# Composition and Structural Perfection of $(A^{III}, Mn)B^{V}$ and $MnB^{V}$ (A = Ga, In; B = Sb, As, P) Nanolayers

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**Abstract**—We have determined the elemental composition of laser-deposited (Ga,Mn)Sb, (In,Mn)As, MnP, MnAs, and MnSb layers. The InMnAs layers were not single-phase and contained MnAs clusters. Active Ga and Mn diffusion to the substrate and arsenic diffusion from the substrate during the GaMnSb growth process is accompanied by the formation of a GaMnAs intermediate layer.

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## INTRODUCTION

Recent years have seen increasing interest in spintronics because the use of the spin, a fundamental property of electrons, along with their charge, is expected to open up new possibilities for semiconductor devices and logic circuits.

A key requirement for spintronic devices is efficient injection of spin-polarized carriers into their active region. Spin injection from a ferromagnetic metal into a "conventional," nonmagnetic semiconductor is an attractive approach because a number of ferromagnetic metals (for example, Fe and Co) possess a sufficiently high Curie temperature, but they have one serious drawback: as a result of the conductivity mismatch between the metallic spin injector and semiconductor channel, the spin injection efficiency is typically no higher than 1% [1].

The use of magnetic semiconductors allows semiconducting properties to be combined with properties of ferromagnetic materials (for example, spin injection across a *p*-*n* junction). Most interest has centered on so-called diluted magnetic semiconductors of the (A<sup>III</sup>,Mn)B<sup>V</sup> type containing up to 5–10 at % Mn [2], which have a rather high Curie temperature ( $T_{\rm C}$ ) [3]. Also attractive in this context are the binary compounds MnB<sup>V</sup>, which have high Curie temperatures ( $T_{\rm C} = 298$  K for MnP, 318 K for MnAs, and 587 K for MnSb [4]).

There are a number of physics and technology issues pertaining to the formation of  $(A^{III},Mn)B^V$  structures, which have not yet been studied in suffi-

cient detail. One major problem is the lack of data on the composition—depth profile in such structures in relation to the substrate material, deposition temperature, and impurity concentration. Other important issues are structural perfection and the effect of interdiffusion from the substrate into the layer and from the layer into the substrate during the growth process on the properties of the material.

In this paper, we report the elemental composition of layers of the (Ga,Mn)Sb and (In,Mn)As semiconductors and MnP, MnAs, and MnSb magnetic halfmetals produced by laser deposition in a horizontal quartz reactor.

#### **EXPERIMENTAL**

(In,Mn)As and  $MnB^{V}$  (B = P, As, Sb) layers were grown on *i*-GaAs(100) substrates at substrate temperatures in the range  $t_g = 300-450^{\circ}$ C, and (Ga,Mn)Sb layers were grown on *i*-GaAs(100) and *p*-InAs(100) substrates at  $t_{g} = 400^{\circ}$ C. Metallic Mn and undoped semiconductor (InAs or GaSb) targets were sputtered alternately by a 1.06-µm pulsed Nd:YAG laser. The sputtering process was run in a hydrogen + arsine flow in the case of (In,Mn)As and in flowing hydrogen in the case of (Ga,Mn)Sb. The process parameter that determined the Mn content  $(Y_{Mn})$  of the (Ga,Mn)Sb and (In,Mn)As layers was the ratio of the sputtering times of the metallic (Mn) and semiconductor (s) targets:  $\tau_{Mn}/(\tau_{Mn} + \tau_s)$ . In addition, MnSb layers were grown through alternating laser sputtering of Mn and Sb metallic targets. The MnP and MnAs layers were

Material	Preparation procedure	t <sub>g</sub> , °C	<i>d</i> , nm	Atomic percent	
				Mn	$B^V$
MnSb/GaAs	Alternating sputtering of Mn and Sb, $\tau_{Mn}/\tau_{Sb} = 5$	300	110	71	29
MnP/GaAs	Mn sputtering in flowing phosphine	350	100	33	67
MnAs/InP	Mn sputtering in flowing arsine	370	320	45	55

**Table 1.** X-ray microanalysis results for  $MnB^V$  magnetic half-metals

produced through reactive laser sputtering of manganese in flowing phosphine and arsine, respectively.

The structural perfection of the layers was assessed by double-crystal X-ray diffraction on a DRON-4 diffractometer (Ge (400) monochromator,  $CuK_{\alpha}$ , radiation). Elemental concentration profiles were obtained using secondary ion mass spectrometry (SIMS) on a TOF.SIMS-5 system (dual beam principle) equipped with a time-of-flight mass analyzer. Compositiondepth profiles across the (In,Mn)As structures were obtained using etching with  $O_2^+$  ions (energies of up to 1 keV), and those of the (Ga,Mn)Sb structures were obtained using etching with Cs<sup>+</sup> ions. The probe beam was a nanosecond (1 ns) 25-keV Bi<sup>+</sup> ion pulse. In the former instance, In<sup>+</sup>, Mn<sup>+</sup>, As<sup>+</sup>, and Ga<sup>+</sup> secondary positive ions were recorded. In the case of the (Ga,Mn)Sb layers, we recorded MnSb<sup>-</sup>, GaSb<sup>-</sup>, MnAs<sup>-</sup>, and GaAs<sup>-</sup> negative cluster ions. The parameters of the craters (depth, lateral dimensions, and surface roughness) were measured with a Talysurf CCI 2000 system. The elemental composition of the  $MnB^{V}$ films was determined by X-ray microanalysis on an SEM-515 scanning electron microscope equipped with an EDAX 9900 energy dispersive spectrometer system. The key features of this method (escape depth of characteristic X-rays, 1 µm or more; thickness of the layer to be analyzed,  $\approx 100$  nm) impose additional limitations on the structures under consideration. Layer/substrate combinations were selected so that the layer and substrate differed completely in elemental composition (for example, MnAs/InP). Relative concentrations were determined by standardless analysis (with an accuracy on the order of 10-15%).

## **RESULTS AND DISCUSSION**

Using X-ray microanalysis, we determined the elemental composition of the  $MnB^{V}$  layers. The results are presented in Table 1.

The MnSb layers were grown at ratios of the sputtering times of the Mn and Sb targets in the range  $\tau_{Mn}/\tau_{Sb} = 2.5-10$  because the sputtering rate of metallic antimony considerably exceeded that of metallic manganese. It was found, however, that the Mn content of the deposit was 69—87 at % and was a weak function of substrate temperature in the range 200– 300°C. Clearly, we failed to take into account the Sb loss in the gas phase. X-ray diffraction patterns of the layers showed, in addition to a reflection from the substrate, 002 GaAs, a rather strong peak at  $2\theta \simeq 29.3^{\circ}$ , which could be indexed as 200 GaSb. The full width at half maximum of the latter peak was on the order of  $0.5^{\circ}$  at  $t_{g} = 300^{\circ}$ C. It should be taken into account that the lattice parameter of (Ga, Mn)Sb decreases slightly with increasing manganese concentration [5]. It is, therefore, reasonable to assume that the peak in question is due to a (Ga,Mn)Sb layer with a low Mn concentration epitaxially grown on the GaAs (100) substrate. As the deposition temperature decreases to 200°C, the intensity of the peak at  $2\theta \approx 29.3^{\circ}$ decreases considerably, and its full width at half maximum increases (up to  $5.5^{\circ}$ ). It seems likely that interdiffusion of the components of the  $Mn_xSb_{1-x}/GaAs$ layer and substrate produces a (Ga,Mn)Sb transition layer at the  $Mn_xSb_{1-x}/GaAs$  interface. In addition, the X-ray diffraction pattern showed rather broad, weaker peaks, in particular, one at  $2\theta \approx 43.6^{\circ}$ , which were attributable to MnSb.

The composition of the MnP layers produced by laser-sputtering Mn in flowing PH<sub>3</sub> was found to be a weak function of  $t_g$ : the manganese content increased from 31.4% at a growth temperature of 300°C to 35.5% at 450°C. Therefore, the layer contained approximately one manganese atom for two phosphorus atoms. We have found no data on a compound of composition MnP<sub>2</sub> or its magnetic properties in the literature.

The MnAs layer grown by reactive laser sputtering of Mn in flowing  $AsH_3$  at 370°C had a nearly stoichiometric composition, with a slight arsenic enrichment (Table 1).

Taking into account the key features of the deposition process, namely, the fact that the MnAs and MnP layers were produced by laser-sputtering metallic Mn in a gas flow, we conclude that the composition of these layers was governed by the chemical reaction between Mn and the Group V element (arsenic or phosphorus), in contrast to MnSb, whose composition was determined by the sputtering times of the targets.

Whereas X-ray microanalysis provides information about the overall content of a particular element in an entire layer, SIMS can be used to obtain composition—depth profiles of structures. Unfortunately, the TOF.SIMS-5 instrument has no absolute calibration



**Fig. 1.** Mn concentration profiles across (In,Mn)As layers grown at  $t_g = 320^{\circ}$ C:  $Y_{Mn} = (1) 0.05$ , (2) 0.09, (3) 0.16, (4) 0.20, (5) 0.26. Inset: overall Mn content as a function of  $Y_{Mn}$ .

for elemental analysis, so only relative compositional changes with depth can be assessed. Figure 1 shows the Mn concentration profiles across the (In,Mn)As layers. The process parameter  $Y_{\rm Mn}$  was varied from 0.05 to 0.26. In all cases, we observed a slight Mn enrichment in the surface layer. At a low Mn content ( $Y_{Mn} = 0.05$ ), the Mn distribution is uniform over most of the thickness of the layer. For  $Y_{\rm Mn} \ge 0.09$ , the depth profiles have a well-defined maximum ( $x_{\rm max} \simeq 75$  nm at  $Y_{\rm Mn} =$ 0.09). With increasing dopant concentration, the maximum shifts toward the substrate ( $x_{max} \simeq 135$  nm at  $Y_{\rm Mn} = 0.26$ ), which is caused by the increase in the thickness of the layer and the broadening of the interface as a result of the interdiffusion of the components of the layer and substrate during the growth process. One possible cause of the maximum in the manganese concentration profiles is the formation of an additional manganese-containing phase (for example, MnAs clusters). MnAs clusters on the order of 20 nm in size were found by Ganshina et al. [6] using transmission electron microscopy in a layer grown near an InMnAs/GaAs interface for structures from a series of samples studied by us.

The inset in Fig. 1 illustrates the effect of the process parameter  $Y_{Mn}$  on the overall Mn content of the layers (measured in counts × centimeter). The relationship between the two parameters is seen to be almost linear up to the highest value of  $Y_{Mn}$ .

In addition, our results demonstrate that increasing the Mn content of InAs layers increases the thickness of the transition layer (from 13 nm at  $Y_{Mn} = 0$  to 70 nm at  $Y_{Mn} = 0.26$ ), which is due to Ga diffusion from the GaAs substrate to the layer. For this reason, a layer of an InGaMnAs solid solution may grow near the interface. A comparative analysis of X-ray diffraction data for the InMnAs and undoped InAs layers showed that the X-ray diffraction patterns of the InMnAs layers with high  $Y_{Mn}$  values contained, in addition to the 200 peak from the GaAs substrate and the 002 peak from the InAs layer at  $2\theta = 31.6^{\circ}$  and  $29.5^{\circ}$ , respectively, peaks close in angular position to peaks from the hexagonal phase MnAs ( $10\overline{12}$  peak at  $42.3^{\circ}$  and  $11\overline{20}$  peak at  $48.9^{\circ}$ ). Given that the peak from the layer was rather narrow, we conclude that the InMnAs layers were single-crystalline but not single-phase.

Consider now the SIMS depth profiling results for structures with GaMnSb layers. The growth conditions of the structures are summarized in Table 2. The variable parameters were the manganese content (from 0 to  $Y_{\rm Mn} = 0.33$ ) and growth temperature (300 and 400°C). SIMS depth profiles for four samples (undoped and manganese-doped, grown on two types of substrates) are presented in Figs. 2 (*i*-GaAs sub-

Table 2. Growth parameters of GaMnSb layers

Sam- ple	Substrate	t <sub>g</sub> , °C	$Y_{\rm Mn} = \tau_{\rm Mn} / (\tau_{\rm GaSb} + \tau_{\rm Mn})$	Gaseous en- vironment
Ι	GaAs	400	0	H <sub>2</sub>
II	GaAs	400	0.06	H <sub>2</sub>
III	GaAs	300	0.33	H <sub>2</sub>
IV	GaAs	300	0.33	$H_2 + AsH_3$
V	GaAs	400	0.33	H <sub>2</sub>
VI	InAs	400	0	H <sub>2</sub>
VII	InAs	400	0.33	H <sub>2</sub>



Fig. 2. SIMS depth profiles for structures (a) I and (b) II containing a GaMnSb layer (*i*-GaAs substrate) with  $Y_{Mn} = 0$  and  $Y_{Mn} = 0.06$ , respectively.

strate) and 3 (*p*-InAs substrate). Analysis of the elemental concentration profiles across the (Ga,Mn)Sb layers revealed considerable arsenic diffusion from the substrate to the layer at nonzero Mn concentrations on both the InAs and GaAs substrates. In addition, in the layers with  $Y_{Mn} \neq 0$  near the interface at  $x \approx 200$  (GaMnSb layers on *i*-GaAs, Fig. 2) and 125 nm (GaMnSb layers on *p*-InAs, Fig. 3) we identified peaks of the MnAs<sup>-</sup> and GaMnAs<sup>-</sup> cluster ions with identical concentration profiles. Moreover, the MnSb concentration profile and arsenic diffusion indicate that the composition of the layer depends on the distance

from the substrate. Most likely, Mn diffusion into the substrate during the growth process initiates arsenic diffusion into the layer (arsenic is then incorporated into the Sb site), leading to the formation of a thin ( $\approx$ 50–100 nm in thickness) Ga<sub>1-x</sub>Mn<sub>x</sub>Sb<sub>1-y</sub>As<sub>y</sub> layer near the nominal GaMnAs/GaAs interface.

It is also worth noting active Ga diffusion into *p*-InAs substrates, which broadens the transition layer from approximately 40 to 80 nm (Fig. 3).

The GaMnSb layers were characterized by X-ray diffraction. The results (Fig. 4) demonstrate that the diffraction patterns of samples IV and V contain, in



Fig. 3. SIMS depth profiles for structures (a) VI and (b) VII containing a GaMnSb layer (*p*-InAs substrate) with  $Y_{Mn} = 0$  and  $Y_{Mn} = 0.33$ , respectively.

addition to major peaks (from the GaAs substrate and GaSb layer at  $2\theta = 31.6^{\circ}$  and  $29.4^{\circ}$ , respectively), extra peaks. In the X-ray diffraction pattern of sample IV, such peaks are attributable to polycrystalline GaAs (27.3°, 111; 45.5°, 220) and MnAs (40.4°, near 112; 42.5°, 202 and/or 211). The reason for the formation of MnAs as an additional phase is that the layers were grown in an AsH<sub>3</sub> atmosphere. The broad peak at  $2\theta = 43.4^{\circ}$  in the X-ray diffraction pattern of sample V is

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**Fig. 4.** X-ray diffraction patterns of GaMnSb layers: samples (*1*) I, (*2*) V, (*3*) IV, and (*4*) III (see Table 2).

attributable to metallic Mn. The GaMnSb structures characterized by SIMS were grown in a hydrogen atmosphere, so the MnAs<sup>-</sup> secondary cluster ions identified (Figs. 2, 3) were most likely unrelated to the formation of the MnAs phase and originated from the transition layer.

## CONCLUSIONS

Reactive laser deposition allows one to produce  $MnB^{V}$  layers whose composition is governed by the chemical reaction between their components and, possibly, by diffusion of atoms from the substrate during the growth process. At high magnetic impurity concentrations, the Mn concentration profile across epitaxial InMnAs layers is nonuniform, which seems to be caused by the formation of MnAs clusters during the growth process. The GaMnSb layers are not single-phase, which is most likely due to arsenic diffusion (in the presence of Mn) from the substrate to the layer on both *i*-GaAs and *p*-InAs substrates and to Ga diffusion from the layer to the *p*-InAs substrate.

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#### REFERENCES

- Lee, T.H., Koo, H.C., Kim, K.H., et al., Temperature Dependence of Spin Injection Efficiency in an Epitaxially Grown Fe/GaAs Hybrid Structure, *J. Magn. Magn. Mater.*, 2009, vol. 321, pp. 3795–3798.
- Matsukura, F., Ohno, H., and Dietl, T., *Handbook of Magnetic Materials*, Buschow, K.H.J., Ed., Amsterdam: Elsevier, 2002, vol. 14, chapter 1, pp. 1–88.
- Danilov, Yu.A., Kudrin, A.V., Vikhrova, O.V., et al., Ferromagnetic Semiconductor InMnAs Layers Grown by Pulsed Laser Deposition on GaAs, *J. Phys. D: Appl. Phys.*, 2009, vol. 42, paper 035 006.
- 4. *Tablitsy fizicheskikh velichin. Spravochnik* (Tables of Physical Quantities: A Handbook), Kikoin, I.K., Ed., Moscow: Atomizdat, 1976, p. 526.
- Basu, S. and Adhikari, T., Bulk Growth, Composition and Morphology of Gallium Manganese Antimonide—A New Ternary Alloy System, *J. Alloys Compd.*, 1994, vol. 205, pp. 81–85.
- Ganshina, E.A., Golik, L.L., Kovalev, V.I., et al., Resonant Enhancement of the Transversal Kerr Effect in the InMnAs Layers, *J. Phys.: Condens. Matter*, 2010, vol. 22, paper 396 002.