ELSEVIER

Surface Science xxx (2002) xxx–xxx

SURFACE SCIENCE

www.elsevier.com/locate/susc

Corrosion of epitaxial Fe(0 0 1) films studied with CEMS and AFM

I. Flis-Kabulska [a], B. Handke [b,c], N. Spiridis [b], J. Haber [b], J. Korecki [b,c,*]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*
[b] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland*
[c] *Department of Solid State Physics, Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy (AGH), al. Mickiewicza 30, 30-059 Kraków, Poland*

Abstract

Epitaxial Fe(0 0 1) films of a high crystalline and surface quality, as checked in situ with AES, low energy electron diffraction and STM, were grown on MgO(0 0 1). Such films show an exceptional corrosion resistance remaining metallic for years at the ambient atmosphere, except of 5–10 nm, as found using the conversion electron Mössbauer spectroscopy (CEMS). For more systematic corrosion studies, 50 nm iron films were prepared of the ^{57}Fe isotope. As-prepared Fe films, exposed to the atmosphere did not show clear morphological and compositional changes, which could be associated with the oxide formation, as checked with contact AFM in air and with CEMS. After exposure of the film to HNO_3 or HCl vapors corrosion was observed with AFM. It resulted in two different types of surface modifications. The first one was seen as a homogenous granular layer with the height amplitude of about 15 nm. Corrosion-induced changes of the second type have a localized character resulting in micrometer sized porous protrusions. The corrosion products were identified as γ-FeOOH. Controlled oxidation of surface iron layer to epitaxial Fe_3O_4 passivated the film. © 2002 Published by Elsevier Science B.V.

Keywords: Atomic force microscopy; Scanning tunneling microscopy; Mössbauer spectroscopy; Low energy electron diffraction (LEED); Corrosion; Oxidation; Iron; Epitaxial thin film

1. Introduction

Room temperature atmospheric corrosion of iron and its alloys is probably one of the most common processes touching all of us. Fe exposed to the atmosphere is subjected to different reactions that are governed by the structure and composition of a surface layer and atmospheric pollutants. Real processes have a complex character and are difficult to be recognized as elementary reactions like passivation, oxidation or corrosion. Whereas wet corrosion under electrochemical conditions has been intensively studied and fairly well understood, less is known about atmospheric corrosion and especially its initial stages. STM and AFM which is used extensively in studies of the surface structure, give new insight in understanding of dissolution and passivation of metals and alloys proceeding during corrosion processes [1–4], including oxidation and passivation of iron, especially in solutions [5–9].

* Corresponding author. Tel.: +48-12-617-2911; fax: +48-12-634-1247.
E-mail address: korecki@uci.agh.edu.pl (J. Korecki).

0039-6028/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0039-6028(02)01364-X

Numerous factors determine corrosion processes. Beside of the individual features of the environment (temperature, humidity, pH), structure of the sample plays a crucial role [3]. A prerequisite for understanding the course of the process is the use of well defined surfaces, which are offered by single crystals. It is due to strong sensitivity of chemical reactions to the coordination, local composition, impurities and defects. In the previous paper [10], corrosion of polycrystalline Fe films in acid vapors was studied using AFM, whereas presently, we extend these studies to corrosion in epitaxial Fe(0 0 1) films. The sensitivity of the applied experimental methods—conversion electron Mössbauer spectroscopy (CEMS) and AFM—allowed to follow in nanoscale local changes in composition and morphology of the film surface exposed to air, HNO_3 and HCl atmosphere.

The reaction of HNO_3 with the as-prepared films was compared with that occurring on a film, which was oxidized epitaxially to Fe_3O_4.

2. Experimental

Fe(0 0 1) films were grown by molecular epitaxy in a multichamber UHV system described in details elsewhere [11]. To enable further studies with Mössbauer spectroscopy, isotopically pure iron, ^{57}Fe and ^{56}Fe was used. Iron was evaporated from thermal sources on polished MgO(0 0 1) substrates ($10 \times 10 \times 1$ mm^3) at elevated temperature that was optimized for a flat growth [12]. The film thickness (typically a few tens of nm) was controlled by a quartz balance. The film composition and structure was checked in situ by the Auger electron spectroscopy and low energy electron diffraction (LEED). For in situ Mössbauer measurements samples were transferred into a CEMS UHV chamber. Compared to standard surface sensitive characterization methods, CEMS has the advantage of probing deeper layers (down to 100 nm) with a monolayer resolution [13]. In the course of an UHV experiment, samples could be exposed to a controlled oxygen atmosphere (up to 10^{-4} Pa). Freshly prepared samples were taken out from the UHV system through a load-lock, which allowed division of the sample into pieces, usually four. Then the samples were placed in containers under pure N_2 and stored for further studies. Ex situ experiments comprise exposure of the samples to a controlled acidic atmosphere, AFM measurements in ambient atmosphere and Mössbauer spectroscopy.

AFM topography was examined in a contact mode with Si_3N_4 cantilevers using TopoMetrix Discoverer TMX 2000 system. In another UHV system [14] Fe(0 0 1) films obtained under similar conditions as described above, were characterized with STM (Aris 1100, Burleigh, with nanoscope control) at different stages of the thermal and chemical treatment.

3. Samples

On MgO(0 0 1) Fe grows with epitaxial relations: Fe(0 0 1)//MgO(0 0 1) and Fe[1 1 0]//MgO[1 0 0], i.e. by 45° rotation of the (0 0 1) surface unit cell. A flat growth is reported for Fe on MgO at elevated temperatures [12], but to prevent an island growth, nucleation should proceed at low temperature (e.g. 300 K) and then temperature can be risen gradually up to 620 K at the final thickness. Fig. 1 documents structure of a 50 nm film obtained according to the above receipt. The LEED pattern (not shown) reveals a low background and sharp spots corresponding to monoatomic terraces seen in the STM image (Fig. 1(a)).

Epitaxial Fe(0 0 1) films present an exceptional resistance to atmospheric corrosion. Our long-term observation indicates that only after months long storage in laboratory environment, the samples show traces of oxidation. Fig. 1(b) and (c) exemplify the influence of the atmosphere by comparison of CEMS spectra of 50 nm $^{57}Fe(0\,0\,1)$ films taken after one week and one year storage in laboratory air. The spectra are dominated by a six-line pattern of metallic iron. Any oxide phases can be easily detected by contribution in the central part of the spectra for paramagnetic oxides or hydroxides (FeO, γ-FeOOH) or high splitting components for magnetite, hematite, maghemite or goethite. The magnetic phases in a highly dispersed state often give rise to "nonmagnetic"

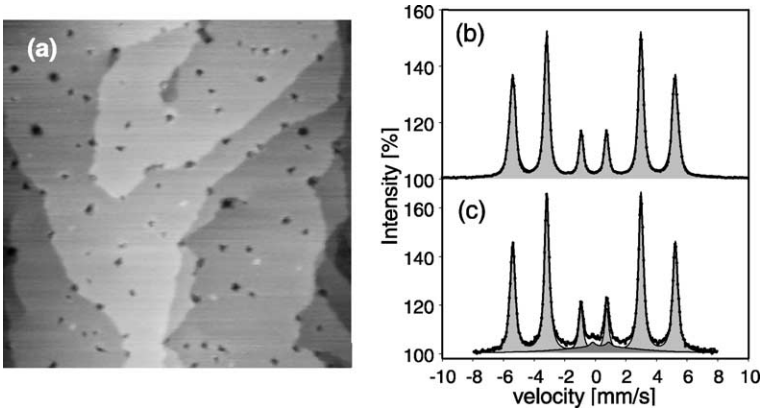

Fig. 1. 50 nm epitaxial Fe(0 0 1) film on MgO(0 0 1) as characterized by STM and CEMS: (a) 100×100 nm^2 topographic STM image, (b) and (c) CEMS spectra one week after preparation and one year after preparation, respectively.

spectra due to superparamagnetism. In the CEMS detection limit ($\sim$1% of the total film thickness) an oxide layer after one week storage is certainly thinner than 0.5 nm, whereas after one year at variable conditions of humidity and temperature, the layer of unidentified oxides is 6 ± 1 nm thick.

4. Results and discussion

To simulate a passive layer formed on Fe(0 0 1) surfaces [15], a Fe(0 0 1) film was subjected to oxidation at 10^{-4} Pa in UHV chamber by annealing for 15 min at 550 K. To enhance the surface sensitivity, the sample was engineered by placing a 5 nm ^{57}Fe probe layer on top of a 20 nm ^{56}Fe film. The oxidation resulted in the formation of a new epitaxial phase observed in a LEED pattern (Fig. 2(a)). The pattern symmetry indicates that the layer could be magnetite. STM image showed distinct changes of the film topography (Fig. 2(b) and (c). Small irregular grains transformed after annealing to monoatomic terraces with atomically resolved structures characteristic for magnetite [16], as shown in the inset on Fig. 2(b). Unambiguous identification of the layer formed is given by a CEMS measurement shown in Fig. 2(d). The spectrum could be fitted with four components. The components (A) and (B) come from magnetite representing Fe ions in tetrahedral and octahedral

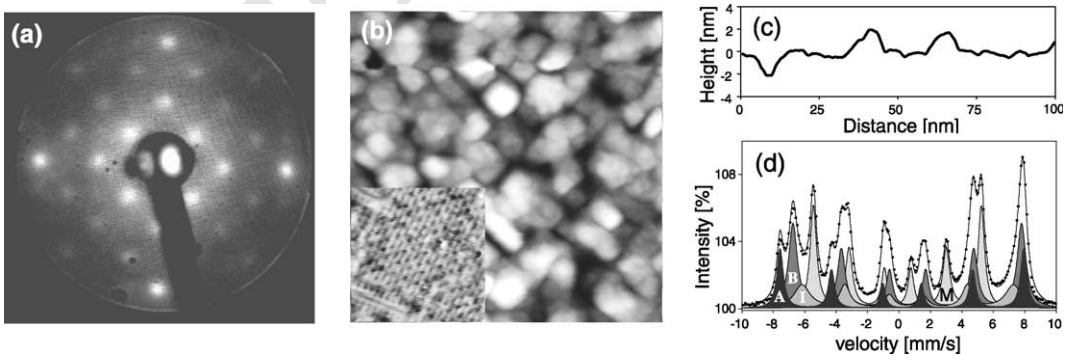

Fig. 2. Oxidized 20 nm ^{56}Fe/5 nm ^{57}Fe epitaxial film on MgO(0 0 1) as characterized by LEED, STM and CEMS: (a) LEED pattern at 94 eV, (b), (c) 100×100 nm^2 topographic STM image with a section along the marked line and (d) in situ CEMS spectrum. Inset on (b) shows the 12.5×12.5 nm^2 atomically resolved scan of the film annealed at 750 K.

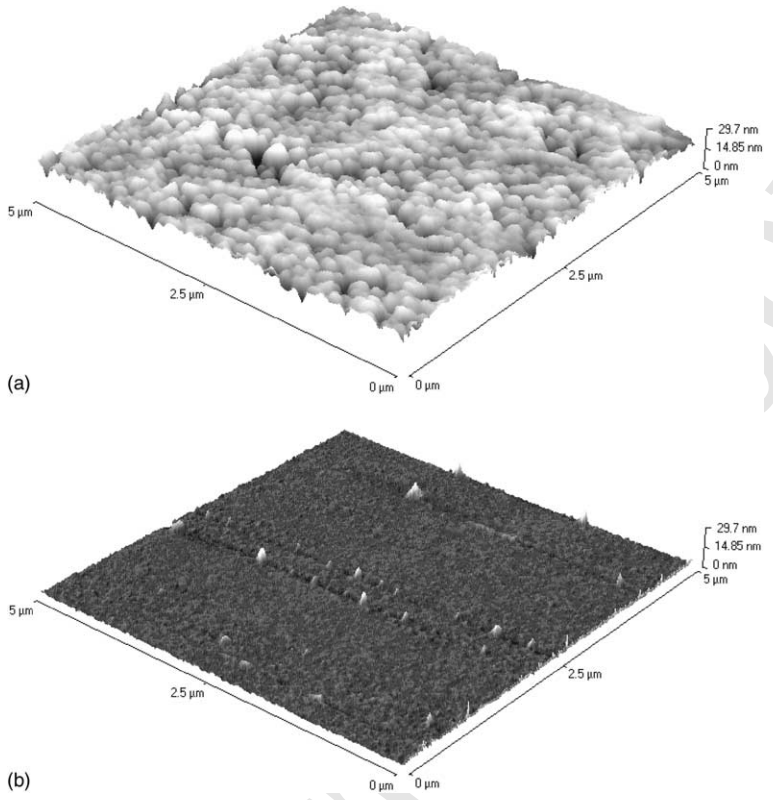

Fig. 3. AFM image of an epitaxial Fe(0 0 1) film on MgO(0 0 1): (a) after 25 h exposure to 1 M HNO_3 vapors and three weeks storing in air and (b) shortly after preparation.

sites, respectively. Component (M) is due to metallic iron. Apparently, the oxidation affected only a part of the top ^{57}Fe layer. Component (I) comes probably from an interfacial layer present between Fe_3O_4 and metallic iron. Neglecting differences in recoilless fractions, the thickness of the oxide layer can be estimated by comparing the relative intensity of the spectral components, which yields that the magnetite layer formed on the epitaxial Fe(0 0 1) film is 3 nm thick. In the following text this sample will be referred as Fe/Fe_3O_4.

To intensify the corrosion process, the samples were exposed for 1 min to 25 h to the atmosphere in equilibrium with vapors of 1 M HNO_3 or 1 M HCl at room temperature. After exposure to corroding agents samples were stored in a desiccator. In the saturated atmosphere, an electrolyte is adsorbed on the film surface (presumably in form of separated droplets) as a result of the vapor condensation. In such an experiment, contrary to the processes conducted in a bulk solution where corrosion products partly dissolve, initial stages of localized corrosion could be observed.

Corrosion resulted in two different types of surface modifications as observed with AFM. The first one, presented in Fig. 3(a) for a selected 5×5 μm^2 area, is seen after a long time exposure (25 h, followed by storing for three weeks in air) as a continuous layer of granules with the height amplitude of about 15 nm. For comparison, the AFM topography of the Fe(0 0 1) surface before chemical treatment is shown in Fig. 3(b). The surface observed at the initial stage corresponds to the in situ STM image (Fig. 1(a)). Few structures (nanometer sized) appearing on the atomically flat iron film are probably impurities adsorbed during the sample handling.

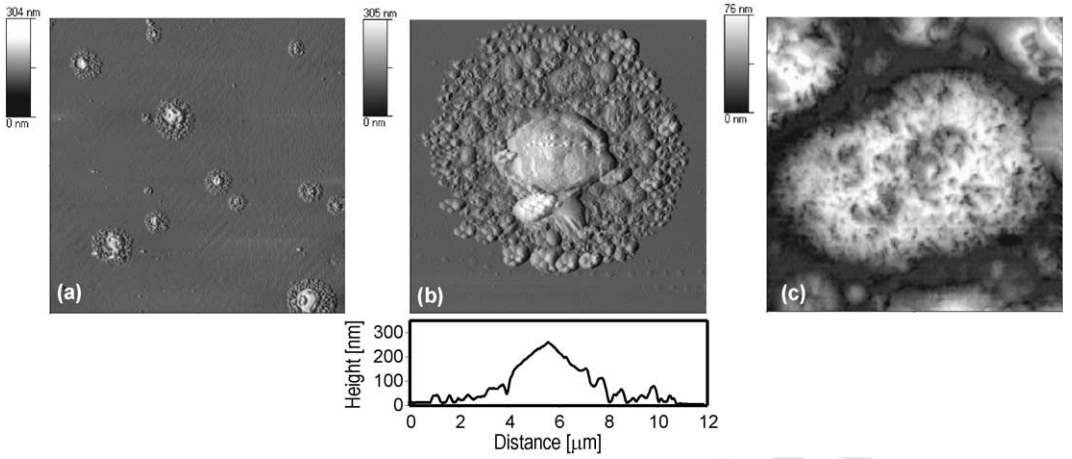

Fig. 4. AFM image of an epitaxial Fe(0 0 1) film on MgO(0 0 1) after 1 min exposure to 1 M HNO_3 vapors and a subsequent 24 h storing in air: (a) large area 70×70 μm^2 scan (b) 12×12 μm^2 and a selected cross-sectional scans (c) 2×2 μm^2 scan indicating porous structure of corrosion products.

Corrosion-induced changes of the second type have a localized character. They are seen even after exposure to HNO_3 vapors as short as 1 min and a subsequent storing in air for 24 h (Fig. 4). Most of the surface remained unchanged, however, a few protrusions indicating corrosion appeared. The protrusions grew in the form of regular structures of the overall diameter 2–12 μm, with a high central part surrounded by numerous lower circular structures. Fig. 4(b) shows the typical shape of the corrosion product. The central part is a uniform structure of the height of about 250 nm, whereas its surrounding is formed by granules with the sizes diminishing when going further from the center. The porous surface of some protrusions (Fig. 4(c)) suggests the location of the corrosion gas exits (NO_2, water vapor). It is worth to note that the height of the protrusions considerably exceeds the Fe(0 0 1) film thickness (50 nm) which means that the reaction products extend into the film bulk and that they have a porous structure of a dispersed oxide/hydroxide.

The regular form of the corrosion products suggests that the corrosion proceeded on the sites of acid vapor condensation. The protrusions are distinctively higher in the central part than at the edge, obviously due to longer exposure to the aggressive solution in the center of the condensate droplet. The central part of the protrusion might be also formed by the coalescence of smaller granules. Many of the corrosion centers reveal a hexagonal shape, which was reported previously by Oelkrug et al. [6].

Exposure of iron to HCl vapors resulted in similar effects as in the case of HNO_3. Additionally, we noticed enhanced localized corrosion along scratches of a mechanical origin (Fig. 5). Scratches can be more reactive than the intact surface for several reasons: (a) a bare metal, free of oxides could be exposed at scratches; (b) geometrical irregularities of the surface might be preferred condensation centers of vapors, and (c) kinks and steps on scratches are probably the most active reaction sites.

Corrosion products were identified by CEMS. Fig. 6(a) and (b) show CEMS spectra of 50 nm Fe(0 0 1) film after 25 h exposure to HNO_3 (compare Fig. 3(a)) and after 72 h exposure, respectively. The only noticeable change of the spectra, in comparison with the as-prepared sample (Fig. 1(b)) is a doublet in the central part. The hyperfine parameters of the doublet, the isomer shift IS = 0.35 mm/s relative to metallic iron and quadrupole splitting QS = 0.74 mm/s indicate for a Fe^{3+} origin of the doublet, and are typical for different corrosion products observed on Fe surfaces [13]. In a low temperature spectrum (85 K) the doublet remained magnetically unsplit, which

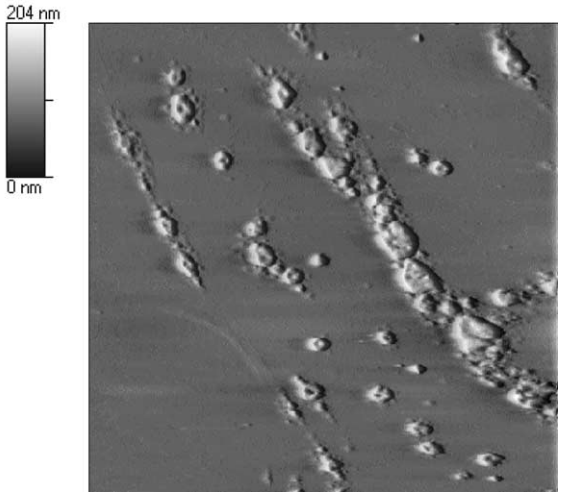

Fig. 5. AFM image (25×25 μm^2) of an epitaxial Fe(0 0 1) film on MgO(0 0 1) after 1 min exposure to 1 M HCl vapors and subsequent 27 h storing in air. Corrosion products were formed on defects (scratches).

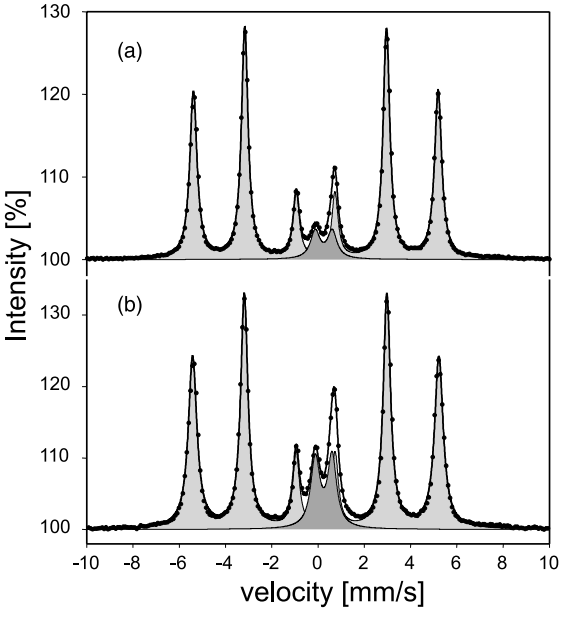

Fig. 6. CEMS spectra of a 50 nm epitaxial Fe(0 0 1) film on MgO(0 0 1) after exposure to 1 M HNO_3 vapors: (a) 25 h and (b) 72 h.

means that the corrosion product is most probably γ-FeOOH. Prolongation of the exposure time from 25 to 72 h increases the thickness of an oxyhydroxide layer from 3.8 to 7.4 nm, as estimated from the intensity of the spectral components.

Exposure of the Fe/Fe_3O_4 film to HNO_3 vapors resulted in much less pronounced changes of the surface morphology and composition than it was observed for a clean Fe(0 0 1) film. A post-exposure STM topography revealed only a homogeneous increase of the surface roughness as compared to in situ observation of the freshly prepared surface. Similarly, no signs of chemical surface modifications in the CEMS spectrum were found after 15 min exposure. Further studies of the Fe(0 0 1) surfaces passivated with the epitaxial Fe_3O_4 layer are in progress.

The same corrosion product, γ-FeOOH, was found by CEMS on the iron sample treated with HCl vapors. However, the average depth of the oxyhydroxide layer formed after 6 min exposure to HCl vapors was two times larger than that after 72 h exposure to HNO_3.

5. Conclusions

Epitaxial Fe(0 0 1) films exposed to ambient atmosphere are highly resistant to corrosion. No oxide layer thicker than 0.5 nm was found after a one week exposure, which means that natural passivation is very slow. Short exposure (minutes) to HNO_3 and HCl vapors resulted in the appearance of localized corrosion centers which cannot be associated with any structural details and are explained as coming from condensation of vapors. Longer exposure (hours) results in the formation of a homogeneous layer that was interpreted as γ-FeOOH basing on CEMS measurements. The corrosion process was studied previously on polycrystalline iron films [10]. The oxide morphology was highly diversified and the nucleation of the corrosion products occurred at active sites like steps, grain boundaries etc. On the surfaces of the epitaxial films the localized corrosion is connected probably with point defects (also mechanical). Controlled oxidation of a surface iron layer to epitaxial Fe_3O_4 passivates the film.

Acknowledgements

This work was partially supported by the Polish State Committee for Scientific Research, grant no. 7 T08A 002 20.

References

[1] H.W. Pickering, T. Sakurai, NACE Conference "Corrosion '91", Cincinnati, OH, 11–15 March, 1991, paper no. 81.
[2] P. Marcus, V. Maurice, in: K.E. Heusler (Ed.), Passivation of Metals and Semiconductors, Trans Tech, Switzerland, 1994, p. 221.
[3] P. Marcus, Electrochim. Acta 43 (1998) 109.
[4] W.J. Lorenz, W. Plieth (Eds.), Electrochemical Nanotechnology. In situ Local Probe Techniques at Electrochemical Interfaces, Wiley-VCH, Weinheim, 1998.
[5] J. Karunamuni, R.L. Kurtz, R.L. Stockbauer, Surf. Sci. 442 (1999) 223.
[6] D. Oelkrug, M. Fritz, H. Stauch, J. Electrochem. Soc. 139 (1992) 2419.
[7] B. Müller-Züllow, S. Kipp, R. Lacmann, M.A. Schneeweiss, Surf. Sci. 311 (1994) 153.
[8] O. Khaselev, J.M. Sykes, Electrochim. Acta 42 (1997) 2333.
[9] J. Li, D.J. Meier, J. Electroanal. Chem. 454 (1998) 53.
[10] I. Flis-Kabulska, J. Electroanal. Chem. 508 (2001) 89.
[11] J. Korecki, M. Kubik, N. Spiridis, T. Ślęzak, Acta Physica Polonica A 97 (2000) 129.
[12] S.M. Jordan, J.F. Lawler, R. Schad, H. van Kempen, J. Appl. Phys. 84 (1998) 1499.
[13] K. Nomura, Y. Ujihira, A. Vertes, J. Radioanal. Nucl. Chem., Articles 202 (1996) 103.
[14] J. Korecki, N. Spiridis, B. Handke, J. Prokop, J. Haber, Electron Technol. 29 (1996) 269.
[15] M.F. Toney, Phys. Rev. Lett. 79 (1997) 4282.
[16] B. Stanka, W. Hebenstreit, U. Diebold, S.A. Chambers, Surf. Sci. 448 (2000) 49.