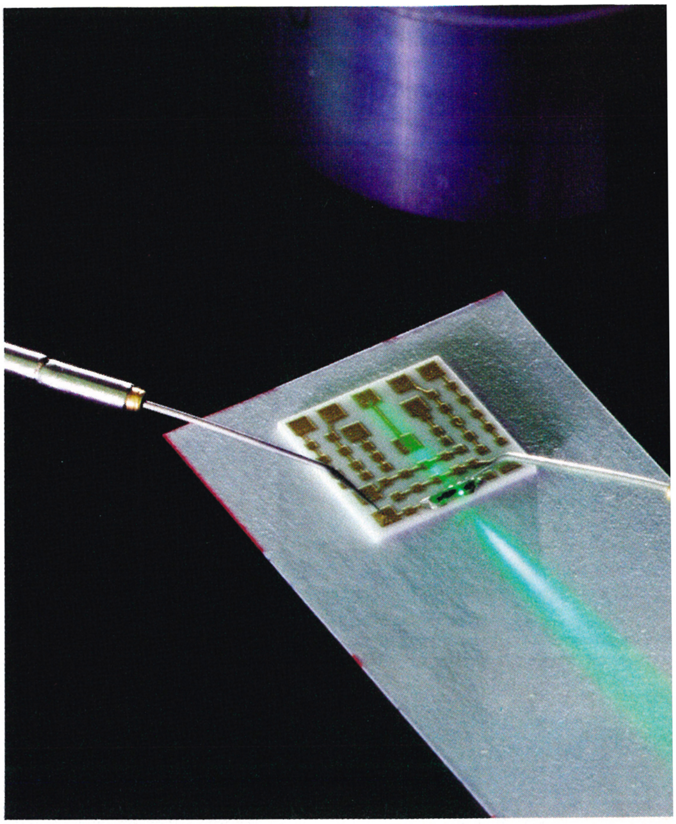
BLUE–GREEN DIODE LASERS



The road to the realization of short-wavelength, wide-bandgap, II–VI semiconductor diode lasers was fraught with scientific challenges.

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The development of compact, reliable and inexpensive short-wavelength lasers is certain to have profound effects on virtually any technology that uses coherent visible light. Although the impact of such devices will be far-reaching, the primary driving force behind efforts to develop blue–green diode lasers is without question optical recording. The demand for increased data storage capabilities is continually forcing the recording industry to increase storage densities.

In today's optical recording systems, bits of information are recorded and read by semiconductor lasers whose output is a focused, diffraction-limited spot. Because the diameter of a diffraction-limited spot is directly proportional to the wavelength of light used to produce it, one can realize significant gains in recording density as well as in data transfer rates simply by using lasers that operate at shorter wavelengths. Other technologies that will derive significant benefit from blue and green diode lasers include printing, communications, displays and numerous sensor applications.

Both scientific and technological interest in short-wavelength light sources were revived recently, following the first demonstration of 490-nm diode lasers fabricated from zinc selenide-based wide-bandgap II–VI compound semiconductors.[1] (Figure 1 shows such a device.) II–VI materials are compounds formed by combining elements from group II and group VI of the periodic table, ZnSe being an example. III–V compound semiconductors such as GaAs and InP are more familiar and have been more extensively developed for technological applications. The particular II–VI compounds of interest here are the ZnSe-based compounds, which have wide bandgaps. The term "wide bandgap" is chosen arbitrarily to refer to semiconductors having bandgaps larger than about 2 electron volts.

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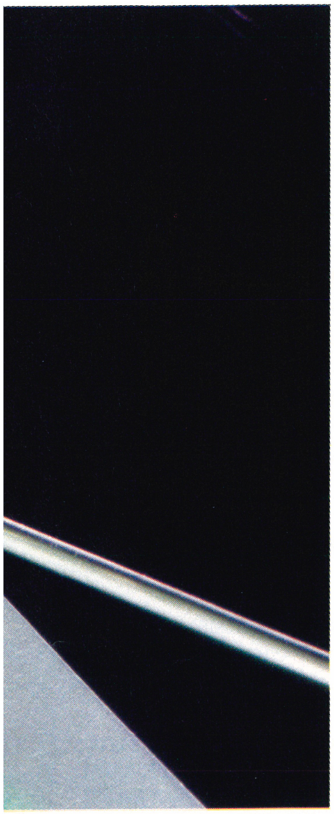
Diode lasers

As the name implies, diode lasers are constructed from p–n junctions. Under forward bias, charge carriers (electrons and holes) are injected into the active (light emitting) region that exists at the junction. The injected electrons and holes recombine either radiatively or nonradiatively. Nonradiative recombination is undesirable and is suppressed when possible through materials engineering techniques. An emitted photon can leave the active region and be absorbed, resulting in a loss, or it can interact with an electron in the conduction band, stimulating it to recombine with a hole in the valence band, producing a second, identical photon.

Placing the active layer within a waveguide, as indicated in figure 2, increases the likelihood of stimulated emission. The waveguide can be artificially constructed through the use of heterojunctions (junctions between materials having different bandgaps and thus different refractive indexes) or it can arise naturally in a homojunction (a p–n junction involving a single material) from the small refractive index changes due to doping, temperature gradients or carrier injection. The effect of incorporating waveguide and carrier confinement structures is to reduce the threshold current density for lasing. It was only recently that suitable waveguide and carrier



3M COMPANY

Blue–green diode laser. This wide-bandgap II–VI semiconductor device is shown operating at room temperature. Its active region is a CdZnSe single quantum well. **Figure 1**

confinement structures were developed in the wide-bandgap II–VI materials.

If the injected carrier densities are large enough, gain through stimulated emission can exceed the losses in the system, and lasing can occur. A laser cavity can be formed with cleaved facets at both ends of the waveguide; frequently the reflectivity of the facets is increased with dielectric coatings. Reflection from the facets provides positive feedback to the cavity, and laser oscillation occurs. The lasing threshold condition is achieved when the gain equals the total loss, including the light emerging from the end of the cavity—the laser beam itself. (Reference 2 contains a complete discussion of diode laser fundamentals.)

In constructing a diode laser, one must be able to dope the materials and to create carrier confinement and waveguide structures in the particular material system of interest. Also, the total series resistance of the laser device, including electrical contact resistance, should be kept small to minimize the drive power and resistance heating effects.

Although these issues were quite readily addressed in, for instance, near-infrared (GaAs based) diode lasers, the wide-bandgap II–VI materials have presented considerable difficulties. In particular, it has proved extremely difficult to achieve p-type doping of wide-bandgap II–VI semiconductors (with the exception of ZnTe); only recently has the p-type doping problem been solved sufficiently for ZnSe-based materials to allow blue–green diode lasers to be demonstrated. Forming low-resistance electrical contacts to p-type material also is a nontrivial problem with wide-bandgap II–VI compounds. However, significant progress is being made in this area, which is contributing to the ongoing improvement in the operating characteristics of ZnSe-based blue–green diode lasers.

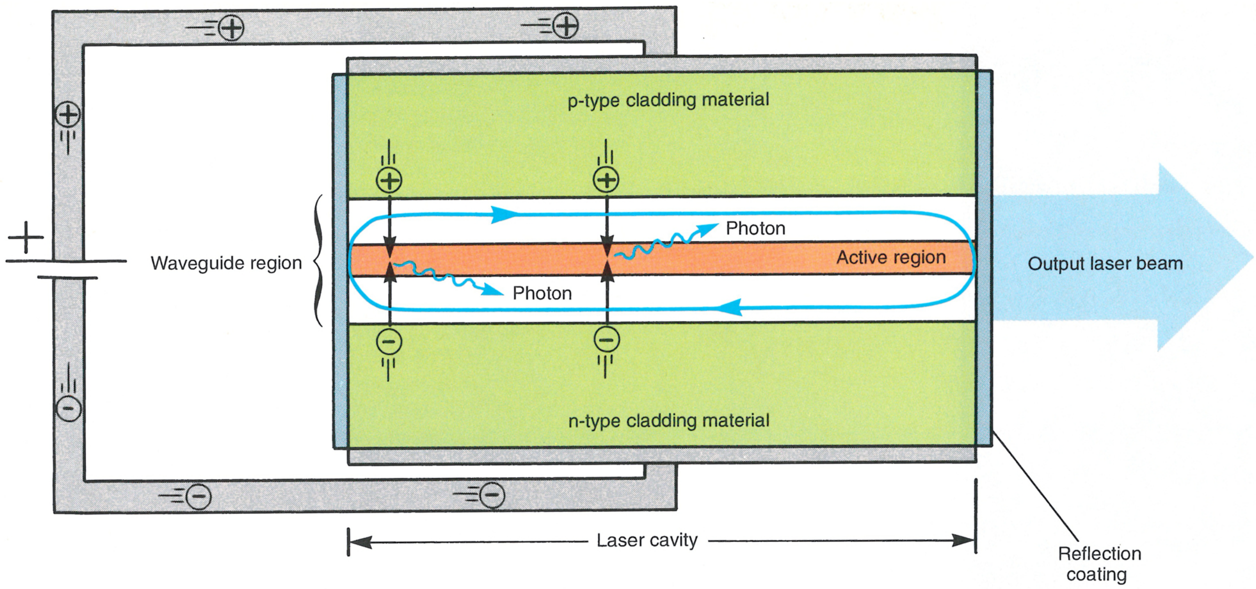
Doping

One introduces appropriate concentrations of dopants (impurities) in semiconductors to obtain good conductivity. These impurities can be either donors or acceptors. Donors are elements that have one more valence charge than the host and thus introduce extra electrons, or negative charge carriers, giving n-type material. Acceptors have one less valence charge, resulting in missing electrons, or "holes"—positive carriers—giving p-type material. Acceptors are said to be dopants of the opposite type to donors, and vice versa.

Historically, obtaining adequate doping for good "bipolar" conductivity in wide-bandgap semiconductors (that is, being able to produce both n-type and p-type material) has been a problem, and not just for II–VI materials. A particularly puzzling aspect of the problem is that good doping can be obtained in some but not all cases.[3] For many years some of these materials could be produced with good n-type conductivity, and some with good p-type conductivity, but none with both. Good n-type but not p-type material has long been available, for example, for ZnSe, which has a bandgap E_g of 2.7 eV at room temperature. By contrast, ZnTe ($E_g = 2.25$ eV) is available in p-type but not n-type form.[4]

In general, good conductivity requires, first, dopants with energy levels close to the respective band edges—donors close to the conduction band and acceptors close to the valence band. With such "shallow" levels, the dopants are easily ionized at device operating temperatures, resulting in free carriers in the respective bands. Second, good conductivity requires a concentration of such shallow dopants sufficiently in excess over any "compensating" (opposite type) species to give the desired concentration of free carriers.

Unfortunately, wide-bandgap semiconductors display a strong tendency toward "self-compensation"—that is, compensation that results from the incorporation of the dopant itself. One can understand the detrimental effects of wide bandgaps by looking at figure 3, which illustrates the case for donor doping. The higher an electron is located in this diagram, the higher is its energy. The average electron energy is denoted by the Fermi level. The zero of electron energy is conventionally taken at the valence band edge. For a material containing only donors, the electrons and the Fermi level are close to the conduc-



Operating principles of a semiconductor diode laser. The schematic is of a separate confinement structure in which the active region (usually a quantum well) is positioned at the center of an optical waveguide created by semiconductor heterostructures. **Figure 2**

tion band edge—that is, at an energy of about E_g. If acceptor-type compensating species are now introduced, an electron will have a lower energy state available (since acceptors are missing an electron with respect to the host) and will in fact lower its energy by dropping down into the acceptor state. Thus the free-carrier concentration will be reduced, lowering the conductivity of the semiconductor. Equal numbers of compensating acceptors and donors would lead to a Fermi level at approximately mid-gap—that is, at $E_g/2$. (A general review is given in reference 5.) The system therefore gains an energy of about $E_g/2$ per electron, and this gain increases in magnitude with increasing bandgap energy.

To obtain this gain, the system must "acquire" such compensating defects. A classic suggestion[5] to account for compensation is the formation, upon introduction of the dopants, of native defects—vacancies, interstitials or antisites—or complexes of the dopant with these defects. A second postulate is that a dopant may be "amphoteric"—that is, it may occupy different lattice sites where it produces levels of opposite type. Such behavior has long been known, for certain dopants, in the case of little or no lattice relaxation, but recent work by James Chadi and his coworkers at NEC in Princeton, New Jersey, shows that it can also take place for previously unexpected cases via large lattice relaxations.[6] Regardless, however, of the detailed mechanism, the electronic gain of $E_g/2$ is not "free": The system must "pay" the energy of formation of the compensating species.

Theories concerning electronic gain and the formation energies of compensating defects were developed in the 1950s and 1960s. However, the details of the energy trade-off between the electronic and formation energies have been clarified only recently. Specifically, recent work[7] has emphasized the role of the chemical potentials of both the host and dopant in controlling solubility. Moreover, further research at Columbia University has shown that the optimum chemical potentials for dopant incorporation also tend to lead to the optimum incorporation of at least one type of compensating species.

For example, in the case of nitrogen-doped ZnSe, which should provide p-type material, a high Zn pressure (large Zn chemical potential) favors the desired incorporation of nitrogen on Se sites, but this condition also favors the formation of Zn interstitials, which behave as donors. Because the appropriate chemical potential must be subtracted from the "standard" formation energy resulting under stoichiometric conditions, the ease of doping a particular system depends on small differences in relatively large energy values. This explains, finally, why good doping can readily be obtained in *some* cases but not in others, and why marginal cases (which p-type ZnSe, for example, appears to be) require careful selection of dopants and of growth conditions.

Novel doping technique for ZnSe

Blue–green diode laser development is due in large measure to recent successes in the p-type doping of ZnSe and related alloys using nitrogen as the dopant element.

Nitrogen-doped ZnSe epitaxial films displaying p-type conductivity of a suitable magnitude for diode laser devices were first grown by researchers at the University of Florida[8] in late 1989. Other research groups have since duplicated the University of Florida doping technique and have measured free-hole concentrations in ZnSe epilayers in the $10^{17}/cm^3$ range.[9–11]

The key to the p-type doping technique in question is the use of a radio-frequency plasma discharge source to generate a flux of highly reactive nitrogen atoms. This source (a product of Oxford Applied Research) is used in a molecular-beam-epitaxy crystal growth system to dope the ZnSe with nitrogen acceptors during growth. Figure 4 is a schematic diagram of a typical MBE growth chamber in which an rf plasma discharge nitrogen free-radical source has replaced a conventional effusion source. In growing p-type ZnSe layers doped with nitrogen, a flux of nitrogen atoms generated in the remote plasma is incident on a heated GaAs wafer, as are Zn and Se fluxes in the form of molecular beams. The nitrogen atoms react chemically at the growing surface and ideally (with regard to creating free holes) occupy Se sublattice sites.

The conclusion that the species responsible for efficient p-type doping in this case is nitrogen atoms produced by the free-radical source is based on optical emission spectroscopy analysis of the discharge plasma itself. The emission spectrum, as reported by the University of Florida group, had bands in the visible and near-infrared regimes.[12] Park has suggested that the emission bands in the visible regime correspond to the so-called first positive system of nitrogen, indicating recombination of ground-state nitrogen atoms in the plasma.[12] He also suggested that the near-infrared bands might be associated with the so-called Y bands of nitrogen; more recently, however, researchers at North Carolina State University proposed an alternative interpretation of the near-ir bands, based on higher-resolution optical emission spectroscopy of the plasma.[13] Those scientists concluded that the near-ir bands correspond to various direct atomic nitrogen transitions (as opposed to molecular transitions).

Considered together, the optical emission spectroscopy analyses of the Florida and North Carolina State groups suggest that the discharge zone of the Oxford Applied Research source contains significant equilibrium concentrations of ground-state and excited-state nitrogen atoms together with ground-state N_2 and various excited-state N_2 molecular species. Thus the flux emanating from the discharge zone (through a perforated-disc aperture) comprises a similar population of nitrogen atoms and molecules. And because the mean free path in a 10^{-6}-torr environment (typical for MBE growth of ZnSe using an rf plasma source) is greater than the 6–8-inch distance between source and substrate, the species emanating from the source will not undergo collisions en route to the substrate and consequently will preserve their states. Although nitrogen doping of ZnSe by means of molecular species that have dissociated locally at the substrate cannot be completely ruled out, it is believed that the atomic nitrogen content in the flux from the free-radical source is responsible for the efficient nitrogen doping seen in this technique.

Nitrogen-doped ZnSe epilayers grown at the University of Florida using the nitrogen source described above were first shown to exhibit p-type conductivity by researchers at the 3M Company in Saint Paul, Minnesota, who employed a capacitance–voltage measurement technique that revealed large net acceptor densities in the films.[8] They performed capacitance–voltage measurements because a procedure for making low-resistance contacts to p-type ZnSe was not available at the time.

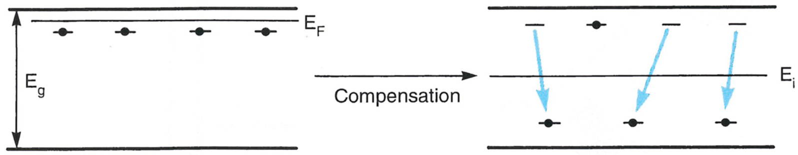
Free-hole concentrations

More recently the development of various low-resistance contact schemes has made it possible to perform Hall effect measurements, which reveal free-carrier concentrations, on nitrogen-doped ZnSe epilayers. Those measurements suggest that the upper limit to the free-hole concentration in nitrogen-doped ZnSe material grown by the above method is in the mid-10^{17}/cm^3 range at room temperature. Although carrier concentrations in that range are suitable for the injection layers in diode lasers, it would be desirable to achieve larger free-hole concentrations in p-type ZnSe, particularly to minimize the electrical contact problem.

While free-hole concentrations are only in the 10^{17}/cm^3 range, nitrogen impurity concentrations approaching 10^{19}/cm^3 have been measured in nitrogen-doped ZnSe epilayers by secondary-ion mass spectrometry. This discrepancy can be explained at least in part by assuming that significant amounts of compensating species involving nitrogen exist in the material; however, the specific species has not yet been identified.

A second issue to consider in the context of free-hole concentrations is the rather large ionization energy—about 110 meV—of the nitrogen acceptors in ZnSe. As Harry Ruda of the University of Toronto has pointed out, such a large ionization energy means that only a fraction of the total nitrogen acceptors in the ZnSe will be ionized at room temperature.[14] Thus both self-compensation and the large dopant ionization energy appear to limit the maximum free-hole concentration attainable in nitrogen-doped ZnSe.

Identifying the compensating species in nitrogen-doped ZnSe epilayers and developing a technique to minimize self-compensation in this material (assuming that nature will allow us to influence the compensation) represent a challenge for future research. In the meantime, the new nitrogen-doping technique discussed above has allowed fabrication of the first blue–green diode lasers employing ZnSe-based materials, and as discussed below, some interesting schemes are being developed to circum-



Energy changes due to compensation. E_g is the bandgap energy; E_F is the Fermi level in uncompensated (n-type) material; E_i is the intrinsic Fermi level, located at about $E_g/2$. In strongly compensated material the Fermi level is expected to be close to the intrinsic value. The electronic energy difference is given by the difference in Fermi levels. **Figure 3**

vent the apparent upper limit on the free-hole concentration, particularly the limit's effect on making contacts to p-ZnSe material.

Carrier and optical confinement

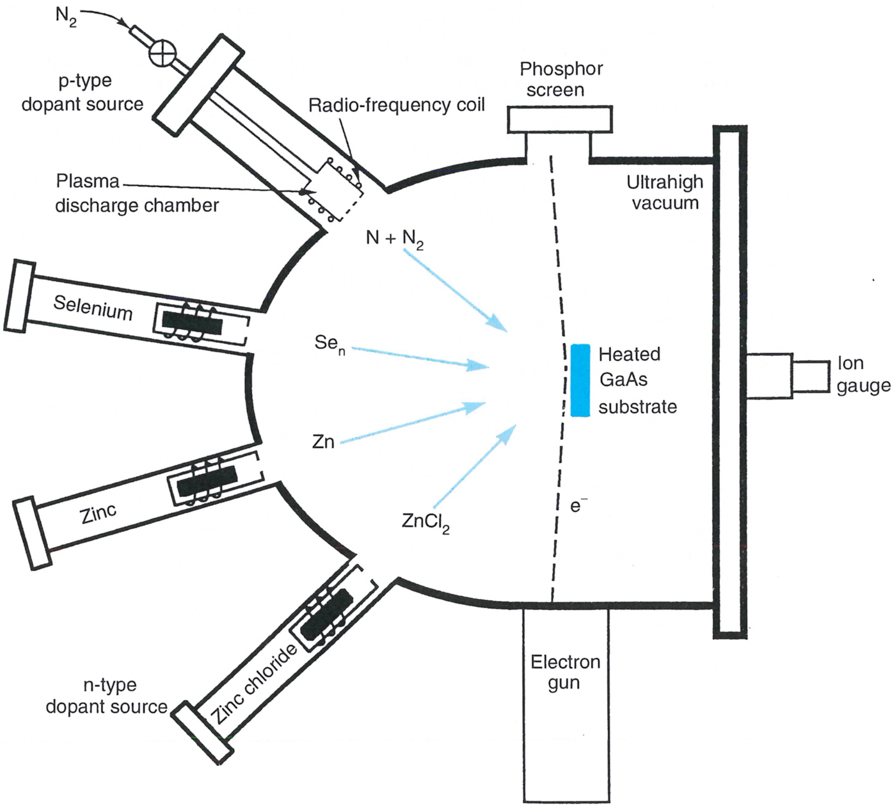
To achieve a carrier density in the active layer large enough for laser oscillation to occur, the current per unit area that passes through the p–n junction must exceed a certain value. One can substantially reduce this threshold current density by confining the carriers to a volume smaller than that naturally produced by carrier diffusion across the junction. Usually one accomplishes this confinement by placing in the junction a thin layer of material that has a smaller bandgap than the surrounding junction material. If the thickness of this small-bandgap layer is reduced to the point where quantum mechanical effects become significant—that is, comparable to the electron wavelength—then the heterostructure is referred to as a quantum well. (See figure 5.) Quantum wells are frequently used in very-low-threshold laser diodes.

One of the challenges faced by researchers working with II–VI materials was the identification of a suitable quantum well system. A quantum well material with appropriate crystal structure and bandgap was not obvious among the naturally occurring II–VI compounds. Researchers at Notre Dame University made a major advance in this area when they demonstrated that one could force $Cd_xZn_{1-x}Se$ to exist with the zincblende structure for $0 \leq x \leq 1$ by growing the crystals epitaxially on a substrate having the zincblende structure.[15] This was not an obvious result, because CdSe occurs naturally with the wurtzite crystal structure. The Notre Dame group also demonstrated that one could continuously tune the bandgap from 2.67 eV (ZnSe) to 1.67 eV (cubic CdSe) and that one could form $Cd_xZn_{1-x}Se$ quantum wells surrounded by ZnSe barriers with reasonably good crystalline quality.

CdZnSe/ZnSe quantum wells

One important aspect of the CdZnSe/ZnSe quantum well system is that CdSe and ZnSe have very different lattice constants. In a lattice-mismatched epitaxial system, the difference in lattice constants can be accommodated by elastic deformation of the lattice of a thin epitaxial layer, resulting in an energy due to strain; the layer is then said to be pseudomorphic. The strain energy increases with the thickness of the epilayer, and above a certain critical thickness, it exceeds the energy required to form a dislocation. Thus for epitaxial films with thicknesses greater than the critical thickness, the system relaxes by forming dislocations. Dislocations, however, cannot be tolerated in the active layer of a laser, because they lead to the efficient nonradiative recombination of minority carriers and are a known failure mechanism.

Luminescence from quantum wells is quenched at elevated temperatures, because carriers are thermally activated out of the well. Therefore, in addition to keeping the well pseudomorphic, the composition and thickness of the CdZnSe must be such that they provide enough difference in bandgap energy to adequately confine electrons at room temperature.[9] Specifically, thermodynamic con-



Molecular-beam-epitaxy growth chamber configured for the deposition of p-type ZnSe (using a flux of atomic nitrogen) and n-type ZnSe (using chlorine atoms derived from $ZnCl_2$). Doping by the incorporation of N and Cl allows the formation of light-emitting ZnSe p–n junctions. For diode laser structures, additional thermal effusion sources are required to deposit elements such as Cd, S and Mg. **Figure 4**

siderations dictate that the well composition must be chosen so that its effective bandgap is approximately 300 meV smaller than the bandgap of the surrounding ZnSe barrier. (The effective bandgap is the actual bandgap of the semiconductor plus contributions due to quantum confinement and strain.) A single 50-Å quantum well with 30% Cd meets both requirements.

The usefulness of the CdZnSe quantum well system was first illustrated at Brown University in optical pumping studies done on multiple-quantum-well structures.[16] Although there had been earlier reports of both electron-beam and optically pumped operation of ZnSe-based lasers, this was the first time that thresholds began to approach those needed for practical devices. The thresholds obtained for pulsed excitation were about 30 kW/cm^2, and continuous operation up to temperatures of 100 kelvin was achieved.

The first wide-bandgap II–VI diode lasers

The first demonstration of diode lasers fabricated from wide-bandgap II–VI semiconductors took place in April 1991 at the 3M Company. The device structure provided for both electrical and optical confinement. (See figure 5.) The carriers were confined with ZnSe barriers to a 100-Å-thick $Cd_{0.2}Zn_{0.8}Se$ quantum well, where they recombined, generating light. The ZnSe also served as the light-guiding layer, with the optical cladding provided by thick $ZnS_{0.07}Se_{0.93}$ layers. That ZnSSe composition was selected because it provided lattice-matching to the GaAs substrate.

These "gain-guided" lasers were fabricated using 20-micron-wide gold electrodes in a polyimide insulator layer. Gain-guided devices are the simplest to fabricate, because no artificial structure has to be formed to provide optical confinement in the plane of the layers: The lateral confinement is due only to index changes resulting from heating, carrier injection and gain that occur under the metal electrode during operation. The mirrors at the ends of the cavity were formed by cleaved facets.

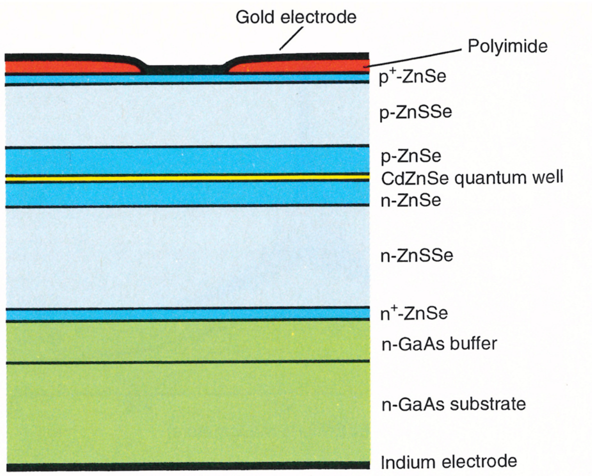
Laser oscillation occurred when these devices were given 500-nsec pulses with a 2-kHz repetition rate at 77 K. The intensity of the output light as a function of current (figure 6) clearly showed the onset of laser oscillation at 75 milliamps. In these first devices the output power was greater than 100 mW per facet, and the quantum efficiencies were in excess of 20%. (The quantum efficiency is the slope of the curve of output power versus current.) Figure 7 shows the lasing spectrum together with the spontaneous-emission spectrum recorded below the threshold current density.

The first II–VI diode lasers did not lase at room temperature, because the quantum wells were not deep enough to produce sufficient carrier confinement. But by increasing the Cd content in the CdZnSe quantum well, researchers obtained room temperature lasing at 520 nm. A more serious problem with this type of device, however, was that the lattice constants of the cladding and guiding layers were mismatched: Dislocations formed to relax the misfit, some of which propagated into the quantum well.

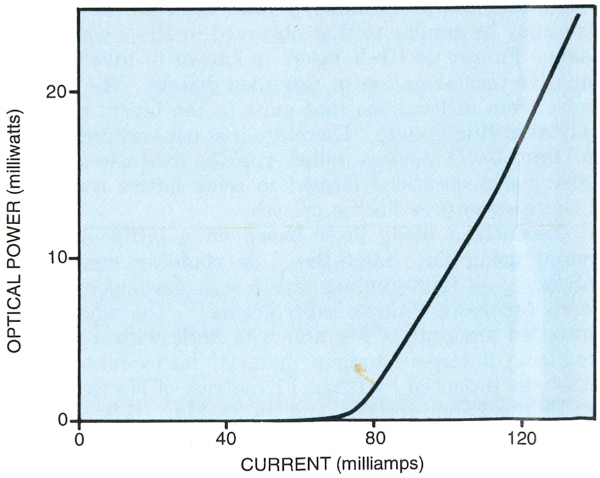
Ohmic contacts

Heat dissipation is an important consideration for all diode lasers. It is especially so for II–VI devices, because making low-resistance ohmic contact to p-type II–VI compounds is extremely difficult. The applied voltages needed to reach threshold conditions in early II–VI lasers exceeded 15 volts, with most of the potential drop occurring at the p-side contact. This difficulty has its origin in the very deep position of the valence band in these materials. Because the valence-band maximum for ZnSe is approximately 6.4 eV below the vacuum level and no metal has a work function larger than 5.6 eV, it is impossible to make simple metal contacts with negligible Schottky-barrier heights to p-type ZnSe.

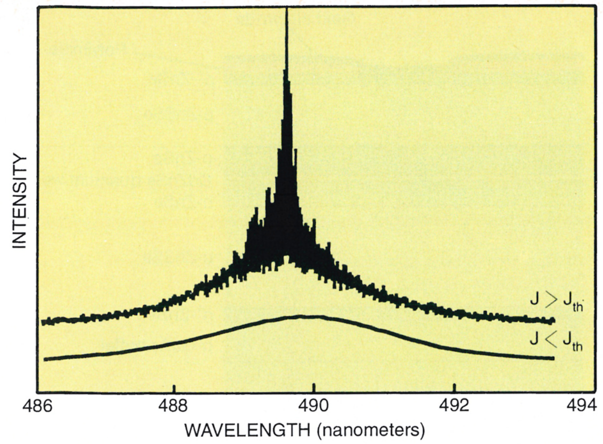
Conventional approaches to circumventing this obstacle, such as alloying the contact metal with the semiconductor or doping the layer immediately under the contact metal extremely heavily to facilitate tunneling, have not succeeded, because doping techniques have been unable to increase the net acceptor density beyond 10^{18}/cm^3 and



Schematic cross section of the first wide-bandgap II–VI diode laser: a separate confinement structure with a $Cd_xZn_{1-x}Se$ quantum well active layer. **Figure 5**



Light intensity as a function of injected current for the first II–VI diode laser. This gain-guided CdZnSe/ZnSe/ZnSSe device, operated at 77 K, had a threshold current of 75 milliamps and an emission wavelength of 490 nm. **Figure 6**



Lasing spectrum recorded at 77 K from the device shown schematically in figure 5. The lower curve is the spontaneous-emission spectrum recorded below the threshold current density J_{th}. **Figure 7**

because the materials are unstable during thermal annealing. Progress toward a viable contact technology using semimetallic HgSe or a graded ZnSeTe pseudoternary scheme has recently been reported. The HgSe contacts, developed at North Carolina State University,[10] rely on the large electronegativity of that material; the valence-band offset between it and ZnSe is expected to be less than 0.6 eV.

For graded contacts, the ideal approach is to change the composition continuously from the starting material to a material that can easily be contacted—for example, grading from ZnSe to ZnTe using $ZnSe_{1-x}Te_x$. But because continuous grading has not yet been achieved in this material system, researchers at Purdue University[11] developed a discrete approach, inserting layers of ZnTe with increasing thickness in ZnSe. They demonstrated contacts with resistances in the $2\text{–}8 \times 10^{-3}\ \Omega\ cm^2$ range.

Device lifetimes

Currently, the biggest limitation of II–VI lasers is their very short lifetimes. Devices have been operated at room temperature in the pulsed mode with 50% duty cycles; however, they typically fail in less than a few seconds in this mode.

The failure mechanism in II–VI devices is not fully understood, but preliminary studies indicate the mechanism may be similar to that observed in III–V compound lasers. Failure of III–V lasers is known to involve nonradiative recombination at extended defects. The defects evolve from dislocations that exist in the layers immediately after film growth. Therefore it is not surprising that the first II–VI devices failed rapidly, because a large density of dislocations formed to relax lattice mismatch in those structures during growth.

Recently a diode laser based on a lattice-matched system using $Zn_{1-x}Mg_xS_ySe_{1-y}$ as cladding layers and ZnS_zSe_{1-z} as light-guiding layers was developed at the North American Philips Laboratories.[17] The addition of controlled amounts of Mg and S to ZnSe with a view to producing a larger-bandgap material lattice-matched to ZnSe was proposed by Brian Fitzpatrick of North American Philips Laboratories,[18] and the $Zn_xMg_{1-x}S_ySe_{1-y}$ alloy was first grown by MBE at Sony in Japan.[19] The absence of lattice mismatch reduces the concentration of dislocations formed during growth significantly compared with that in the previous, lattice-mismatched devices. The performance of devices containing $Zn_{1-x}Mg_xS_ySe_{1-y}$ has improved accordingly, and pulsed operation up to 394 K has been demonstrated. Even with perfectly lattice-matched structures, however, device lifetime is still a problem.

The recent achievements in p-type doping, carrier and optical confinement structures and ohmic contacts have allowed the demonstration of blue–green diode lasers, revitalizing interest in wide-gap II–VI semiconductors. However, additional advances appear to be necessary at the materials level to dramatically increase the operating lifetimes of wide-gap II–VI diode lasers. In particular, methods of controlling the generation and propagation of defects under device operating conditions need to be developed before these devices can be considered practical.

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