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PROPERTIES OF GaAs EPITAXIAL LAYERS GROWN IN WATER VAPOUR ASSISTED TRANSPORT PROCESS

SZILÁRD VARGA and KÁROLY SOMOGYI

Research Institute for Technical Physics of the Hungarian Academy of Sciences,
Budapest, P. O. B. 76, H-1325 Hungary

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GaAs homoepitaxial layers have been grown in close-spaced transport conditions. The transport process was activated by the presence of water vapour in hydrogen at temperatures about 730 − 760 °C and 800 − 900 °C. GaAs wafers were used as solid sources. A distance of about 0.3 − 1 mm from the substrate was kept with silica spacers. High growth rates have been reached (up to 2 μm/min) and carrier concentrations at 2×10^{17} and 2×10^{16} cm^{-3} were found at the above two growth temperatures, respectively. The electron mobilities are relatively low suggesting high compensation rations, typically 0.3-0.5. Photoluminescence spectra show peaks corresponding to complexes formed with participation of peaks corresponding to complexes formed with participation of intrinsic point defects, what is in agreement with the growth rates and electric parameters.

1. Introduction

Many techniques of epitaxial growth of semiconductor layers have been developed in the last ten years. Revival of some nearly forgotten methods is also observed. One of the most promising revivals is the close-spaced vapour transport (CSVT) technique [1-3]. The great interest can be explained by the fact that this method is cost-efficient and does not require toxic source materials compared to the sophisticated and advanced technologies.

Though promising results are published on growing of different heteroepitaxial structures for photovoltaic and solar cell applications [e.g. 4, 5], the basic questions of the CSVT technology are discussed on the basis of GaAs homoepitaxial growth [1,6]. Questions of the growth mechanisms and the relation between the properties of the "end product" and the growth (chemical, kinetic, etc.) processes are still discussed. In this work, typical physical properties of a great series of CSVT grown GaAs homoepitaxial layers are summarised.

2. *Experimental conditions*

Two different concepts have been realised in CSVT setups. One of them is a "barrel" type system, with a (nearly) stagnant H_2 ambient, with the possibility of a vacuum pretreatment [1]. In our work an experimental reactor was built of the second type, i.e. an open tube and continuous flow system [2]. The scheme of this CSVT equipment is described in Ref. 7, and it is very similar to that shown in Ref. 5. The heating system consisted of either two 1 kW or two 2 kW tungsten halogen lamps. Temperatures of $T_1 = 760$ °C and $T_2 = 730$ °C of the source and substrate, respectively, were reached by using 1 kW lamps (process type I). The corresponding temperatures were 900 °C and 800 °C when using 2 kW lamps (process type II). These temperatures were measured by chromel-alumel thermocouples inside the directly heated graphite blocks.

Fused silica spacers were used of thickness d=0.3, 0.5, 0.7 and 1 mm, of the forms of a ring or a semi-ring. The diameter of the spacers was 1 cm and they were placed directly between the source and substrate wafers. Saturation with H_2O vapour was assured by bubblers up to 610 Pa.

Layers grown on Si-GaAs substrates underwent also Hall measurements. Layer thicknesses have been determined by the C-V profilometry and by alphastep measurements, which was possible owing to the spacers: the surface below the spacers remained practically unaffected. Surface morphology was investigated by optical and scanning electron microscopy. Also X-ray topography and Laue patterns were studied. 77 K photoluminescence spectra offered additional informations.

3. *Growth and morphology*

The role of the water vapour in the transport process is described more or less unambiguously in the literature. There are ambiguities concerning the moment of introduction and on the choice of the optimum temperature of introduction of the water vapour. Our experiments were directed in this direction.

Fig. 1. Scanning electron micrographs of a typical surface of a GaAs *layer grown at water partial pressure* ≈ 20 Pa, *applying only heating and cooling periods. (a) and (b) show different areas. Sample 18 n.*

Fig. 2. Two typical 77 K *photoluminescence spectra of samples of process I.*

(i) Growth cycles were carried out without water (i.e. palladium end-purified H_2, with the partial pressure $p_{H_2O} \approx 6$ Pa) in processes of both type. No epitaxial growth was detected. However, it is striking that the surfaces of the wafers kept their mirror like smoothness.

(ii) Introducing H_2O vapour at partial pressure ≈ 20 Pa from the beginning of the heating process resulted in the growth of GaAs layers. The surface studies have shown significant differences between processes of types I and II. In the case of the high temperature process, the surface was usually found mirror like and the growth rate was very high, up to $> 1\mu$m/min. In the low temperature process, usually dull surfaces were obtained. Figure 1 shows typical surface defect structures for this case. A porous like surface suggest an amorphization of the layer. Nevertheless, X-ray topograms and also Laue patterns prove a monocrystalline structure and a relatively low extended defect concentration in the layers. Figure 2 shows two typical photoluminescence spectra with very definite, intense and sharp band edge exciton peaks, which also demonstrate an appropriate crystalline quality of the GaAs layers.

Fig. 3. Scanning electron micrographs of two typical surface areas (a. and b.) of an epitaxial GaAs layer grown at high water partial pressure (≈ 50 Pa), but heated up at low water pressure (≈ 20 Pa). Sample 21 n.

(iii) Figure 3 shows the morphology of two typical surface structures grown at $p_{H_2O} \approx 500$ Pa, introduced at about 700 °C for the time of the growth period, while the water pressure was kept 20 Pa during the heating and cooling periods in processes of type I. The thickness of the layer is 3 μm, the growth rate was $\approx 0.15\mu$m/min. In the high temperature processes, the surface morphology was significantly improved, the growth rates were significantly increased, but dependent on the main flow.

4. *Galvanomagnetic and photoluminescence properties*

Galvanomagnetic and C-V profilometry studies have shown that in the low temperature processes n-type layers were always obtained with a carrier concentration around 10^{17} cm^{-3}, independently of the technological circumstances and of the type of the source material (either n, p or SI type). These results are not evident. In the high temperature processes, high resistivity and p-type layers have also been obtained (from SI and p-type sources, respectively). Using n type sources, the electron concentration in the grown layers, near 10^{16} cm^{-3}, was lower than that in the low temperature processes. This is probably due to the more perfect crystal formation in the growth process, in agreement with the more perfect morphology.

Independently of the technological circumstances, a low electron mobility in n type layers has been obtained. Figure 4. shows plots of the electron concentration versus temperature. These curves and the maxima indicate not only the low value of the mobility, but high compensation ratios typically of 0.3–0.5, as well. The mobility results are in good agreement with the existing literature data.

Fig. 4. Plots of electron mobilities versus temperature covering the whole electron concentration range of CSVT grown GaAs layers.

In photoluminescence (PL) spectra, three peaks were found and at the gap.

All of them are strongly connected with crystalline point defects. The first one is at 1.45 eV and it is an electron-acceptor type transition, related to the combination of the Si acceptor and stoichiometry defects. The best electron-acceptor type transition at 1.34 eV is very typical of GaAs vapour phase epitaxial layers and is related to Cu on Ga sites. Electron-acceptor transitions at 1.26 eV can be related to shallow acceptors (Zn, Ge, Sn) on As sites and intrinsic defects. Halfwidth of these peaks indicates the presence of different complexes, based on or related to different stoichiometry point defects.

5. *Discussion*

Literature data are consistent in publishing a critical temperature difference T_1-T_2 of about 50 °C, which is necessary for layer growing. In our case for processes I, this difference is not more than 30 °C, and growth was observed. The SEM picture (Fig. 3) indicates that the density of nucleation centres is small and the coalescence of the crystallites (probably 3D type growth [5]) is not perfect. Low partial water pressure indicates also less effective surface kinetics (Fig. 1).

Concerning the temperature of the introduction of the water into the reactor, two moments have to be mentioned. The measured temperatures are not equivalent to the temperatures of the surfaces of the (GaAs) wafers serving as sources and substrates. This fact makes the explanation of the results more difficult. Moreover, the thickness of the spacers can influence on the surface temperatures what it is not indicated by thermocouples. On the other hand, the vapour introduced into the system through an inlet must reach the closed ambient between the two wafers, a problem that concerns the question of the structure of the reactor system itself.

The high compensation ratio and the independence of the conductivity type on the source wafer can only be explained with a very high (dominating) density of point defects, suppressing the direct influence of impurities. PL measurements are in agreement with this explanation of the growth results (Fig.2).

That is supported also by the observations that all the measurements and studies showed that the samples are laterally inhomogeneous. Temperatures, H_2 flux, spacer thickness and geometry, water pressure, etc. can be varied, but thicknesses, electrical properties, surface morphology, etc. are still nonuniform along the wafer. Publications in the literature report also on small surfaces, but usually do no speak about uniformity. It seems that the nonuniformity of the layers is one of the main reasons that this process is not used by industry.

6. *Conclusions*

Easy feasibility and cost-effectiveness of the CSVT process is very attractive for epitaxy growers. A simple setup was constructed and some basic properties of the layers were investigated. Results show some peculiar and some general properties of such GaAs epitaxial layers. It turns out that neither the transport process, nor the growth processes are clear in details.

The main conclusion is that GaAs epitaxial layers can be grown with acceptable crystalline quality. High growth rates can be reached and very thick layers can be grown. The intrinsic and growth defects seem to dominate the properties of CSVT grown layers, probably due to the intensive growth of the layers. Therefore, further efforts have to be made to elucidate processes of the growth and to improve the technological conditions. On the other hand, a search for applications can be continued to exploit properties, which are given or which are realisable with CSVT technique, since this method is probably the simplest, cheapest and safest method among the semiconductor epitaxial technologies.

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SVOJSTVA EPITAKSIJSKIH SLOJEVA GaAs NAČINJENIH PRENOŠENJEM UZ POMOĆ VODENE PARE

Homoepitaksijski slojevi GaAs načinjeni su u uvjetima malog razmaka (0.3-1 mm). Prijenos je u vodiku aktiviran vodenom parom na temperaturama $730-760$ °C i $800-900$ °C. Ustanovljene su velike brzine rasta (do 2 μm/min) s koncentracijama nositelja 2×10^{17} i 2×10^{16} cm^{-3} za gornja dva temperaturna područja. Elektronska vodljivost slojeva je relativno niska što ukazuje na visoku kompenzaciju.