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Structural and magnetic properties of nanocomposite iron-containing SiC_xN_y films

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ABSTRACT

New ferromagnetic films with composition $SiC_xN_yFe_z$ were synthesized using chemical vapor deposition technique. Films were deposited using ferrocene, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and hydrogen gaseous mixture. Chemical and phase composition of the films were studied by FTIR, Raman spectroscopy and X-ray diffraction with grazing incidence (GI-XRD). FTIR spectra analysis confirmed the existence of Si-C and Si-N bonds. Graphite inclusions and amorphous carbon were determined by Raman spectra analysis. The surface of the $SiC_xN_yFe_z$ films studied by SEM is covered by nanocrystallites of iron oxide Fe_3O_4 phase. The main purpose of GI-XRD analysis is to describe the layered structure of the films in detail. It was shown by GI-XRD study, that phase composition of the $SiC_xN_yFe_z$ films varies from iron oxide Fe_3O_4 to iron silicide Fe_3Si and silicon carbide SiC with the deposition temperature growing. It was established, that $SiC_xN_yFe_z$ films are perspective for application in the spintronic field.

1. Introduction

According to Moore's law, the potential of modern microelectronics is close to its limit nowadays. With this problem unsolved for some time, new fields of science appeared, such as spintronics. This phenomenon is based on the fact of electron's spin being able to orient into an external magnetic field and to carry out this orientation through the insulator layer. The main thing about spintronics is a necessity for new materials which can be electron's injectors. Currently, there are few types of materials which are promising for spintronics application, such as, Heusler alloys and diluted ferromagnetic semiconductors. At the same time, the diluted ferromagnetic semiconductors (DMS) class includes different materials with various compositions [1,2]. This fact allows scientists to vary the composition and, as a consequence, properties of synthesized materials in a wide range. The most crucial problem of modern spintronic materials is their Curie temperature being lower than the room temperature. One of the examples of DMS is magnetic semiconductors containing manganese as a ferromagnetic additive. Mn-doped chalcopyrites $CdGeAs_2$, $ZnGeAs_2$ and $ZnSiAs_2$ were obtained by the vacuum-ampoule method [3]. Heusler alloy with composition Fe_2MnGa was obtained by melting elements in arc-furnace [4]. Another example of DMS is Fe, Co – doped materials based on other semiconductors such as ZnO [5]. Also, there are examples of ZnO doped with Mn atoms [6,7]. To put it another way, a variety of diluted magnetic semiconductors could be obtained within the combination of

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transition metal and a semiconducting material. One of the major spintronics issues is the question of the compatibility of new materials with existing silicon technology. It would be a very painful process to refuse from existing technology to develop the new one suitable for "exotic" spintronic material. With the material being able to suit modern Si-technology, it will be much easier to implement spintronic technology into the devices. So, the materials containing silicon and films of DMS deposited on the silicon wafers are promising structures for the spintronic devices being built on their base.

In this publication, we present our results on the synthesis of new ferromagnetic semiconducting films with composition $SiC_xN_yFe_z$ using a chemical vapor deposition technique. It is worth mentioning, that magnetic ceramics based on SiC_xN_y, silicon carbide either silicon nitride were obtained [8–12]. Nevertheless, films with such composition were not obtained, but SiC_xN_y coatings with the inclusion of different elements, such as Ti, Zr, Al or without it, are of a great interest for various technological applications [13–17]. Recently, we reported about $SiC_xN_yFe_z$ films synthesis from tris(diethylamino)silane [18]. The synthesis procedures were carried out in the temperature interval of 1073–1273 K at low pressure. In present work, we used common substance – hexamethyldisilazane. We made a significant advance in composition and properties characterization. The chemical composition of the films obtained at different deposition temperatures was studied using different modern chemical analysis techniques. The main focus of this work is an investigation of films phase composition using grazing incidence XRD analysis. It turned out that the phase composition on the film's surface differs from the one inside the film. The saturation magnetization for iron-containing SiC_xN_y films was determined.

2. Experimental part

The $SiC_xN_yFe_z$ films were obtained using a chemical vapor deposition technique by the thermal decomposition of a gaseous mixture of 1,1,1,3,3,3-hexamethyldisilazane (HMDS), ferrocene and hydrogen. The deposition procedure was carried out in the horizontal flow-type reactor and described in detail elsewhere [19]. While the hexamethyldisilazane and ferrocene were the sources of Si, C, N and Fe, respectively, hydrogen was selected as a reducing gas. The excess of carbon results in contamination of deposited films with carbon containing phases, such as graphite and amorphous carbon. The deposition conditions are described as follows: the deposition temperature range of 1073–1273 K, partial pressure of HMDS $P_{HMDS} = 5 \times 10^{-2}$ Torr, $P_{Ferrocene} = 5 \times 10^{-2}$ Torr and $P_{H2} = 1.5 \times 10^{-2}$ Torr. The residual pressure was about $(7–8) \times 10^{-4}$ Torr. The preliminary cleaning of the Si (100) wafers was used for all the films obtained. The silicon wafers were subjected to the following pregrowth treatment procedure:

1. degreasing their surfaces in various solvents (trichloroethylene, acetone)
2. treatment in NH_3-H_2O_2 and HCl-H_2O_2 and HF solution in order to remove SiO_2 oxide layer.

The microstructure of the films surface was studied by scanning electron microscopy (SEM) with a JSM-6700F microscope with a resolution of 1 nm, and the elemental composition was examined by energy dispersive spectroscopy (EDS) with an EX-23000VU detector for this microscope.

The phase composition of the samples was studied by grazing incidence X-ray diffraction (GI-XRD) using a high-precision PANalytical X'Pert PRO MRD high-resolution XRD system with $CuK\alpha_1$ radiation. The grazing incident angle varied from 0.5 to 2.5° for all the samples.

All the IR absorption spectra of the films were recorded on an FTIR SCIMITAR FTS 2000 spectrometer in the range 300–4000 cm^{-1}. All the FTIR spectra were normalized to the film thickness.

The recording of Raman spectra was carried out on PHILIPS PU-95 and Triplemate, Spex spectrometers. The Raman spectra were recorded using the argon ion laser wavelength of 488 nm.

Magnetic properties of the films were investigated with torque magnetometer. The procedure of the measurements is described elsewhere [20]. The equation

$$\frac{\Psi H}{L} = \frac{1}{M_s V} + \frac{H}{2K_\perp V},$$

where L is the torque moment, H – external magnetic field, M_s – saturation magnetization, V – specimen volume, $K_\perp$ - perpendicular anisotropy constant, is suitable in the case when the direction of the magnetic field being applied to the specimen forms a small angle Ψ with the specimen plane. Studying the $\Psi H/L$ as a function of H gives us an opportunity to determine a M_s and $K_\perp$. All measurements were carried at room temperature in the magnetic field range of 2000–10000 Oe.

3. Results and discussions

3.1. Elemental composition

Energy dispersive spectroscopy technique is a semiquantitative technique allowing us to determine the approximate chemical composition of the deposited films. Fig. 1a represents a dependence of the $SiC_xN_yFe_z$ films chemical composition on the deposition temperature. It can be seen, that carbon is a dominant element in the film's composition. In order to determine the form of carbon in the films, it is necessary to use other techniques, such as Raman spectroscopy and XRD investigations.