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Damage in gallium arsenide crystals produced by ion implantation, abrasion and ball-milling

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Gallium arsenide single crystals implanted with tellurium and cadmium ions at 50 and 150 keV at room temperature were examined using RHEED. Damage depth profiles were measured. Annealing was carried out to investigate the effect of temperature on the implantation damage. These effects which proved to be very complicated, included decomposition of the gallium arsenide, formation of beta gallium oxide and gallium telluride, and preferred orientation of the gallium arsenide. Comparisons were made with the annealing behaviour of ball-milled gallium arsenide using X-ray diffraction line broadening. The effects of various types of mechanical damage associated with specimen polishing of the gallium arsenide single crystals were also investigated.

1. Introduction

The use of ion implantation to produce doping in semiconductors was foreseen as far back as 1954 in a patent filed by W. Shockley [1]. Development work has since been carried out in a number of academic and industrial centres throughout the world. The main interest at present is in electronic devices, in which the controllability of the production process is important. The Science Research Council has formed a special panel to help support this research at three university centres and, at Surrey, work is proceeding into the controlled implantation of various ions into gallium arsenide, and also the resultant properties of the implanted material [2].

One important aspect of the implantation process is the damage produced in the single gallium arsenide crystals by the implanted ions. This damage is mainly confined to the surface of the crystals and can greatly affect their electrical properties. The crystals are annealed at temperatures over 650° C to remove this damage, but the effects are complicated by decomposition of the gallium arsenide, and possible loss of arsenic and oxidation of the gallium. The investigation of these effects requires techniques which are effective on surfaces. The method mostly used at present is Rutherford back-scattering. This technique enables a determination of the damage depth profile to be made. The surface composition and the presence of impurities can also be determined. Some use has been made of electron microscopy [3] and electron spectroscopy [4] in the study of the surface structure and composition of the ion-implanted gallium arsenide crystals.

During the study of ion implantation in progress at Surrey, it was felt that a detailed knowledge of the damage produced by the implantation process was essential. Such factors as the extent and nature of the damage, and the effect of annealing temperature, were not fully known because the Rutherford back-scattering technique previously used is essentially spectroscopic and can only detect elements, and the resolution is only about 200 Å. Both X-ray and electron diffraction methods can be used to study damage but the character of the information given by each is different, and an investigation of the usefulness of both methods was undertaken. Neither method gives much information about point defects, but both give information about long-range defects, such as dislocations. The X-ray diffraction line-broadening method seemed best to try first to study annealing effects, as the theory and practice of the technique are well established. However, this method cannot be used to study ion-

implantation damage because of the excess penetration of the X-rays.

It was felt that useful information concerning the depth and nature of mechanical damage produced by cutting and polishing of the gallium arsenide crystals could also be investigated simultaneously, as the annealing procedures for mechanical damage removal would be similar to that for ion-implantation damage removal.

2. Mechanical damage and thermal decomposition in GaAs powders

X-ray line-broadening methods have been intensively developed in the study of crystal damage. Many theoretical treatments of varying complexity have been used in this work, but they usually result in the obtaining of two parameters, one a measure of the crystal mosaic size, and the other a measure of the crystal "strain", or dislocation density. The presence of dislocations in ion-implanted gallium arsenide has been established by electron microscopy [5], so that it seemed worthwhile to study the crystal size and strain in gallium arsenide produced by mechanical deformation, and the effect on these of annealing temperature.

For this purpose, mechanical damage was produced by ball-milling gallium arsenide powder in a vibratory mill using an agate pot and balls. The gallium arsenide powder was milled for 40 h. It was then annealed in an evacuated tube at temperatures ranging from 200 to 800° C, for 1 h. Chart-recorded X-ray diffraction profiles were obtained using a Philips powder diffractometer with Ni-filtered Cu$K\alpha$ radiation. A scanning speed of $\frac{1}{8}°$ min^{-1} in deviation angle, 2θ, was chosen. Rachinger's method [6] was used to resolve the $K\alpha_1$ and $K\alpha_2$ lines. The integral breadth method of Wagner [7] was used to measure the microstrains and crystal sizes.

Broadening due to the specimen β_s^* was obtained by subtracting the instrumental broadening obtained from large-grained undamaged GaAs powder, β_I^*, from the total broadening, β_T^*, using the equation:

$$\beta_s^* = \beta_T^* - \frac{[\beta_I^*]^2}{\beta_T^*} \qquad (1)$$

where $\beta^* = \beta \cos \theta_0/\lambda$; β = integral breadth; θ_0 = Bragg angle; λ = wavelength of X-rays.

Values of microstrain, ϵ, and crystallite size, D, were obtained from the equation:

$$(\beta_s^*)^2 = \frac{1}{D^2} + \frac{16\epsilon^2 \sin^2 \theta_0}{\lambda^2} . \qquad (2)$$

The plot of $(\beta_s^*)^2$ against $(d^*)^2 = (2 \sin \theta_0/\lambda)^2$ gave the values of crystallite size, D, and microstrain, ϵ. $d^* = 1/d$; d = interplanar spacing of the crystal.

The amount of arsenic diffusing out during the annealing was estimated by using calibrating mixtures of various known weights of arsenic and gallium arsenide. The same diffractometer procedures used previously were employed to scan the profiles using the various As/GaAs mixtures. A calibration curve was plotted by taking the ratio of the weight of As to GaAs against the ratio of corresponding areas of the X-ray diffraction profiles. The percentages of out-diffusing As at different temperatures were then estimated (Table I).

TABLE I Dislocation densities and percentage of As in GaAs after various heat-treatments (X-ray results)

Treatment	Dislocation densities ($\times 10^{10}$ cm^{-2})	% As
Ball milled 40 h	62.90	None
Annealed 200° C	33.90	None
Annealed 300° C	22.30	2.7
Annealed 400° C	10.00	10.7
Annealed 500° C	1.00	21.1
Annealed 600° C	0.83	None
Annealed 700° C	0.52	None
Annealed 800° C	0.25	None

3. Results of X-ray examination

Decomposition of the GaAs took place at about 300° C when arsenic was detected, but this disappeared at 600° C. No sign of free gallium was detected. Above 600° C, the out-diffusing arsenic evaporated to the other end of the specimen tube, leaving no signs of free arsenic in the specimen.

Fig. 1 shows the variation of microstrain and crystallite size with temperature. The rate of microstrain relief increased with temperature up to 400° C with little increase in crystallite size. Above 400° C, the microstrain showed little change while the crystallite size increased up to ten times the original value.

Dislocation densities shown in Table I were estimated using the equation [8]:

$$\rho = 16.1 \frac{\epsilon^2}{b^2} \qquad (3)$$

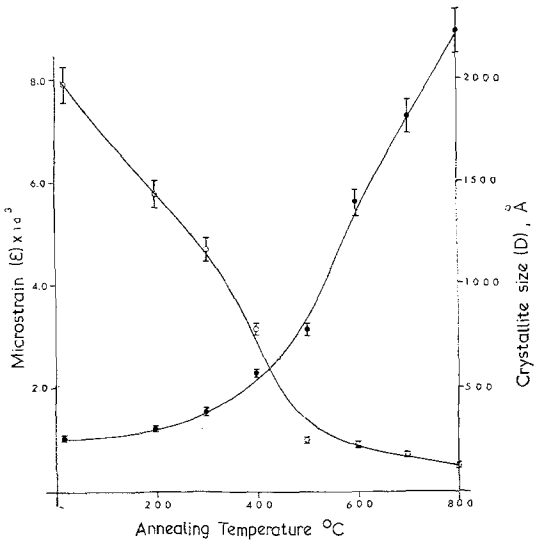


Figure 1 Effect of annealing on microstrains (ϵ) and crystallite sizes (D). Annealing time 1 h; ● – crystallite size, ○ – microstrain.

where ρ = dislocation density; ϵ = microstrain; $\boldsymbol{b}$ = Burgers vector ($a/2$ ⟨110⟩) [9]. Thus this part of the work clearly showed the stages of strain removal and crystal growth associated with different annealing temperatures in mechanically damaged gallium arsenide. Information concerning decomposition was also obtained. However, it must be assumed that these results would be more applicable to the removal of mechanical damage due to cutting and polishing than to implantation damage. The fact that the specimens were in powder form instead of the single crystal form usual in implantation should be borne in mind.

4. Surface mechanical and implantation damage in GaAs single crystals

X-ray diffraction is not a suitable method for investigating surface damage in gallium arsenide single crystals owing to the great penetration of the X-radiation. Therefore, it was decided to use reflection high-energy electron diffraction (RHEED) for single crystal studies. This was carried out in an apparatus built along the lines recommended by Kehoe [10]. The conditions of working were 35 kV and 15 μA.

4.1. Mechanical damage

In the first part of this work, mechanical damage was introduced into the surface of single gallium arsenide crystals by methods likely to correspond with those used in the preparation of crystals for ion-implantation studies. These were: abrasion by fine grade energy paper; abrasion by diamond wheel cutting; rubbing on a polishing pad. The surfaces were examined by RHEED. The variation of the damage with depth was examined by etching off the damaged surface using a 0.1 to 0.2% bromine methanol solution. A typical RHEED pattern of mechanically damaged GaAs single crystals is shown in Fig. 2. After each etch the specimen surface was cleaned using concentrated hydrochloric acid and methanol [11]. The average etch rate was estimated by etching a partially masked smooth crystal surface under the same conditions, and estimating the step height formed using a Rank Taylor-Hobson Talystep.

The patterns obtained varied from continuous rings for highly damaged surfaces, arcs and spots for slight damage, and sharp spots after the damage was completely etched away. The indexing of the patterns was carried out according to Cho [12]. The intensities of the 220 rings and the 220 spots were estimated using a microdensitometer, so that the ratios of the areas under the profiles could be estimated. These ratios were converted into percentages of polycrystalline material present by relating them to RHEED patterns obtained from calibration samples of single crystals of GaAs with powdered GaAs scattered on the surface.

To achieve this calibration, five samples were prepared with various amounts of very finely powdered gallium arsenide powder, particle size

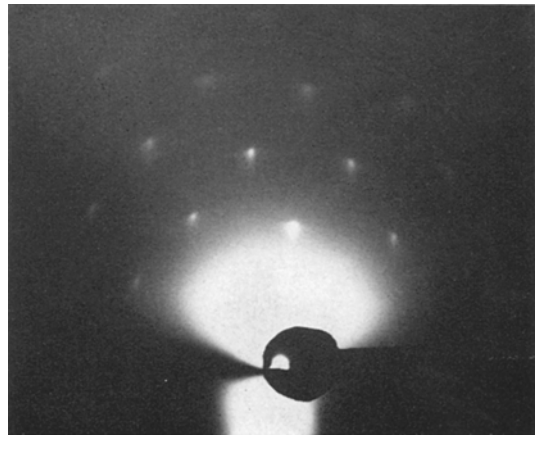


Figure 2 RHEED pattern of GaAs after abrasion with emery paper and removal of a layer 2600 Å thick by etching.

about 200 Å, spread evenly over a gallium arsenide single crystal. A RHEED diffraction pattern and a stereoscan picture were taken from each sample. The proportion of single crystal to polycrystal material in each sample was obtained from the stereoscan pictures, by estimating the powdered crystal areas of the photographs. The ratios of the intensities of the 220 rings and the 220 spots on the RHEED pictures were estimated on a microdensitometer. A calibration curve was then drawn. It was not intended to obtain absolute values of the percentage of polycrystalline material present from this calibration, as the diffraction conditions of powder spread over the surface of a single crystal are different from polycrystalline material formed in the single crystals as the result of damage. However, relative values of the ratio of single to polycrystalline material were obtained for varying amounts of deformation, and small changes could be detected. The general appearance of the calibration RHEED photographs was similar to those obtained by the mechanically damaged and the ion-implanted gallium arsenide crystals, but the calibration results could be expected to be lower than the correct values in damaged crystals because of the possibly greater shielding effect of the powder on the crystal surface as opposed to polycrystalline material actually in the surface. In fact, the single crystal spots were undetectable with 50% powder on the surface, thus indicating a maximum error of about two. This error was assumed to be uniform, thus giving self-consistent relative values.

From the mechanically damaged specimens showing arcs on their RHEED patterns, the dislocation densities were estimated using the method of Sarkar and Towner [13] with their equation:

$$\rho = \theta/t\boldsymbol{b}$$

where ρ = dislocation density; θ = angular arcing of spots; t = crystallite size; $\boldsymbol{b}$ = Burgers vector.

4.2. Ion-implantation damage

Cd^+ and Te^+ ions were implanted into gallium arsenide single crystals at room temperature and the resultant damage was studied using RHEED. The variation of damage with depth in the crystal was examined using similar etching methods to the mechanical damage procedure. The RHEED patterns obtained from the implanted GaAs consisted mainly of broad rings and spots.

Annealing experiments to remove the implantation damage were carried out on GaAs crystals implanted with Te ions at a density of 1.25×10^{14} ions per cm^2, the ion energies being 50 keV and also 150 keV. The heat-treatment was carried out in evacuated tubes in the temperature range 150 to 700° C in steps of 50° C. The annealing time was 15 min.

The specimens were approximately 4 mm × 4 mm × 1 mm in size and the quartz tubes were 7 mm diameter and 10 cm long. They were evacuated to a pressure of 10^{-3} mm mercury. The quartz was Thermal Syndicate of 99.9% purity. For anneals below 500° C 9 mm diameter Pyrex tubes were used, these were from Jobling and Co and were 80.6% silica and 12.6% boric oxide. No differences in behaviour in the specimens with the different annealing tube materials could be detected. The specimens were examined by RHEED after each anneal.

5. Results of the RHEED examination

Fig. 3 shows the effect of various forms of damage on the gallium arsenide single crystals in terms of the fragmentation of the single crystals into a polycrystalline mosaic structure. The depth of such damage is also shown. The dislocation densities as a function of depth are shown in Table II.

TABLE II Dislocation densities at various depths in damaged GaAs single crystals

Method of damaging	Depth (Å)	Dislocation densities ($\times 10^{11}$ cm^{-2})
Emery paper	1 000	14.99
	2 600	9.55
	5 000	6.8
	9 800	6.48
	11 000	3.90
Diamond saw	200	12.99
	400	10.827
	600	7.73
	1 000	5.902
	1 200	3.39
	1 400	3.03
	2 000	3.25
	6 800	1.68
	10 600	1.62

Fig. 4 shows the effect of ion energy on the depth of damage for tellurium ions. The depth of damage for cadmium ions is also shown. The effect of annealing the tellurium implanted

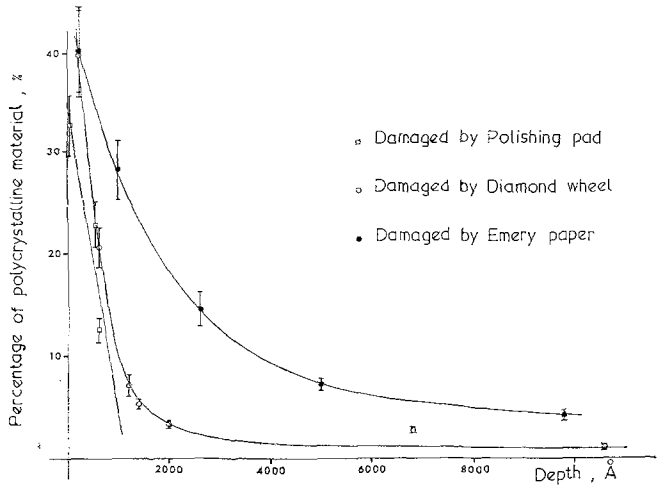


Figure 3 Depth of damage in GaAs crystals produced by various forms of abrasion.

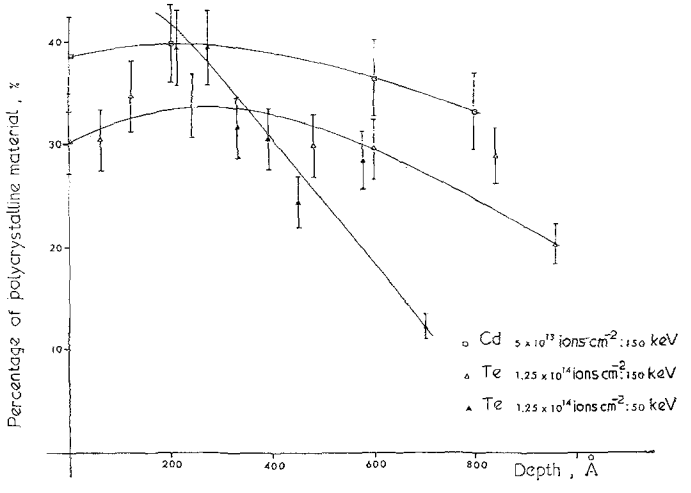


Figure 4 Effect of implantation conditions on damage depth in GaAs crystals.

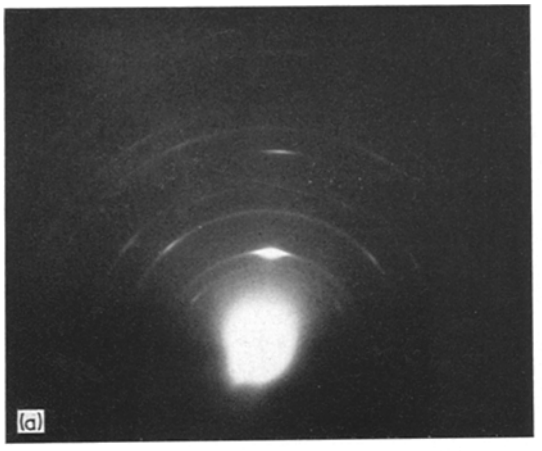
crystal is shown in Table III. A large number of changes occurred in the RHEED patterns exhibited by these crystals on annealing, indicating conditions of great complexity. In general, the highly damaged GaAs crystals gave sharp diffraction rings and spots at 400°C and above (Fig. 5). Arsenic diffused onto the surface up to about 500°C, after which Ga_2Te_3 could be seen. At higher temperatures, arsenic reappeared and another compound identified as β-Ga_2O_3 also appeared. These identifications were made by comparison with the intensities and "*d*" values given in the Powder Diffraction File. Although the File is for X-ray results, reasonable agreement was obtained with the RHEED values in this work (Figs. 6 and 7).

The same annealing process for unimplanted perfect GaAs crystals gave no arsenic on annealing until 400°C, at which temperature GaAs arcs were observed.

Preferred orientation was shown by some crystals annealed at temperatures of 400°C and over. Unimplanted gallium arsenide crystals gave a preferred orientation about the [110] axis, whereas crystals implanted with Te^+ at 50 keV gave orientation about the [100] axis. Crystals implanted with Te^+ at 150 keV showed no preferred orientation on annealing. There seems to be a great field for study in this aspect of the problem alone.

6. Discussion

Interest in the properties of small and highly deformed crystals in such fields as sintering and catalysis has resulted in the production of a



certain amount of information on the behaviour of some materials under conditions of heavy ball-milling and subsequent annealing. A summary of some of this information is given in Table IV.

It may be seen from this tabulation that gallium arsenide, silicon and germanium under annealing behave similarly, although silicon does require rather a high temperature for crystal growth. Values obtained for alumina and tungsten carbide are included, and it would appear that temperatures for the removal of strain and the increase of crystal size on annealing relate to the melting point of the material.

Some work has been carried out on pure

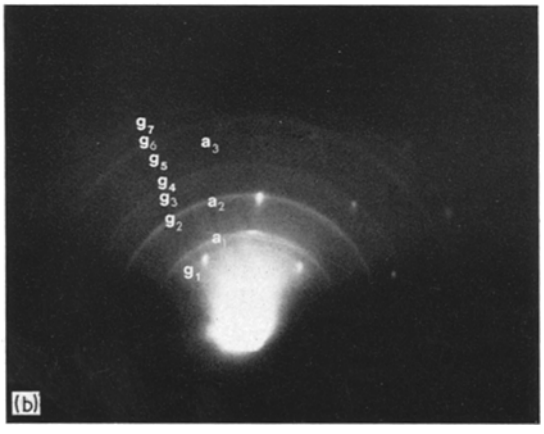


Figure 5 Te implanted GaAs, annealed at 400°C. (a) 50 keV implantation, (b) 150 keV implantation. g = gallium arsenide: $g_1 = (111)$; $g_2 = (220)$; $g_3 = (311)$; $g_4 = (222)$; $g_5 = (400)$; $g_6 = (420)$; $g_7 = (422)$. a = arsenic: $a_1 = (102)$; $a_2 = (014)$; $a_3 = (204)$.

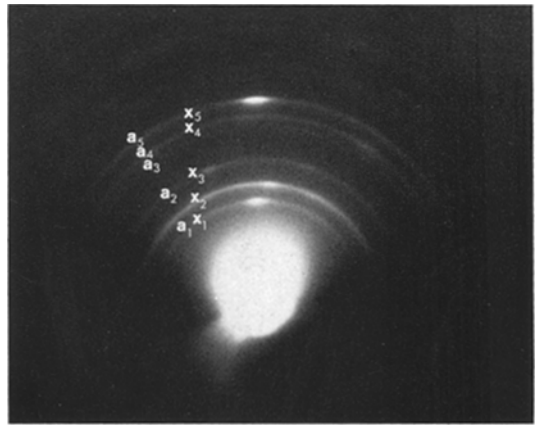


Figure 6 Te implanted GaAs, annealed at 700°C. a = arsenic: $a_1 = (102)$; $a_2 = (014)$; $a_3 = (105, 006)$; $a_4 = (022)$; $a_5 = (204)$. X = β-Ga_2O_3: $X_1 = (10\bar{4}, 200)$; $X_2 = (111, 104, 11\bar{3})$; $X_3 = (10\bar{6}, 006, 211)$; $X_4 = (311, 10\bar{8})$; $X_5 = (12\bar{2}, 215)$.

TABLE III Unimplanted and Te^+ implanted GaAs crystals, after various heat-treatments and examination by RHEED

Annealing temperatures (°C)	Te^+ implanted (50 keV)	Te^+ implanted (150 keV)	Unimplanted single crystal
150–200	Diffuse rings and spots	Diffuse rings and spots	Spot pattern
250	Diffuse rings and spots	Diffuse GaAs rings and spots; sharp strong As arcs	Spot pattern
300–350	Diffuse rings and spots	GaAs spot pattern; faint As rings	Spot pattern
400–450	As and GaAs sharp rings both having preferred orientation (Fig. 5)	As rings, GaAs rings and spot pattern (Fig. 5)	As and GaAs sharp rings both having preferred orientation
500	No change from 400°C	No change from 400°C	Amorphous
550	Ga_2Te_3 present	Ga_2Te_3 present	Faint arcs possibly arsenic and β-Ga_2O_3
600–700	Arsenic with other compound probably β-Ga_2O_3	Arsenic with other compound probably β-Ga_2O_3	Arsenic with other compound probably β-Ga_2O_3

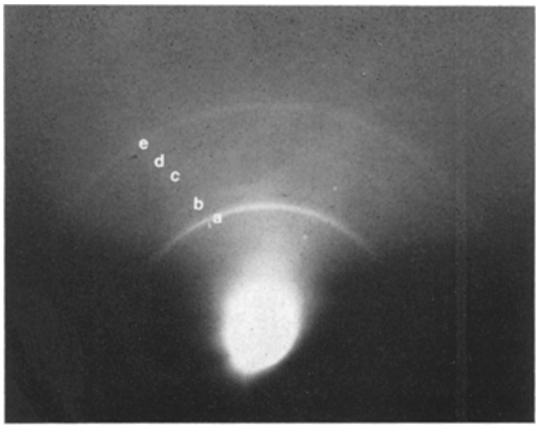


Figure 7 Te implanted GaAs, annealed at 550° C. Ga_2Te_3: a = (220); b = (311); c = (400); d = (311, 420); e = (422).

sintered tungsten carbide to measure the depth of deformation produced by grinding [14] and it is interesting to see that the general micro-strain distribution with depth corresponds quite well with that produced in the gallium arsenide crystals in this work. None of these other materials were affected by decomposition problems on annealing as severely as gallium arsenide.

Values of microstrains obtained from ball-milling can be interpreted in terms of dislocation density, and these results are presented in Table I. Some values for dislocation density for GaAs annealed at 600° C have been obtained by Sealy [15] using electron microscopy, and these are quite similar to the values obtained in this work using X-ray diffraction methods.

The method of estimating dislocation densities developed by Sarkar and Towner [13] using arc spread in electron diffraction was used in this work for surface studies in GaAs single crystals to estimate dislocation densities produced by mechanical working. The results obtained here were similar to those of Sarkar and Towner for ball-milled alumina, but rather higher (2 to 3 times higher). This is not surprising as their method averaged the deformation throughout the body of the particles, they used transmission diffraction on small particles, whereas we have used reflection diffraction on single crystals, which is more responsive to the outer layers of the surfaces. These might be expected to be more deformed than the inner layers.

In Fig. 4 a comparison is made between the damage distribution with depth for gallium arsenide crystals bombarded by tellurium ions with energy of 50 and 150 keV. It will be seen that the damage maximum for the 50 keV ions is very close to the surface, whereas for the 150 keV ions the damage maximum is at a depth of about 300 Å below the surface. These results are in good agreement with the theoretical values of projected range statistics in semi-conductors predicted by Lindhard *et al.* [16] for 50 and 150 keV Te ions in gallium arsenide crystals, where the projected range maxima in the range distribution curves are given as 173 Å for the 50 keV ions, and 400 Å for the 150 keV ions.

The cadmium 150 keV ions show a similar damage-depth distribution curve to the tellurium 150 keV ions. For cadmium ions at 150 keV in gallium arsenide crystals, Lindhard *et al.* predict the projected range maximum at 422 Å. The average level of damage for the cadmium ions was rather more than for the tellurium ions, although the dose rate was lower. This could be due to experimental error, although as it is known that the gallium arsenide crystals become quite warm under the ion bombardment, the higher dose rate will also produce a relatively higher temperature and thus a possibility of more recrystallization.

TABLE IV Annealing characteristics of various materials after ball-milling

	Strain temperature* (°C)	Crystal size temperature† (°C)	Strain‡	Crystal size‡ (Å)	Melting points (°C)
Ge [17]	500	500	4×10^{-3}	400	958
GaAs	300	400	8×10^{-3}	250	1240
Si [17]	650	1100	4×10^{-3}	400	1410
Al_2O_3 [18]	800	1100	6.8×10^{-3}	300	2024
WC [17]	1100	1300	9×10^{-3}	150	2870

*Temperature to relieve strain to half the maximum value.
†Temperature to double the crystal size.
‡Values attained after heavy ball-milling.

7. Conclusions

The process of ion implantation initially involves the cutting, polishing and etching of the gallium arsenide crystals in preparation for the implantation. The diffraction results on mechanical damage show that unless the whole process is conducted with great care, the possibility of some residual damage remaining is quite high. The next stage in the implantation process is the bombardment of the crystals by the ions selected. Judging from the RHEED patterns, and comparing these with RHEED and X-ray diffraction patterns of mechanically damaged crystals, the crystal structure is very severely disturbed by the ion bombardment. The spots become diffuse, and diffuse arcs also appear, indicating that up to half of the single crystal material in the surface has become polycrystalline.

The final stage in the implantation process is the annealing of the implanted crystals to temperatures of over 600° C. The changes in the crystals occurring here are of great complexity and should it prove necessary to obtain a detailed knowledge of all these changes, a very substantial amount of work will be required. In general, the processes occurring on annealing could include some or all of the following depending on the previous implantation treatment:

(1) removal of microstrains;
(2) crystallite growth;
(3) formation of preferred orientation;
(4) decomposition of the GaAs;
(5) diffusing of arsenic to the surface;
(6) formation of Ga_2Te_3, β-Ga_2O_3 and possibly other compounds.

The damage caused by the implantation was far closer to the surface for 50 keV implantation of Te^+ than for the 150 keV implantation. Free arsenic was detected at temperatures as low as 250° C when annealing the 150 keV implanted crystals, which may imply that the higher energy ions break down the GaAs structure more readily than the 50 keV ions. At 400° C the decomposition is probably due to thermal effects.

The various effects of annealing mentioned above depend greatly on the previous damage given to the crystal structure. Many of these effects modify the electrical properties of the implanted crystals. It thus seems that ion implantation and subsequent annealing of GaAs crystals can produce complicated changes in structure and electrical properties. This work, therefore, indicates the great importance of close quality control in the production of ion-implanted crystals, and also shows that RHEED could play a very important role in such control. The surfaces of the implanted materials investigated here were unprotected. Some of the undesirable effects due to annealing could be prevented under proper encapsulation conditions, and much work is also required here to find the best conditions and methods for encapsulation.

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