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Quantitative measurement of impurities in gallium arsenide

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The chemical concentrations of Be, O, Si, S, Zn and Sn have been measured in epitaxial layers of GaAs grown by the molecular-beam and vapour-phase techniques and also in bulk crystals grown by the Bridgman technique. Spark source mass spectrometry calibrated using atomic absorption spectrometry was used to give quantitative results with high detection sensitivities for a large range of elements. For doped layers containing no significant background impurities ($< 10^{16}$ cm^{-3}) the chemically determined dopant concentrations relate directly to the measured free carrier concentrations in the range 10^{16} to 10^{19} cm^{-3}. Impurity elements such as O, Ti, Fe, Mo and W act as trapping centres and must be considered when interpreting the electrical results.

1. Introduction

The direct measurement of impurity concentrations is important in the characterization of semiconductor materials. Whilst direct electrical measurements can be used to determine the electrically active impurity concentration, the actual chemical identity of the impurity, giving rise to a particular type of electrical conduction is not revealed. Where several unknown active impurities are present in the semiconductor lattice, additional qualitative and quantitative chemical impurity information is required for the interpretation of the electrical data.

In these laboratories chemical characterization of semiconductor materials is carried out using a combination of analytical techniques. These have been selected to give sufficient sensitivity in the range of interest in semiconductor work (down to 10^{14} cm^{-3}) combined with broad element coverage. The principal techniques used are spark source mass spectrometry (SSMS), flame and flameless atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES).

We present, in this paper, impurity measurements made on GaAs in the form of thin epitaxial films grown by the molecular-beam epitaxy (MBE) technique [1] and measurements on bulk GaAs crystals. The combination of chemical and electrical data will be shown to be essential for the full understanding of the measured free carrier concentrations.

2. Experimental details

The analytical procedures for the analysis of thin epitaxial layers by SSMS using the scanning device developed at these laboratories has been reported previously [2]. This consists of using an AEI MS7 mass spectrometer, with photoplate detection, to provide overall element coverage with high detection sensitivity. The source region of the MS7 is cryogenically pumped with liquid helium [3] to reduce residual gas interference and to give reliable O, Si and S values. Bulk GaAs samples were etched with HCl/HNO_3 followed by Br_2/MeOH and sparked as conventional rod electrodes.

The flame AAS measurements for Sn, Zn and Si were carried out using a Pye-Unicam SP1900 and the flameless AAS measurements for Be were made on a Varian Model 63 carbon rod atomizer mounted on a Varian AA5 instrument, both instruments being connected on-line to a mini computer giving full data handling facilities [4]. Bulk samples were etched as for MS7 analysis to remove surface contamination and subsequently dissolved in HCl/HNO_3. The Be-doped MBE layers were etched with 50% HNO_3 to remove the epitaxial layer. The effective concentration in the layer was calculated from the mass of Be deter-

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mined and a knowledge of the layer thickness and area. Film thicknesses were measured by optical and scanning electron microscopy (SEM) on cleaved edges.

The doped GaAs layers, of thickness between 1 μm and 4 μm, were grown on semi-insulating GaAs substrates of approximate size 2 cm x 2 cm. Hall effect measurements were made at room temperature on part of each layer using the Van der Pauw technique.

3. Results and discussion

The key feature of this work lies in the method of calibration of the SSMS response. Selected samples of GaAs, doped in the high concentration range ($\sim 10^{18}$ cm^{-3}), are analysed by absolute chemical methods and subsequent SSMS analysis then gives the calibration factors for particular elements. The linear response of the mass spectrometer is then used to determine concentrations down to 10^{14} cm^{-3} with an absolute reliability of about ± 30%.

We first present results from a series of Sn-doped layers. These were grown as part of an investigation into the performance of the Sn molecular beam effusion cell used for doping layers [1]. The results given in Fig. 1 were obtained from calibrated SSMS measurements and it can be seen that the experimental points are uniformly distributed about the line calculated from the cell temperature and system geometry over the concentration range 5×10^{15} to 1×10^{18} cm^{-3}. These results support the quantitative reliability of the determination of the chemical concentrations of the dopant element in the layers independent of electrical measurements.

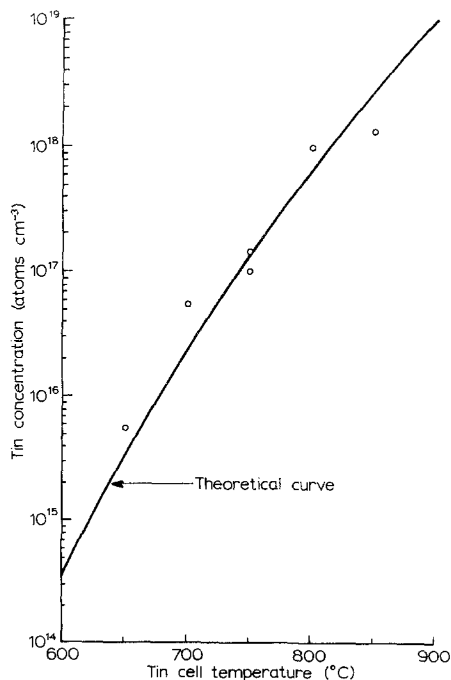

Figure 1 Tin doping concentration in GaAs as a function of MBE cell temperature.

As an extension of this work, we have investigated the relationship between the number of free carriers and the chemical dopant concentrations in a series of Sn-doped layers. SSMS survey analyses on these layers showed that in most cases no other electrically active impurities (e.g. Si, S, Cu, etc.) were present at concentrations above 10^{16} cm^{-3}, so that the combined activity of other impurity elements was significantly smaller than the concentrations of Sn added to the layers ($> 10^{17}$ cm^{-3}). Given the ideal situation where each Sn atom gives rise to one conduction electron, then a one-to-one relationship would be expected between the electron and dopant concentrations. The results of these measurements are given in Fig. 2 where it can be seen that a proportional relationship exists over a concentration range 1×10^{17} to 4×10^{18} cm^{-3}. The absolute reliability of the SSMS data after calibration (± 30%) does not enable us to comment on the extent of Sn auto-compensation in this concentration range except to say that it is not a dominant factor. The upper point on this graph does show a significant displacement from the line and could suggest that some of the Sn is electrically inactive, possibly in the form of precipitates.

Some of the layers in this investigation were

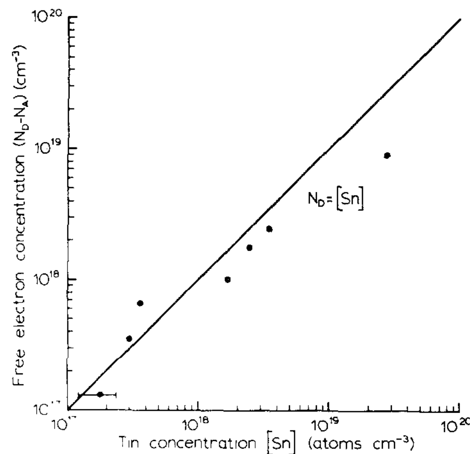

Figure 2 Relationship between free electron concentration and total tin concentration for a series of Sn-doped GaAs layers.

found to be non-conductive with no measurable free carrier concentration. The SSMS survey analyses showed the presence of a range of background impurities which could be traced to an accidental source of contamination during growth. These included Ti, Mn, Fe, Mo and W in the concentration range 10^{16} to 10^{18} cm^{-3}. In all cases the total concentration of these impurities was comparable to the Sn content. This suggests that these elements acted as deep level centres and trapped the conduction electrons from the Sn dopant. SSMS impurity measurements on normal Sn-doped MBE material shows that the background impurity levels are consistently less than 10^{16} cm^{-3}, which is in agreement with free carrier and mobility measurements made at 77 K [5].

We now consider some results from the analysis of Be-doped layers. Since flameless AAS shows a high detection sensitivity for Be, accurate measurements could be made down to 2×10^{18} cm^{-3}. For SSMS calibration, one sample was divided into two parts and analysed by both techniques. The comparison of total Be content with free carrier measurements ($N_A - N_D$) is shown in Fig. 3. The line represents the case for Be generating one hole per atom; the error bars show the absolute errors in both chemical techniques. The closed symbols on the graph show that [Be] exceeds ($N_A - N_D$) by about 1×10^{18} cm^{-3} in all but one case. Examination of the mass spectra of two of these samples showed the presence of significant quantities of Al (2 to 7×10^{18} cm^{-3}) and O (1×10^{18} cm^{-3}). Al is isoelectronic in GaAs whereas oxygen is thought to be a deep centre which could trap out the holes from the Be acceptors. The absolute amount of oxygen found by SSMS shows acceptable agreement with the apparent deficiency in the electrical values. These impurities were subsequently shown to originate from an Al_2O_3 ceramic used in the growth system and elimination of this source of contamination reduced the Al content of the layers to about 1×10^{16} cm^{-3} with a significant reduction in the oxygen level ($< 10^{17}$ cm^{-3}). The two measurements shown by the open symbols in Fig. 3 were obtained from layers produced in the improved growth system and it can be seen that both points lie close to the theoretical line.

In conclusion, some additional chemical and electrical measurements on other GaAs samples are given in Fig. 4. The open symbols show chemical results (± 5% accuracy) obtained from flame AAS and an AES measurement on Bridgman material and the closed symbols represent uncalibrated SSMS data on material grown from the vapour phase [6]. The graph shows that zinc is a well behaved acceptor in GaAs while the Sn- and Si-doped samples have chemical concentrations about 25% greater than the corresponding electrical values. This difference is significantly greater than the measurement uncertainties in the chemical and electrical techniques and is consistent with the known amphoteric behaviour of both dopants [7, 8] again suggesting that auto-compensation is present but not dominant. The results of the S-doped layers are displaced from the line by a constant factor of approximately 2 owing to a

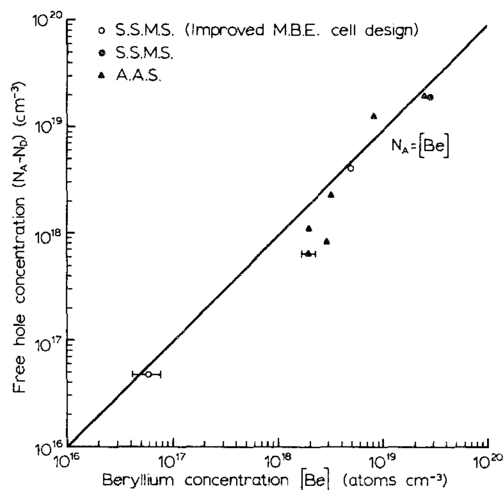

Figure 3 Relationship between free hole concentration and total beryllium concentration for a series of Be-doped GaAs layers.

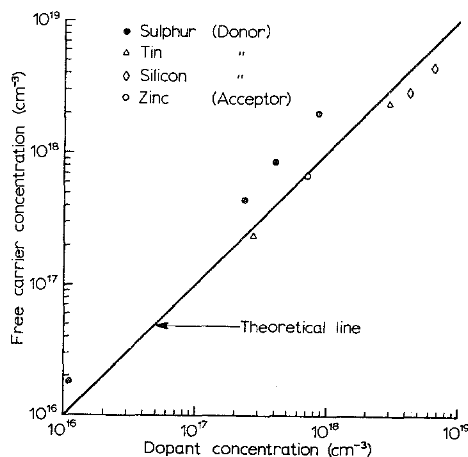

Figure 4 Relationship between free carrier and chemical dopant concentrations in GaAs.

systematic bias in the uncalibrated SSMS results for sulphur. These results do, however, illustrate the versatility of the SSMS technique as we have consistently found that measurements in GaAs and related semiconductor compounds [9] can be made for a broad range of impurities with an uncertainty of a factor of two, without the use of calibration samples.

4. Conclusions

Our experience with the analysis of GaAs has shown that free carrier data can be related directly to measured chemical impurity concentrations for elements such as Be, O, Si, S, Ti, Mn, Fe, Cu, Mo, Sn and W present in the lattice in the concentration range 10^{16} to 10^{19} cm^{-3}. In this concentration range it has not been necessary to postulate the presence of electrically inactive compounds [10] to account for the measured electrical values with the exception of Si-doped GaAs grown by the boric oxide encapsulating technique [11].

These investigations are only possible when reliable chemical impurity data are obtained from several independent analysis techniques.

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