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GRAZING INCIDENCE X-RAY DIFFRACTION (GIRXD) STUDY OF THE PHASE COMPOSITION OF SiC_xFe_y AND $SiC_xN_yFe_z$ THIN FILMS

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Films of various composition are synthesized by chemical vapor deposition under low pressure using the thermal decomposition of the following initial gas mixtures: ferrocene $Fe(C_5H_5)_2$ and helium; ferrocene, tris(diethylamino)silane $[(C_2H_5)_2N]_3SiH$ (TDEAS) and helium; ferrocene, 1,1,1,3,3,3-hexamethyldisilazane $[(CH_3)_3Si]_2NH$ (HMDS), and helium. The chemical composition of the films obtained is analyzed by FTIR and Raman spectroscopies. The phase composition of the films is studied by grazing incidence X-ray diffraction (GIXRD). It is determined that the films grown from the gas mixtures of organiosilicon compounds (TDEAS or HMDS), ferrocene, and helium have the same chemical and phase composition ($SiC_xN_yFe_z$), while the films obtained from the mixture of ferrocene and helium have another composition (SiC_xFe_y).

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Films with the complex composition $SiC_xN_yFe_z$ combining the ferromagnetic properties of iron and its compounds and also the electronic properties of silicon carbonitride semiconductor are very promising for the creation of spintronic devices where the electron spin is an active element for information storage and transfer [1, 2]. In addition to the abovementioned properties, this material has good thermal and chemical stability. $SiC_xN_yFe_z$ is also an environmental friendly material. There are references in the literature [3-5] to the synthesis of $SiC_xN_yFe_z$ ceramics, but there are no references to the synthesis of films with this composition.

In the present work we have elaborated a synthesis of thin $SiC_xN_yFe_z$ films and determined their chemical and phase compositions. For comparison the films were synthesized using the thermal decomposition of the initial gas mixture of ferrocene and helium, which were also analyzed with the abovementioned methods.

Experiment. The SiC_xFe_y and $SiC_xN_yFe_z$ films were grown by chemical vapor deposition under low pressure in a horizontal quartz reactor in a temperature range of 1073-1273 K. We have studied high-temperature deposition processes of the following three gas mixtures: ferrocene and helium (1); ferrocene, HMDS, and helium (2); ferrocene, TDEAS, and helium (3). Helium was used as carrier gas. Si (100) wafers were used as substrates.

The phase composition of the samples obtained was studied by grazing incidence X-ray diffraction (GIXRD) using a high-precision PANalytical X′Pert PRO MRD high-resolution XRD system with Cu$K\alpha_1$ radiation. The grazing angle was set at 1° for all samples measured. A Ge(220) hybrid monochromator was used in the incident beam.

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All the IR absorption spectra of the films were recorded on a FTIR SCIMITAR FTS 2000 spectrometer in the range 300-4000 cm^{-1}. 32 scans with an aperture of 4 at the achieved resolution of 2 cm^{-1} were used for measurements. For each set of experiments an uncoated silicon substrate was used as a background for each spectrum; the substrate was preliminary subjected to the same pregrowth chemical treatment as the Si(100) substrates with the films. All the silicon substrates were of one type (series) of materials, which guarantied the similarity of the spectral background. All the FTIR spectra were normalized to the film thickness.

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

Results and discussion. GIXRD is a useful method to measure diffraction patterns at low incidence angles: the signal from the thin film improves (increases) and the effect of the substrate material is minimized. Fig. 1*a* presents the diffraction pattern from the film grown from mixture 1. The diffraction line shown in Fig. 1 belongs to the α-$FeSi_2$ phase [6]. It is supposed that during a high-temperature process the silicon atoms from the substrate react with iron atoms produced during the decomposition of ferrocene.

The SiC_xFe_y films were additionally studied by FTIR and Raman spectroscopies with the aim to clarify their composition and structure. The FTIR spectra of these layers have peaks corresponding to the stretching vibrations of Fe–Si bonds (480 cm^{-1}, 630 cm^{-1}, 1070 cm^{-1}) [6], and the sharp peak at 1550-1600 cm^{-1} belongs to the stretching vibrations of C–C bonds [7]. The presence of carbon nanotubes within the SiC_xFe_y films was confirmed by Raman spectroscopy.

Fig. 1*b*, *c* depicts the diffraction patterns of $SiC_xN_yFe_z$, films grown from initial gas mixtures 2 and 3. The diffraction lines correspond to the crystals of the following phases: α-Si_3N_4, β-SiC, α-$FeSi_2$, FeSi, and graphite [8-12]. These results were confirmed by the FTIR and Raman spectroscopic studies. It was previously found that the films grown from TDEAS or HMDS are nanocomposite [13], so one can suppose that the above mentioned nanocrystals (α-Si_3N_4, β-SiC, α-$FeSi_2$, FeSi and graphite) were introduced into the amorphous silicon carbonitride matrix. The similar results, including also the formation of the amorphous phase of silicon carbonitride during the chemical vapor deposition with organosilicon compounds as precursors, were obtained and described in [14, 15]. Thus, in particular, in [14] the synchrotron radiation X-ray diffraction analysis confirmed the formation of α-Si_3N_4 nanocrystals, and HRTEM and electron diffraction demonstrated the existence of the amorphous phase due to the presence of halo and ring system in the electron diffraction images. In [15]

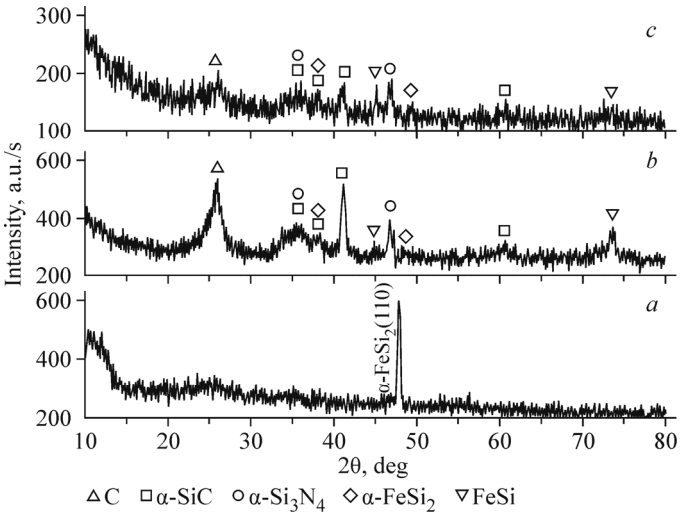

Fig. 1. GIXRD diffraction patterns of the following films: SiC_xFe_y obtained from the gas mixture of ferrocene and helium (*a*); $SiC_xN_yFe_z$ obtained from the gas mixture of HMDS, ferrocene, and helium (*b*); $SiC_xN_yFe_z$ obtained from the gas mixture of TDEAS, ferrocene, and helium (*c*). All the films were synthesized at a temperature of 1273 K.

a more detailed study of the material was carried out by HRTEM and selected area electron diffraction. Therefore, the formation of the α-Si_3N_4 phase and the presence of the amorphous component in silicon carbonitride films have been proved by two methods.

The α-$FeSi_2$ phase crystal size was estimated to be 20-25 nm, according to the Selyakov – Scherrer formula: $D = \lambda/\beta \times \cos\theta$, where D is the crystal size; λ is the wavelength of 1.5405 Å; β is the diffraction line broadening in radians; θ is the diffraction angle.

Conclusions. The deposition of the SiC_xFe_y and $SiC_xN_yFe_z$ films from the gas mixtures of ferrocene and helium, TDEAS (or HMDS), ferrocene and helium was studied by experiments using chemical vapor deposition under low pressure (10^{-1}-10^{-2} Torr) within the temperature range of 1073-1273 K. The phase and chemical compositions of the films were studied by GIXRD, FTIR and Raman spectroscopies. It is demonstrated that the films contain nanocrystals of the following phases: α-Si_3N_4, SiC, α-$FeSi_2$, FeSi, and graphite, which seem to be introduced into the amorphous matrix of silicon carbonitride layers.

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