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Stoichiometry and doping in large gap compound semiconductors (*)

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Résumé. — Les théories courantes sur l'autocompensation des semiconducteurs composés à large bande interdite (travaux de Kröger en particulier) qui font appel à l'intervention de défauts de stœchiométrie expliquent relativement bien les propriétés électriques sans intervention des impuretés. Un certain nombre de résultats récents montrent au contraire que celles-ci jouent en fait un rôle déterminant au moins à température ambiante. On tentera de comprendre qualitativement, à partir d'un matériau particulier (ZnTe), la physicochimie réelle de l'autocompensation et les raisons du succès apparent des théories simplifiées qui supposent le cristal pur.

Abstract. — Current theoretical models on self-compensation in large gap semiconductors assume that intrinsic stoichiometric defects dominate and explain electrical properties quite satisfactorily without any contribution from impurities. Some recent results show on the contrary that impurities are in fact dominant at least at room temperature. The paper, starting from one particular material (ZnTe), is an attempt to understand the real physicochemistry of self-compensation and the reasons for the success of simplified theories assuming the crystal to be very pure.

1. **Introduction.** — It has been realized long ago that large gap semiconductors are very difficult to obtain with the desired conductivity, most of them being available with only one type of conductivity, even when large amounts of impurities are introduced in attempts to obtain the opposite type. This self-compensation is common to all large gap materials ($E_g > 2$ eV) and has been extensively studied in particular in the highly ionic alkali halides and in the partly covalent II-VI. In what follows, we will largely use specific results from studies on ZnTe, a II-VI compound with $E_g = 2.394$ eV at 4.2 K and accordingly write chemical equations referring to this particular material for the sake of definiteness, although it should be understood that the basic defect chemistry mechanisms are similar in all compounds.

2. **The classical self-compensation theory.** — Most of the current understanding derives from work initiated by Kröger and coworkers [1, 2] in which the basic assumption is that intrinsic stoichiometric defects play a major role in the electronic doping of the large gap materials. Metal vacancies and interstitial anions are expected to be acceptors (doubly charged in the case of a II-VI material), anion vacan-

cies and metal interstitials are donors. The formation energies of all these defects are different and one is dominant, controlling the conductivity type. In the case of (p-type) ZnTe, the dominant defect was considered to be the zinc vacancy V_{Zn}^- , mostly in the doubly charged form V_{Zn}^{--} . Quasi-chemical equilibria relating these species with the electronic carriers and outside atmosphere can be written, using standard notations, as :

resulting in the mass action equations

$$\begin{aligned} [V_{Zn}^0] &= K_1 p_{Zn}^{-1} \\ [V_{Zn}^{--}] &= K_2 [V_{Zn}^0] p^{-2} = K_2' p^{-2} p_{Zn}^{-1} \end{aligned} \quad (1)$$

where p_{Zn} is the zinc partial pressure specifying the composition of the atmosphere and p the hole density introducing the coupling to the electronic system.

The third condition defining equilibrium is the electrical neutrality equation which in our simplified case yields $[V_{Zn}^{--}] \simeq 2p$. The resolution of the system with these assumptions is straightforward and leads to a carrier (hole) density proportional to $p_{Zn}^{1/3}$ in good agreement with experiment.

The introduction of impurities in the framework of the above model (and similar ones elaborated for

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other compounds) does not create unsurmountable difficulties and has of course been attempted. Two conclusions then emerge :

1) Self-compensation results directly from the mass-action laws. For instance, introduction of a donor reduces p and thus increases the concentration of V_{Zn}^- acceptors.

2) Assuming a given (constant) impurity concentration results in carrier densities which differ from the simple laws corresponding to the pure crystal, but the agreement with experiment is usually rather poorer in the case of undoped crystals.

3. Microscopic studies on ZnTe. — The good agreement between the theory presented above and the experimental values of acceptor concentrations, along with the presence of two persistent shallow acceptor levels at ~ 60 and ~ 150 meV above the valence band in crystals of different origins led Aven and Segall [3] to attribute them to the two levels of the zinc vacancy. This identification was then used by others and gained the status of a widely accepted theory, although no microscopic arguments were available.

More recently, extensive studies were made on a number of crystals grown by a Bridgmann-Stockbarger method in Te solvent. Detailed descriptions of the experiments may be found in the references [4, 5, 6, 7] but the main results for our purpose are the following :

1) For crystals grown in the same thermal conditions, higher purity of the starting elements generally leads to lower hole concentration in non intentionally doped samples.

2) Acceptor profiles measured *versus* depth after anneal in a controlled atmosphere and quench cannot be explained by diffusion of one species (V_{Zn}) into or out of the crystal. Their reproducibility from sample to sample is good for the very short and very long times, poor for intermediate values.

3) Luminescence spectra show clearly that excitons can be trapped on two dominant acceptors at $E_v + 61$ meV (labelled « b ») and $E_v + 149$ meV (labelled « a »), both behaving as simple acceptors. Other acceptors are also visible depending on annealing parameters and starting crystal.

4) The intensities of the spectra related to « a » and « b » during various anneals vary differently, showing that they are not due to the same centre.

5) Scanning electron microscopy in the cathodoluminescence mode shows large spatial variations in the luminescence yield, related to the annealing and quenching conditions, explaining the lack of reproducibility in acceptor profiles (see section 2) above). These variations are clearly related to the distribution of excess Te in precipitates and/or inclusions dispersed in the ZnTe matrix.

Results 1) and 2) suggest that stoichiometric defects are not the only species responsible for the electronic doping even in high purity crystals. Results 3) and 4) definitely show that no double acceptors, i.e. no V_{Zn}^{2-} , are involved (a double acceptor cannot trap an exciton on its singly ionized state). However, result 5) shows that the Te excess does play an important role. From complementary experiments involving in particular diffusion doping with various impurities, a consistent picture finally emerged, the essential features of which are :

A) Acceptors « a » and « b » are due to Cu and Li respectively, presumably as substitutional species Cu_{Zn} and Li_{Zn} . The bulk of these impurities is contained in the Te precipitates at growth and may be released during anneals according to the thermal history of the sample. Some silver is also present, although usually less prominent, and may be released as $Ag_{Zn}(E_v + 123 \text{ meV})$ with a behaviour similar to that of Cu.

B) Lithium has a relatively simple behaviour and has been observed only as Li_{Zn} . It is released from the Te precipitates as they are dissolved, especially during heat treatments in zinc vapour and disappears completely during long anneals, presumably by evaporation at the surface since its vapour pressure is high.

C) Copper has a more complicated behaviour, being observed both as Cu_{Zn} and as part of various complex centres. It is released from Te precipitates during anneals before the Li, but is not extracted from the crystal into the vapour phase, probably because its vapour pressure is too low.

The effect of anneals is thus due to a complex interplay of chemical reactions between the ZnTe matrix and both the outer atmosphere (Zn or Te vapour in most cases) and the Te precipitates.

4. Discussion. — The most important point to discuss is probably the explanation of why the simple model involving V_{Zn} was successful. To understand this, we should first remember that the hole density is almost systematically governed by the concentration of substitutional copper, so that electrical measurements in fact give the amount of Cu in solid solution in the ZnTe matrix. The recent measurements bearing on acceptor « a » after Cu diffusion are indeed in good agreement with previously published values of concentrations of *zinc vacancies*. If we then realize that Cu is always present in a Te-rich precipitate phase, it becomes clear that we should add to the set of equations (1) chemical equations describing the exchange of Cu between the matrix and the precipitates, which may be represented as Cu_2Te in Te solution. The simplest way of describing this exchange while conserving equal varia-

tions in the number of sites for both sublattices is to write the equilibrium reaction as :

The reaction conserves the number of acceptors so that zinc vacancies can be stored in the form of Cu_{Zn} . The replacement of $[V_{Zn}]$ by $[Cu_{Zn}]^2$ in equation (1) leads to an exponent $-1/4$ instead of $-1/3$ in the hole density as a function of p_{Zn} . The difference is small and difficult to ascertain experimentally, so that it is very difficult to discriminate on the basis of electrical measurements alone between the models based on equation (1) alone or on equation (1)+equation (2) at least as long as Cu_2Te is present. Differences will appear only when the chemical purity is high enough for the available Cu_2Te to be exhausted, or when more selective techniques are used to probe the atomic structure of the defects.

Of course reactions similar to (2) can be written involving all monovalent impurities, i.e. all substitutional acceptors on zinc sites. Corresponding equations involving potential simple donors can also be written, for instance :

for zinc site donors or for Te site donors :

Clearly the introduction of donors creates zinc vacancies which may subsequently be stored as acceptors. The set of reactions (2), (3) and similar ones can thus mimic the simple situation described by (1) without any detectable concentration of intrinsic defects (V_{Zn}).

The good quantitative agreement between different experimental groups thus rests essentially on the fact that all crystals contained enough copper to saturate them and even contained a precipitate phase⁽¹⁾. The lack of success of models involving impurities can be traced to the assumption of a definite amount of impurities in the matrix (distributed among charge states) which is not valid in the presence of a second phase.

The other main interest in the discussion is what can be expected in the future development of large gap semiconductors if there is no sizable contribution of intrinsic defects to the doping and self-compensation. One important point that should be kept in mind is that, although the classical models are not microscopically correct, they still give a good description of experimental results and will continue so as long as the impurity content of the crystals is

above saturation at the effective quenching temperature (500-600 °C in the case of $ZnTe$). If we compare for instance equations (2) and (3) the mass-action law will result in

$$\frac{Al_{Zn}}{Cu_{Zn}} = KV_{Zn}^{-1} = K' p_{Zn} .$$

Since p_{Zn} can vary only within limits imposed by the existence domain of the compound, there is a corresponding domain for Al_{Zn}/Cu_{Zn} . The fact that the crystal is always p-type then simply means that this domain does not include the value 1. The only way to obtain n-type material is thus to render equation (2) inoperative by decreasing the total amount of available Cu below the solubility limit in Zn-rich conditions (i.e. minimum Cu solubility and maximum Al solubility).

The above discussion bears on neutral species only. It is clear that the Fermi level position will also influence the total amount of impurities in solution, including the ionized species. The discussion will be directly applicable if two conditions are met simultaneously :

- 1) The donor and acceptor levels involved are both shallow, thus at almost equal distances from the midgap and intrinsic Fermi level.
- 2) The net doping is below n_i at the effective quenching temperature.

If these conditions are not satisfied, corrective factors have to be applied. These can be derived from the classical models. The condition 2 is the main problem in the control of doping since the correction factor eventually generated is always in the direction of making self-compensation more efficient and since the value of n_i is a strongly decreasing function of energy gap.

Recently Bhargava *et al.* [8] and Neumark [9] have examined the possibility of self-compensation by amphoteric impurities such as Li which may be present as substitutional (Li_{Zn}) or interstitial (Li_i) species. The same type of arguments involving storage of V_{Zn} can be developed in this case, using the reaction :

The same general conclusion can be drawn, i.e. that high chemical purity and/or high quenching rates are necessary if type conversion is to be obtained in large gap semiconductors.

5. Conclusion. — We have shown that the relatively simple behaviour of large gap semiconductors can be misleading and often derives from their being saturated with impurities. Good control of electronic doping will thus be possible only after very careful

⁽¹⁾ Note that silver has a behaviour very similar to copper, so that a dominant contamination by Ag instead of Cu will not change the results drastically.

consideration of the chemical equilibria during crystal growth and during subsequent thermal treatments. In particular the growth technique is a very important parameter to consider since it always involves some kind of selection between impurities.

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