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AMORPHISATION OF SEMICONDUCTORS BY BALL-MILLING

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Résumé - Des travaux récents ont montré que, contrairement à l'opinion générale, le broyage mécanique pouvait produire une amorphisation partielle de semiconducteurs cristallins purs, tel le silicium. Dans une série d'expériences préliminaires, nous montrons qu'une amorphisation partielle de l'arséniure de gallium peut aussi être obtenue. En utilisant un broyeur planétaire, nous avons obtenu une poudre, mélange de microcrystallites et de grains amorphes qui représentent environ 11% du volume. Nous avons effectué des mesures du spectre de diffraction X, l'analyse thermique différentielle à balayage (DSC) et la microscopie électronique à balayage. La DSC nous a permis de donner un ordre de grandeur de l'enthalpie de recristallisation.

Des expériences analogues effectuées sur des cristaux de CdTe n'ont pas permis de mettre en évidence une amorphisation de ce composé, nonobstant le fait que le CdTe liquide présente une structure tétracoordonnée et semiconductrice.

Abstract - Recent results have demonstrated that ball-milling may produce a partial amorphisation of a pure crystalline semiconductor such as silicon, contrary to the general belief. In a series of preliminary experiments, we show that a partial amorphisation is also observed for the GaAs crystalline compound. X-ray diffraction, differential scanning calorimetry (DSC), SEM observations and EDX/SEM analyses have shown that the ball-milled powder (using a planetary ball-milling system) is a mixture of microcrystallites and an amorphous phase which amounts to 11% of the volume fraction. DSC analyses give an estimate of the crystallisation enthalpy. Similar experiments performed on CdTe crystals have not shown any tendency to amorphisation, in spite of the fact that liquid CdTe exhibits a four coordinated structure and is semiconducting.
Introduction

The aim of this paper is to investigate the capabilities of the ball-milling technique (referred to in the following as BM) as a method of amorphisation. Traditionally, the BM technique allows amorphising metallic alloys of large enthalpy of formation /1,2/ eventually starting from the components, provided that one of the two components is a fast diffuser /3/.

Using conventional techniques, group IV semiconductors are amorphised as bulk materials, even unhydrogenated, whereas III-V compounds are produced as thin films; on the contrary, II-VI compounds have not been amorphised by any preparation method, to the authors' knowledge (but a single reference /4/).

Recently, it has been shown that ball-milled silicon is partially amorphised /5/. It is therefore interesting to investigate the possibilities of the BM method regarding the above mentioned semiconductors.

Experimental procedure.

Ball milling procedure: 10 g of pure GaAs (or CdTe) are introduced in a cylindrical tempered steel container of capacity 45 ml. This procedure occurs in a glove box filled with purified argon. Each container is loaded with five steel balls 1.5 cm in diameter and 14g in mass. The container is sealed in the glove box with a Teflon O-ring. BM is carried out using two FRITSCH planetary high energy BM equipments (Pulverisette P7/2 and P5/2). For the latter, the intensity settings is mentioned between brackets, e. g. P5/2(10). The highest energetic condition are obtained with P7/2. The durations of the continuous milling processes have been respectively: 93h. for GaAs (P7/2), 127h. for GaAs (P5/2(10)) and 96h. for CdTe (P5/2(10)).

SEM observations and EDX/SEM analyses: Some GaAs particles have been extracted from the vial for further electron microscopy investigations: the particle morphology has been characterized using a Digital Scanning Electron Microscope (Zeiss DSM 950) in the secondary electron image mode. In order to evaluate the possible container contamination which may occur during the friction of the particles on the balls and on the walls of the container, E.D.X analyses have been performed using the Si - Li detector and the Tracor EDX analyzer which equips the Scanning Electron Microscope. A semi-quantitative program with internal references (SQ from TRACOR) has been used to analyze the EDX spectra. Cr impurities are not detected in any of the experiments whereas Fe impurities amount to at most .4% for GaAs (P5/2(10)) and 2.6 at.% for GaAs (P7/2).

X-ray investigations: After milling, a small amount of BM powder (0.3 to 0.6 g) is extracted from the container and glued onto a SiO2 plate for X-ray investigations. The X-ray diffraction patterns of the BM powders have been obtained using a (θ - 2θ) Philips diffractometer with CoKα radiation (λ = 1.7889 Å). A numerical method (The ABFFit program /6/) has been used in order to analyze the X-ray diffraction patterns and to obtain the position and the full-width at half height of the various peaks. The procedure has been
successfully used in the data reduction of BM amorphised Si and is reported in a review paper /7/. The peak width $B$ is related to the particle diameter $D$ through the Scherrer's formula

$$B(2\theta) = \frac{0.91 \lambda}{D \cos \theta}$$  \hspace{1cm} (1)

**Experimental results**

**GaAs**

Figure 1 show the GaAs particles observed by Scanning Electron Microscopy: the distribution of sizes ranges from microparticles (more than 1 mm in diameter) to nanoparticles.

![SEM observations (Secondary electron image mode) of the ball milled powder of GaAs for two different milling conditions (a)P5/2 (left), least energetic milling conditions and (b)P7/5 (right), high energy milling). The smallest grains corresponds to the amorphous phase and the largest grains are microcrystallites.](image)

Figure 1: SEM observations (Secondary electron image mode) of the ball milled powder of GaAs for two different milling conditions (a)P5/2 (left), least energetic milling conditions and (b)P7/5 (right), high energy milling). The smallest grains corresponds to the amorphous phase and the largest grains are microcrystallites.

The raw diffraction data are shown in Fig. 2 in the range $20^\circ < 2\theta < 120^\circ$ or $1.2 < k < 6.1$ A$^{-1}$. The Bragg peaks, broadened by the size effect, are the only relevant features seen by the eye. However, the ABFfit program analyses the diffraction peaks in different gaussian contributions and an underlying spectrum, characteristics of an amorphous phase is put forward; it amounts to 11% in both cases. The position of the first peak in the amorphous spectrum is respectively $q_1 = 1.936$ A$^{-1}$ (P7/2) \[ and 1.956 $A^{-1}$ (P5/2)], the second broad peak at $q_2 = 3.24$ A$^{-1}$ is characteristic of the amorphous state, it is located in between the (220) and (311) Bragg peaks; this gives a ratio $q_2 / q_1 = 1.67$ in excellent agreement with the value obtained from flash-evaporated GaAs. This is the signature of a tetracoordinated structure with even membered rings /11/.
Figure 2. Raw diffraction data obtained from Table 1. Results of the ABFfit program analysis of figure 2.

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<th>2θ</th>
<th>Δ(2θ)</th>
<th>q(Å⁻¹)</th>
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DSC measurements (Fig. 3 a and b) have been performed with a temperature variation of 40°C/min; they show a small endothermic effect below 200°C and an exothermic effect above 200°C which contains two contributions, a diffuse contribution starting at low temperature (150°C) and extending to 500 - 600°C. A narrower contribution in the temperature range 400°C - 600°C is attributed to the recrystallisation heat. Similarly to ball-milled silicon, the

Figure 3. DSC measurements on the two different ball-milled GaAs samples (a) and (b).
recrystallisation starts at higher temperature compared to amorphous GaAs produced by conventional means (310° C, /8/). On the basis of 11% relative volume of amorphous phase, the recrystallisation heat is estimated to be between 10 and 20 kcal/at. g., in relative agreement with ref. /8/.

**CdTe**

A similar experience performed on CdTe were not able to show the existence of an amorphous phase (within the limit of 1% ). The diffraction spectrum is entirely analysed in terms of Bragg peaks broadened by the size effect (Figure 4). The average value of the particle diameter deduced from the Scherrer formula (1) is 85 Å. No broad peak is observed in between the (220) and (311) Bragg peaks.

![Figure 4. Raw diffraction data of the CdTe stoechiometric compound.](image)

**Discussion**

From these investigations, we conclude that the BM technique gives a partial amorphisation of the semiconductors that have already been produced by other techniques, but in our experimental conditions, it was not possible to produce amorphous semiconductors that were not obtained already amorphous by other techniques. We believe that other III-V semiconductors will behave the same way. On the other hand, CdTe which has not been produced in amorphous phase, cannot be amorphised either by BM. This asks an intriguing question because it has been shown that liquid CdTe /9/ (and similarly ZnTe /10/) is fourfold coordinated and its liquid structure can be described by a Connell-Temkin model valid for amorphous GaAs. The reason why rapid solidification of the liquid phase does not produce amorphous CdTe is not well understood. CdTe has a strong tendency to crystallise and our BM
experiments confirm that its crystalline phase is relatively more stable than that of GaAs, even under ball-milling conditions. A possible explanation is the difference in ionic character of the III-V and II-VI compounds.

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