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Review
Problems in optoelectronic semiconductors

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Some of the current problems of optoelectronic semiconductors are reviewed by selecting compounds which typify materials at different stages of development. Even relatively well established materials present obstacles to a proper understanding of material growth. Their solution will aid the progress of more complex compounds. Most of the understood properties of the materials are covered in this review via references to representative publications in the literature.

1. Introduction

Problems associated with new materials have always been with us. With the passage of time, as newer materials are devised to overcome the shortcomings of others, the difficulties seem to multiply. In addition, materials growers are faced, nowadays more than ever before, with problems which are not only chemical or physical. A decision to initiate a growth programme for any particular material represents the culmination of a period of research into feasibility, techniques, effectiveness and even motives. For the pressures to grow or not to grow are not derived solely from scientific considerations.

Attitudes to materials can be assigned broadly to three schools of thought. These are that current materials are adequate for the purposes originally envisaged for them, they are not yet adequate but by a form of research by attrition they may be forced to an acceptable level of performance, or that they form a short term solution awaiting the advent of radically new materials. The position adopted by any one individual naturally depends on the problems he faces. He will have to have due regard for financial pressures which may militate against embarking on a long programme of research, pointing to investments of time and money on some material which has not come up to expectations, rightly or wrongly.

In the semiconductor field, more familiar to this author, silicon, germanium, gallium phosphide and to some extent gallium arsenide are materials which have benefited greatly from a period of history which has allowed thorough and painstaking programmes of research to provide solid understanding of material behaviour. This has had its due reward. The current foreshortening of the time scale between conception and useful application now demanded of materials has caused the rejection of some of the newer materials, some might say prematurely. The need to project the properties of materials yet to be researched is greater than ever before.

To attempt a review of the whole field of optoelectronic materials would be daunting indeed. The world of semiconductors alone is vast. Having regard to reviews already available [1-7] it would seem preferable to take a selective look at some of the newer materials as well as the problems of some of the more established ones. The book by Bergh and Dean in particular [2] discusses in great detail the properties of light emitting diode materials. In the present review, emphasis will be placed on the difficulties associated with a material rather than presenting a catalogue of its understood properties, which will be covered only by references to the literature.

The topics covered in this review are divided into two general areas. The first part serves as an introduction to the modes of preparation and crystal structure characteristic of the materials, which in the end limit the quality of the final product. It does not pretend to be exhaustive, yet it does point to the origins of some of the problems encountered with the materials when they are put to use. It deals largely in general principles, avoiding specific details, leaving a number of these to be covered by way of example in the second part (beginning at Section 4), a succession of sections dealing with progressively more difficult materials. By discussing a cross section of the problems and the ways they are investigated it is hoped to convey an idea of the general considerations which apply when researching a new material.

Luminescence measurements receive a deal of attention not only because of the wealth of information available (if only it could all be analysed) but also because it can readily distinguish between different defects (e.g. zinc or calcium centres) rather than merely between different kinds of defect (e.g. donors or acceptors) and that with relatively low cost, rapid turnover and non-destructive handling. Quite a large amount of what is said concerning the defect or impurity content of optoelectronic materials at the present time is backed by results of optical experiments, included in which are the hybrid optoelectrical experiments of photoconductivity and photocapacitance with again a high resolution of energy levels. This is not to deny the existence of other analytic techniques which are particularly useful for locating defects which are neither optically nor electrically active (e.g. mass spectrography) or for investigating the nature of surfaces, for which where is a whole range of experimental machinery, some of it highly commercially developed.

Following the sections on structures and growth techniques is a section on gallium arsenide, representing a class of materials which has been relatively long established. There is still a real need for a proper understanding of the growth of this material, a problem which may yield to the development of new analytical techniques, which will find application in the cases of a whole range of materials, new and old. One section deals with the III-V alloys, principally indium gallium phosphide, representing a group of compounds which have enjoyed a deal of investment of time and money, but not always realizing their full potential. Finally, some of the very problematical compounds are discussed, from silicon carbide through gallium nitride to the ternary compounds, all united by a common lack of understanding of their optical properties particularly with regard to the impurities they contain and sometimes even of the salient features of their intrinsic band structure.

2. Structure

The semiconductors covered in this review are tetrahedrally co-ordinated [8, 9] and normally crystallize in either the wurtzite or the zinc blende form. The wurtzite form of a binary compound is readily visualized as a hexagonally close packed lattice of one component, (more strictly a basic group – see Fig. 1) with the other component occupying a similar lattice, displaced perpendicularly to the basal plane to occupy tetrahedral interstitial sites of the former. There appears to be an instability associated with this kind of lattice which causes a small distortion along one of the four equivalent trigonal axes to give a unique *c*-axis.

Viewed along the *c*-axis, the wurtzite lattice reveals a hexagonal-like structure, rather similar to graphite, except that atomic identities alternate around the hexagon rings and also vertically in depth through the crystal. If one could "clip" the vertical bonds of the lattice (Fig. 1) and allow the atoms to relax into the nearest basal plane delineated by atoms of the other type, the boron nitride (layer) structure would result. From this point of view, the real (distorted) so-called wurtzite structures are really intermediate between the true wurtzite and boron nitride lattices.

Whereas the stacking sequence of the wurtzite lattice is abab . . . that for the zinc blende (sphalerite) structure, regarded as hexagonal, is abcabc . . . (Fig. 2). It is more usual to regard the zinc blende structure as cubic however, since the four equivalent trigonal axes are, in fact, the diagonals of a cubic unit cell. The atoms of one component occupy the lattice of a face-centred cubic structure with those of the other component lying on the sites of an identical lattice shifted one quarter of the way along the cube diagonal [8]. Both lattices together, carrying the same kind of atom, constitute the diamond structure. An interesting feature of both of these structures is that a slab of crystal cut perpendicular to the trigonal axis will have front and rear surfaces exposing atomic layers of opposite kinds of atom.

Apart from details of growth technique, the considerations which determine whether the wurtzite or zinc blende form appears were first stated by Mooser and Pearson [10]. The empirically most important parameters appear to be the mean principal quantum number (n) of the valence electrons of the constituent atoms and their electronegativity difference (x). As xn

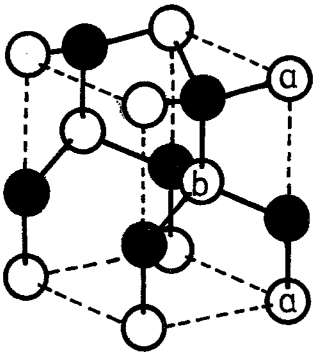

Figure 1 Part of the wurtzite structure. The basal unit is a 60° rhombus. The outlines of the unit cell are shown dotted. The letters a, b indicate the stacking.

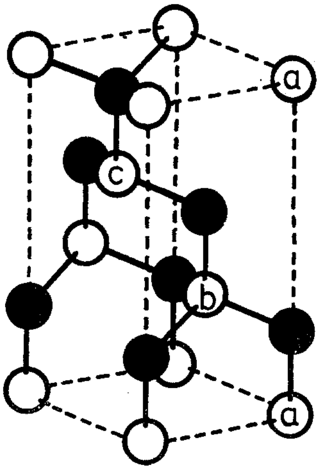

Figure 2 Part of the zinc blende structure, viewed hexagonally for comparison with Fig. 1.

increases the bonds lose their directionality. For $xn < 3$ the structure tends to be zinc blende (with some exceptions). For $3 > xn > 4.5$ both wurtzite and zinc blende forms are found, with an increasing tendency to wurtzite and even a common salt structure for $x > 1.2$. A rationalization of these properties, particularly the change of co-ordination number, is given in the recent book by Phillips [7].

The shift towards the wide band gap octahedrally co-ordinated compounds is accompanied by an increasing tendency to form native defects. This has a profound effect on the development of the materials industry, particularly where specific conductivity levels and types are required. We shall return to this aspect later.

Even in the most well behaved of these compounds one must guard against the perils of polytypism – the ability of tetrahedrally co-ordinated compounds to grow with regular stacking sequences of different patterns. The zinc blende and wurtzite structure may be regarded as different polytypes. Silicon carbide provides the prime example of this property, but even zinc sulphide, the archetypal zinc blende compound has been observed in forms with stacking sequences up to 263 layers deep [11].

Continuing the progression from diamond to zinc blende by dividing the occupancy of one of the component sites equally between two elements of different valency we reach the chalcopyrite ($CuFeS_2$) structure. The division may be orderly, as in $CuFeS_2$, or random as in $MgGeP_2$. The disorder in the latter case allows the unit cell to be identical to that of zinc blende. Corresponding wurtzite forms also exist, e.g. $BeSiN_2$ (ordered) and $AgInS_2$ (disordered). Clearly, new compounds may be imagined on an ever increasing scale of complexity [8], generally reflected in a rapidly decreasing understanding of their properties and methods of preparation to an acceptable standard.

Where the division of occupancy of a lattice site is between elements belonging to the same group of the periodic table, there results the ternary alloy, a boon to the band structure engineer who refuses to be tied to the properties of the rational compounds. Interestingly enough, alloys of the group IV elements, such as (SiGe) [7, 12], have not attracted anywhere near the same amount of attention as the III-V alloys. Of course the number of possible varieties is far smaller and it does not need many objections on the grounds of properties or growth problems to rule out the whole series. The proportion of III-V alloys which have found themselves a useful role in society is indeed small.

3. Growth

In the life of a specimen of material it is at the growth stage where the problems are in-built. The two things which militate against the production of a pure and perfect crystal are impurity incorporation and non-stoichiometry. Dislocations and stacking faults can still present problems, but many crystal growers, even of the "well established" gallium arsenide system, would give much to understand the processes controlling the first two, let alone control them.

Such is the scale of the problem even in the simplest systems.

Apart from cases like indium atimonide, germanium and silicon, much of the best material is produced by epitaxy. The crystal is built up progressively by deposition on an appropriate surface which provides an atomic bonding base of the proper periodicity and symmetry. Provision of such a surface is not a trivial matter. Uncontaminated free surfaces with atomic arrangements characteristic of the bulk material are the exception rather than the rule and special arrangements must be made to clean the surface immediately prior to growth. Even epitaxial growth of a material onto a substrate of the same compound can be fraught with difficulties apart from that mentioned above. The whole point of growing epitaxial material is to produce high purity, low dislocation count crystals often perforce on relatively poor quality substrates. The presence of significant quantities of impurities and defects can change the lattice parameter and present a lattice mismatch to the purer material. This leads to strains which may or may not be relieved by dislocations, and impurity and other defect problems at the interface.

The success of an epitaxial technique depends, amongst other considerations on the extent to which such interface problems propagate themselves into the growing layer. Devices which require the passage of carriers across such interfaces can be subject to unacceptable varying production problems. When the substrate is not of the same composition as the layer, the situation is frequently disastrous, as will be seen in the discussion of specific materials below.

Nevertheless, the advantages of epitaxy are manifold. Growth temperatures are well below the material melting point, which reduces reactivity of surrounding surfaces and in general reduces concentrations of vacancies. Epitaxial growth may be from the liquid [13, 14] (liquid phase epitaxy) or from the vapour [15-17] (vapour phase epitaxy). Both of these methods have received considerable attention in the literature [18] and it is not proposed to discuss them again in detail here. It is worthwhile pointing out, however, that the growth environments in the two cases differ considerably. In the liquid phase, for example in the case of gallium arsenide grown from gallium solution, there is a vast preponderance of the group III constituent whereas the reverse tends to apply in the vapour phase method. The kinetics of impurity and vacancy incorporation thus differ markedly and this is reflected in the optical properties of the resulting material [19].

Where larger volumes of crystal are required, there is a variety of established bulk growth procedures available, again widely discussed in the literature. The highly developed Czochralski ("pulling") technique [20] involves growth by solidification at the melting point as a seed crystal is slowly withdrawn from the melt. Very great problems relating to structural uniformity and dislocations have yielded to intensive research. Naturally, in common with all other high temperature procedures, the necessity to grow at the melting point of the material greatly increases the vapour pressures of the constituents and the equilibrium concentrations of native defects in the crystals. The reactivity of the materials in the growth equipment is increased, leading to higher impurity levels. This and the problem of volatility have been met partly by the liquid encapsulation technique [21]. In the case of gallium arsenide, as with several other III-V compounds, a liquid layer of boric oxide is floated on top of the melt in the presence of an inert atmosphere at the appropriate pressure. This effectively prevents the loss of arsenic, removing the need to keep the whole of the growth equipment at a high temperature. Naturally, such a procedure does not improve the resultant material purity against boron or oxygen content.

Another melt growth technique which may be mentioned is the Bridgeman method [22]. It is applicable to a whole range of materials and variations are introduced according to the requirements of individual systems. The necessary constituents are sealed into an evacuated ampoule and held at a high temperature (above the melting point) for often a considerable time. Crystallization is induced by lowering the temperature. The quality and size of the crystals may be very dependent on the stability of the temperatures and temperature gradients, and on the cooling rate. The difficulty with bulk growth procedures is that they generally do not produce materials of acceptable quality for refined applications. Nor are they suited to production of devices requiring planar variations of doping, as are epitaxial methods.

Whereas the former methods represent attempts to prepare materials with acceptable optical properties by isolating the purest, perfect form, i.e. single crystals, it has been recognized that the powder form too can have very desirable properties.

For some phosphor applications, relatively crude methods of large scale manufacture are quite suitable and indeed appear mandatory. Such a state of affairs seems to correlate with a woeful understanding of the detailed operation of the device under construction. This is not to say that the devices do not work well. That they do, is of course the justification of the means.

4. Established compounds – gallium arsenide

The casual reader may be forgiven for believing that, in view of the long and intensive research programmes on gallium arsenide culminating in the present output level of devices, there must be little scope for an improvement in the quality of this material. A quick look at the quality of silicon readily available in bulk to manufacturers will surely rapidly convince him otherwise. The volume of silicon production is overwhelming and greatly to its advantage compared with that of gallium arsenide, which nevertheless can be regarded as a successful materials development. It can be grown readily by liquid phase epitaxy from a melt of gallium saturated with arsenic [13, 14], or by vapour phase epitaxy using any one of a variety of vapour phase reactions [15-17]. Routine impurity concentrations in undoped material have been whittled down to below the 10^{14} cm^{-3} level aided by the application of a whole variety of analytical techniques. Here we reach the seat of the problem in this class of material. To further improve material quality, new, quick, reliable and highly sensitive techniques are urgently required, so that the effectiveness of modifications to growth programmes can be properly assessed.

One such technique, photoluminescence, was recognized at a very early stage as providing a sensitive indicator to the presence of certain impurities. The consequent floods of papers provide a fitting memorial to this belief. For indeed, the variety of spectra produced from a variety of samples grown under a variety of (often unspecified) conditions and assigned to a variety of elements caused disenchantment with the technique and eventually killed the belief that photoluminescence would provide a useful method of assessment, as opposed to an interesting one.

At these low levels of impurity, conventional analytical methods of assessment are failing and it has become a tradition to characterize samples principally by the results of electrical measurements – mobilities, carrier concentrations and resistivities. The behaviour of these quantities as a function of temperature and as a function of growth conditions can give estimates of the relative total numbers of donors and acceptors present, but only very poor indications of the individual numbers and identities of these impurities [23]. Nevertheless, such information can be applied empirically to reduce net impurity concentrations. The bigger advance will be when the impurities are individually identified, traced to particular aspects of the growth programme and eliminated.

As the quality of materials improved, photoluminescence measurements gradually worked their way back to recognition and respectability. Spectra are examined more critically before publication and the fluctuations in the reported binding energy of zinc acceptors for example in gallium arsenide now amount to about 1 %, and assignments are much more reliable.

The current availability of samples of gallium arsenide with impurity concentrations at the 10^{14} cm^{-3} level has allowed the observation of bound exciton spectra [24]. Recombination of an exciton bound to an impurity centre gives rise to sharp emission lines which do not have the broadening which is associated with the thermal or even "hot" motion of free excitons, even below 2 K. For most of the electrically active impurities, this is the breakthrough long awaited by analysts.

Gallium arsenide is a direct gap material with a low effective mass (Fig. 3). The orbital sizes of bound electronic states are correspondingly large (several hundred Ångstrom units). It turns out that the penetration of the impurity containing cell of the lattice is so small that the localization energies of excitons bound to different impurities are almost independent of the nature of the impurity, that is, most donor bound excitons have almost the same recombination energies, and similarly for acceptor bound excitons [19, 25]. This situation is quite different to that found in gallium phosphide [6] or silicon where these emission lines can be readily used to identify different impurities and does not auger well for a parallel programme in gallium arsenide or similar compounds, for example indium phosphide.

There is, however, a saving property [19].

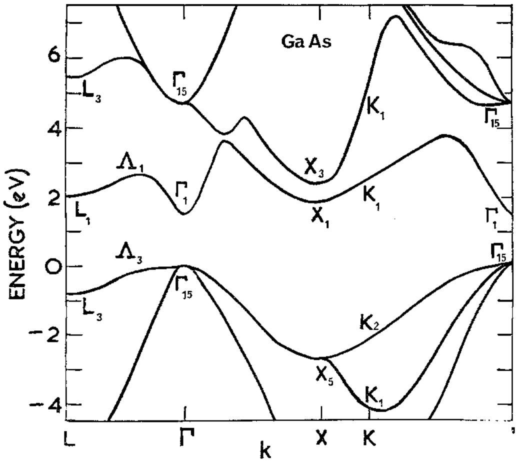

Figure 3 The band structure of gallium arsenide. The general features are the same for all the zinc blende compounds. The direct gap at Γ is more sensitive to composition, pressure etc. than the other features, in particular the gaps at L and X. Small differences in the atomic parameters for different compounds slightly affect the absolute energies of the band extrema so that in indium phosphide (still direct, Γ lowest) L is below X, while in gallium phosphide the order is reversed. Since electrons occupy the lowest minimum, such small modifications dramatically affect the material properties. As gallium phosphide is added to indium phosphide the Γ minimum rises rapidly in energy while the X minimum remains relatively static (see Fig. 5). (From Jones and Lettington [104].)

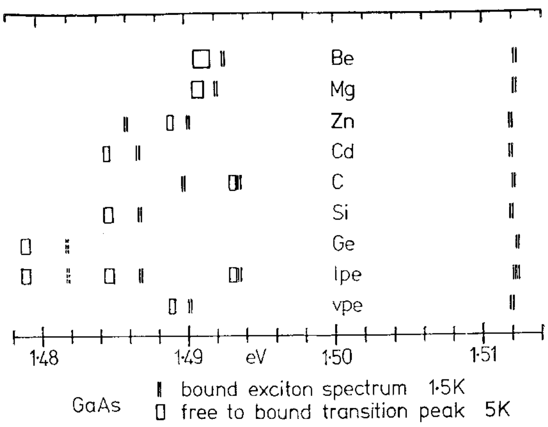

Figure 4 The distribution of bound exciton lines and their shifted replicas due to recombinations leaving acceptors in gallium arsenide in excited states. The exciton ground state is double, leading to the doublet emission. For zinc and carbon acceptors, the presence of more than one excited state is detected in the purest material. Free-to-bound transitions are observed when conduction electrons are captured by neutral acceptors and give much broader emission lines whose peaks can only be established to the accuracy shown.

Recombinations to higher energy excited states, of acceptors for example, are necessarily shifted in energy by amounts which are dominated by differences in central cell effects between ground and excited levels of the acceptor. The position of the shifted (replica) emission is an unambiguous pointer to the presence of different acceptors and is characterized readily by deliberate doping experiments. The whole situation is a spectroscopist's dream, with lines as sharp as 0.1 meV shifted from one another by several meV (Fig. 4).

The most striking conclusion to be drawn from this work is that the dominant impurity amongst acceptors in vapour grown gallium arsenide is zinc (a group II element on a group III site), as in vapour grown indium phosphide. In liquid grown gallium arsenide, carbon, silicon and germanium acceptors are all commonly found (group IV elements on group V sites) but never zinc [19]. The correlation of impurity with growth method has been established from an examination of samples from a wide variety of laboratories and is nearly, but not quite perfect. The way that growth conditions affect the incorporation of different valency acceptors can now be monitored, making it possible to ask serious questions about the details of reaction kinetics which would have been impossible to answer a year ago. The important point is that answers to these questions are confidently expected soon to give valuable insight into the incorporation of other troublesome entities such as vacancies and donors.

So far, gallium arsenide has yielded quite readily to this approach. Success is achievable only when the material quality exceeds some threshold so that exciton spectra can be observed properly. Indium phosphide is expected to benefit greatly from the experience gained in gallium arsenide. To set against the increased difficulty of preparing doped samples of adequate quality we have the knowledge that vapour phase grown indium phosphide does show bound excitons apart from that due to zinc and we have the benefit of experience gained from gallium arsenide in the field of reaction kinetics. In comparing gallium arsenide and indium phosphide it is appropriate to comment here that the former material appears to suffer from surface problems in the form of a high carrier surface recombination velocity, not so apparent in indium phosphide [26, 27]. The cause of this is quite unclear, but it must contribute to the difficulties of contacting problems and may very well repay some investigation.

Analysis of donors is not quite so straightforward due to the smallness of the chemical shifts involved (less than 1 cm^{-1}). In that case the improved resolution afforded by far infra-red photo-excitation experiments is more appropriate [28, 29]. The conduction band minimum of gallium arsenide is simply spin-only degenerate, in contrast to the situation at the valence band edge. Shallow (i.e. normal) donors have wide electron orbits which have little penetration of the core of the centre so that different donors all have closely similar energy level systems, excellently represented by a hydrogenic scheme in both magnitudes and in the classification of the orbital states. Nevertheless the observation of the 1s — 2p transition in the far infra-red (~ 250 μm) does reveal small central cell shifts characteristic of different donor elements. The quantity measured is photoconductivity, since a judicious choice of temperature ensures thermal ionization following photo-excitation. The most commonly observed donors so far identified are tin and silicon although there are a number of others still being investigated. The wide electron orbits which are responsible for such small chemical shifts inevitably sweep out relatively large volumes of crystal and in effect sample the purity of the material over a much larger region than applies in the case of acceptors. This aspect and the more difficult experimental arrangement inevitably slow the development of the technique for routine analysis, relative to the simple acceptor experiment. But as in that case, the knowledge of the donor elements in general incorporated as a result of a particular growth programme will be invaluable.

The photocapacitance experiment is not new, but is currently enjoying renewed popularity due to the applications it provides in locating deep traps in device materials and which are not necessarily radiative [30, 31]. A depletion layer is first formed within the material to be investigated, either by formation of a junction or a Schottky barrier. This is itself not without problems, for as in all techniques which require sample processing before measurements can be made, there is a danger of introducing centres not characteristic of the virgin material. Depending on the carrier concentration in the material, a depletion layer is set up, represented by a movement of the conduction band edge (in n-type material) away from the Fermi level as the free carriers redistribute themselves. There is a resulting space charge (ionized donors in n-type material) balancing the removed carriers.

Centres with levels deep in the forbidden gap can have their charge states changed, by the application of light of appropriate wavelength for example. This changes the space charge which is then compensated by a movement of the depletion edge, ionizing or neutralizing a number of donors, according to the circumstances. The change in the depletion width is detected as a change in the small signal high frequency capacitance (hence photocapacitance). The liberated carriers produced when the charge state of a centre is altered can also be detected (transient photoconductivity). Traps can also be resolved via their characteristic lifetimes which can be varied by altering the temperature of the material. By arranging a detection system which is sensitive to time constant effects, a whole spectrum of traps can be displayed by simply sweeping the temperature of the sample over a wide range [32].

Such techniques have the particular merit of being quantitative in that densities, distributions and cross-sections of deep centres can all be determined. Particularly troublesome impurities in gallium arsenide, oxygen and copper are currently receiving attention using these methods. It seems likely that as more laboratories take up the method it will become accepted as a useful analytic tool for investigating some of the hitherto inaccessible characteristics of these materials.

So here we appear to have some problems with a real chance of solution. There is a real prospect of getting the concentration of electrically active impurities in gallium arsenide at least, routinely down to the 10^{12} cm^{-3} level. Having removed this somewhat random effect, we may then see which other problems are limiting material quality.

5. The ternary alloys

As soon as one moves away from the regular binary compounds in an effort to engineer some particular band structure arrangement, problems multiply. Substitution of only a small fraction of one component by an isoelectronic element immediately introduces a randomness into the lattice and the clear picture we have been forming blurrs immediately. It is not only a matter of less well resolved luminescence features. It has been found that the introduction of as little as 1% of arsenic into gallium phosphide reduces luminescence efficiency by $\sim 90\%$ [33]. This rate of decrease is not maintained however and the gallium arsenide phosphide alloy Ga(AsP) is a commercially well developed light emitting semiconductor [18, 34-39], embodying in one compound the direct gap of gallium arsenide (Fig. 3) but with a magnitude nearer to the indirect gap of gallium phosphide. Although an admirable material, having reached a full production status because of its competitive emission properties relative to other compounds, principally gallium phosphide, it falls a long way short of its theoretical potential as a direct gap emitter [39, 40]. Despite much research, this problem does not yield. The magnitude of the difficulty is magnified in that it is not clear exactly what the problem is.

Such a difficulty was encountered in the famous heterostructure (close carrier confinement) laser, in which the active region of gallium arsenide is bounded by layers of (GaAl)As alloy [41-43]. Such lasers, although having an admirably low threshold with high efficiency and low loss, had a notoriously short life. It always seemed a telling point that gallium arsenide, aluminium arsenide and, therefore, also the alloy matched each other exceedingly well so far as lattice parameter was concerned. Certainly, the match is close enough to allow ready growth of the mixed alloy onto gallium arsenide substrates.

The trouble is, good though the match may be, it is just not good enough [44, 45]. A mismatch in expansion coefficients can be as bad as a mismatch in lattice parameter, for the structures are prepared at temperatures near 900°C, yet used at room temperature. Strains of the order of 10^{-3} are built in at the interface and were ultimately identified as the seat of the problem. In this case, problem identified was as good as problem solved, for the strains can be avoided by modifying the aluminium content of the alloy or by introducing a further degree of freedom in the form of phosphorus atoms to tailor the lattice parameter of the resulting quaternary alloy to an exact match. It is an interesting feature that the latter step also reduces further the laser thresholds [46]. It has been a salutary experience. The difficulties encountered in such a well understood and simply prepared system tend to depress hopes of early successes with more exotic materials.

Of course, when the subject of the alloy (InGa)P was raised, as a material with better potential than Ga(AsP), the troubles of that material and the fact of lattice mismatch were already recognized. Hindsight shows us that to embark on (InGa)P was an act of faith indeed. It is a material with a very rapid compositional dependence of the direct gap and, therefore, requires exceptional control during growth [47-54]. The lattice mismatch between the constituent compounds is twice as great as for Ga(AsP) [55], a difficulty scarcely alleviated by employing gallium arsenide substrates. These provide a lattice match at an alloy composition near to 51% gallium phosphide, too low to provide the required material properties (achieved nearer a composition of 60 to 70%).

Liquid phase epitaxial methods have shown up a tendency for the layer composition to lock on to that required for exact lattice match with the substrate, irrespective of the composition of the liquid [56]. This property may yet be utilized by the quaternary alloys. The preferred method for vapour growth would appear to include a rapidly grown, graded composition, thick buffer layer. This is not easily done, however, for the chemical differences between indium and gallium compounds cause considerable difficulties in arranging a reasonable control of growth of a layer of definable composition. They are such that questions concerning non-regular solutions and miscibility gaps can arise. The sheer magnitude of all these problems has led to such an industrial disenchantment with the material that any further discussion of problems would seem to some to be of academic interest only.

Nevertheless, it is not inappropriate to recall a simple and clearcut question which this alloy has posed for some time. The raison d'être of such alloys is to find a direct gap material with as large an energy gap as possible. From an early stage the critical composition at which the nature of the energy gap changed from direct (indium phosphide like) to indirect (gallium phosphide like), that is, the crossover composition, was sought. A number of laboratories, not all dealing in epitaxial material conclude that the composition is close to 63% gallium phosphide (molecular fraction) [57-59]. A second group, relying on luminescence measurements again not wholly on one type of material, prefer a composition near 74% [36, 48, 51, 60, 61] and support it with admirable confidence [54]. There is a genuine problem here, however, which must surely lie in the methods of interpretation of different properties to establish band edge positions. It is difficult to believe that all the differences can be ascribed to poor compositional homogeneity, a criticism that might have been levelled at earlier work.

More recently, measurements of the pressure dependence of Hall coefficient and resistivity have brought to light a quirk of the band structure [62] that may yet satisfy both camps. The conduction band minimum associated with the indirect transition in this alloy has always been regarded as being that minimum (strictly the set of minima) at the X point in the Brillouin zone (see Fig. 3). It has been customary to relate experimental phenomena to such a picture. Such a practice may be the seat of the controversy however. It now transpires that the conduction band edge at the L point intrudes upon the scene in such a way that the rapidly composition dependent direct minimum at Γ crosses the L indirect minimum energy near 63% composition. At a stroke the direct/indirect crossover is released from any connection with the X minimum. A further crossover occurs near the 75% composition when the L minimum rises above the X minimum, (Fig. 5).

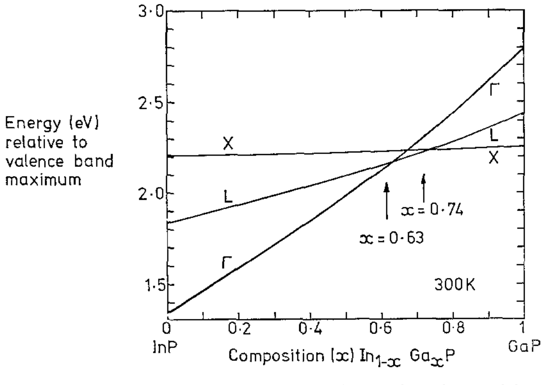

Figure 5 The conduction band-valence band transition energies for the (InGa)P alloy as a function of composition. This diagram is to be viewed in conjunction with Fig. 3. (From Pitt *et al.* [59].)

While this behaviour may account for a number of observations, the interpretation still awaits universal acceptance. Perhaps in view of the waning commercial interest in this system an interchange of samples may be in order. Whatever the conclusion on this point, the major problem of mismatch will still be with us and buried beneath that, the vexed question of the random occupation of the substitutional sites. It seems likely that, from any advances which are made, it will be Ga(AsP) which will reap the benefit.

6. Exotica

Research aimed at generating wider band gap materials amongst the simple semiconductor compounds has led to a number of materials which appear to offer a great deal, but have so far proved very disappointing. One of the most successful of these in the past has been silicon carbide [63-67]. It is classed here as exotic in the sense that although it has been used to prepare commercial devices on a limited scale, there is only a minimal understanding of its optical properties and of the limiting factors in device operation. It is an indirect gap material with a band gap of 2.8 eV when prepared in its most common form. It is an extremely stable compound with a high thermal conductivity. Its mechanical strength, the extreme conditions necessary for its preparation and the poor understanding of the energy level systems and transitions associated with impurities and defects remind one very much of that tetrahedrally co-ordinated form of carbon, diamond, with its large band gap and still more intractible properties.

No doubt the problems of silicon carbide, saturation effects, traps and other impurity effects, at present the major stumbling blocks to further exploitation, could gradually yield to a continuation of the already prolonged spectroscopic investigation. But its other disadvantages, principally high growth temperatures with slow growth rates and also its famous capability of polytype growth – a puzzle in itself (repeat distances of up to 1500 Å!) would lead some to argue that the material has poor commercial prospects.

Endemic in most wide band gap materials are the problems of self compensation [68-73]. This phenomenon occurs when the energy required to form a native defect of donor-like character (say), is more than compensated for by the energy released by trapping the resultant electron at a nearby acceptor site. The general result is that it is very difficult and often impossible to dope the material p-type (n-type in some cases). A simple enough problem, but its effects are quite disastrous so far as all devices requiring amphoteric doping are concerned. It has been the subject of numerous theoretical investigations [74] the results of which indicate that where data on the thermodynamics of defect formation are known, the experimental problems are justified, and are likely to be so in other cases as well.

Efforts to beat the problem have not abated however. The direct approach involving implantation by ion bombardment [75-78] is largely foiled by the creation of damage centres which cannot be annealed out at sufficiently low temperatures. This is not to say that the technique does not work at all, for a usable type conversion has been achieved in some of the zinc chalcogenides [79-81] which appear to be more amenable to p-type doping than most of the II-VI compounds.

Of course, for electroluminescence purposes it is not essential to manufacture a p–n junction. The II-VI compounds give good illustrations of how the difficulty can be avoided. Zinc selenide has responded to an approach involving the use of Schottky barriers and metal-insulator-semiconductor (MIS) structures [82-84]. Nevertheless, it seems that controlled barrier experiments on zinc selenide may indeed provide a back door method of solving the very difficult questions concerning the luminescence mechanisms in the zinc sulphide system. Understanding of the optical processes taking place in zinc selenide has advanced markedly with the interpretation of these experiments, and with the assignment of a large number of pair transitions [85] of the type so well known in gallium phosphide [6].

Zinc sulphide has gained a new lease of life in recent years in the field of DC electroluminescence [86]. It is prepared by improved phosphor techniques, questions about the precise excitation mechanisms having been left behind as the phosphor performance has steadily improved. Possible mechanisms include simple carrier injection processes taking place at built-in junctions occurring inside the particles due to some unidentified aspect of the preparation, but involving phases of cuprous sulphide, or impact ionization effects due to metal-semiconductor barriers at copper precipitates [87]. The luminescence properties of zinc sulphide have been investigated over a long period of time. Conversion of samples of phosphor material to single crystal form in a high temperature furnace have allowed a luminescence investigation of the nature of the transitions to yield firm conclusions concerning the roles of impurities within the lattice [88]. It may be that further single crystal investigations will aid the understanding of participating processes and lead to useful developments in phosphor chemistry, even if the crystals themselves are not good phosphors.

Gallium nitride is another wide gap material which has made some progress [89-92] and suffered some disenchantment. Like the nitrides of indium and aluminium it crystallizes in the wurtzite form. It has a band gap near 3.5 eV [93, 94] and a pathological antipathy to being p-type. Typical undoped material contains more than 10^{18} donors per cm^3 most of which are probably nitrogen vacancies. This really is the problem of gallium nitride. If it is ever solved, one is still faced with severe substrate difficulties. The excessive defect concentration tends to generate broadband luminescence which does not help spectroscopic investigation. Nevertheless, successful barrier devices have been made [95, 96] and the material survives while further information on the doping characteristics and energy level systems [97] is gathered.

The chalcopyrite derivatives of the III-V or II-VI compounds have attracted some attention. Relative to the problems of gallium arsenide however, the difficulties encountered in this field are truly astronomical. It is not clear even if the optimum conditions for growth of single crystals have been established. Correlation of experimental measurements with band structure calculations appear problematical. The ordered division of occupation of the sites of one of the components leads to an extension of the unit cell by a factor of two in the cubic $\langle 100 \rangle$ direction. This leads to a collapse in the size of the associated Brillouin zone and a folding over of the bands so that certain levels at the edge of the zinc blende zone now appear at the zone centre [98]. Transitions which may be expected to become allowed without phonon co-operation only do so to the extent that the potentials of the substituting elements are different. It seems that a confirmation of this simple conclusion is proving difficult. It is recognized that there is a slight tetragonal distortion which effectively reduces the symmetry and introduces complications (cf. the trigonal distortions of wurtzite crystals).

In spite of the difficulties associated with level assignments it does seem clear that the general rule is that the band gaps [99, 100] of these materials are somewhat lower than those of the corresponding binary compounds from which they are derived. That, and difficulties associated with controlling their electrical properties [101] means that they tend to be disregarded for light emitting applications, although they may well have a future in non-linear optical devices [102]. At present, however, they present formidable crystal growth problems, and it is not clear how they will develop.

Beyond the chalcopyrite structures the number of varieties of materials explodes. Many of the more likely ones, including the defect structures (e.g. gallium selenide [103]) have received some preliminary assessment. The difficulty with all new materials is to know how much refinement of growth technique is necessary in order to obtain a reliable estimate of the device potential of the samples obtained. How many lamp or CRT phosphors, for example, have been prepared, assessed and rejected on the basis of the results from one or two samples? At the very least, good reasons should be sought for poor performance. Apparently good growth techniques for one material may not be so for allied and similar, but nevertheless different materials.

7. Conclusion

In this brief review we have commented on the rapid proliferation of problems arising out of the search for materials to supersede the simpler semiconductors which have led the field for so long. The tremendous start gained by a material like silicon in terms of research time and investment embodied in the quality of current material places newer materials at a dreadful disadvantage unless they offer completely new properties (for example efficient emission of visible light). Nevertheless, the research by attrition mentioned earlier does produce dividends, often by spin-off from investigations under quite different briefs. An example of this is the rise of photocapacitance and exciton and pair luminescence techniques, which are clarifying our ideas on the practicalities of vapour and liquid phase growth mechanisms, and will have impact on all materials grown by these methods. As the general quality of materials improves, then the characteristics of bulk grown material will be drawn into the net. Finally, we must remember to keep an open mind about that new, exotic material which might, with a reasonable amount of development, produce just the solution we seek.

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References

1. T. S. MOSS, G. J. BURRELL and B. ELLIS, "Semiconductor Optoelectronics" (Butterworth, London, 1972).
2. A. A. BERGH and P. J. DEAN, "Light Emitting Diodes" (Clarendon, Oxford, in press).
3. *Idem, Proc. IEEE* **60** (1972) 156.
4. A. ONTON, *Festkörperprobleme* **13** (1973) 59.
5. *Idem, J. Lum.* **7** (1973) 95
6. P. J. DEAN, "Progress in Solid State Chemistry", Vol. 8 (Pergamon, Oxford, 1973) p. 1.
7. J. C. PHILLIPS, "Bonds and Bands in Semiconductors" (Academic Press, New York, 1973).
8. E. PARTHE, "Crystal Chemistry of Tetrahedral Structures", (Gordon and Breach, New York, 1964).
9. R. W. G. WYCKOFF, "Crystal Structures", Vol. 1 (Wiley, New York, 1963).
10. E. MOOSER and W. B. PEARSON, *Acta Cryst.* **12** (1959) 1015.
11. P. WORTHINGTON, *J. Mater. Sci.* **8** (1973) 1194.
12. R. BRAUNSTEIN, A. R. MOORE and F. HERMAN, *Phys. Rev.* **109** (1958) 695. The bracket notation indicates alloying.
13. H. NELSON, *R.C.A. Rev.* **24** (1963) 603.
14. A. R. GOODWIN, J. GORDON and C. D. DOBSON, *Brit. J. Appl. Phys.* **2** (1968) 115.
15. J. R. KNIGHT, D. EFFER and P. R. EVANS, *Solid State Electron.* **8** (1965) 178.
16. J. J. TIETJEN and J. A. AMICK, *J. Electrochem. Soc.* **113** (1966) 724.
17. R. E. ENSTROM and C. C. PETERSON, *Trans. Met. Soc. AIME* **239** (1967) 413.
18. M. CRAFORD, "Progress in Solid State Chemistry", Vol. 8 (Pergamon, Oxford, 1973) 127.
19. A. M. WHITE, P. J. DEAN, D. J. ASHEN, J. B. MULLIN, M. WEBB and B. DAY, *J. Phys.* **C6** (1973) L243.
20. R. GREMMELMAIER, *Z. Naturforsch.* **11a** (1956) 511.
21. J. B. MULLIN, B. W. STRAUGHEN and W. S. BRICKELL, *J. Phys. Chem. Solids* **26** (1965) 782.

22. P. W. BRIDGEMAN, *Proc. Amer. Acad. Arts Sci.* **60** (1925) 305.
23. H. BROOKS, *Adv. Electronics Electron Phys.* **7** (1955) 158.
24. A. M. WHITE, P. J. DEAN, L. L. TAYLOR, R. C. CLARKE, D. J. ASHEN and J. B. MULLIN, *J. Phys.* **C5** (1972) 1727, references and discussion.
25. A. M. WHITE, P. J. DEAN, K. M. FAIRHURST, W. BARDSLEY, E. W. WILLIAMS and B. DAY, *Solid State Commun.* **11** (1972) 109
26. R. D. BURNHAM, N. HOLONYAK JUN, D. L. KUENE and D. R. SCRIFRES, *Appl. Phys. Letters* **18** (1971) 160.
27. A. M. WHITE, P. J. DEAN, B. D. JOYCE, R. C. CLARKE and L. L. TAYLOR, Proceedings of the 11th International Conference on Physics of Semiconductors 1972 (PWN, Warsaw, 1972) p. 190.
28. C. M. WOLFE, D. M. KORN and G. E. STILLMAN, *Appl. Phys. Letters* **24** (1974) 78.
29. R. A. STRADLING, L. EAVES, R. A. HOULT, N. MIURA, P. E. SIMMONDS and C. C. BRADLEY, Proceedings of the IVth International Symposium on GaAs, Boulder, Colorado, 1972 (Inst. Phys., Bristol, 1973) p. 65.
30. C. T. SAH, L. FORBES, L. L. ROSIER and A. F. TASCH JUN, *Solid State Electr.* **13** (1970) 759.
31. C. H. HENRY, H. KUKIMOTO and G. L. MILNER, *Phys. Rev.* **B7** (1973) 2499.
32. D. V. LANG, *J. Appl. Phys.* **45** (1974) 3014, 3023.
33. R. A. LOGAN, P. J. DEAN, H. G. WHITE and W. WIEGMANN, *ibid* **42** (1971) 2328.
34. A. ONTON and L. M. FOSTER, *ibid* **43** (1972) 5084.
35. J. I. PANKOVE, H. NELSON, J. J. TIETJEN, I. J. HEGYI and H. P. MARUSKA, *R.C.A. Rev.* **28** (1967) 560.
36. C. J. NUESE, J. J. TIETJEN and J. J. GANNON, *J. Electrochem. Soc.* **116** (1969) 248.
37. A. H. HERZOG, W. D. GROVES and M. G. CRAFORD, *J. Appl. Phys.* **40** (1969) 1830
38. M. G. CRAFORD, R. W. SHAW, A. H. HERZOG and W. O. GROVES, *ibid* **43** (1972) 4075.
39. R. J. ARCHER, *J. Electr. Mater.* **1** (1972) 128.
40. *Idem*, Spring Meeting of the Electrochemical Society (1970).
41. H. KRESSEL, *J. Quantum Electronics* **8** (1972) 632.
42. H. C. CASEY JUN and M. B. PANISH, *J. Appl. Phys.* **40** (1969) 4910.
43. K. J. LINDEN, *ibid* **40** (1969) 2325.
44. M. ETTENBERG and R. J. PAFF, *ibid* **41** (1970) 3926.
45. F. K. REINHART and R. A. LOGAN, *ibid* **44** (1973) 3171.
46. G. A. ROZGONYI and M. B. PANISH, *Appl. Phys. Letters* **23** (1973) 533.
47. G. J. NUESE, D. RICHMAN and R. B. CLOUGH, *Met. Trans.* **2** (1971) 789.
48. Y. OKUNA, K. SUTO and J. NISHIZAWA, *Jap. J. Appl. Phys.* **10** (1971) 388.
49. H. ITOH, K. HARA, A. TANAKA and T. SUKEGAWA, *Appl. Phys. Letters* **19** (1971) 348.
50. A. LAUGIER and J. CHEVALLIER, *Phys. Stat. Sol.* **7** (1971) 427.
51. A. ONTON, M. R. LORENZ and W. REUTER, *J. Appl. Phys.* **42** (1971) 3420.
52. M. B. PANISH and M. ILEGEMS, "International Symposium on GaAs, Aachen 1970" (Inst. Phys., Bristol, 1971) p. 67.
53. B. W. HAKKI, *J. Electrochem. Soc.* **118** (1971) 1469.
54. H. M. MACKSEY, N. HOLONYAK JUN, R. D. DUPUIS, J. C. CAMPBELL and G. W. ZACK, *J. Appl. Phys.* **44** (1973) 1333.
55. I. KUDMAN and R. J. PAFF, *ibid* **43** (1972) 3760.
56. G. B. STRINGFELLOW, *ibid* **43** (1972) 3455.
57. R. Z. BACHRACH and B. W. HAKKI, *ibid* **42** (1972) 5102.
58. C. ALIBERT, C. T. BORDURE, A. LAUGIER and J. CHEVALLIER, *Phys. Rev.* **B6** (1972) 1301.
59. A. W. MABBITT, *J. Mater. Sci.* **5** (1970) 1043.
60. D. R. SCIFRES, H. M. MACKSEY, N. HOLONYAK JUN and R. D. DUPUIS, *J. Appl. Phys.* **43** (1972) 1019.
61. D. R. SCIFRES, H. M. MACKSEY, N. HOLONYAK JUN, R. D. DUPUIS, G. W. ZACK, C. B. DUKE, G. G. KLEIMAN and A. B. KUNZ, *Phys. Rev.* **B6** (1972) 2206.
62. G. D. PITT, *Solid State Commun.* **14** (1974) 621.
63. R. M. POTTER, J. H. BLANK and A. ADDAMIANO, *J. Appl. Phys.* **40** (1969) 2253.
64. H. K. HENISCH and R. ROY (Eds.), "Silicon Carbide 1968" (Pergamon, London, 1969).
65. G. F. KHOLUYANOV, *Sov. Phys. Solid State* **7** (1966) 2620.
66. H. L. DUNLAP and O. J. MARSH, *Appl. Phys. Letters* **15** (1969) 311.
67. P. J. DEAN and R. L. HARTMANN, *Phys. Rev.* **B5** (1971) 4911.
68. G. MANDEL, *ibid* **134A** (1964) 1973.
69. R. S. TITLE, G. MANDEL and F. F. MOREHEAD, *ibid* **136A** (1964) 300.
70. G. MANDEL, R. S. TITLE and F. F. MOREHEAD, *ibid* **136A** (1964) 826.
71. F. F. MOREHEAD and G. MANDEL, *ibid* **140A** (1965) 924.
72. H. J. VINK, *Festkörperprobleme* **4** (1965) 205.
73. W. ALBERS, "Physics and Chemistry of II-VI Compounds", edited by M. Aven and J. S. Prener (Wiley, New York, 1967) p. 165.
74. C. H. HENRY, K. NASSAU and J. W. SHIEVER, *Phys. Rev.* **B4** (1971) 2453.
75. F. CHERNOW, G. ELDRIDGE, G. RUSE and L. W. AHLIN, *Appl. Phys. Letters* **12** (1968) 339.
76. B. TELL and W. M. GIBSON, *J. Appl. Phys.* **40** (1969) 5320.
77. W. W. ANDERSON and R. M. SWANSON, *ibid* **42** (1971) 5125.
78. B. TELL, W. M. GIBSON and J. W. ROGERS, *Appl. Phys. Letters* **17** (1970) 315.
79. Y. S. PARK, H. F. LOCKWOOD and F. Z. HAWRYLO, *ibid* **18** (1971) 45, 99.

80. J. DIELMAN, *ibid* **19** (1971) 84.
81. J. MARINE and H. RODOT, *ibid* **17** (1970) 352.
82. J. W. ALLEN, M. D. RYALL and E. M. WRAY, *Phys. Stat. Sol.* **17***a* (1973) K101.
83. K. TURVEY and J. W. ALLEN, *J. Phys.* **C6** (1973) 2887.
84. A. W. LIVINGSTONE and J. W. ALLEN, *ibid* **C6** (1973) 3491.
85. J. L. MERZ, K. NASSAU and J. W. SHIEVER, *Phys. Rev.* **B8** (1973) 1444.
86. A. VECHT, *J. Lum.* **7** (1973) 213.
87. A. G. FISCHER, "Proceedings of the International Conference on Luminescence", Vol. 12 (Akademiai Kiada, Budapest, 1968) p. 1765.
88. A. SUZUKI and S. SHIONOYA, *J. Phys. Soc. Japan* **31** (1971) 1455, 1462, 1719.
89. H. P. MARUSKA and J. J. TIETJEN, *Appl. Phys. Letters* **15** (1969) 327.
90. R. B. ZETTERSTROM, *J. Mater. Sci.* **5** (1970) 1102.
91. H. J. HOVEL and J. J. CUOMO, *Appl. Phys. Letters* **20** (1972) 71.
92. M. ILEGEMS, *J. Crystal Growth* **13/14** (1972) 360.
93. J. I. PANKOVE, H. P. MARUSKA and J. E. BERKEYHEISER, *Appl. Phys. Letters* **17** (1970) 197.
94. D. L. CAMPHAUSEN and G. A. N. CONELL, *J. Appl. Phys.* **42** (1971) 4438.
95. J. I. PANKOVE and P. E. NORRIS, *R.C.A. Rev.* **33** (1972) 377.
96. H. P. MARUSKA, D. A. STEVENSON and J. I. PANKOVE, *Appl. Phys. Letters* **22** (1973) 303.
97. J. I. PANKOVE, *J. Lum.* **7** (1973) 114.
98. A. SHILEIKA, *Surface Sci.* **37** (1973) 730.
99. G. C. BHAR and R. C. SMITH, *Phys. Stat. Sol.* **13A** (1972) 157.
100. J. L. SHAY, B. TELL and H. M. KASPER, *Appl. Phys. Letters* **19** (1971) 366.
101. B. TELL, J. L. SHAY and H. M. KASPER, *J. Appl. Phys.* **43** (1972) 2469.
102. G. D. BOYD, E. BUEHLER, F. G. STORZ and J. H. WERNICK, *J. Quantum Electronics* **8** (1972) 419.
103. A. MERCIER, E. MOOSER and J. P. VOITCHOVSKY, *J. Lum.* **7** (1973) 241.
104. D. JONES and A. H. LETTINGTON, *Solid State Commun.* **7** (1969) 1319.

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