Electric Conductivity and Gas-Sensing Properties of Nickel Ferrite Thin Films Formed by Ion-Beam Sputtering Deposition

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Abstract

Ferrites with composition of $NiMn_xFe_{1-x}O_4$, (with x = 0 ÷ 1.0) have been synthesized by self-propagating high-temperature synthesis (SHS). The particle size of the synthesized ferrite powder was about 10 nm. Additional heat treatment at 1270 K during 50 min allowed us to obtained product with the single phase composition $NiFe_2O_4$.

We found out that the increasing of the manganese content (x) increased the lattice constant of the ferrites from 0.833896 nm (x = 0) up to 0.836369 nm (x = 1). The synthesized powder contains two types of ferrite particles that are varied in size and shape. The magnetic properties significantly depend on the microstructure and chemical composition of synthesized ferrites. It has been found that the coercive force H_c increased from 1.75 (x = 0.2) to 2.85 (x = 1).

By using of IBSD technology thin film of $NiFe_2O_4$ was sputtered on the Si (100) substrate. All sputtered films were X-ray transparent. The structure of ferrite films consisted of agglomerate less than 35 nm. The thickness of the sputtered film was about 600 nm. Additional heat treatment at 770 K during 90 min resulted to homogeneity of the film microstructure. The temperature range 400-750 K corresponds to working temperature range of gas-sensing devices.

The ferrite compounds were studied by TOF-SIMS (Time-of-Flight Secondary-Ion-Mass-Spectrometry) for all depth of film. The resistivity *R* of synthesized film was 39 kΩ. Measurement of gas-sensing sensitivity R_{CH4}/R_{air} for gas ($2\%_v$. CH_4) – air mixture showed increase of *R* up to 12% at the present of methane at 403 K. For further research we plan to replace iron to manganese ions in chemical compounds of ferrite.

Introduction

Oxide compositions based on nickel ferrites are known due to their magnetic properties. However, during recent years scientific investigative directions concerning the electrical properties of ferrites have been intensely studied. In particular, the perspectives of employment of the $NiFe_2O_4$-based ferrites as sensitive components of gaseous sensors are noticeably developing [1]. The mechanism of the oxide material sensitivity is based on the alteration of the electrical conductivity of a thin layer of the material upon adsorption of the molecules of the gas under registration. Therewith the range of the gases analyzed in the sensitive compositions of the ferrites includes such substances as methane, propane-butane mixtures, and the like. At the same time, design of the gas-registering unit incorporating a sensitive ferrite-based element meets a number of difficulties. First of all those are instability and ambiguity of the physical properties manifested during obtaining thin nano structural layers of the oxide materials. Ferrites are spinels in their structure and their physical properties are strongly dependent on the lattice parameters as well as on the type and character of ion distribution within it [2, 3]. At present a certain progress has been achieved that allowed development of methods of thin films production based on laser cooling aerosol pyrolysis, sol-gel processes, and ion-beam sputtering [4]. Investigation of thin ferrite films and improvement of the methods of their production will help to finding the dependence of the structural and physical characteristics on the gas-sensitive parameters of the given material.

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Within the scope of the discussed problem, the possibility of production of the $NiFe_2O_4$ material with the predictable properties and stable compositions by the method of ion sputtering of the ferrite powder has been investigated in the present study. The method allows formation of thin films of oxide materials both on the conducting and silent materials. The main advantage of the method is the possibility of one-stage deposition of an order of 1 μm thick layers.

It should be noted that the oxide layers consisting of nanosized particles are predominantly used in the sensor gases. In this case, one of the most important factors that determine the gas sensibility of the layer deposited on the support is its high specific surface, since the main mechanism of the sensor layer operation is alteration of electroconductivity during adsorption of the molecules of the detected gas [5]. Therefore it should be kept in mind that since adsorption occurs in the near-surface region and the sensor layer is commonly deposited onto a silent support with registering electrodes, a minimum thin layer is required with a highly developed surface of the ferrite intended to be used as a gas-sensing material. At the account made of the above reported problems the present study was aimed at the electroconductivity characteristics of the films deposited on the supports made of glass and silicon and the influence of certain gas concentrations on the electroresistance behavior of the thin ferrite film.

Experimental

In the experiments a green powder of nickel ferrite produced by the method of self-propagating high-temperature synthesis (SHS) was used for the film deposition onto the support [6]. The synthesis was performed according to the following scheme at room temperature under air with the use of simple oxides, metallic iron powder, and sodium perchlorate:

$$NiO + Fe + 0.5Fe_2O_3 + (0.2NaClO_4) \rightarrow NiFe_2O_4 + (0.2NaCl) \quad (1)$$

The target (100 × 100 mm) was composed of pressed pellets (Ø20/5 mm) of the synthesized powder. Deposition of the ferrite films onto the supports of monocrystalline silicon Si (100) was a procedure of ion-beam sputtering. This approach is characterized by an exceptional novelty among the methods of the film deposition onto the silent supports. Residual vacuum in the reaction chamber was provided by a turbomolecular pump and did not exceed 1 mPa. The focus of the circular beam of argon ions formed with an accelerator with an anodic layer [7] was directed to the ferrite target. The mean Ar ion energy in the beam constituted *ca*. 750 eV at the current density on the target 10-12 mA/cm^2. Under the force of the ion bombarding the target was pulverized and the substance was transferred onto the support. Spatial distribution of the beams of the powdered substance determined by both the beam structure and the material, structure, and the target topology was evaluated in the experiment. The most intensive material transfer was observed towards the direction corresponding to the angle of 40-47 degrees, i.e. to the zone of the target location, thus providing formation of an equally thin layer.

The microstructure, morphology, and relief of the surface of the resultant samples were analyzed by the methods of the scanning and tunneling electron microscopies. The concentration profiles and the element distribution in the samples were plotted with the use of secondary ion mass spectrometry (*SIMS*) on the time-of-flight mass spectrometer (*TOF-SIMS*).

Electroconductivity was measured by a standard four-contact method in a special measuring cell equipped with gilded both conducting and potential electrodes. Investigation of the ferrite films sensitivity to the methane-air mixture was performed in a hermit chamber with a measuring cell and the sample inside. The sample was heated up to the temperatures within the range of 300-800 K at the heating/cooling rate of 10 K/min. The concentration of the combustible gas was set at 2.0%, what corresponded approximately to 40% of the lower concentration limit of the flame propagation.

Results and Discussion

Submicron ferrite films were deposited onto supports of Si (100) as a result of ion sputtering of the $NiFe_2O_4$ powder. The supports were 0.59 mm thick and the film had a surface glassy surface without any visible defects and inclusions. To be used in further investigations the plates were carefully cut with a diamond disk without distortion of the deposited layer into small specimens with the dimensions of 3 × 10 mm^2. Microstructural studies showed that the structure of the initial powder was not inherited in the films formed.

The green powder had a specific ferrite morphology of rounded particles sized no less than 2 μm (Fig. 1a), while after ion-beam sputtering a continuous film was formed of nanostructures particles on the supports. The result was achieved due to the fact that during ion-beam sputtering the energy of the atoms deposited onto the support was much higher than the thermal one. The film formed was under the high-energy influence of the ions rejected by the

target [8] and bombarding the deposit, therefore its uniform growth was hindered. In all cases, the film thickness formed on the sample did not exceed 600 nm. The microstructure was a uniform layer without fractures or any other flaws. The resultant coating consisted of agglomerated particles with the size of no less than 35 nm and was a continuous polycrystalline film with a definitely pronounced tubular texture directed towards the material formation (Fig. 1 b,d). The typical transverse dimensions of the tubular structures of the silicon support were equal to 30-50 nm. Meanwhile, the growth of the textured crystallites set on right from the silicon surface and was probably initiated by the support surface.

All films obtained were X-ray transparent independent of the conditions of sputtering or the support characteristics. The view of the diffraction pictures of the X-ray phase analysis (XRPA) was characteristic of amorphous materials, since the size of the grains constituting the film was rather small for X-ray diffraction and formation of the corresponding peaks for the nowadays sensitivity of the XRPA method.

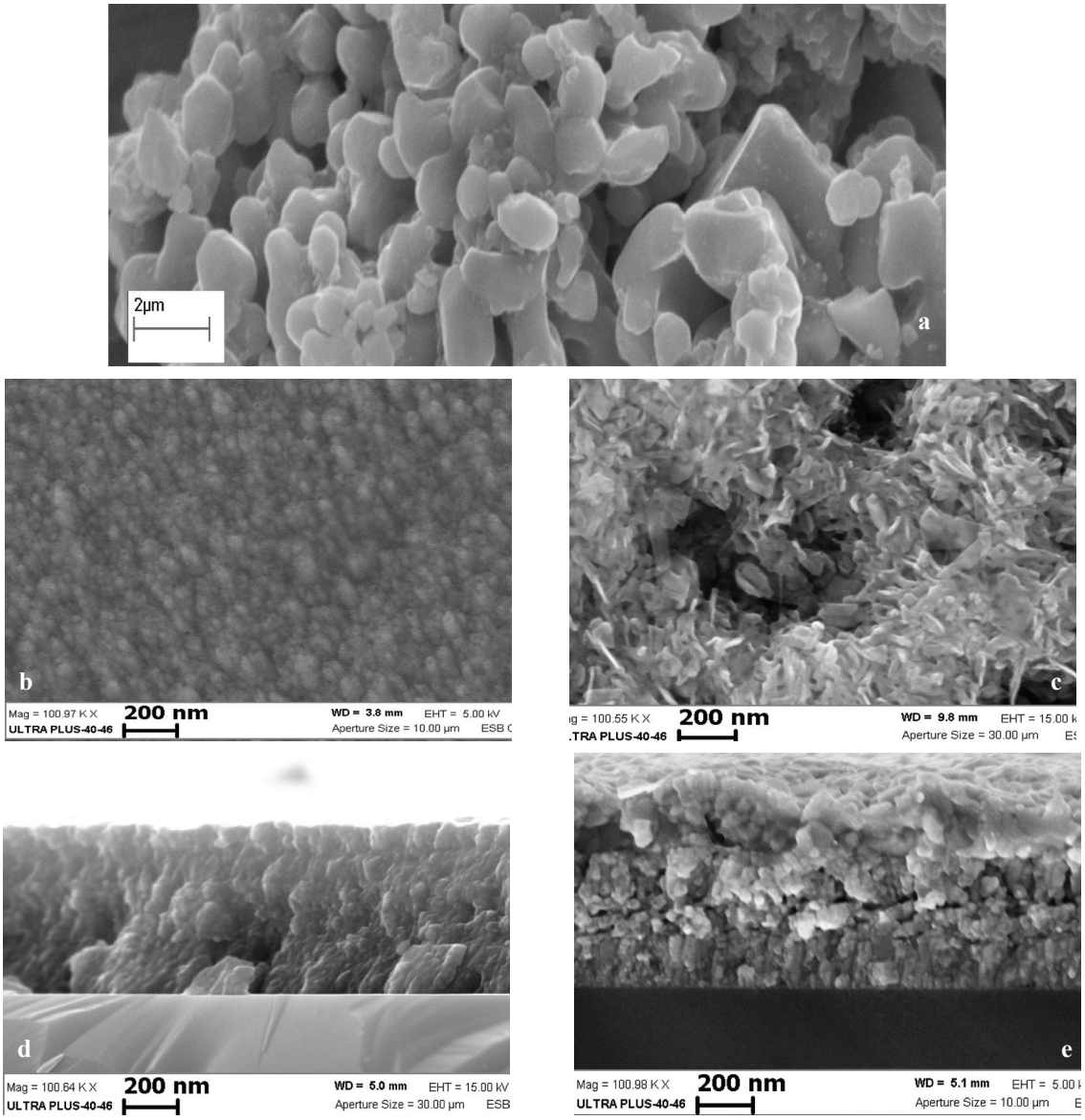

Fig. 1. Microstructure of the green powder (a) and a thin film of $NiFe_2O_4$ ferrite on the support Si (100) after ion-beam sputtering (b – surface, d – transverse fracture) and after annealing at 770 K/90 min in the air (c – surface, e – transverse fracture).

In the further experiments all samples were subjected to annealing for 90 min at 770 K under air with the heating/cooling step of 20 K/min. The procedure was aimed at stabilization of the properties of the ferrite layer, since when used as a gas-sensor material the ferrite gets heated up to the temperatures of

400-700 K, which are characteristic of the maximum values of gas-sensing oxide materials [9]. Under ambient conditions the electroresistance of the post-annealed sampled increased up to 39 kOm as compared to the value of 30 kOm observed before annealing of the ferrite films deposited onto the support.

To determine the temperature dependence of the resistance of the annealed samples $R = R(T)$ measurements were carried out via a triple cycle of heating-cooling within the range of 350-470 K (Fig. 2). Curves 1 and 2 therein belong to the measurements of resistance in the $NiFe_2O_4$ film under air and in the mixture containing 2.0 vol.% CH_4, respectively. Temperature dependence R is seen to have a specific bent at 384 K, which is also retained in the case of air-methane mixture. However, in the course of the temperature elevation the values of R_{air} and R_{CH4} keep different up to 421 K. The ratio $S = R_{CH4}/R_{air}$ exhibits a linear temperature dependence growing up to 403 K followed with a further drop in the range within 403-421 K. The S value in the maximum constituted 1.12. At the further temperature growth, the shape of curves 1 and 2 coincides ($S = 1$), i.e. the film sensibility has not been detected within this temperature range. It can be supposed that upon reaching the critical point at 384 K in the given material, there occurs a change of the mechanism of the charge transfer in the thin ferrite film. According to the reported data on the gas-sensitive materials [10], at certain temperatures the number of adsorbed molecules of the detected gas is achieved that makes the electrons of the mentioned molecules donate a significant contribution to the conductivity of the undersurface region of the material-adsorbent (a thin nickel ferrite film, in the present case). At the same time, the run of the plotted temperature dependence of electroresistance of the ferrite film $NiFe_2O_4$ corresponds to the data characteristic of the nickel-zinc films obtained according to the thick-film production technology [11], however in that case the bent was observed at 600 K. Such a displacement of the critical point can be attributed to the fact that according to the thick-filmed technology the films yielded are 20-60 μm thick. Thus the change of the mechanism of the ferrite film can be an activator of conductivity in the undersurface region of $NiFe_2O_4$ with participation of the adsorbed molecule of gaseous methane. This results in the appearance of the above described effect of the increase in the gas sensibility at 403 K. The further decrease in the S value and smoothing of the methane influence can be caused both with the process of desorption of the gas molecules from the oxide surface and the increase in the material conductivity.

Since the observed effects are essentially dependent on the morphological particularities of the film and the material composition, all samples were investigated by the methods of electron microscopy and time-of-flight mass spectroscopy. The microstructure obtained after the film annealing is shown in Fig. 1c,e. The texture disappearance was characteristic of all post-annealed films. In the case of the Si (100) support, formation of a porous structure and the particle size enlarging were observed. The film surface was looser (Fig. 1c) as compared to the initial one (Fig. 1b). The film was covered with non-through surface pores with a specific size of 300 nm. During observation of the sample fracture such large pores were not detected across the film thickness. In the film bulk (Fig. 1e) formation of small pores comparable in their size with the particles did not disturb the film continuity. Formation of small pores was probably provoked by reorganization of the film texture during annealing and by some enlarging of the particle size. Their presence appeared to be a positive factor for the increase in the specific area and, consequently, the material sensibility towards the detected gas. Thus, one may gain the formation of an optimum structure of the film by choosing the annealing mode which could allow regulation of the pore quantity by means of involving the intermediate layer to the texture reorganization.

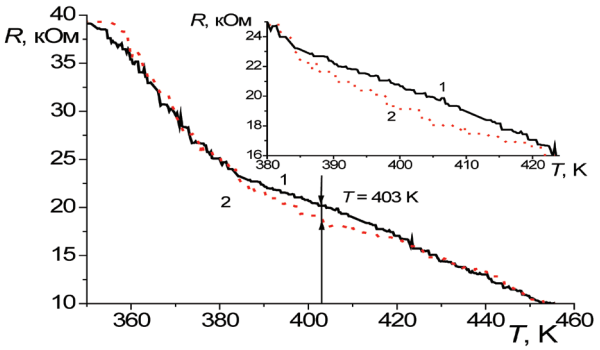

Fig. 2. The temperature dependence of the electrical resistance of the $NiFe_2O_4$ thin film deposited on the Si (100) support.

Since time-of-flight mass spectrometry is one of the most reliable tools of determination of the thin-film chemical composition, it was used to study element distribution in the ferrite films. The results obtained in the TOF SIMS analysis of the surface and depth of the annealed samples (Fig. 3) were harvested in the regime of sputtering for 10 min from the 150 × 150 μm^2 square. Graphic representation of the results of the analysis of the element distribution over the material surface as well as the microphotographs made with an electron microscope showed that the surface was a uniform substance layer composed of

nanosized particles without significant defects. The highest concentration in the near-surface region belonged to the ferrite-forming oxides $FeO:Fe_2O_3$ (a most light area) and NiO (a red area, according to the coloration scale) against the background of the rest substances having more dark coloration. The layer was mainly formed of oxides involved into the nickel ferrite formula $NiO:FeO:Fe_2O_3$ (Fig. 3). Herewith their ratio did not practically change along the thickness and corresponded to the nickel ferrite composition. The main specific feature was the presence of free elements of transition metals in the film composition. They could probably appear under the condition of incomplete oxidation during sputtering of the material because of the oxygen loss.

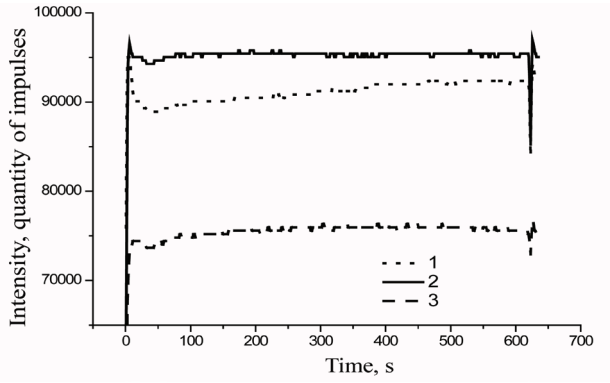

Fig. 3. Concentration profiles of distribution of the oxides-components of the ferrite over the $NiFe_2O_4$ film depth: 1 – Fe_2O_3; 2 – FeO; 3 – NiO.

Thus the proposed mechanism of gas sensibility is based on the presence of a developed surface of the ferrite film formed of nanostructured particles on the silent support. In this case, technological annealing did not cause undesired grain growth and gave the possibility of the pore formation inside the film material. These factors led to the increase in the surface and, consequently, in the gas-sensibility of thin $NiFe_2O_4$ films. Further investigations are supposed to be aimed at the influence of the manganese content on sensibility of the $NiMn_xFe_{2-x}O_4$ ferrite. This can be important since substitution of the iron ions with those of manganese brings about an extra charge exchange and should excite a stronger response of a sensor material towards the fixed concentration of the detected gas.

Conclusion

The first case of deposition of thin films of $NiFe_2O_4$ ferrite with thickness of an order of 600 nm onto the silent supports of Si (100) silicon with the use of ion-beam sputtering of the SHS-produced ferrite powder was described. The mean size of the particles forming the film was equal to 35 nm. The film annealing regimes, within which the ferrite grain size was not enlarged and the properties and composition remained were stable (770 K for 90 min), were experimentally determined. The temperature dependence of electroresistance of the obtained films was for the first time found to have a descending character both under air and in the presence of methane (the resistance of the samples of the given size diminished from 39 kOm at room temperature to 10 kOm at 450 K). The character of the effect produced by the morphological particularities, microstructure, and composition on the electroresistance and gas sensibility of the obtained ferrite films was investigated. It was found that the temperature interval of the $NiFe_2O_4$ film sensitivity towards the methane-air mixture 2.0 vol.% was T = 384-421 K ant the maximum ratio $S = R_{CH4}/R_{air} = 1.12$ was achieved at 403 K.

References

1. Kazin A.P., Rumyantseva M.N., Prusakov V.E., Suzdalev I.P., Maksimov Yu.V., Imshennik V.K., Novichikhin S.V., and Gaskov A.M., Neorgan. Mater., 2000, v. 46 (11), p. 1381-1386.
2. Maqsood A., Khan K., Anis-ur-Rehman M., Ali Malik M. J. Supercond. Nov. Magn. 2011. v. 24 (1-2). p. 617-622.
3. Sathishkumar G., Venkataraju C., Sivakumar K. J. Mater. Sci.: Mater. Electron. 2011, v. 22 (11), p. 1715-1724.
4. Su H.-Ch., Dai J.-Y., Liao Y.-F., Wu Y.-H., Huang J.C.A., Lee C.-H. Thin Solid Films, 2010, v. 518, p. 7275–7278.
5. Solid State Gas Sensing (Eds. E. Comini, G. Faglia, G. Sberveglieri), Springer:NY, 2009, – 337 p.
6. Busurin S.M., Busurina M.P., Kovalyov Yu.D., Kuznetsov M.V., and Morozov Yu.G. Abstr. VII Vseros. Conf. Ceramics and Composite Materials (Syktyvkar, June 21-25, 2010), p. 26.
7. V. Zhurin, Industrial Ion Sources, Wiley-VCH, ISBN 978-3-527-41029-3, 2011.
8. Sputtering of Solid Substances with Ion-Beam Bombarding (Ed. R. Berish), Mir: M., 1984, -336 p.
9. Satyanarayana L., Madhusudan Reddy K., Manorama S.V. Sensors and Actuators B, 2003, v. 89, p. 62-67.
10. Vasilyev R.B., Ryabova L.I., Rumyantseva M.N., and Gaskov A.M. Usp. Khimii, 2004, v. 75 (10), p. 1019-1038.
11. Bush A.A., Shkuratov V.Ya., Chernykh I.A., and Fetisov Yu.K. Zhl. Teor. Fiziki, 2010, v. 80 (3), p. 69-76.

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