GaAs p^+-n^--n^+ DIODES MADE BY Zn DIFFUSION OUT OF A SPIN-ON FILM

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Abstract

Diffusion technology, which is well introduced for silicon, is still problematic for GaAs and other compound semiconductors. Spin-on films containing the dopant and protecting at the same time the surface might bring a solution to the problems. We examined a commercially available spin-on film containing Zn as p-dopant for the production of deep diffused p-n-junctions and of pin diodes. The technological problems - mainly a very slow diffusion but also contamination with other materials - are discussed in detail. The electrical characteristics of the manufactured diodes are presented and the dependence of different parameters on diode size and n^--layer thickness is discussed.

Introduction

pin diodes have found wide applications in microwave and power circits [1] and also in optoelectronics. One of the most common ways to produce p-i-n diodes is the diffusion of acceptors in an intrinsic layer. Since intrinsic layers are very difficult to produce on GaAs, $p^+n^-n^+$ diodes are more common for this material. One possibility to produce a p layer is to diffuse in an acceptor. As Zn is very rapidly diffusing into GaAs it is the most commonly used p-dopant. Diffusion into GaAs and other compound semiconductors is not as easy as into Si or Ge, since the group V element (As in GaAs) is usually volatile. Different technologies have emerged to prevent surface damage due to the outdiffusion of As: originally substrate, dopant and some of the volatile element (to build up a high partial pressure) were enclosed together in a closed tube and heated up, mostly with a temperature gradient between dopant and substrate [2]. The proposed open tube diffusion [3] works similarly but only for lower temperatures with the disadvantage that the diffusion time to produce the same junction depth is increasing dramatically. A third possibility is the deposition out of a solid protective coating which contains the dopant. This coating might be a CVD deposited glass [2], an oxide [4], or a spin-on film [5]. In spite of much work done in this field, doping techniques for GaAs using diffusion are not yet wide spread [6], because of the problems due to the surface damage during the diffusion. So far also the spin-on films have not found wide application, although they can prevent the surface damage and do not need expensive vacuum equipment for processing. We have performed Zn diffusion out of a two component spin-on film and we will discuss technological aspects of this kind of diffusion and the electrical characteristics of $p^+n^-n^+$ diodes produced in this way.

Technology of the diffusion

The starting material was n^+ GaAs substrate (Si doped) with a 5μm n^- MOCVD epitaxial layer ($n < 5 \cdot 10^{13} cm^{-3}$). The wafers were cleaned in boiling trichlorethylene, acetone, and methanol. A two component spin-on film containing 10% Zn supplied by Demetron, which was tested already on InP and other compound semiconductors [5], was spun on the substrated which were heated up to 150°C beforehand. A 500 nm thick glass coating formed during a 30 minutes heating at 150°C in air. A second prebake at 400°C in air for 10 minutes improved the surface after the diffusion and made it easier to etch away the glass after the diffusion. The diffusion itself was performed at 700°C in a nitrogen stream, the samples being covered by a quartz glass plate. After diffusion the glass was etched away with concentrated HF.

The layers were examined electrically (diode characteristics, van der Pauw measurements) and physically (etching of cleaved samples, SIMS, in-depth photoluminescence, and light induced current).

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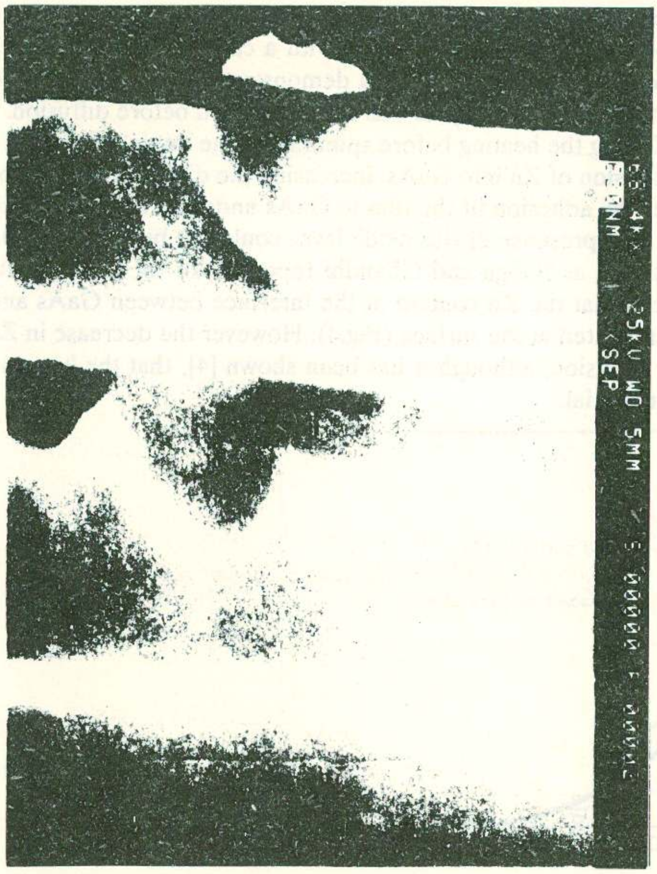

Fig.1: Cleaved and etched sample after diffusion at 700°C for 4 hours

< = Spin-on film

< = p-layer (620 nm thick)

< = n^--layer

Samples were cleaved and etched with Wright etchant [7] revealing dislocations and junctions. Junction depths between 185 and 490 nm were measured in a SEM after 1 hour of diffusion. Fig.1 shows the junction (depth 620 nm) diffused for 4 hours. These values are very low compared to the results of other authors who diffused out of ZnO layers [4], or by evaporation of different Zn containing materials [3,8] (Fig.2).

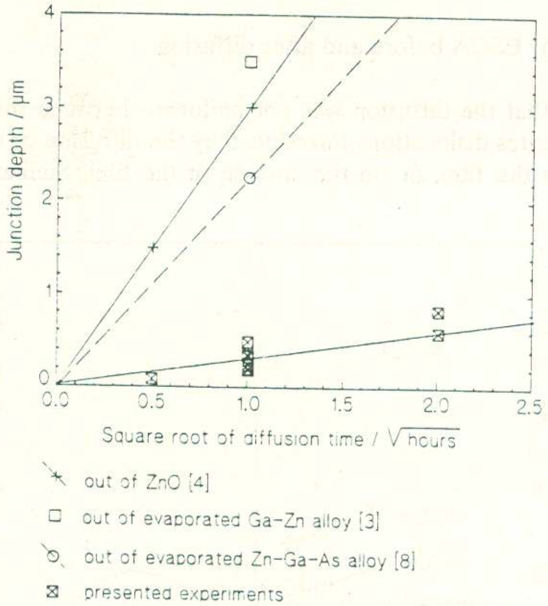

Fig.2: Junction depth at different diffusion experiments at 700°C

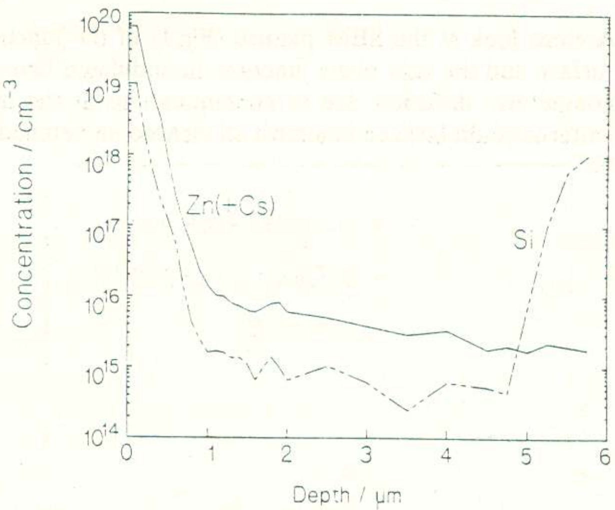

Fig.3: SIMS profile of Zn and Si of a sample diffused at 700°C for 1 hour

Also SIMS measurements (Fig.3) showed a junction which is very shallow and not as sharp as expected. Furthermore it can be seen that together with Zn also Si diffuses into the sample with a concentration ten times lower than Zn. This might indeed be one reason for the slow diffusion of Zn and demonstrates on the other hand that in spite of the 400°C prebake the formation of a temperature stable glass was not completed before diffusion. Other two possible reasons for the slow diffusion are: During the heating before spinning on the doping emulsion a thin oxide layer is formed. This layer is inhibiting the diffusion of Zn into GaAs, increasing the diffusion time up by a factor 4 [9]. However, heating up the sample increases the adhesion of the film to GaAs and assures the absence of organic solvants from the initial cleaning procedure. The presence of this oxide layer could not be detected. On the other hand a depletion of the source could be possible, as Baliga and Ghandhi reported for tin doped oxide films on GaAs [10]. ESCA measurements showed indeed that the Zn content at the interface between GaAs and the film is decreasing with diffusion time and Zn is accumulated at the surface (Fig.4). However the decrease in Zn concentration is not strong enough to explain the slow diffusion, although it has been shown [4], that the junction depth is proportional to the surface concentration of a material.

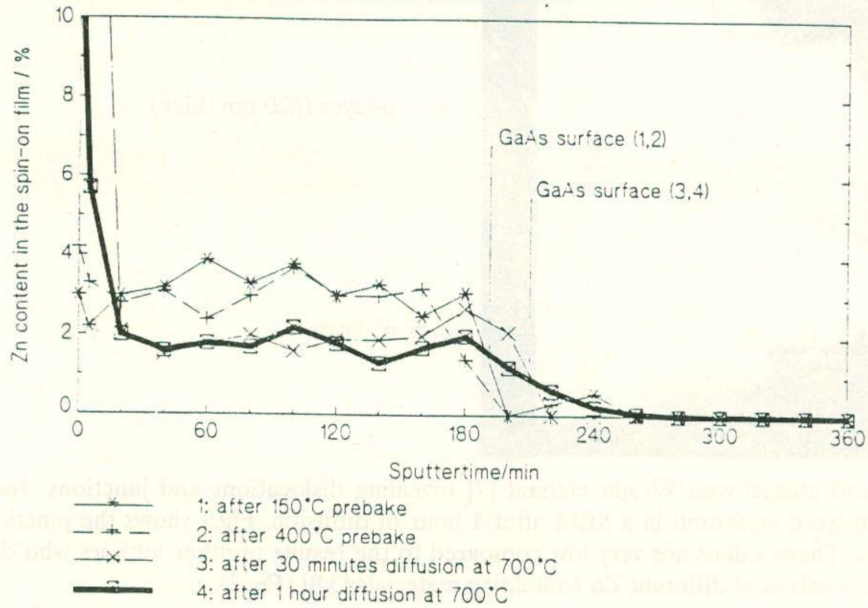

Fig.4: Zn content in the spin-on film as measured by ESCA before and after diffusion

A close look at the SEM picture (Fig.1) of the junction shows that the diffusion was not uniform - between the surface and the very plane junction an ondulated line either indicates dislocations introduced by the diffusion or a nonuniform diffusion due to contaminations at the interface, in the film, or on the surface of the film. Similar patterns could be seen in almost all cleaved and etched samples.

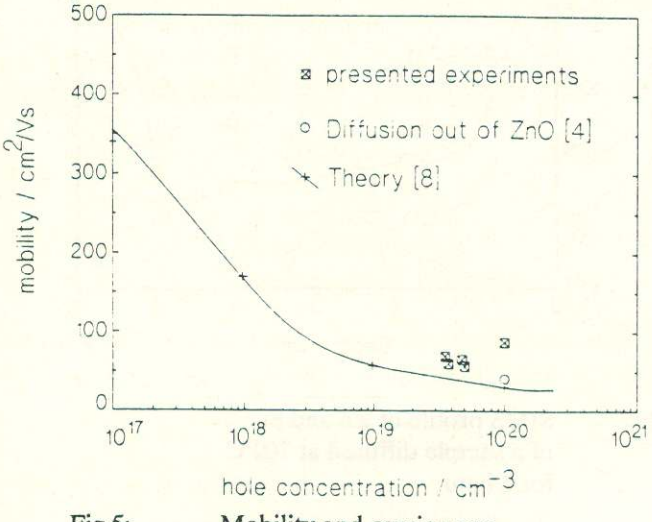

Fig.5: Mobility and carrier concentration compared to theory and other experimental results

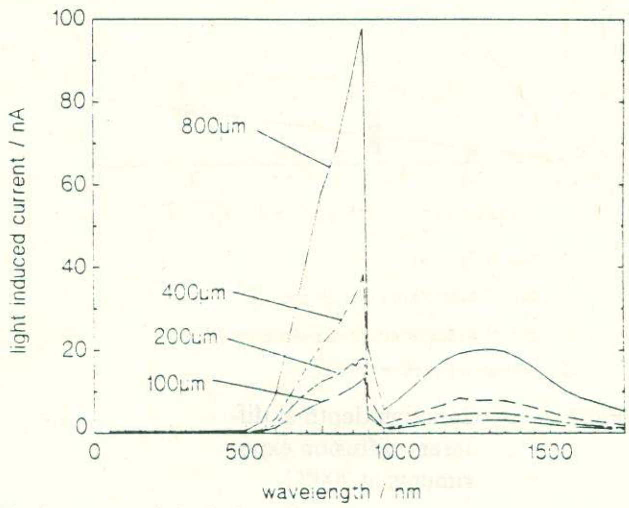

Fig.6: Light induced current of several $p^+n^-n^+$ diodes

Van der Pauw measurements (cmbination of four point probe and Hall measurements) gave somewhat integral but more precise information about the characteristics of the diffused layer. A carrier concentration of $2\text{-}6 \cdot 10^{19} cm^{-3}$ and a carrier mobility of 50-60 was typical. Fig.5 shows several samples in the mobility versus carrier concentration plane, the theoretical curve [8] and experimental results of other authors [4]. The good electrical properties of the produced p-layers is thus demonstrated.
A further indication which impurities are present is given by the photocurrent as a function of the incident wavelength. Fig.6 shows the current at zero voltage as a function of the incident wavelength. A clearly pronounced peak at 886 nm with a sharp decrease towards greater wavelengths (corresponding to smaller energies) corresponds to the energy gap of GaAs. A second flat peak has its maximum at 1300 nm wavelength corresponding to 0.95 eV, which can perhaps be identified with an oxide level [1] or a trap due to dislocations.

Contact technology of diodes

The back side of the substrate was contacted with a Ni-AuGe-Ni ohmic contact, on the p layer dots of different diameters (100μm, 200μm, 400μm, and 800μm) consisting of a 60 nm In layer and a 150 nm Ag layer were deposited. Back side and front side contacts were annealed in a RTA oven at a peak temperature of 510°C. InAg contacts are known to form good ohmic contacts on highly doped p-GaAs [11]. The diodes were subsequently separated by wet etching.

Electrical characteristics of the diodes

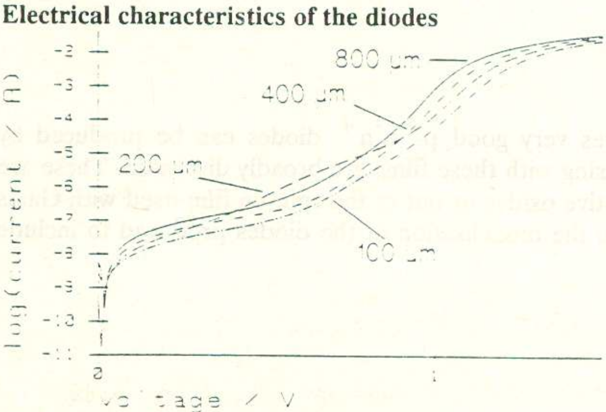

Fig.7: Forward characteristics of diodes with different diameter

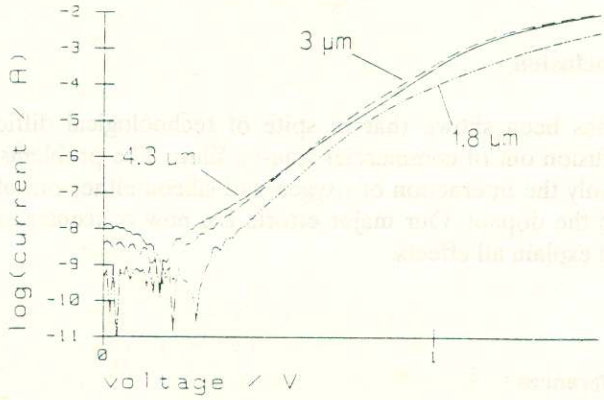

Fig.8: Forward characteristics of diodes with different n^--layer thickness

The forward characteristics (Fig.7) show a strog recombination current, most probably thermally induced - measurements were made in the dark. Recombination and drift current are proportional to the diode diameter. Some diodes also show a second tilt in the slope indicating two distinct mechanisms of recombination (e.g. the 200μm diameter diode in Fig.7), perhaps caused by some Si in the p^+-layer. However, the ideality factor is usually very poor, most probably also because of the strong recombination. Diodes with thinner n^--layer show less importance of recombination current and also a better ideality factor (Fig.8).

n^--layer thickness	ideality factor	recombination current (0V)	breakthrough voltage theory	mean
1.8μm	2.2	$40 mA/cm^2$	60V	42V
3μm	1.9	$17 mA/cm^2$	85V	60V
4.3μm	1.6	$0.7 mA/cm^2$	110V	82V

Table 1: Comparision of diodes with different n^--layer thicknesses

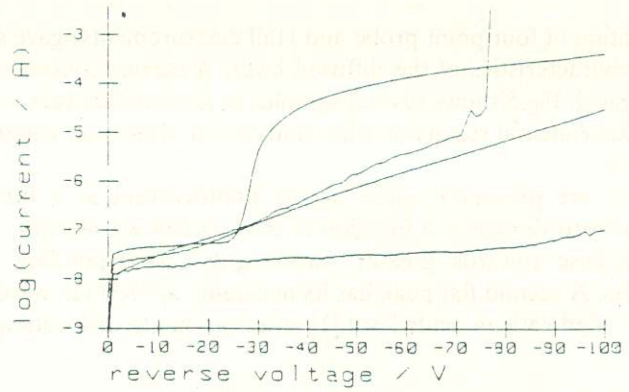

Fig.9: Reverse characteristics of several diodes with different reverse voltage behaviour

On the other hand the reverse characteristics (some examples are shown in Fig.9) are far better for thick n^--layers: Breakthrough voltages are usually about -100V, as predicted [1] for a 5μm n^--layer. As expected the breakthrough voltage is not depending on the diode size, any differences between diodes on the same wafer are due to surface defects or dislocations. Table 1 shows that the mean breakthrough voltages are significantly decreased for thinner n^--layers, still according to theory. Larger diodes often show a step in their reverse characteristics. Most probably this step is due to defects in the diffused layer, which are more probably covered by the larger diode surface. So far no high frequency measurements were made.

Conclusion

It has been shown that in spite of technological difficulties very good $p^+n^-n^+$ diodes can be produced by diffusion out of commercial spin-on films. The problems arising with these films are broadly discussed. These are mainly the interaction of oxygen and silicon either out of native oxides or out of the spin-on film itself with GaAs and the dopant. Our major efforts are now concentrated on the modelisation of the diodes produced to include and explain all effects.

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