Annealing of GaSb single crystals in ionised hydrogen atmosphere

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ABSTRACT

GaSb undoped wafer were annealed in flowing ionised hydrogen atmosphere at temperature range between 100 – 350°C for 1 – 50 hours. The free carrier concentration and resistivity were measured. It was found out that the wafers being treated at a temperature of 150°C for 24 hours reached the resistivity of about $10^2 - 10^3$ Ω.cm and the free carrier concentration was lower than 1 x 10^{15} cm^{-3}. However, the thickness of the passivated layer was only 0.4 – 0.6 μm.

1. INTRODUCTION

Gallium antimonide (GaSb) single crystals are promising candidates for a variety of military and civil applications in the 2 - 5 and 8 - 14 μm ranges, among others infrared (IR) imaging sensors for missile and surveillance systems (so-called focal plane arrays), fire detection and monitoring environmental pollution and other light diodes and lasers. In comparison with traditional GaAs, InSb, InP, for which the semi-insulating as well as conductive material is available, GaSb has a disadvantage: its conductivity that is usually very high due to the large amount of p-type natural defects in the lattice, which puts very serious limits on the construction of GaSb-based devices. To develop high-resistive GaSb, intensive optimisation of doping and growth conditions was undertaken[1,2]. Doping by the following elements Cu, Zn, Cd, In, Si, Ge, Sn, N, As, S, Te, Mn was investigated[3,4,5,6] systematically using the Czochralski method of growth without encapsulant in a hydrogen flowing atmosphere as well as by diffusion studies[7]. The limit of the doping concentration of each dopant was measured indicating the lowest solubility for S, N, Cu, and the highest for In, Ge, Te, As[8]. Extensive thermodynamic evaluation were also carried out and directed to analyse some binaries and ternaries, such Ga-Sb-S (Te, Cu), etc.[3,4,5].

However, in spite of big affords, the desired low conductivity material was not obtained yet. Therefore a special and rather unique method has been developed using the passivation of active donors of n-type (Te-doped) crystals by protons during the inherent growth realised in the ionised hydrogen atmosphere generated in situ by deuterium lamp radiation[9,10]. From a thermodynamic point of view the ionised hydrogen passives a part of donors and shifts equilibrium between passivated and active donors depending on the starting concentration of n- and p-dopants to the intrinsic-like position. The preparation of stable GaSb with sufficiently high resistivity would open unique perspectives in the construction of integrated IR-optoelectronic devices of a new generation.

A major drawback of GaSb substrates is their higher concentration of residual acceptors that reach, in the pure undoped GaSb single crystal, a value[11] of about 1.7 x 10^{17} cm^{-3}. The acceptors are identified as $V_{Ga}Ga_{Sb}$ complexes (where V is the vacancy) with a double ionised structure[12]. The resulting resistivity of undoped GaSb single crystals is about 10^{-2} Ω.cm. Many researchers have tried to reduce the residual acceptor concentration and to increase the resistivity of GaSb.

The achieved results of growth under the ionised hydrogen atmosphere were sufficiently stimulating to encourage us in opening the question of annealing of GaSb wafers in ionised hydrogen a to study influence of this treatment on change of free carrier concentration and resistivity.

2. EXPERIMENTAL AND DISCUSSION

Hydrogen passivation of different defects and impurities was studied in many III-V compounds[13,14]. Polyakov et al[15] treated GaSb samples either undoped or Zn- or Si-doped both in hydrogen and in deuterium atmosphere in the temperature range between 100 - 250°C and with the exposure times of 0.5 - 1 hour with interesting results. In the case of the undoped GaSb

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the carrier concentration decreased as much as to the value of about 1 x 10^{16} cm^{-3} and the resistivity increased by one order of magnitude. Polyakov et al.'s method showed that this way is likely to successfully manage the preparation of least high-resistivity GaSb crystals with a low carrier concentration.

Using the Czochralski method without encapsulant in a hydrogen flowing atmosphere the undoped GaSb single crystals were grown having a carrier concentration of (1.70 - 1.80) x 10^{17} cm^{-3} and a resistivity of (6.50 - 6.70) x 10^{-2} Ω.cm. The crystal bowl was cut to the wafers with a thickness of 200 μm. The samples were treated in a quartz tube at temperatures of 100, 120, 150, 180, 200, 220, 250, 280 and 350°C for 1-50 hours. Hydrogen ionised by means of a deuterium lamp flew through this annealing reactor. After cooling the quartz ampoule, the carrier concentration and the resistivity were measured on the treated wafers in the first step by means of van der Pauw method. Then the layers of about 10 μm on both sides of the wafers were ground out and the electrical measurements were repeated.

It turned out that in the case of the temperature range 200 - 350°C (Fig.1.); the values of the measured parameters were the same, both before and after the temperature annealing. However, when the temperature was lower than 200°C, mainly at 150°C, and the duration of the annealing procedure exceeded 10 hours, the carrier concentration in the nonground wafers achieved the value of (1.20 - 1.30) x 10^{17} cm^{-3} (i.e. about 40%). After grinding a 10 μm layer, the carrier concentration was the same as in the case of the untreated samples.

This method of measurement, however, is influenced by a high inaccuracy because the total volume of the samples was measured for only a small passived layer. For this reason, the resistivity and free carrier concentration were studied by the spreading resistivity procedure. It has been found that in the case of the wafers being treated at a temperature of 150°C for 24 h, the thickness of the passived layer was only 0.4 – 0.6 μm and its resistivity reached value of 10^{2} - 10^{3} Ω.cm. The free carrier concentration was lower than 1 x 10^{15} cm^{-3} and with increasing time of temperature treatment the values of free carrier concentration does not change essentially. It seems the optimal duration to be about 20 – 30 hours only. However, such a thin layer of high-resitivity GaSb crystals would be difficult to fabricate because, on the one hand, the thickness of the layer was not uniform on the surface of the wafers and, on the other hand, the spreading of the resitivity was very inhomogeneous.

3. CONCLUSIONS

The results of electrical measurements show that the ionised hydrogen does effect the resistivity of GaSb. However, the effect of temperature is not fully clear (Fig.2.). We only suggest that the temperature influence, on the one hand, the diffusion of ionised hydrogen into GaSb material and, on the other hand, the evaporation of hydrogen from the crystal. The equilibrium could create between these effects and for this reason the temperature of 150°C seems to be the most suitable for obtaining GaSb with low free carrier concentration. Diffusion of ionised hydrogen into GaSb wafers play very important role in decrease of free carrier concentration during the temperature treatment and could be said that the diffusion is the limiting factor. Of course, higher temperature speed up the diffusivity, however, in the case of our procedure the ionised hydrogen also starts either to recombining to molecular hydrogen or evaporating from material. It seems that annealing in higher pressure of hydrogen could help to stimulate diffusion and prevent evaporation from GaSb.

Next study will be mainly oriented to look for new methods how to increase ionised hydrogen concentration in GaSb material and if it is still possible to work in the region of higher temperature, especially at melting point of GaSb (712°C), i.e. during crystal growth.

It is worth noting that we are in process to study this effect in more detail and to use special thermodynamic procedure.

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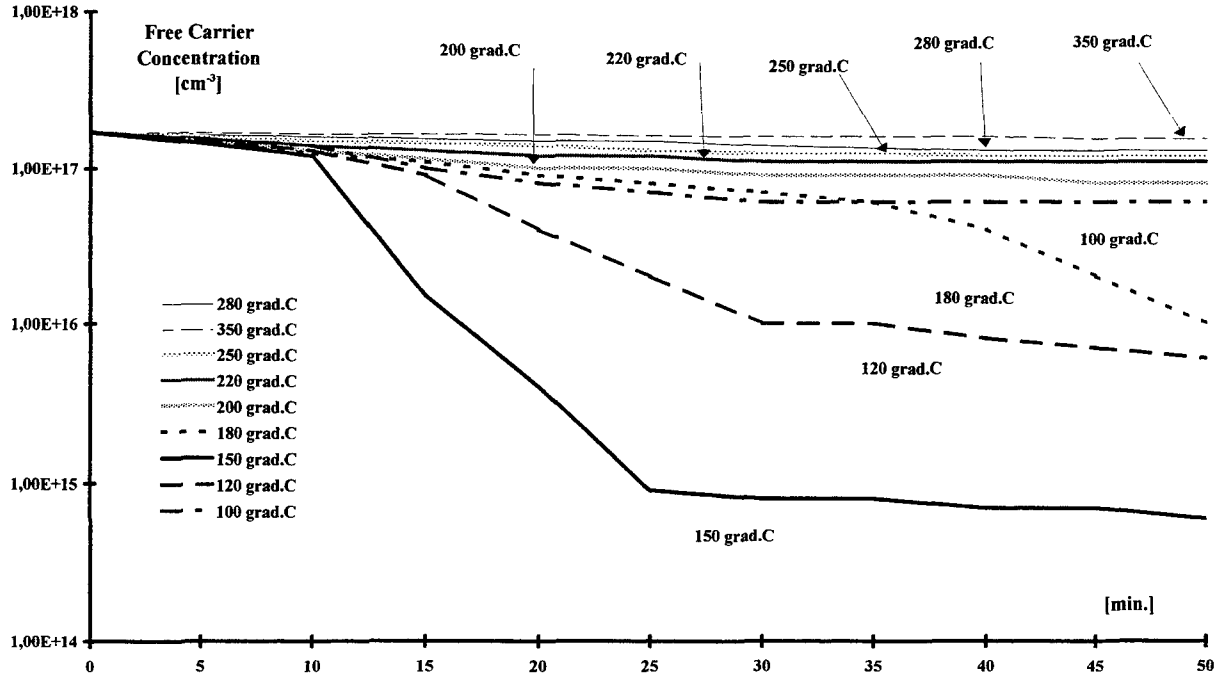

Fig. 1. Dependence of free carrier concentration on temperature and duration of annealing.

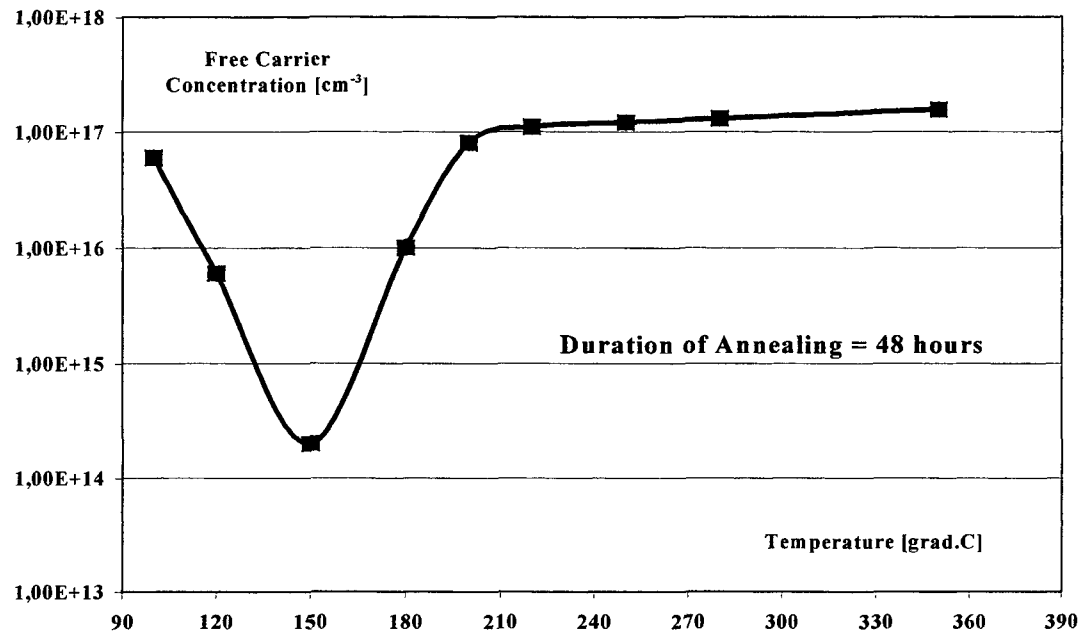

Fig. 2. Dependence of free carrier concentration on temperature of annealing of 48 hours.

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