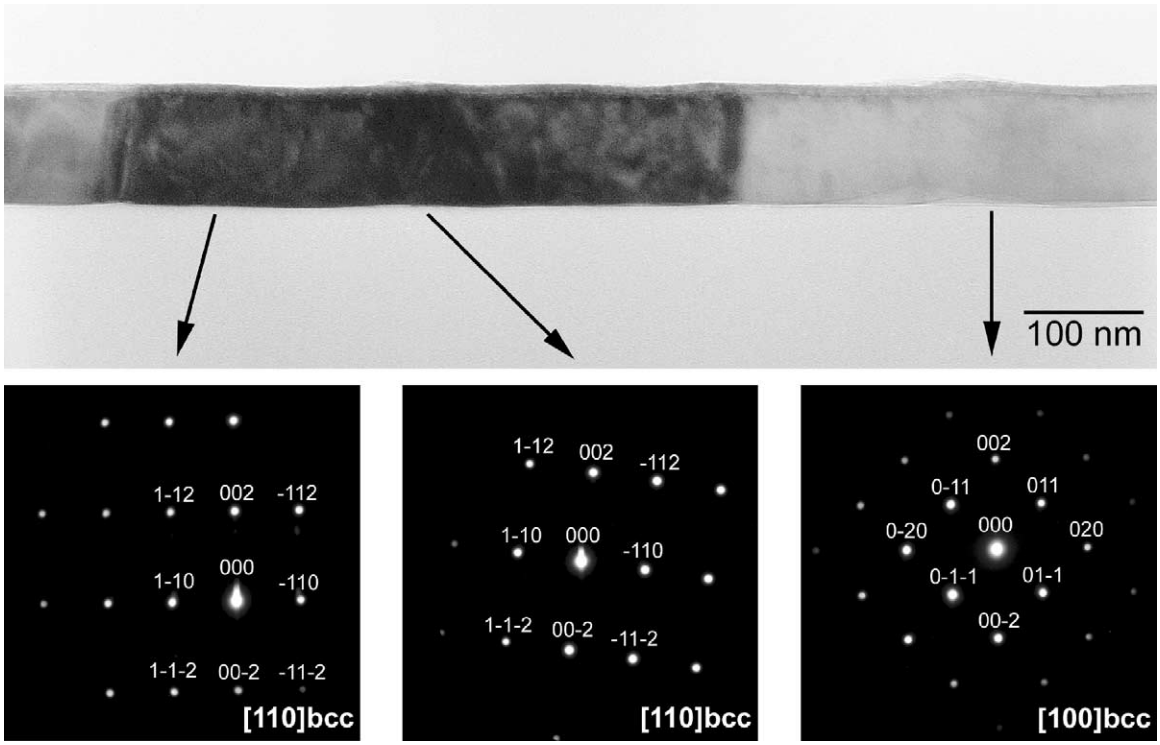

Fig. 5. Electron diffraction patterns of distinguishable areas (marked by arrows) in the cross-section of the Fe film (top image). The Fe film was annealed in vacuum continuously from 330 to 1000 K in 30 min.

consider a partial rearrangement of our films. The roughness factor of the Fe film annealed at 330 K, based on the results of volumetrical adsorption of deuterium and nitrogen at 78 K, was estimated to be 8 ± 1 [16], whereas the roughness factor of the Fe film warmed up to 195 K was higher than 15 [20]. A difference in curvature of the surface was postulated earlier to be a driving force for surface self-diffusion [21]. The activation energy of surface self-diffusion (E_d) was found to be relatively low (<1 eV) on the low-index planes of various metals [22]. Thus, this process seems to be the main one at low annealing temperatures. However, although at $\tau = 0.18$ the Fe surface self-diffusion just becomes appreciable [17,22], the duration of annealing (30 min) is too short to complete them. Therefore, in Figs. 1(a) and 2(a) one can observe features characteristic for a film evaporated at very low temperatures ($\tau < 0.1$): small grains adopt random orientation and the microvoids are visible. Microvoids are expected to be formed during the film growth on a substrate maintained at 78 K [17,21]. Iron atoms evaporated from a hot source are quenched on the cold substrate as they condense and lose energy rapidly. Gaps formed between crystallites cannot be filled in due to low migration of Fe atoms at this temperature. Porous films obtained in such a process are easily accessible to gases. Warming the Fe films from 78 to 330 K causes the sorbed gases to be released, and the pressure of the gas phase to be increased from 10^{-8} to 10^{-5} Pa.

Heating the Fe film to 700 K ($\tau = 0.38$) accelerates the self-diffusion of Fe atoms leading to a filling-up of the narrow gaps in the film. We observe the granular structure of the film surface (Fig. 1(b)) accompanied by a much better distinguishable columnar microcrystalline bulk structure (Fig. 2(b)). Direct comparison of iron films annealed at 330 K (Figs. 1(a) and 2(a)) and at 700 K (Figs. 1(b) and 2(b)) seems to be ambiguous because the thickness of both films differs significantly. Nevertheless, one can observe grain growth at 700 K resulting in a continuous film which consists of a columnar crystalline structure. Careful analysis of

the electron diffraction patterns taken from a cross-section plane of the film (Fig. 3) shows no texture in the film annealed in these conditions. The grains contain clearly defined crystallographic facets implying that recrystallisation proceeds already at this temperature.

Increasing the annealing temperature to 1000 K ($\tau = 0.55$) activates the recrystallisation process. The mean grain size increases (Figs. 1(d) and 2(d)) and the grain facets exhibit mainly low-index diffraction patterns (Fig. 4). The analysed cross-section areas of the Fe film show also that the columnar crystallites are oriented towards the (0 0 1) direction (Fig. 4). The same trend was mentioned in [6] for Fe films deposited at 573 K on an annealed GaAs substrate. We did not observe evident influence of a substrate state on the film structure during annealing, although at 1000 K ($\tau = 0.55$) such influence of the state of the substrate could be possible [17]. The rate and duration of heating as well as the Fe film structure before annealing seem to play a crucial role in the microstructural transformation within the Fe layer. Rapid annealing from 330 to 1000 K, performed in 30 min, causes the small crystal grains to aggregate into larger crystallites (Fig. 1(c)). However, a spread in the larger grained crystallites is limited by the relative short time in the annealing procedure, resulting in a vague and incomplete columnar formation (Fig. 2(c)). Annealing at 1000 K, preceded by 1 h heating at 700 K, causes the crystalline columnar structure of the Fe film to become more distinct and the Fe crystallite size to become larger with an average value of 400 nm (Fig. 2(d)).

Ex situ analysed iron films are covered by a thin layer of native iron oxide as a result of exposure to air after vacuum annealing. Scanning Auger microscopy (SAM) depth profile analysis showed that a layer of native iron oxide approximately 4 nm thick covers all

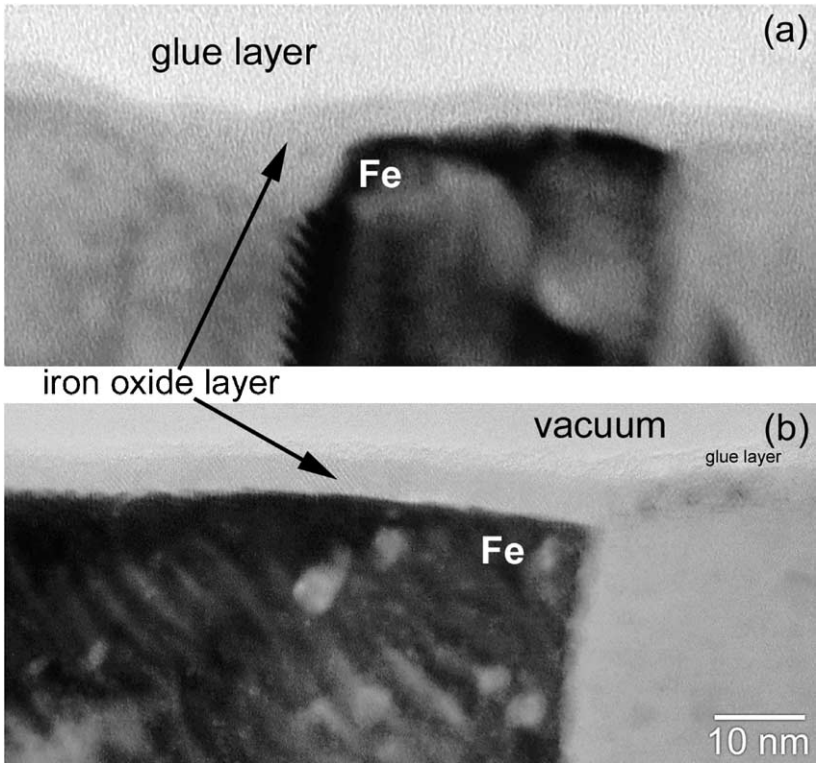

Fig. 6. Bright field TEM images of the Fe film cross-section at high magnification. The Fe film was annealed in vacuum at 700 K (a) and 1000 K (b), respectively, and then exposed to air. The arrows mark the native iron oxide layers. Whereas the glue layer in the image of (a) is fully intact, in (b) only part of the glue layer is visible; the upper part is vacuum. The thickness of the films was 54 ± 2 nm (a) and 57 ± 2 nm (b).

our Fe films annealed at various temperatures. The thickness of this iron oxide layer is very well confirmed by a direct investigation of the TEM images of the cross-sectional Fe/quartz samples (Fig. 6). The bright field TEM image allows to differentiate between the roughness originating from the Fe surface and that formed by the native oxide layer. It can be seen (Fig. 6) that the native iron oxide top layer apparently smoothes out the Fe film roughness. The roughness of the iron oxide top layer covering the relatively rough Fe film sintered at 700 K is significantly less than that of the pure Fe film surface itself (Fig. 6(a)). The roughness of the relatively smooth Fe film annealed at 1000 K is reproduced by the roughness of native oxide layer (Fig. 6(b)). This observation seems to be essential for the interpretation of the roughness factor [16], which is determined for metal samples exposed to air. Essentially, the native oxide layer smoothes out the rough metal surface.

5. Conclusions

The following conclusions can be drawn:

- Vacuum annealing of Fe films evaporated at low temperature on a quartz substrate in the temperature range 330–1000 K, leads to microstructural transformations in both the surface and the bulk. The rate and duration of annealing play a crucial role in this process. A polycrystalline structure with fine, randomly distributed crystallites accompanied by a fine-grained surface and formation of microvoids was observed after annealing the Fe film at 330 K. Ordering of the polycrystalline Fe film occurred at annealing temperatures between 700 and 1000 K resulting in columnar microstructure.
- Cross-section TEM analysis revealed a randomly oriented microcrystalline structure of the Fe films annealed at temperatures $\leq$700 K and a well oriented columnar structure in the (0 0 1) direction after annealing at 1000 K.
- Annealing performed at 1000 K, leads to a reduction in the high-index Fe bcc diffraction patterns. Low-index planes were observed mainly in selected cross-section areas of the Fe film indicating a monocrystalline structure of well separated Fe grains.
- Direct observation of the Fe film roughness smoothed out by its native oxide layer has been performed using the cross-sectional TEM analysis at high magnifications.

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