The formation of epitaxial p-i-n structures on the basis of (In,Fe)Sb and (Ga,Fe)Sb layers

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The multilayer structures on the basis of n-type (In,Fe)Sb and p-type (Ga,Fe)Sb magnetic semiconductors were fabricated on GaAs substrates by pulsed laser deposition technique. The transmission electron microscopy and energy-dispersive X-ray spectroscopy investigations reveal that the phase composition of the (In,Fe)Sb compound have a strong dependence on a growth temperature. The growth temperature increase from 200 to 300 °C leads to Fe atoms coalescence and a second crystalline phase formation in the In0.9Fe0.1Sb layer, in the same time, the Ga0.9Fe0.1Sb layers obtained at 200 and 300 °C are the single phase. The three-layer (In,Fe)Sb/GaAs/(Ga,Fe)Sb structure obtained on a GaAs substrate at 200 °C with the Fe content in the single-phase (In,Fe)Sb and (Ga,Fe)Sb layers being equal to about 10 ± 1 at. % has a rather high crystalline quality and can be considered as the prototype of bipolar spintronics device based on Fe-doped III-V semiconductors.

Presently the formation of III-V semiconductor layers heavily doped with Fe atoms, (in particular (In,Fe)As [1,2], (Ga,Fe)Sb [3,4,5], (In,Fe)Sb [6,7], (Al,Fe)Sb [8]) is a new and very promising trend in the field of semiconductor spintronics. The (Ga,Fe)Sb and (In,Fe)Sb layers fabricated by molecular beam epitaxy [3,4,7] and pulsed laser deposition [5,6] demonstrate the intrinsic ferromagnetism up to room temperature. At present, the electrical activity of iron in the InSb and GaSb matrices is not completely clear. According to the data available, Fe impurity in InSb and GaSb forms a level within the valence band. This should exclude the manifestation of donor or acceptor properties for Fe dopant in these semiconductor matrices [3,6]. However, the investigations reveal n-type conductivity for (In,Fe)Sb layers [6,7] and p-type conductivity for (Ga,Fe)Sb layers [3,5]. This is due to the effect of electrically active structure defects in these semiconductor hosts, the presence of which leads to the formation of n-type InSb layers and p-type GaSb layers without the introduction of electrically active dopants. Thus, on the basis of (In,Fe)Sb and (Ga,Fe)Sb layers one can fabricate a prototype of room temperature bipolar spintronics device in the form of a multilayer heterostructure. For the fabrication of n-p or p-i-n diode structures, it is necessary to develop the technology of the semiconductor layers epitaxial growth on the surface of heavily Fe-doped III-V magnetic semiconductors. In particular, an undoped GaAs is a suitable material for the i-region of a p-i-n structure. In addition, GaAs is a suitable material as a substrate as well. One of the main problems of the formation of multilayer structures based on (In,Fe)Sb, (Ga,Fe)Sb and GaAs semiconductors is a large lattice mismatch, which is 14.6% in the InSb/GaAs pair and 7.8% in the GaSb/GaAs pair.

In this work we present the results of investigations of the structural properties and elemental composition of multilayer epitaxial heterostructures based on the layers of (In,Fe)Sb and (Ga,Fe)Sb magnetic semiconductors.

The samples were grown by pulsed laser sputtering of InSb, GaAs, GaSb and Fe targets in a vacuum chamber with a background gas pressure of about 2×10⁻⁷ Pa. The presence of an additional Sb target allowed us to introduce an additional amount of antimony during the sputtering process. The n-type (001) GaAs was used as a substrate. The technological Fe content was set by the growth parameter \( Y_{Fe} = t_{Fe}/(t_{Fe} + t_{InSb/GaSb}) \), where \( t_{Fe} \) and \( t_{InSb/GaSb} \) are the ablation times of the Fe and InSb (or GaSb) targets, respectively. \( Y_{Fe} \) value in the (In,Fe)Sb and (Ga,Fe)Sb layers was \( Y_{Fe} = 0.13 \). Two samples named A and B were grown. These samples differed in the number of layers and a growth temperature \( T_g \).

The sample A: the GaAs buffer layer, the (In,Fe)Sb layer, the GaAs spacer layer, the (Ga,Fe)Sb layer and the GaAs cap layer. The GaAs layers were undoped. The growth temperature was 300 °C.

The sample B: the (In,Fe)Sb layer, the undoped GaAs spacer layer, the (Ga,Fe)Sb layer. The growth temperature was 200 °C.

During the (In,Fe)Sb layers formation, the introduction of an additional amount of Sb was carried out for the suppression of the indium precipitates formation on the surface as a consequence of the Sb deficiency [6]. Our previous studies revealed that the formation of a relatively smooth (Ga,Fe)Sb layer within method used is possible without the introduction of an additional amount of antimony.

The structural properties of the samples were investigated by Bruker D8 Discover X-Ray Diffractometer and high-resolution transmission analytical electron microscope Jeol JEM-2100F. The distribution of constituent elements was obtained by energy-dispersive X-ray spectroscopy (Oxford instruments X-Max Silicon Drift Detector) during microscopy investigations.
Figure 1(a) shows the $\theta$-2$\theta$ scans for the samples A and B obtained at room temperature using Cu K$_{\alpha}$ radiation. The X-ray diffraction curves contain three reflections: the high intensity (400) reflection from GaAs substrate (overlapped with the reflection from the GaAs spacer layer) and the (400) reflections from (In,Fe)Sb and (Ga,Fe)Sb layers. The $\theta$-2$\theta$ scans reveal that the growth character of all layers is epitaxial for both samples. Note that peak from the (In,Fe)Sb layer for the sample B ($T_g = 300$ °C) is narrower than for the sample A ($T_g = 200$ °C), therefore the crystalline quality of the (In,Fe)Sb layer in sample B is higher.

Figure 2(a) shows the overview cross-section transmission electron microscopy (TEM) image of the sample A. The image was obtained from a 270 nm long region. The image clearly reveals the grown layers: the GaAs buffer layer ($\approx 25$ nm-thick), the (In,Fe)Sb layer (with varying thickness in the range of 30 - 50 nm), the GaAs spacer layer ($\approx 60$ nm-thick), the (Ga,Fe)Sb layer ($\approx 35$ nm-thick) and the GaAs cap layer ($\approx 17$ nm-thick). It is noteworthy that there is a relatively high thickness variation for the (In,Fe)Sb layer. Figure 2(b) shows a high-resolution TEM (HRTEM) image of a 105 nm long region containing a part of the GaAs buffer, the (In,Fe)Sb layer and a part of the GaAs spacer. The image reveals areas with a Moire-like contrast within the (In,Fe)Sb layer (the area in dashed circles on Fig. 2(b)). These areas are Fe-enriched regions i.e. the second phase inclusions. The presence of the second phase inclusions in the (In,Fe)Sb layer and its relatively significant roughness indicates that $T_g = 300$ °C is not optimal. Despite the roughness and multi-phase character of the (In,Fe)Sb layer the growth of subsequent layers is epitaxial. As can be seen in Fig. 2(b) the atomic rows of the GaAs spacer are the continuation of the atomic rows of the (In,Fe)Sb layer. The GaAs spacer contains large number of stacking faults on the {111} planes, that appear in the image as the assemblage of straight lines at an angle of $\approx 70^\circ$ with respect to each other (Fig. 2(b)). The stacking faults generation is the consequence of the large lattice mismatch between the (In,Fe)Sb and GaAs matrixes [6]. Figure 1(c) shows HRTEM image of a 105 nm long region containing a part of the GaAs spacer, the (Ga,Fe)Sb layer and the GaAs cap layer.

Both the (Ga,Fe)Sb and GaAs cap layer are epitaxial. The preservation of crystal rows from the GaAs spacer layer to the surface is observed (Fig. 1(c)). In contrast to the (In,Fe)Sb layer the formation of the second crystalline phase in the (Ga,Fe)Sb layer is not observed, probably due to the better stability of (Ga,Fe)Sb with respect to formation of Fe-enriched second phase. The HRTEM images reveal that the (In,Fe)Sb, (Ga,Fe)Sb and GaAs spacer layers are fully relaxed. The lattice mismatch between the GaAs buffer and the (In,Fe)Sb layer and also between the (In,Fe)Sb layer and the GaAs spacer in the growth direction and in the plane (detected from HRTEM images) is equal to $\approx 14$ %. The lattice mismatch between the GaAs spacer and the (Ga,Fe)Sb layer in
the growth direction and in the plane is equal to \( \approx 8 \% \). This values coincide with the \( \Delta a/a \) values for GaAs/InSb and GaAs/GaSb pairs. Geometric phase analysis method allows one to estimate the relaxation layer thickness (the layer in which the transition to the maximum lattice mismatch occurs). For the GaAs (buffer)/(In,Fe)Sb heterojunction the relaxation layer thickness within (In,Fe)Sb layer is \( \approx 3 \) nm. For the (In,Fe)Sb/GaAs (spacer) heterojunction the relaxation layer thickness within GaAs spacer is \( \approx 9 \) nm. For the GaAs (spacer)/(Ga,Fe)Sb heterojunction the relaxation layer thickness within (Ga,Fe)Sb layer is \( \approx 4 \) nm.

Figure 3 presents a scanning cross-section TEM (STEM) image of the sample A and the energy-dispersive X-ray spectroscopy (EDS) mapping of Ga, As, In, Sb, and Fe constituent elements. The data reveal a non-uniform distribution of Fe atoms within the (In,Fe)Sb layer, which is consistent with TEM studies (Fig. 2(b)).

![Fig. 3. STEM image and corresponding EDS mapping of Ga, As, In, Sb, and Fe constituent elements in the structure A.](image)

Figure 4 shows the EDS concentration profile of In, Sb, and Fe atoms in the (In,Fe)Sb layer of the sample A along the line named “Profile” on the STEM image (Fig. 4). The profile reveals that the Fe content in the Fe-enriched regions is up to 70 at. %. In the Fe-enriched regions a decrease in the In and Sb content is observed, at that the concentration of In and Sb atoms approximately coincides. The absence of detectable Fe atoms between the regions with high Fe concentration attracts attention (Fig. 4). According to Springer Materials database [9], crystalline chemical compounds \( \text{Fe}_{0.7} \text{Sb}, \text{FeSb}_2, \text{FeSb}_3 \) and compounds with a strong Fe predominance (\( \text{Fe}_{0.07} \text{Sb}_{0.93}, \text{Fe}_{0.97} \text{Sb}_{0.03} \)) are known. The chemical compounds of Fe and In were not reported in the literature. Taking into account the concentration profile (Fig. 4), it is most probable that at \( T_g = 300 \) °C the Fe atoms coalesce and form the crystalline clusters of pure Fe (or \( \text{Fe}_{0.7} \text{Sb}_{0.93}/\text{Fe}_{0.97} \text{Sb}_{0.03} \)-like clusters with a strong predominance of Fe) in the InSb matrix. The cluster diameter is about 20 nm. The appearance of areas with a Moire-like contrast within the (In,Fe)Sb layer (Fig. 2(b)) is a consequence of the (In,Fe)Sb host and Fe cluster lattices overlapping.

![Fig. 4. EDS concentration profile of In, Sb, and Fe atoms in the (In,Fe)Sb layer of the sample A.](image)

The average Fe content in the (Ga,Fe)Sb layer detected by EDS investigations is \( \approx 10 \pm 1 \) at. %.

Figure 5(a) exhibits the overview cross-section TEM image of the sample B. The image was obtained from a 190 nm long region. The image clearly reveals the formed layers: the (In,Fe)Sb layer (\( \approx 27 \) nm-thick), the GaAs spacer layer (\( \approx 27 \) nm-thick) and the (Ga,Fe)Sb layer (\( \approx 17 \) nm-thick). Figure 5(b) shows HRTEM image of a 78 nm long region. The sample B demonstrates a significantly higher crystalline perfection as compared to the sample A. The (In,Fe)Sb layer grown at the lower temperature \( T_g = 200 \) °C with respect to the structure A is rather smooth and does not contain regions with a Moire-type contrast i.e. the layer is single-phase. In the (Ga,Fe)Sb layer the presence of a second crystalline phase was not detected also. The growth character for all layers is epitaxial. The preservation of atomic rows from the GaAs substrate to the surface is observed (Fig. 5(b)). Similarly to the sample A the sample B contains a large number of stacking faults grown through all layers up to the surface. This, as was mentioned above, is the consequence of the large lattice mismatch between the (In,Fe)Sb and GaAs matrices. The (In,Fe)Sb, (Ga,Fe)Sb, and GaAs spacer layers, as in the sample A, are completely relaxed. The values of the relaxation layers thickness are similar to the values in the corresponding heterojunctions of the structure A.

Figure 5 shows the STEM image of the sample B and the EDS mapping of Ga, As, In, Sb, and Fe constituent elements. In contrast to the structure A (Fig. 3) there are no obvious areas with the greatly increased content of Fe. This, together with HRTEM investigations, allows us to conclude about the relatively uniform distribution of Fe in the (In, Fe) Sb and (Ga, Fe) Sb layer without the Fe atoms coalescence and clusters formation. The average Fe content in the (In,Fe)Sb and (Ga,Fe)Sb layer detected by EDS investigations is \( \approx 10 \pm 1 \) at. %.
FIG. 5. (a) Overview TEM image of the structure B. (b) HRTEM image of a 78 nm long region (the enlarged area in dashed square (b) on Fig. 4(a)).

FIG. 6. STEM image and corresponding EDS mapping of Ga, As, In, Sb and Fe constituent elements in the structure B.

The investigation reveals that the growth temperature is a critical parameter in the formation of InSb layers heavily doped with iron. For the used method of pulsed laser deposition, the $T_g$ increase from 200 to 300 °C (for the Fe content about 10 at.%) leads to Fe atoms coalescence and a second crystalline phase formation in the (In,Fe)Sb layer. At that, the (Ga,Fe)Sb compound is more resistant to the formation of Fe-enriched second phase. The (Ga,Fe)Sb layer with the Fe content about 10 at.% obtained at $T_g = 300$ °C, in contrast to the (In,Fe)Sb layer, is a single phase (Fig. 2). By choosing the optimal growth temperature it is possible to form single-phase multilayer epitaxial structures based on III-V semiconductors heavily doped with Fe.

In summary, the $p-i-n$ epitaxial structures based on $n$-type (In,Fe)Sb and $p$-type (Ga,Fe)Sb layers were formed using the method of laser sputtering in a vacuum. The TEM and EDS investigations reveal that the phase composition of the (In,Fe)Sb compound depends on the growth temperature. The $T_g$ increase from 200 to 300 °C leads to Fe atoms coalescence and a second crystalline phase formation in the In$_{0.9}$Fe$_{0.1}$Sb layer. In the same time, the Ga$_{0.9}$Fe$_{0.1}$Sb layers obtained at 200 and 300 °C are the single phase. The three-layer (In,Fe)Sb/GaAs/(Ga,Fe)Sb structure deposited on a GaAs substrate at 200 °C with the Fe content of about 10 ± 1 at.% has a rather high crystalline quality and can be considered as the prototype of bipolar spintronics device based on Fe-doped III-V semiconductors.

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