JOURNAL OF MATERIALS SCIENCE 12 (1977) 1827–1833

Scanning electron microscope EBIC and CL micrographs of dislocations in GaP

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The SEM EBIC (or charge collection) method using a surface Schottky barrier was applied to GaP specimens to obtain dark spot micrographs revealing dislocations present in the specimens. We describe the experimental procedures and electron probe parameters necessary to obtain such micrographs for specimens ranging from LEC substrate material to doped and undoped VPE layers, and compare the results obtained with analogous results for the SEM CL method. A one-to-one correspondence between the dark spots in corresponding EBIC and CL micrographs was demonstrated. Factors affecting the spatial resolution of the micrographs are discussed; a best resolution of ~ 1 μm was obtained.

1. Introduction

Dislocations in GaP specimens used for light emitting diodes (LEDs) can cause a decrease in luminescence and poor device performance [1, 2]. It is important, therefore, that methods are available for accurately assessing the dislocation density and distribution in the various GaP specimens corresponding to the different stages of manufacture of such devices. LEDs are generally made by growing doped epitaxial layers on (1 0 0) substrates, or on substrates cut typically 10° off (1 0 0). This is followed by a number of fabrication stages such as diffusion, nitriding, metallization, etc.

Chemical etching and subsequent optical microscope examination of the resulting etch pits is the method most commonly used to reveal dislocations in semiconductor specimens. However, there is considerable difficulty in finding etchants suitable for GaP specimens with the crystallographic orientations generally used for LEDs. For example, the Richards–Crocker (RC) etch [3] or Abrahams–Buiocchi (AB) etch [4] are successful for (1 1 1 B) specimens, but cannot be used for specimens of other orientations. An etchant [5] was recently developed that is suitable for (1 0 0) specimens, but it is not satisfactory for specimens cut 10° off (1 0 0) [6].

The SEM cathodoluminescent (CL) method can be used for GaP specimens to obtain micrographs exhibiting dark spots [1, 7, 8] (or lines), which indicate regions where increased non-radiative recombination of carriers is taking place. These dark spots have been shown [1, 9] by etching and TEM studies to correspond to individual dislocations.

The SEM electron beam-induced conductivity (EBIC) (or charge collection) method has been used for many years with semiconductor specimens to obtain micrographs with dark spots [2, 10] (or lines), which indicate regions where increased electrical recombination of carriers is taking place. These dark spots are again considered to correspond to individual dislocations.

The EBIC method has mostly been used for collecting the electrical carriers, generated in the specimen by the incident electron beam, at a p–n junction in the specimen. However, this has the disadvantage that the junction needs to be fabricated, and this may modify the dislocations present or introduce new dislocations. The EBIC method has more recently been used for collecting the carriers at a Schottky barrier formed by depositing a thin metal layer on the specimen surface [2, 11]. This has the advantage that it can be used with any type of semiconductor specimen (providing a suitable Schottky barrier can be made).

These SEM methods can be applied to specimens of any crystallographic orientation, as long as sufficient luminescent signal (for CL) or

TABLE I Minimum SEM probe currents needed to obtain acceptable EBIC and CL micrographs

Specimen			Probe current (A)	
Code	Type	Dopant	EBIC	CL
A	LEC Substrate	S, 1×10^{17} cm^{-3}	10^{-7}	Acceptable micrographs difficult to obtain
B	VPE layer	nominally undoped	10^{-8}	10^{-6} to 10^{-5}
C	VPE layer	S, 1×10^{17} cm^{-3} N, 1×10^{19} cm^{-3}	10^{-8}	10^{-8}
D	VPE layer	S, 1×10^{17} cm^{-3} N, 1×10^{19} cm^{-3} Zn diffused, 2×10^{18} cm^{-3}	10^{-8}	10^{-8}

electrical signal (for EBIC) can be generated by the incident electron beam and collected. The CL method has been successfully used during the last two or three years to investigate a number of GaP specimens [1, 7–9]. However, there have been few reports of the application of the EBIC/Schottky barrier method to GaP specimens, possibly because there is little published information concerning the experimental procedures that need to be used.

The aim of the present work is to draw attention to the advantages of the EBIC/Schottky barrier method for investigating dislocations in GaP specimens, describe the experimental conditions necessary to obtain such EBIC micrographs for different types of GaP specimen, compare the EBIC method with the CL method, and briefly comment on some of the results obtained.

2. Experimental procedures

In the present work, four types of GaP specimen were examined by the SEM EBIC and CL methods (Table I). Three of the specimens (A, C and D) correspond to successive stages in the fabrication of a particular type of LED, and the fourth specimen (B) was grown to obtain additional information concerning the epitaxial growth process.

The specimens consisted of liquid encapsulated Czochralski (LEC) GaP substrate slices cut 10° off (1 0 0) and doped with 1×10^{17} cm^{-3} of S atoms (specimen A), vapour phase epitaxial (VPE) GaP layers nominally undoped grown on LEC substrates (specimen B), VPE layers doped with $\sim 1 \times 10^{17}$ cm^{-3} of S atoms and $\sim 1 \times 10^{19}$ cm^{-3} of N atoms grown on LEC substrates (specimen C), and similarly doped VPE layers grown on LEC substrates and subsequently diffused with Zn atoms to give a Hall concentration of 2×10^{18} cm^{-3} (specimen D). The LEC substrates had been mechanically and chemically polished by standard procedures. The other specimens had not been subjected to any treatments following the layer growth or subsequent diffusion.

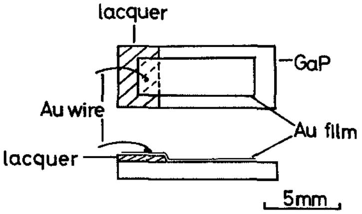

Figure 1 Diagrams showing method used to make electrical connection to the evaporated Au layer.

For the EBIC micrographs, the surfaces of all the specimens were degreased with organic solvents and treated with aqua regia to remove any oxide that might be present. A thin film of electrically insulating lacquer was applied to a portion of the specimen (Fig. 1). A gold film typically 50 nm thick was evaporated onto the specimen using a mask so that a portion of the film was on the GaP surface and a portion on the lacquer film. The vacuum in the evaporator during deposition was less than 10^{-5} torr. The lower side of the specimen was cemented to a standard SEM metal stub using silver conducting paint, and a gold wire attached to the portion of the gold film on top of the lacquer also using silver conducting paint. This procedure for attaching the wire to the gold layer avoids possible damage to the gold/GaP junction.

The specimen was inserted in the SEM and reverse-biassed in the range 1 to 5 V. The particular value of the voltage used in this range generally had little effect on the quality of the resulting EBIC micrographs from any of the specimens investigated. Breakdown mostly occurred between 5 and 6 V. For specimens A, B and C the gold wire was made negative (Fig. 2), and for specimen D positive. Different electron probe currents were used for the different examinations, and these were obtained by suitable selection of the SEM lens currents and final aperture diameter (Table II). Such differences gave different probe diameters, but in all cases these diameters were $< 2\,\mu$m (Table II). The electron/hole pairs generated by the

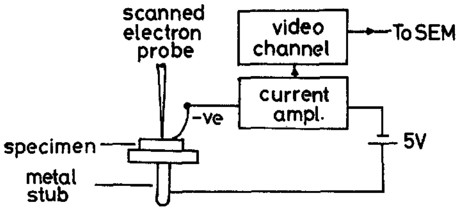

Figure 2 Diagram showing electrical circuit used for n-type semiconductor materials for EBIC Shottky barrier method.

electron probe in the junction region were separated by the junction field, and the resulting junction current was fed to a Keithley Model 427 current amplifier and used as the video signal to produce the EBIC micrograph on the viewing screen. The electron probe was generally scanned over the specimen using a standard square raster, but line traces were sometimes made to aid measurements.

For the CL micrographs, the specimens were examined in the SEM without performing any special surface treatments (except for the specimen used to obtain the CL micrograph of Fig. 4b). The electron probe currents required were sometimes significantly different from those used for the corresponding EBIC examinations (Table I). The emitted light was collected in the standard manner using a perspex light-pipe coupled to an EMI Ltd. type S11 photomultiplier and video amplifier to produce the CL image. No wavelength selection was used, other than that imposed by the spectral response of the photomultiplier.

In general, for the EBIC examinations, the specimen was set with the surface perpendicular to the SEM electron optical axis, while for the CL examinations, the specimen was tilted typically 30° towards the light-pipe collector to provide a larger signal. The SEM was operated with a standard tungsten hairpin filament, and mostly at an accelerating voltage of 30 kV. The EBIC and CL dark spot micrographs were recorded after using the black level control (d.c. background level suppression) and increasing the amplifier gain until the signal as viewed on the line-trace monitor was only just not clipping at either the top or bottom. Photographic exposures were typically 40 sec. The diameters of the dark spots referred to later in the text were measured on photographic prints processed in the standard manner.

TABLE II SEM probe diameters used

Probe current (A)	Probe diameter d (μm)	
	200 μm diameter final aperture	no final aperture
10^{-8}	0.5	–
10^{-7}	1.6	–
10^{-6}	–	0.6
10^{-5}	–	1.8

3. EBIC and CL micrographs

At each initial examination, the electron probe current was progressively increased until dark spot EBIC or CL micrographs of acceptable quality resulted. This occurs when the electrical or luminescent signal collected for the micrograph is sufficiently large to overcome signal/noise limitations. The probe currents obtained in this way for the different types of specimen are those given in Table I, and these currents were then used for the remainder of the work.

Acceptable EBIC micrographs were obtained for specimens B, C and D with a probe current of 10^{-8} A, while for specimen A a probe current of 10^{-7} A was required. The dark spot micrographs from specimens B, C and D (VPE layers) were similar to one another, Fig. 3a from specimen B being typical, while those from specimen A (LEC substrate) were significantly different (Fig. 3b).

The reason why it is more difficult to obtain sufficient electrical signal from specimen A is thought to be related to the smaller minority carrier lifetime τ and diffusion length L for this specimen. Typical measured bulk values of τ for specimens B, C and D were ~ 50 nsec, and for specimen $A < 5$ nsec. Calculation shows that these correspond to L values of $\sim 3.5\,\mu$m and $< 1.0\,\mu$m respectively. Hence, when the minority carriers are generated in specimen A by the incident electron probe, they recombine more rapidly and so fewer are available for collection at the junction.

Acceptable CL micrographs were obtained for specimens C and D with a probe current of 10^{-8} A, while for specimen B a probe current of 10^{-6} to 10^{-5} A was required. Acceptable CL micrographs could not be obtained from specimen A, the micrographs that did result being noisy even when a probe current of 10^{-5} A was used, the practical maximum. The general appearances of the CL micrographs from the individual specimens were similar to those of the EBIC micrographs from

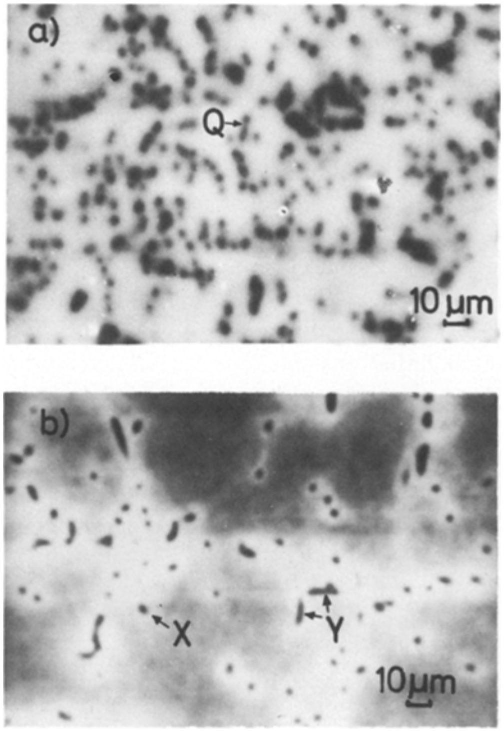

Figure 3 EBIC/Schottky barrier dark spot micrographs from (a) undoped VPE GaP layer (specimen B), (b) doped LEC GaP substrate (specimen A).

the corresponding specimens, except for the poorer CL micrograph quality in some instances.

Sufficient luminescent signal could readily be obtained from specimens C and D because they were N-doped, this creating large numbers of isoelectronic centres and giving high luminescence. More difficulty was experienced with specimen B because it did not contain N. Still greater difficulty occurred with specimen A because it did not contain N and it possessed smaller values of τ and L.

The above results demonstrate that acceptable EBIC micrographs can be obtained using the Schottky barrier method from either n- or p-type GaP specimens. They also show that for all of the specimens examined, the probe current required for the EBIC micrograph is similar to or less than that required for the corresponding CL micrograph. Smaller probe currents are advantageous because less surface contamination and heating of the specimen occurs. Furthermore, a smaller electron probe diameter can then in general be used, and this could in some cases result in micrographs with better spatial resolution (see later).

4. Correlation of EBIC dark spots with dislocations

In one instance for specimen C, the GaP specimen that had been used to give EBIC micrographs was also used to give CL micrographs. The light that was emitted from the GaP specimen and transmitted through the gold surface layer was collected by the light-pipe and fed to the photomultiplier and then to a second video channel. EBIC and CL micrographs from the same area of the GaP specimen, and corresponding to the same electron probe conditions, were simultaneously displayed on adjacent viewing screens. A pair of micrographs obtained in this way is shown in Figs. 4a and b. The micrographs are of similar quality. For each dark spot in the EBIC micrograph, there is a corresponding dark spot in the CL micrograph, and vice-versa, i.e. there is a precise one-to-one correspondence between the dark spots in the two types of micrograph.

Previous work by Titchmarsh *et al.* [9] investigating a liquid phase epitaxial (LPE) GaP layer showed that there was a precise one-to-one correspondence between dark spots obtained in

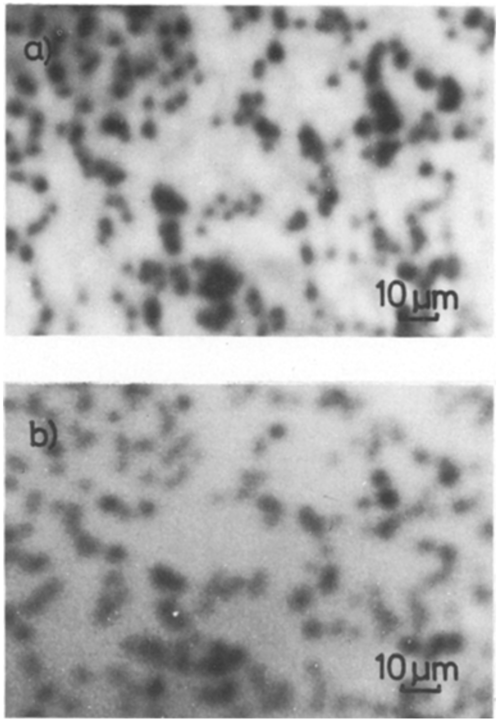

Figure 4 Dark spot micrographs from the same area of a doped VPE GaP layer (specimen C) using (a) EBIC/Schottky barrier method, (b) CL method. Note the one-to-one correspondence of dark spots.

CL micrographs and dislocations observed using the TEM method, and that all possible types of dislocation, namely, screw, 30°, 60° and edge, gave CL dark spots. Consideration of the present results illustrated in Figs. 4a and b, in conjunction with the above results of Titchmarsh *et al.*, leads to the conclusion that when EBIC micrographs are obtained using the Schottky barrier method, each EBIC dark spot corresponds to a dislocation, and all dislocations are revealed.

5. Spatial resolution of EBIC and CL micrographs

In the present work, the experimental results showed that for both the EBIC and CL micrographs, and for all types of GaP specimens examined, the dark spot diameters tended to fall in the same general range, 4 to 7 μm. All of these micrographs were obtained using a beam voltage of 30 kV.

Several parameters may limit the spatial resolution of the EBIC and CL micrographs, and hence determine the diameter of the dark spots, these being as follows. Firstly, the spots will be blurred out by an amount directly related to the diameter Δ of the effective generation volume of the carriers within the specimen. The value of Δ is in turn determined by the probe diameter d, which depends on SEM instrumental parameters, and the diameter Δ_0 of the carrier generation volume corresponding to zero probe diameter, which depends on the material of the specimen and the electron beam accelerating voltage. To a first approximation, Δ can be taken to be whichever is the larger of d and Δ_0. In the present work, the values of d that were used are given in Table II, and values of Δ_0 for GaP interpolated from experimental measurements made by Woolf [12] are given in Table III. Hence, for the present work on GaP using 30 kV electrons, Δ was $\sim 6\,\mu$m.

Secondly, the spots will also be blurred out by an amount dependent on the minority carrier diffusion length L. The diameter of a dark spot arising from this effect is generally taken to be $\sim L$. In the present work, the maximum value of L was 3.5 μm.

TABLE III Generation volume diameters for GaP (for zero probe diameter)

Electron probe accelerating voltage (kV)	Generation volume diameter Δ_0 (μm)
30	6
25	4
20	2.5
15	1.5

Consequently, the resolution that will occur for EBIC and CL micrographs will depend on Δ and L, and can be taken as a first approximation to correspond to whichever of the two parameters is the larger. In the present work on GaP using 30 kV electrons, $\Delta \simeq 6\,\mu$m and $L \leqslant 3.5\,\mu$m. Hence, the dark spot diameters for all of the specimens examined should be $\sim 6\,\mu$m, and this is in reasonable agreement with the experimental observations. These results suggested that the parameter limiting the spatial resolution of the micrographs in this work was the 30 kV electron accelerating voltage.

In order to verify this, a series of EBIC micrographs was obtained for specimen B for electron accelerating voltages of 30, 25, 20 and 15 kV, and the mean diameters of the resulting dark spots proved to be 5, 3.5, 1.5 and 1.5 μm respectively. The probe diameter d for all of these micrographs was 0.5 μm. The values of Δ_0 were $\sim 6, 4, 2.5$ and 1.5 μm respectively, and so these should also be the values of Δ. The value of L was 3.5 μm. Consequently, as the accelerating voltage was decreased from 30 to 15 kV, the resolution should have progressively decreased from $\sim 6\,\mu$m (limited by the voltage) to $\sim 3.5\,\mu$m (limited by L). The experimental observations showed this general trend, but the eventual resolution was $\sim 1.5\,\mu$m, i.e. considerably less than L.

In the case of the EBIC micrographs obtained using the Schottky barrier method, the spatial resolution may also depend on the junction depletion region width W, which is determined by the doping concentration in the GaP specimen and the reverse-bias voltage applied. There are various cases to consider, e.g. those in which the diameter Δ of the effective carrier generation volume is either greater or less than the depletion region width W. Both of these cases were thought to be encountered in the present work. For example, for specimen D (Zn-diffused VPE layer) and 30 kV accelerating voltage, $\Delta \gg W$. Conversely, for specimen B (undoped VPE layer) and 15 kV accelerating voltage, $\Delta < W$.

In the latter case, after the carriers are generated in the specimen, they begin to diffuse while under the action of the junction electric field, which is perpendicular to the specimen surface. The probable result is that the mean diffusion length L' measured parallel to the surface will be significantly less than the standard bulk diffusion length L. Consequently, because L' rather than L determines the spatial resolution of the EBIC micrographs, this is a possible reason as to why the mean dark spot diameter (1.5 μm) for specimen B and a 15 kV accelerating voltage was less than the bulk value of L (3.5 μm) for this specimen. However, further work is required to investigate this effect.

Some consequences of the above work when obtaining EBIC and CL micrographs from GaP specimens containing dislocations are as follows. The use of a 30 kV accelerating voltage is convenient because it gives dark spots of large diameter, which can be readily observed with the SEM at low magnifications (150 ×). However, a 15 kV accelerating voltage gives better spatial resolution (~ 1 μm) enabling dislocation densities up to 10^7 cm^{-2} to be measured, and gives a more correct indication of the amount of luminescent emission lost due to the dislocations. For example, the fraction of the area of any particular micrograph that is dark (due to dislocation dark spots) can be decreased by a factor of 5 to 10 simply by decreasing the accelerating voltage from 30 to 15 kV.

6. Structural Information

The EBIC micrographs showing dark spots provide the following information concerning the dislocations in the specimens examined. For the VPE layers (Fig. 3a), the dark spots are almost always circular, indicating that the dislocations are steeply inclined to the specimen surface. The dislocation density is typically 8×10^5 cm^{-2}. The regions between the dark spots are in general uniformly grey, suggesting that the material between the dislocations is of uniform quality. The micrographs also occasionally showed that two dark spots occurred close together with a faint dark line joining them (Fig. 3a, Q). These are interpreted to be stacking fault defects, the two dark spots corresponding to the two steeply inclined bounding partial dislocations, and the line to the fault itself.

For the LEC substrates (Fig. 3b), there are two kinds of dislocations. The circular dark spots (X) correspond to dislocations steeply inclined to the specimen surface, and the elongated dark spots (Y) to dislocations shallowly inclined to the surface. The latter are oriented mainly along two directions approximately perpendicular to one another. The dislocation densities for types X and Y are typically 2×10^5 and 2×10^4 cm^{-2} respectively. The regions immediately surrounding the dark spots are bright, while further away the regions are darker with a mottled appearance. The latter contrast suggests that these regions consist of less uniform material. Davidson *et al.* [7] have observed similar contrast in CL micrographs from LEC GaP substrate material, and have suggested that the bright regions arise because impurities have diffused from these regions to the dislocations, leaving material of higher luminescence.

The structural results deduced from the EBIC micrographs of the present work are in good agreement with the results of a comprehensive TEM investigation recently performed on the same and similar GaP specimens by Palolil [13].

7. Conclusions

(1) The SEM EBIC method using a Schottky barrier can be routinely applied to GaP specimens to obtain dark spot micrographs revealing the number and distribution of dislocations in the specimen.

(2) The method is satisfactory for all types of GaP specimen irrespective of doping and crystallographic orientation.

(3) A best spatial resolution of ~ 1 μm was obtained and so the method is suitable for dislocation densities up to 10^7 cm^{-2}.

(4) To obtain this spatial resolution for VPE GaP layers, the optimum SEM instrumental conditions were electron accelerating voltage 15 kV and probe current 10^{-8} A.

(5) The diameter of the dark spots in the micrographs can be less than the minority carrier diffusion length in the specimen.

(6) A one-to-one correlation was demonstrated between dark spots in the EBIC micrographs and dark spots in the corresponding CL micrographs for an undoped VPE GaP layer.

(7) When applied to dislocations, the SEM EBIC method using a Schottky barrier has definite advantages for some types of specimen over other methods of examination; (a) the SEM EBIC method using a p–n junction fabricated within the specimen (the fabrication may modify the defects and electrical behaviour), (b) the SEM CL method (the luminescence may be insufficient to give good quality dark spot micrographs), and (c) etch pit methods (suitable etchants are often not available).

Acknowledgments

The authors wish to thank Mr. D. G. Jenkins and Mr. J. Palolil for help with the experimental techniques, and Dr. R. M. Gibb, Mr. D. J. Stirland and Mr. J. Palolil for useful discussions and for supplying specimens. This work is part of a collaborative project performed with the Allen Clark Research Centre, Plessey Company Ltd., Towcester.

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Received 24 November 1976 and accepted 4 January 1977.