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DEGREE OF Bachelor of Science in Chemistry

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**Theory and Uses of Low Temperature
Photoluminescence Spectroscopy**

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Abstract

The use of photoluminescence spectroscopy for the characterization of semiconductors is an important process that can be confusing for the undergraduate student. Many times a simple or novel concept is lost in the jargon that is used by scientists in the field. The concept becomes "available" for only the scientists or students that understand this lingo. The purpose of this paper is to explain the theory and uses of photoluminescence spectroscopy using as little math as possible and in simplified terms making this novel spectroscopic technique accessible to non-electrical engineers.

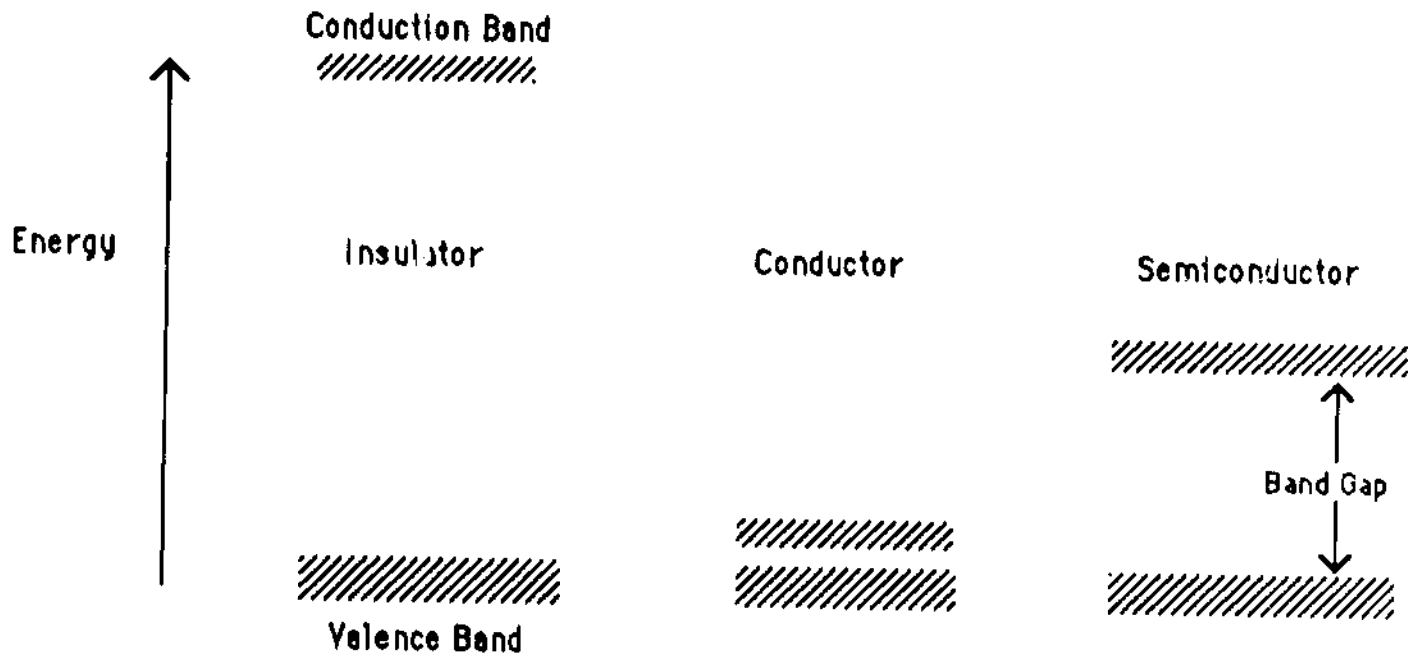
Introduction

Semiconductors are used in solid state electronic devices such as microwave circuits, visible and infra-red sources for optical communications and electro-optic devices. As the use of these devices becomes more widespread, the need for improved performance and reliability increases. These demands can be met only with increasingly higher purity and highly uniform materials.

A widely used method for characterizing the purity and uniformity of semiconductor material and devices is photoluminescence spectroscopy. Photoluminescence spectroscopy provides a contactless, non-destructive and very sensitive means for detecting certain chemical impurities in the material. This paper is intended for the non-electrical engineer who needs to understand the theory and uses of photoluminescence spectroscopy. The paper will include a brief introduction to semiconductors, photoluminescence theory and use, and interpretation of photoluminescence spectroscopic data.

Semiconductors

If a material allows electrons to flow easily across a charge separation it is referred to as a conductor. If the material restricts the flow of electrons it is an insulator. A semiconductor, as the name implies, lies between these two extremes. Electrons will not flow in a semiconductor until they have a discrete amount of energy. Thus, a semiconductor acts like an insulator until it is given a discrete amount of energy. When this energy level is achieved the semiconductor acts as a conductor. This energy is referred to as the band gap. The band gap for conductors is quite small while the band gap for insulators is large. The high energy state is called the conducting band and the lower state the valence band. The electrons are restricted to a single atom when they are in the valence band (this is not exactly true but will do for the scope of this paper¹) but when enough energy is put into the electron it frees itself from the atom and can move throughout the crystal lattice. The electron is now in the conducting band (see figure 1).

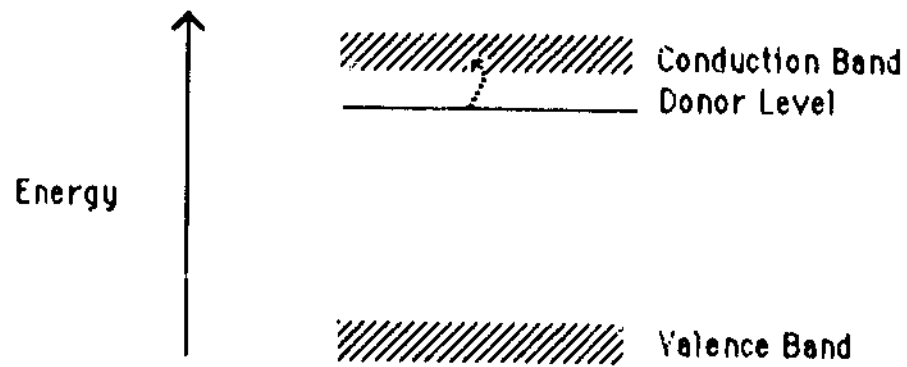


Energy level diagram for an insulator, a conductor, and a semiconductor 1.

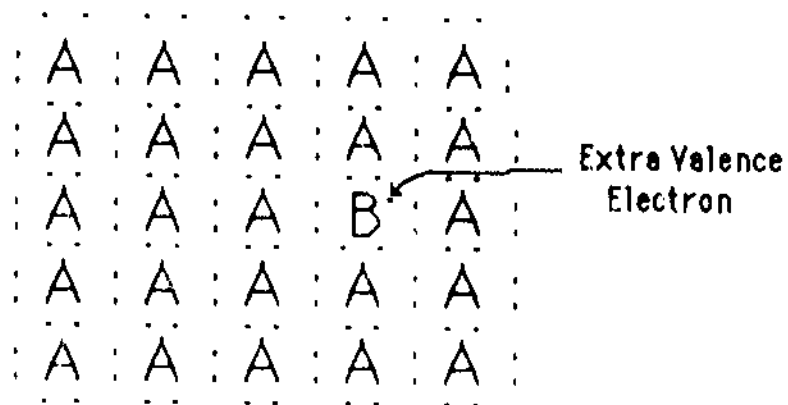
Fig. 1

If a chemical impurity occurs or is introduced into a semiconductor, isolated electronic levels in the band gap may appear. When the atom that is acting as the impurity has more valence electrons than the atoms that make up the crystal and its valence electronic level lies near the conduction band in the band gap, the impurity is known as a donor or n-type impurity (see figure 2). A donor can donate its excess free electron to the semiconductor's conduction band. When the impurity has fewer valence electrons than the atoms that make up the crystals and its electronic level lies near the valence band in the band gap, the impurity is called an acceptor, or p-type impurity. An acceptor can accept electrons from the semiconductor's valence band leaving "holes" in the valence band. Holes can move through the valence band by an electron from an adjoining atom, filling the hole and thus leaving a new hole behind it (see figure 3).

In semiconductors there are three processes of conduction. Intrinsic conduction is when equal numbers of electrons and holes are operative, these being created by excitation of electrons across the band gap.

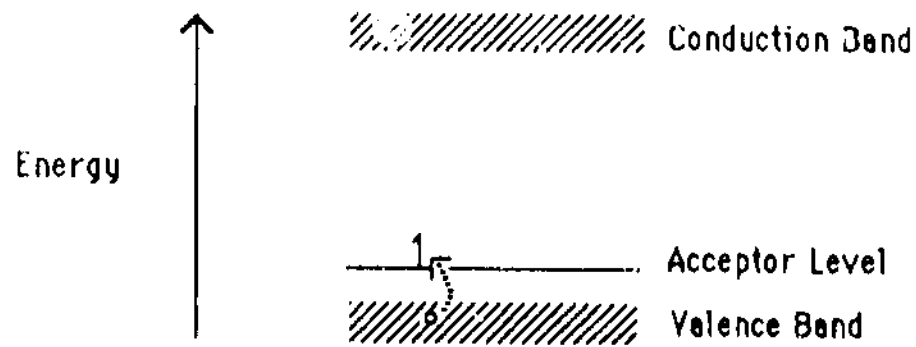


This diagram is an energy level diagram of a donor level in the band gap donating its excess electron to the conduction band¹.

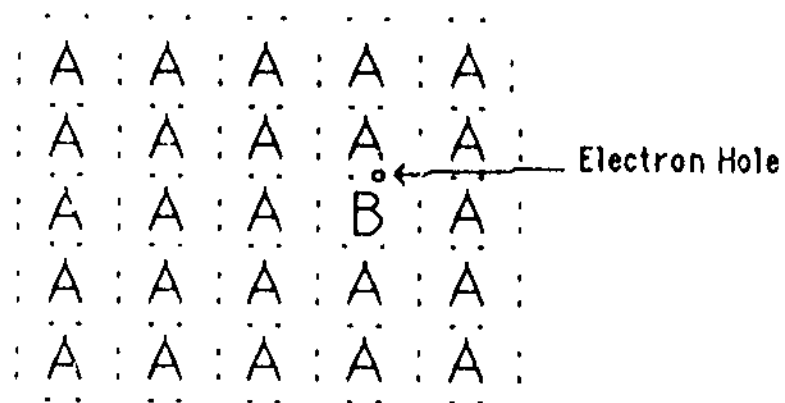


This diagram shows a crystal lattice of atom A with a donor impurity B and its extra valence electron².

Fig. 2



This is an energy level diagram of an electron from the valence band jumping into the acceptor level leaving behind a "hole" in the valence band¹.



This diagram shows a crystal lattice of atom A with an acceptor impurity B and its electron hole².

Fig. 3

Electron or n-type conduction is when only electrons from donor levels are excited into the conduction band. Hole or p-type conduction is when only holes are produced by excitation of electrons from the valence band into acceptor levels. All three processes will take place simultaneously but usually one or another predominates².

An electron and a hole can move through a crystal lattice as a unit. This unit is called an exciton and has distinct energy levels associated with it that exist in the band gap. Excitons can be bound at low (liquid He) temperatures to electrically active impurities and recombine. When an electron and a hole recombine, the electron fills the hole and energy is released. In photoluminescence spectroscopy, recombinations at impurity sites are identified.

Semiconductor technology's forefront is research on the III- V group of semiconductors, such as GaAs and InP. These semiconductors are important because they can be optically activated (activated with light waves) and can emit light photons. These semiconductors have a diamond

crystal lattice structure and are "grown" by many different methods.

These methods are Liquid Phase Epitaxy (L.P.E.), Vapor Phase Epitaxy (V.P.E.), Metalorganic Chemical Vapor Deposition (M.O.C.V.D), and Molecular Beam Epitaxy (M.B.E.)³. After a crystal is grown it can be "doped". In doping, an impurity is added in small amounts to increase the number of acceptors or donors in a crystal lattice. This increases the number of electrons or holes available for conducting and creates n-type (electron enhanced) or p-type (hole enhanced) semiconductors.

Photoluminescence Spectroscopy

Low temperature photoluminescence spectroscopy is the simplest and most useful technique for identifying impurities in GaAs and InP. Both donors and acceptors can be chemically identified and the sensitivity of the technique is extremely high. Under favorable conditions, concentrations of individual acceptor species can be detected as low as 10^{11}cm^{-3} ⁴. No sample preparation, besides cooling, is required, and small irregular shaped pieces can be used. Good signal to noise ratio, rapidity of measurement (after cooling), and quick data analysis all make photoluminescence attractive. The major limitation of the method is the high sample purity that is required for a discernable spectra. For n-type material, $n < 10^{15}\text{cm}^{-3}$, and for p-type, $p < 10^{16}\text{cm}^{-3}$, are required to identify acceptors using non-selective excitation in GaAs⁵. In heavily doped material, the shallow donor levels are broadened and merge with the conduction band. The peaks of other transitions are no longer well

resolved and acceptor identification is not reliable. The inability to study non-radiative centers and the complexity of the spectra also limit the usefulness of photoluminescence.

Photoluminescence is accomplished by using an excitation light with a photon energy larger than the band gap of the material. This light is strongly absorbed near the front surface of the sample creating electron hole pairs. These pairs diffuse into the sample and recombine through an enormous variety of radiative and non-radiative channels. This creates a highly complex spectra that escapes back through the front surface of the sample.

The spectra that results is first analyzed by determining the physical nature of the recombinations that are observed. These identifications have been determined by studying photoluminescence peak behavior as a function of measurement (such as temperature, excitation intensity, excitation wavelength, and external electric or magnetic fields) or sample parameters (such as donor or acceptor concentrations).

The next step is identifying the chemical or metalurgical nature of the defects and impurities which participate in these recombination processes. Defects, in general, are quite difficult to determine. Some defects can be intentionally created and then studied, but the exact nature of the defect is hard to determine. Identification of impurities is more straightforward. High purity samples are intentionally back doped with low levels of impurities and the resulting spectra compared.

The final step is to utilize the knowledge gained in the first two steps to identify impurities and defects that show up on the spectra of undoped high purity material. Certain impurities are common for different growth methods (see figure 4). These impurities come from the atmosphere, contaminants in the source material, and in the containers the material is grown in. After the impurities are identified, techniques can be developed and tested to minimize these contaminants.

Recombination

Electron-hole pairs have many different ways to recombine. Certain

The following is a list of commonly found acceptors and donors, in order of importance, that occur as impurities in different growth techniques^{4,5,13,14,15}.

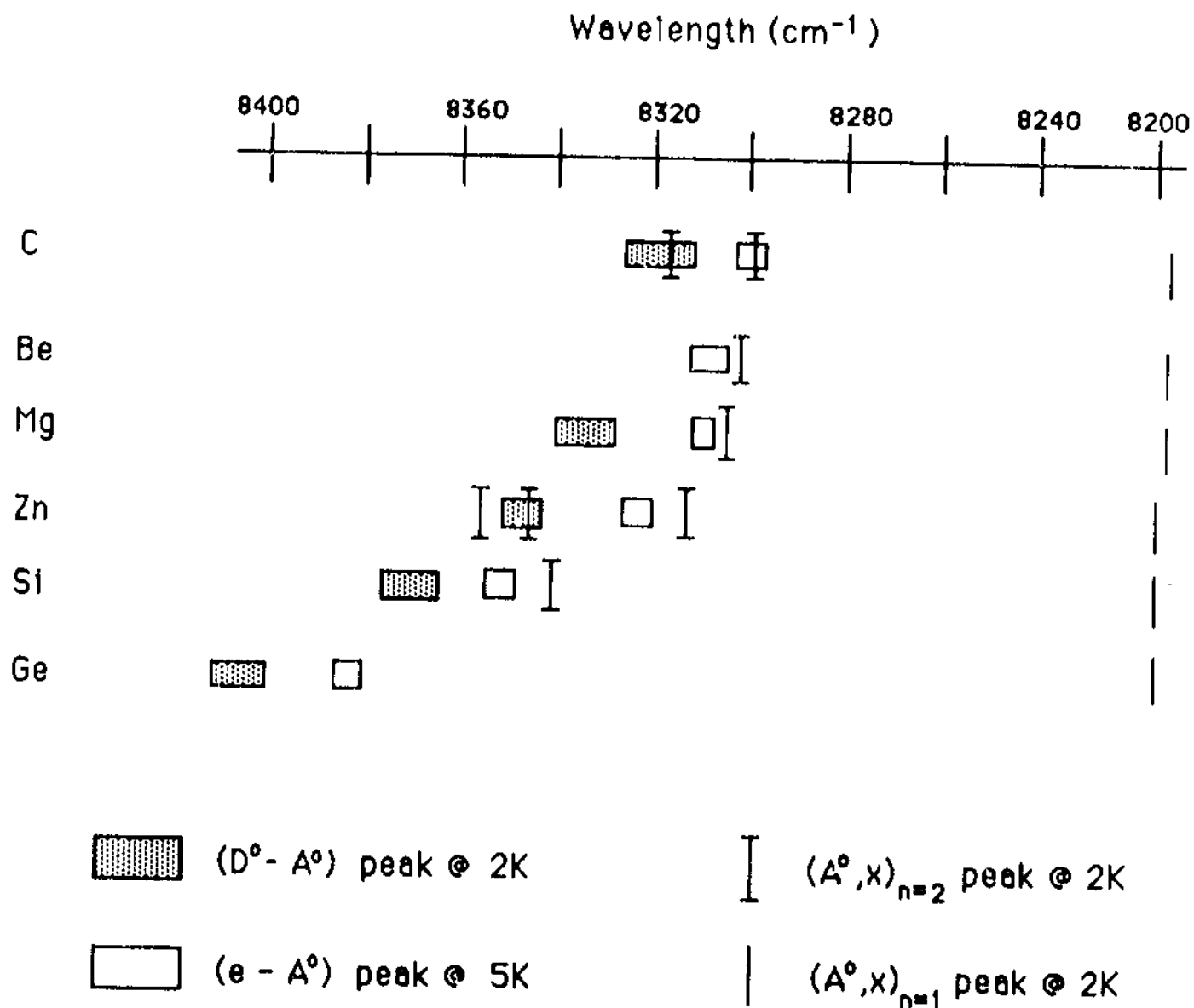
	<u>Acceptors</u>	<u>Donors</u>
Liquid Phase Epitaxy	Carbon Magnesium Silicon Germanium	Sulfur Silicon Selenium or Tin Lead or Tellurium
Vapor Phase Epitaxy (AsCl ₃ source)	Zinc Carbon Silicon Germanium	Silicon Sulfur Germanium Selenium or Tin
Vapor Phase Epitaxy (AsH ₃ source)	Carbon Zinc Silicon Germanium	Sulfur Silicon Germanium
Metalorganic Chemical Vapor Deposition	Carbon Zinc Germanium	Germanium Tellurium Silicon Selenium or Tin Sulfur
Molecular Beam Epitaxy (solid As source)	Carbon Magnesium or Beryllium Silicon Germanium	Tellurium or Lead Silicon Tin Sulfur
Molecular Beam Epitaxy (cracked As source)	Carbon Magnesium or Beryllium Silicon Germanium	Tellurium or Lead Silicon Tin Sulfur

Fig. 4

recombinations have been identified in GaAs and InP. These include free excitons and excitons bound to neutral shallow donors (this is designated by (D^0, X) , D^0 for donor, X for exciton), neutral shallow donor acceptors (A^0, X) , and ionized donors (D^+, X) . Donor to acceptor pair recombination (D^0-A^0) and conduction band to acceptor $(e-A^0)$ is also observed. The donor to valence band transitions (D^0, h) are virtually degenerate with the (D^+, X) transition. Excited-final-state or "two-electron" replicas of the (D^0, X) peak and "two-hole" transition replicas of the (A^0, X) peaks have been observed in both GaAs^{5,6} and InP⁴. Binding energies for typical shallow acceptors are five times those of donors so that the chemical shifts produce experimentally resolvable differences between different acceptor free-to-bound transitions but not for the donors⁷. These recombinations appear at different wavelengths for different chemical impurities. Some of these transitions are shown for GaAs in Figure 5.

Temperature

Photoluminescence spectroscopy is done at Liquid Helium and Helium



Peak positions for various acceptor impurities in GaAs⁵. The position of the $(D^0 - A^0)$ peaks are by Ozeki et al¹¹. The $(A^0, X)_{n=1}$ and $(A^0, X)_{n=2}$ peaks are doublets while the rest appear as singlets.

Fig. 5

Vapor temperatures which are below 20k. At this low temperature spectral broadening due to anti-stokes luminescence is eliminated and the electron or holes are frozen out on electrically active centers⁴. Peak narrowing is also increased due to the reduced thermal energy distribution of free particles⁸. By varying the temperature, some overlapping peaks can be further discerned, especially (D^0-A^0) and $(e-A^0)$ ⁴.

Excitation Levels

Good resolution for most peaks can be accomplished by using low excitation levels (\sim few mW/cm^{-3} or less)⁴. At high excitation energies, the electron system can begin to be heated with resulting broadening of peaks⁹. High excitation levels are used to study excitons bound to minority dopants such as (A^0,X) in n-type material or (D^0,X) in p-type material and to bring out some peaks like $(A^0,X)_{n=2}$ or deeply bound exciton peaks which can be superimposed on (D^0-A^0) and $(e-A^0)$ peaks¹⁰.

Experimental Apparatus

The experimental apparatus has an Argon laser that provides the

excitation energy. The Argon laser is focused through quartz windows on the liquid Helium dewar onto the sample. The sample is loosely held in place in a copper V-block. The sample must be mounted in a strain-free manner since even small strains can distort the spectra. The luminescence is collected and focused into a spectrometer that detects the wavelength and intensity. The instrumental resolution must be high since some peaks in GaAs and InP can have widths of $\sim 0.6 \text{ \AA}$ or less¹². The spectra is then fed into a computer where it can be stored and graphed out on a printer.

Conclusion

Photoluminescence spectroscopy is a novel spectroscopic technique that uses the special characteristics of semiconductors to detect impurities and defects in the material. It is used extensively by crystal growers to evaluate semiconductor growth techniques and to study the physics of radiative recombination. Hopefully, this discussion has helped introduce photoluminescence spectroscopy to the non-specialist.

References

1. R.A. Smith, Semiconductors, (University Press, Cambridge, 1964), chapter 1.
2. M.M. Cirovic, Semiconductors : Physics, Devices and Circuits, (Prentice Hall, New Jersey, 1971), chapter 1.
3. S.M. Sze, Semiconductor Devices : Physics and Technology, (John Wiley and sons, New York, 1985).
4. B.J. Skromme, Thesis : Low Temperature Photoluminescence Characteristics of High Purity Gallium Arsenide and Indium Phosphide, (1984).
5. D.J. Ashen, P.J. Dean, D.T.J. Hurle, J.B. Mullin, A.M. White, and P.D. Greene, *J. Phys. Chem. Solids* **36**, 1041 (1975).
6. A.M. White, P.J. Dean, L.L. Taylor, R.C. Clarke, D.J. Ashen, and J.B. Mullin, *J. Phys. C* **5**, 1727 (1972).
7. S.G. Bishop, *S.P.I.E.* **276**, 4 (1981).
8. P.J. Dean and D.C. Herbert, in Excitons, edited by K. Cho, (Springer-Verlag, New York, 1979), chapter 3.
9. H.B. Bebb and E.W. Williams, in Semiconductors and Semimetals, edited by R.K. Willardson and A.C. Beer, (Academic, New York, 1972), Vol. 8, chapter 4.
10. R.J. Almassy, D.C. Reynolds, C.W. Litton, K.K. Bajaj, and G.L. McCoy, *Solid State Commun.* **38**, 1053 (1981).
11. M. Ozeki, K. Nakai, K. Dazai, and O. Ryuzan, *Jpn. J. Appl. Phys.* **13**, 1121 (1974).

12. P.J. Dean, Prog. Cryst. Growth Charact. 5, 89 (1982).
13. Y Seki, K. Tanno, K. Iida, and E. Ichiki, J. Electrochem. Soc. 121, 1108 (1975).
14. T.S. Low, B.J. Skromme, and G.E. Stillman, in Gallium Arsenide and Related Compounds, 1982, edited by G.E. Stillman, (Institute of Physics, Bristol, 1983) p. 515.
15. K.L. Hess, P.D. Dapkus, H.M. Manasevit, T.S. Low, B.J. Skromme, and G.E. Stillman, J. Electron. Mater. 11, 1115 (1982).