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Thermal Stability of $Hg_{1-x}Mn_xTe$ Compound Semiconductors

By

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The thermal behaviour of $Hg_{1-x}Mn_xTe$ single crystals is investigated by means of the RBS/channeling technique. The stoichiometry parameter x ranges from 0.08 to 0.2. An important release of Hg atoms is observed after annealing in hydrogen atmosphere at 240 °C for 10 min. Backscattering spectra for crystals with $x = 0.2$ revealed quite a sharp Hg edge proceeding towards greater depth with increasing annealing temperature, the shallower region being completely depleted of Hg. Somewhat different behaviour is noticed for samples with $x < 0.1$. Although the Hg edge is also observed, the intensity of the Hg portion of the spectra diminishes with increasing annealing temperature or time. The latter effect is also observed for all samples after the second and further annealings. The examination by means of the optical microscopy reveals the presence of small cracks and pits which are apparently formed upon annealing. The Hg release through the crack walls is therefore responsible for the lowering of the Hg portion in the backscattering spectra.

Das thermische Verhalten von $Hg_{1-x}Mn_xTe$-Einkristallen wird mit der Rutherford-Rückstreuungs-Methode (RBS) untersucht, wobei der Parameter x zwischen 0,08 und 0,2 liegt. Intensives Freisetzen von Hg-Atomen wird nach dem Tempern in Wasserstoff-Atmosphäre bei 240 °C für 10 min festgestellt. Eine scharfe Hg-Kante in den RBS-Spektren wird beobachtet, die sich mit wachsender Temperatur in größere Tiefen verschiebt. Daraus folgt, daß der Bereich nah an der Oberfläche von Hg verarmt ist. Ein etwas unterschiedliches Verhalten wird an Kristallen mit $x < 0{,}1$ beobachtet. Obwohl die Hg-Kante immer noch zu sehen ist, nimmt die Zählrate vom Hg-Teil in den RBS-Spektren mit steigender Temperatur oder Zeit ab. Der gleiche Effekt wird für alle Proben nach dem zweiten und weiterem Tempern festgestellt. Eine Untersuchung mit dem optischen Mikroskop weist die Bildung von Poren und Rillen während des Temperns nach. Daraus kann man schließen, daß der Hg-Verlust über diese Strukturen für die Absenkung der Hg-Zählrate in den RBS-Spektren verantwortlich ist.

1. Introduction

Ternary semimagnetic semiconductors have attracted increasing attention in recent years because of their new magneto-optical and magnetotransport properties. The term semimagnetic semiconductor (SMSC) refers generally to any semiconducting alloy which is partially composed of magnetic ions. This class of materials exhibits a number of unusual magnetic, magneto-optical and magnetotransport properties which have been extensively reviewed elsewhere [1 to 3]. Hg-based II–VI compounds are currently used for infrared detector applications. The wavelength regions of 3 to 5.5 and 8 to 14 μm are largely dominated by $Hg_{1-x}Cd_xTe$ alloys, whereas $Hg_{1-x}Mn_xTe$ is proposed as an alternate material for

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these regions [1, 4]. The semiconducting properties of this alloy are similar to those of the well-known "sister material" $Hg_{1-x}Cd_xTe$. The exchange interaction between band electrons and Mn^{2+} d-electrons modifies its band structure making it strongly dependent on composition, temperature, and magnetic field [4]. $Hg_{1-x}Mn_xTe$ exhibits a Hg–Te bonding stability exceeding the one observed in $Hg_{1-x}Cd_xTe$, so that it should be considered a priori as a better candidate for device fabrication [5]. The characteristics of semiconductor devices, in particular narrow-band-gap semiconductors, are largely governed by the properties of the semiconductor surface [6]. One should point out that in $Hg_{1-x}Mn_xTe$ difficulties in processing and junction formation may also occur due to both volatility and rapid diffusion of Hg in the material. The behaviour of atomic migration of Hg in $Hg_{1-x}Mn_xTe$ should depend on heat treatment, composition, and surface passivation.

In this paper the thermal stability of the $Hg_{1-x}Mn_xTe$ compound was studied in detail for the stoichiometry parameter x ranging from 0.08 to 0.2.

2. Experimental

$Hg_{1-x}Mn_xTe$ single crystals were grown from Te-rich solution by a vertical modified Bridgman method [7]. A pulling rate of 0.4 mm/h and a temperature gradient of 50 K/cm were applied. No impurities were introduced intentionally and no post growing annealing was applied. The analyzed samples were of p-type having carrier concentration at 77 K

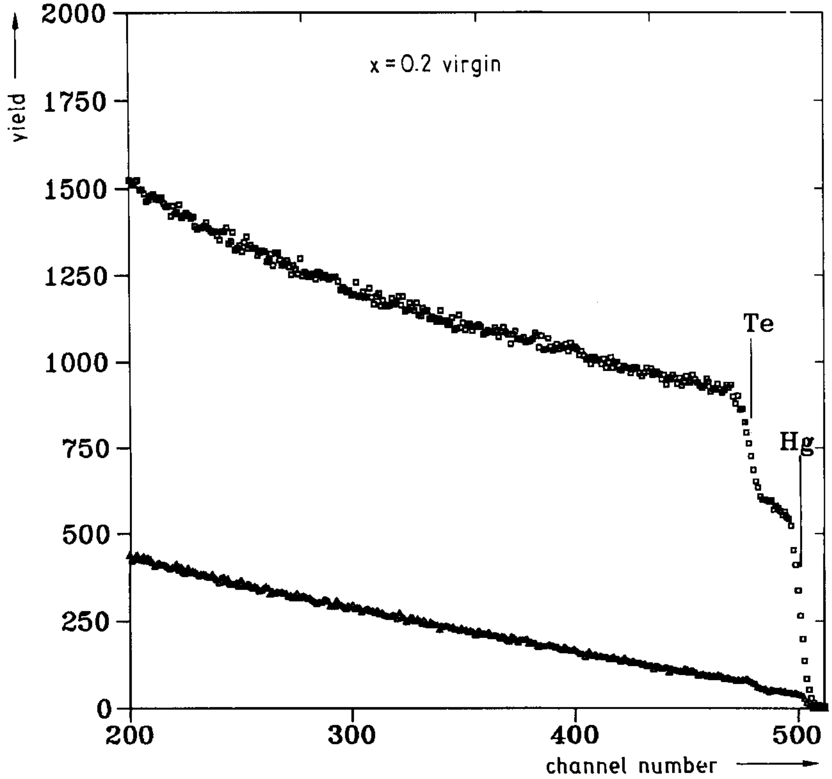

Fig. 1. Random (□) and aligned (△) spectra for a ⟨111⟩ $Hg_{0.8}Mn_{0.2}Te$ single crystal

between 5×10^{16} and 2×10^{16} cm^{-3}. The carrier mobility was of the order of 500 cm^2/Vs. Discs of about 1 mm thickness were cut out from the grown slab. Their surfaces were chemomechanically polished and solvent cleaned. Surfaces of samples for channeling analysis were additionally etched with bromine in ethylene glycol.

Annealing was carried out in flowing hydrogen in the temperature range 260 to 320 °C. The samples were analyzed before and after heat treatments by Rutherford backscattering spectrometry (RBS) using 2 MeV $^4He^+$ ions [8]. In order to check the quality of their crystallinity some samples were also measured in ion channeling mode [9]. Changes of the state of sample surfaces upon thermal treatment were also studied using optical microscopy.

3. Results

Fig. 1 shows random and aligned spectra for a ⟨111⟩ $Hg_{0.8}Mn_{0.2}Te$ single crystal. Two characteristic steps in the random spectrum corresponding to the Hg-ion scattering by Hg and Te atoms are clearly visible. One notes the lack of the Mn signal which should appear in the vicinity of channel 279. This is due to the much lower scattering cross section of Mn atoms and the much higher concentration of heavier components.

The minimum channeling yield close to the sample surface of χ = 12% indicates a reasonable quality of the crystal and the lack of a large amount of intrinsic defects.

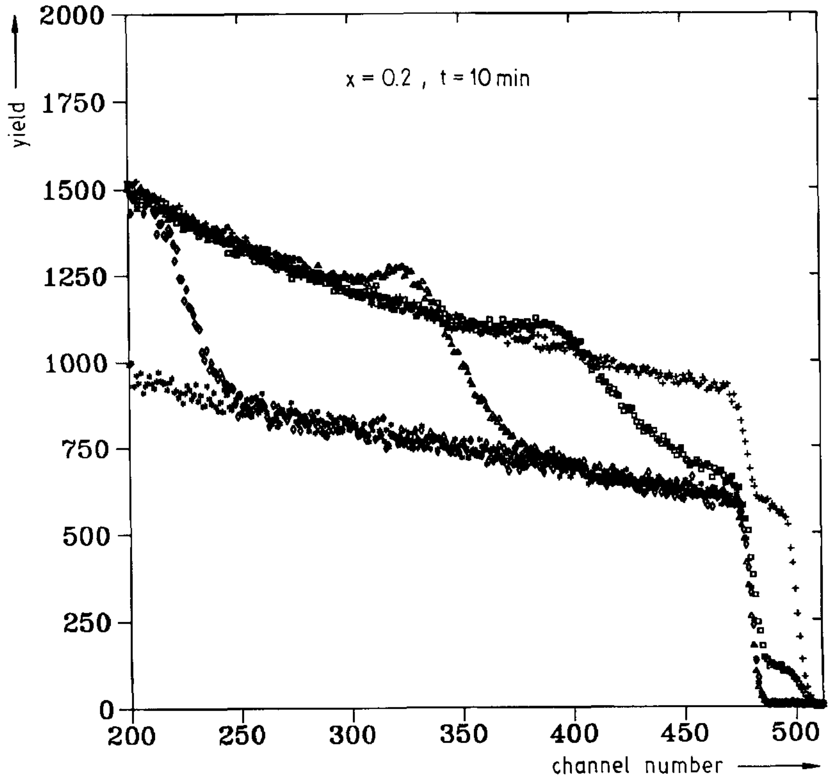

Fig. 2. Backscattering spectra obtained for $Hg_{0.8}Mn_{0.2}Te$ sample after isochronal annealing (t = 10 min) at different temperatures. + show the curve for the virgin sample other curves are for 260, 280, 300, 320 °C (from top to bottom)

Thermal treatment did not produce visible changes of the spectra up to 240 °C. The important decomposition of the sample begins at 260 °C. In Fig. 2 a set of backscattering spectra obtained after isochronal annealing ($t = 10$ min) at different temperatures is shown.

The Hg release is clearly visible already after annealing at 260 °C. The rapid decrease of the step in the vicinity of channel 500 indicates important depletion of the near-surface region in Hg atoms.

The Hg release proceeds with increasing temperature. One notes the formation of a completely Hg-depleted surface region. The region contains only Mn and Te atoms. The sharp step between Hg-depleted and nondepleted regions clearly indicates that Hg release is controlled by a process occurring at the interface between these two regions. The released Hg atoms diffuse rapidly through the depleted layer and eventually evaporate from the surface. It was hoped that the measurement of the release kinetics may elucidate this process. Fig. 3 shows the backscattering spectra for isothermal annealing of a $Hg_{0.8}Mn_{0.2}Te$ sample at 260 °C. Somewhat surprisingly the backscattering yield for Hg-containing portions of the spectra for times exceeding 10 min was lower than expected. One notes the unchanged yield of the high energy portion of the spectra.

Even more irregular Hg behaviour was observed for the $Hg_{0.91}Mn_{0.09}Te$ sample. Fig. 4 shows the backscattering spectra for such a sample after isothermal annealing at 260 °C.

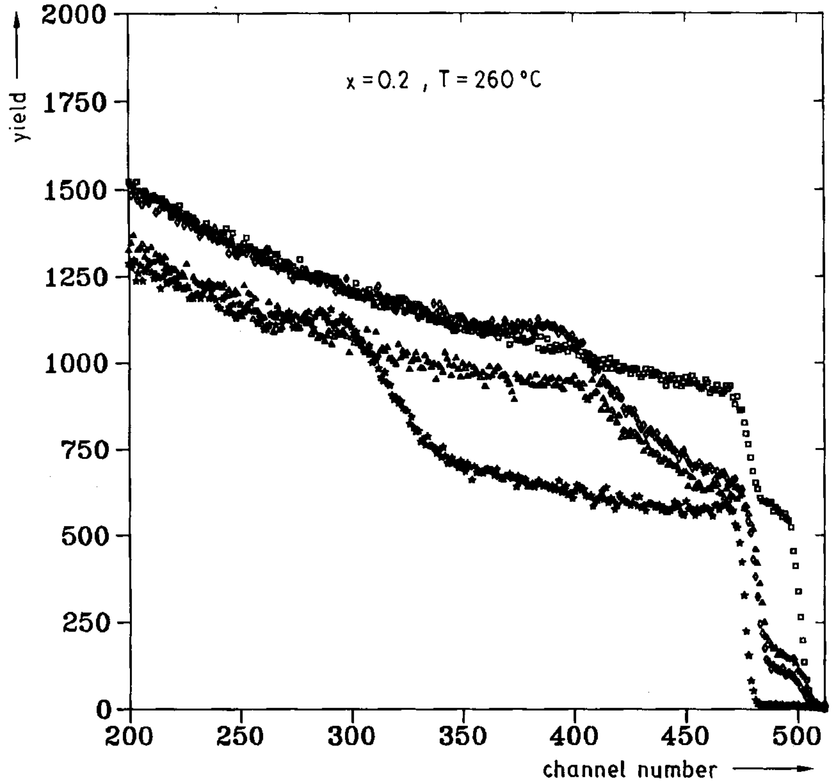

Fig. 3. Backscattering spectra obtained for $Hg_{0.8}Mn_{0.2}Te$ sample after isothermal annealing at 260 °C. □ Virgin, ◇ 10, △ 20, ⋆ 35 min

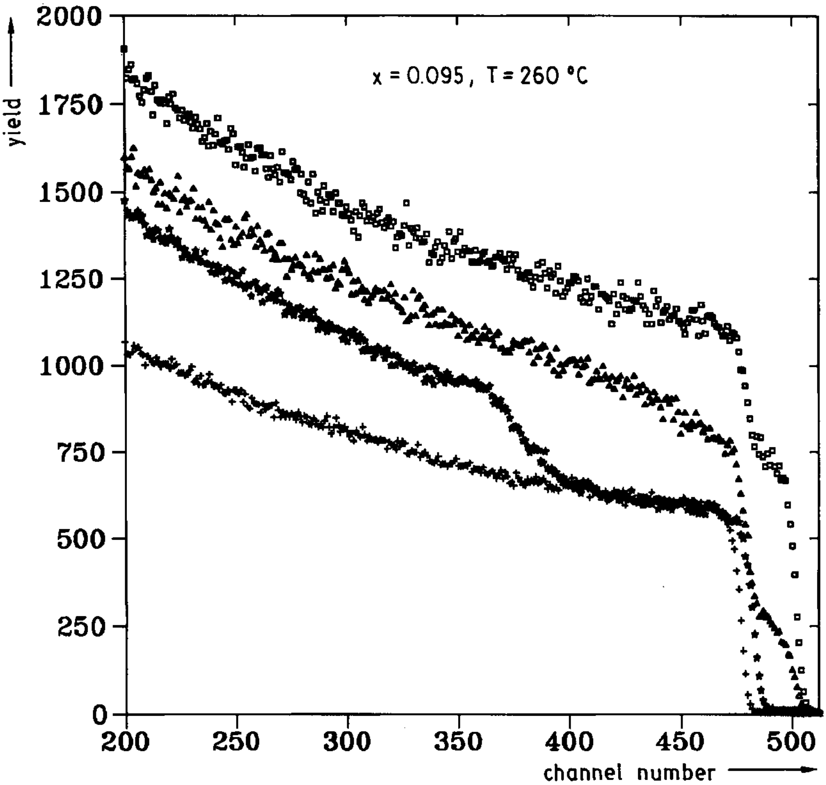

Fig. 4. Backscattering spectra obtained for the $Hg_{0.91}Mn_{0.09}Te$ sample after isothermal annealing at 260 °C. □ Virgin, △ 10, ⋆ 20, + 30 min

With increasing annealing time not only the Hg interface proceeds deeper, but also the Hg yield decreases continuously. This fact clearly indicates that Hg release does not only take place at the Hg interface, as can be concluded from Fig. 1, but other release channels are effective.

In order to check the state of the sample surface and its development upon annealing the samples were also examined by means of an optical microscope (magnification 200 ×). Fig. 5 shows two pictures obtained in this way: before and after annealing at 260 °C for 10 min. Dramatic changes occurred due to annealing. On the previously flat surface a large amount of pits and cavities was formed. The quantity of these deformation objects increases as a function of duration and temperature of annealing. The state of the surface is particularly sensitive to repeated cycles of heating and cooling as applied for the isothermal annealing. The number of cavities increases after each cycle.

The channeling investigation of annealed single crystals turned out to be impossible. The crystalline structure of surface layers was apparently destroyed at the moment when the Hg release begins. As a consequence no channeling pattern was observed.

4. Discussion and Conclusions

The Hg loss measurements described in the previous section were made as a function of several parameters: annealing time, annealing temperature, and composition *x* of

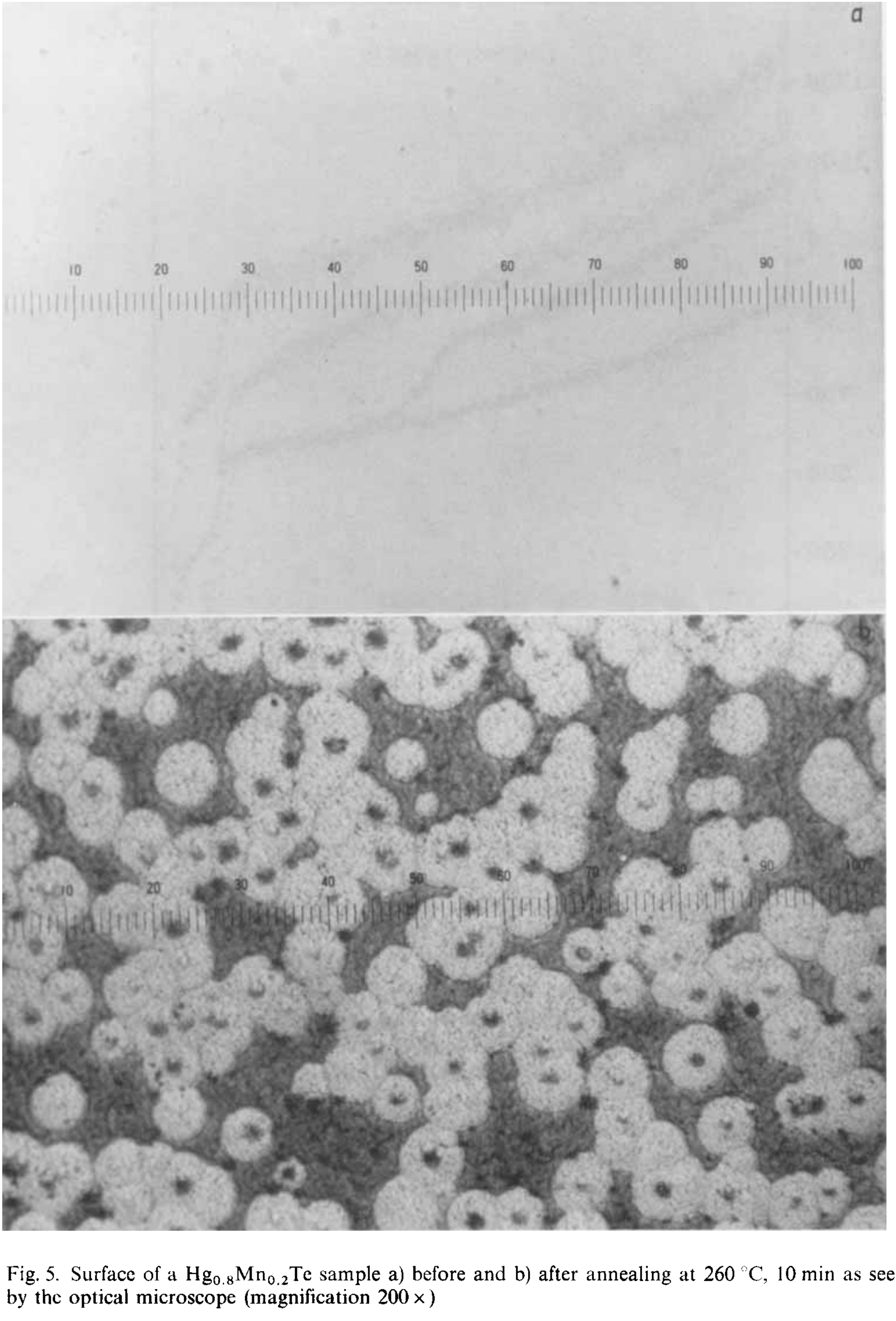

Fig. 5. Surface of a $Hg_{0.8}Mn_{0.2}Te$ sample a) before and b) after annealing at 260 °C, 10 min as seen by the optical microscope (magnification 200 ×)

$Hg_{1-x}Mn_xTe$ crystals. Hg release is a complicated process which cannot be described by simple out-diffusion models [10]. It should be pointed out that the results reported here are for large amount of total Hg loss, i.e. $\approx 10^{18}$at/cm^2. Optical microscope and SEM investigations [11, 12] revealed important structure transformations of the annealed samples. Most probably the structures observed by Mikułko and Szummer [12] are formed. Using SEM they observed the appearance of well-developed ducts running parallel to each other and perpendicular to the sample surface. With increasing temperature and/or time the number of ducts increases and finally a spongy, porous layer is created. The RBS analysis of such structures cannot yield reliable quantitative results. The ducts are apparently easy paths for Hg release: it evaporates to the inside of ducts where rapid diffusion towards the real surface occurs. Somewhat surprisingly we observed enhanced formation of cavities for samples of small x ($x \approx 0.1$). For $x = 0.2$ the cavities appear usually after repeated annealing. Taking into account this mechanism one can conclude that Hg loss is suppressed for samples with larger Mn content.

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