MnSb ferromagnetic films synthesized by vacuum thermal evaporation

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Abstract. By the original method, using the sequential high-purity Mn and Sb metals evaporation, followed by annealing under high vacuum conditions, MnSb semiconductor films were synthesized. It is shown that the high chemical activity of nanostructured Mn and Sb films significantly reduces the manganese antimonide evaporation temperature. Films are p-type and have a high charge carriers mobility.

1. Introduction
Manganese antimonide is a ferromagnetic semimetal with a high Curie temperature up to 600 K. This compound attracts attentions due to unique properties, such as ferromagnetism, magneto-optical effect and high magnetic anisotropy [1-7]. Nowadays hybrid structures of ferromagnetic semimetal-semiconductor are widely investigated [4-12]. Such structures synthesis is possible both as films and as system with ferromagnetic micro- and nanoclusters embedded in semiconductor matrix. It was predicted that the superconducting state in MnSb compound will be at low temperatures under the external pressure influence. The crystalline and electrical MnSb properties compatibility with semiconductor compounds is valuable for the hybrid structures at the effective spin diodes or transistors production.

Manganese antimonide films are generally synthesized by molecular-beam epitaxy [13-16]. This method is complicated and does not allow obtaining films with a thickness more than 10-15 nm. Due to the low manganese antimonide concentration, the films have a low sensitivity to the magnetic field. The films with bigger thickness could be synthesized by vacuum thermal evaporation [17-20]. The method limitation is the incongruent character of the manganese antimonide evaporation MnSb_con = Mn_1+xSb_con + Sb_gas.

2. Experiment
Manganese and antimony evaporation temperatures for achieving the MnSb stoichiometric composition were selected based on the metal vapor flux density calculations. MnSb synthesis, taking into account the Mn and Sb films nanocrystallinity, was carried out at temperatures much lower than the melting points of these metals. The synthesis was carried out by thermal annealing under high vacuum conditions. The investigation of temperature influence on adhesion and structural perfection showed that the optimum temperature range for films annealing was from 380 to 420 °C. At
temperatures below 380 °C, the compound synthesis did not occur, and at temperatures above 420 °C the films were flaked off from the substrates. The composition, structure, and nanocrystallites size in the films were determined by X-ray diffraction and microstructural analysis.

Manganese and antimony vapor condensation fluxes density calculations, as well as the films growth rates, were carried out under molecular evaporation conditions using the Langmuir equation, for the density of evaporation fluxes (1) and condensation (2), film growth rate (3), respectively:

\[
\dot{j}_{ev} = 3.16 \cdot 10^{-3} \cdot \alpha_{ev} p_0 / (2 \pi R T_{ev} M)^{1/2}
\]

\[
\dot{j}_{con} = \alpha_{con} \dot{j}_{ev} F_{ev} / \pi l^2
\]

\[
\omega_p = 6 \cdot 10^5 \dot{j}_{con} M / \rho_{con}
\]

where \(\dot{j}_{ev}, \dot{j}_{con}\) - the density of the evaporation and condensation fluxes, respectively (mole∙cm\(^{-2}\) s\(^{-1}\)); \(\omega_p\) - the film growth rate (μm / min); \(p_0\) - the saturated vapor pressure of metals (Pa) at evaporation temperature \(T_{ev}\); \(R\) - the universal gas constant 8.314 (J ∙ mol\(^{-1}\) ∙ K\(^{-1}\)); \(M\) - the molecular (atomic) vapor mass of the evaporating component (g / mol); \(\alpha_{ev}\) and \(\alpha_{con}\) - the evaporation and condensation coefficients; \(F_{ev}\) - the surface area of the evaporator (cm\(^2\)); \(l\) - the distance between the substrate and the evaporator (cm); \(\rho_{con}\) - the condensate density (g / cm\(^3\)).

The condensation fluxes density of the source and the substrate surface was 0.5 and 3 cm\(^2\), respectively. The substrate location was symmetrical to the vertical axis and perpendicular to the evaporator surface.

3. Result and Discussion

These equations solutions at equal fluxes make it possible to choose the metals evaporation temperatures at which the MnSb stoichiometric composition can be obtained. Based on these results, the temperature dependences of the antimony and manganese evaporation rates in the temperature range 900-1700 K were obtained, the distance from the evaporator to the substrate varied from 3 to 15 cm (figure 1).

![Figure 1. Temperature dependence of the materials deposition rate on the substrate](image)

Evaporation was carried out in vacuum (5 ∙ 10\(^{-4}\) Pa) using high-purity metals Mn (5N) and Sb (5N) as sources from resistively heated conical spiral evaporator (after annealing in high vacuum). Separate evaporation is more convenient for controlling the stoichiometric composition of the films. Source temperatures were selected based on data on the manganese and antimony vapor condensation streams density. Measuring the films thickness and using data on the metal vapor condensation fluxes density, the evaporation temperatures of the source were corrected, which made it possible to obtain identical flux densities. For the experiment it is more convenient to fix the evaporator temperature when the distance between the substrate and the evaporator is varied. Evaporation was carried out on the sittall
and single-crystal silicon substrates at room temperature. The evaporation time was chosen so that the films thickness was 200-250 nm.

The structure of the films, their composition and elements distribution were investigated by X-ray phase analysis (XRD), optical and scanning electron microscopy (SEM). XRD was carried out on a Bruker D8 Advance diffractometer (CuKα radiation, $\lambda = 0.1540$ nm, $U = 40$ kV, $I = 40$ mA). The diffractograms were recorded in the information reading mode with a step $\Delta \theta = 0.014^\circ$ in the angles range $2\theta$: 20 $^\circ$ - 90 $^\circ$ and holding for 1 s. The films microstructure was investigated using an optical microscope EPIQUANT and a scanning electron microscope JSM-6610LV with an equipment for energy dispersive X-ray spectroscopy.

Firstly, the sitall and silicon substrates diffraction patterns were obtained, then – for Sb films on the sitall (figure 2a) and on the Si substrates (figure 2b).

![Figure 2. X-Ray diffraction patterns: a) Sb film on Sitall substrate; b) Sb film on Si substrate.](image)

Annealing was carried out in vacuumed quartz ampoules, in an electric furnace. Ampoules were placed in the isothermal part of the furnace. The effect of the annealing temperature and time on the manganese antimonide compound synthesis was investigated. The MnSb phase synthesis according to XRD data (figure 3) and microstructural investigations (figure 4) began at a temperature 380 $^\circ$C.

![Figure 3. Mn + Sb films diffraction patterns after annealing at 400 $^\circ$C.](image)
Figure 4. a) film microstructure with Mn and Sb layers, d ~ 400 nm; b) the same film after annealing at 400°C.

According to SEM (figure 5a, b), it was detected that the optimum conditions for MnSb synthesizing from Mn and Sb films were: the temperature - 400 ± 20 °C and time - 2 h.

Figure 5. a, b) Mn + Sb films microstructure after annealing at 400 and 430 °C.

Further temperature increase led to a breakdown in the mechanical strength of the film. XRD, optical microscopy, and SEM results confirmed the temperature dependences of the electrical resistivity.

Unannealed and annealed films on the sitall substrate were investigated. Electrical properties measurements were carried out in the temperature range 14-300 K. At the same time, the annealed films resistance was approximately 3-4 times higher than for unannealed ones, and that is another
indication of the interaction between manganese and antimony with the manganese antimonide synthesis. Figure 6 shows the temperature dependences of the annealed films resistance in the cooling-heating mode.

![Figure 6](image)

**Figure 6.** Temperature dependence of films resistivity

4. Conclusion

The high chemical activity of nanostructured metal films make it possible to synthesize the MnSb compound at low temperatures by annealing in high vacuum. It was detected the optimum conditions for MnSb synthesizing from Mn and Sb films.

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