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1992 J. Phys.: Condens. Matter 4 5825

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A positron annihilation study of defects in cadmium mercury telluride semiconductor

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Received 10 October 1991, in final form 13 April 1992

Abstract. Doppler broadening measurements of the 511 keV positron annihilation line-shape have been carried out to study the nature of vacancy-type defects in samples of cadmium mercury telluride. Results from annealing in the temperature range 300–450 K indicate an unusual, reversible variation with temperature which is attributed to the role of impurities or native defects in the sample. Further annealing (to 570 K) produces an increase in the vacancy concentration due to the formation of a new type of defect. Extensive annealing at this temperature gradually changes the sample to a coral structure of CdTe as Hg and Te are lost from the sample.

1. Introduction

The mixed crystal cadmium mercury telluride, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (CMT) is an important infrared detector material. From the viewpoint of the device physics it is in many respects an ideal substance. By altering x , the mole fraction of CdTe, the forbidden energy gap can be varied continuously from that of the semi-metal HgTe (–0.3 eV at 0 K) to that of CdTe (1.6 eV at 0 K) and within this bandgap range detectors can therefore be tailored for a specified spectral response with optimum performance. Most interest is in detectors operating in the atmospheric windows lying between the spectral wavelengths 8–14 μm and 3–5 μm requiring CMT with x -values around 0.2 and 0.3 respectively. The lower value leads to a very small electron effective mass and a very high electron mobility ($>10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Detectors made from small-bandgap material generally require cooling, usually to liquid nitrogen temperature, to reduce the thermal generation of carriers, but current research is aimed at raising the operating temperature. Both photoconductive and photovoltaic detectors are required—hence the need to make n- and p-type CMT with specified properties.

From the materials aspect, CMT is a very difficult substance to prepare with the necessary degree of uniformity in composition and electrical properties, especially when relatively large areas are required for the fabrication of detector arrays. In recent years improvements in the defect structure have resulted from the lower temperatures associated with the epitaxial growth techniques (liquid and vapour phase) which have, to a large extent, replaced bulk growth. However, since CMT is a defect semiconductor, native defects play a large part in determining the electrical properties. As-grown CMT usually has a fairly high concentration of mercury vacancies which

act as acceptors. Post-growth annealing is used to alter the concentration to give the hole concentrations required for a particular detector. At sufficiently low levels the material becomes n-type as residual donor impurities become dominant. Current research is aimed at producing the 'p' and 'n' regions of the photovoltaic detectors by incorporating dopants during growth. However, complex reactions between dopants or impurities with native defects may be detrimental to device performance. Point defects in CMT have not been extensively studied due to lack of suitable techniques. Most of the methods used with wide-bandgap materials cannot be applied for one reason or another. Carrier lifetimes are too short for EPR and photoluminescence although the latter has been used with higher- x -value CMT (Lusson *et al* 1990, Werner *et al* 1990) and the small bandgap prevents the attainment of good Schottky barriers which would be required for DLTS to be used. Some progress has been made with radiotracer diffusion (Chen 1985, Archer *et al* 1991) but most of the information has been inferred from electrical properties determined from measurements of the Hall effect. Positron annihilation spectroscopy offers a possible means of complementing the electrical measurements with direct determination of the concentration of certain defect species.

2. Positrons in semiconductors

The use of positrons as probes for studying lattice defects in semiconductors is a powerful technique which is sensitive to relatively low concentrations. Energetic positrons from radioactive sources rapidly slow down in solids to thermal velocities, then diffuse and after a period typically 200–400 ps eventually annihilate and emit gamma rays in the process. Lattice defects, especially open-volume defects such as negatively charged vacancies, are potential wells, which are liable to trap a fraction of the positrons prior to annihilation. The trapping probabilities are governed by the density of electrons experienced by the positron, and this will vary according to its circumstances: positrons trapped in vacancies will encounter a lower electron density than those free in the lattice and hence will have a longer lifetime. The early work on positron trapping in semiconductors was done with lifetime measurements, by Dannefaer *et al* (1976) on silicon, and by Dannefaer (1982) on gallium arsenide. In such studies the time taken from the birth to the eventual annihilation of each positron is recorded and the statistical distribution plotted. Each distribution is an exponential and can be characterized by a mean lifetime that reflects the constant probability of annihilation for a particular defect and gives an indication of its concentration.

So far, only a few studies have been made on II–VI semiconductors. Krause *et al* (1990) found with lifetime measurements in $\text{Cd}_{0.22}\text{Hg}_{0.78}\text{Te}$ that they could observe mercury vacancies ($\text{V}_{\text{Hg}}^{2-}$) in the concentration range between 10^{15} and 10^{18} cm^{-3} . After a sequence of post-growth annealings, with estimates of concentrations of defects based on thermodynamical equations and comparisons with Hall effect measurements, their positron measurements led to an estimate for the specific positron trapping rate $\mu_{\text{V}}^{\text{Hg}}$ of $(6 \pm 0.5) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \equiv (9.0 \pm 1.0) \times 10^{14} \text{ s}^{-1}$ where the bulk lifetime $\tau_{\text{b}} = 264 \pm 1 \text{ ps}$. In another study, the Beijing group (He *et al* 1989) found a value of $(5 \pm 1) \times 10^{14} \text{ s}^{-1}$ for the specific trapping rate for $\text{V}_{\text{Hg}}^{2-}$.

3. Experimentation with Doppler broadening

An alternative approach to investigating defects is to exploit the Doppler broadening

of the 511 keV photons arising from the motion of the electron participating in the annihilation. This is a well established technique for defects in metals (see, e.g., Hautojärvi 1979, Rice-Evans *et al* 1978). Positrons trapped in vacancies are more likely to couple with an outer rather than a core electron and these will narrow the observed distributions. For a particular defect the broadening will vary in a characteristic way with the defect concentration and hence may be used as an indication of the change in the concentration. By varying the temperature of a material the defect concentration can be altered as can the type of dominant defect. Positron annihilation offers the potential to monitor the evolution of such changes in semiconductors.

In this study of CMT a 20 μCi ^{22}Na positron source was used; this precluded the use of epitaxial material (typically $\simeq 10 \mu\text{m}$ thickness) since positrons produced by the source penetrate a mean distance of $\simeq 300 \mu\text{m}$ into this material. Recourse was made to slices cut from bulk material grown by the cast-recrystallize-anneal (CRA) process (Vere *et al* 1982) with an x -value of 0.22 corresponding to a bandgap of 0.19 eV at 300 K. The starting materials were Cominco quadruply zoned Cd and Td and 7N purity Hg. The major impurities found by spark source mass spectroscopy in samples similar to that from which the slices used in this study were cut were Li at around 3×10^{15} atoms cm^{-3} and Na at 4×10^{15} – 2×10^{16} atoms cm^{-3} . Our as-grown material is p-type with a hole concentration of $\simeq 2 \times 10^{17}$ cm^{-3} and a mobility of $280 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. It is interesting to note that after an isothermal anneal at 250 °C in Hg vapour the material converts to n-type with an electron concentration which is typically mid 10^{14} cm^{-3} and a mobility of $1.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The slices were cut with a reciprocating blade and carborundum polished with Linde A alumina and then etched in a 2% solution of Br in methanol to remove work damage caused by cutting and polishing.

The positron source was contained between two leaves of Al foil 3 μm thick and sandwiched between two slices of CMT ($8 \times 6 \times 0.6 \text{ mm}^3$). Two experiments were undertaken, each requiring its own sample structure which was positioned in a continuously evacuated furnace. In the first experiment the sample was heated in steps from ambient to 460 K and then cooled in a similar way. The sample was then reheated in steps from ambient to 590 K which resulted in some degradation. The behaviour at the lower end of the temperature range was studied in the second experiment using a fresh sample. The temperature was again changed in steps and cycled with the maximum temperature in each cycle being successively increased from 418 K to 550 K by approximately 20 K per cycle with a total of six cycles. In both experiments at each stabilized temperature a spectrum was accumulated over a period of one hour using a germanium detector of resolution 1.1 keV at 514 keV. Rather than conduct a separation of each photopeak into its components we have used the conventional line-height parameter S , changes in which will indicate linearly the variations in the numbers of positrons being trapped. S is defined as the ratio of the counts in the central fifteen channels to the counts in the whole line (40 channels) after background subtraction (Chaglar *et al* 1981).

4. Results

Figure 1, curve A shows the response of the as-grown sample as the temperature is raised from 300 K to 460 K. The S -parameter remains constant to about 380 K suggesting no changes in the defect concentration, a specific trapping rate for positrons

that is independent of temperature, and traps that are relatively deep. Above 380 K, the declining value of S , shown in broadening of the photopeak, indicates a reduction in the number of traps.

However, taking the sample down from 460 K back to 300 K results in the curve seen in the lower part of figure 1, curve B: its negative slope is most unusual as is the fact that it is reversible.

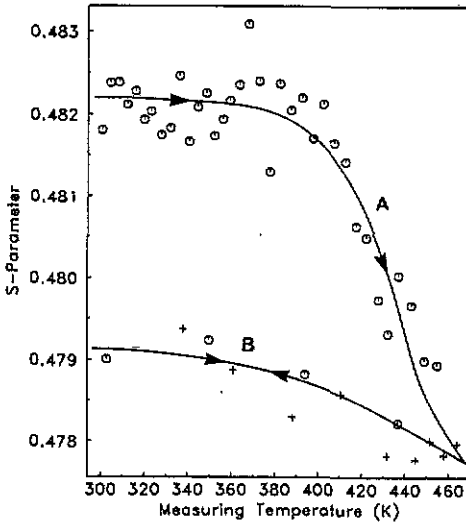


Figure 1. The effect on the Doppler S -parameter of raising the original CMT crystal temperature from 300 to 460 K, and the subsequent values as the temperature was cycled back to 300 K and back up to 460 K again.

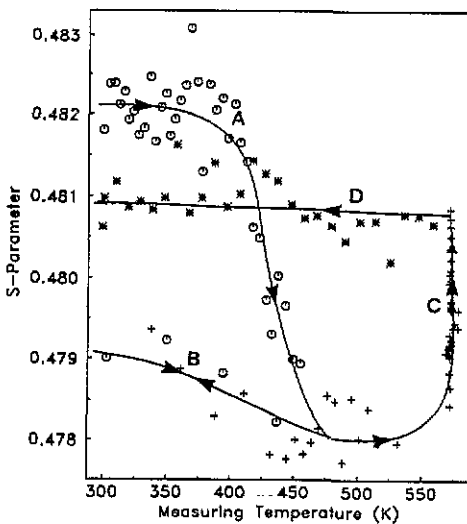


Figure 2. The effect of raising the temperature further (460–570 K), annealing at 570 K for 56 hours, and then subsequently reducing the temperature to 300 K.

Figure 2, curve C shows the results of raising the temperature to 570 K. Up to 530 K the annealed sample initially holds a steady value of S at about 0.478 indicating little change in the CMT. At the highest temperatures S rises slowly (each point corresponds to one hour) indicating the creation of new traps. After about 56 hours, the sample was measured as it was taken back to 300 K, curve D. The flat curve ($S \approx 0.481$) supports the assumption of the temperature independence of the trapping rate.

The study of the transition region, curve A in figures 1 and 2, by taking a similar sample through a number of temperature cycles is shown in figure 3. By using the two-state trapping model (West 1973) the vacancy concentration C_V can be determined from the S -parameter:

$$C_V = (\lambda_b/\mu)(S - S_b)/(S_V - S)$$

and, adopting the values of Krause *et al*, we have

$$C_V = 6.21 \times 10^{16}(S - S_b)/(S_V - S).$$

Taking the original vacancy concentration for the as-grown sample as $1.0 \times 10^{17} \text{ cm}^{-3}$, where $S = 0.4822$, and the expected concentration of $2.5 \times 10^{15} \text{ cm}^{-3}$ at 475 K where $S = 0.478$, we obtain values of S_b and S_V and hence the relation for the vacancy concentration at any temperature in the range 300–500 K:

$$C_V = 6.21 \times 10^{16}(S - 0.477)/(0.485 - S).$$

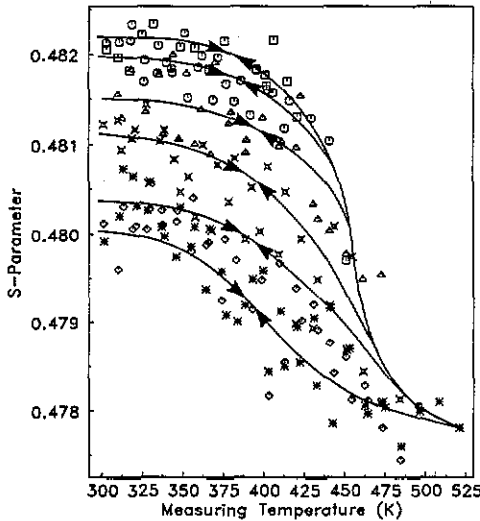


Figure 3. A second identical CMT sample showing the variation of the S -parameter for the temperature cycles (300–400–300–420–300–440–300–460–300–490–300–510–300–550–300 K). The lines are drawn as a guide to the eye only.

In obtaining this relation we have taken the hole concentrations at 475 K from Destéfani *et al* (1987) and assumed the vacancies to be doubly ionized. Using this expression the information can be replotted in terms of the vacancy concentration and this is demonstrated in figure 4 where two of the cycles from figure 3 are shown.

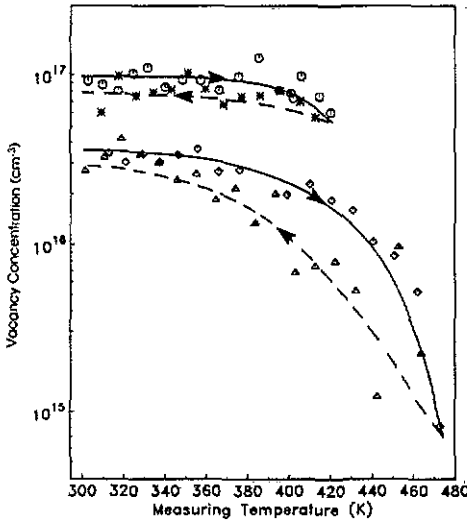


Figure 4. The defect concentration derived from the S -parameter for the cycles 300–400–300 K, and 300–490–300–K in figure 3 (solid lines: as the temperature is raised in each case; dotted lines: as the temperature is reduced).

5. Discussion

Originally, the samples of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ are expected to have had a hole concentration of $2 \times 10^{17} \text{ cm}^{-3}$, which currently is believed to be due to Hg vacancies that have been 'frozen-in' during growth; hence in this explanation the material is not in equilibrium. In figure 1 it is thus tempting to interpret the decline in S as an indication that the vacancies become mobile at about 380 K and anneal out by migrating to sub-grain boundaries or the like where they are annihilated. However, the cyclic behaviour in figures 3 and 4 is inconsistent with this explanation. The cycles are repeatable and reversible. In metal physics, reversible negative slopes are rare, and are often hypothesized to correspond with detrapping of positrons from shallow traps as temperatures are raised (Smedskjaer 1980). However, in the present case, the fact that negative slopes are seen in figure 3 long before the deep traps have annealed out casts doubts on this interpretation—the deep traps would dominate and merely cause flat 'go back' lines.

Vacancies in semiconductors, unlike metal vacancies, can exist in one of several charge states. Elizarov *et al* (1990) have shown that at low temperatures the vacancies are singly ionized, but they become doubly ionized above 200 K. This contradicts the findings of Vydyanath (1981) who concluded that mercury vacancies are doubly ionized in the range 77–300 K, but it is possible that the latter study related to too high a dopant level. It is interesting to note that Corbel *et al* (1988) have observed a reduction in the positron trapping in arsenic vacancies for gallium arsenide due to the transition from V_{As}^{2-} at 100 K to V_{As}^{-} at 200 K. However, according to both Elizarov and Vydyanath at 300 K the mercury vacancies in CMT are in the V_{Hg}^{2-} state, and it therefore seems unlikely that the observed temperature dependence in figure 3 is due to the change in the ionization state.

Puska *et al* (1990) have discussed the influence of temperature on the positron trapping rates of negatively charged vacancies in semiconductors. They predicted

a $T^{-1/2}$ dependence. However, we are not aware of any evidence to support this model; our own Doppler results with identical as-grown material indicate a constant trapping rate between 77 and 300 K (Smith *et al* 1992b), and Gély *et al* (1990) find a similar flat response with positron lifetime measurements between 15 and 300 K. In any event, the magnitudes of the negative slopes between 300 and 500 K in figure 3 exceed the $T^{-1/2}$ dependence by a factor of about 5. We therefore prefer to advance another hypothesis.

It can be seen that in each cycle the vacancy concentration falls as the temperature is raised, then increases above the lowest value as the temperature falls and, when back at ambient temperature, exhibits a value slightly less than at the start of the cycle. If the positrons are indeed annihilating at Hg vacancies—as we have good reason to believe because of the correlation found with measured hole concentrations (Krause *et al* 1990, Smith *et al* 1992a)—then this quasi-reversibility must imply that the core of the sample is close to thermodynamic equilibrium. This being so, the Hg vacancy concentration cannot be ‘frozen-in’ but must be controlled by another point defect such as an impurity or native defect that is relatively immobile.

It is suggested that as the temperature is raised it becomes energetically favourable for the controlling defect to switch to a new atomic site. This could be a Na atom, initially on a Hg site, moving to an interstitial position. In this new configuration the Hg vacancy concentration rapidly adjusts to comply with the prevailing charge neutrality condition by falling in value, and when the temperature is reduced it should return equally rapidly to its original value. However, the core of the sample cannot be regarded as a completely isolated system, hence while in the high-temperature state the controlling defect can diffuse to a region that acts as a sink, and it will effectively be removed from the system. Examples of such sinks are Te precipitates which are present in bulk-grown CMT (Williams 1986) and are known (in CdTe) to getter many impurities (Pautrat *et al* 1982) and also the surfaces of slices that accumulate impurities such as the more mobile alkali metals Li, Na (Astles *et al* 1988, Blackmore *et al* 1990) and Cu (Jin *et al* 1990). Should the controlling centre be a native defect (e.g. a Te antisite), then presumably this can similarly be removed. This loss from the system means that the Hg concentration cannot return to its original value but must always be less than at the start of a cycle unless new types of defect-controlling centres are created. The process will continue until the vacancy level falls to a value determined by non-mobile controlling defects or the equilibrium value that would pertain in their absence.

As the maximum temperature experienced in a cycle increases above 530 K there is a slight increase in the defect concentration on cooling back to ambient. Again this is reversible and the increase continues in each succeeding cycle. This could be due to the creation of another type of defect which may not be mobile and is possibly shown in an advanced state of development in figure 2, curve D. The observed reliability would thus be related to the continuing decay of the original defect (Hg vacancy) concentration.

For the lower maximum temperature cycles the difference in Hg vacancy concentration between the start and end of a cycle is in good agreement with what would be predicted using the empirical equations of Destéfani (1987) (taking into account the time spent at each temperature), given by

$$(P - P_t)/(P_0 - P_t) = \exp[-10^6 t \exp(-1.0/kT)]$$

where P_0 and P are the acceptor concentrations at $t = 0$ and t respectively, and P_t

is the equilibrium acceptor concentration at temperature T , given by

$$P_f = 1.07 \times 10^{21} \exp(-0.5/kT) \text{ cm}^{-3}.$$

However, for the cycles with higher maximum temperatures the difference is not as large as predicted due to the counter-effect of newly created defects. As an example, applying the Destéfani's equations to cycle 5, figure 4, where initially the defect concentration is $5 \times 10^{16} \text{ cm}^{-3}$ and the temperature changes in 8 K increments from 305 K to 489 K and then returns, dwelling at each temperature for 1 hour, the integrated difference in concentration is $3 \times 10^{16} \text{ cm}^{-3}$ but a difference of about $1 \times 10^{16} \text{ cm}^{-3}$ is all that is observed indicating the generation of $2 \times 10^{16} \text{ cm}^{-3}$ new defects.

The concept of point defect centres controlling the low-temperature Hg vacancy concentration can be used to explain the discrepancy between the low-temperature hole concentration and the vacancy concentration at elevated temperatures (670–870 K) determined by a mass-loss method (Wiederman and Gao Sha 1990). Wiederman and Y measured vacancy concentrations two to three orders of magnitude greater than the low-temperature hole concentrations. He argues that at low temperatures only a fraction of the vacancies are measured electrically because a preponderance of them are neutral and there is a high degree of self-compensation. However, since both Elizarov and Vydyanath agree that Hg vacancies are fully ionized above 200 K the high concentrations observed by Wiederman would be revealed by room temperature (300 K) Hall measurements. An alternative explanation is that the number of controlling centres present is very much less than is needed to retain the high vacancy concentrations found at elevated temperatures. The excess vacancies quickly migrate to suitable sinks and disappear from the system, leaving only those associated with controlling centres.

Large hole concentrations have, however, been measured in bulk ($> 10^{18} \text{ cm}^{-3}$, $x = 0.2$, Vydyanath (1989) and $> 2.5 \times 10^{17} \text{ cm}^{-3}$, $x = 0.4$ Schmit and Stelzer (1978) and LPE ($> 10^{18} \text{ cm}^{-3}$, $x = 0.2$, Vydyanath (1989) CMT after high-temperature annealing (773–873 K) in a mercury atmosphere followed by quenching. Further work is required on similarly prepared material to ascertain whether these acceptor-like defects behave in the same way as those that arise during growth.

The effect of further heating is shown in figure 2 where little effect is observed until 560 K is reached, and successive measurements at 570 K reveal a slow increase in the amount of positron trapping up to an S -parameter of 0.481 after 56 hours. This increase can be explained by the results of Farrow *et al* (1979), who have shown that significant quantities of mercury are lost above 363 K, which leaves tellurium-rich material. Above 593 K both Hg and Te diffuse out at equal rates until the HgTe component is depleted and hence tellurium-rich CdTe remains. Micrographs taken by Farrow *et al* show that at these high temperatures in vacuum a porous surface layer of tellurium-rich CdTe develops which grows with time, and it is this development that is being recorded by the S -parameter. The final reduction in temperature in figure 2, curve D, yielding a flat response in S , suggests a fixed concentration of deep traps.

6. Conclusions

The reversible behaviour of the S -parameter with temperature for temperatures less than 500 K is taken to indicate that the system is close to thermodynamic equilibrium.

As a consequence it is suggested that the mercury vacancy concentration is not 'frozen-in' but is controlled by some other defect, which may be a native defect or a mobile impurity such as sodium. Hence high mercury vacancy concentrations at low temperatures will be determined by the number of controlling centres. As the number of these centres diminishes as a result of diffusion to sinks during heat treatment, so the low-temperature vacancy concentration will similarly decrease.

In the region 590 K the defect concentration increases with time and does not alter on cooling. This can be taken as evidence of the creation of a different type of defect whose onset may occur at a lower temperature around 530 K. Prolonged heating at 590 K alters the structure of the material and a coral layer of CdTe slowly grows from the surface (Farrow *et al* 1979).

Acknowledgments

The authors thank the Science and Engineering Research Council and the DRA (Electronics Division), RSRE Malvern, for their support of this work.

References

- Archer N A, Palfrey H D and Willoughby A F W 1991 *Proc. II-VI Conf. (Japan)*
- Astles M G, Hill H, Blackmore G, Courtney S and Shaw N 1988 *J. Cryst. Growth* **91** 1-10
- Blackmore G W, Courtney S J, Astles M G and Shaw N 1990 *Surf. Interface Analysis* **15** 617-20
- Chaglar I, Rice-Evans P C, El Khangi F A R and Berry A A 1981 *Nucl. Instrum. Methods* **187** 581
- Chen J S 1985 *PhD Dissertation* University of Southern California
- Corbel C, Stucky M, Hautojärvi P, Saarinen K and Moser P 1988 *Phys. Rev. B* **38** 8192
- Dannefaer S 1982 *J. Phys. C: Solid State Phys.* **15** 999
- Dannefaer S, Dean G W, Kerr D P and Hogg B G 1976 *Phys. Rev. B* **14** 2709
- Destéfánis G L 1988 *Proc. II-VI Conf. (1987) J. Cryst. Growth* **86** 1-4
- Elizarov A L, Bogoboyashchii V V and Berchenko N N 1990 *Sov. Phys.-Semicond.* **24** 3
- Farrow R F C, Jones J R, Williams G M, Sullivan P W, Boyle W J O and Wotherspoon J T M 1979 *J. Phys. D: Appl. Phys.* **12** L117
- Gély C, Corbel C and Triboulet R J 1990 *J. Phys.: Condens. Matter* **2** 4763
- Gough J S and Mullin J B 1982 *Proc. II-IV Conf. (1982); J. Cryst. Growth* **59** 121-9
- Hautojärvi P (ed) 1979 *Positrons in Solids* (Berlin: Springer)
- He Y J, Li X F, Li L H, Yu W Z and Xiao J R 1989 *J. Phys.: Condens. Matter* **1** SA91
- Jin M H, James K M, Jones C E and Merz J L 1990 *Mater. Res. Soc. Symp. Proc.* **161** 45-50
- Krause R, Klimakow A, Kiessling F M, Polity A, Gille P and Schenk M 1990 *J. Cryst. Growth* **101** 512
- Lusson A, Fuchs F and Marfaing Y 1990 *Proc. II-VI Conf. (1989); J. Cryst. Growth* **101** 673-7
- Pautrat J L, Magnea N and Faurie J P 1982 *J. Appl. Phys.* **53** 8668-77
- Puska *et al* 1990 *Phys. Rev. B* **41** 9980
- Rice-Evans P, Chaglar I and El Khangi F A R 1978 *Phil. Mag.* **A 38** 543
- Schmit J L and Stelzer E L 1978 *J. Electron. Mater.* **7** 65
- Smedskjaer L C, Manninen M and Fluss M 1980 *J. Phys. F: Met. Phys.* **10** 2237
- Smith C, Rice-Evans P C, Shaw N and Smith D L 1992(a) to be published
- 1992(b) unpublished
- Vere A W, Straughan B W, Williams D J, Shaw N, Royle A, Gough J S and Mullin J B 1982 *Proc. II-VI Conf. (1982); J. Cryst. Growth* **59** 121-9
- Vydyanath H R 1981 *J. Electrochem. Soc.* **128** 2609
- 1989 *J. Appl. Phys.* **65** 3080-8
- Werner L, Tomm J-W, Tilgner J and Hermann, 1990 *Proc. II-VI Conf. (1989); J. Cryst. Growth* **101** 787-91

West R N 1973 *Adv. Phys.* **22** 263

Wiedemeier H and Gao Sha Y 1990 *J. Electron. Mater.* **19** 761-71

Williams D J 1986 *PhD Thesis* University of Birmingham