Structural and magnetic studies of thin Fe$^{57}$ films formed by ion beam assisted deposition

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Thin Fe$^{57}$ films with the thickness of 120 nm have been prepared on glass substrates by using the ion-beam-assisted deposition technique. X-ray diffraction, electron microdiffraction and Mössbauer spectroscopy studies have shown that as-deposited films are in a stressfree nanostructured state containing the nanoscaled inclusions of α-phase iron with the size of ~10 nm. Room temperature in-plane and out-of-plane magnetization measurements confirmed the presence of the magnetic α-phase in the iron film and indicated the strong effect of residual stresses on magnetic properties of the film as well. Subsequent thermal annealing of iron films in vacuum at the temperature of 450 °C stimulates the growth of α-phase Fe crystallites with the size of up to 20 nm. However, electron microdiffraction and Mössbauer spectroscopic data have shown the partial oxidation and carbonization of the iron film during annealing. The stress disappeared after annealing of the film. The magnetic behaviour of the annealed samples was characterized by the magnetic hysteresis loop with the coercive field of ~10 mT and the saturation magnetization decreased slightly in comparison with the α-phase Fe magnetization due to small oxidation of the film.

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1. Introduction

At present the synthesis and study of nanostructured materials are of high scientific and practical interest because they exhibit properties that are substantially different from the properties of single-crystal or bulk polycrystalline samples [1–3]. The development of new methods for the formation of nanostructured materials and the study of the effect of size effects (nanostructuring) on properties of the material is a topical problem.

Ion-beam and ion-plasma methods of the deposition of thin films and coatings should be separated among the variety of methods for producing nanostructured materials, since they are the most technologically advanced and easily controllable. It is possible to produce films and coatings with a wide range of structural characteristics, different phase structures and physical and performance properties by varying such parameters as the deposition rate, substrate temperature, composition of the reaction gas, composition of the sputtering target, etc. Earlier we used these techniques to synthesize and modify diamond-like carbon films [4,5], to form silver nanoparticles in the silica glass matrix [6,7], to prepare nanocomposite films of barium titanate-based multiferroics with magnetic cobalt nanoparticles [8], to fabricate thin germanium layers on silicon [9,10] and nanostructured ZnO and Al$_2$O$_3$ films [11]. The characteristic feature of above-listed single-elemental or composite films and layers is the nanocrystalline structure (when the dimensions of the crystallites of different phases are in the nanometer range), which determines their optical, magnetic and electro-physical properties.

In the past decade, interest in magnetic thin films of pure 3d-metals (in particular to iron films) have experienced a tremendous boost due to the high potential of thin-film magnetic heterostructures for existing and emerging technological applications [12]. Different techniques such as thermal evaporation in ultra-high vacuum [13], magnetron sputtering [14], electrodeposition [15] etc. [16,17] are used usually to produce thin iron films on the different substrates. However the application of the ion-beam-assisted deposition technique (IBAD) for the preparation of thin films of pure iron is of special interest. Unlike above methods, in the IBAD technique the material of iron film deposited on the substrate is
subjected additionally to the irradiation by the low-energy Fe\textsuperscript{57} flow (E < 1 keV). Finally, the effect of the ion beam on the formation process and the crystal structure of the deposited film and consequently on its properties can be fundamentally different. On the one hand, as a result of the intense ion-mixing of the metal atoms during the film formation, the iron film can be found in the thermodynamically unstable amorphous state. On the other hand, on the contrary, the low-energy ion beam impact on the material film can stimulate the crystallization of the film and formation of different iron phases including non-equilibrium ones. This specifies the main aim of our work—the studies of phase composition and magnetic properties of the thin iron films obtained by IBAD, and the same films is then subjected to thermal annealing under vacuum.

2. Experimental

A wide-aperture ion source of the Kaufman type with the divergent ion beam (beam angular divergence of ∼20°) was used for the deposition of thin iron films. Using this source the Fe\textsuperscript{57} isotope foil with the diameter of 65 mm was sputtered and the deposited film was ion-stimulated at the glancing incidence angles of ions on the film surface. The chemically pure xenon was used as the working gas. The energy of xenon ions was 1 keV at the ion current density of 150 mA/cm\textsuperscript{2}. The deposition of films was performed in high vacuum (10\textsuperscript{-3} Pa). Vacuum was provided by two diffusion pumps. Two nitrogen traps were used to reduce the partial pressure of the diffusion oil vapour in the working chamber of the setup. The substrate temperature during deposition was no higher than 50°C. Preliminary studies showed that the residual oxygen content in the working chamber affects substantially the elemental and phase compositions of the deposited iron films, as a result the composite film is typically formed from iron and iron oxides. To avoid this, special measures were taken to reduce the partial pressure of oxygen in the working chamber of the setup. To this end, the vent of nitrogen and pumping were repeated after the preliminary pumping of the chamber. The films were deposited on silica glass substrates which were attached to a water-cooled holder. This holder was rotated in order to ensure the uniform film thickness. The thickness of the deposited films was measured on an interference microscope “MII-11” and by observing the cross-section of the film on a scanning electron microscope (SEM). It was on the order of 120 ± 7 nm. For transmission electron microscopy studies thinner film samples with the thickness of ∼50–60 nm were fabricated by depositing iron on the surface of a freshly cleaved surface of sodium chloride NaCl crystals followed by dissolving the substrate (salt) in distilled water and the transfer of the film on the microscopy grids.

Subsequent thermal annealing of the samples was performed under vacuum of ∼10\textsuperscript{-2} Pa at the temperature of 450°C for 15 min. The elemental composition and surface morphology of the films were studied on a scanning electron microscope (SEM) “Zeiss EVO 50 XM” equipped with energy-dispersive X-ray (EDX) spectrometer “Oxford Inca Energy-350”. The phase composition was studied by X-ray diffraction (DRON-7, CuK\textalpha{} radiation with a beta-filter), transmission electron microscopy (TEM) on microscope “Zeiss Libra 120” and Mössbauer spectroscopy of conversion electrons (MSCE). The speed scale in MSCE spectra was calibrated with respect to metallic iron (α-phase Fe). Magnetic properties were studied on an experimental magnetometer [18]. The sample with the rectangular shape 5.0 × 5.0 mm was used in the magnetic studies in order to exclude the effect of the sample shape on the magnetic characteristics. The dependence of the induced magnetic moment on the values of the magnetic field applied either in the plane (in-plane geometry) or perpendicularly to the plane (out-of-plane geometry) of the sample was measured at room temperature with the magnetic field

**Fig. 1.** X-ray pattern and electron microdiffraction (inset) for: (a) as-deposited Fe\textsuperscript{57} thin film and (b) the same film after thermal annealing in vacuum at 450°C for 15 min.

<table>
<thead>
<tr>
<th>No. of ring</th>
<th>α-Fe* (hkl)</th>
<th>d (Å)</th>
<th>1 (%)</th>
<th>FeO* (hkl)</th>
<th>d (Å)</th>
<th>1 (%)</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a [before annealing]</td>
</tr>
<tr>
<td>1</td>
<td>(110)</td>
<td>2.026</td>
<td>100</td>
<td>(111)</td>
<td>2.47</td>
<td>50</td>
<td>2.46</td>
</tr>
<tr>
<td>2</td>
<td>(200)</td>
<td>2.14</td>
<td>100</td>
<td>(200)</td>
<td>2.14</td>
<td>100</td>
<td>2.02</td>
</tr>
<tr>
<td>3</td>
<td>(110)</td>
<td>2.026</td>
<td>100</td>
<td>(220)</td>
<td>1.51</td>
<td>63</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>(200)</td>
<td>1.433</td>
<td>19</td>
<td>(311)</td>
<td>1.293</td>
<td>15</td>
<td>1.28</td>
</tr>
<tr>
<td>5</td>
<td>(211)</td>
<td>1.17</td>
<td>30</td>
<td>(222)</td>
<td>1.238</td>
<td>8</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 1

Interplanar spacing in as-deposited Fe\textsuperscript{57} film and in the same film after thermal annealing in vacuum. Here the asterisk marks the tabular values [19].
sweep to 500 mT. When processing the results of magnetic measurements, the diamagnetic contribution from the glass substrate was subtracted, and the magnetic moment value was reduced to the volume of the deposited film.

3. Results and discussion

3.1. Structural analysis

SEM studies showed that the morphology of the film surface as a whole is sufficiently smooth at the submicron scale. The elemental microanalysis data indicate the absence of any other (in addition to iron) chemical elements in the films.

The phase composition of the films was studied by X-ray diffraction and electron microdiffraction (Fig. 1). There is only one reflex in the X-ray pattern of the as-deposited film which is obtained in the conventional 2θ measurement geometry. Since no other features, a reduced portion of X-ray pattern is presented in the range 35°–55° for better evaluation of the details (Fig. 1a). It can be seen in figure there is a broad diffraction peak, the position of which corresponds to the interplanar spacing \(d_{\text{exp}} = 0.2064\) nm. If these data are compared with tabular values (\(d_{110} = 0.2026\) nm) for \(\alpha\)-phase iron (Fig. 1a, dotted line), it can be concluded that there are considerable in-plane compressive stresses in deposited iron film, which lead to the increase in the interplanar spacing in the direction perpendicular to the film plane and, accordingly, to the shift of the observed peak to the low-angular region of the X-ray pattern. Moreover, an in-plane stress in iron films may be calculated by using equation [15]:

\[
\sigma = - \left( \frac{E}{2

\nu} \right) \varepsilon,
\]

where \(E\) denotes Young modulus and \(\nu\) is the Poisson ratio, \(\varepsilon = (d_{\text{exp}} - d_{110}) / d_{110}\) is relative lattice strain, \(d_{\text{exp}}\) and \(d_{110}\) are the interplanar spaces of the sample and stress-free bulk iron, respectively. For iron \(E = 211.4\) GPa and \(\nu = 0.29\) [15]. In as-deposited film a stress was calculated to be \(\sigma = -0.68\) GPa. Here a negative sign of \(\sigma\) indicates a compressive stress in as-deposited iron film. Note
that residual stresses occurring in as-deposited film are common feature for all sputtering techniques.

The size of the X-ray coherent scattering region (~10 nm) was estimated from the width of the observed reflex by using the Scherrer formula. Thus, from the data of the X-ray diffraction follows that iron films formed by ion-beam assisted deposition technique is a nanocrystalline structure with a lot of stress and which does not have the sufficiently extended long-range order. This conclusion is in agreement with the TEM experimental results for iron films. Fig. 1a, inset shows the electron microdiffraction pattern of the iron film and its interpretation is given in Table 1. The analysis of the location of the rings 3 and 5 indicates the presence of α-phase Fe crystallites in the film and the considerable broadening of microdiffraction rings indicates their small size. The central most intense ring 1 is related to the iron oxide which is apparently formed in the process of the sample preparation and the surface oxidation of the iron film during the dissolution of the NaCl substrate in distilled water.

Fig. 1b shows the X-ray pattern of the iron film after thermal annealing at T = 450 °C under vacuum. The observed diffraction maximum became more intense, and its width is significantly decreased compared with the same reflex in the virgin sample. The position of the diffraction maximum is completely consistent with the tabular arrangement of the reflection (110) for α-phase iron and the coherent scattering region increases to ~20 nm. Consequently, in general, post-annealing leads to the increase in the crystallinity of the film and removes residual mechanical stresses. The same is indicated by the electron microdiffraction pattern (Fig. 1b, inset). The diffraction rings from the iron α-phase and iron oxide (FeO) become sharper indicating the increase in sizes and decrease in the number defects of the corresponding crystallites.
Table 2

Hyperfine parameters and the percentage of various Mössbauer spectrum components in iron films before and after thermal annealing in vacuum. In the brackets, the standard deviations of the measured values are presented as a variation of last digits.

<table>
<thead>
<tr>
<th>No. of component</th>
<th>$I_s$ (mm/s)</th>
<th>$Q_s$ (mm/s)</th>
<th>$B_s$ (T)</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Before annealing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 ( sextet), α-Fe</td>
<td>0.00(6)</td>
<td>−0.00(7)</td>
<td>33.1</td>
<td>54</td>
</tr>
<tr>
<td>2 ( sextet), intergranular Fe</td>
<td>0.02(2)</td>
<td>−0.1</td>
<td>32.5</td>
<td>46</td>
</tr>
<tr>
<td>b) After annealing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 ( sextet), α-Fe</td>
<td>0.00(2)</td>
<td>0.00(4)</td>
<td>32.9</td>
<td>57</td>
</tr>
<tr>
<td>2 ( sextet), Fe/C</td>
<td>0.20(4)</td>
<td>0.06(6)</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>3 ( sextet), close to γ-Fe2O3</td>
<td>0.24(5)</td>
<td>−0.00(8)</td>
<td>47.5</td>
<td>4</td>
</tr>
<tr>
<td>4$^*$ (doublet), FeO$_{1-x}$</td>
<td>0.70(9)</td>
<td>(0.0-1.4)</td>
<td>0</td>
<td>18</td>
</tr>
</tbody>
</table>

$^*$ Superposition of doublets with a wide distribution of the quadrupole splitting.

3.2. Mössbauer spectroscopy of conversion electrons

Fig. 2a shows the Mössbauer spectrum of conversion electrons for the as-deposited Fe$^{57}$ film, which represents the superposition of the two sub-spectra (two sextets) with hyperfine parameters shown in Table 2. The values of the isomer shift ($I_s \equiv 0$), quadrupole splitting ($Q_s \equiv 0$) and hyperfine magnetic field on the Fe$^{57}$ nucleus for the first sextet ($B_s = 33.1$ T), in fact, correspond to the parameters of the crystal α-phase Fe [20]. The second, less intense and noticeably broadened sextet with $B_s = 32.5$ T was observed earlier [16,21] in the studies of nanocrystalline iron and according to its parameters was referred to iron atoms, which are located in the region of boundaries between nanocrystallites. Thus, the analysis of the hyperfine parameter values of Mössbauer spectrum components confirms the X-ray analysis data. In addition, these data indicate that iron atoms in the as-deposited film are in two states, i.e., they are located either in crystalline lattice or in the disordered state between crystallites. Note that both these states are magnetically ordered and according to the hyperfine field value on the Fe$^{57}$ nuclei can be related to the magnetic phase close to α-phase Fe.

After thermal annealing of the film the Mössbauer spectrum (Fig. 2b) undergoes significant changes associated not only with the structural changes in the iron film but also with its partial oxidation and carbonization in the annealing process. First of all, the intensity and percentage of the first sextet corresponding to the crystalline α-Fe phase increase. Secondly, the sextet, which in the as-deposited film was attributed to the intergranular iron atoms, disappears completely after thermal annealing. At the same time, there are two additional sextets and a broad doublet that according to their parameters can be attributed to iron carbide and oxides (see Table 2). Note that the carbon arises into iron film after annealing procedure only due to either contamination of the sample during storage or in result of the annealing in a vacuum chamber equipped with oil diffusion pump.

3.3. Magnetic properties

Studies of magnetic properties of the as-deposited iron film confirm the presence of the ferromagnetic α-Fe phase and strong mechanical stresses. Fig. 3 shows the magnetization curves of the film recorded at room temperature in the plane and perpendicularly to the film plane. The field dependence of the magnetization in the film plane shows the magnetic hysteresis with the coercive field value $B_c \approx 12.2$ mT characteristic for nanocrystalline iron films. The saturation magnetization value in the film is $M_s \approx 1.65 \times 10^6$ A/m (1650 G in the CGSM system) which is very close to the magnetization value of the α-phase of metallic iron at room temperature ($M_{α-Fe} = 1707$ G [22]).

Detailed studies of the angular dependence of the shape and parameters of the magnetic hysteresis loop showed that the magnetic behaviour of the obtained film, in general, is typical for thin-film magnetic materials and all studied samples exhibit the magnetic anisotropy of the shape. In the plane (in-plane geometry) the film is magnetically isotropic and easily magnetized, while the saturation is not achieved even at the maximum magnetic field sweep of 500 mT during scanning of the field along the normal to the sample plane (out-of-plane geometry). However, there are two features in the magnetic behaviour of Fe$^{57}$ films obtained by ion-beam assisted deposition. In particular, on the one hand, the linear region unusual for magnetic films is observed in the field dependence of the film magnetization during the detection of the magnetic hysteresis in the film plane in the range of the middle magnetic fields. On the other hand, the magnetization step is observed in the range of low (zero) fields during the detection of the field dependence of the magnetization perpendicularly to the film plane. Both features can be understood if we assume that the surface magnetic anisotropy associated with the presence of significant stresses in the film contributes considerably to the total magnetic energy of the Fe$^{57}$ films obtained by ion-beam assisted deposition. It is known [23,24] that the compressive and tensile stresses of the magnetic film lead to the appearance of the uniaxial perpendicular magnetic anisotropy with the “easy” magnetization axis directed along the normal to the film surface. As a result, the equilibrium orientation of magnetization goes out of the film plane and the linear section associated with the “rotation” magnetization vector in the film plane (in-plane geometry) and the magnetization step in the out-of-plane measurement geometry are observed during the magnetization process of the film. After thermal annealing the mechanical stresses in the film are almost completely removed, and the perpendicular magnetic anisotropy disappears and magnetic field dependences of the magnetization typical for ferromagnetic films are observed, which are shown in Fig. 3b. Due to the increase in the size of the α-phase Fe crystallites annealed samples exhibit the magnetic hysteresis with the coercive field of 10 mT in the film plane, the high residual magnetization value and the summary saturation magnetization slightly reduced in comparison with the magnetization of the pure α-Fe phase that is associated with the formation of iron oxides and carbidates on the film surface during thermal annealing.

4. Conclusions

Thin Fe$^{57}$ films prepared by the ion-beam assisted deposition on the glass substrate exhibit a number of features in microstructure and magnetic characteristics. The as-deposited films have nanocrystalline structure containing two different phases of iron:
the nanoscale crystallites of α-Fe and an intercrystalline disordered phase of iron atoms situated between the crystallites. The films are in the stress state that has a significant impact on the magnetization curves of the films and appears in the form of the uniaxial magnetic anisotropy. Subsequent annealing in vacuum stimulates the crystallization of the whole film volume and the sizes of crystallites of α-Fe phase increase up to ∼20 nm. Residual mechanical stresses in the film are removed and annealed samples exhibit the magnetic behaviour typical for polycrystalline films of iron.

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