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Langmuir-Blodgett technology to obtain semi-magnetic photosensitive materials

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Abstract. We studied the technological modes of obtaining of nanoscale coatings containing a controlled number of iron atoms on a semiconductor substrate by Langmuir-Blodgett technology. We determined the regime of obtaining a monolayer of iron arachinate with the maximum content of iron atoms into monolayer. The analysis of compression isotherms made it possible to determine the surface density of the of iron atoms. Modeling the processes of diffusion taking into account the limited solubility Fe in CdS makes it possible to estimate the number of iron arachinate monolayers required to form a heterophase material that exhibits magnetic properties. The diffusion coefficient of Fe atoms in CdS was determined experimentally from the profile of iron distribution in CdS obtained using secondary ion mass spectrometry.The model allows to predict the density and depth of the occurrence of the nanosized iron -containing phases. It was obtained that 30 monolayers of iron arachinate obtained at pH = 5.83 provide the formation of nanosized phases at a depth of up to 300 μm. The annealing was for 30 minutes at a temperature of 450 °C.

Keywords: Langmuir-Blodgett technology, heterophase material, ferromagnetic phase, semi-magnetic material, monolayer, diffusion

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Материалы конференции
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Технология Ленгмюра-Блоджетт для получения полумагнитных фоточувствительных материалов

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Аннотация. Проведено исследование и апробация технологических режимов получения на полупроводниковой подложке наноразмерных покрытий, содержащих контролируемое количество атомов железа, по технологии Ленгмюра-Блоджетт. Моделирование процессов диффузии атомов Fe позволяет прогнозировать с высокой точностью плотность и глубину залегания наноразмерных железосодержащих фаз.

Ключевые слова: технология Ленгмюра-Блоджетт, гетерофазный материал, ферромагнитная фаза, полумагнитный материал, монослой, диффузия

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Introduction

Of special interest are the materials whose properties can be controlled by various external effects (for example, a magnetic field and an optical range radiation). This possibility increases the functionality of devices made on the basis of these materials. Such materials are soft magnetic homogeneous and semi-magnetic heterophase materials [1], which have a perspective for use in modern industries and are interesting for science due to the variety of their properties. Previously, massive monocrystals of solid solutions were mainly investigated [2]. But in recent years, significant attention is paid to the study of the film and nanolayer [3] of soft magnetic materials and structures. Heterophase semi-magnetic photosensitive materials are not enough studied due to the lack of reproducible (proven) technology and modelling views about obtaining such material with optimal and reproducible characteristics. Cadmium sulfide (CdS) can be used as a semiconductor matrix to create soft magnetic structures, because CdS has high photosensitivity, and its technology is well detailed for film polycrystalline forms and monocrystalline substrates. We have demonstrated [4] that the Fe-doping of CdS makes it possible to obtain heterophase structures based on a paramagnetic matrix of a solid solution CdS:Fe with ferromagnetic inclusions of FeS and Fe_2O_3, which are formed as a result of the processes of self-organization and decomposition of a supersaturated solid solution due to the limited solubility of Fe in CdS.

Previously, we created a semi-magnetic heterophase material based on a CdS:Fe solid solution by thermal evaporation of all components of this material [4]. As a result, a film sample with the properties of a semi-magnetic material was obtained. However, the method of thermal evaporation does not allow us to obtaine materials with a predictable arrangement of nanoscale phases and to control the size of these phases.

The aim of this work is the study and testing of technological modes and conditions for producing of nanoscale coatings containing a controlled number of iron atoms on a semiconductor substrate by Langmuir-Blodgett technology. The modeling of diffusion processes of Fe atoms in a photosensitive substrate allows us to predict density and depth of the occurrence of nanoscale iron-containing phases to high precision.

Materials and Methods

The Langmuir-Blodgett technology makes it possible to form multilayer nanoscale layers of surface-active substances at the liquid-gas interface with a thickness of each monolayer of one molecule. Monolayers play the role of an organic matrix, which can include various functional elements. This feature of the formation of monolayers is used for dosed transfer of metal atoms onto a solid substrate. It is possible to obtain clusters of a size-defined by changing the mode and conditions of filming process.

In our work, arachic acid (AA) $C_{19}H_{39}COOH$ was used as an organic matrix. We have chosen arachic acid because the length of the carbon chain ensures its almost complete insolubility in water. This circumstance determines the production of a monolayer stable in time with a high ordering of molecules in the layer, which makes it possible to obtain high reproducibility of the processes of formation and transfer of monolayers. $FeCl_3$ salt was used as a source of iron. To obtain Langmuir--Blodgett films we used equipment of monolayer deposition KSV-Nima LBThrough Medium KN 2002 (KSV-Nima, Finland). This trough is equipped with two moving barriers that provide symmetrical bilateral compression, with an accuracy of positioning the barriers and determining the area occupied by the monolayer, up to 0.1%. The measurement of surface tension was carried out by weighing the Wilhelmy plate, while the accuracy of determining the surface pressure was 0.01 mN/m.

The arachic acid was diluted in chloroform to a concentration of 0.001 mol/L and injected in a volume of 50 μl onto the surface of an aqueous solution of $FeCl_3$ to obtain monolayers. The amount of iron and its the distribution density in the layer of a surface-active substances depend on the pH of the subphase where films were formed and the concentration of $FeCl_3$. In our experiments, the concentration of $FeCl_3$ was 10^{-3} mol/L. To develop the most efficient regime for obtaining an iron-containing coating, the pH value of the aqueous subphase was varied in the range from 3.7 to 8.

After preparing the solution and introducing the surfactant, the monolayer was compressed by a moving barrier at a rate of 1 cpm until a close-packed layer was formed, which was recorded by the π–A isotherm. The monolayer was transferred to the substrate surface by the Langmuir-Schaeffer method. The temperature, surface pressure π of the monolayer, and the average area A per molecule in the monolayer were controlled during the process of obtaining a close-packed monolayer. The optimal technological parameters are air and subphase temperature – 23 ± 1 °C, surface pressure – 18 mN/m, which were kept constant in the process of obtaining the layer. Under these conditions, iron-containing monolayers were transferred onto a solid substrate.

Semiconductor single-crystal wafers (CdS) were used as solid substrates for transferring the obtained iron-containing films. The surface quality of the wafers and low specific resistivity made it possible to comprehensively study the resulting nanoscale coatings.

Auger electron spectroscopy combined with layer-by-layer ion etching of the substrate was used to characterize the distribution of Fe in the obtained heterophase samples "organic coating-semiconductor substrate", annealed at a temperature of 450 °C for 30 minutes. The bombardment was by argon atoms with an energy of 3 keV, which made it possible to introduce minimal distortions into the chemical composition of the measured layer.

Results and Discussion

Fig. 1 shows the π–A isotherms of iron arachinate monolayers obtained at different pH values of an aqueous $FeCl_3$ solution and for an impurity-free arachic acid monolayer.

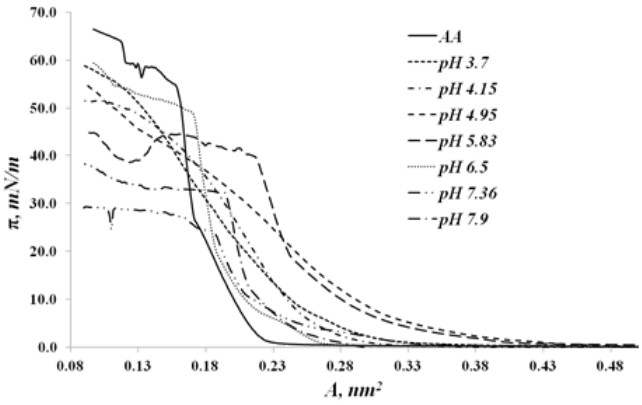

Fig. 1. Dependences of the surface pressure π of a monolayer on the area A per one molecule for arachic acid (*AA*) and its salts at different pH values of the solution

The values of the average area per molecule were determined in monolayers of iron arachinate obtained at different pH values by approximating the sections on the compression isotherms corresponding to the solid-crystalline state (Fig. 2).

The area per molecule for an arachic acid monolayer is 0.22 nm^2. For iron arachinate films, the packing density of molecules was varied across the entire range of pH values. Changes in the area per molecule A ranged from 0.25 nm^2 to 0.32 nm^2. Moreover, at pH from 3.7 to 5.8, the value of A increased, then practically stabilized at a value of 0.32 nm^2. Starting from pH = 6.5 the area per molecule began to decrease and at pH = 7.36 it reached a minimum value of 0.22 nm^2.

Most researchers explain the increase in the area per molecule with the incorporation of metal atoms into the surfactant monolayer. The proportion of acid molecules converted to salt changes with pH variation: the larger this proportion, the greater the average area per molecule

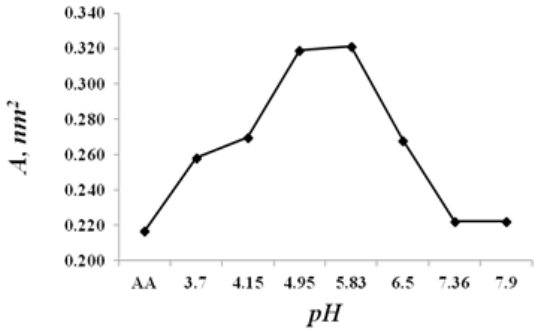

Fig. 2. Average area per molecule in monolayers of arachic acid (*AA*) and its salts at different pH values

in the monolayer. In an alkaline medium, metal clusters can attach to the film and metal can precipitate. In the first case, there is an increase in the area per molecule A, and in the second case, the value of A can decrease almost to the value corresponding to arachic acid without metal inclusions. Analysis of Fig. 2 shows that the maximum number of Fe atoms is incorporated into the monolayer in the range of pH values from 5 ± 0.2 to 6 ± 0.2. The stabilization of the maximum value of the area per molecule suggests that all acid molecules in the monolayer have attached Fe and converted to salt.

Fig. 3 shows the iron distribution profiles in single-crystal CdS wafers with 30 deposited monolayers of iron arachinate, obtained at pH = 5.83. The measurements were carried out before and after high-temperature annealing at a temperature of 450 °C.

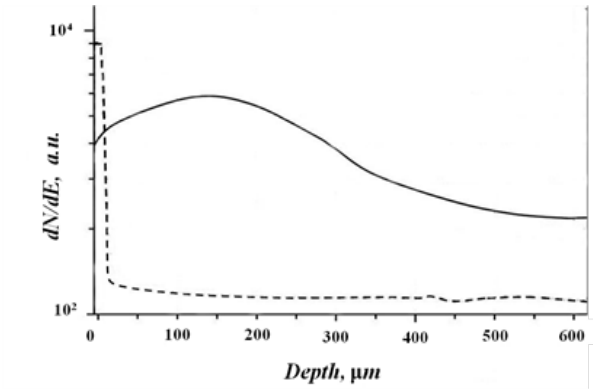

Fig. 3. Iron distribution profiles before (dashed lines) and after high-temperature annealing (solid lines)

It follows from the graph that the thickness of the Fe layer is less than 10 μm for an unannealed sample that corresponds to the film thickness of iron arachinate. After annealing, Fe is recorded over the entire thickness of the substrate (600 μm), but an increased content of Fe is observed in the layer up to 300 μm. If before annealing the profile was a step function, then after annealing it is a part of the Gaussian function. Therefore, the Gaussian equation can be used to describe diffusion:

$$N(x,t) = \frac{nN_s}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (1)$$

where $N(x, t)$ is the impurity concentration at a depth x from the surface after diffusion for time t; N_s is the surface density of Fe atoms in a monolayer; n is the number of monolayers; D is the diffusion coefficient (in this case, iron atoms).

The value of N_s was calculated based on the area per molecule of iron arachinate, on the basis of $\pi-A$ isotherms. The calculated average area per one molecule was 0.32 nm^2, then $N_s = 3.125 \cdot 10^{14}$ cm^{-2}. Annealing time $t = 1800$ s. The diffusion coefficient D obtained using these parameters is $0.16 \cdot 10^{-10}$ cm^2/s, which corresponds to the literature data.

The model of the diffusion of metal atoms in a semiconductor substrate taking into account the limited solubility [5] allows us to confirm the formation of iron solid solutions over the entire thickness of the substrate and the possible precipitation of iron atoms at the depth up to 300 μm with the formation of a ferromagnetic phase.

Conclusion

The researched technology allows us to obtain a heterophase nanostructured photoconductor with ferromagnetic phases. The use of organic nanoscale coatings structured by iron ions as a source of impurity makes it possible to set the required depth of formation of the ferromagnetic phase. Model of diffusion of metal atoms in a semiconductor photosensitive substrate taking into account the limited solubility Fe in CdS makes it possible to estimate the number of iron arachinate monolayers required to form a heterophase material that exhibits magnetic properties.

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