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Approaches Toward a Blue Semiconductor Laser

I. Ladany
Planning Research Corporation
Aerospace Technologies Division
Hampton, Virginia

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ABSTRACT

This paper surveys approaches which can be used to obtain semiconductor diode laser action in the blue region of the spectrum. Included is a discussion of diode lasers in general, and a review of the current status of "visible" emitters, presently limited to about 670 nm. Various methods are discussed for shifting laser emission toward shorter wavelengths, including the use of II-VI materials, the increase in the bandgap of III-V materials by additions of low atomic number elements, for example nitrogen; changing the band structure from indirect to direct by incorporating interstitial atoms or by constructing certain superlattices. Non-pn-junction injection methods are surveyed, including avalanche breakdown, Langmuir-Blodgett diodes, heterostructures, carrier accumulation, and Berglund diodes. A discussion is given of the prospects of inventing new multinary semiconducting materials, and a number of novel materials described in the literature are tabulated. New approaches available through the development of quantum wells and superlattices are discussed, including resonant tunneling, which may have applications to materials not having pn-junction capability, and the synthesis of arbitrary bandgap materials through multiple quantum wells. Also included is a review of the current status of some materials often considered in discussions of semiconductor lasers or emitters (SiC, ZnO, ZnS, ZnSe, GaN and InN, Diamond, CdS).

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SUMMARY

Short wavelength lasers, especially in the blue spectral region, are of interest wherever high power density is to be delivered to a surface, for example in laser recording devices. This report attempts to survey various approaches available for making such a device. Beginning with a review of the main properties of diode lasers which make them attractive in such applications, the discussion covers the state of the art in diode lasers, currently limited to about 670 nm. This limitation arises out of the lack of semiconductor materials having the requisite bandgap while being capable of both p- and n-type doping to high levels. Certain II-VI materials, for example ZnO, ZnSe, and CdS, have the required bandgap, and have been made to lase using electron beams and other methods; however, they cannot be made to have efficient p-n junctions. A section of this report therefore deals with alternate injection mechanisms which might be applicable to such materials. Although some of these are found to be promising, none are as efficient as p-n junctions.

Consideration is next given to modifications which might be imposed on existing laser materials to make their emission reach the desired wavelength. These include increasing the bandgap by additions of low atomic number elements, e.g., nitrogen to III-V materials, such as GaAlAs, the possibility of making ambipolar II-VI materials through use of non-equilibrium growth methods, and the change of bandstructure from indirect to direct, by for example constructing superlattices using GaP and AlGaP, or

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by the incorporation of interstitial atoms into a suitable crystal, also typically GaP.

The next section examines the possibility of inventing (or discovering) new multinary compound semiconductors, and concludes that the number of possible direct bandgap compounds with bandgaps in the 2.5-3.0 eV region is very large.

Evidently, this field will prove to be extremely fruitful in the future, although it will also require a significant effort.

A more direct approach to the possibility of developing new materials is to consider some of those which have already been studied, but which have so far not been successful. A table of such materials, binaries, ternaries and a few quaternaries, provides a listing some of the pertinent data, such as bandgaps and crystal structures. Examples are CdGa_2S_4 , CuGaS_2 , and $\text{ZnSe}_{1-x}\text{Te}_x$.

Another approach consists of constructing devices incorporating p- and n-type heterostructures between dissimilar materials. This process has never been successful in the past, but new insights obtained in recent years in the field of strained layer structures combined with new methods of growth, could lead to ways of overcoming the lack of p-doped materials which has limited the usefulness of II-VI compounds.

Two sections, one on frequency multiplication and one on electron beam pumped lasers, are included in order to cover these very active fields, although neither of them is attractive as a substitute for diode lasers.

Quantum well lasers and superlattice structures are surveyed, and it is shown that they offer improved performance and the

possibility of novel developments, such as new injecting methods and the synthesis of desired bandgap materials.

The final section of the report consists of a survey of the present state of development in a number of materials sometimes thought of as promising light emitters. These include SiC, ZnO, CdS, ZnSe, GaN and InN, and Diamond.

Section I.

INTRODUCTION

The possibility of developing a shorter wavelength diode laser is attracting the attention of a number of laboratories throughout the world. Besides applications which particularly require such wavelengths (strong or weak absorption in specific regions), the advantage of shorter wavelengths resides in the greater power density which such a laser can deliver into an optical system.

The main objective of the present study is to provide a survey of devices which have the potential to generate such short wavelength laser radiation in a solid-state diode structure. The ideal device fitting this description would be a laser similar to the well-known AlGaAs heterostructure type, but emitting in the blue region of the spectrum. Such a device would operate at room temperature at a current of less than 100 mA, with a bias of about 2.5 volts. Although this device cannot now be made, continued efforts in this direction are likely to lead to eventual success. It is hoped that the present report will provide an outline of the various ways this goal can be pursued.

The principal reason for NASA's interests in these short wavelength lasers is their use in recording applications¹. Currently, studies of erasable optical recording seem to be aimed at three different approaches: magneto-optical (MO), dye-polymer (DP), and phase change (PC). Of these, MO appears to be the most advanced, but the other two are also being pursued intensively.

In magneto-optical recording, the laser heats a small region on the disc, and a coil is used to align the direction of magnetization in this region. For read out, a polarized light beam is needed to sense the state of polarization. Thus, a higher power source of light which need not be polarized, and a lower power source which must be polarized are required for the operation, and this is clearly available from a single laser whose power can be modulated by varying the applied current. For the PC method, in which the reflectivity of a suitable material is changed by taking it from the crystalline to the amorphouse state, the light source is used to generate the required amount of heat only. Similarly, in the DP method, a plastic film is distorted through the application of heat, again imposing no requirements on the polarization of the light source. It must therefore be allowed, that there may be ways of achieving rapid optical recording using non-lasing light sources, provided they are intense enough and have a short enough wavelength². Nevertheless, a laser beam has a much higher radiance, and is therefore more efficiently focused into a spot. In this review we will, therefore, be mostly interested in direct bandgap materials capable of generating stimulated emission in semiconductors, although occasionally there will be mention of indirect materials if they have some especially interesting properties.

Excluded from this survey are large classes of lasers, such as gas lasers, ion lasers, dye lasers, excimer lasers, and flash-lamp pumped solid state lasers, the exclusion being due entirely to their large size and low efficiency. However, it is recognized that the distinction is not well defined, and that in the future

some heretofore excluded lasers may have to be considered. Partly because of their position at the border between these two classes, we include electron beam pumped lasers and diode-pumped frequency-conversion lasers in this review.

Using the AlGaAs laser as a model, it is possible to state the requirements for developing a useful laser in a new wavelength regime. Mainly, this will require material with a direct bandgap of the correct magnitude, the ability to make p-n junctions, and the ability to achieve high doping levels with high electrical conductivity.

Looking at III-V compounds used in all currently successful structures, it appears that there are none capable of satisfying all of these requirements. Thus the only III-V material known to have a large enough direct bandgap is GaN, although it lacks a number of other properties from the list, particularly that of forming p-n junctions. The prospects for this as well as a number of other materials, especially compounds of the II-VI composition, would be much improved if other injection processes not based on p-n junctions could be used. It seemed useful, therefore, to include a review of various non-p-n junction injection mechanisms described in the literature.

A part of this review deals with possible approaches toward modifying existing lasers in suitable directions, for example by modifying III-V materials through additions of nitrogen. A section is devoted to a listing of relatively new materials discussed in the literature, which show some promise of yielding shorter wavelength lasers.

The last class of devices to be considered are based on

quantum wells (QW), superlattices, and their prospects in the development of short wavelength lasers. The concluding section of the review deals with a number of materials which were at one time considered promising, and which for various reasons have not yet lived up to their potential. This includes diamond, GaN, InN, SiC, and a series of compounds from columns II-VI: ZnSe, ZnS, ZnO, and CdS.

Section II.

THE DIODE LASER

A laser light source has certain unique properties: emission in the form of a fairly tight, linearly polarized beam with a narrow range of wavelengths. Further, the phase front of the beam along the axis of propagation is approximately planar, and the beam intensity distribution is Gaussian and lends itself to efficient focusing into a small area. Furthermore, the laser as a source of light is very efficient. Thus, overall power efficiencies (light power out divided by electrical power in) for diode lasers can exceed 50 percent, a value unmatched by any other light source. It is for these reasons that one wishes to apply laser technology in various areas, including that contemplated in this work, the recording of data.

A. BASIC STRUCTURE OF THE DIODE LASER

In order to construct a laser it is necessary to produce an excited state with an inverted population, and this population must be capable of returning to the equilibrium state through

giving up energy in the form of light. The process of light generation in semiconductors is called radiative recombination. The excited state of electrons or holes can be produced in different ways, for example by optical pumping (flash lamp), by bombardment with an electron beam, or by the injection of minority carriers by means of a p-n junction. Whatever the method, the excited electrons must also be placed into an optical resonator which selects some particular mode into which optical energy will be continuously fed by the recombining electrons.

A simple structure of a diode laser is shown in figure 1. The active layer, where recombination takes place, is GaAs, and this layer is surrounded on two sides by layers of AlGaAs. These two layers have a lower refractive index than GaAs, and a higher bandgap - these characteristics serving to contain both electrons and photons within the GaAs slab. The optical resonator is formed by cleaving the ends of the crystal to give two perfectly flat and parallel surfaces, having a reflectivity of about 30 percent. The lateral boundaries in this structure are the sides of the slab, which is not a desirable arrangement for various reasons. Improvements are effected by a) restricting the current flow to a narrow region in the middle of the slab through use of a stripe contact, b) by reducing the size of the active region in the lateral direction by etching out a mesa, c) by building in refractive index steps in the lateral direction, and d) by introducing back-biased junctions in the lateral direction in order to restrict the current flow exclusively to the center portion.

Any and sometimes all of these techniques are used in the same device, and their effect is to concentrate the current, the

injected carriers, and the generated photons into the smallest possible volume. The exact form of these lateral modifications is not important for the present purposes; it is sufficient to assume that one can always introduce some form of lateral confinement by the proper application of technology.

A light-output-power versus current-input curve of a typical laser with some lateral confinement is shown in figure 2. The value of the current where the light output begins to increase rapidly is called the threshold current, and that value divided by the active area is the threshold current density. The threshold current shown is about 20 mA; some commercially available units have a threshold current of a few mA. If one knows or if one can estimate the size of the active area, the threshold current density provides a way of comparing the quality of different lasers. For sustained performance, this value should be well below 2000 A/cm²; in the better lasers it is below 1000 A/cm², and in the latest quantum well lasers it can be less than 250 A/cm². The lower this value, the more efficient the laser and the more power can be generated with it (although this may require that the geometry of the structure be designed for that purpose).

The quantum well laser is a radical modification of the structure discussed so far, based on making the active layer extremely thin (say 5 nm). These lasers, and the related superlattice lasers, will be discussed further below.

B. STATE OF THE ART IN DIODE LASERS

The present section offers a review of the state of the art in short wavelength injection lasers. As will be seen, these lasers are rapidly approaching commercial exploitation, and are likely to displace He-Ne lasers in many applications. However, their wavelength is in the vicinity of 670 nm.

1. AlGaAs Lasers

The emission wavelength of an AlGaAs laser can be changed by increasing the ratio of Al to Ga. This is a consequence of the fact that the bandgap of the alloy increases with increasing Al. In order to maintain the bandgap and index steps at the hetero-interfaces, it is also necessary to increase the Al concentration in the cladding layers. The limiting aluminum concentration in the active layer is that for which the material becomes indirect³, which, according to figure 3, corresponds to an Al mole fraction of 0.38 and a bandgap of 1.96 eV. However, various difficulties arise as the bandgap approaches this value, such as an increase in threshold; and what is more serious, the operating life also appears to decline with increasing aluminum content. It seems that the shortest wavelength achievable using DH lasers in this system without any effect on device design or performance is near 720 nm.

Progress in AlGaAs has been achieved by using quantum wells (see Section VIII below). The first step in the realization of this structure is to make the active layer extremely thin, typically 3-5 nm. This already requires a profound change in the crystal growth apparatus, since liquid-phase-epitaxy (LPE) is not

capable of providing the layer flatness and uniformity required. Rather, one uses organo-metallic vapor phase epitaxy (OMVPE) or molecular beam epitaxy (MBE). Another modification is made in the structure outside the active region, which in these devices consists of a graded index region serving the purpose of further confining the radiation to the vicinity of the active region⁴, while discouraging higher-order mode excitation (see figure 4). The single, very thin layer in a quantum well laser can also be replaced by a stack of alternating high and low bandgap layers, forming the multiple quantum well laser, further discussed in Section VIII. Using such graded index quantum well lasers, a threshold current density of approximately 1.1 kA/cm^2 was obtained at 680 nm, but no data was supplied concerning life⁵.

2. InGaAsP

The active layer here is composed of the same elements as the long wavelength (1.3 and 1.5 μm) communications lasers. However, the proportions are different, and the lattice constant of InP does not match the lattice constant of InGaAsP having the bandgap corresponding to this wavelength. In order to have a strain-free system, the cladding has to be InGaP, which is grown on a suitable composition of GaAsP⁶. A threshold current density of 4.5 kA/cm^2 and a threshold current of 56 mA were obtained at 671 nm.

3. AlGaInP

This material is also a promising candidate for short wavelengths, and can be taken as a derivative of the InGaP system. At a wavelength of 662 nm, a threshold current of 120 mA and a

threshold current density of 6.7 kA/cm^2 were obtained⁷.

4. Quantum Well InGaP/AlGaInP

This laser is composed of multiple InGaP wells and AlGaInP barrier layers⁸. The threshold current and threshold current density are 70 mA and 3.5 kA/cm^2 respectively, at 668 nm. Another recent result, in the same system, is a threshold current of 55 mA or 4.4 kA/cm^2 at 646 nm⁹. Work with optically pumped lasers suggests that the AlGaInP QW system could be pushed to a wavelength as short as 625 nm¹⁰.

A summary of these results is presented in the table below:

TABLE 1: Recently Published Results
for Short Wavelength Diode Lasers.

System	J_{th} (kA/cm^2)	Wavelength (nm)
AlGaAs QW	1.1	680
InGaAsP	4.5	671
InGaAlP	6.7	662
InGaP/InGaAlP QW	3.5	668
	4.4	646

The best threshold results seem to have been achieved in the AlGaAs system. Nevertheless, probably because of reduced life, visible lasers now becoming available commercially are based on InGaAlP.

Table 2 shows properties of those lasers advertised by NEC and Toshiba:

Table 2: Visible Diode Lasers
Available Commercially.

composition	InGaAlP
threshold current	76-100 mA
rated power	3 mW
wavelength	670 nm
life	>2500 h @ 3 mW, 50 C

Section III.

INJECTION MECHANISMS

Carrier injection in typical semiconductor lasers occurs via p-n junctions. This method appears to be the most efficient known, in the sense of requiring the smallest power consumption for its operation¹¹. However, there are presently very few semiconductors which are capable of supporting p-n junctions while possessing the required bandgap value for short wavelength emission. This is thought to be a consequence of the low enthalpy for vacancy formation¹², these vacancies often acting as electrically active centers which can compensate the usual doping impurities. The general tendency for wide bandgap semiconductors (for example CdS, ZnS, ZnSe) is that while n-type materials can be obtained, it is difficult to obtain significantly doped p-type material. It appears, therefore, that progress in developing shorter wavelength lasers using such materials may require the introduction of minority carriers without benefit of p-n junctions. (It must be pointed out that more recent developments suggest that this situation may be changing; see for example the section

dealing with ZnSe below). The importance of these non-junction methods comes about because, in the words of H. Hensch¹³, "any nonequilibrium situation that involves an excess of carriers can support luminescence". As will be discussed later on, there is evidence that such non-junction injection methods have already been used to make a diode laser (although an unstable and short-lived one).

The present section provides a brief review of p-n junctions, followed by a discussion of a number of other methods which may be used to introduce excess carriers into semiconductors.

A. P-N Junction

Carrier injection in a p-n junction can be visualized as follows: consider an n-type and a p-type sample of semiconductor material brought together at an interface. This causes electrons to diffuse from the n-side into the p-side, and holes to diffuse from the p-side into the n-side, thereby uncovering the charge of the fixed dopants built into the material, the space charge. The space charge in turn generates an electric field across the junction region, which causes a drift of carriers across the junction, in opposition to the diffusion of carriers. In equilibrium, the net current across the junction is zero, and this requirement then determines how much space charge there will be. By this means one obtains a potential barrier to the motion of carriers, i.e. no carriers in addition to those required to establish equilibrium can flow across the interface.

When a forward bias is applied to the structure, the electrostatic potential across the junction is reduced, thus reducing

the drift current. The effect of this is that the current due to diffusion predominates, and extra minority carriers traverse the junction and show up on the other side.

The process is controlled by the requirement for current continuity across the barrier, together with charge neutrality in some regions, and built-in fields in others. The extra carriers appearing across the junction are available for use, for example to drop down to the valence band, and in so doing emit light.

Although this description is generally valid and leads to quantitative formulations for carrier injection, it is also cumbersome when a number of structures are to be compared. A much simpler, qualitative approach is to use band diagrams, which will be illustrated in the case of p-n junctions, and thereafter used to discuss other injection mechanisms as well.

Figure 5(a) shows the structure of a p-n junction diode without applied bias, the corresponding energy band diagram, and the Fermi level (a line marking that energy level which has a probability of 0.5 of being occupied by electrons). The principal requirement in drawing these bands is that the Fermi level with no applied bias has to be flat across the interface between the two materials. Figure 5(b) shows the same structure under a forward bias of V_f . Now the Fermi level shows a displacement equal to the applied voltage multiplied by the electronic charge, q (assuming no voltage drops across other regions of the device). For an intrinsic (lightly doped) semiconductor, the Fermi level is near the center of the bandgap, and for a well doped n-type semiconductor, the Fermi level moves up to or even past the edge

of the conduction band. Thus, the position of the Fermi level indicates the doping level. Injection of carriers is indicated by the height of the energy barrier that carriers must overcome, and by the concentration of carriers available for climbing the barrier. Thus, in figure 6(a), we see the barrier for holes and electrons is approximately the same, and the availability of carriers is also about the same, as indicated by the position of the Fermi level relative to the band edges. Therefore, the amount of hole and electron injection will be about the same, as indicated by equal-sized arrows. In figure 6(b), showing an unsymmetrically-doped junction, the barrier height (from the Fermi level to the band edge) is different, and the availability of electrons is much lower, as shown by the deep position of the Fermi level on the n-side. This structure will have mostly hole injection.

B. Schottky Barrier

This is the interface between a metal and a semiconductor. The semiconductor is described as in Section I above, but the description of a metal requires some new terms¹⁴. Referring to figure 7, we first note the energy difference called the work function, which is the energy required to take an electron from the Fermi level clear out of the metal (this is taken to be the vacuum level). The work function for a semiconductor (or any other material) will in general have a distinct value. Under equilibrium, the band structure will appear as shown in figure 7(a), where we see that the Fermi level is flat. The semiconductor electron affinity is the energy difference between the

vacuum level and the conduction band edge. The vacuum level in equilibrium must always be drawn without interruptions, and it must be parallel to the band edges. The barrier between the metal and the semiconductor is given by the difference between the metal work function and the semiconductor electron affinity, and should thus increase with the metal work function. It should therefore be possible to obtain a wide range of barrier heights by using metals with different work functions. In practice, the metal work function only exerts a minor effect on the barrier height because of states on the semiconductor surface, so that the barrier is largely determined by the semiconductor alone.

Figure 7(b) shows the Schottky barrier under forward bias. It is apparent that electrons will be injected into the metal, resulting in no increase in the net carrier concentration in the semiconductor. At large forward bias there can be significant minority carrier injection, but it is not possible to obtain this while maintaining a high donor concentration in the semiconductor.

C. Metal-Insulator-Semiconductor (MIS) and Metal Oxide Semiconductor (MOS) Devices

These devices are related to Schottky barriers, the difference being the presence of an intermediate oxide or insulating layer. In general, there is again no injection of carriers in such a device, its utility coming as a method of controlling the electric field. However, a special version of this structure is discussed next.

D. Langmuir-Blodgett or Tunneling-MIS Devices

If the insulating layer in an MIS device is made thin enough,

there exists the possibility of minority carrier injection, i. e. injection of holes from the metal into the semiconductor. One method of depositing such films is based on the work of Langmuir and Blodgett with thin organic films, and some of the recently described light emitting devices of this type are called Langmuir-Blodgett diodes¹⁵. An analysis of the mechanism has been presented by Card and Rhoderick¹⁶. Figure 8(a) shows a relatively large step between the metal Fermi level E_f and the valence band. Under a forward bias the metal Fermi level remains pinned at the surface. When an insulator is applied between the metal and the semiconductor the situation changes as shown in figure 8(b). Now part of the applied bias develops across the insulator, the metal Fermi level can move, and the energy step between the metal and the valence band is reduced, thus favoring the injection of holes into the semiconductor. Ordinarily this would not lead to any current flow, but tunneling through very thin insulators, on the order of 10-50 nm, is possible and produces significant hole injection. It can be seen that the two mechanisms, barrier lowering and tunneling, require a thick insulator for the first case, and a thin one for the second. Injection efficiencies as high as 0.2 have been obtained in such electroluminescent devices, although the current density was well below 1 A/cm².

In order to construct a laser based on the tunneling-MIS process it will be necessary to a) greatly increase the current density, or b) use a very efficient material not requiring high current densities, such as a II-VI compound, or c) use a radically different geometry to increase the injected carrier density.

E. Heterojunction Barrier

This structure refers to the junction of two materials having different bandgaps. A typical device might be the AlGaAs/GaAs interface shown in figure 9(a). The spike ΔE_c and the discontinuity ΔE_v arise because of the differences in the bandgap on the two sides of the interface. Both of these can be minimized by some grading of the junction, and indeed, are not very prominent in the case of AlGaAs/GaAs and InGaAsP/InP. Nevertheless, they are thought to be the reason for the failure in many other heterostructure devices. Figure 9(b), which indicates the same structure under forward bias, shows that very strong electron injection into p-GaAs can occur, with at the same time, reduced hole injection into the n-type AlGaAs. This effect is taken advantage of in double heterostructure lasers to build up the carrier density in the active layer. Heterojunctions can also occur between two quite dissimilar materials. This subject will be taken up separately in Section V.

F. Electron Beam Injection

When energetic electrons impinge on a semiconductor material, they enter the lattice, contributing to the majority carriers present, but in addition they also ionize a large number of atoms and create electron-hole pairs above the equilibrium concentrations. The recombination of these pairs leads to light emission which is usually very similar to that produced in the same material by minority carrier injection across a p-n junction (differences can arise due to the additional excitation of high energy photons arising from other recombination paths).

Typical electron energies are between 20 and 40 keV. The average energy required for generating a hole electron pair is about three times the bandgap energy, or 8 to 10 eV in the present case. This also means that most of the energy put into the material is wasted as heat and only about 30 percent is useful in generating carriers. Finally, it should be noted that typical electron beam current densities are on the order of a few A/cm², and typical threshold carrier concentrations generated in the material by such a beam are similar to those of conventional p-n junction lasers, i.e. on the order of 10¹⁸-10¹⁹ cm⁻³. It is believed that every p-n junction laser can be excited by using an electron beam, and an electron beam can also excite a number of materials not amenable to p-n junction fabrication.

G. AC Electroluminescence

This mechanism is the one operating in phosphors used in various flat panel displays. Since these phosphors consist of materials like ZnS, the mechanism of their excitation clearly touches on the issues considered important for diode lasers. In discussing these devices one has to consider the process of "forming" which usually precedes their use, and which plays a profound role in the mechanism. According to the discussion by Dean¹⁷, a typical ZnS EL cell consists of ZnS particles coated with Cu_xS, sandwiched between two electrodes, one of which is optically transparent. During forming, a high resistance region is formed within this cell, near one of the electrodes, due to the migration of copper within the cell. The high electric field in this region, caused by the applied voltage, results in

electrical (avalanche) breakdown within the ZnS. The luminescent centers associated with the dopant (activator) such as Mn or Cu or Cl, then capture these carriers which emit radiation upon release.

It is to be noted that for electron-beam pumped lasing in similar materials, e.g. ZnS, very lightly doped or pure crystals are used. Thus, the excitation process involves the lattice and band to band recombination. In AC electroluminescence, an activator is required, just as for LED's made from indirect materials, like red-emitting GaP. In direct materials suitable for lasers, no activator is required, since the mechanism is band-to-band recombination.

H. Carrier Accumulation

This process is the increase of minority carriers above the equilibrium value, which occurs when a drift field accelerates minority carriers toward an electrode or other barrier, which prevents them from escaping¹⁸. It seems that local carrier excesses can be obtained this way, which should yield electroluminescence in suitable materials, even without p-n junctions¹⁹. However, the process is inefficient compared to a p-n junction, because of the power consumed in creating the drift current.

I. Spark Gap Excitation

This process is based on developing an RF or DC spark across an electrode held a small distance away from the semiconductor, both being placed in a vacuum or some other insulator. The excitation is due to electrons generated in the spark discharge which pump the semiconductor²⁰. This method, therefore, while similar to electron beam pumping, removes the need for a vacuum tube, a

thin window, and a focusing element, but it leaves open the question of laser life due to the deleterious effects of the bombardment. The mechanism of excitation may be more complicated than stated above, since the emission differs in a fundamental way from that obtained in similar materials by E-beam excitation. Thus, in some cases²¹, the material is only excited in thin filaments along certain preferred orientations, a process discussed in a number of Soviet publications under the name of "streamer" lasers²².

J. Avalanche Multiplication (Impact Ionization)

In this process¹⁴, available carriers are accelerated by a high electric field, and then cause impact ionization of the material. The resultant hole-electron pairs are also accelerated and cause impact ionization and hole-electron pair creation, the process rapidly building up and resulting in a high carrier concentration available for radiative recombination. Even though the efficiency of the process is generally low, it is the origin of light emission in many intractable materials, for example Mn-doped ZnSe, NaI, and KI¹³.

K. Berglund Effect

This involves the application of an alternating voltage across an electrode separated from the semiconductor by an insulating film, essentially a MIS structure. Carriers are generated by avalanche multiplication during one half cycle, and allowed to diffuse into the semiconductor and recombine during the other half cycle²³. It is therefore an AC method, but it is capable of stable emission, as demonstrated for GaP. A study of

the power efficiency of this process shows that it has between 1/5 and 1/10 of the efficiency of a p-n junction¹¹.

In conclusion, it can be stated that p-n junctions remain the most efficient devices for carrier generation. However, other methods, for example avalanche multiplication, may eventually provide an alternative approach, provided that sample heating and thermal runaway can be controlled.

SECTION IV.

LASER MATERIALS

A. Modifications of Existing Materials

The most direct approach which can be taken toward obtaining short wavelength lasers is to look for relatively simple modifications which could be applied to currently used laser materials. The advantage of this method is that one hopes to have many of the requirements already satisfied by the "standard" structure, so that only one new property needs to be obtained.

Before proceeding it might be useful to restate, in a slightly more precise way, the basic requirements one wishes to have satisfied by any new laser material:

- 1) The material should be an ambipolar semiconductor.
- 2) The bandgap must be at least 2.5 eV at room temperature, and should not be greater than 3.0 eV.
- 3) The bandgap should be direct.
- 4) There should exist a "compatible" material, to be used for carrier and optical confinement, which has approximately the same crystal structure and lattice constant, but a higher

bandgap and a lower refractive index.

5) There should be available a bulk crystal material or an epitaxial layer which can be used as a substrate, and which has a lattice constant and crystal structure similar to that of the active layer.

6) It should be possible to dope the material (both p- and n-type), to levels exceeding 10^{18} cm^{-3} , with a mobility above $100 \text{ cm}^2/\text{volt sec}$.

7) The material should have adequate thermal conductivity, on the order of that for GaAs (0.5 W/cm deg C).

With these requirements in mind, one may be looking for a) materials obtained through an increase of the bandgap in existing laser materials, b) materials generated through the modification of an existing large bandgap semiconductor so as to yield both n- and p-type conductivity, and c) the modification of an existing indirect material with p-n junction capability and efficient radiative recombination, so as to have a direct bandgap.

a) Bandgap Increase

It is known that the replacement of an element of a compound semiconductor by an element of lower atomic number in the same column of the periodic table causes the bandgap to increase²⁴. (A well known example is the partial replacement of Ga with Al in GaAs, or of As by P in AlGaAs.)

In considering such replacements, it is reasonable to start with a well-behaved material, such as AlGaAs, and to consider additions of the lightest elements from columns III and V, Boron or Nitrogen. The difficulty here is metallurgical, compounds of

these elements proving intractable by conventional growth methods. GaN itself is not under good control at present; however, AlN and GaN have been grown as films²⁵, and films of AlGa_N²⁶ have also been made, and these show strong cathodoluminescence and a direct bandgap. However, the value of the bandgap is much too large, being above 4.4 eV, which would make efficient injection less likely. A theoretical study of AlGaAsN has been presented²⁷, the calculations showing that the bandgap is direct over a broad range of values, depending on the composition. In general, these results suggest that modest lattice incorporations of nitrogen into well known laser materials are possible, although it may require new approaches in crystal growth to achieve this.

The growth of boron containing compounds appears somewhat more difficult²⁴. Boron phosphide is a translucent crystal of the sphalerite structure, which is also the structure assumed by boron arsenide. Thus, the prospects for bandgap modification using B are somewhat more distant than those using N.

Additions of N and B may also be considered in GaAsSb and its alloys, but this seems less promising because of the smaller bandgap of the starting material.

To summarize, the incorporation of nitrogen into existing, well studied materials, such as InGaAsP or AlGaAs, seems feasible, although the metallurgical problems may not be trivial.

b) Attainment of p-n Junctions in Wide Gap Materials

The main interest here is in the modification of II-VI compounds which have all the desired attributes except that they cannot be made p-type. Good examples are ZnO, CdS, and ZnSe, all

of which have yielded excellent lasers under E-beam pumping, i.e. using a non-junction method for generating carriers.

It is a universal observation that the difficulty of obtaining ambipolar conduction (conduction by electrons and holes) increases with increasing bandgap. As mentioned earlier, this is generally felt to be due to the tendency for self-compensation, which is driven by the large energy gain from compensation and the small energy required for native defect creation.

Another possible difficulty arises because the usual acceptors are much too deep in the bandgap to be ionized at room temperature¹². However, Li is a shallow acceptor in CdS²⁸; it has also been used to obtain p-type doping and blue light emitting p-n junctions in ZnSe²⁹. Recently, using metalorganic VPE, p-type carrier concentrations of 10^{17} - 10^{18} cm⁻³ as well as light emitting diodes have been achieved³⁰. However, because of the tendency of Li to drift rapidly through most semiconductors, it is not yet clear whether this is a useful approach.

Since the tendency for self-compensation in wide bandgap materials is an equilibrium process, it may be possible to overcome it by using a strongly nonequilibrium growth process, such as MBE. Thus, new attacks on the growth of II-VI materials may prove fruitful.

In summary, there is a good possibility that many wide gap semiconductors, particularly those of the II-VI classes, may be successfully grown to have ambipolar conduction. However, it appears wise not to use a material with a bandgap unnecessarily large. The interesting candidates, from the present point of view, are materials showing efficient lasing under cathodo-

luminescence.

c) Conversion to Direct Bandgap

Although the modification of the band structure to produce a direct bandgap may appear difficult, alteration of the band-structure is not unknown, for example through the application of hydrostatic pressure. According to a recent analysis³¹, it was shown that a quantum-well superlattice composed of layers of an indirect semiconductor separated by suitable barrier layers should have a direct bandgap. The change in the bandstructure is attributed to the presence of the new periodicity of the superlattice. While there has been no experimental confirmation of this idea, it is true that AlGaAs/GaAs superlattice structures do show a reduction of the threshold for short wavelength devices, as expected if the direct/indirect crossover had been shifted to higher energies. On the other hand, the threshold reduction has also been explained on the basis of a more conventional analysis. What is wanted is a convincing demonstration of the concept, using an indirect material available in both conductivities, and known to be capable of efficient radiative recombination (such as GaP/-AlGaP or just AlGaP, where the two components of the superlattice could be obtained through changing the ratio of Ga to Al).

Another proposal, also based on a theoretical study, is to introduce small interstitial atoms into the sphalerite type lattice of a typical indirect semiconductor³². It was calculated that GaP, for example, would become a direct semiconductor through the insertion of helium atoms, although this structure was not considered to be stable. However, stable compounds of the I-II-V

type, such as LiZnP and LiZnN were also predicted to have a direct energy gap³³.

In summary, two possibilities have been mentioned for changing an indirect to a direct bandgap, and thereby achieving lasing transitions in suitable materials. Up to now, these possibilities have not been verified experimentally.

B. Prospects for the Synthesis of New Materials

It is certainly possible that new materials may be invented which will yield p-n junction type lasers at shorter wavelengths. The enormous success of compound semiconductors has shown that no penalty need be paid in using a multi-component material, compared to elementary or even binary compounds. Thus, InGaAsP lasers have been brought to a very high degree of perfection, in spite of early predictions of difficulties associated with non-radiative recombination. The two aspects of new materials to be discussed are the likelihood of there existing untried combinations of elements showing semiconductor behavior, and the likelihood of such a new material having a direct bandgap.

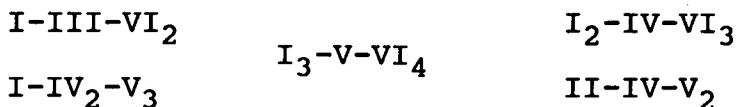
The question of how many semiconductors there are is one of considerable importance, which has been explored by several authors. Goryunova's rules²⁴ are based on the need to have a tetrahedral atomic arrangement in the lattice as this shows the covalent bond, characteristic of semiconductors. For the tetrahedral arrangement in diamond-like structures, the first rule is that the average number of valence electrons per atom must equal four. The second rule is that the binary analogues of group IV semiconductors must have a "normal valence", i.e. that the number

of electrons given up by the cation must equal the number of electrons needed to achieve a total of eight on the anion. These rules lead to three classes of binary compounds, namely III-V's, II-VI's, and I-VII's. If we assume that there are four elements in each column of the periodic table which participate in "interesting" compound formation, we obtain a total of 48 possible compounds in the binary series. Table 3 lists the total number of possible compounds for some higher multinary combinations, based on Goryunova's deduction of acceptable classes:

Table 3: Number of Possible Semiconductor Compounds.

Material type	Number of possible compounds
binary	48
ternary	320
quaternary	9472
quinary	43,008

It can be seen that the number of possibilities, without going beyond quinary, is already very large. The ternary classes are:



For the list of quaternaries and quinary, it is best to consult the original reference²⁴.

However, the above list is not yet complete, because there are also "defect" crystal structures which include vacancies in certain lattice positions. For these substances, the number of

valence electrons per atom need not equal four. Thus, a more general rule²⁴ is that the number of electrons per atom in binary compounds with possible semiconducting properties must be between 2 and 7, and this now includes both filled and defect type structures. For binaries, the expanded list of classes now numbers 23 instead of the previous 3, and the total number of substances will be a great deal larger than estimated above. Past experience also indicates that a large fraction of these compounds will have their bandgaps in the visible range, as long as elements near the first or second rows of the periodic table are used.

A more recent approach to similar problems, with slightly different rules is given by Mooser³⁴. In addition to the compounds crystallizing in the diamond, wurtzite or sphalerite structures discussed so far, he also considers transition element compounds crystallizing in the pyrite, marcasite and arsenopyrite structures, which may also show semiconducting behavior.

It is seen that the number of possible semiconducting compounds, when allowance is made for multinary structures and for classes of materials not previously thought of as semiconducting, becomes too large to be enumerated.

Predicting whether a hypothetical multinary compound has a direct bandgap requires extensive work. Van Vechten³⁵ has presented calculations of direct and indirect bandgaps of a number of binary, tetrahedrally coordinated compounds of the diamond, sphalerite and wurtzite structures. This approach, based on electronegativity differences, provides a very good estimate of the bandstructure of such compounds, and has been used to derive the crystal structure and bandgap of AlGaAsN²⁷.

For existing materials, this determination is usually made experimentally, through the study of absorption or electroreflectance spectra. Occasionally, if all available members of a certain class of compounds have a direct bandgap, one may expect that as yet unsynthesized members will have a similar band structure. In general, however, it requires detailed calculations to predict the bandstructure of new multinary compounds. It is likely, however, based on the experience obtained with existing materials, that a large number of new materials will have a direct bandstructure. Thus, the prospects for synthesizing new materials with desirable properties are very good, but it is difficult to make predictions concerning their composition.

The next section takes a different approach, necessitated by the difficulties discussed above, in providing a tabulation of materials culled from the literature. Among these are compounds which have shown promise as light emitters or lasers without having reached practical levels, and in general materials which might, after further development especially by using improved growth processes, become useful as short wavelength lasers.

C. A Table of Materials

Various compounds of interest in developing new laser materials have been described in the literature. The table below lists some of these, and for a considerable number of them also supplies the bandgap in eV, an indication of whether they are direct (D) or indirect (I), the crystal structure, and comments.

BINARIES

Material Class	Bandgap	D/I, structure	Comments	Ref. no.
II-V₂				
CdP ₂	2.1	I, chalcop.		36
ZnP ₂	2.14	I, chalcop.		37,37a
II-VI				
ZnSe	2.7	D, sphal./wurtz.	p-n junct., LED, E beam laser	29,30
CdS	2.4	D, sphal./wurtz.	E beam laser, diode? laser	39,40,41
CdSe	1.77	D, wurtz.	Opt.pump laser	41
BeTe	2.9	D, sphal.	unstable	37b
ZnS	3.8	D, sphal./wurtz.	E beam laser, LED	37c,37d
ZnO	3.25	D, wurtz.	E beam laser	118
ZnTe	2.3	D, sphal.	E beam laser	37e
III-V				
GaN	3.5	D, wurtz.	n-only; Be, Li, Dy are promising p-dopants	38,42
InN	1.9	D, wurtz.		43
BN	6.4	I, cubic	pn junct., LED in UV	44
BP	3(2)	I, sphal.		24
III-VI				
GaS	2.5	I, layered	injection EL @77K	45,46
GaS ₂	3.5	I		37
GaSe	2.1	D, layered		46,47

III ₂ -VI ₃			
Al ₂ S ₃	4.1	wurtz.	48
Al ₂ Se ₃	3.1	wurtz.	48
Ga ₂ S ₃	2.5	wurtz.	24,48
Al ₂ Te ₃	2.2	wurtz.	48
Ga ₂ Se ₃	1.9	sphal.	48
In ₂ O ₃	2.75	D, corundum?	37
Ga ₂ O ₃	2.5	I, corundum	37f
IV-VI ₂			
SnO ₂	3.6	D, rutile	37,37g

TERNARIES

Material Class	Bandgap	D/I, structure	Comments	Ref. no.
II-VI				
ZnS _x Se _{1-x}	2.9-3.0	D, sphal.	E beam las.@430 nm	49,50
ZnSe _{1-x} Te _x	2.3-2.7	D, sphal.	E beam laser ambipolar, weak EL	51
Zn _{1-x} Cd _x Se	2.6	D, sphal.	E beam laser	51
Zn _{1-x} Cd _x S	2.95	D, sphal.		50,51,52
CdMgTe	1-2.5		ambipolar,LED	53
CdSSe	2.1	D, wurtz.	opt.pump laser	41
III-V				
Al _x Ga _{1-x} N	>=3.5	D, wurtz.	sharp CL in U.V.	26
GaN _{1-x} P _x	< 3.5	wurtz.	n only	54,55
I-II-V				
LiZnAs	(2.1)			33

I-III-VI ₂				
CuAlS ₂	3.5	D, chalcop.	ambipolar, red PL	56
CuAlSe ₂	2.7	D, chalcop.	ambipolar	56
CuGaS ₂	2.5	D, chalcop.	orange EL, pn jun., las. 500 nm by opt. pump	57, 58, 59
AgGaS ₂	2.7	D, chalcop.	n-only, EL, CL, las. 462 nm by opt. pump	58, 60, 61
I ₂ -II-VII ₄				
Ag ₂ HgI ₄			yellow color	48
II-III ₂ -VI ₄				
ZnGa ₂ S ₄	3.18	D, stannite/ chalcop.		62
CdGa ₂ S ₄	3.58	D, chalcop.	ambip., EL, las. by E-beam	48, 62, 63
CdGa ₂ Se ₄	2.57	D, chalcop.	EL	48, 62, 64
CdIn ₂ S ₄	2.3	I, spinel	n, EL.	65
ZnIn ₂ S ₄	2.86	D, polytypes	layered, ambip.	48, 62
HgGa ₂ S ₄	2.79	D, chalcop.		48, 62
ZnGa ₂ Se ₄	2.17	D, stannite/ chalcop.		62
II-IV-V ₂				
ZnSiP ₂	2	I, chalcop.		66, 67, 68
CdSnP ₂	1.17	D, chalcop.	n-only; las. by opt. pump	69, 70
CdGeP ₂	2-5	D, chalcop.		66
CdSiP ₂	2.21	(D), chalcop.		71, 72
ZnGeP ₂	2.25	(D), chalcop.		71, 73
MgSiP ₂	2.24	D, chalcop.		74
MgSiN ₂ :Eu			green EL	61

CdMnSe	1.95	II-VI-VII		75
		D	opt.pump.las.638nm magnet. tunable	
III-V-VI				
(GaP) _{3x} ⁻ (Ga ₂ S ₃) _{1-x}	2.24-2.5		0.3 < X < 1	76

QUATERNARIES

Material Class	Bandgap	D/I, structure	Comments	Ref. no.
III-V				
AlGaAsN	>2	D, sphal.	theory only	27
II-III-VI₄				
CdInGaS ₄	2.7	I, layered	Red PL	77
II-III₂-VI₄				
Cd(InGa) ₂ S ₄	2.6-3.2	D, layered		78
ZnCdIn ₂ S ₄	2.76-2.86	D, layered	PL	79
II₃-III-VI₆				
Cd ₃ InGaS ₆	2.43	D, layered	green PL	77
Zn ₃ InGaS ₆	3.26	D		80
III-V-II-VI				
ZnSe-GaP	2.24-2.7	D, sphal.	ambipolar	81,82

SECTION V. HETEROSTRUCTURES

The interest in using heterostructures is that by this means one may construct a device using a p-type semiconductor of one material and an n-type of another, and thus hope to obtain minority carrier injection without having both p- and n-type doping in the same crystal. Thus, if one could deposit a wide bandgap p-type semiconductor onto a crystal of n-type ZnO, hole injection into ZnO might be obtained.

A difficulty with heterostructures is that a change in composition at the heterointerface usually creates a defect layer which causes nonradiative recombination, and thus reduced efficiency for the device³. This effect is characterized by a surface recombination velocity, S , which then plays a role in determining the laser threshold. If S is large enough, the threshold will be increased, and if it is below 10^3 cm/sec, its contribution to the threshold will be negligible³. The usual view of interface recombination is that it is reduced by selecting both materials to have the same lattice constant and crystal structure, as is the case with GaAs and various combinations of AlGaAs. According to this model, the thickness of the active layer also contributes to the effect, a thinner layer leading to increased surface recombination. It has been shown⁸³ that the recombination velocity at a presumably typical AlGaAs/GaAs interface is 450 cm/sec, in other words well below the critical value given above. However, as first pointed out by Ettenberg and Kressel⁸⁴, for active layers with thicknesses in the 50 to 100 nm range the low threshold current densities actually measured indicate that the recombi-

nation velocity has to be less than one would expect.

Recent studies⁸⁵ of a similar effect in quantum well lasers attribute the decrease of the interface recombination velocity to quantum phenomena occurring in thin layers, particularly the peaking of the electronic wave function at the center of the layer (well), away from the interfaces. Quantum well lasers may therefore show much more tolerance for faults at heterointerfaces than the lasers studied so far.

Another feature of heterostructures is the presence of an energy spike caused by the difference in bandgaps and work functions between the two sides of the structure⁸⁶. As shown in figure 9, this shows up mostly in the conduction band (for AlGaAs/GaAs), and is usually assumed to occur in the conduction band in other systems as well. As mentioned earlier, grading the transition region reduces the magnitude of these energy discontinuities. Nevertheless, their presence can impede the injection process, which is why one prefers heterojunctions with only a modest difference in bandgap energies.

It is clear that in regard to structural perfection, the AlGaAs/GaAs and the InGaAsP/InP interfaces satisfy the requirements imposed by laser operation. So far, no pairs of larger bandgap materials seem to have been found which show similar perfection. However, it appears that the losses at heteroboundaries in many novel systems have not been studied sufficiently to know if they can be reduced by special growth techniques.

The following table shows some heteropairs in the short wavelength regime which have been discussed in the literature:

Table 4: Short Wavelength Heteropairs.

Active layer	cladding layer	emitted wavelength	Ref.
AlGaInP	AlInP	550 nm	87
ZnSTe	ZnSe or ZnSSeTe	500 nm	87
ZnTe	ZnSe	540 nm	88
CdS	CuGaS ₂	510 nm	89

None of these structures have so far produced stimulated emission, nor do they approach the AlGaAs/GaAs system in efficiency. Thus, much work remains to be done in this area.

SECTION VI.

FREQUENCY MULTIPLICATION

Changing the output frequency of a semiconductor laser is another approach to obtaining short wavelength emission. Although this can be done by converting the diode laser output directly, most presently used devices go through an intermediate stage, in which the diode laser is used to pump a crystal laser, such as Neodymium YAG. (The reason for this is that the direct output of the diode laser does not possess the modal purity required for high conversion efficiency. Thus, diode lasers can mode jump, i.e. switch the wavelength; they may have a complicated lobe structure in the output beam which may change during operation, and their power output as well as wavelength depend on the temperature).

The diode-pumped YAG output is passed through a non-linear

optical material which generates the second harmonic frequency, with phase matching used for both the fundamental and the harmonic frequencies. One popular nonlinear optical material is MgO:-LiNbO₃, which can be placed inside the cavity. The YAG emission⁹⁰) at 1.047 μm is converted to 523.6 nm, but with two conversions; the overall efficiency is low. A schematic diagram of the arrangement is shown in figure 10.

Another recent result, using an external cavity for the doubler, is an output of about 30 mW at 532 nm from an input of 52.6 mW from a diode laser pumped Nd:YAG laser⁹¹. The overall power efficiency was on the order of a few percent. The highest output power yet reported is the achievement of 180 mW at 532 nm from a Nd:YAG laser pumped with several laser diode arrays combined via a fiber optic bundle⁹². The overall efficiency was 4.4 percent. Blue emission by frequency doubling has also been obtained. Thus, Matsushita Co. has reported direct conversion of 60 mW of diode laser emission to an output of 0.2 mW at 420 nm⁹³. Frequency doubling of a diode laser pumped Nd:YAG to 473 nm using KNbO₃ has yielded 3.1 mW⁹⁴.

Another scheme is to use frequency summing in a nonlinear crystal, the output from two lasers producing the sum frequency. Output in the blue, although at a small power level, has actually been demonstrated⁹⁵. This may have some advantage if the phase matching condition requires a particular frequency. Related to this scheme is parametric mixing in a suitable crystal, but this does not offer any obvious advantages.

A different approach is based on two photon pumping (also called upconversion), where for example, one photon pumps near

792 nm and the other near 840 nm, with laser output at 550 nm⁹⁶. The levels are provided by Er^{3+} in YAlO_3 . As both pump wavelengths are reachable with current diode lasers, this scheme may yet turn out to be useful. Two photon pumping has also been used to generate 380 nm lasing⁹⁷. Pumping of a suitable phosphor (for example $\text{LaF}_3:\text{Yb}$, Er) with multiple photons near 930 nm has been tested a number of years ago as a way of obtaining visible LED's^{98,99}.

SECTION VII.

ELECTRON BEAM PUMPED LASERS

All of the usual semiconductor laser materials can be excited with electron beams, and several II-VI materials, particularly CdS , CdSe , ZnSe , and ZnO , have been used to construct E-beam lasers. Because of heat dissipation problems, pumping is typically by 50 ns pulses.

The main objections to this method of laser pumping is the cumbersome high voltage supply, the need for a vacuum tube device to generate the electron beam, the limited life of the window for this beam, and questions about life in the semiconductor exposed to electron bombardment. The important question is whether these lasers are practical devices, i.e. do they meet the criterion of small size, easy modulation, and life?

Addressing some of these concerns, workers at Phillips Laboratories¹⁰⁰ have shown very small, sealed tube designs operating at room temperature. Very large power outputs have been obtained from electron beam pumped lasers (100 kW peak)¹⁰¹, and

the literature abounds in descriptions of devices.

Papers dealing with degradation processes in these lasers are more scarce. There appears to be a reversible degradation due to the charging of various impurity centers, and an irreversible process due to the generation (in the case of CdS) of sulfur vacancies¹⁰². Thus, the life is specified in terms of the irradiation dose, which can introduce damage (for 50 keV electrons) at a value as low as a few times 10^{17} electrons/cm². In addition there is a catastrophic degradation threshold at a laser output power of 0.2-3 MW/cm². These results are considered due to the faults in the quality of the CdS crystals used, so that there is hope of greatly improved life based on materials and engineering advances.

SECTION VIII.

QUANTUM WELLS AND SUPERLATTICES

If the active layer in a conventional double heterostructure injection laser is made thin enough, the carrier distribution and energy levels in this region become subject to quantum mechanical laws. Such a device is called a single quantum well (SQW) laser¹⁰³. The active layer is now looked on as a potential well, with energy levels quantized to a few allowed values selected out of the continuum of states in the standard bandgap model. In particular, since the lowest allowed level is above the minimum allowed without the well, the emission wavelength should be shorter. Some of the other advantages expected from this structure are a lower sensitivity to temperature, and a lower

threshold current. Figure 11 shows the first two energy levels in an infinite one dimensional potential well, and the first two levels in the more realistic finite well occurring in the semiconductor laser.

The dimension being considered is the layer thickness, which is also the growth direction. In this direction, there is only limited freedom of motion for carriers because of various restrictions due to the quantization; the carriers are free to move in the other two directions. Weisbuch¹⁰³ calls this a quasi-two-dimensional system, in contrast with true two-dimensional systems such as planar waveguides. A consequence of this restricted dimensionality is that the density of states is also restricted to a series of discrete values, as shown in figure 12. Therefore, the density of states function never reaches zero, even at low temperatures. Other advantages flowing from the restricted density of states function are a higher gain at low injection levels, a smaller gain dependence on temperature, a lower absorption coefficient in unexcited material at the lasing wavelength, and an overall lower value for the density of states function compared to the three dimensional case. All of these factors are such as to suggest that the threshold current in quantum well lasers will be reduced. However, the maximum possible gain is also reduced, implying that SQW lasers are more useful in high quality materials with few nonradiative centers.

The deposition of a series of thin layers of alternating bandgaps results in a multi quantum well (MQW) structure, which has the advantage that the net density of states (being the product of the one-well density of states by the number of wells)

is increased. It is possible to reach much greater population inversions in such devices. The optical overlap between the gain region and the mode in SQW tends to be very small, and this also can be increased by going to MQW's.

The design of quantum well lasers has been greatly advanced by Tsang^{4,104,105} in developing separate confinement heterostructures combined with a graded index region, both together being called the GRIN-SCH-QW laser (graded-index separate-confinement-heterostructure quantum-well).

This structure, briefly discussed in section II and shown in figure 4, combines the advantages of a single quantum well laser with the improved optical overlap caused by the index grade, to yield the most advanced laser structure available at present. Together with one or another scheme for lateral confinement, it has been used in many current devices with record setting performance. The demands for perfection in layer growth for these devices are severe, MBE being the growth method usually employed.

In the MQW's discussed so far, the layer thicknesses are assumed large enough to prevent interactions, but if the layers are thin, tunneling between them can occur. In this case, and assuming the layers are regular enough, there arises a new coherent structure called a superlattice state.

If the alternate layers are composed of materials of different bandgaps, then the superlattice assumes a bandgap which is intermediate between these two values, the actual value depending on the layer thicknesses. One can see therefore, that a material with any desired bandgap can be constructed. This has been demonstrated in InGaAsP, made up from alternating layers of

InP and InGaAs¹⁰⁶.

So far, superlattice devices have not shown the spectacular results of SQW or MQW lasers, but they are the focus of tremendous activity, particularly in areas where conventional approaches have been pushed to the limit. Stimulated emission has been obtained by optical pumping of superlattices composed of alternate layers of ZnSe and ZnMnSe^{107,108}. Emission was obtained in the 451-455 nm range at temperatures as high as 80 K. Based on a theoretical analysis, it has been claimed that direct optical transitions can be obtained in a certain superlattice geometry assembled from materials having only indirect transitions in their normal state³¹.

Doping superlattices are structures obtained by spatial modulation of doping (so called n-i-p-i structures)¹⁰⁹. In these, non-radiative recombination rates are strongly suppressed, compared to more moderate suppression of radiative recombination. Thus, the possibility exists that emission in some indirect gap semiconductors may be enhanced over that occurring in standard bulk geometries. It has also been speculated that such devices made from indirect material may be overcompensated to yield a direct bandgap¹⁰⁹.

Another new phenomenon is "resonant tunneling"¹⁰³. Referring to figure 13, this occurs when the Fermi level of the injecting material (GaAs) on the left side of a structure composed of two barriers and a quantum well, is at the same energy as the lowest allowed energy state of the well. This is achieved by applying the correct bias to the device, in which case there is a peak in the current flow through the structure, as demonstrated both

theoretically and experimentally. Resonant tunneling is the basis for a new approach to the injection of hot carriers, based on a staircase of energy levels obtained from a series of quantum wells with progressively changing widths. Carriers traverse each well by resonant tunneling and are able to enter the semiconductor at an elevated potential. Such a structure is called a "variable spaced superlattice"¹¹⁰.

As mentioned elsewhere, hot electron injection is a satisfactory method for excitation of many II-VI compounds, such as CdS, ZnO, ZnSe. Brennan and Summers¹¹¹ propose variable spaced superlattice injection into Mn activated ZnSe in order to obtain an electroluminescent display. The distinction between this and the requirement for stimulated emission in a similar structure may be one of geometry only. The reason for this is that besides the impact ionization of an activator center, which is the case in the above scheme, hot electrons may also ionize the crystal, and in so doing generate hole-electron pairs. These are soon thermalized and thus recombine across the bandgap in the usual way, producing near band edge luminescence or lasing.

Strained layer quantum wells or strained layer superlattices are obtained when there is a lattice mismatch between the layers which is not allowed to be accommodated through dislocations. This is accomplished by keeping the layers thin enough and thereby limiting the amount of strain energy built up. The lattice misfit is on the order of a few percent, and the layer thickness is typically less than 5 nm.

Besides further increasing the range of available materials combinations, new effects are expected to arise through the

tetragonal strains now occurring in the structure; for example the change of certain indirect gap transitions into direct transitions¹¹², a decrease or increase of the bandgap¹¹³, and the blocking of misfit dislocation motion by these strained layer superlattices. Strained layer quantum well lasers in InGaAs/GaAs have been made and their properties studied¹¹⁴. It appears that they are well behaved, with promising early life test results.

SECTION IX.

SPECIAL TOPICS

This section deals with certain materials which have been studied for some time, by many different groups, with the object of developing electroluminescent devices or lasers. Their inclusion here is in the nature of a status report.

A. SiC

A well known difficulty with this material is the great number of crystal structures which occur. The 6H polytype configuration has been much studied as an electroluminescent material because of its large bandgap and the ability to dope it both p- and n-type. It also has notable drawbacks, namely an indirect band structure, a tendency toward polymorphism, and great difficulties in growth.

This situation has been improved in recent years by growing it from the vapor or by LPE onto substrates of SiC obtained by other methods¹¹⁵. Using Al for the acceptor and N for the donor, a quantum efficiency of 0.01 percent has been achieved. Cathodo-

luminescence studies of p-n junction type diodes show spectra similar to those found in EL, with no evidence of stimulated emission. Injection electroluminescence has also been obtained from amorphous SiC¹¹⁶, but not at wavelengths as short as the blue.

None of the polytypes of SiC have a direct bandgap¹¹⁷, and the main interest in this material is therefore as a component in multinary compounds.

B. ZnO

This material is a semiconductor with a direct bandgap large enough (3.2 eV) to satisfy the requirements for blue emission. Unfortunately, it has not so far been possible to grow the material with p-type doping.

However, ZnO shows intense laser emission when excited by an electron beam¹¹⁸. In diode form, experiments have been reported for N-I-Metal diodes, where the N layer is ZnO and the I layer is obtained by oxidation of the crystal surface¹¹⁹. The emission has a peak near 5100 Å, and the external quantum efficiency is estimated to be on the order of 0.001 percent. The current-voltage characteristic is quadratic rather than the exponential characteristic of minority carrier injection.

A study has also been made of a Schottky (i.e. metal-semiconductor) diode¹²⁰. In this case the spectrum was much broader, and the efficiency was similar to the above value.

It seems reasonable to conclude that it is the lack of an efficient injection system which has hindered progress using ZnO. This material therefore becomes a prime candidate for experiments with novel injecting methods. It is also possible that p-type

material may be achieved through methods similar to those currently applied to ZnSe (new dopants, e.g. lithium, ion implantation, etc.).

C. ZnS

In this material it has also proven impossible to make well-doped p-type layers, thus precluding p-n junction devices. Blue emission was obtained from MIS type structures with a quantum efficiency of 0.05 percent¹²¹. Lasing was obtained at 345 nm using pulsed electron beam excitation¹²². Lawther and Woods prepared both Schottky type^{122a} and MIS type¹²³ diodes, the I region in the latter being generated by E-beam evaporation of ZnS. Electroluminescence at 445 nm was attributed to injection of holes from the metal into the semiconductor. The effect of different thicknesses of the I layer was also investigated. Efficiency was limited by shortage of minority carriers, and the devices were characterized by relatively high series resistance.

In the above study¹²³ and in a later one¹²⁴, it was shown that the electroluminescence is much weaker, or vanishes if there is no interfacial insulating layer, and that the peak brightness occurs for relatively thick I layers (500 Å or more). These findings suggest that the operating mechanism is much like the one discussed in the section on Langmuir-Blodgett diodes.

D. ZnSe

This is probably the most interesting compound semiconductor in the II-VI system. Its bandgap is 2.67 eV at room temperature, and it is direct, so that recombination is obtained through the efficient band-to-band process. It suffers from the usual problem

that p-type material is difficult to make, so that efficient p-n junction type of injection has so far not been realized.

In a fairly recent paper¹²⁵ it is shown that growth of ZnSe from Se solution yields p-type crystals, and that p-n junctions can be made by diffusing Ge into such material. Resultant diode properties appear entirely consistent with this interpretation. Edge emission at 480 nm was obtained at room temperature, and the intensity increased linearly with current in the range studied. No output efficiency is given, but the brightness of 2 mcd at 2 mA suggests that the efficiency was low. ZnSe can be made to lase at room temperature when excited with an electron beam, and when photopumped¹²⁶. Methods of growth of ZnSe (and ZnS), and of heterostructures on ZnSe films have been reported¹²⁷.

It has been shown that MOCVD grown films of ZnSe can be excited into stimulated emission with an electron beam¹²⁸. When such films were assembled into Langmuir-Blodgett diodes, band-to-band recombination radiation was observed¹²⁹. Short wavelength emission at room temperature consisted of peaks at 460 and 500 nm. This was achieved by growing a film of ZnSe onto a GaAs substrate using MOCVD, and then depositing a thin organic insulator under the metal electrode. The 460 nm peak is due to band-to-band recombination, but the presence of the 500 nm emission suggests a strong influence of defects.

Recently¹³⁰, p-type ZnSe was obtained by MOCVD growth onto GaAs, using lithium nitride as the dopant source. Aluminum doped ZnSe was then grown by the same method on top of the p-type material. The emission at room temperature peaked at 467 nm, and

there is a lower intensity broad band peaking near 540 nm. In this experiment, substantial p-type conductivity with a carrier concentration up to 9×10^{17} (resistivity = 0.2 ohm-cm) has been obtained. In order to improve the lasing performance of ZnSe it is helpful to sandwich the material between layers of lower index. ZnS has been proposed for this purpose, and stimulated emission was obtained at room temperature by electron beam pumping such a structure¹³¹.

A significant observation is that most ZnSe growth processes lead to the generation of defects, presumably vacancies. One exception was the growth by liquid phase epitaxy, from melts of Bi or Sn¹³². One of the newest attacks on this material is the growth of strained layer superlattices. The materials used were ZnS and ZnSe, with a lattice misfit of 5 percent¹³³.

E. GaN, InN

GaN is a semiconductor with a bandgap of 3.5 eV, and if suitably doped, could serve as emitter for any visible wavelength. Since its band structure is direct, it was expected to be a good short wavelength laser material. To date, these hopes have not been realized because of the difficulty in obtaining p-type material. There have been a number of studies of EL in various configurations; a typical work¹³⁴ uses MIS contacts, the insulator being Al_2O_3 or NaI, and the metal Au. The ohmic contact to the n-type GaN was In, and GaN was deposited by a vapor phase process onto sapphire substrates. Emission in the blue region was observed at room temperature and at 77K, with low efficiency.

Another approach is to produce a near intrinsic layer of GaN, thus making a i-n or even n-i-n structure¹³⁵. The i region is produced by doping GaN with zinc during growth. Some of the interesting observations concerning that structure are the variation of the emission wavelength between red and blue depending on the drive current, and the emission of polarized radiation. The spatial dependence of the luminescence was investigated, both by CL and by EL studies. However, no lasing emission was reported.

InN is a direct bandgap semiconductor with $E_g = 1.9$ eV, and alloys of InGaN allow the selection of intermediate bandgaps. Good results in the growth of InN have been reported using microwave excited MOCVD⁴³. It is interesting to note a significant recent result in a similarly intractable material, Boron Nitride. UV emitting p-n junctions in the cubic form of this material have been obtained by a special high pressure growth process¹³⁶.

Since GaN exists in both the wurtzite and the sphalerite (cubic) form, it may be advantageous to consider the cubic structure, and such material has recently been grown using MOCVD¹³⁷. Thus, GaN and its alloys remain promising materials, but because of difficulties in growth which presumably are responsible for reduced efficiency in compensated material, there has been no progress so far toward achieving stimulated emission.

F. Diamond

This material is of interest because it is an elemental semiconductor with a bandgap of 5.6 eV. Current experiments are conducted on naturally occurring p-type semiconducting type IIb

material¹³⁸. With silver paint contacts it is possible to obtain EL at the many contact points between the individual silver grains and the diamond. The mechanism is associated with the existence of high (at least 105 V/cm) electric fields, and is likely an impact excitation process. Luminescence has been observed in n-type synthetic diamonds¹³⁹ when a current is passed between silver electrodes. Neither this nor the above process are apparently efficient.

Diamond has been used as a host for a color center laser, the center being due to nitrogen. Stimulated emission at 530 nm at room temperature has been obtained under optical pumping¹⁴⁰. The electroluminescent brightness observed in synthetic diamond doped with boron or arsenic¹⁴¹ behaves in a manner consistent with impact ionization, which can occur if there are internal barriers. The field intensity at these crystal irregularities is considered to be sufficient to excite color centers.

Electron beam excited diamond produces luminescence similar to that obtained in electroluminescence experiments. In neither case is there any evidence of high efficiency. Another difficulty is the well known complexity of growth requiring very high pressures.

G. CdS

With a direct bandgap near 2.4 eV, this material has yielded electron beam and optically pumped lasers at 490 - 530 nm. Furthermore, it has been the subject of various attempts to obtain more directly excited diode lasers. Lasing has been obtained by driving a sample with a vacuum arc which supplies electrons doing

the pumping²⁰. This is basically a scheme for electron beam pumping without an electron gun and focusing lens. Stimulated emission was also obtained by using RF pulses of 10-15 kV applied to a 200 um gap between the crystal and an electrode²¹. Here again, it is possible that electrons were generated by an air breakdown mechanism. However, emission was observed to occur along certain preferred directions in the crystal, yielding what is now called a streamer laser²².

Directional breakdown is thought to be caused by the applied electric field, (which has to be on the order of 10^6 V/cm) and may be initiated by microinhomogeneities in the crystal. It has been argued by the Soviet workers, that it might be possible to obtain this conduction in a streamer channel without causing damage to the material, by preventing excess current flow after breakdown. The applied voltage is in the kV range, but very high powers have been obtained from such devices.

Some form of breakdown seems to be the source of pumping carriers in Nicoll's⁴⁰ early attempt to obtain diode lasing in CdS. Two closely spaced metal electrodes were deposited onto the surface of the crystal, and the structure was formed by the application of a voltage. After forming, the device showed a diode characteristic, and emitted intense blue light at a forward bias in the range of 10 - 40 V. Under pulsed conditions, the spectrum showed strong similarities to the lasing spectrum obtained from the same sample under cathodoluminescence. Although this device was not sufficiently stable for practical use, it appears to have demonstrated hot-carrier-induced diode lasing in CdS.

There are several lasing mechanisms in CdS, as evidenced by the varieties of emission spectra for different doping levels and temperatures. For lightly doped material, electron beam pumped laser emission at room temperature is thought to be due to free exciton recombination, whereas in doped material it may be due to free electron to acceptor recombination¹⁴².

A study of degradation processes in electron beam pumped CdS has already been mentioned¹⁰².

SECTION X.

CONCLUSIONS

It may be asked whether there is any one approach which is more promising than the others, in the sense that a reasonable amount of development is likely to lead to well performing devices. As it is hard to avoid subjective factors from entering such an assessment, it is only possible to offer the following comments. Certain approaches can be criticized on the grounds that they do not provide the advantages of diode lasers, namely small size and high efficiency. This would remove from the top contenders frequency multiplication and summing, and electron beam pumped lasers. Non-p-n junction devices are faulted because of their reduced injection efficiency, although this may eventually be overcome by developments in both laser structures and injection methods. Other approaches can be thought of as requiring a considerable amount of development. Thus, the invention of new materials appears to require a long-term program, with a number of uncertainties. The same observations can be made

about the development of unmatched heterojunctions, and about the effort required to develop direct bandgap materials using new superlattice structures or interstitial doping. Perhaps the most promising short-term approaches are the modification of existing III-V materials through the addition of nitrogen as in the growth of AlGaAsN, and a renewed attack on certain well known materials, for example GaN and ZnSe, using novel growth techniques, perhaps microwave excited MOCVD or reactive MBE.

SECTION XI.

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SECTION XII.

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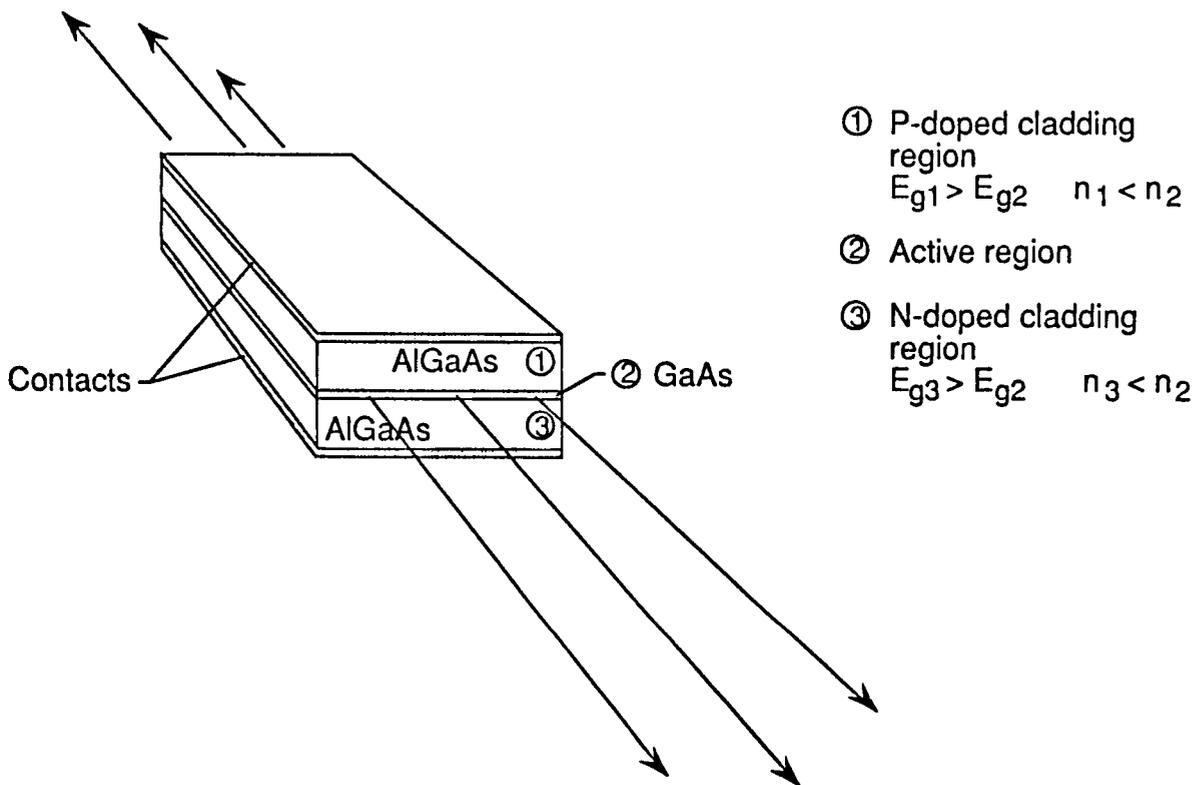


Fig.1 Basic structure of a Diode Laser.

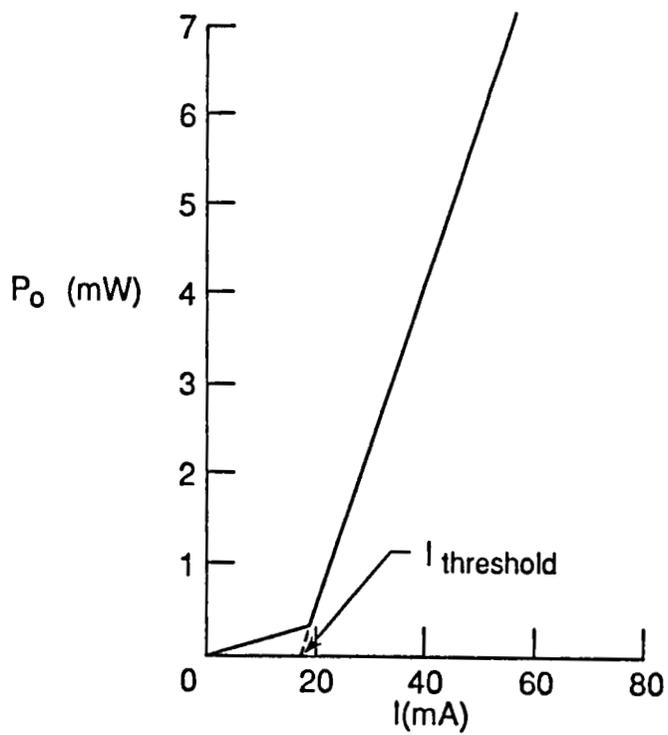


Fig.2 Power curve of a typical InGaAsP Laser.

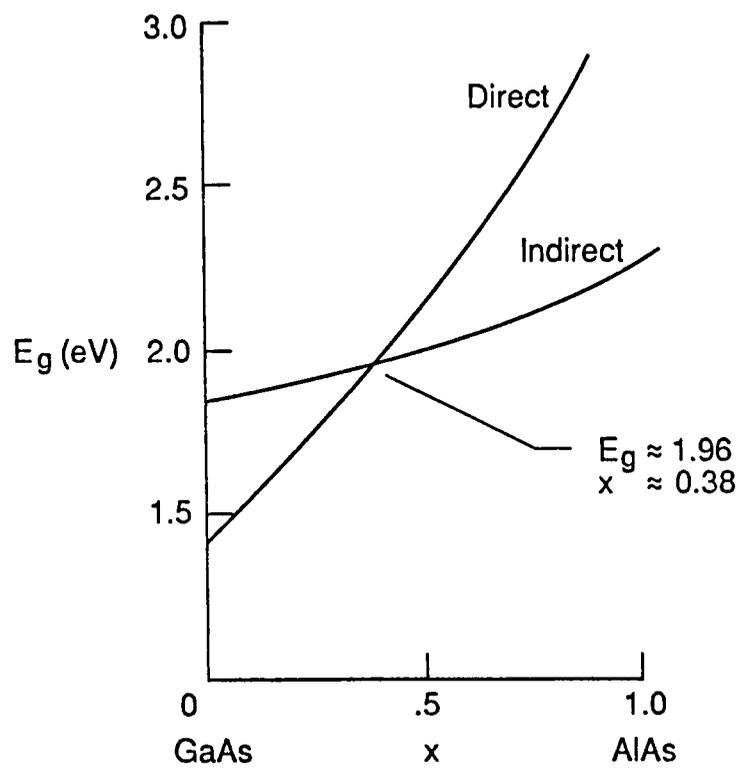


Fig.3 Direct and Indirect Bandgaps in AlGaAs.

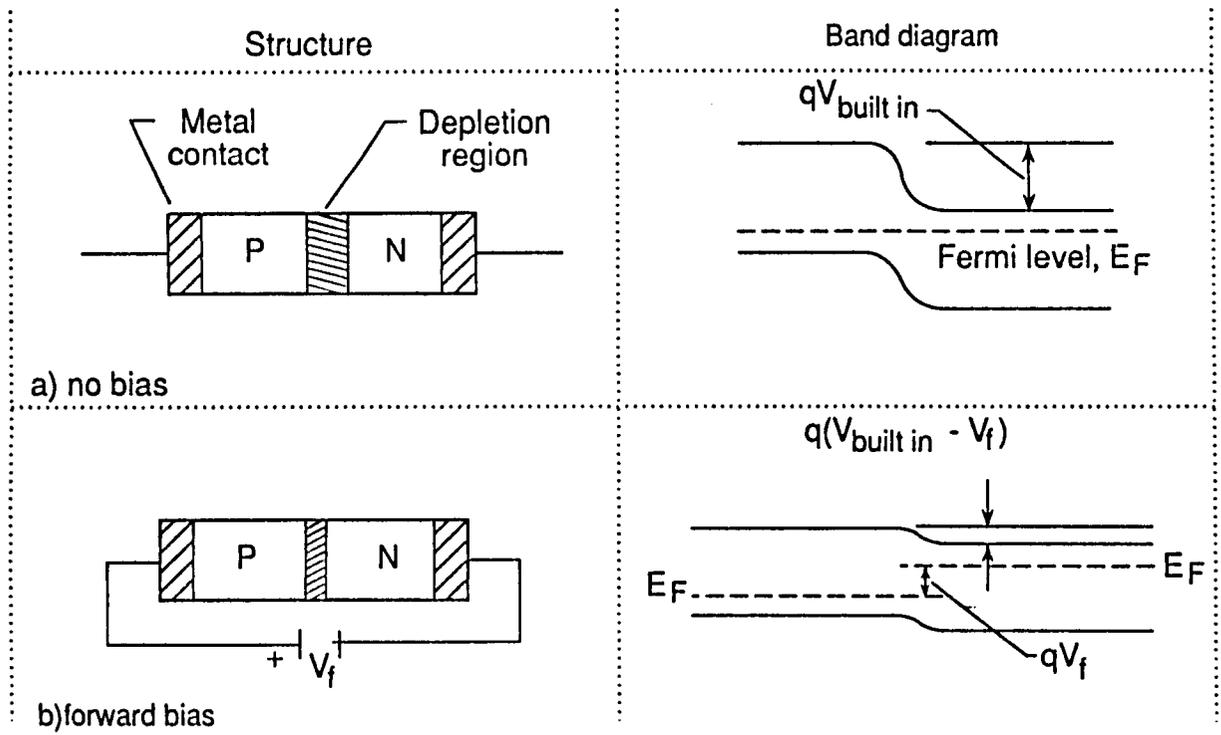


Fig.4 Graded-Index Separate-Confinement Quantum-Well structure.

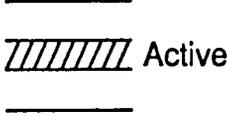
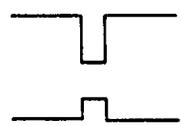
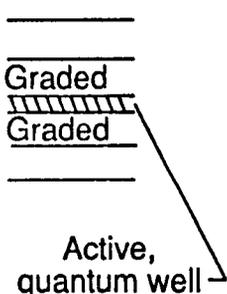
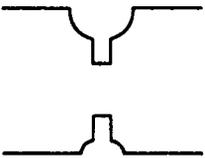
Type of laser	Structure	Band diagram	Refractive index
Standard			
Graded index separate confinement			

Fig.5 Structure and Band-Diagrams of a p-n Junction.

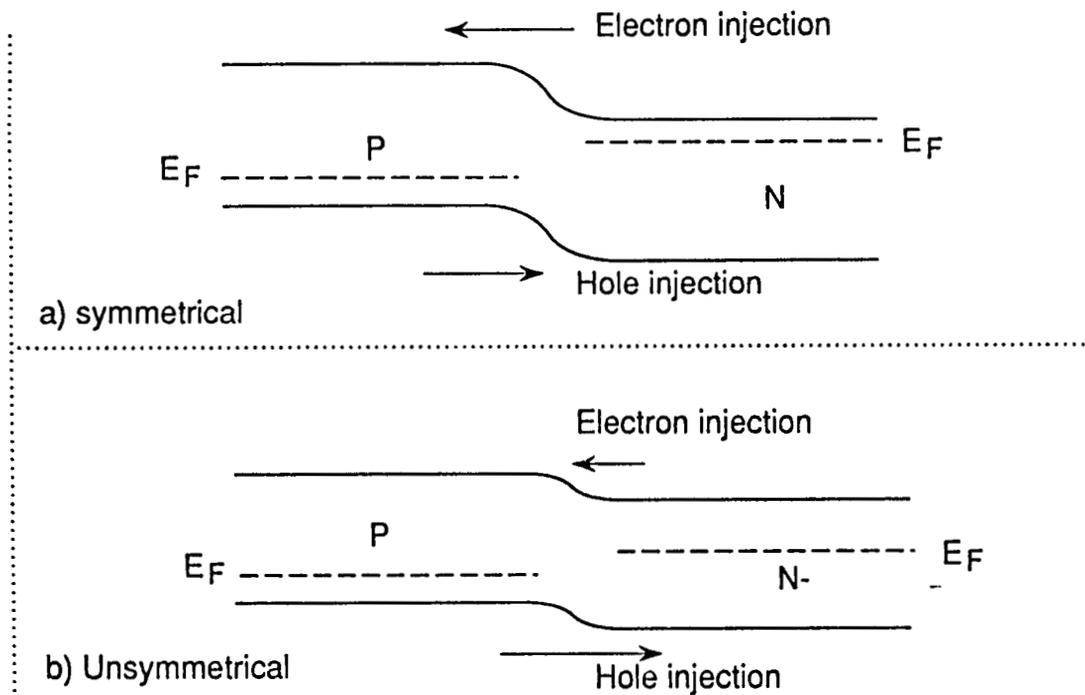
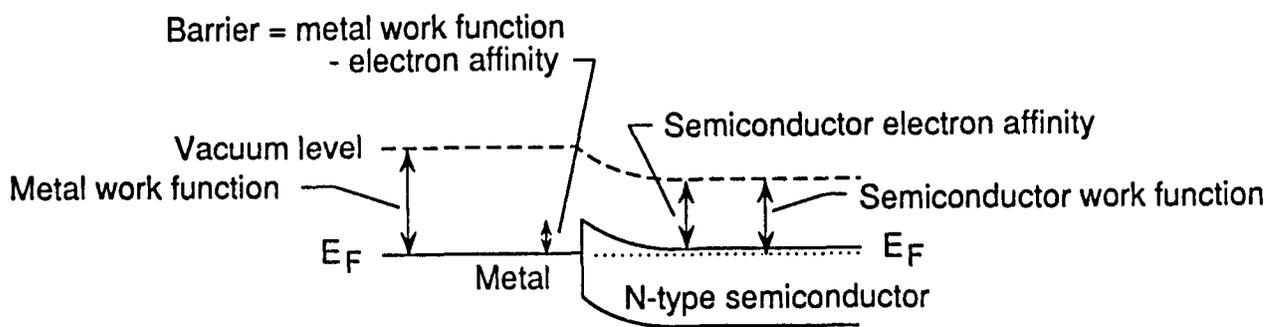
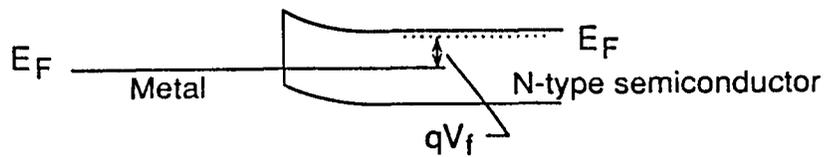


Fig.6 Electron and Hole Injection in a p-n Junction.



(a) No bias



(b) Forward bias

Fig.7 Metal-Semiconductor Barrier, a) without and b) with forward bias.

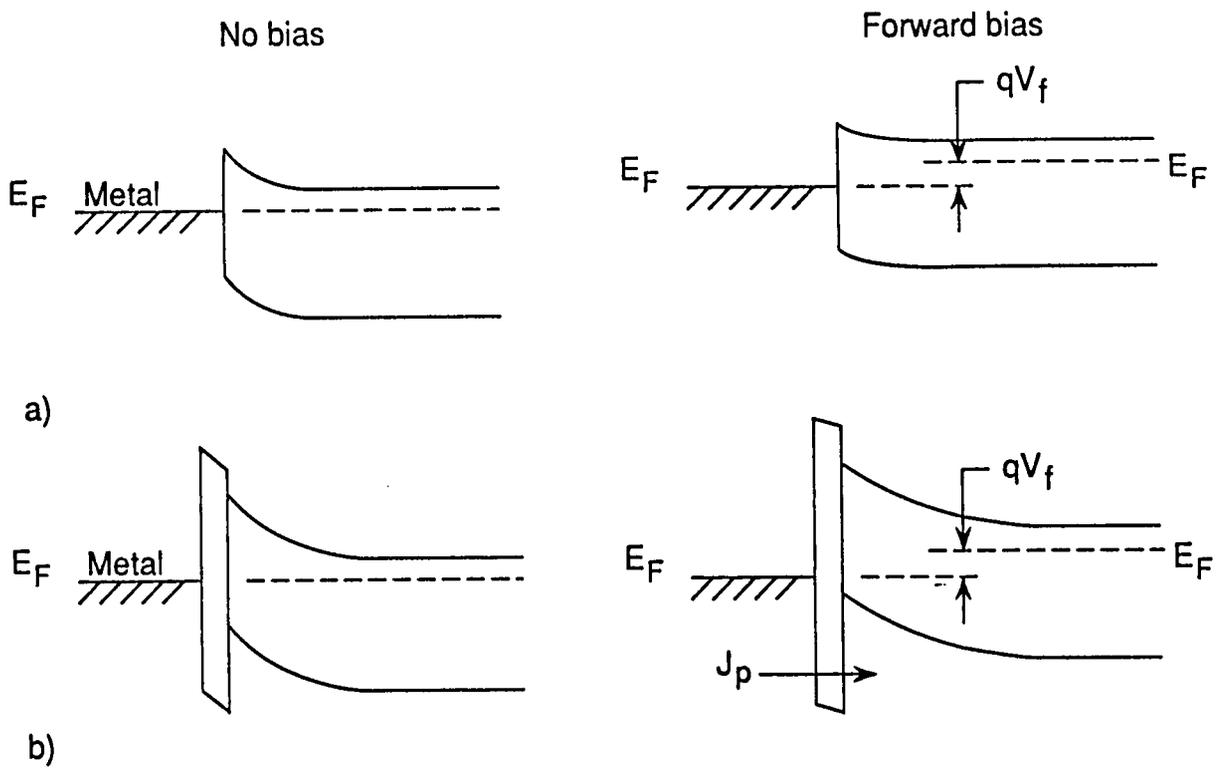


Fig.8 Mechanism of the Tunneling MIS diode.

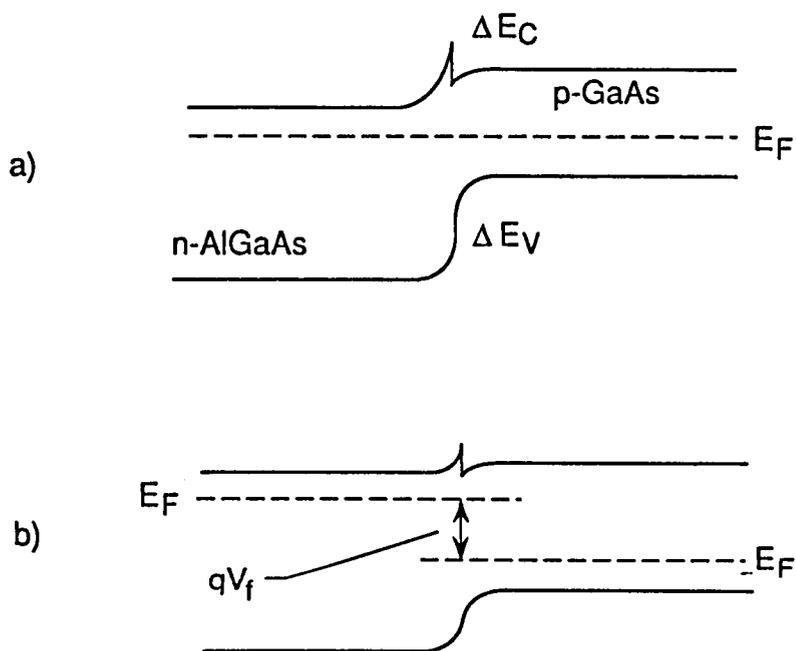


Fig.9 AlGaAs/GaAs Heterointerface, a) without and b) with forward bias.

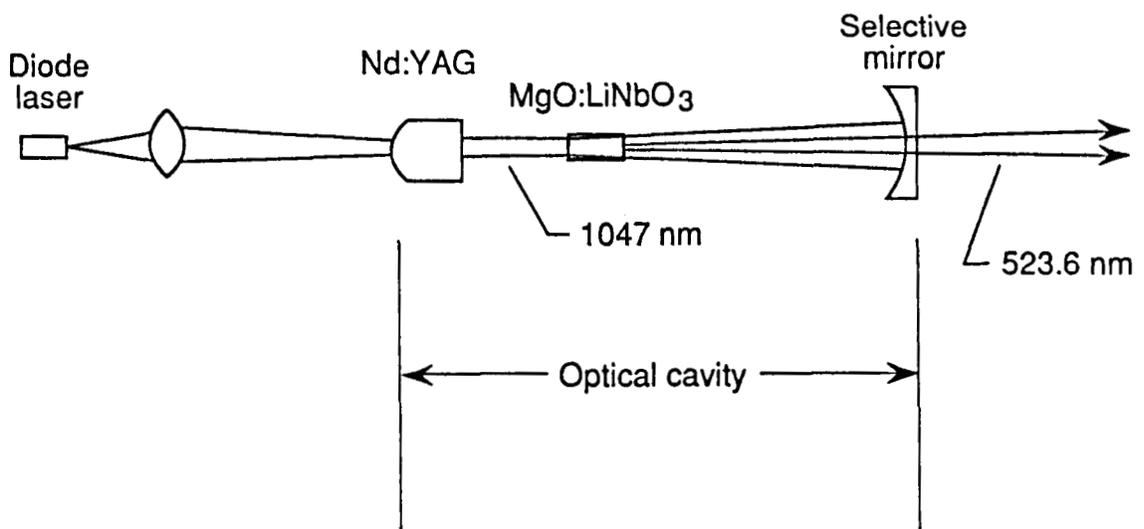


Fig.10 Structure of a Frequency-Conversion Laser.

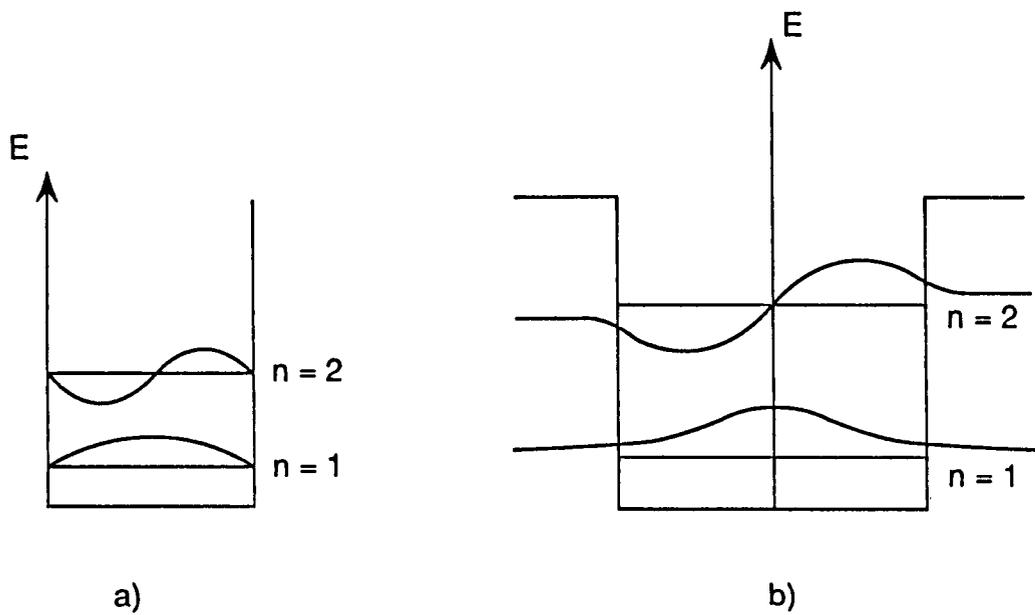


Fig.11 First two energy levels in the a) infinite, and b) finite Potential Well.

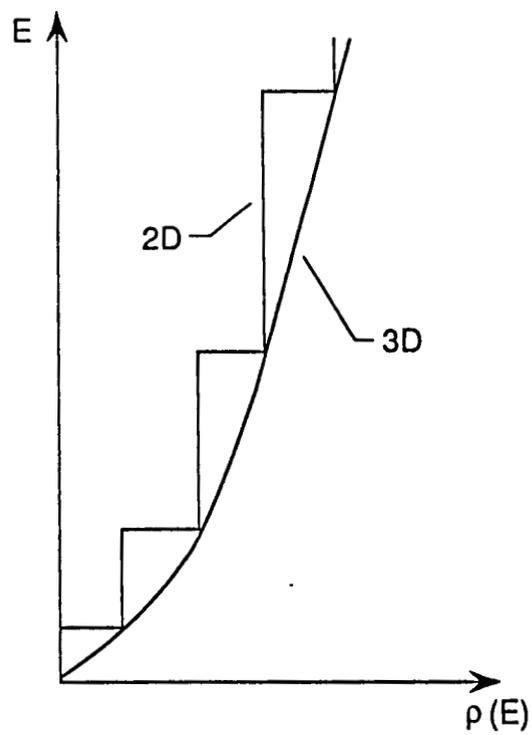


Fig.12 Density of States function in the conventional (3 dimensional) structure, and in a single Quantum Well (2 dimensional) structure.

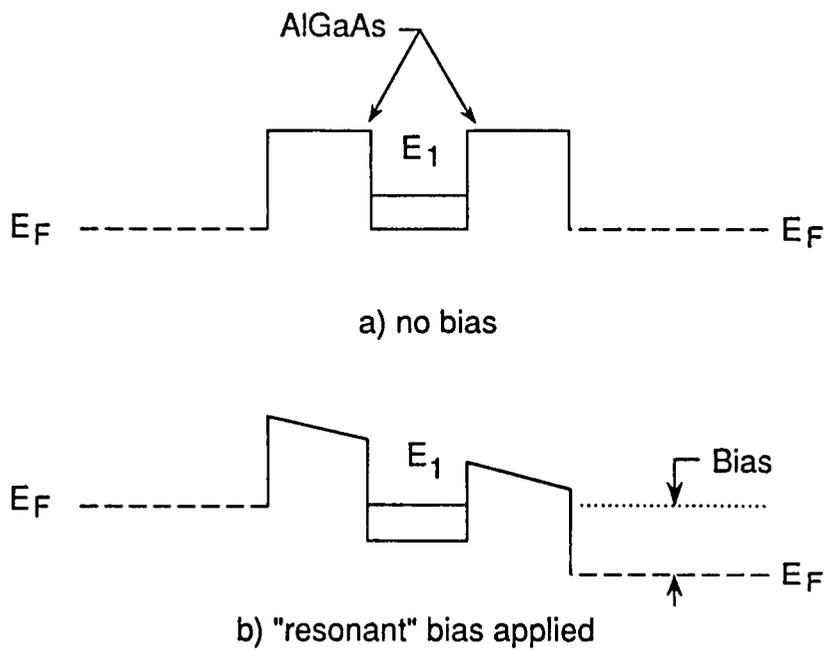


Fig.13 In Resonant Tunneling, application of the correct bias lines up the Fermi level with the first allowed level in the Quantum Well.



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16. Abstract Possible approaches for obtaining semiconductor diode laser action in the blue region of the spectrum are surveyed. Included is a discussion of diode lasers, and a review of the current status of "visible" emitters, presently limited to 670 nm. Methods are discussed for shifting laser emission toward shorter wavelengths, including the use of II-VI materials, the increase in the bandgap of III-V materials by additions of nitrogen, and changing the bandstructure from indirect to direct by incorporating interstitial atoms or by constructing superlattices. Non-pn-junction injection methods are surveyed, including avalanche breakdown, Langmuir-Blodgett diodes, hetero-structures, carrier accumulation, and Berglund diodes. Prospects of inventing new multinary semiconducting materials are discussed, and a number of novel materials described in the literature are tabulated. New approaches available through the development of quantum wells and superlattices are described, including resonant tunneling and the synthesis of arbitrary bandgap materials through multiple quantum wells. Also included is a review of the status of some well-known materials of interest for semiconductor lasers or emitters (SiC, ZnO, ZnS, ZnSe, GaN and InN, Diamond, CdS).					
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