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Thermal treatment effects on Cr centers in GaAs : Cr (*)

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Résumé. — On étudie les paramètres qui régissent l'équilibre entre les centres Cr^+ et Cr^{2+} en fonction de divers traitements thermiques oxydo-réducteurs en employant la résonance paramagnétique électronique pour évaluer les teneurs en chrome.

On discute les implications des résultats quant à l'élaboration de GaAs : Cr qui serait stable aux conditions thermiques rencontrées lors de la fabrication de dispositifs.

Abstract. — The parameters, governing the equilibria between the Cr^+ and Cr^{2+} centres, as a function of various oxydoreductive thermal treatments are investigated using electron paramagnetic resonance for assessing the chromium contents.

Consequences for the preparation of stable semi-insulating GaAs : Cr during device processes are discussed.

1. Introduction. — Much attention has been given recently to the semi-insulating GaAs : Cr material, as it is to be used on a large scale for FET's and high speed IC logic. The chromium is added to compensate the shallow donors, always present even in the purest melt-grown crystals [1]. Electron paramagnetic resonance (EPR) measurements have shown that Cr may be present with three valence states, and the spectra of Cr^+ , Cr^{2+} and Cr^{3+} are now well known [2-7]. Thus Cr acts as a double acceptor. The aim of this work was to study the influence of thermal treatments on the equilibrium between the Cr centres, in order to assess the operation of the compensating redox buffers $\text{Cr}^+ - \text{Cr}^{2+}$ and $\text{Cr}^{2+} - \text{Cr}^{3+}$.

2. Experimental. — A series of crystals A, B and C, purposely doped with decreasing Cr amounts from A to C were grown using a sealed horizontal gradient freeze technique.

The samples were cut into bars of

$$2.5 \times 2.5 \times 10 \text{ mm}^3,$$

orientated along the [011] direction.

Annealing treatments were performed by heating the samples in sealed silica ampoules, evacuated

(10^{-6} torr), or in presence of various atmospheres (As, H_2 , Ga_2O_3 powder) in order to get various reductive or oxidative conditions. All anneals were at 600 °C for 24 hrs.

EPR spectra were recorded with a Thomson-CSF THN 252 spectrometer working at 9.2 GHz. The samples were kept in the dark while cooling down to 4.2 K in order to take spectra before, during and after photoexcitation (PE). The latter was done *in situ*, using white light from an unfiltered OSRAM HBO 200 W mercury lamp.

3. Results. — The Cr^+ and Cr^{2+} spectra have been recorded over the 0-5 kG range. Their relative $[\text{Cr}^{n+}]$ concentrations were determined by the product of the square of the peak to peak magnetic field difference times the peak to peak amplitude taken on the EPR derivative curve. Thus these products are given in arbitrary units (a.u.). (The order of magnitude of one a.u. may be estimated to $\sim 10^{15} \text{ cm}^{-3}$.)

The Cr^{3+} spectrum is very strain sensitive [5] and thus its intensity yields no reliable data for a concentration estimate. Further some intensity data suffer from the fact that the samples were no longer semi-insulating after the anneal.

The $[\text{Cr}^{n+}]$ varies with PE as is already known. But this variation is also sample and treatment dependent, as is shown on table I, which summarizes the experimental results.

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(**) Associé au C.N.R.S. n° 232.

Table I. — *Remarks : All anneals at 600 °C for 24 hrs.*

Samples	[Cr ⁺] in a.u.		[Cr ²⁺] in a.u.		[X] in a.u.
	before PE	during PE	before PE	during PE	
<i>A samples</i> (RT 123)					
as-grown	4.5	10.5	0.6	1.3	
vacuum-annealed	7.0	9.0	0.5	1.5	< 0.5
As-annealed (*)	< 0.5	9.0	2.3	3.1	
Ga ₂ O ₃ -annealed	< 0.5	10.1	4.8	4.7	
H ₂ -annealed (**)	~ 1	~ 1	< 0.5	< 0.5	7
<i>B samples</i> (RT 193)					
as-grown	< 0.3	~ 0.5	1.0	1.0	
As-annealed (*)	1.0	4.8	3.4	2.5	4.0
<i>C samples</i> (RT 399)					
as-grown	< 0.3	1.3	2.0	1.0	1.2
vacuum-annealed (***)	< 0.5	0.5	< 0.5	< 0.5	
As-annealed (*)	0.5	1.3	2.5	1.3	1.0
Ga ₂ O ₃ -annealed	< 0.5	1.0	1.7	1.6	2.7
H ₂ annealed (**)	0.5	0.5	0.6	0.6	10

(*) *Saturating pressure at 600 °C.*(**) *PH₂ = 300 torr.*(**) *Highly conductive sample, therefore faint signals.*

Furthermore a new line, labeled X, corresponding to a till now unknown centre, has been observed in several samples. Its concentration is also given on table I.

In the A samples before PE, [Cr⁺] decreases with an oxidative and increases with a reductive anneal; conversely, [Cr²⁺] increases with an oxidation and decreases with a reduction. After the H₂ anneal, the [Crⁿ⁺] drop by one order of magnitude.

Both [Cr⁺] and [Cr²⁺] are increased by PE (Fig. 1).

Fig. 1. — EPR of a as-grown A sample without (solid line) and with PE (dotted line). The difference shows the appearance of Cr⁺ and the increase of the Cr²⁺ line.

Surprisingly all samples, but the H₂ annealed one, reach an identical [Cr⁺] during PE.

On the B samples (Fig. 2), the As anneal induces an increase of both [Cr⁺] and [Cr²⁺] before PE contrary to the former case. But during PE, only an increase of [Cr⁺] is observed, whereas [Cr²⁺] diminishes.

Fig. 2. — EPR of a As-annealed B sample. a) without PE; b) with PE; c) and d) which indicate the Cr⁺ and Cr²⁺ line variations, show that the Cr²⁺ decreases (compare to Fig. 1).

In the C samples, before PE, there is only little effect of anneals on [Cr⁺], but [Cr²⁺] increases with oxidation and decreases with reduction; in the latter

case the crystals are no more semi-insulating. The behaviour during PE is similar to the B samples.

The new X line (Fig. 3) has been observed either in as grown or annealed crystals. However its intensity is strongest in reduced samples, especially after the H_2 anneal. Its g value occurs at $g = 2.002 \pm 0.001$. Its linewidth decreases from 30 to 4 G, whereas the line intensity increases. Etching of the sample reduces the intensity of the line.

Fig. 3. — X-EPR line as observed on a H_2 annealed C sample.

4. Discussion. — The equilibrium between $[Cr^+]$ and $[Cr^{2+}]$ obviously depends upon the total amount of Cr incorporated into the material, and must involve the $[Cr^{3+}]$.

In highly doped A material, whatever the treatment, carriers are transferred to the Cr^+ and Cr^{2+} levels during PE. For low doping, on the contrary,

carriers are transferred from the Cr^{2+} to the Cr^+ levels; hence we expect that for the latter the Fermi level stays between the Cr^+ and Cr^{2+} levels; for the former, it should lie below the Cr^{2+} level. The Cr^{3+} concentration, and the Cr mean valency, should therefore be higher in the former, highly doped, samples.

On the other hand, only the highly doped material may be reduced up to a point such that stable Cr^+ may be observed, without becoming conductive.

The X-line intensity is consistently higher in low doped and reduced samples, and may therefore be ascribed to a donor. An isolated substitutional centre should yield EPR linewidths of about 50 G, as in GaAs : Fe^{3+} [8]; therefore we conclude that the linewidth is motionnally narrowed. This is consistent with the intensity dependence of the linewidth. It corresponds to a high local density of centres, and is likely to originate from a shallow surface layer, as the intensity decrease after etching confirms.

Finally the strong $[Cr^{n+}]$ decrease in H_2 annealed A sample, which is not observed in vacuum annealed material, can be explained by a further Cr reduction or a Cr exodiffusion. As concerns the former hypothesis, we have however not been able to observe any signal corresponding to isolated Cr centres, but on the other hand evidence for a Cr depleted layer has been obtained [9].

5. Conclusion. — The present results show that in order to remain semi-insulating under any chemical reductive or oxidation heat treatment the electrical redox buffer should be the Cr^{2+} - Cr^{3+} system in GaAs : Cr.

It turns out that this high mean valency of the Cr centres is only observed with the higher doping levels; obviously the latter will be limited by the actual segregation coefficients for the various Cr compounds.

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