The GaAs is a binary III-V semiconductor compound composed of gallium and arsenic components. It does not occur in nature and for the first time it was synthesized experimentaly in the laboratory in 1950. It has the sphalerite crystal structure. GaAs is suitable for making various optoelectronic devices because of its suitable direct energy band gap (1.43 eV) and dielectric constant (13.1) value. In addition, it is used as the basis for useful series of ternary and quaternary compounds. Semiconductor GaAs is used as a circuitry common in mobile phones, in satellite communications, in microwave point-to-point links, and in some radar systems. The toxicological properties of GaAs have not been thoroughly investigated, however, it is considered to be highly toxic and carcinogenic. The main component in GaAs is rare element Ga discovered in 1875. Ga is an element which has an unusual phase diagram that like in Bi, Sb, and water, and it expands during solidification. The second component is As element, naturally occuring element in the Earth's crust. The main use of As is for pesticides, weed killers, wood preservatives, etc. Most arsenic compounds are manufactured using arsenic trioxide (As₂O₃) as a raw material. Due to the high economic value of Ga and its limited resource in nature, a number of recovery procedures applied to GaAs system have been developed and tested over the years, but yet none have been applied for in-plant pollution prevention and for a recycling and reuse of Ga. The ball-milling (BM) is suitable method because of its efficacy, easiness of use and versatility, to be applied to process all sorts of materials. BM method allows preparation of a wide variety of entirely new non-equilibrium, metastable materials that might possess nanocrystalline or even amorphous structures, as well. The present contribution is a report on the study of the non-equilibrium phase transformations in GaAs system induced by BM and subsequent heat treatment (HT) of the milled sample by applying X-ray powder diffraction (XRD) method.

Milling of GaAs wafer scraps was carried out by a planetary micromill Pulverisette type 7 (Fritsch, Germany) with cylindrical agate containers, having internal volume of 45 cm³, and twelve agate balls (10 with 10 mm and 2 with 12 mm in diameter) in air at ambient temperature. The balls to powder mass ratio (BPR) was ~40:1. The XRD analysis was performed using a Philips PW 1820 X-ray diffractometer with a graphite monochromatised Cu Kα radiation (λ = 0.154 nm). Powder XRD patterns were recorded in the angular region 10° ≤ 2θ ≤ 48°. The observed d-spacings and the relative intensities of XRD peaks, as well as the cell parameters were compared with the literature values reported in [5]. The XRD results obtained in our investigation are presented in Figs. 1 and 2. On Fig. 1 (a-f) a series of XRD patterns of GaAs taken after 10 min, and 1, 2, 3, 6 and 10 h of milling are presented, respectively. A brief analysis of the XRD patterns reveals that the single-phase crystalline structure of GaAs is stable up to 1 h of milling. In the sequence of milling times after 2, 3, 6 and 10 h, an obvious reduction in diffraction line intensity accompanied with a line broadening takes place. At the same time new diffraction lines, indexed as crystalline arsenic oxide As₂O₃ phase, are present. Also, on the patterns Fig. 1 (d-f) one can observe formation of a broad maximum around 33° (2θ), probably connected with the formation of Ga₂O₃ amorphous phase. So, the final product after 10 h of milling of GaAs is a mixture of oxides of the constituent metals, i.e., amorphous Ga₂O₃ and
crystalline As$_2$O$_3$ phases. On Fig. 2 are shown the results of post-annealing of the milled GaAs samples. From Fig. 2 is evident that there are no more lines belonging to the As$_2$O$_3$ crystalline phase and simple explanation could be that As$_2$O$_3$ escaped from the sample during post-annealing treatment. At the same time the new system of lines appears in patterns (b-d) on Fig. 2, and a careful analysis of the XRD patterns reveals that the single Ga$_2$O$_3$ crystalline phase is formed from the earlier amorphous phase which had appeared during milling treatment. So, in contrast to the above results connected with the As$_2$O$_3$ oxide phase, fully developed single crystalline powder of Ga$_2$O$_3$ oxide phase was obtained only after post-annealing of the milled samples (see Fig. 2). According to the authors’ present knowledge the BM method has been applied to GaAs system under argon atmosphere [1], and it has been revealed that only partial amorphisation of crystalline GaAs was possible. The results similar to those described in the present communication have been obtained during milling the single crystalline GdNi$_5$ phase [2]. In this case the product phases observed after milling were a mixture of amorphous gadolinium (Gd$_2$O$_3$) oxide and crystalline nickel oxide (NiO). Heat treatment of the milled samples induced crystallization of amorphous phase into crystalline. In our present experiments for the separation of gallium and arsenic oxides we plan to use the simple vacuum apparatus described in [3]. Also, it is interesting to note here that it is possible, if one uses the mixture of metal oxides and carbon powder, the pure metals will be obtained by applying ball milling method [4]. Namely, in this case the mechanically activated reduction process takes place. Similar experiments with the gallium oxide are now in progress in our laboratory. Based on the results presented up to now in this contribution the following can be concluded:

(i) High-energy dry ball milling is an efficient processing method even when used at room temperature. It induces the structural changes from the crystalline GaAs single phase to the mixtures of amorphous Ga$_2$O$_3$ and crystalline As$_2$O$_3$ phases, if the mill processing was continued long enough. The formation process was complete after milling up to 10 h, and no intermediary phase was detected.

(ii) In the course of subsequent HT processing of the milled GaAs samples, formed earlier the As$_2$O$_3$ crystalline phase escaped from the samples, and at the same time the amorphous Ga$_2$O$_3$ phase crystallized if samples were milled long enough, and then post-annealed long enough at the appropriate temperatures (e.g. milled for 10h and post-annealed for 1h at 750 °C).

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References
Fig. 1. A set of the typical X-ray powder diffraction patterns of GaAs milled up to: (a) 10 min, (b) 1 h, (c) 2 h, (d) 3 h, (e) 6 h and (f) 10 h, respectively.

Fig. 2. Series of the representative XRD powder patterns of GaAs samples: 10 min milled and subsequently post-annealed for 1 h at 450 °C (b) and 750°C (c); and 10 h milled and subsequently post-annealed for 1 h at 450 °C (a) and 750°C (d), respectively.