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ANISOTROPY IN SULPHUR DOPING OF GaAs GROWN BY V.P.E.

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Abstract. - The doping behaviour of sulphur during the vapour growth of GaAs using the GaAs/AsCl₃/H₂ method is investigated for the following orientations of the substrate: (100), (110), (111)A, (111)B. A linear relationship is found between the measured electron concentration n and the sulphur partial pressure up to a saturation limit for n at about $5 \times 10^{18}$ at.cm$^{-3}$. This value of the effective solubility limit for S is found to be the same for the four different substrate orientations. However, the strong dependence of the effective distribution coefficient with the crystalline orientation puts forward the importance of the surface and adsorbed layer structure in the rate limiting step for dopant incorporation.

1. Introduction. - The elemental mechanisms involved in the dopant incorporation during GaAs crystal growth from the vapour have not yet been well established. In fact, the way how the local structure of the vapour - crystal interface acts on the rate limiting process for the dopant incorporation remains an unresolved and very puzzling problem.

Nevertheless, some previous studies have pointed out the effects of the substrate orientation and the process parameters such as: deposition temperature, reactants partial pressure, on the dopant concentration in the grown solid. A paper by Mullin has been devoted to a review of the parameters modifying the element incorporation in III-V compounds grown from the vapour.

Our study has been limited to the case of sulphur which is an n-type dopant in GaAs. In order to cover as well as possible the different possible surface structures, we have chosen a substrate orientation for each type of crystalline face following Hartman's theory. The polarity of the (111) face leads us to examine both A and B orientations.
2. Experimental results. - The growth experiments have been performed in a conventional V.P.E. reactor. We used undoped polycrystalline GaAs as a source, for simplicity, and H₂ as a carrier gas. For each run, the samples with the four different orientations were placed together on the substrate holder providing identical conditions for each of them. Sulphur doping was achieved by passing an H₂ flow over elemental sulphur thermostated at a temperature ranging from 45 to 95°C. The values of the experimental parameters were the following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source temperature Ts</td>
<td>830°C</td>
</tr>
<tr>
<td>Deposition temperature Td</td>
<td>760°C</td>
</tr>
<tr>
<td>Total pressure P</td>
<td>1 atm.</td>
</tr>
<tr>
<td>Total flow rate D</td>
<td>25 l/h</td>
</tr>
<tr>
<td>Dopant flow rate d</td>
<td>3 l/h</td>
</tr>
<tr>
<td>AsCl₃ bubbler temp. O</td>
<td>41°C</td>
</tr>
<tr>
<td>AsCl₃ mole fraction MF</td>
<td>10⁻²</td>
</tr>
</tbody>
</table>

The samples were characterized by Hall measurements using the Van der Pauw method, photoluminescence at 300 K and by optical measurement of the layer thickness.

The electron concentration measured as a function of the sulphur temperature are shown in figure 1 for the four different wafer orientations. The following remarks may be pointed out:

(i) the electron concentration (n) measured on each sample show a linear dependence with the sulphur generator temperature in the range 40 to 80°C. According to Veuhoff, this dependence is a first order one in the case of H₂S doping.

(ii) In this linear regions, the sulphur incorporation is strongly dependant upon the substrate orientation: n (100) < n (110) < n (111)A = n (111)B

The electron concentration measured for the (100) oriented wafer is about 15 times lower than for the (111)A and (111)B ones. Contrary to Veuhoff measurements, we found about the same electron concentration for the two polar directions of the (111) orientation. This behaviour can only be explained by a strong effect of the impurity uptake of the experimental parameters such as AsCl₃, MF, T, III/V ratio.

(iii) For a sulphur temperature in excess of 80°C, the electron concentration saturates at a value of 5.10¹⁸ at.cm⁻³. This saturation limit is found to be the same for the 4 substrate orientations and must be considered as an effec-

![FIG. 1: Measured electron concentration n versus sulphur generator temperature.](image1)

![FIG. 2: Growth rates versus electron concentration n for the experimental points of fig. 1.](image2)
tive solubility limit of sulphur in GaAs under our experimental conditions. In figure 2, the growth rate is plotted as a function of $n$ for the experimental points of figure 1. There is no noticeable change in the growth rate with the increase of the sulphur partial pressure, except at the very high values of $n$ for the (110) and (111) B growth directions. However, it should be pointed out that there is about an order of magnitude of difference between the (111)A and (111)B growth rates.

Finally, figures 3 and 4 show the variations of the 300 K electron mobility and of the integrated 300 K photoluminescence intensity with the electron concentration in the layers. As reported before$^6$, the electron mobility decreases abruptly for $n$ values near the saturation limit, and so does the photoluminescence intensity. This result may be understood if we suppose a change in the sulphur incorporation at the saturation. In fact, the total sulphur concentration has been measured in similar layers by Veuhoff$^6$, and his results show that the sulphur incorporation goes on after the saturation up to a "metallurgical solubility limit" in the high $10^{19}$ cm$^{-3}$ range. He suggests that beyond $5.10^{18}$ cm$^{-3}$ sulphur atoms are incorporated in a new S rich phase or as interstitials to form S precipitates.

### 3. Discussion

The dramatic effect of the substrate orientation on the effective vapour-crystal distribution coefficient emphasises the particular importance of the surface processes for the dopant incorporation. Some previous works highlight a number of specific effects, such as: the misorientation around the exact (100) orientation$^2$, the reactants partial pressures (HCl, As$_2$, AsH$_3$, GaCl$_3$...), the deposition temperature$^1$,$^7$, the III/V ratio$^8$, the supersaturation$^9$. All of these parameters affect the interface properties and especially the surface coverage in vacant sites or adsorbed species. But unfortunately, the reported investigations have been made under various growth conditions and slightly different reactor configurations, so that absolute comparisons between the data are difficult to make. Furthermore, any variation of one of those parameters has also an effect on the growth rate and in consequence it seems difficult to discriminate between purely kinetic and surface induced effect. Indeed, a change in growth rate can affect either

![FIG. 3: Hall mobility $\mu$ at 300 K versus electron concentration $n$.](image1)

![FIG. 4: Integrated photoluminescence intensity at 300 K versus electron concentration $n$.](image2)
the mass transfer to the incorporation site of the source species with respect to the dopant, or the impurity incorporation surface reaction itself.

In this matter, Reif \(^{10}\) for the case of As doped silicon, and Jakobs \(^{1}\) for Te doped GaP, have applied successfully a "first order" kinetic model to give an explanation for the growth rate effect on the dopant concentration.

In the case of GaAs, works on growth mechanisms \(^{12}\) have provided us with an analytical tool to study the effects of the process parameters on the growth rate for the (100) growth direction, and more recently also for the (111)A and (111)B directions \(^{12}\). All these studies have pointed out the role of the surface kinetic processes occurring in a dense adsorbed monolayer, on the growth rate limitation. Furthermore, it has been possible to separate the contribution of the mass transfer in the gas phase close to the interface, to give a more accurate description of the surface kinetics \(^{13}\).

The growth mechanisms for the three different orientations should be different in theory, but they are strongly dependent on Cl adsorption \(^{12}\). It has been demonstrated that the coverage by Cl atoms is very important on both (100) and (111)A and on (111)B surface steps \(^{12}\). The adsorbed Cl atoms play the chief role in the (100) growth rate limitation, and can explain the difference in growth rate for the two (111) directions and then can affect the dopant incorporation.

Finally, the relationship often found between the dopant concentration and the growth rate tells that the growth limiting step may also play the fundamental role in impurity incorporation. Nevertheless, the growth rate cannot be chosen as an independent parameter and we will have to look closer to the surface physical parameters.

4. Conclusion. - Sulphur doping of GaAs is strongly dependant on the substrate orientation. The (111) oriented wafers show the higher sulphur uptake, and the (100) oriented ones the lower. The measured electron concentration increases linearly with the sulphur partial pressure up to a saturation at about 5 \(\times 10^{18}\) at.cm\(^{-3}\). This limit is found to be the same for each orientation and is only a function of the growth parameters.

The dependence of the sulphur incorporation with the surface orientation and coverage leads to the conclusion that the process is kinetically controlled, in the same way than the growth rate is. Thus, the dense adsorbed monolayer existing at the vapour-crystal interface during the growth of GaAs in a chlorine ambient, may well play the dominant role in impurity incorporation. Nevertheless, to draw a final conclusion, we need more experimental work on the subject in order to correlate the impurity incorporation with the local surface structure.

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