

GRANULAR METAL- POLYMER COMPOSITES FORMED BY ION IMPLANTATION TECHNOLOGY

**B.Rameev^{a,b}, R.I.Khaibullin^{a,b}, B.Aktaş^a, and
V.A. Zhikharev^b, A.L.Stepanov^b, Yu.N.Osin^b, V.V. Bazarov^b, I.B. Khaibullin^b**

^a *Gebze Institute of Technology, P.K.141 41400, Gebze/Kocaeli, Turkey*

^b *Kazan Physical-Technical Institute, Sibirsky Trakt 10/7, 420029 Kazan, Russia*

ABSTRACT

Thin metal-polymer composite films were synthesized by high-dose implantation of 40 keV Fe⁺ and Co⁺ ions into epoxy and silicone polymers. The influence of both an initial relaxation state (viscosity) of polymer target and a dose of implantation on microstructures and magnetic properties of ion synthesized composite materials was investigated. The process of nucleation and growth of metal nanophase in polymer volume with dose increasing were observed by transmission electron microscopy. It was shown that various metal nanostructures (isolated particles with different morphology and sizes, multi-particles clusters, fractal-type agglomerates) and quasi-continuous monocrystalline films are formed at different initial viscosity of the targets, kinds of implanted ions and doses of implantation. Magnetic properties of metal-polymer composite films were studied by ferromagnetic resonance (FMR) method. The observed FMR spectra and their orientation dependencies reflect the essential differences in the magnetic properties of the composite films formed in the epoxy and silicone substrates at different viscosity and doses. The dose dependencies of effective magnetization are presented for iron-implanted silicone films synthesized at different relaxation state of polymer substrate. The dependence of FMR spectra on a type of implanted atoms (iron or cobalt) is also discussed.

1. INTRODUCTION

High-dose implantation of metal ions into insulators leads to an excess of the dopant, which is unstable in the form of metal atoms dispersed in the volume of dielectric substrate. The system relaxes into precipitates of metal which are variously termed colloids, granules or nanoparticles. In this way the metal granular films and nanostructures may be formed in the near-surface layers of irradiated insulators. The production of the inclusions is not limited to metals, and precipitates of other nanophase materials can be obtained in insulators by ion implantation method. However, the study of magnetic films and nanostructures in polymers is particularly interesting due to a high potential of these composite materials for applications in the magnetic data storage industry and for magnetosensor electronics.

A series of papers [1-4] deal with synthesis Cu, Ag, and Fe granular films by ion implantation in polymers. In these works the different polymers in solid glassy-like state were used as matrices for ion synthesis of metal nanoparticles. The feature of the present work is that the method of ion implantation into polymer matrix of *variable viscosity* is developed to form thin metal

granular films and nanostructures. Epoxy and silicone substrates of different viscosity were used as a target for implantation by the iron and cobalt ions at different doses. We present the structural and magnetic studies of ion-synthesized composite materials by electron microscopy and magnetic resonance methods.

2. EXPERIMENTAL

The ion-beam synthesis of metal-polymer composites was performed by implantation of 40 keV Fe⁺ and Co⁺ ions into the epoxy and silicone polymers being under different stages of curing process in the dose range $(0.1-1.8) \times 10^{17}$ ions/cm² and with the current density 4 μ A/cm². The implantation was carried out on ILU-3 ion-beam accelerator at room temperature with the residual vacuum of 10^{-5} Torr. For implantation the following polymer matrixes were used:

Epoxy: The epoxy substrates were prepared by hand deposition of the mixture of the commercial epoxy resin (ED-20, 93 weight %) and the hardener (polyethylenepolyamine, 7 %) on glass plates. The thick of produced epoxy films was equal near 1 mm. During the curing process (polymerization) the epoxy mixture was passing the different relaxation states: from the viscous-flow through viscoelastic to the solid glassy state. The first viscous-flow stage of epoxy was characterized by measuring of the dynamical viscosity (η) by using a capillary viscometer with the accuracy of 10%. Epoxy viscosity varied in the range 20-180 Pa s during the first 250 min of cure process (Fig.1). A set of epoxy-based samples was prepared by Co⁺ implantation during this stage. The glassy-like solid substrates (received after 24 hours of the cure process) were used for preparation of another set of Co-implanted samples.

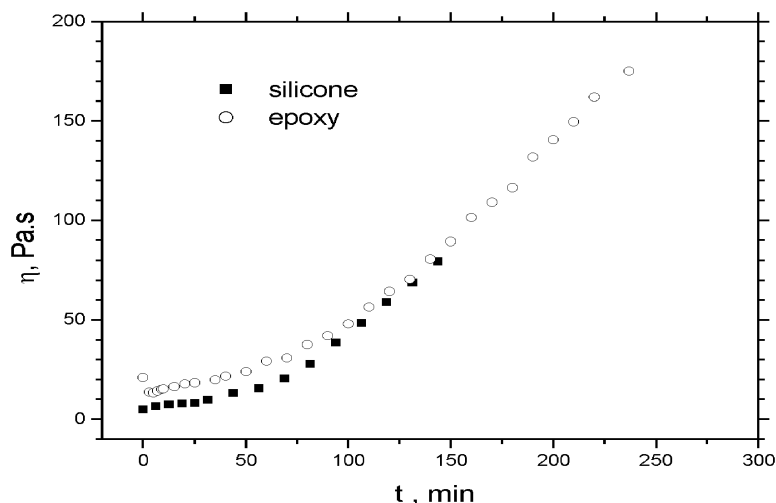


Figure 1. Viscosity of epoxy composition vs. time of the cure process at the room temperature.

Silicone: Commercial silicone polymer (SKTN-F) were used as substrate for implantation. A mixture of viscous silicone resin (low-molecular methyl-phenyl-siloxane, 97 weight %) with curing agent (diethyl-dicaprilat of tin, 3%) was prepared, and thin (150 μm) silicone films were deposited on glass plates by centrifugation of the viscous mixture. Then, the implantation of Fe^+ and Co^+ ions into both viscous-flow substrates at initial stage of curing process and fully cured resin-like silicone films was carried out. The dynamic viscosity of viscous substrates measured by a capillary viscometer was equal to 20 Pa·s at an initial moment of the implantation. The viscosity of cured silicone polymers had a value of the order of 10^3 - 10^4 Pa·s [5].

For microstructure studies the thin surface layers of irradiated polymers were obtained by chemical etching. The morphology and the crystalline phases of the synthesized metal granular films were studied in the plane of irradiation by electron diffraction and transmission electron microscopy (TEM) on the TESLA-BS500 and EM-125 microscopes. The specimens for cross-section TEM were prepared by using microtome LKB. Magnetic resonance spectra of the metal-polymer composites were recorded at temperatures ranging from 4.2 K to 300 K with IRES-1003 and Bruker EMX spectrometers operating in X-band (≈ 9.5 GHz). As usual, the field derivative of microwave power absorption (dP/dH) was registered as a function of the applied magnetic field H .

3. RESULTS AND DISCUSSION

3.1. Microstructure of Cobalt Epoxy Composites

It is established that high-dose cobalt ion implantation in the near subsurface volume of both viscous and solid epoxy matrices results in the formation of the thin films of nano-size cobalt particles dispersed in the epoxy matrix. Data on TEM cross-section showed that the synthesized metal-organic composite films are about 300-500 Å of thickness and occur at the depth of 150-200 Å from the principal surface of the irradiated polymer. Figure 2 shows TEM images and diffraction for a series of films synthesized at different parameters of the ion beam and epoxy viscosity. It is seen that the morphology, the average size and size dispersion of cobalt granules, and their crystalline structure to a great extent depend on the epoxy viscosity. In the viscous matrices at implantation doses in the range of 1.2 - $1.5 \times 10^{17} \text{ cm}^{-2}$ we have observed formation of particles having various forms: wormlike ($\eta=20$ Pa·s, Fig. 2a), spherical ($\eta=30$ Pa·s, Fig. 2b), cubic ($\eta=90$ Pa s, Fig. 2d), and bands of ultra small cobalt particles ($\eta=50$ Pa·s, Fig. 2c). In the solid-state epoxy only drop-like grains (Fig. 2e) were grown as a result of implantation in the range of dose 0.3 - $2.5 \times 10^{17} \text{ cm}^{-2}$. The particular interesting result was obtained in the experiment when cobalt ions were implanted into the viscous matrix ($\eta=170$ Pa s) at the enhanced dose of $1.8 \times 10^{17} \text{ cm}^{-2}$ and the current density $10 \mu\text{A}/\text{cm}^2$. Micron particles in the form of plates with regular hexagonal form and crystal structure corresponding to the monocrystal phase α -Co were obtained (Fig. 2f).

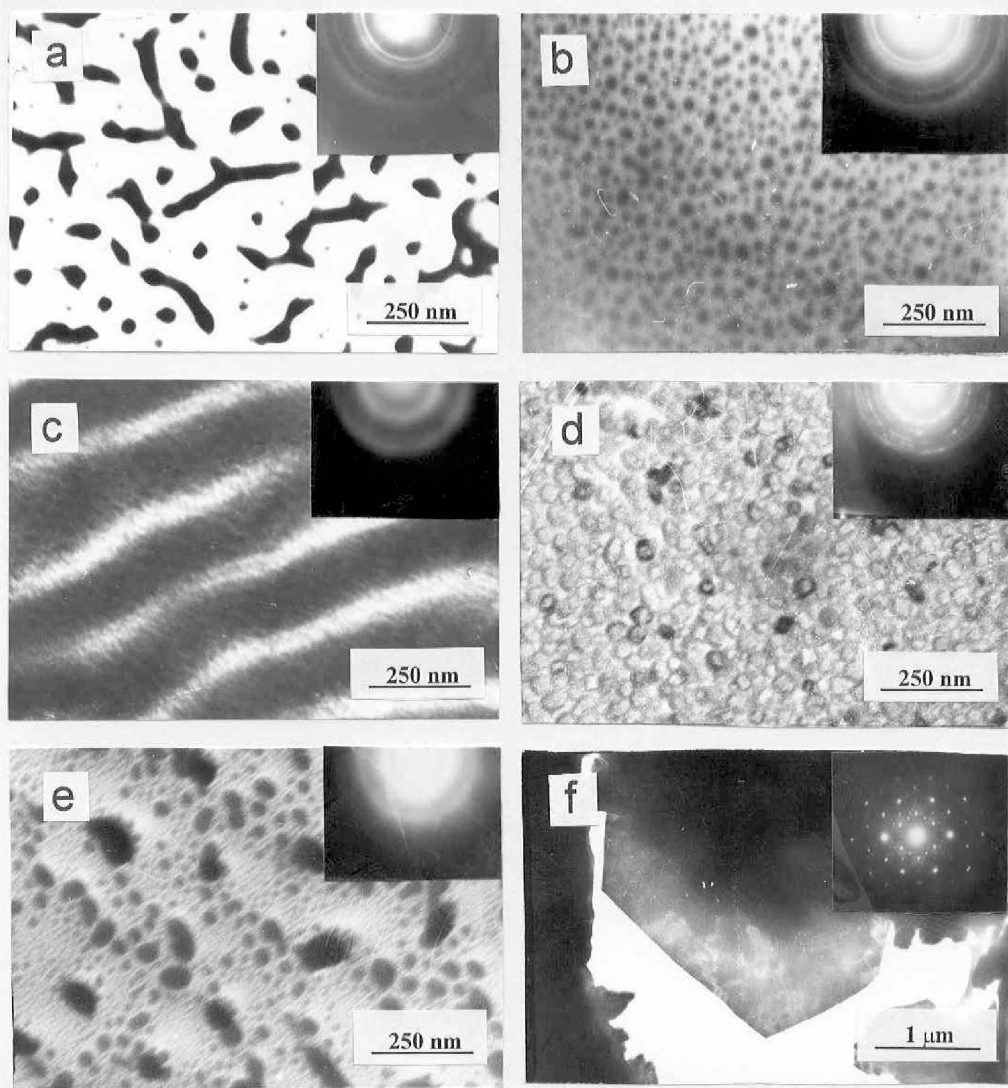


Figure 2. Bright field TEM images of cobalt films formed by Co⁺ implantation in epoxy matrix at different viscosity (η): a) 20 Pa s, b) 30 Pa s, c) 50 Pa s, d) 90 Pa s e) solid state polymer. The implantation parameters for films: (a), (d), (e) - $F=1.5 \times 10^{17} \text{ cm}^{-2}$, $J=4 \text{ } \mu\text{A/cm}^2$; for (b) and (c) - $F=1.2 \times 10^{17} \text{ cm}^{-2}$, $J=4 \text{ } \mu\text{A/cm}^2$. Tablet hexangular plates (f) were formed at $F=1.8 \times 10^{17} \text{ cm}^{-2}$, $J=10 \text{ } \mu\text{A/cm}^2$ and viscosity $\eta=170 \text{ Pa s}$.

Electron diffraction measurements enabled us to establish (see insets in Fig.2) that the crystal structure and phase composition of the films formed, to a great extent, depend on the relaxation state of the matrix during irradiation. It is amorphous in the solid-state matrix (Fig.2e), and polycrystalline (pure α -Co phase for films in Figs.2a-2c, mixed α -Co / β -Co phase for those in Fig. 2d) or even monocrystal (Fig. 2f) for the samples obtained by implantation into the viscous matrix.

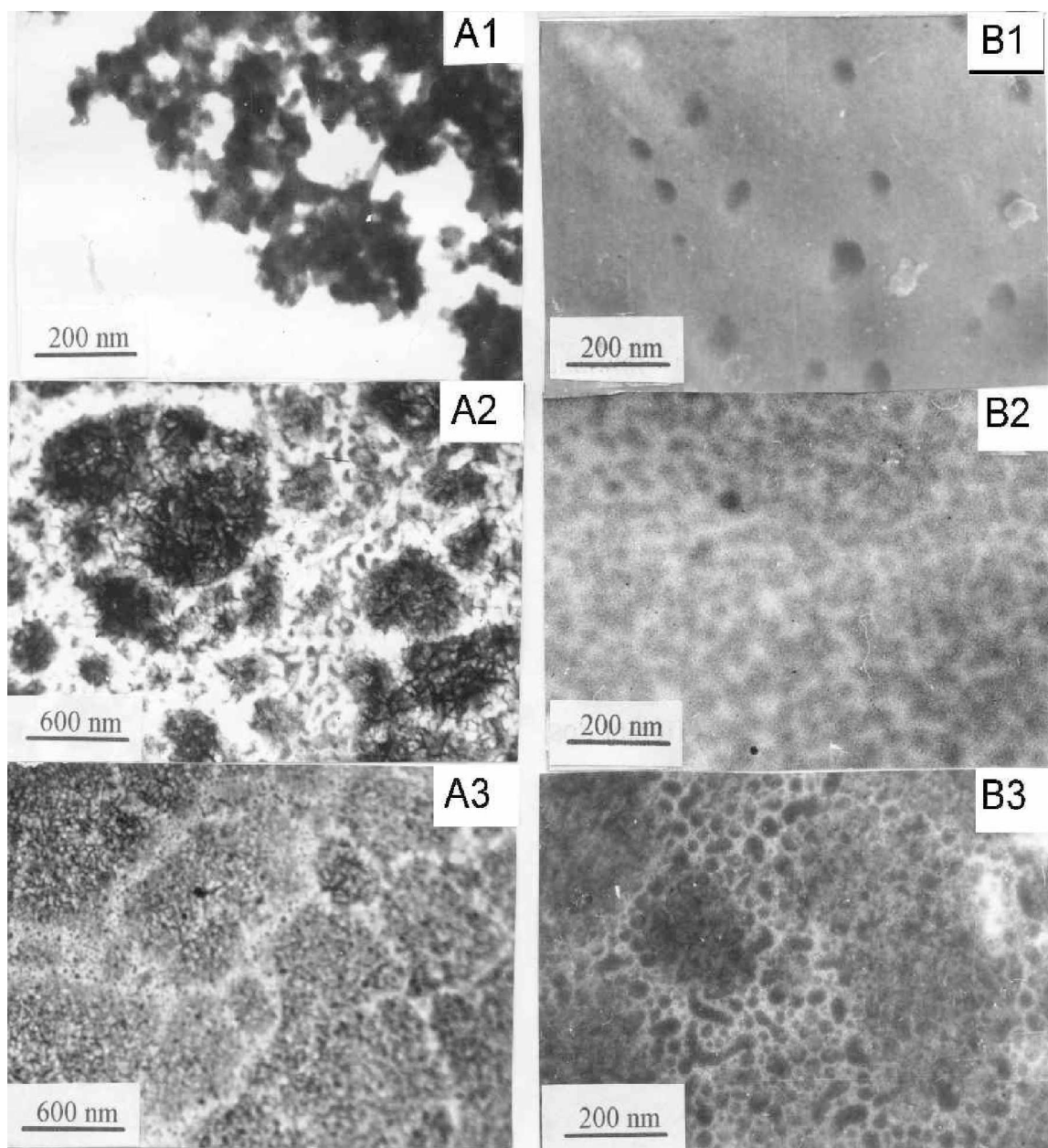


Figure 3. TEM images of iron granular films formed by Fe⁺ implantation in viscous (A1-A3) and solid (B1-B3) silicone polymers at different dose: 1) 0.6×10^{17} , 2) 1.0×10^{17} , 3) 1.4×10^{17} ions/cm².

3.2. Microstructure of Iron/Cobalt Silicone Composites

As established by TEM, the iron and cobalt granular films are formed in the near-surface volume of silicone polymers at implantation doses higher than 0.3×10^{17} ions/cm². The TEM cross-section views of implanted polymers showed that synthesized metal films are about 30-50 nm thick and they are buried at a depth 20-25 nm.

Figure 3 present TEM plan view images of iron films created at different doses in viscous (a) and solid (b) silicone substrates. It is seen that the kinetics of film growth and film structure depend on the relaxation state of the implanted silicone polymer.

The iron granular films formed in viscous silicone consist of nanoparticles agglomerates. These agglomerates present a set of connected iron nanoparticles and they are already formed at a dose equal to 0.6×10^{17} ions/cm² (Fig.3-A1). With increasing dose, the average size of these agglomerates increases and they begin to touch each other to form a connecting network of needle-like iron nanoparticles (Fig.3-A2,A3). In the irradiated solid-state silicone matrix, the isolated drop-like iron particles with an average size of 20-25 nm were observed at low doses (Fig.3 B1). With increasing dose, the number of nanoparticles increases (Fig. 3-B2,B3).

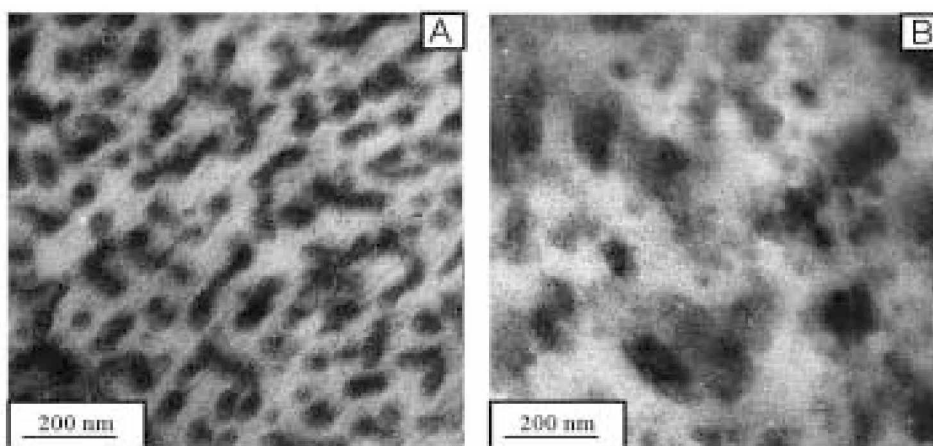


Figure 4. TEM images of cobalt granular films formed by ion implantation in viscous (A) and solid (B) silicone polymers at a dose of 1.25×10^{17} ions/cm².

Fig. 4(A,B) shows the microstructure of cobalt granular films produced in viscous (A) and solid (B) polymers implanted with a dose of 1.25×10^{17} ions/cm². It is seen that large (100-200 nm) Co groups of closely packed particles are formed in viscous substrates. In implanted solid polymers the cobalt granular film consists of widely separated fine particles and their size being spread in rather broad range until 100 nm.

For both type of films, Fe and Co implanted, the electron diffraction measurements were also performed. The electron diffraction pattern exhibited the rings for polycrystalline bcc α -Fe structure in iron films, and the hexagonal α -Co metallic phases in the polymers implanted by cobalt.

3.3. *Magnetoresonance Properties of Co/Fe - Epoxy/Silicone Composite Films*

The magnetic resonance signals were detected in all types of the epoxy/silicone Co/Fe films. The dependence of magnetic resonance spectra on orientation (θ) of the static magnetic field

(H) relative to the normal of film (n) was measured. A resonance spectrum for all samples starting from some threshold implantation dose contained the component which orientation dependence was typical for ferromagnetic resonance (FMR) in thin granular magnetic films: when $H \parallel n$ ($\theta=0^\circ$), then absorption lines are shifted to the high field side, when $H \perp n$ ($\theta=90^\circ$) they are shifted to the low field side. Threshold where the FMR signal appeared were different for various films. For example, the cobalt-epoxy composites exhibit the signal only for implantation doses higher than $1.8 \times 10^{17} \text{ cm}^{-2}$, even the iron and cobalt implanted silicone composites showed a resonance signal at much smaller dose as $0.6 \times 10^{17} \text{ cm}^{-2}$. As an example, the FMR spectra of iron films synthesized in viscous (A) and solid silicones (B) at a dose value equal to $0.6 \times 10^{17} \text{ ion/cm}^2$ are presented on Fig.5 for different magnetic field orientation. As one would expect with increase of the implantation dose the intensity of the FMR signal also increased.

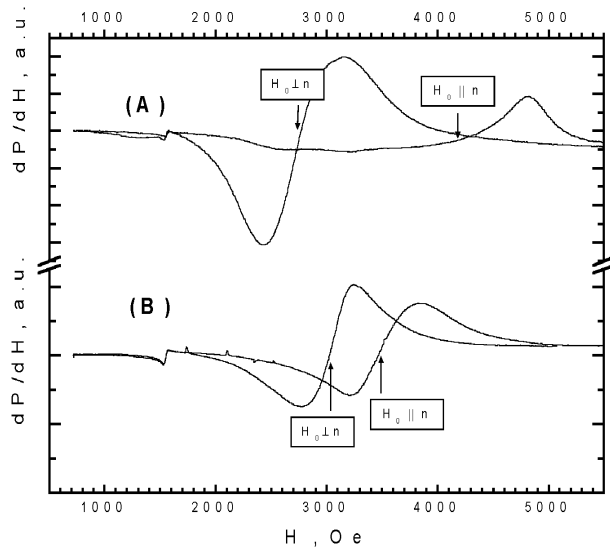


Figure 5. The FMR spectra of iron granular films formed by Fe+ implantation in viscous (A) and in solid (B) silicone polymers at dose of $0.6 \times 10^{17} \text{ ion/cm}^2$ and for two orientations of the applied magnetic field relative to normal of film plane.

The typical spectra dependence on temperature is illustrated by the example of silicone films implanted by iron and cobalt ions. Fig.6 is showing the spectra for viscous and solid samples implanted with Fe and Co ions with a dose of $1.25 \times 10^{17} \text{ ions/cm}^2$ under perpendicular orientation ($\theta = 0^\circ$) with respect to magnetic field. In the viscous samples (Fe and Co both) the FMR signal (H_{FMR}) shifts to the high field side for the orientation $\theta = 0^\circ$ with the temperature decrease (and to lower fields for the parallel orientation, not presented here). For all samples the signal gradually broadens, excepting the

Co- implanted viscous one, where at lower temperatures a sort of “structure” of FMR absorption evolves under orientation $\theta = 0^\circ$. Besides the FMR signal, there are some extra resonance signals in the spectra (Fig.6):

- 1) Narrow signal at $H=1600 \text{ Oe}$ with paramagnetic behaviour and small linewidth was identified as a signal of glass plate and excluded from further consideration.

Low-field absorption signal (H_L) is observed in the range 1000- 2500 Oe (Fig.6) for the perpendicular orientation. The signal of low-field absorption was also found in some other implanted samples with smaller doses and exhibits the similar behavior. Even the origin of the signal is not well understood, as possible reason for the low-field absorption the effect of magnetic dipolar fields could be considered.

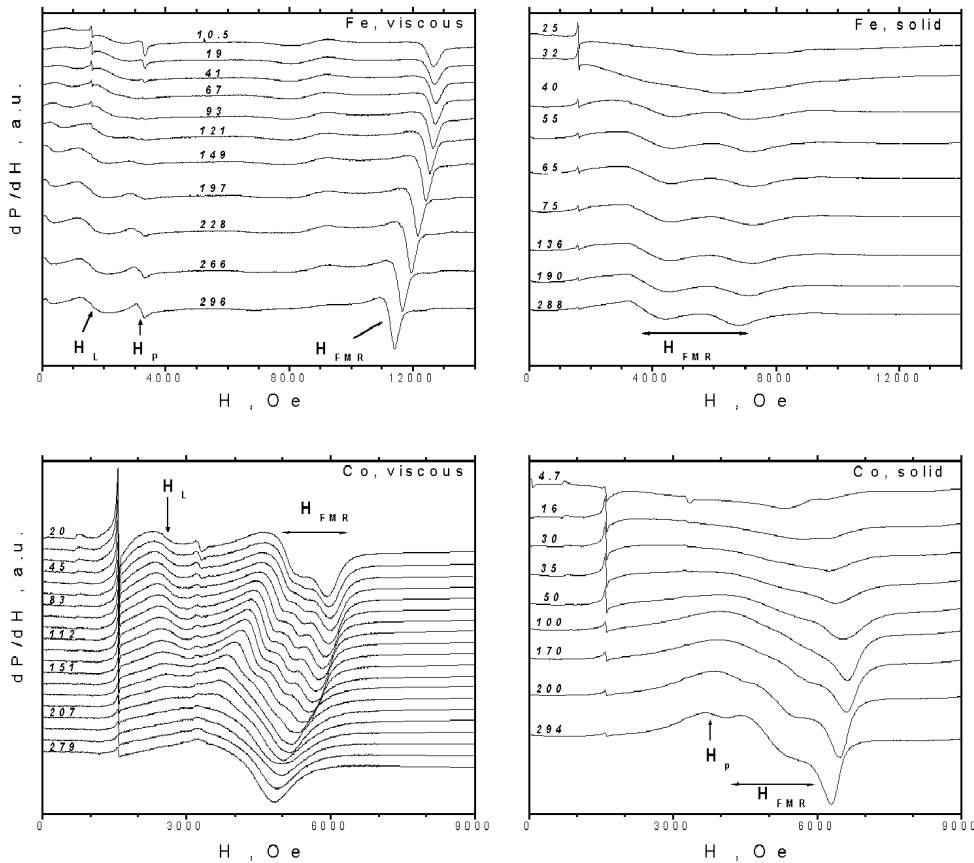


Figure 6. The temperature dependencies of FMR spectra of iron and cobalt granular films synthesized in viscous and solid silicone polymers at a dose of 1.25×10^{17} ions/cm². The FMR absorption H_{FMR} , low field absorption H_L and isotropic paramagnetic signal at $g=2$ H_P are labelled.

2) The isotropic signal with $g=2$ (H_P) is observed for Fe-implanted viscous sample and Co-implanted solid sample at temperatures more than 100-200K*. The signal was associated with the resonance response from the fraction of fine particles, which are well isolated from the

* The signal is much more pronounced for samples with smaller implantation dose. For example, in Co-implanted samples this signal clearly observed above 200K for both viscous and solid samples with implantation dose 1.0×10^{17} ions/cm².

particle agglomerates, and exhibit the superparamagnetic (SPM) properties [6]. At higher temperatures the magnetic moment direction of these particles fluctuates quickly in the film plane. As the averaging effect of thermal fluctuations of magnetization is reduced under decreasing temperature the signal disappears.

Here we would like to mark only the most important results:

As can be seen from Figs.5-6, the values of magnetic resonance field, FMR line shapes and their orientation and temperature dependencies strongly depend on the relaxation state of the substrate during the implantation and the type of implanted ions (Fe or Co). The FMR signal of the granular magnetic film results from the single particles entering the film. (Only at highest doses of implantation, when the continuous metal layer start to form, the anisotropy of the FMR signal due to the shape of sample as whole would be essential [7].) An isolated spherical magnetic particle should provide the Lorentzian-like line shape of the resonance absorption at $H=3400$ Oe. According to the electron microscopy studies the shape of particles essentially deviate from spherical (typical size of particles is about 100 nm in plane of the thin film compared with the thickness of granular layer about 30 nm) and one can expect the contribution of particle shape anisotropy in FMR. Besides, magnetocrystalline anisotropy (together with the orientational distribution of the easy axes of anisotropy) and the interparticle magnetic dipolar interaction may contribute to the shifts mentioned above and the FMR lines broadening. In this way the analysis of the FMR spectra peculiarities observed in the implanted silicone samples should be performed with respect to the structure features of the synthesized granular metal films.

Structural investigations showed that in the Fe- implanted viscous silicone samples the planar agglomerates of iron needle-like particles are formed, while the solid silicone samples consist of widely separated nanoparticles of oblate ellipsoidal metal particles [8]. As seen from Fig. 5, a value of resonance field of FMR signal for Fe- implanted solid sample is smaller than for the viscous- implanted one. The magnitude of the shift of FMR line results from following factors: the effective magnetization and the particle shape anisotropy. The effective value of magnetization M_{eff} of the granular thin films may be calculated from magnetic resonance data by using a modified Kittel's equation [9]. In a rough approximation, $M_{eff} = Q \times M$, where Q is the volume percentage of magnetic metal particles in a composite metal-polymer film and M is the magnetization of the particles. In the case of isolated drop-like iron particles of the solid samples, the value M_{eff} is expected to be smaller than for large planar agglomerates of viscous silicone samples (Figs. 3 and 4) as well as the value of the particle shape anisotropy. In Fig. 7, the ion dose dependencies of calculated M_{eff} values for iron films synthesized in viscous and solid silicone matrices are presented. It is seen that the effective magnetization is larger and increases rapidly with increasing implantation dose for iron films formed in viscous matrix.

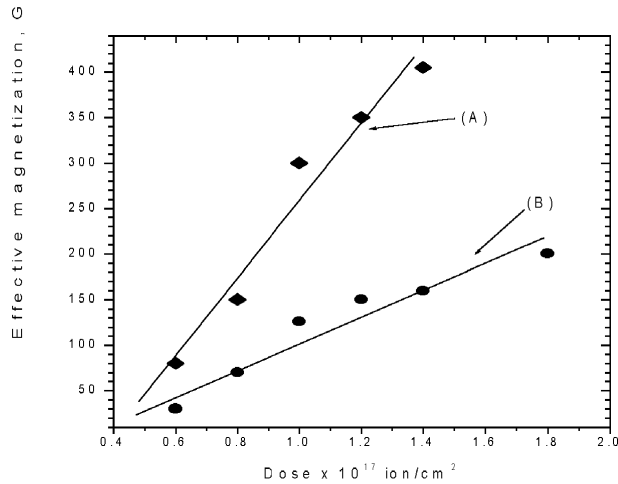


Figure 7. Ion dose dependencies of the effective magnetization of iron granular film formed by Fe⁺ implantation in viscous (A) and in solid (B)

The temperature shift of FMR line in the Fe- implanted sample is apparently related to the increase of effective value of magnetization of the agglomerates with the temperature lowering.

In viscous silicone Co- implanted samples the closely packed cobalt agglomerates are also formed, consisting of particles of oblate ellipsoidal or spherical form, but they do not touch each other as do the Fe particles at the same doses.

As for the epoxy polymer the FMR

response was observed only at highest implantation doses, because the extraordinary structures formed under some values of epoxy viscosity are either highly non-homogeneous (as worm-like structures on Fig.2A) or also consisted of ultra small non-contacting metal particles (as "bands" on Fig.2C). The tendency of Co ions to coagulate in the particles with the shape close to spherical is favoured by more high value of the surface tension energy compared with magnetostatic energy in the metallic cobalt rather than iron. That is the reason why the thin plates of cobalt ions in epoxy polymer were grown only under condition of high magnitude of implantation current and for high values of polymer viscosity. The same tendency is observed in the implanted silicone polymers. As seen from the Fig.6, in the case of the silicone samples the shift of the FMR line for viscous sample is smaller than for the solid one. This is due to the shape of individual Co-nanoparticles is much more close to sphere in the viscous polymer than in the solid one. On the other hand, the granular metal films formed in the solid samples characterized by considerable dispersion of granule sizes, that results in formation of "structure" of FMR absorption in the Co- implanted solid sample and in the appreciate FMR response from granules with largest sizes in high field range.

A shift of resonance signals with decreasing temperature under orientation $\theta = 0^\circ$ for both Fe and Co solid samples is much smaller than for the viscous ones. Besides the above-mentioned fact that for the Fe- implanted samples M_{eff} for solid polymer much smaller than for the viscous, there is another reason. For both Fe and Co solid samples the temperature shift of the signal is determined by the average value of dipole-dipole interactions between individual granules, which are more diluted than the particle agglomerates of viscous sample. On another hand, the considerable inhomogeneity of microstructure of the solid samples result in broad dispersion of the magnitude of the dipolar fields. As result, a reduction of thermal fluctuations of magnetic moments and SPM blocking in the particles produce in solid samples the much pronounced broadening (Fig.6) of the resonance lines at lower temperatures [10].

Acknowledgements

This work was supported by the grant No 99-03-32548 of the Russian Basic Research Foundation and by the grant No 99-A-01-02-14 of Research Fund of Gebze Institute of Technology. We are also grateful to the TUBITAK-NATO PC Advanced Fellowship Programme for financial support of Dr. R.I. Khaibullin at the Gebze Institute of Technology.

REFERENCES

-
1. J.H. Das, J.E. Morris, J. Appl. Phys. **66** (1989) 5816.
 2. N. C. Koon, D. Weber, P. Penrsson, and A. I. Shindler, Mat. Res. Soc. Symp. Proc. 27 (1984) 445
 3. K. Ogava, United State Patent, N 4.751.100 (1988).
 4. V. Petukhov, V. Zhikharev, M. Ibragimova, E. Zheglov, V. Bazarov, and I. Khaibullin, Solid State Commun. **97** (1996) 361.
 5. M. Schatz, in *Silikonoviy kauchuk*, edited by A.L. Klebanckij (Khimiya press, Leningrad, 1975) (in Russian).
 6. L. Neel. C R Acad Sci **228**, 664 (1949); C.P. Bean, J. D. Livingston. J Appl. Phys. **30**, 120S (1959).
 7. Netzelmann U. J Appl Phys 1990; 68: 1800
 8. Petukhov V, Zhikharev V, Ibragimova M, Zheglov E, Bazarov V, and Khaibullin I. Solid State Commun 1996; 97: 361.
 9. Rubinstein M, Das BN, Koon NC, Chrisey DB, Horwitz J. Phys Rev B 1994; 50: 184
 10. Sharma VK, Baiker A. J Chem Phys 1981; 75: 5596.