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Magnetic properties of heterophase film coatings based on a solid solution of cadmium sulfide and iron

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Abstract. In this work, we measured and analyzed the magnetic susceptibility and the isotherms of magnetization of a semimagnetic material based on CdS: Fe with nanosized inclusions of FeS and Fe_2O_3 phases. These measurements made it possible to divide the ferromagnetic and paramagnetic phases. Measurements of magnetic force microscopy showed manifestations of magnetic properties mainly at the boundaries of CdS grains, which is explained by the predominance of the mechanism of diffusion of iron atoms along the boundaries of crystallites. The displacement of Cd atoms with the formation of FeS or the oxidation of Fe to the state of maghemite occurs at the boundaries of these crystallites.

Keywords: semimagnetic material, heterogeneous material, magnetic force microscopy, magnetization isotherms, magnetic susceptibility, magnetic hysteresis

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Материалы конференции
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Магнитные свойства гетерофазных пленочных покрытий на основе твердого раствора сульфида кадмия и железа

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Аннотация. В настоящей работе проведены измерения и анализ изотерм намагниченности и магнитной восприимчивости полумагнитного материала на основе CdS:Fe с наноразмерными включениями фаз FeS и Fe_2O_3. Данные измерения позволили разделить ферромагнитную и парамагнитную фазы. Измерения магнито-силовой микроскопии показали проявление магнитных свойств в основном на границах зерен CdS, что объясняется преобладанием механизма диффузии атомов железа по границам кристаллитов, где и происходит замещение атомов Cd с образованием FeS или окисление Fe до состояния маггемита.

Ключевые слова: полумагнитный материал, гетерогенный материал, магнито-силовая микроскопия, изотермы намагниченности, магнитная восприимчивость, магнитный гистерезис

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Introduction

A semimagnetic material can be obtained in the case of partial displacement of metal atoms of the base material (for example, cadmium chalcogenide) by dopant atoms (for example, Fe) [1, 2]. At present, the study of the properties of semimagnetic materials is very important, because the specific properties of these materials significantly depend on the concentration of dopant atoms and their interaction. At the same time, nanoparticles showing ferromagnetic properties are no less interest [3]. Of particular interest are ensembles of such particles included in a semiconductor matrix with paramagnetic or semimagnetic properties.

This paper presents the research results of heterogeneous film samples based on CdS obtained by thermal evaporation in vacuum. Doping with iron atoms from a nanosized film on the back surface of CdS occurred by thermal annealing. During annealing, the diffusion of iron atoms occurs deep into the CdS sample with the formation of a substitutional solid solution $Cd_xFe_{1-x}S$ based on the cubic modification of CdS [4]. Also there is recrystallization of CdS which is attended by a polymorphic transformation of its crystal lattice from sphalerite to wurtzite. The resulting significant differences in the crystal lattices of the photosensitive modification of CdS, iron and its sulfide during annealing lead to a limitation in the solubility of the components and the formation of a heterogeneous material based on a $Cd_xFe_{1-x}S$ solid solution.

A significant change in the electrical and optical properties is observed for heterogeneous CdS: Fe materials under the action of an applied magnetic field. This is of interest for modern micro- and nanoelectronics, and can be used to create semiconductor devices with magnetic field-controlled characteristics [5].

Materials and Technology

The object of study in this work is thin-film polycrystalline samples of cadmium sulfide doped with iron. There are many ways to obtain CdS films and their doping [6, 7]. For this research, we obtained samples with a multilayer structure created by successive deposition of layers by thermal evaporation in vacuum.

Initially, we deposited a layer of chemically pure iron 30–50 nm thick on a glass substrate at a pressure of $6 \cdot 10^{-5}$ Torr for 5 minutes, then, on top of it, a layer of chemically pure cadmium sulfide 0.6–0.8 μm thick. The mixture of CdS also contained the $CuCl_2$ activator at a ratio of 20 mg $CuCl_2$ per 1 g CdS. Thus, the film, which is the source of iron during diffusion, is located between the glass substrate and the CdS film. Further, the samples were annealed in a furnace in an air atmosphere at a temperature of 450°C for 15 minutes. As a result of such high-temperature annealing of samples consisting of components with low mutual solubility (the solubility of Fe in CdS is less than 9%), one can expect the formation of precipitates from iron atoms, FeS, and iron oxides.

Results and Discussion

To study the magnetic properties of the obtained heterogeneous CdS: Fe material, we used magnetic force microscopy (MFM) and methods for measuring of magnetization curves and of the dependence of magnetic susceptibility on temperature.

Fig. 1 shows the results of measurements of the magnetization isotherms of heterogeneous materials samples based on $Cd_xFe_{1-x}S$ solid solutions. The measurements were made on a magnetometer with a vibrating sample.

The presence of hysteresis indicates about a ferromagnetic phase, and an increase of the specific magnetization M_S with increasing magnetic field intensity indicates about a paramagnetic phase.

An analysis of the experimental magnetization isotherms makes it possible to separate the ferromagnetic and paramagnetic phases (Fig. 2).

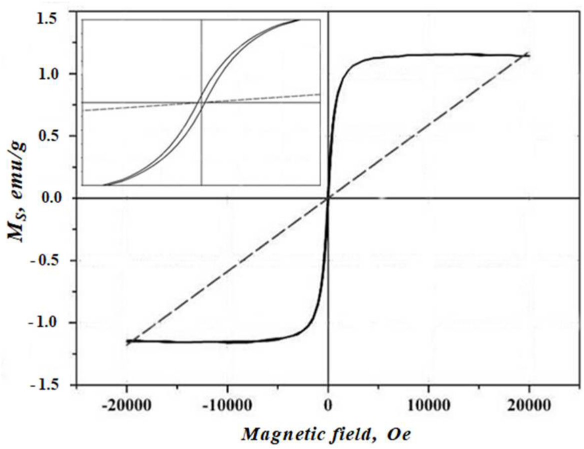

Fig. 1. Experimental magnetization isotherm of an annealed heterophase CdS:Fe sample with a selected hysteresis area in the range from -1500 Oe to +1500 Oe

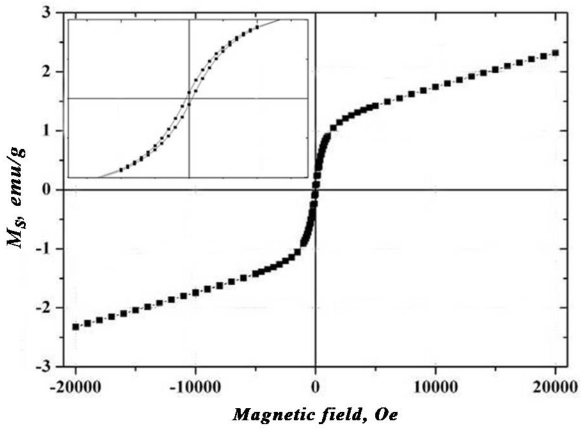

Fig. 2. Separation of paramagnetic (dotted line) and ferromagnetic (solid line) components from the experimental graph in Fig. 1.
The area on the fragment is increased in the range from -1500 Oe to +1500 Oe

The ferromagnetic phase is a soft magnet, characterized by a coercive force H_C = 44 Oe, with a value of specific magnetization M_S = 1.15 emu/g. The area of the hysteresis loop determines the amount of energy losses required to remagnetize the sample, which are used to heat the sample. As we can see, the hysteresis loop is quite "narrow". Narrow magnetic hysteresis loops are observed in soft magnetic materials, which also indicates that this material belongs to the class of soft magnetic materials.

Fig. 3 shows the temperature dependence of the magnetic susceptibility χ of heterogeneous semiconductor film samples of CdS:Fe. The dependence was obtained using a magnetometer with a vibrating sample under the influence of an external magnetic field of 1500 Oe.

Different classes of substances have different ranges of magnetic susceptibility values. These values are on the order of 10^{-4}–10^{-6} for diamagnets and paramagnets. But at the same time, diamagnets and paramagnets are practically independent of the intensity of the applied magnetic field. The magnetic susceptibility can reach very large values from several tens to many thousands of units for ferromagnets. Also there is a strong dependence on the intensity of the applied field for ferromagnets. Therefore, for convenience, we use the differential magnetic susceptibility, which is equal to the derivative of the magnetization of a unit volume of a substance on the magnetic field intensity. The magnetic susceptibility of paramagnets decreases with increasing temperature, obeying the Curie–Weiss law. The magnetic susceptibility of ferromagnets, increases with increasing temperature, reaching a sharp maximum near the Curie point.

In our research at room temperature, the sample shows paramagnetic properties, but as the temperature increases, the shape of the curve differs from the curve observed in the Curie–Weiss law. In addition, we observe a local peak at a temperature of about 212 °C, which is characteristic of ferromagnetic samples. These measurements confirm the heterogeneity of the annealed CdS: Fe sample and the presence of paramagnetic and ferromagnetic phases in these samples.

We used magnetic force microscopy (MFM) to characterize the magnetic properties of the surface of heterophase CdS:Fe samples. Measurements of magnetic force microscopy make it possible to study magnetic domain structures with a high spatial resolution of recording and reading information in a magnetic medium, magnetization reversal processes, etc.

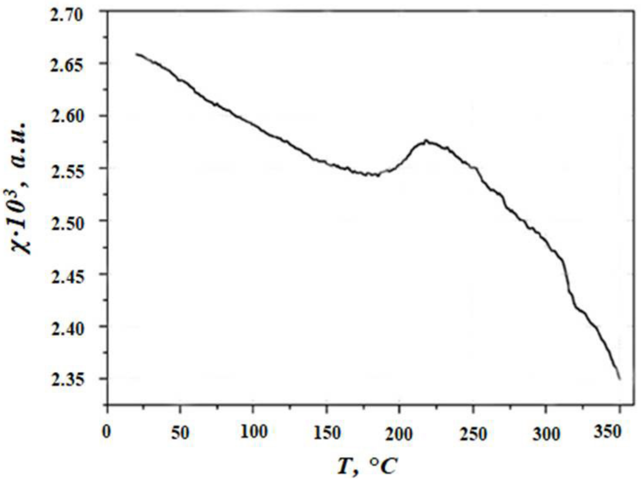

Fig. 3. Temperature dependence of magnetic susceptibility χ for an annealed heterophase CdS:Fe sample

When obtaining MFM images, an external magnetic field was applied to the samples in the range from 0 to 500 Oe with the intensity vector parallel to the plane of the sample. Fig. 4 shows MFM images of the surface of a CdS:Fe sample in the absence and in the presence of an external magnetic field of 500 Oe.

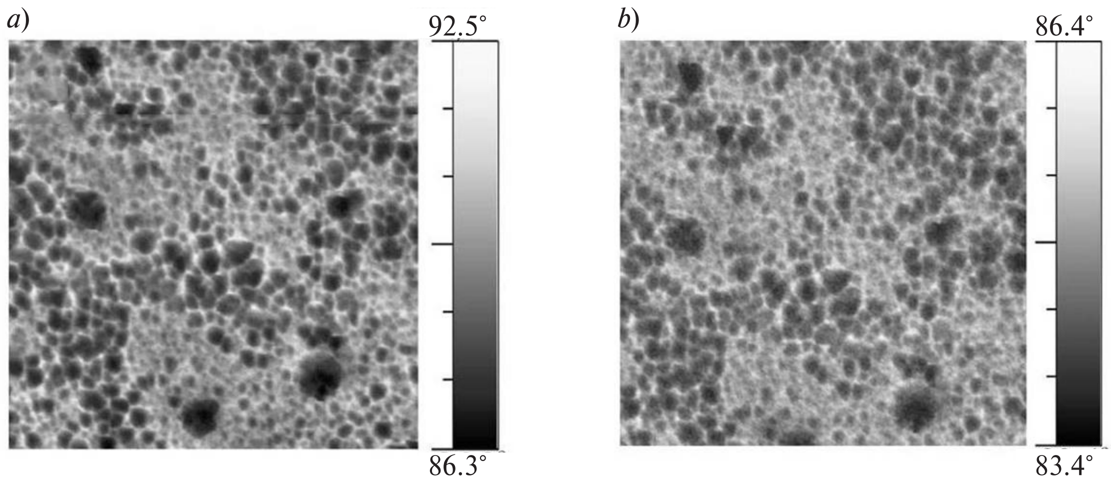

Fig. 4. MFM images of the surface of an annealed heterophase CdS: Fe sample without (*a*) and with (*b*) a magnetic field. The scan size is 10×10 μm

The application of an external magnetic field leads to a decrease in the contrast of the MFM image that can be explained by an increase in the magnetization of the inner regions. That is, there is another ferromagnetic phase inside the film along with a ferromagnetic phase on the surface. The ratio of MFM signals indicates a significant (up to 9.2%) change in the signal for the intercrystalline space and insignificant (1.5%) for large crystallites on the surface. This fact can be explained by the diffusion of iron atoms to the surface during annealing. Iron accumulates at grain boundaries where magnetic particles grow. At the same time, the external magnetic field has a slight attachment on large CdS crystallites.

Conclusion

Thus, measurements of the magnetic hysteresis and magnetic susceptibility showed the presence of paramagnetic and ferromagnetic phases in a heterogeneous material based on a $Cd_xFe_{1-x}S$ solid solution after high-temperature annealing. Based on the data of magnetic force microscopy, it can be concluded that there are various ferromagnetic phases inside the annealed samples of the heterogeneous CdS:Fe material and on its surface. Magnetic properties mainly appear at the boundaries of CdS grains that is explained by the predominance of the mechanism of diffusion of iron atoms along the boundaries of crystallites. The displacement of Cd atoms with the formation of FeS or the oxidation of Fe to the state of maghemite (Fe_2O_3) occurs at the boundaries of these crystallites. The oxidation process dominates on the surface, while the sulfur replacement process dominates inside heterogeneous samples. This circumstance explains the presence of one ferromagnetic phase on the surface and another ferromagnetic phase in the bulk of the sample.

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