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Fabrication of Monocrystalline CoFeMnSi Heusler Alloy Film on MgO Substrate

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The pulsed laser deposition method has been used for the growth of CoFeMnSi thin films on an atomically smooth MgO (100) substrate, which is of interest in spintronics applications. Optimization of substrate temperature, laser energy, and pulse frequency allowed for the formation of continuous, uniformly thick monocrystalline films without subsequent high-temperature annealing process. Electron microscopy and diffraction analysis of cross-sectional specimens of the grown films revealed that they exhibit a perfect cubic crystalline atomic structure. It was demonstrated that the atomic planes of CoFeMnSi {202} align with the parallel planes of the MgO substrate {020}, and a misfit of 4.65% between their interplanar spacings relaxes with the formation of misfit dislocations at the interface.

Keywords: Heusler Alloy, Pulsed laser deposition, thin film, TEM.

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Spin gapless semiconductors based on Heusler alloys, which include the CoFeMnSi (hereinafter referred to as CFMS) quaternary compound, are of interest for spintronics applications due to their unique electrical and magnetic properties [1,2]. Their band structure is characterized by the contact between the conduction band and the valence band at the Fermi energy level for carriers with one spin direction and the presence of a band gap for carriers with the opposite spin direction [1]. Therefore, CFMS compounds provide an opportunity to implement 100% spin polarization [3] and use the Hall effect to „separate" spin-polarized electrons and holes. Compared to the Co_2FeSi ternary compound, which was grown on Si substrates in [4], the properties of the CFMS alloy are less dependent on rearrangements of atoms of different types within crystal cells in the process of material growth [5]. CFMS-based films are also characterized by a high Curie temperature ($T_c \approx 763$ K for a bulk sample), and their saturation magnetization M_s is on the order of 3.49 μ_B/f.u. [6] and follows the Slater–Pauling rule [7].

To use Heusler alloys based on quaternary compounds in spintronic devices [2] (e.g., for the fabrication of magnetic tunnel junctions [8]), one needs to form thin single-crystal films on the surface of oxide materials, among which MgO holds a most unique position. The structural and magnetic properties of CFMS thin films grown by magnetron sputtering on „pure" single-crystal MgO (100) substrates and substrates coated with a thin Cr layer were examined in [9,10].

In the present study, crystalline CFMS films were formed on an MgO (100) substrate by pulsed laser deposition (PLD) without subsequent annealing. In the process of growth, their structural perfection was monitored by reflection high-energy electron diffraction (RHEED), and subsequent structural studies of grown films were carried out with the use of a transmission electron microscopy (TEM).

Films were grown by sputtering the CoFeMnSi Heusler alloy with 99.9% pure components in a PLD setup with a CL-7100 KrF laser operating at a wavelength of 248 nm. A mass spectrometer was used to determine the composition of the atmosphere in the growth chamber, and the temperature of the substrate was measured on both sides by two pyrometers. The growth of thin CFMS films was monitored by a RHEED system integrated into the PLD setup. Cross-sectional samples for structural studies of films grown on the substrate were prepared parallel to the MgO (001) plane using the *in situ* lift-out [11] method in a Helios Nanolab 650 dual-beam system. The obtained samples were subjected to electron diffraction and TEM examination in a FEI Titan Themis 200 microscope with a spherical aberration corrector of the objective lens at an accelerating voltage of 200 kV.

Prior to CFMS film growth, chemically pure single-crystal MgO (100) substrates, which were stored in specialized vacuum packaging, were subjected to heat treatment in an oxygen atmosphere in the growth chamber of the setup at a pressure of $P = 10^{-2}$ Pa and a temperature of 1000°C for 3 h. Following this annealing, the substrates were kept in the chamber for approximately 1 h at a temperature of 650°C and a residual pressure of $P = 10^{-5}$ Pa, which was the pressure maintained in the course of subsequent deposition of the films proper.

The temperature of the substrate affects the migration of deposited atoms on its surface. A low temperature level makes it difficult for target atoms to move along the surface and occupy energetically favorable positions, leading to the formation of a layer with a polycrystalline atomic structure. In contrast, if the substrate temperature is too high, the migration mobility of atoms increases. The result is that atoms of the target material may either leave the substrate surface due to desorption or form seeds, which then coalesce into large grains. It was determined experimentally that a substrate temperature of 650°C is the optimal one for CFMS film growth.

Since the duration of laser pulses was constant, the rate of evaporation of the target material and, consequently, film growth was determined by their energy and repetition rate. If the energy of the laser source is too high, a single irradiating pulse knocks out a significant number of atoms (and possibly their conglomerates) from the target. This results in rapid growth of the mass of deposited material on the substrate in the form of individual clusters and precludes one from forming a solid CFMS film. Therefore, a rather low pulse energy of approximately 150 mJ was set as the optimal one.

The growth rate and the atomic structure of the grown film depended heavily on the pulse repetition rate. When it was set to several hertz, films with an imperfect atomic structure were formed on the substrate, since the deposited atoms did not have enough time to occupy energetically favorable positions on the substrate surface. It was found experimentally that a pulse repetition rate of 0.5 Hz provides sufcient time for structuring.

CFMS islands formed first on the substrate surface in the process of growth. This is verified by the RHEED pattern (Fig. 1, *a*) that visualizes point reflections resulting from electron diffraction by CFMS atomic planes. A two-minute gap was introduced after every 65 irradiating laser pulses to implement layer-by-layer CFMS film formation. Such pauses in the film formation process allowed atoms of the deposited material to fill the space between islands. When the CFMS layer thickness exceeded 2 nm, the islands merged into a solid film with a single-crystal structure, which is evidenced by continuous reflections in the RHEED pattern (Fig. 1, *b*).

The TEM image of the cross section of the sample (Fig. 2) demonstrates that the CFMS film grown on MgO (100) is solid and atomically smooth; its thickness does not change in the lateral direction and is close to 12 nm. The left inset in Fig. 2 shows the electron diffraction pattern for the CFMS film and the substrate obtained along the MgO [001] direction with the use of selected area apperture with a diameter of 650 nm. The square in this inset highlights the reflections from planes {200} of the MgO substrate, and the rhombus denotes the reflections closest to the center from the CFMS film. They are point-like, indicating that this film is single-crystal in nature.

The arrangement of reflections in the diffraction pattern suggests that cubic unit cells of the CFMS film (space group $F\bar{4}3m$) and the MgO (100) crystal are rotated relative to each other by an angle of 45° around the MgO [100] direction. This mutual positioning of crystal lattices is indicative of the orienting influence of translational symmetry of the substrate on the arrangement of atoms in the grown film. The CFMS (202) and MgO (020) planes,

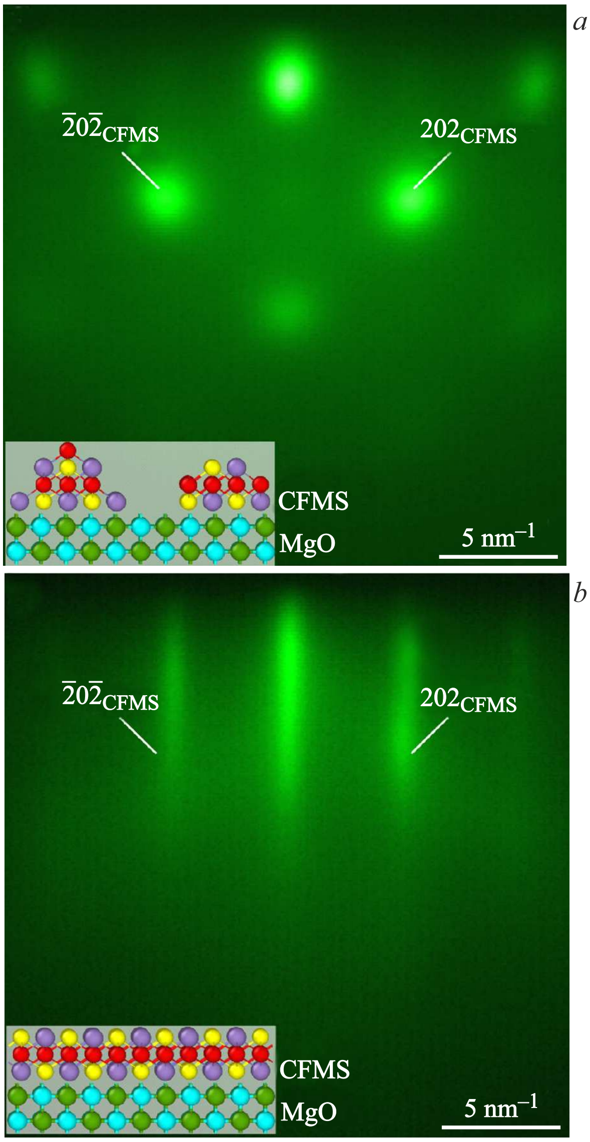

Figure 1. Diffraction patterns for high-energy electrons reflected from the surface of a CFMS film with an island structure (*a*) on the MgO (100) substrate and a single-crystal solid film (*b*). The atomic structures of MgO with formed islands (*a*) and a solid CFMS film (*b*) are shown schematically in the insets.

which have close interplanar spacing, are aligned in this case, inducing the emergence of a compound reflection in the diffraction pattern.

The obtained high-resolution TEM images (see one such image in the right inset in Fig. 2) provided an opportunity to visualize the matching of the CFMS (202) and MgO (020) atomic planes and verify directly that the grown film has a perfect crystalline structure and the boundary between it and the substrate is almost atomically flat. These images and the known lattice parameter of MgO (0.419 nm) were used to determine the lattice parameter of CFMS: 0.565 nm, which is close to the values reported in [10,12]. It can be seen from the right inset in Fig. 2 that a 4.65% mismatch in

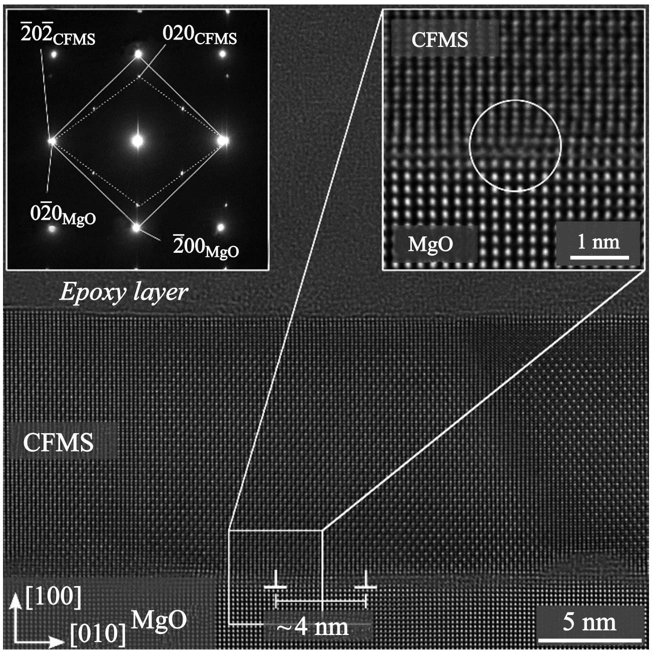

Figure 2. High-resolution TEM image of a CFMS film on the MgO (100) substrate with the positions of two misfit dislocations and the distance between them indicated. The left inset shows a diffraction pattern with 020-type reflections of the substrate connected by solid lines and the reflections from CFMS closest to the center of the pattern connected by dashed lines. An enlarged image visualizing the atomic structure of CFMS in the vicinity of a misfit dislocation with its core located at the center of the circle is presented in the right inset.

interplanar spacing of CFMS (202) and MgO (020) leads to the formation of misfit dislocations at the interface between the substrate and the film, which are located at a distance of 3.98 nm from each other. Several regions of the grown film were subjected to TEM imaging, and the obtained results were similar to those presented in Fig. 2. They indicate that a CFMS film with a perfect crystalline structure forms on the MgO (100) substrate in the examined growth regime.

Thus, it was demonstrated that atomically smooth CFMS films may be grown on the MgO surface at a rate of 2 nm/h by selecting the optimal values of the MgO substrate temperature, the energy of pulsed laser radiation incident onto the CoFeMnSi target, and the pulse repetition rate. The crystalline perfection of these films was confirmed by transmission electron microscopy data. The examined growth regime allows one to exclude annealing from the procedure of formation of single-crystal CFMS films, which is a significant advantage in the context of application of such films in the production of spintronic heterostructures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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