Functional Materials 17, No.4 (2010)

Morphology and optical properties of films with magnetite nanoparticles

O.Korovyanko[*], N.Dmitruk, S.Mamykin, M.Sytnyk[*], O.Lytvyn, P.Fochuk[*]

V.Lashkaryov, Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., 03028 Kyiv, Ukraine
[*]Faculty of Inorganic Chemistry, Chernivtsi National University, 2 Kotsyubynskogo St., 58012 Chernivtsi, Ukraine

Received December 12, 2009

Thin films containing Fe_3O_4 nanoparticles have been prepared by spin coating method on Si substrates and studied by AFM and spectroscopic measurements in the range 0.4–1.1 μm. The films exhibit a significant light scattering due to agglomeration of nanoparticles.

Тонкие пленки с включением наночастиц Fe_3O_4 изготовлены методом центрифугирования на подложках Si и исследованы методами атомной силовой микроскопии и оптической спектроскопии в диапазоне 0,4–1,1 мкм. Пленки демонстрируют значительное рассеяние света благодаря агломерации наночастиц.

1. Introduction

Magnetite in nanoparticular form is used widely in different areas such as liquid seals, optics, spintronics, sensors, biology and medicine due to flexibility in manipulation by magnetic field and biocompatibility. It might be used for magnetic recording media itself [1] or as a precursor for γ-Fe_2O_3 [2]. Some conducting polymers with Fe_3O_4 nanoparticles have been prepared with interesting conductive and magnetic properties [3]. An intermediate step between the synthesis of nanoparticles and their use in practical devices is their organization within solid matrices, such as polymers, glasses, or ceramics. Such combinations of a solid matrix with nanometer sized components of a different material are often referred to as nanocomposites. The optical properties of such nanocomposites depend strongly on the size and shape of magnetic nanocrystals and their aggregates [4]. Different factors can influence the aggregation process. These include the surrounding media, the surfactant used to segregate the particles, temperature and magnetic field. Recently, the multilayered systems where magnetic layers alternate with dielectric ones attract significant attention due to their specific interaction with light. The aim of this work is to study the possibility to use the nanocomposite films with Fe_3O_4 in preparation of magnetic photonic crystals. Magnetic materials are promising as prospective components of magnetic photonic crystals, because they allow tuning of their optical properties under dc magnetic field action [5]. For example, the light polarization state can be changed from elliptical to circular one by variation in magnetization vector.

2. Experimental

In this work, the sol-gel method was used to obtain the magnetite nanocrystals of 10 to 15 nm average size as confirmed by TEM measurements (Fig. 1). The synthesis procedure for Fe_3O_4 nanoparticles based on data from [6] can be described as follows.

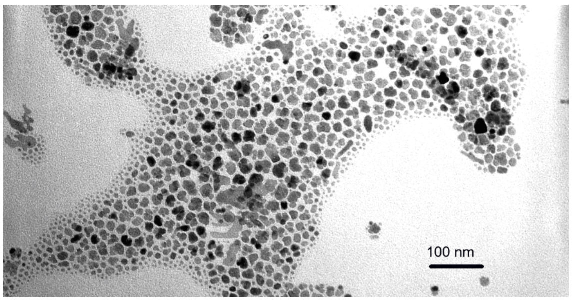

Fig. 1. TEM images of prepared Fe_3O_4 nanoparticles of 10–15 nm average size. The particle shape is octahedral that is typical of magnetite.

For Sample 1 – 100 ml water solution of 0.01 M Fe^{2+}, 0.02 M Fe^{3+} (from iron chlorides) mixed with 12 ml of NH_4OH (20 %) and 10 ml of oleic acid. For Sample 2 – 100 ml of 0.02 M Fe^{2+}, 0.04 M Fe^{3+} mixed with 12 ml of NH_4OH (20 %) and 10 ml undecylenic acid. Oleic and undecylenic acids are used here as surfactants. The reactions occurring can be written as:

$$Fe^{3+} + 3OH^- \rightarrow FeO(OH) + H_2O$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$$2FeO(OH) + Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O.$$

The spin coating technique was used to deposit the films containing Fe_3O_4 nanoparticles onto Si substrate. In this case, the polyvinyl styrene was used as the coating layer and binder. The Sample 1 was prepared by deposition of single layer of magnetite nanoparticles while five layers have been deposited for Sample 2. Some films were thick and flexible enough to peel off the substrate, so there was a possibility to measure the light transmittance therethrough. The reflectance of the films was also measured in the 0.4–1.1 μm range.

Morphological characteristics and specific properties of the obtained composite structures were studied by atomic force microscopy (Fig. 2). The Sample 1 (thin film) demonstrates a large relief formed by agglomerates of nanoparticles with lateral size around ~100 nm. The Sample 2 shows a smooth surface with low roughness, probably because of total film thickness where nanoparticles and agglomerates thereof were hidden and a more suitable surfactant used (undecylenic acid).

Optical properties of thick film (Sample 2) were studied by measuring the transmittance (T) and reflectance (R) of a free nanocomposite film. The film was thick

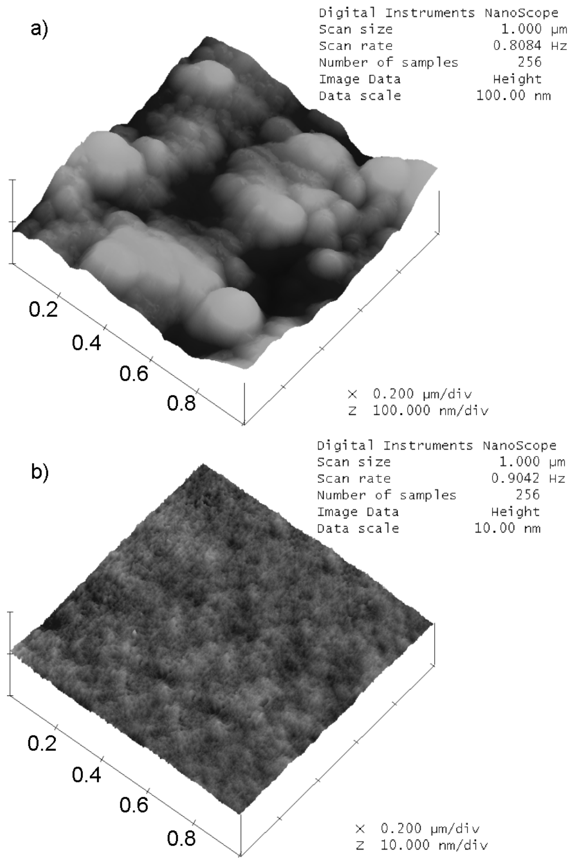

Fig. 2. AFM images of Fe_3O_4 composite films made of Samples 1 (a) and 2 (b) with 1 layer (a) and 5 layer (b) thickness.

enough and it was possible to peel it off from the substrate. Then light absorption (A) (Fig. 3a) for the films was calculated as $A=1-R-T$. The spectral dependence of extinction coefficient $k(\lambda)$ (Fig. 3b) was calculated from the absorption A using the following relations:

$$A = 1 - \exp(-\alpha \cdot d)$$

$$\alpha = \frac{4 \cdot \pi}{\lambda} \cdot k,$$

where α is the absorption coefficient; d, the film thickness; λ, the wavelength.

Optical properties of thin film (Sample 1) were studied by measuring the spectral dependencees of polarized light reflectance only at different angles of incidence. It was impossible to measure the film transmittance, therefore, the calculations were more complicated. The extinction coefficient $k(\lambda)$ (Fig. 3b, curve *1*) was eliminated from reflectance measurements by fitting using Fresnel equations [7]. Then the absorption coefficient α and absorption A were ob-

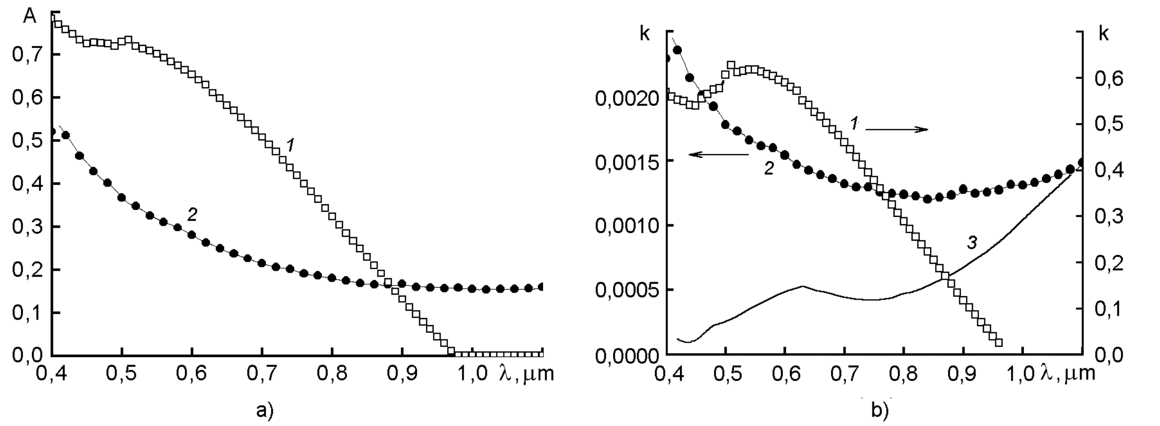

Fig. 3. Measured spectral dependences (a) of the light absorption (A) for thin film (*1*) on Si substrate (Sample 1) and for free film (*2*) prepared from Sample 2. Spectral dependences (b) of extinction coefficient *k* for the thin film (*1*) (Sample 1), free film (*2*) (Sample 2) and for the bulk material [8] (*3*).

tained using the above formulas. The significant film roughness (Fig. 2) comparable with the film thickness and a nonideal fitting resulting therefrom provides a rather rough estimation of the extinction coefficient, but a significant difference from the bulk material properties (Fig. 3b, curve *3*) is nevertheless obvious. The curve shapes differ most in the IR spectral region; perhaps this is connected with nanosized character of magnetite. The fact that the absolute extinction value is even higher than that for bulk material [8] in some spectral regions could be due to light scattering, increased concentration of Fe, FeO components in magnetite nanoparticles, and possibly to incorrect estimation of film thickness.

The obtained dependence $k(\lambda)$ for nanocomposite thick film differs significantly from the corresponding dependence for the bulk material [8] (Fig. 3b, curve *3*) and for the thin film (curve *1*). The curve shape and the milky color of studied films suggests that the light scattering is here of a considerable importance. To check the influence of the scattering, the absorption spectrum $A(\lambda)$ was drawn in coordinates $1/\lambda^4$ (Fig. 4). The linear part of the curves confirms the idea of light scattering significant influence on the film optical properties. The absorption of thin film (Sample 1) (curve 1) exceeds significantly that of thick film (curve *2*). This fact correlates with increased surface roughness observed in Sample 1 by AFM (Fig. 2). The light scattering is proportional to the size of the structures responsible for the surface roughness. There is a power dependence with coefficient 4 [9]. Therefore,

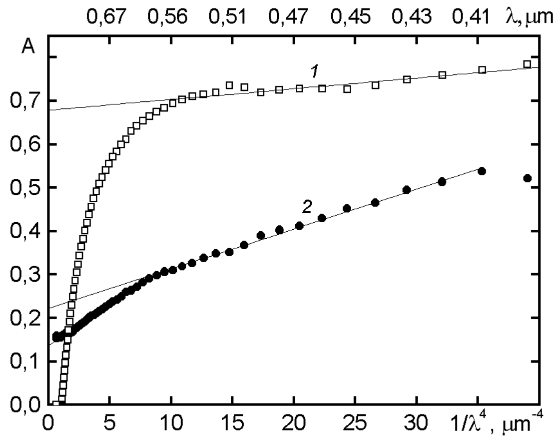

Fig. 4. Recalculated absorption *A* as a function of $1/\lambda^4$ for scattering analyses in thin film (*1*) on Si substrate (Sample 1) and for free film prepared from Sample 2.

Sample 1 which demonstrates a larger roughness shows also a larger scattering and measured absorption. The bend on the curves around 0.6 μm is probably related to the maximum in optical extinction coefficient spectrum $k(\lambda)$ of bulk material (Fig. 3b, curve *3*).

3. Conclusions

The optical properties of nanocomposite films with Fe_3O_4 are mainly defined by scattering on large (as compared to light wavelength) agglomerates of nanoparticles. The average size of such agglomerates as estimated from AFM images is about 100 nm. Such an increased scattering can be used for reflectance decreasing and amplification of light interaction with semiconductor substrate of surface barrier heterostructures for photoelectric applications. These investigations are continued.

Acknowledgments. Authors are thankful to A.Kotko for carefully made TEM measurements.

References

1. W.Eerenstein, L.Kalev, L.Niesen et al., *J.Magn. Magn.Mater.*, **258–259**, 73 (2003).
2. Q.W.Chen, Y.T.Qian, Z.Y.Chen et al., *Mater.Lett.*, **24**, 85 (1995).
3. D.C.Sun, D.S.Sun, *Mater.Chem. and Phys.*, **118**, 288 (2009).
4. K.T.Wu, Y.D.Yao, H.K.Huang, *J.Appl.Phys.*, **87**, 6932 (2000).
5. I.L.Lyubchanskii, N.N.Dadoenkova, M.I.Lyubchanskii et al., *J.Phys.D:Appl.Phys.*, **36**, R277 (2003).
6. P.Berger, N.B.Adelman, K.J.Beckman et al., *J.Chem.Educat.*, **76**, 943 (1999).
7. R.M.A Azzam, N.M.Bashara, Ellipsometry and Polarized Light, North-Holland, Amsterdam, (1987).
8. M.R.Querry, Optical Constants, Pentagon Reports, CRDC-CR-85034 (1985).
9. C.F.Bohren, D.R.Huffman, Absorption and Scattering of Light by Small Particles, Wiley Interscience, New York (1998).

Морфологія та оптичні властивості плівок із включенням наночастинок магнетиту

О.Коров'янко, М.Дмитрук, С.Мамикін, М.Ситник, О.Литвин, П.Фочук

Тонкі плівки із включенням наночастинок Fe_3O_4 виготовлено методом центрифугування на підкладках Si та досліджено методами атомної силової мікроскопії та оптичної спектроскопії у діапазоні 0,4–1,1 мкм. Плівки демонструють суттєве розсіяння світла внаслідок агломерації наночастинок.