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An automatic carrier concentration profile plotter using an electrochemical technique

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A fully automatic system which directly plots semiconductor carrier concentration profiles to any required depth is described. An electrolytic Schottky barrier permits simultaneous controlled dissolution and capacitance-voltage measurements. Examples of profiles obtained in multiple epitaxial layer structures of n-type gallium arsenide are given.

1. Introduction

Recent studies [1, 2] of the electrochemical behaviour of the interface between n-type gallium arsenide, and concentrated KOH electrolyte have demonstrated that, within well-defined limitations, ideal Schottky barrier characteristics are obtained. Thus, it has been possible to derive the mean value of carrier concentration within the semiconductor depletion width from simple capacitance measurements over a range of anodic potentials [2]. At the same time, it was established that on uniformly doped material, reproducible measurements were obtained following the anodic dissolution of up to 10 μm of semiconductor, under specified conditions. The present paper describes a fully automatic system which combines electrochemical dissolution with simultaneous differential capacitance measurement to provide direct plotting of carrier concentration to any required depth. It will be shown that this method readily yields profiles of complex multiple epitaxial layer structures whose analysis is extremely tedious by other available techniques. It should be noted that except where otherwise stated, the description of the technique refers to n-type semiconductors, and the examples given are of gallium arsenide.

2. Measurement principles

2.1. *Carrier concentration measurement*

It will be recalled that the basic Schottky formula [2] for depletion layer capacitance is:

$$C = \left(\frac{qn\epsilon_0\epsilon}{2}\right)^{\frac{1}{2}} \psi^{-\frac{1}{2}} A, \qquad (1)$$

where q = electronic charge, n = net donor concentration, ϵ_0 = permittivity of free space, ϵ = relative permittivity of semiconductor, ψ = barrier height potential, and A = area. Also, the depletion width is given by:

$$W_D = \frac{\epsilon\epsilon_0 A}{C}. \qquad (2)$$

Thus, the average value of carrier concentration within a depletion layer width may be determined from a simple capacitance measurement, provided that the value of the barrier height potential ψ, corresponding to the fixed anodic potential, is known; this relies upon having previously determined this relationship, e.g. by curve fitting, as described in reference [2]. This approach, of making continuous capacitance measurements while dissolving the semiconductor at a fixed anodic potential, was used in a trial version of the system, as reported earlier [3]. However, for greater accuracy and depth resolution, particularly at the lowest values of carrier concentration (i.e. below about 10^{17} cm^{-3}), a modulation technique is employed in the present system. A small modulation of the anodic potential produces a corresponding modulation of the depletion layer width, and hence of the measured capacitance. The carrier concentration at the interface between the depletion layer and the underlying 'field-free' region may be expressed in various equivalent ways [4, 5], the version most appropriate to this work being:

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$$n = \frac{2\epsilon\epsilon_0}{q} \cdot \frac{\delta V}{\delta(W_D^2)}, \tag{3}$$

where δV is the modulation of ψ.

The practical details of this measurement are given in Section 3.

2.2. *Depth measurement*

The depth x below the original semiconductor surface corresponding to the measured value of carrier concentration is given by the depletion layer width W_D added to the thickness of material W_R removed by dissolution. The former is simply derived from the measured value of capacitance, according to Equation 2 above, whilst the latter is obtained from the time integral of dissolution current (Faraday's Law):

$$W_R = \frac{M}{NFDA} \int I dt, \tag{4}$$

where M is the molecular weight of the semiconductor, N is the number of charge carriers transferred per molecule of material dissolved, F is the Faraday ($9{\cdot}64 \times 10^4$ C), and D is the density of the material ($5{\cdot}32$ g cm^{-3}).

Also,

$$x = W_D + W_R. \tag{5}$$

Note that under typical operating conditions W_D is approximately 1·5, 0·15, or 0·015 μm for carrier concentration values, n, of 10^{15}, 10^{17}, or 10^{19} cm^{-3} respectively (as obtained from Equations 1 and 2, assuming $\psi = 1{\cdot}5$ V). In comparison, W_R may vary from fractions of μm to tens of μm's.

3. Description of system

3.1. *Introduction*

The automatic plotting system is shown as a block diagram in Fig. 1. The electrochemical cell (A), and potentiostat (C) are described in Sections 3.2 and 3.3 below. Units (D) to (K) constitute the differential capacitance analysis section (Section 3.4), and (L) to (N) comprise the depth analysis section (Section 3.5). The remaining units are auxiliary control units, shown linked by broken lines.

3.2. *The electrochemical cell*

The cell (A) has not been changed significantly since it was described earlier [1, 2] although an additional cathode has been provided, consisting of a Pt wire inserted through the cell wall close to the sample mount. This is used for capacitance measurements, and reduces the influence of electrolyte series impedance to a negligible level. A further modification has been the use of a moulded PVC mounting ring for the sample, both modifications being shown in Fig. 2. The latter has resulted in a reduction in the outer rim of material which is exposed to electrolyte, whilst being shielded from the illumination which is required for dissolution. Fig. 3a shows an area stripped using the new system, and is to be compared with Fig. 3b which depicts the area definition previously obtained [2].

Further consideration has been given to the illumination source, which, it has been shown, is essential to provide minority carriers for the 'safe' dissolution reaction [2]. It was felt that precautions should be taken to make the dissolution rate as independent of carrier concentration as possible to reduce the effect of lateral variations in doping of the semiconductor upon stripping rate, and hence upon depth resolution in the profile plot. Therefore, for GaAs, a narrowband filter at 550 nm was used in conjunction with the quartz iodine tungsten light source to provide light which is strongly absorbed within a region much narrower than the depletion width (except for very highly doped samples). This ensures that in almost all cases, a similar number of minority carriers are available for the dissolution reaction. The resulting improvement in smoothness of the base of the stripped area shown in Fig. 3a, compared with that in Fig. 3b, which shows the result of using broadband illumination to dissolve similar material, should be noted.

The system of making probe contacts to the back of the sample is used as before, and is indicated on the block diagram (B); the ease with which any sample can be loaded and immediately contacted is an important feature of the equipment. It should be noted that the means of representation of the cell (A) in the block diagram bears no resemblance to the actual construction.

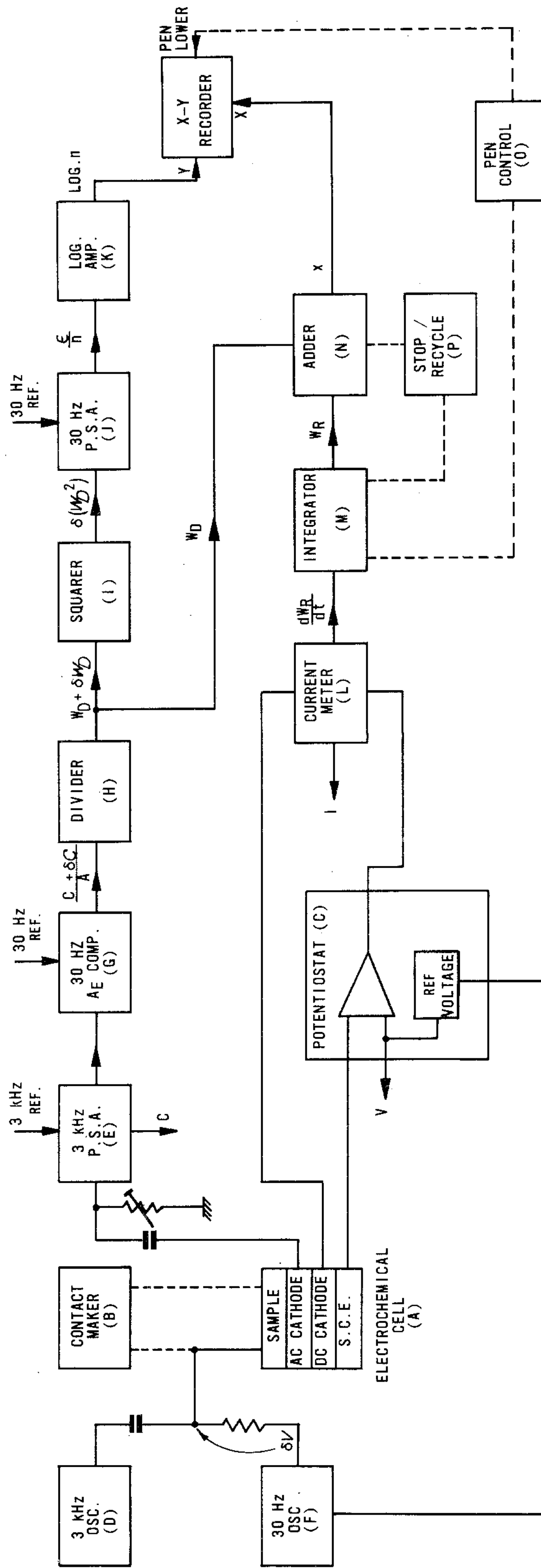


Fig. 1. Block diagram of the automatic profile plotter.

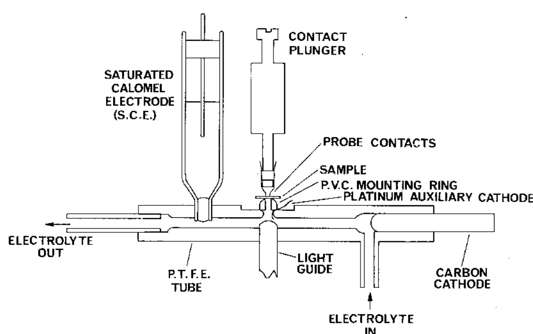
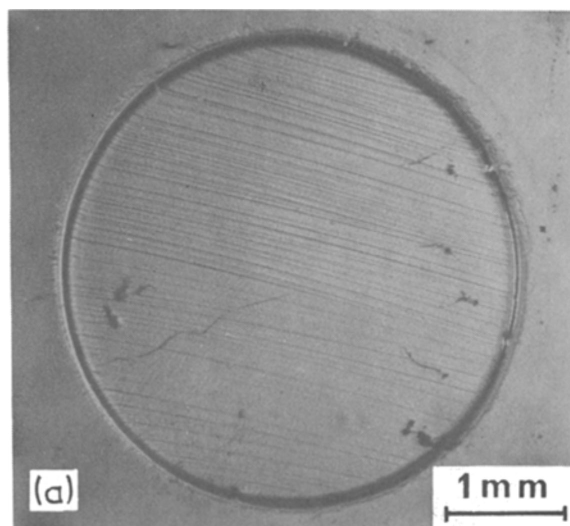


Fig. 2. The electrochemical cell.



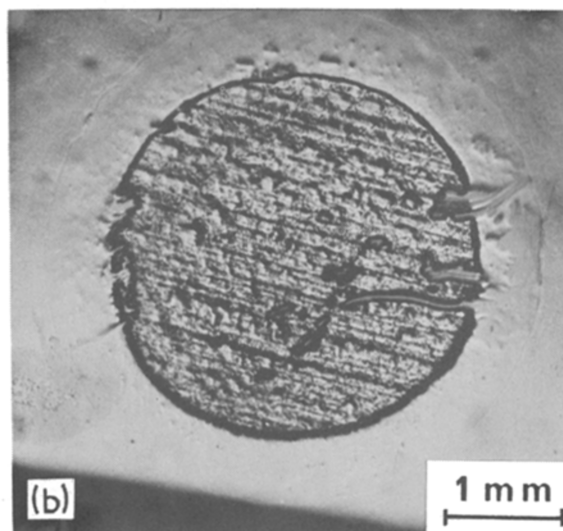


Fig. 3 (a). Region of a gallium arsenide (boat-grown) sample from which 7 μm was removed by dissolution under 550 nm illumination; (b) Region of the same material from which 10 μm was removed by dissolution under broadband (quartz iodine tungsten) illumination, using an earlier method of area definition [2].

3.3. *The potentiostat*

The potentiostatic control unit uses a single integrated circuit operational amplifier to maintain a constant anodic dissolution potential. The required potential is set on a built-in voltage reference source, and the potentiostat controls the current through the cell so that the same potential appears at the saturated calomel reference electrode (SCE). The response time of the potentiostat is arranged to be greater than 100 ms to permit external modulation of the cell potential for differential capacitance measurements. The value of anodic potential must lie within the 'safe' range described in our earlier work [2] to prevent preferential dissolution at regions of material imperfections where premature breakdown may occur. For gallium arsenide, the value chosen is − 0·3 V relative to the calomel electrode, which corresponds to a total band-bending of about 1·5 V, or an effective reverse bias of about 0·5 V.

The potentiostat unit also incorporates switch-controlled relays which permit initial connection to the contact forming unit, followed by a standby position in which the cathode is disconnected so that the rest potential may be checked. This also permits the conductivity-type to be ascertained prior to dissolution since the rest potential of *n*-type material only is sensitive to illumination. Finally, dissolution is allowed to commence by completing all connections between the cell and potentiostat and removing a shutter on the illumination source. The relay control system incorporates fail-safe protection against power supply disruptions.

3.4. *Differential capacitance analysis section*

The depletion layer capacitance is determined by applying a 50 mV rms signal from a 3 kHz oscillator (D) and measuring the imaginary component of current using a 3 kHz phase sensitive amplifier (E). The latter detects the signal across a resistor (preset, for sensitivity calibration) which is in series

with the sample, and whose impedance (tens of Ω) is negligible compared with the lowest sample impedance at 3 kHz. Fully encapsulated modules (Ancom 15 PO and 15 PSA-3) are used for the oscillator and amplifier with the addition of a simple phase-adjust circuit based on an integrated circuit operational amplifier. The phase and sensitivity of the phase sensitive amplifier are adjusted using a standard test capacitor ($\sim$ 10 nF), so that the output represents capacitance per unit area, C/A, of a sample. This, of course, requires a knowledge of the area A which is exposed to illumination, and is hence dissolved during analysis. This area, and the surrounding 'excess' area A_E, also exposed to electrolyte as shown in Fig. 3, are measured on a test sample using a travelling microscope. (It has been established that these areas are highly reproducible). Clearly there is a constant contribution to the measured capacitance from the undissolved area A_E at all times during the measurement of a sample undergoing dissolution. However, it may be assumed that before dissolution commences, the 'excess' capacitance is related to the total capacitance measured, by the same ratio as 'excess' area to total area, provided that lateral uniformity of doping exists. Thus an 'area compensation' control is provided which allows the output of the phase sensitive amplifier (as monitored on a four figure DVM) to be offset by the corresponding fraction of the initial output, measured with the sample in darkness, prior to any dissolution.

Modulation of the depletion width is achieved by means of a 30 Hz Wein Bridge oscillator (F) (based on two i.c. operational amplifiers) connected in the d.c. return path of the potentiostat circuit. The effective output δV (which is influenced by losses via the 3 kHz oscillator connection) is set at 100 mV rms. This results in a 30 Hz component in the d.c. output of the 3 kHz phase sensitive amplifier, corresponding to $\delta C/A$. This also includes a contribution which does not change during dissolution from the 'excess' area A_E, so that a fraction of this signal also has to be offset. This is achieved by adding a 30 Hz offset with 180° phase difference derived from the 30 Hz oscillator via a phase-shifter circuit. The adjustment is performed with the output of the compensation unit (G) temporarily connected to the 30 Hz phase sensitive amplifier (J) (to be described later) with its output being monitored on the digital voltmeter.

The compensated signals representing C/A and $\delta C/A$ (with the latter remaining as a 30 Hz component) are fed into a divider unit (H) based upon an encapsulated analogue divider module (Analog Devices 427 J). This unit provides an output which represents depletion width W_D (with δW_D superimposed) according to Equation 2. It is necessary to calibrate this unit using the known value of relative permittivity (dielectric constant) ϵ of the semiconductor. The output is fed to the depth-scale correction circuit (N) (Section 3.5) and to an analogue squarer unit (I). The squarer, which is an encapsulated module, requiring no external adjustment (Analog Devices 434 B) provides an output at 30 Hz proportional to $\delta(W_D^2)$; the d.c. output is not required.

The 30 Hz signal is converted to a d.c. voltage by means of a purpose built (four i.c.) high sensitivity phase sensitive amplifier (J), having an ultra-low drift, low offset, i.c. operational amplifier output stage with a usable dynamic range of 10^4.

This corresponds to a carrier concentration span of 10^4 (e.g. 10^{15}–10^{19} cm^{-3}) as given by Equation 3. The output strictly represents ϵ/n when the gain of the unit has been set according to the calibration procedure to be described in Section 4.1.

Finally, this voltage is fed into a logarithmic amplifier (K), based on an encapsulated module (Ancom 15 LP-2) which is calibrated taking into account ϵ for the semiconductor. This provides a voltage proportional to log n, which is supplied to the Y-axis input of an X–Y recorder (Hewlett Packard type 7004B).

3.5. *Depth analysis section*

The anodic dissolution current is measured using a purpose-built differential input current meter circuit (four i.c. operational amplifiers) (L). An output is provided which is calibrated to represent dissolution rate (thickness removed per unit of time); the calibration takes into account the parameters given in Equation 4 which include semiconductor material parameters, and the area of dissolution, A.

This signal is fed to an integrator whose input sensitivity is varied by a switch which allows six different values of full scale depth, from 1·8 to 72 μm on the final plot. To permit long integration periods (up to several h), the unit incorporates a

stepping-motor-driven multi-turn potentiometric output stage (M). This output, representing W_R, is added to the depletion width value W_D, via an i.c. operational amplifier (N) to provide a voltage proportional to the total depth x which is fed to the X-axis input of the X–Y recorder. A switch is provided to remove the depletion width correction, W_D, so that the thickness removed by dissolution, W_R, may be checked at any time during plotting.

In practice, the integrator output is stepped approximately 360 times during a complete plot to full-scale depth. The X–Y recorder pen registers a single point for each step by driving the pen lowering mechanism from the integrator via a simple pen plot control circuit (O).

Finally, a control unit (P) is included which senses when full-scale depth has been reached, and may be programmed so that it switches off the system completely at this point, in which case dissolution stops. Alternatively it may be set to continue plotting, in which case the X–Y recorder pen is returned to the beginning of the X-scale; in this mode the effective total depth scale is extended indefinitely.

4. Operation of the system

4.1. *Calibration*

Calibration of the integrator and associated parts of the circuit is simply performed by applying d.c. test inputs and using a digital voltmeter to measure output values. The depletion width measurement circuit up to the output of the 'divider' involves similarly straightforward calibration, requiring reference only to a fixed test capacitor and d.c. measurements. To avoid the need for accurate a.c. signal level measurements (at 30 Hz), the calibration of the 30 Hz phase sensitive amplifier (J) relies upon a final adjustment of phase and gain using an actual semiconductor sample, as follows:

The test sample should be a uniformly doped slice with a doping level about 10^{17} cm^{-3} (mid-range on the logarithmic scale). The precise value need not be known in advance, as this is measured using the electrochemical system. It is first verified that the dark current is negligible, at the usual dissolution potential, so that no conductance component interferes with the measurement. The carrier concentration can then be determined by curve fitting to a C–V plot [2] obtained by sweeping the reference potential over a range of about 0·5 V, and plotting this against the capacitance measured by the 3 kHz PSA (E). (The latter unit provides 5 switched ranges for C measurement, as well as the C/A range described earlier). The gain of the 30 Hz PSA (J) is adjusted until the measured value of n is reproduced on the X–Y recorder. The phase correction is made at the same time whilst monitoring the PSA detector stage output on an oscilloscope. It is, of course, necessary to apply the excess area compensation to the signal levels during this procedure. Having calibrated the system in this way, the test sample may be stripped sufficiently to confirm the original assumption of depth uniformity of n as required for the curve fitting.

4.2. *Routine analysis*

Once the system has been calibrated as described, analysis of n-type samples of the same semiconductor is extremely simple. Loading, contact making and area compensation corrections take only a few minutes, and once dissolution has commenced, no further attention is necessary provided the remote switch-off control has been set. Dissolution rates are of the order of 2 μm h^{-1} for gallium arsenide using the existing illumination source, so that if relatively thick specimens are being analyzed it is convenient to let the system operate overnight. Some examples of profiles obtained from gallium arsenide are shown in Figs. 4, 5 and 7.

5. Discussion

The profile shown in Fig. 4 represents an epitaxial layer structure of n-type GaAs which was grown in an attempt to meet a specification for IMPATT diode fabrication. The structure consists of a low-doped 'active' layer grown on a more heavily doped 'buffer' layer on a highly doped substrate. This continuous profile could not have been obtained by the more conventional solid Schottky barrier methods [6, 7] without resorting to a laborious procedure of measurement and chemical step etching. These methods rely upon probing in depth by increasing the applied reverse bias, and extending the depletion width until limited by reverse breakdown (to about 0·4 and 0·1 μm at donor concentrations of 10^{17} and 10^{18} cm^{-3} respectively); the

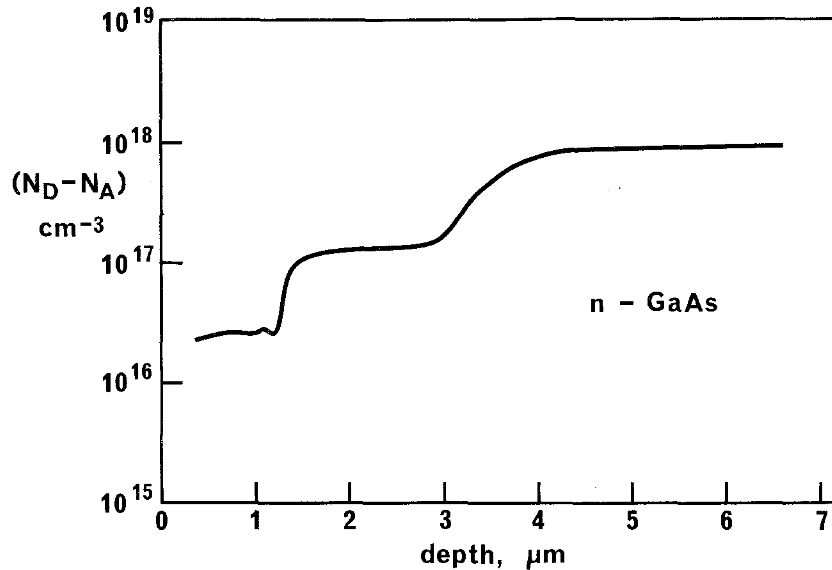


Fig. 4. Profile of a two-layer epitaxial structure of *n*-type gallium arsenide.

effective measurement depth can then only be extended by etch removal of material. Clearly, the new method combines the two features of the old approach into a reliable continuous process by the novel use of an electrolytic barrier medium. Although the principle of differential capacitance analysis is the same as that of Baxandall *et al.* [6], the approach to the electronic circuit design differs, in order to take full advantage of the electrochemical method. It was necessary to incorporate a wide dynamic range in carrier concentration measurement to allow a single continuous plot to cover the whole range of concentrations encountered in a device structure without external manipulation. This has essentially been achieved by performing the analogue operations on the 30 Hz signal rather than detecting it at an earlier stage. It should also be pointed out here that the simplified technique reported earlier by ourselves [3] did not have sufficient depth resolution to distinguish adequately the undulations in carrier concentration at the interface between the 'active' and 'buffer' layers in the profile of Fig. 4.

The resolution of the new modulation technique is limited by the Debye Length, which is a factor of ten smaller than the depletion widths, quoted in Section 2.2, which determined the resolution of our earlier technique. This is rather important; in fact the epitaxial structure given in this example was rejected from IMPATT device processing on the grounds of the features revealed only by the modulation technique.

A further example of a multilayer structure is given in Fig. 5. This represents an attempt to produce material for a Read-type IMPATT device. Once again it is apparent that the wide carrier concentration range and depth capability of the electrochemical system are being fully exploited.

There are certain aspects of the electrochemical system where there is scope for improvement. It is clear that uniformity of illumination is essential for a uniform rate of dissolution across the area examined. The present system of illumination, via a multiple fibre light pipe, provides a uniformity which is quite acceptable for most purposes as illustrated by the 'Talysurf' trace* over the base of a stripped area, shown in Fig. 6. However, since the 'spread' is necessarily a certain fraction of the total amount removed, this places a limit on the ability to resolve sharp interfaces at large depths. An improvement in uniformity is currently being sought by the use of microscope optics. This is being combined with a project to observe directly the revelation of topographic features whilst dissolving material in the 'destructive' mode as described in

* The 'Talysurf' is a moving stylus surface measuring instrument, manufactured by Rank–Taylor–Hobson, Leicester, England.

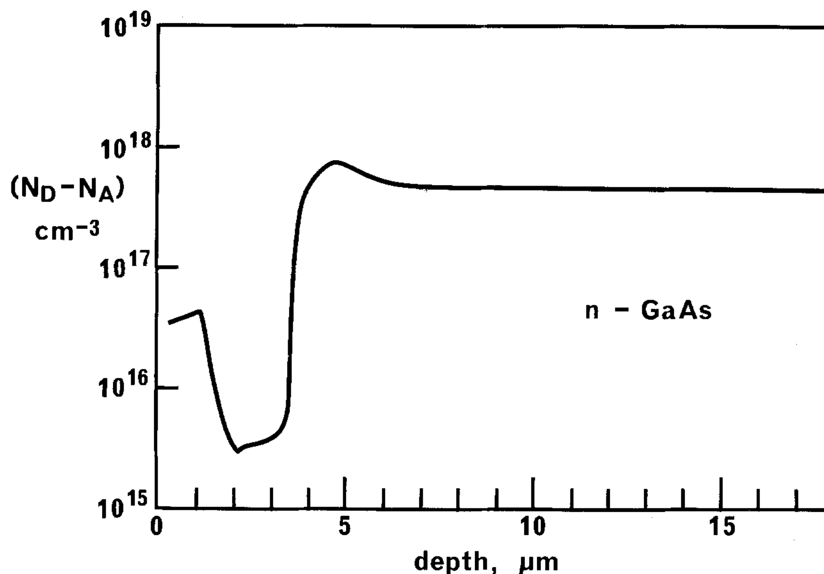


Fig. 5. Profile of a three-layer epitaxial structure of n-type gallium arsenide.

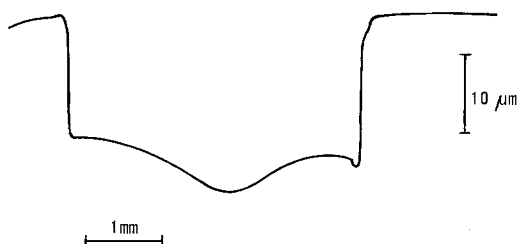


Fig. 6. 'Talysurf' trace over the base of an area stripped to an average depth of 10 μm.

reference [2]. This technique may provide valuable information on material quality, complementary to that given by a profile plot. The possibility of examining smaller areas than at present (about 4 mm diameter) is also being considered. However, it is not practicable to permit the ratio of 'excess' area to 'dissolved' area to increase since the errors in compensation would reduce the accuracy of plots, being particularly significant in the case of a high concentration interface. In certain cases it may be advantageous to employ a contact mask, but this is not an attractive possibility for general use, as it detracts from the simplicity of the present system.

An important question concerns the possible influence of the illumination on the carrier concentration measurement. Fortunately, at the flux used, its effect is apparently negligible. The external photopotential is accommodated by the potentiostat, although there remains a small increase in measured capacitance (typically less than 10%) at a given anodic potential when the illumination is switched on. Thus there appears to be a decrease in impedance in the very-near surface region in which the light is absorbed. However no change can be detected in the apparent value of carrier concentration derived from the modulation of depletion width in regions of uniform doping. At much higher illumination levels (e.g. with the narrowband filter removed from the light source), an apparent change has been observed. This has not yet been studied in detail, however, and the relative influence of illumination wavelength, and intensity has not been established; this is of some interest, since it would be useful in some instances, to be able to increase the dissolution rate.

A limitation which applies to all capacitance methods of carrier concentration analysis is the uncertainty imposed by the possible presence of deep traps. This question was raised in reference [2] in conjunction with the bulk low-doped samples investigated. A recent study by Kimmerling [8] discusses anomalous profiles which can arise from certain trap distributions. The profile shown in Fig. 7 was obtained using the electrochemical plotter, and the feature indicated by the arrow was also revealed similarly in the same gallium

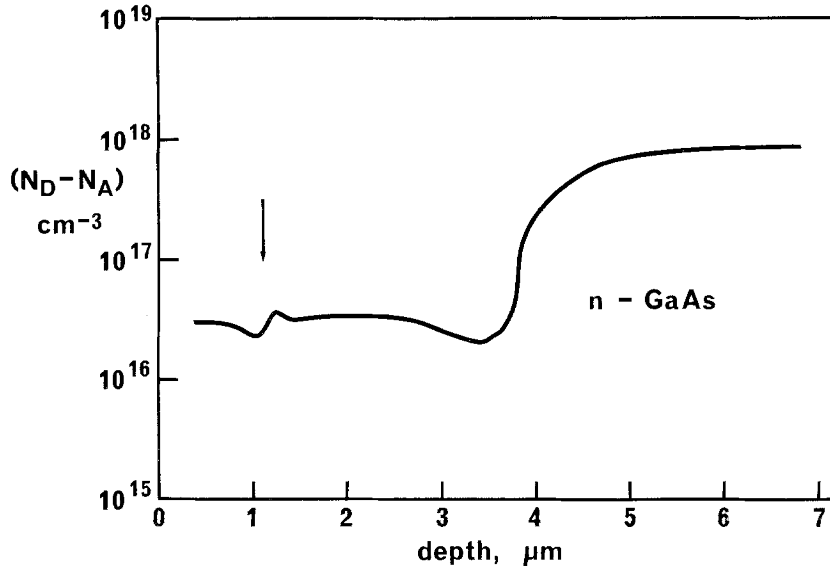


Fig. 7. Profile of an epitaxial structure of n-type gallium arsenide exhibiting a feature which may represent deep trap levels.

arsenide sample by the plotter described by Baxandall *et al.* [6]. The feature is extremely similar to one illustrated in Kimmerling's paper. In the situation described by Kimmerling, such a feature could arise from a triangular trap distribution of acceptor-type levels having a characteristic frequency greater than the modulation frequency employed by the profile plotter. Note that the peak following the dip is purely an anomaly of the analyzing system. It is not known, however, whether our own plot does represent such a case: a detailed study as described by Kimmerling would require a significant variation in sample temperature or analyzing frequency. Thus independent measurements, capable of indicating the presence of deep levels, are desirable in conjunction with a capacitance-type profile plotter. It is hoped that a contribution based on electrochemical techniques involving frequency-dependent measurements or illumination-wavelength dependent photocurrent measurements will be possible.

Finally, let us consider the application of the automatic profile plotter to materials other than n-type gallium arsenide. First, analysis of n-type gallium phosphide has been successfully performed, requiring only simple re-calibration of the plotter, and substitution of a blue-filtered mercury arc illumination source. It is expected that other wide band-gap III–V compounds could also be readily analyzed, although other semiconductors such as silicon may have to be individually treated, requiring an investigation to find suitable electrolytes.

Some preliminary work reported elsewhere [9] indicates that, with a little modification, the technique is suitable for the analysis of p-type material. This, in turn, raises the possibility that structures containing p–n junctions may also be analyzed.

6. Conclusions

A fully automatic carrier concentration profile plotter based upon an electrochemical technique has been described. Its ability to cover a wide range of carrier concentration values up to any required depth has been demonstrated using examples of epitaxial multilayer structures of n-type gallium arsenide. The potential application to other semiconductors, including p-type material, suggests that a plotter of this type could meet many existing demands for a versatile semiconductor characterisation tool.

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