Gallium arsenide deposited on the porous glass

K. S. PATER

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

An MOCVD epitaxy of gallium arsenide on the porous glass has been applied. The results of optical and electrical measurements of the porous glass covered by GaAs are presented.

1. Introduction

In the last years, a series of papers on the porous glasses have been published [1]-[4]. Some of them concern deposition of the semiconductor compounds inside the porous glasses. This is the first step to direct application of these glasses as a substrate in optoelectronics [5].

The porous glass can be obtained as the result of etching the alkaline compounds from the solid glass. After leaching them there remains a silica skeleton with the porous structure. The mean dimension of pores depends on the heat treatment leading to a suitable phase separation in the glass, still before the leaching of the alkaline phase. After leaching the microporous glass can be obtained with pores of a few nanometer diameter. After additional leaching in the KOH the macroporous glass with the pore diameter of a micrometer fraction order has been obtained [6].

The semiconductor compounds are deposited on the glass as a liquid solution or from the gas phase. Evaporation and subsequent heat treatment of zinc phosphide [7] did not give satisfactory results. The better results were obtained for halkogenides, such as CdS and CdSe [8], by depositing them in the low-temperature chemical reactions from the aqueous salt solutions with hydrogen sulphide or hydrogen selenide. The light absorption of the majority of samples, filled with the semiconductor compounds in the way mentioned above, exhibited a sharp edge, as for the solid material.

The aim of this work was deposition of gallium arsenide on the porous glass and investigation of the properties of the impregnated samples, which can be applied to optical filtres. For deposition of the GaAs epitaxial layers on the porous glass the MOCVD (Metal-Organic Chemical Vapour Deposition) [9] method was applied. This technology is expensive, but gallium arsenide is a very important material from the point of view of its applicability.

2. Technology of the sample preparation

Three samples of porous glass of dimensions $20 \times 10 \times 1$ mm³ have been prepared according to the procedure described. The glass samples were etched right across and

the pores were linked. Sample P1 was the reference one. In samples P2 and P3 the GaAs was deposited. The epitaxy was performed at the Institute of Electron Technology, Technical University of Wrocław. The deposition process took place in the standard vertical quartz reactor cooled with water. The support of the substrate was the graphite cylinder of 45 mm in diameter inductively heated. For deposition, trimethyl gallium $(Ga(CH_3)_3)_{(g)}$ and arsine $(AsH_3)_{(g)}$ with hydrogen as a carrier gas were used. The chemical reaction

 $(Ga(CH_3)_3)_{(g)} + (AsH_3)_{(g)} \longrightarrow GaAs_{(s)} + 3CH_{4(g)}$

was performed at the temperature of 850 K for 5 minutes for the P2 sample and 3 minutes for the P3 sample.

3. Experimental results

3.1. Morphology

The colour of the samples after their removal from the reactor was brown and grey. The external surfaces exposed to the gas action were easily distinguishable. The mass of the samples decreased after epitaxy due to desorption of water from the surface of pores. Figure 1a presents the micrograph of the P2 sample surface with the arrow marking the GaAs grain for which the roentgen analysis of composition was made. The results of analysis are presented in Fig. 1b. Besides the peaks characteristic of gallium and arsenium, also a high silicon peak originating probably from the silica substrate is present. This peak dominates in the roentgen spectrum presented in Fig. 2b and obtained from the area limited by a rectangle marked in Fig. 2a. The micrograph (Fig. 2a) presents the cleavage plane of the same sample. No GaAs continuous layer is visible in the bright area on the right-hand side, where epitaxy

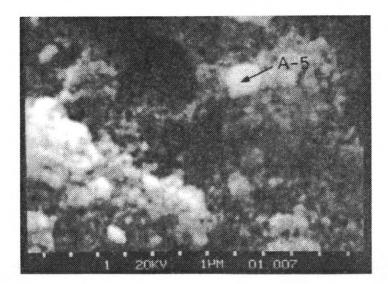


Fig. 1a

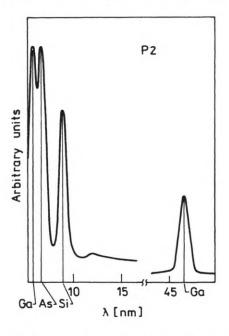


Fig. 1. Micrograph of the P2 sample surface (a) with the arrow marking the GaAs grain for which the roentgen analysis (b) was made

has occurred. The bright spots at the bottom of the micrograph are probably the separate fragments of coverage. The results of roentgen analysis of these fragments are presented in Fig. 2c. It can be generally stated that the nonstoichiometric GaAs grains were observed in the coverage, for which distinctly visible was the arsenium peak only, whereas no grains with dominating gallium peak were observed.

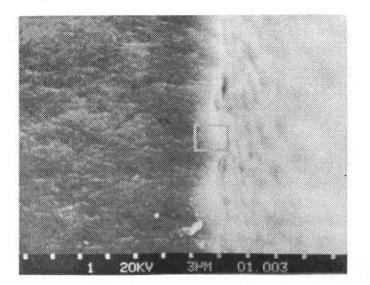


Fig. 2a

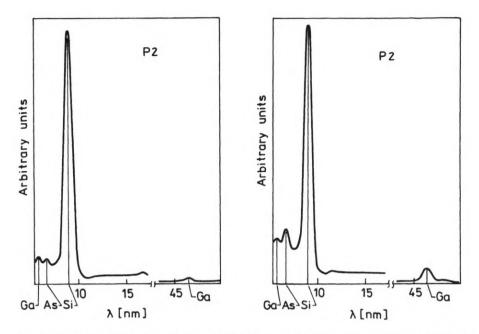


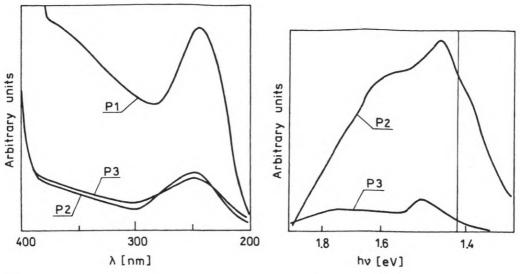
Fig. 2. Micrograph of the cleavage plane of the P2 sample (a), the roentgen spectrum (b) obtained from the area limited by a rectangle and results of roentgen analysis (c) of fragments of the coverage visible as bright spots on the bottom of the micrograph

3.2. Luminescence

The luminescence excitation spectra of glasses covered with GaAs have the shapes similar to the spectra of glass without coverage (Fig. 3). In the whole excitation range under investigation, the signal for both the P2 and P3 samples is about five times lower than that for the reference sample P1. Photoluminescence in the red-orange range, observed at the room temperature, was very weak (Fig. 4). There are no sharp edges of the spectrum. A very broad luminescence peak suggests GaAs coverage. Position of the maximum for both samples varies and is different from that for the epitaxial layer of GaAs substrate. This may be caused by differences in the sizes of coverage grains [9].

3.3. Thermostimulated depolarization

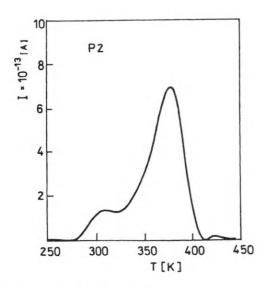
The depolarization current in the sample covered with GaAs (P2) was investigated. The blocking electrodes were applied. The temperature of polarization amounted to about 470 K, and the field strength of polarization to 10^4 V/m. No peaks were observed (Fig. 5) up to the room temperature. Two peaks: at 310 K and 380 K are present for solid glass [10]. It can therefore be supposed that the semiconducting coverage has very little influence on the electrical process in the bulk of the samples investigated.

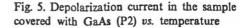


۸

Fig. 3. Luminescence excitation spectra of glasses covered with GaAs (P2, P3) and the spectra of glass without coverage (P1)

Fig. 4. Photoluminescence in the red-orange range, observed at the room temperature for both the samples P2 and P3 covered with GaAs





3.4. Electrical resistance

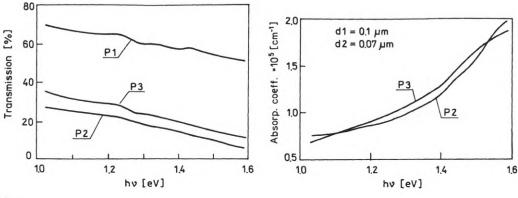
The electrical resistances of the samples as measured in planar configuration are given in the Table. The gold contacts from chloroauric acid were applied. The I-V characteristics were linear for both P2 and P3 samples in the whole measuring range from -20 V to 20 V.

Sample	In air atmosphere	After rinse in hexamethyldisilizane
P1	1.3 × 10 ⁷	> 5.0 × 10 ¹⁴
P2	1.3×10^{9}	3.0×10^{10}
P3	1.3×10^{9}	2.5×10^{10}

Electrical resistance of the samples (ohm per square)

3.5. Absorption

The light absorption in the vicinity of the basic absorption edge of the solid GaAs was investigated. The samples were not stuffed with a material reducing the light scattering (e.g., methyl polymethacrylate). The light transmission was determined by the method described in paper [7]. The results are presented in Fig. 6. The shape of the curves is smooth and the absorption edge is not clearly seen.



۸

Fig. 6. Light transmission for the sample without (P1) and with (P2, P3) cover Fig. 7. Absorption coefficient fitted for the GaAs coverage on the P2 and P3 samples

4. Discussion

The experimental results allow us to suppose that gallium arsenide is deposited on the surface of the porous glass and does not penetrate inside the pores. Fitting the absorption coefficient gives (Fig. 7) as a result the mean layer thickness of about a micrometer fraction. The layer thickness cannot be estimated from the electron microscope photographs because no continuous layer of gallium arsenide is seen on the micrographs. In the structure of the layer one can distinguish grains, part of them being strongly nonstoichiometric with a distinct predominance of arsenium. This is probably caused by a relatively low temperature of epitaxy [11] and, obviously, the high temperature gradients on the sample surfaces thus evaluated. Application of higher temperatures may cause changes in the structure of porous glass. In conclusion, it can be stated that the GaAs coverage is probably composed of nonstoichiometric grains partially connected together. It can be supposed that building a special reactor for GaAs epitaxy on the porous glass using the MOCVD technology could give desirable results. Such a reactor should enable the flow of reacting gases across the glass pores. It seems also that more suitable for MOCVD epitaxy would be the macroporous glass with a possible uniform structure.

Acknowledgement – The author would like to thank Dr K. Marczuk for supplying the porous glass and luminescence excitation measurements and Dr J. Radojewski for photoluminescence measurements. This work was financed by Technical University of Wrocław, Poland.

References

- [1] MACEDO P. B., SANTANA M., SIMMONS J., Patent USA No. 4188196, 1980.
- [2] ALEXEEV-POPOV A. V., ROIZIN YA. O., RYSIAKIEWICZ-PASEK E., MARCZUK K., Opt. Materials 2 (1993), 249.
- [3] ZERDA T. W., VASCONCELOS W. L., HENCH L. L., J. Non-Cryst. Solids 121 (1990), 143.
- [4] KAPS CH, SCHUBERT R., FRANKE G., Proc. XVI Intern. Congress on Glass, Bol. Soc. Esp. Ceram. Vid. 31-C, 3 (1992), 109.
- [5] LONG J. C., BORELLI N. F., Proc. Mat. Res. Soc. Symp. Proc., 1989, p. 144.
- [6] MAZURIN O. V., PORAI-KOTSHITS E. A., Phase Separation in Glass, North-Holland, Amsterdam 1984.
- [7] PATER K. S., Opt. Appl. 24 (1994), 73.
- [8] KAPS CH., SCHUBERT R., Opt. Appl. 24 (1994), 141.
- [9] MANASEVIT H. M., J. Electrochem. Soc. 1725 (1969), 116.
- [10] RYSIAKIEWICZ-PASEK E., PATER K., in press.
- [11] TLACZALA M., private communication.

Received April 6, 1995