CHEMISTRY 5570

Advanced Analytical Chemistry

Lecture 9

LASERS

Semiconductor LED vs LASER

Light Emitting Diode

- Light is mostly monochromatic (narrow energy spread comparable to the distribution of electrons/hole populations in the band edges)
- Light is from spontaneous emission (random events in time and thus phase).
- Light diverges significantly

LASER **Light Amplification by Stimulated Emission of Radiation**

- Light is essentially single wavelength (highly monochromatic)
- Light is from "stimulated emission" (timed to be in phase with other photons
- Light has significantly lower divergence (Semiconductor versions have more than gas lasers though).

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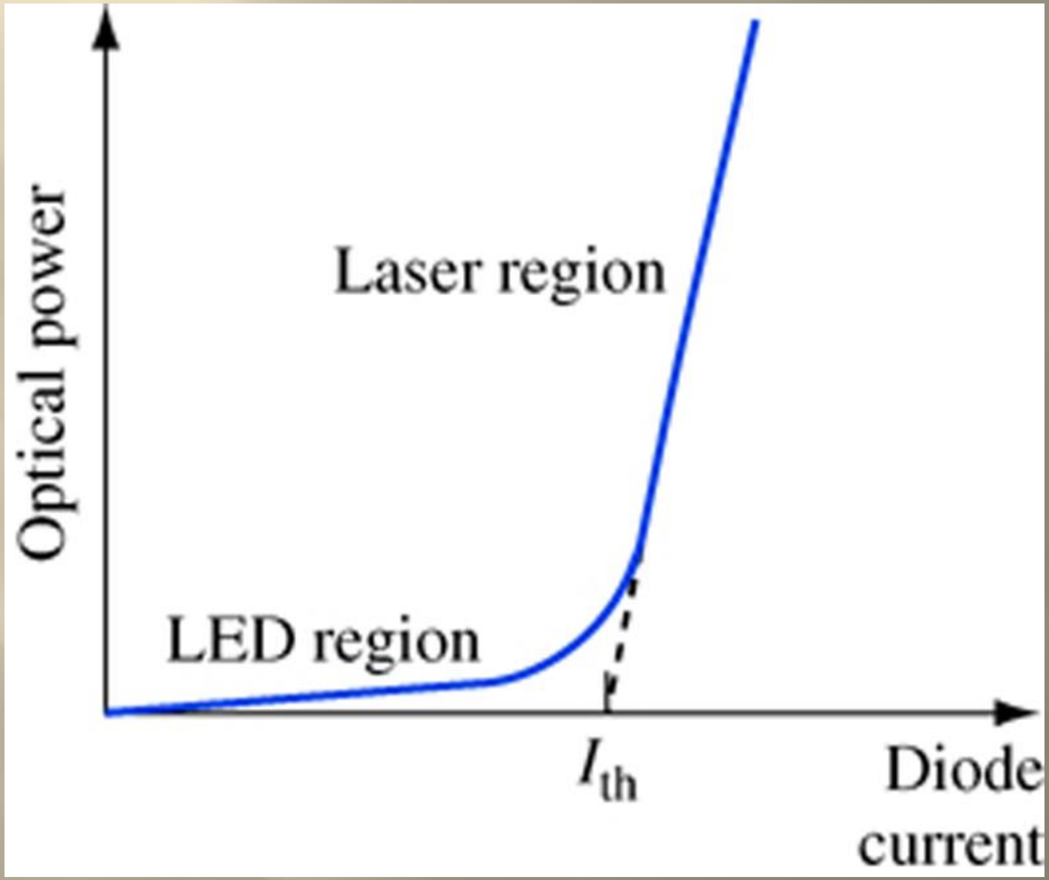
Semiconductor LED vs LASER



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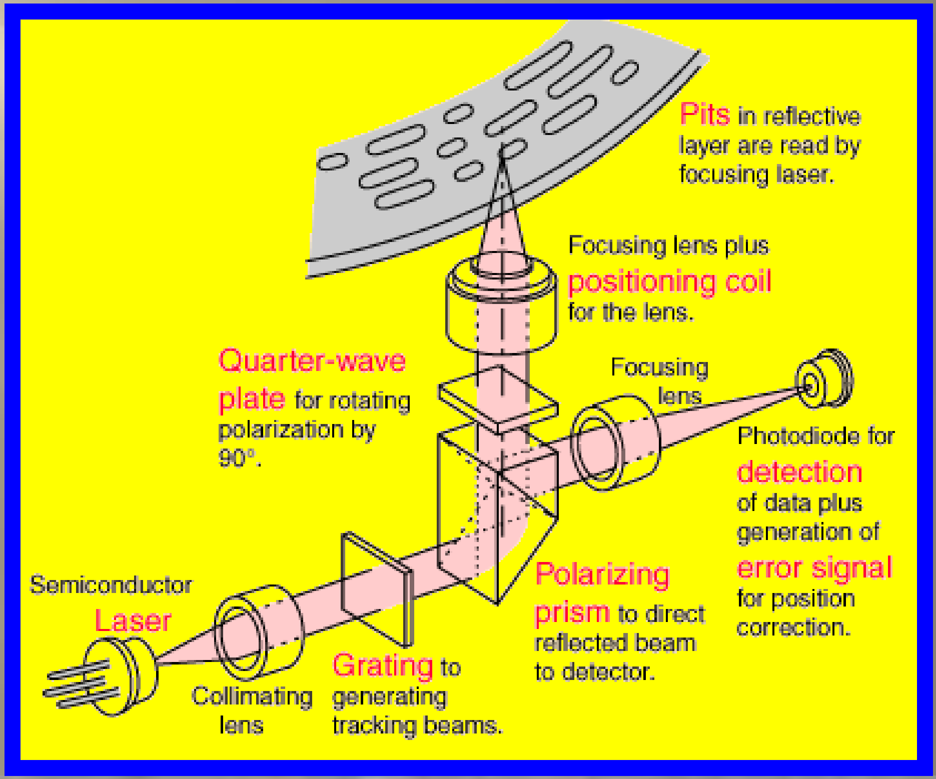
Applications

Readers

CD/DVD Readers
Fiber Optics
Spectroscopy Sources
Material Processing
Photochemistry



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Applications

Fiber Optics - Communication

Light travels down a fiber optics glass.

Light carries with it information.

Dispersion of light at the receiving end is observed to be spread. This is associated with data or information lost.

The greater the spread of information, the more loss.

However, if we start with a more coherent beam then loss can be greatly reduced.

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Laser Sources
in UV, vis, and IR

Used for

- high resolution spectroscopy
- kinetic studies
- routine analysis

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Light Amplification by Stimulated Emission of Radiation

A laser is a device that generates light by a process called STIMULATED EMISSION.

- High Intensities
- Narrow Bandwidths
- Coherent Outputs

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Background

In 1917 Einstein predicted that:

- under certain circumstances a photon incident upon a material can generate a second photon of
  - **Exactly the same energy (frequency)**
  - **Phase**
  - **Polarisation**
  - **Direction of propagation**
- **In other word, a coherent beam resulted.**

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Background

Stimulated emission is the basis of the laser action.

The two photons that have been produced can then generate more photons, and the 4 generated can generate 16 etc… etc… which could result in a cascade of intense monochromatic radiation.

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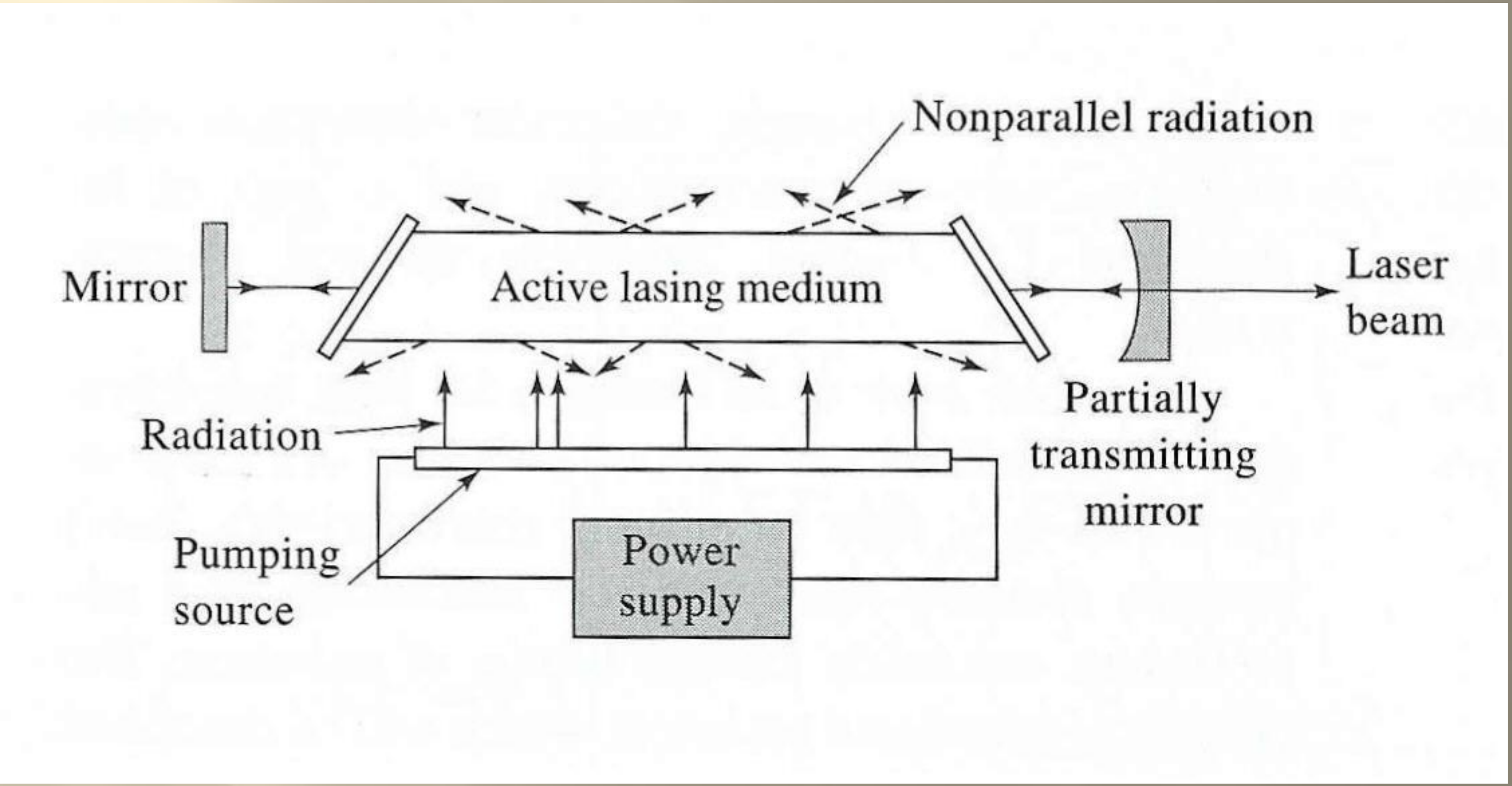

Nonparallel radiation dissipates out the top and bottom of the medium and parallel or coherent radiation is left.

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Mechanism of Light Emission

For atomic systems in thermal equilibrium with their surrounding, the emission of light is the result of:

Absorption

And subsequently, spontaneous emission of energy

There is another process whereby the atom in an upper energy level can be triggered or stimulated in phase with the an incoming photon.

This process is:

stimulated emission

It is an important process for laser action

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Mechanism of Light Emission

Processes include:

- adsorption
- spontaneous emission (fluorescence)
- stimulated emission
- pumping
- population inversion

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Absorption

Process that competes with stimulated emission. Two photons of same energy are absorbed to produce a metastable excited state.

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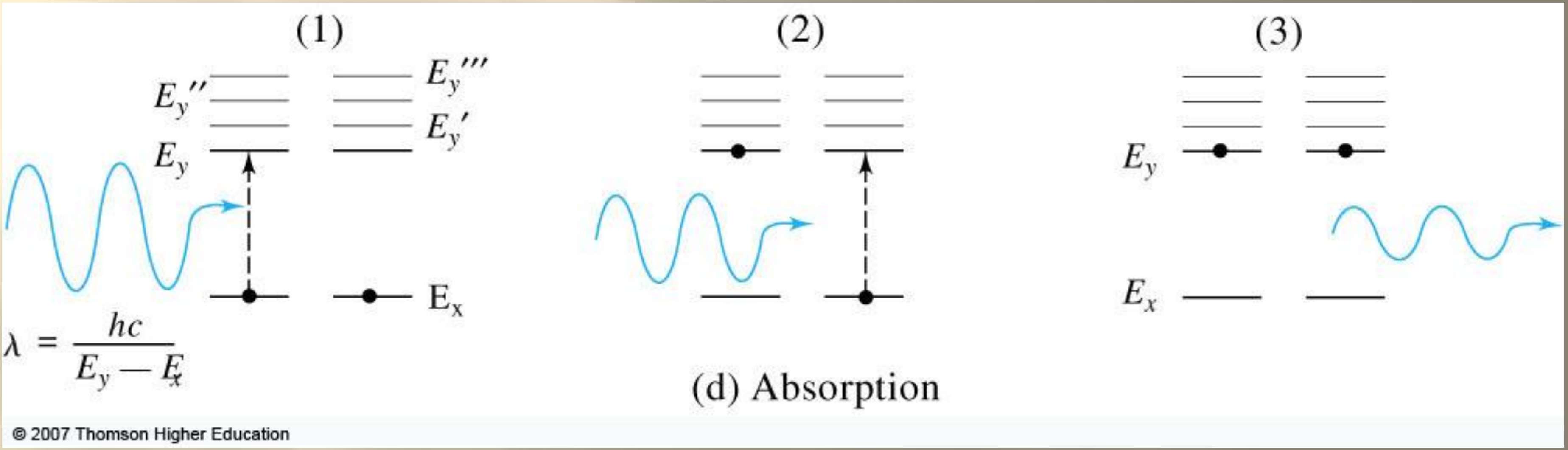
Absorption



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Spontaneous emission

The excess energy in the higher levels is lost by emission of radiation returning to ground state.

This type of emission is incoherent since it is a random process with species differing in direction and phase of emission**.**

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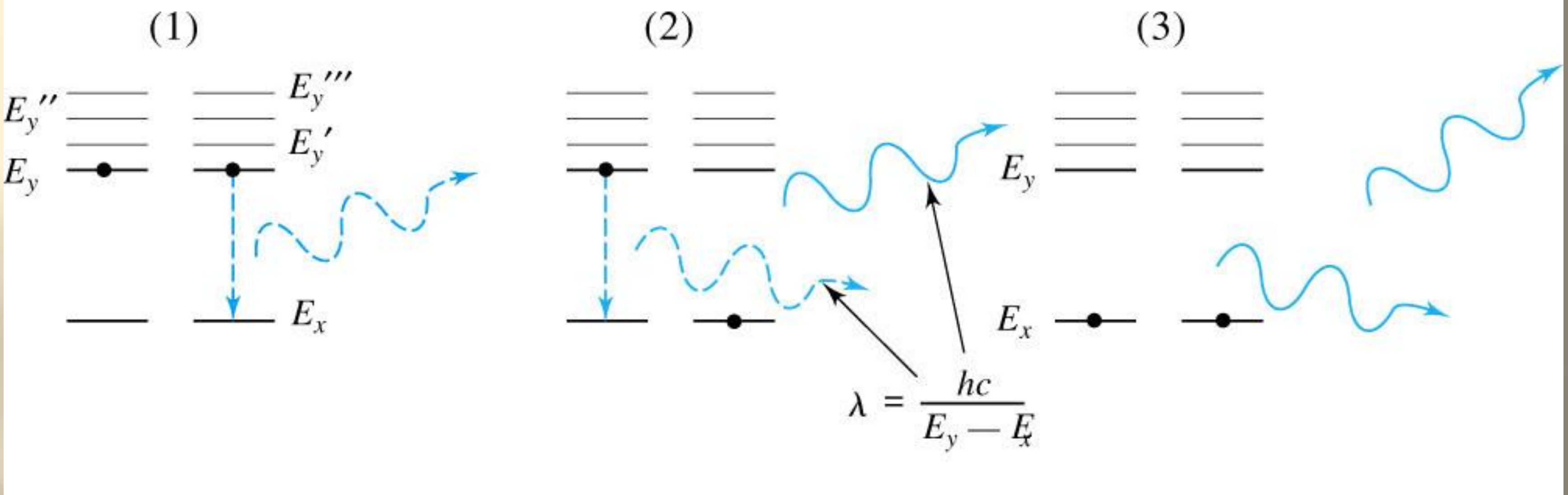
Spontaneous emission



(b) Spontaneous emission

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Stimulated emission

Excited species are struck by photons with the same energy as that of the spontaneous emission energy. Causes immediate relaxation to ground state.

This type of emission is coherent since the photons travel in phase and the same direction.

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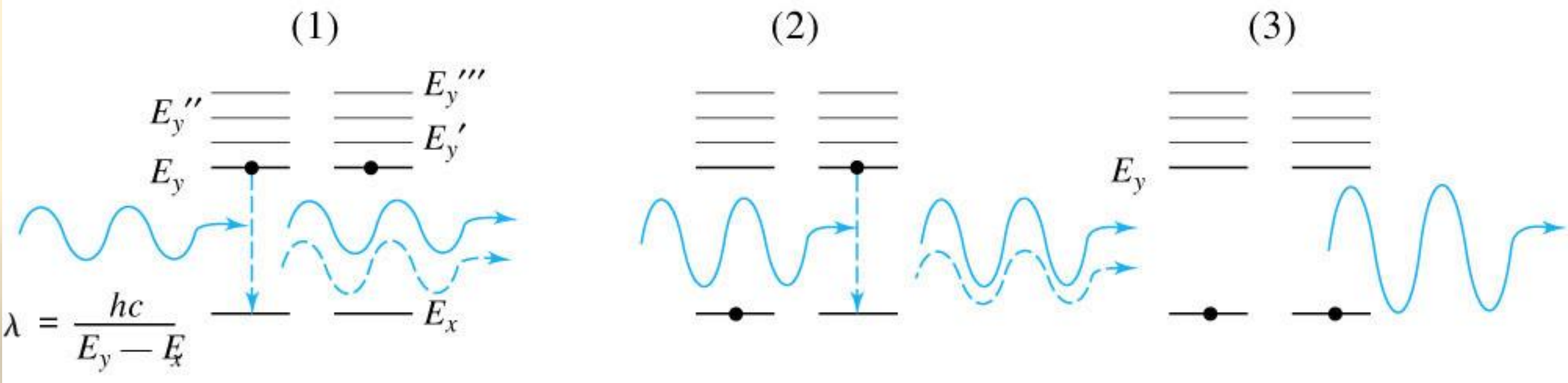
Stimulated emission



(c) Stimulated emission

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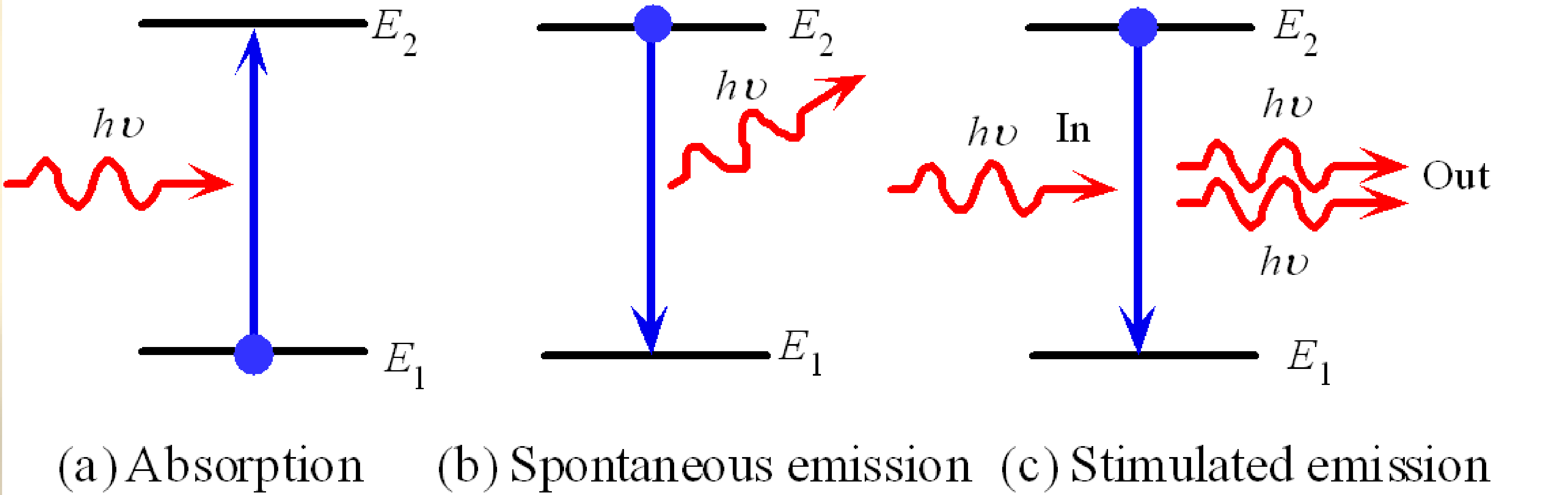

Absorption, spontaneous (random photon) emission and stimulated emission.

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Background

In a system, all three mechanisms occur.

However the stimulated emission is very sluggish compared to the spontaneous emission.

We need to have a much stimulated emission as possible for lasing action.

How?

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For Light Amplification to occur the number of photons produced by stimulated emission must exceed the number lost by absorption.

Stimulated emission > Absorption

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Stimulated emission > Absorption

This can only occur when the number of particles in the higher energy state exceeds the number in the lower.

This process is known as population inversion.

(created by pumping)

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Pumping

Lasing Medium – must be activated or "pumped" using radiation from an external source.

This can be a few photons of the correct energy to trigger a cascade of photons of the same energy. Or could be an electrical discharge into a gas.

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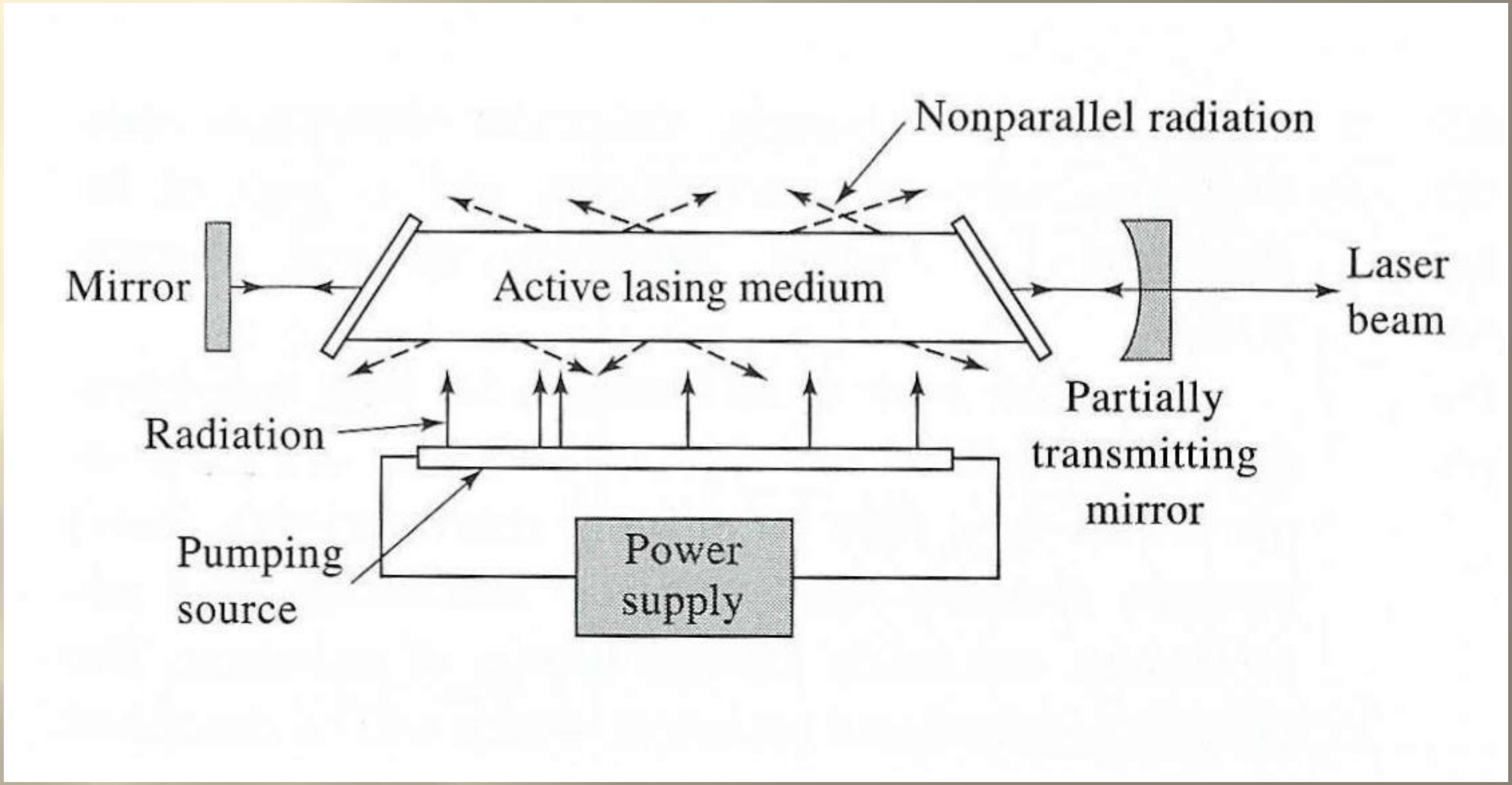
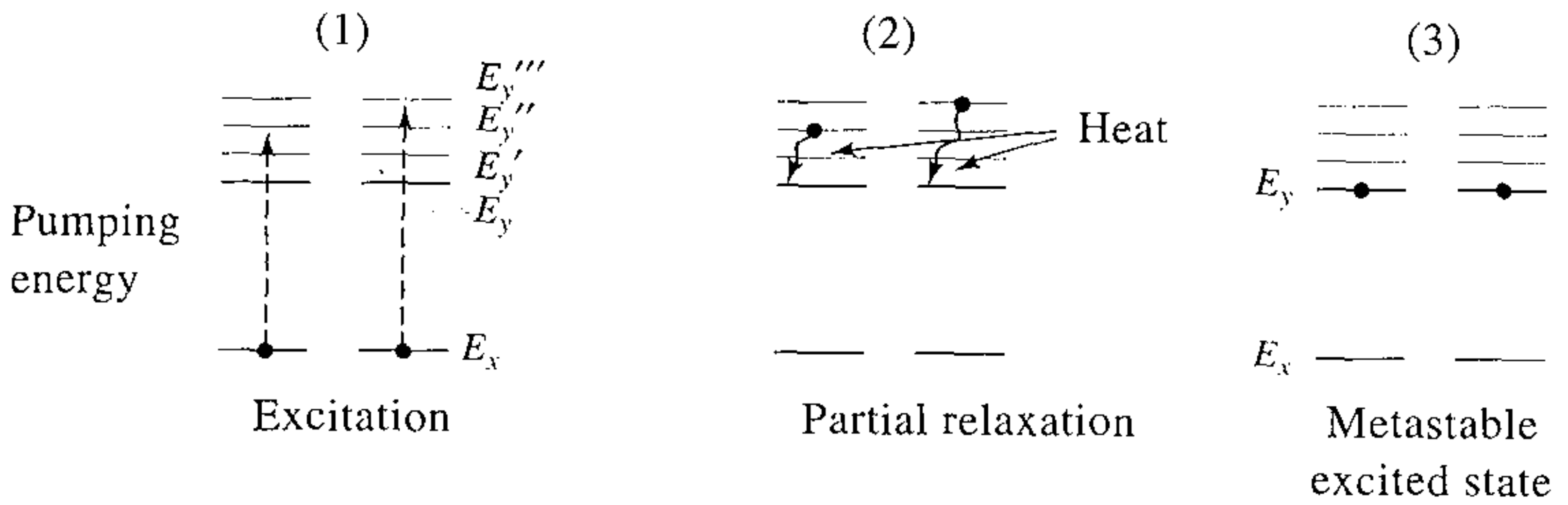

Nonparallel radiation
Mirror
Active lasing medium
Laser
beam
Partially
transmitting
mirror
Radiation
Pumping
source
Power
supply

LASERS

Pumping



(a) Pumping (excitation by electrical, radiant, or chemical energy)

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Pumping

Occurs when the medium is excited by external radiation or electricity.

This action populates higher electronic or vibrational energy levels of the active medium. Relaxation occurs through vibrations to the lowest excited level.

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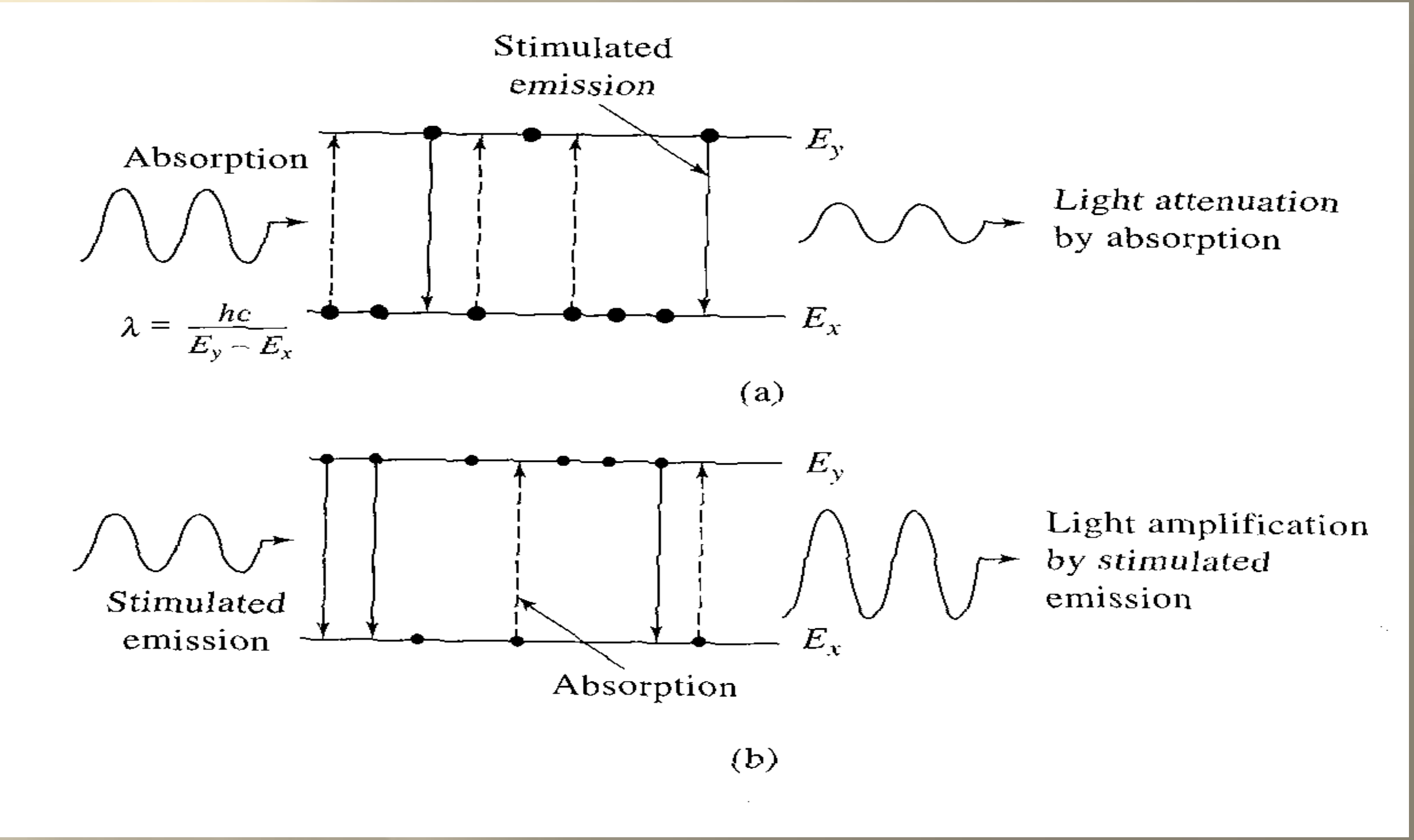
Stimulated emission
Absorption
E_y
Light attenuation by absorption
$\lambda = \frac{hc}{E_y - E_x}$
E_x
(a)
E_y
Light amplification by stimulated emission
Stimulated emission
E_x
Absorption
(b)

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Coherent Photons Production

When one atom in E2 decays spontaneously, a random photon results which will induce stimulated photon from the neighboring atoms.

The photons from the neighboring atoms will stimulate their neighbors and form avalanche of photons.

Large collection of coherent photons result.

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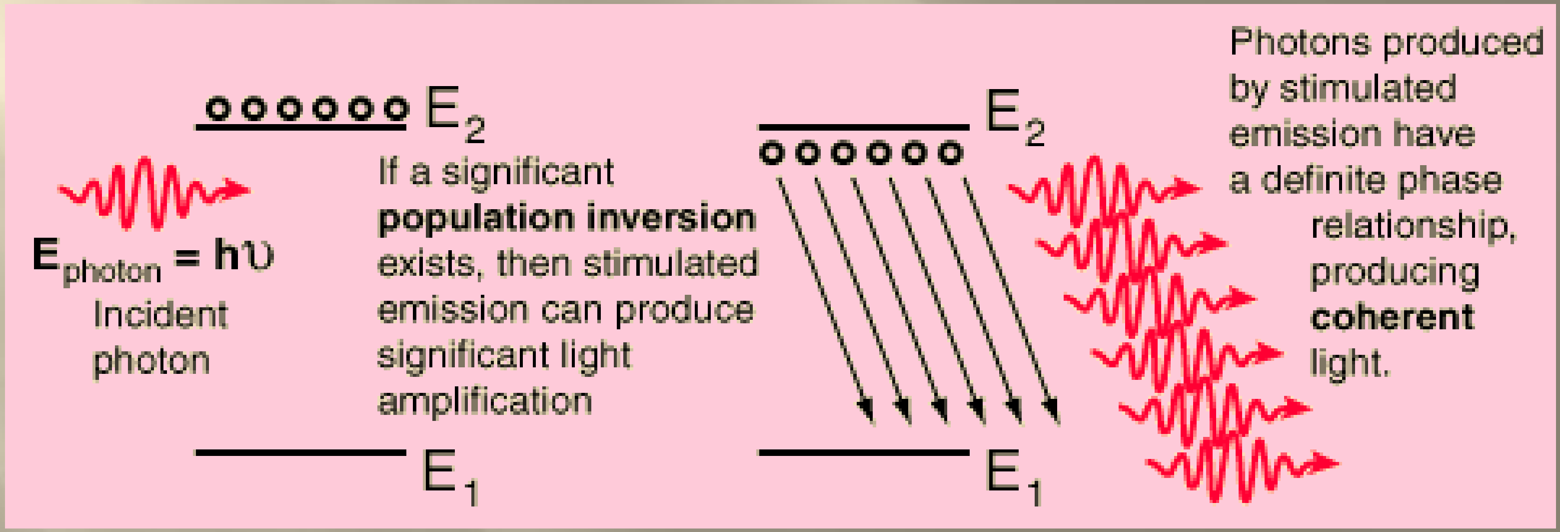
Population Inversion

When a sizable population of electrons resides in upper levels, this condition is called a "population inversion", and it sets the stage for stimulated emission of multiple photons. This is the precondition for the light amplification which occurs in a LASER and since the emitted photons have a definite time and phase relation to each other, the light has a high degree of coherence.



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POPULATION INVERSION

- Mechanism where $N_2 > N_1$
- Population inversion can be created by introducing a metastable centre where electrons can piled up to achieve a situation with more N_2 than N_1
- The process of attaining a population inversion is through pumping and the objective is to obtain a non-thermal equilibrium.
- It is not possible to achieve population inversion with a 2-state system.
- If the radiation flux is made very large the probability of stimulated emission and absorption can be made to far exceed the rate of spontaneous emission.
- But in 2-state system, the best we can get is $N_1 = N_2$.
- To create population inversion, a 3-state system is required.
- The system is pumped with radiation of energy E_{31} then atoms in state 3 relax to state 2 non-radiatively.
- The electrons from E_2 will now jump to E_1 to give out radiation.

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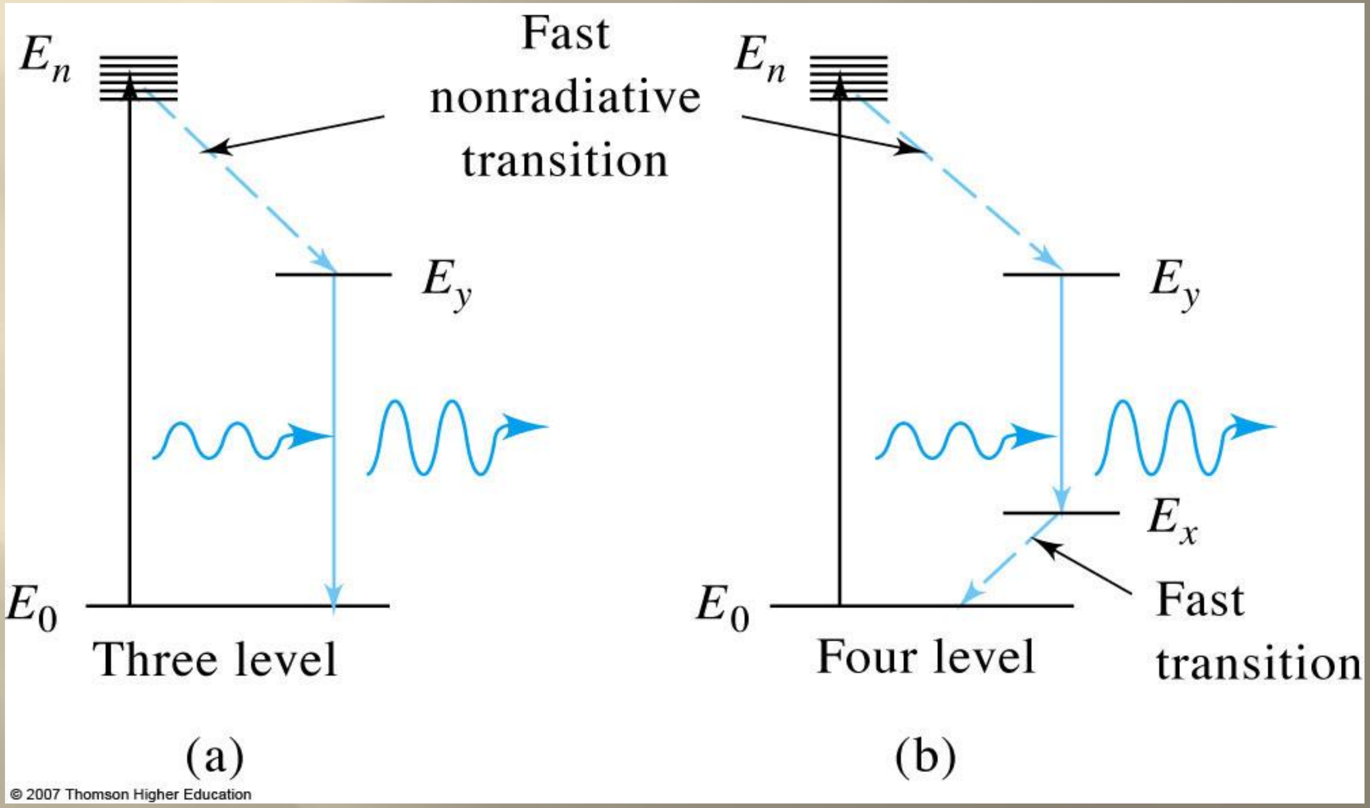
3- and 4- level laser systems



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Optical Feedback

The probability of photon producing a stimulated emission event can be increased by reflecting back through the medium several times.

A device is normally fashioned in such a way that the 2 ends are made highly reflective.

This is term an oscillator cavity or Fabry Perot cavity.

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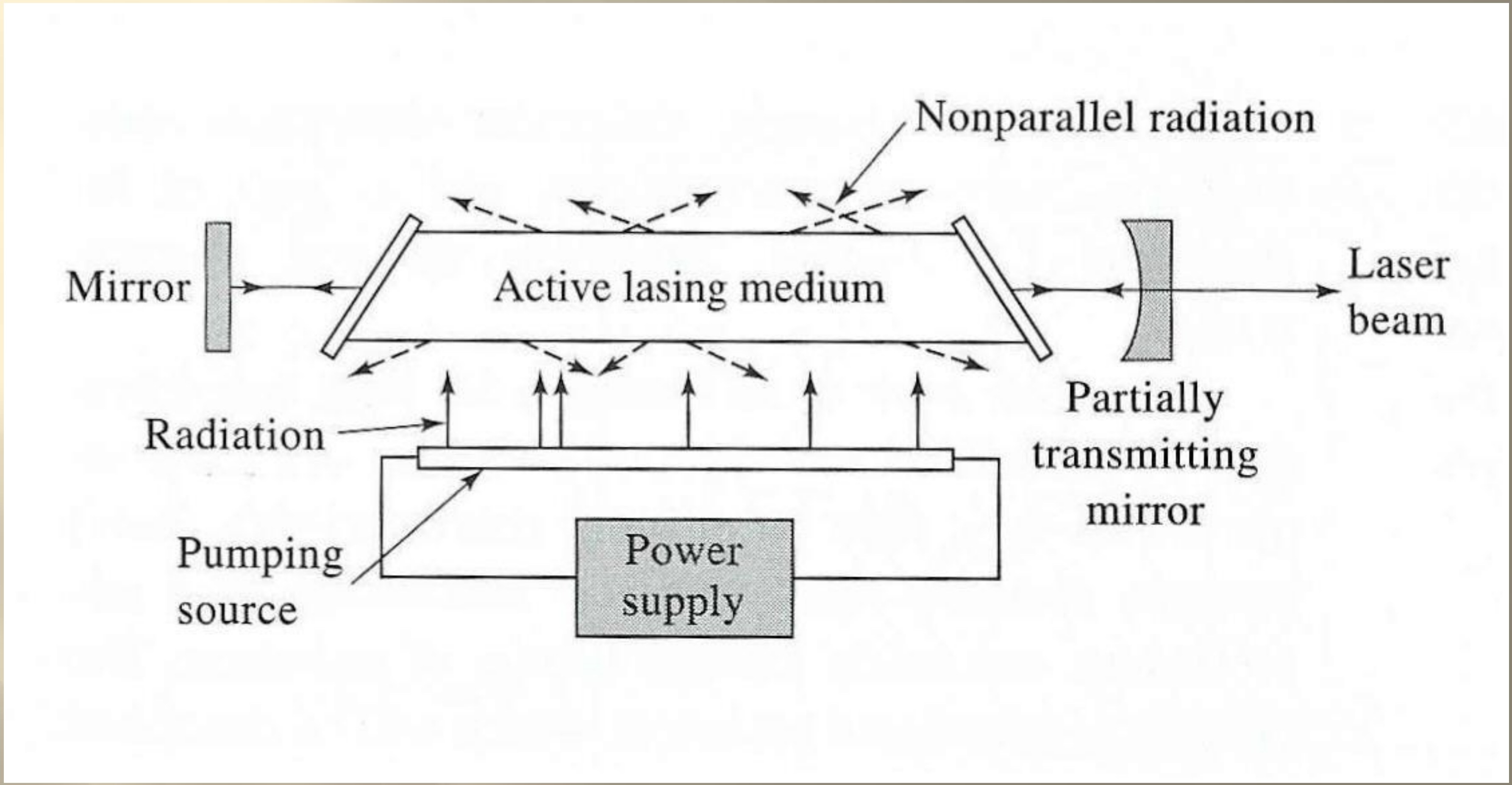

Nonparallel radiation
Mirror
Active lasing medium
Laser beam
Partially transmitting mirror
Radiation
Pumping source
Power supply

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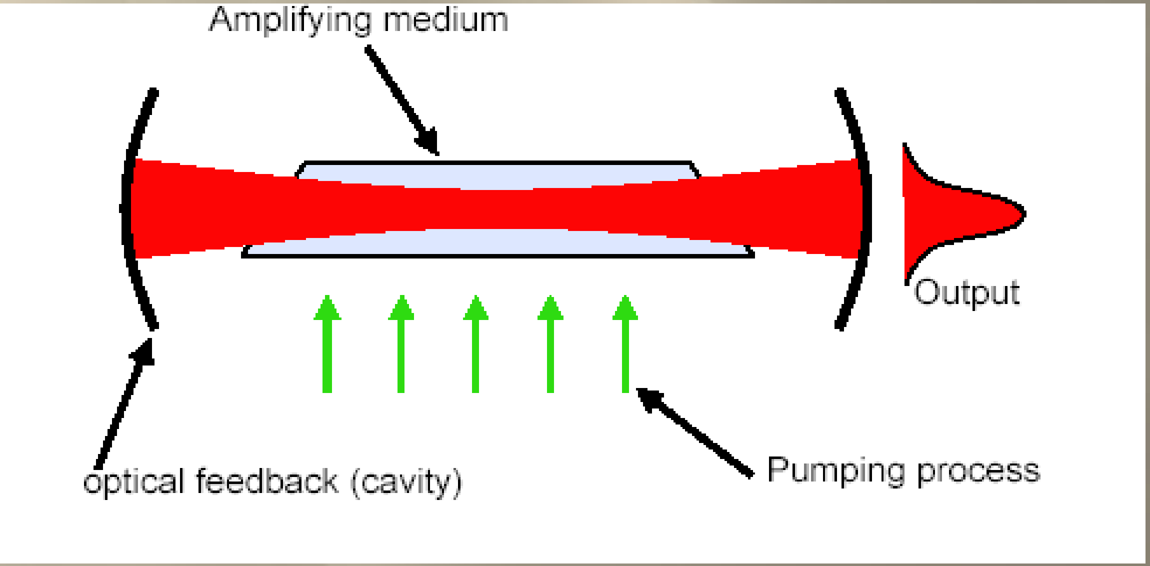
The key elements in a laser

- Pumping process prepares amplifying medium in suitable state
- Optical power increases on each pass through amplifying medium
- If gain exceeds loss, device will oscillate, generating a coherent output



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Once the cascade begins the laser functions as a resonator, passing the radiation back and forth through the medium using mirrors. This generates even more photons – "amplification".

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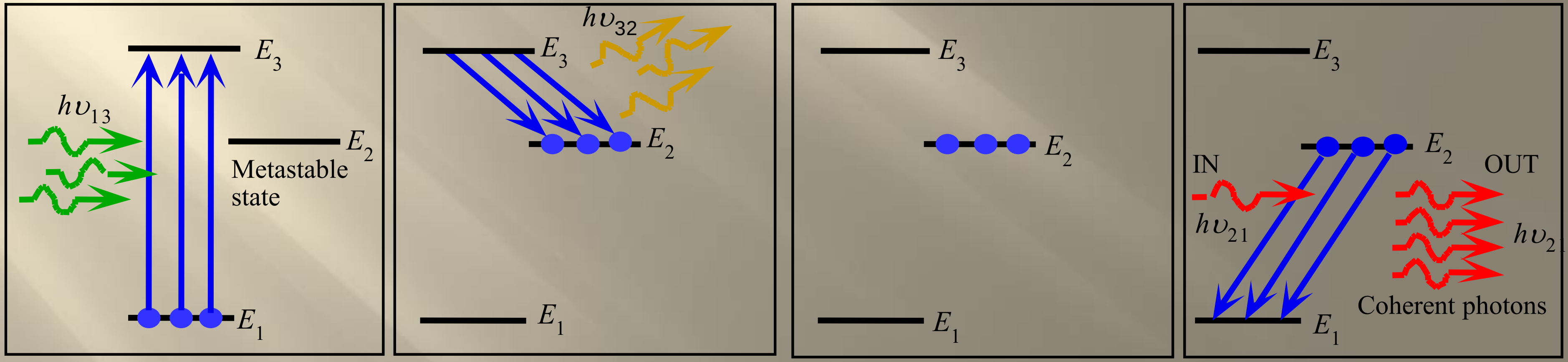
Recap

Excite atoms from E1 to E3.
Exciting atoms from E1 to E3 →optical pumping
Atoms from E3 decays rapidly to E2 emitting hv32
If E2 is a long lived state, atoms from E2 will not decay to E1 rapidly
Condition where there are a lot of atoms in E2 →population inversion.



(a) (b) (c) (d)

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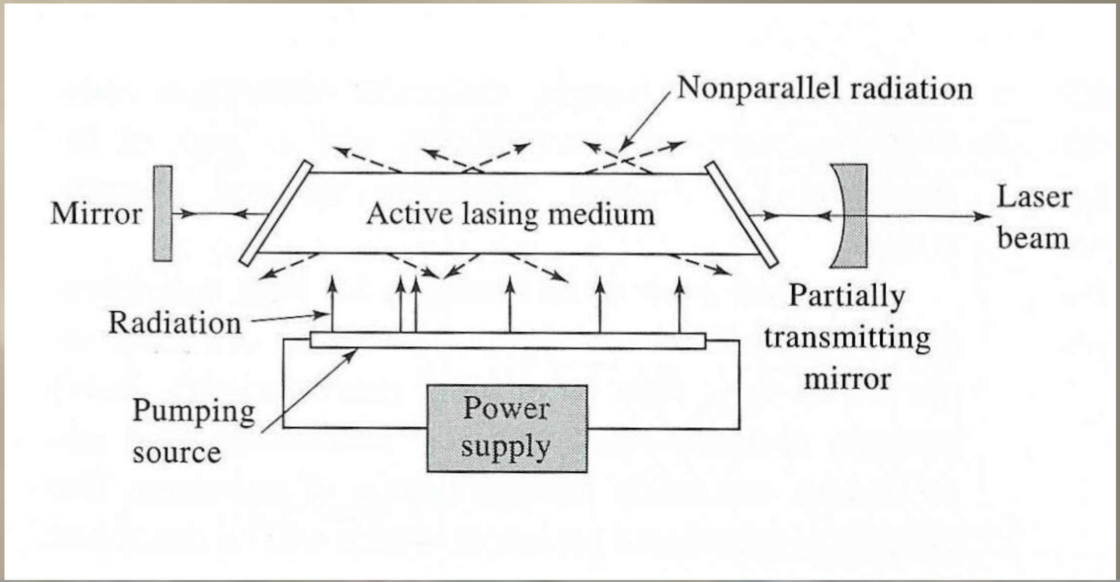
Lasing Medium

solid crystal (ruby)
solution (organic dye)
gas (argon or krypton)
semiconductor (gallium arsenide)



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Crystal

Ruby Laser – one of the first lasers,

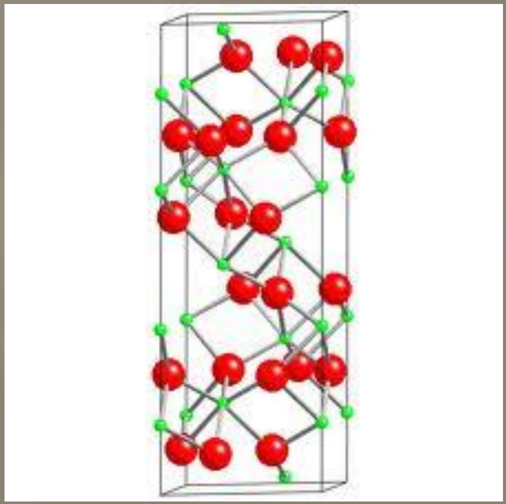
made up of Al_2O_3 with 0.05% Cr(III) in the Al(III) lattice.

The Cr(III) is the active lasing material.

λ = 694.3 nm (has a deep red color)

Al – green

O - red



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Crystal

Nd:YAG Laser – most widely used. (4-level)

Lasing medium is made up of neodymium ion in a crystal of yttrium aluminum garnet. ($Y_3Al_2(AlO_4)_3$, or $Y_3Al_5O_{12}$)

Very high radiant power output at 1064 nm and frequency doubled to give intense line at 532 nm.

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Gas Lasers

Four types

- neutral atom lasers (He/Ne)(most common)
- ion lasers with active species (Ar^+ or Kr^+)
- molecular lasers (CO_2 or N_2)
- eximer lasers (gas mixtures)

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Gas Lasers

- neutral atom lasers (He/Ne)(common)
  - Low cost and maintenance, reliable, low power consumption, 632.8 nm line
- ion lasers with active species (Ar^+ or Kr^+)
  - Ar^+ 514.4 and 488.0 nm lines of high intensity
  - 4-level device
  - Argon ions formed by electrical discharge
  - Go from ground state (3 principle quantum #) to 4p states, lasing occurs when relax to 4s state
  - Very high intensity – used for Raman

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Gas Lasers

- molecular lasers (CO_2 or N_2)
  - CO_2 used in IR 10.6 μm
- eximer lasers (gas mixtures)

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Dye Lasers

Continuously tunable over a 20 - 50 nm range. Bandwidth ~ 0.01 nm.

Active material is an organic dye that fluoresces in the UV, vis, or IR region.

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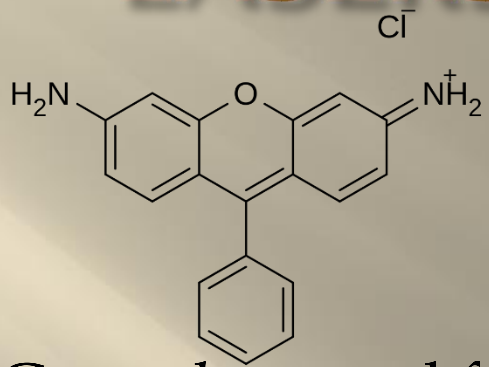
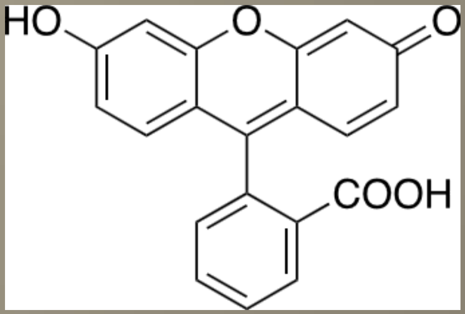
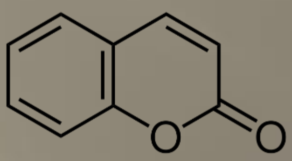


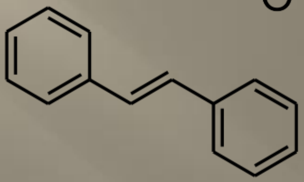


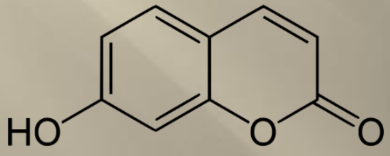
Dye Lasers

Examples:

- rhodamine 6G, can be tuned from 635 nm (orangish-red) to 560 nm (greenish-yellow)
- fluorescein (green, 530–560 nm)
- coumarin (blue 490–620 nm)
- stilbene (violet 410–480 nm),
- umbelliferone (blue, 450–470 nm)







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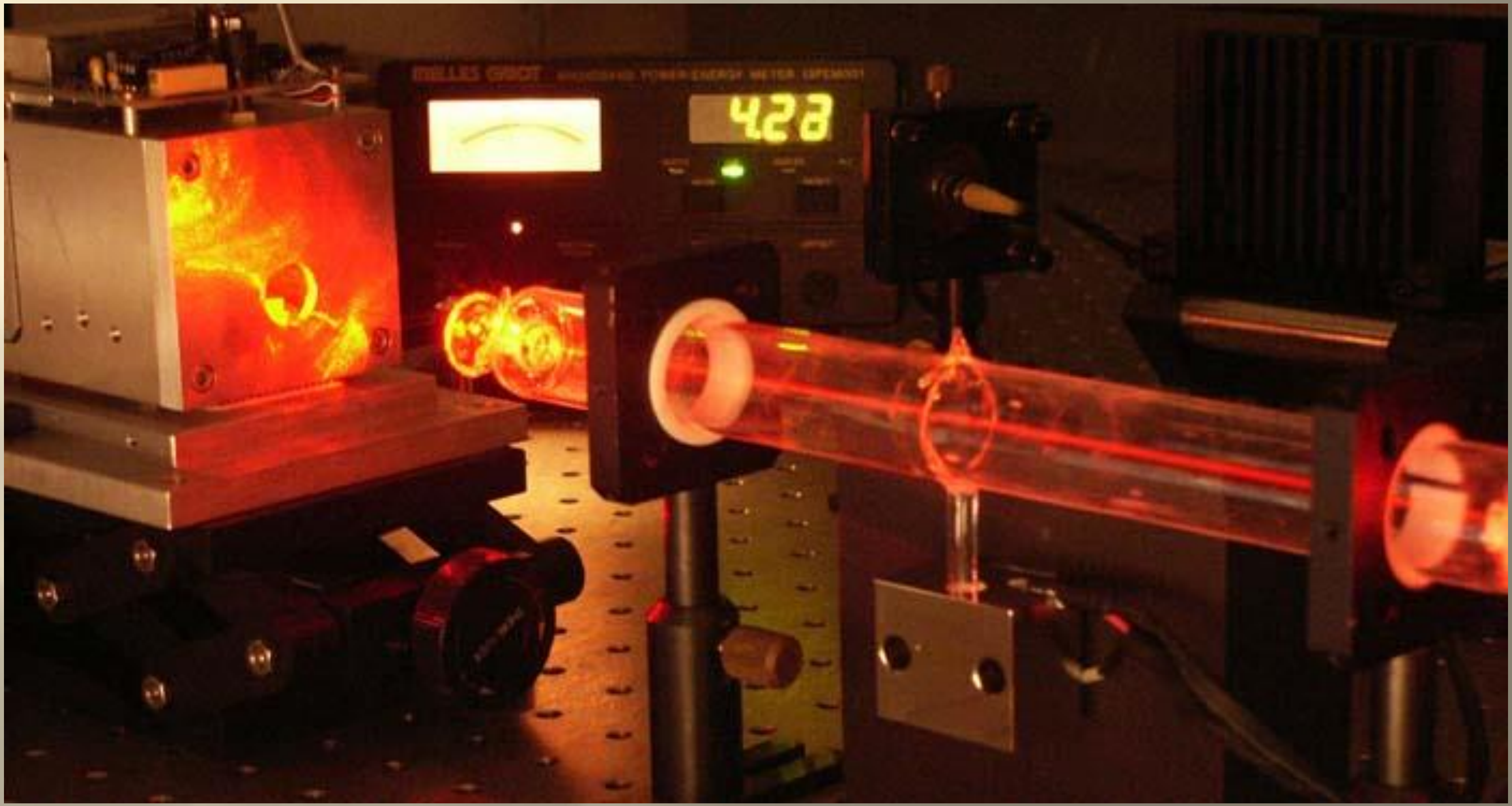
Diode Lasers



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Diode Lasers

Semiconductor laser diodes are double heterostructures (DH) with energy band diagrams similar to LEDs.

In order to design a laser diode, the p-n junction must be heavily doped (p and n materials are degenerate). Degenerate semiconductor is a semiconductor with such a high level of doping that the material starts to act more like a metal than as a semiconductor.

By degenerated doping, the Fermi level of the n-side lies in the conduction band whereas the Fermi level in the p-region will lie in the valance band.

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Diode Lasers

If the degenerately doped p-n junction is forward biased by a voltage greater than the band gap; eV > Eg,

electrons flow to the p-side and holes flow to the n-side.

When a photon with E = Eg strikes, the photon can stimulate an electron to fall down from the CB to VB.

The incoming photon stimulates emission rather than absorption.

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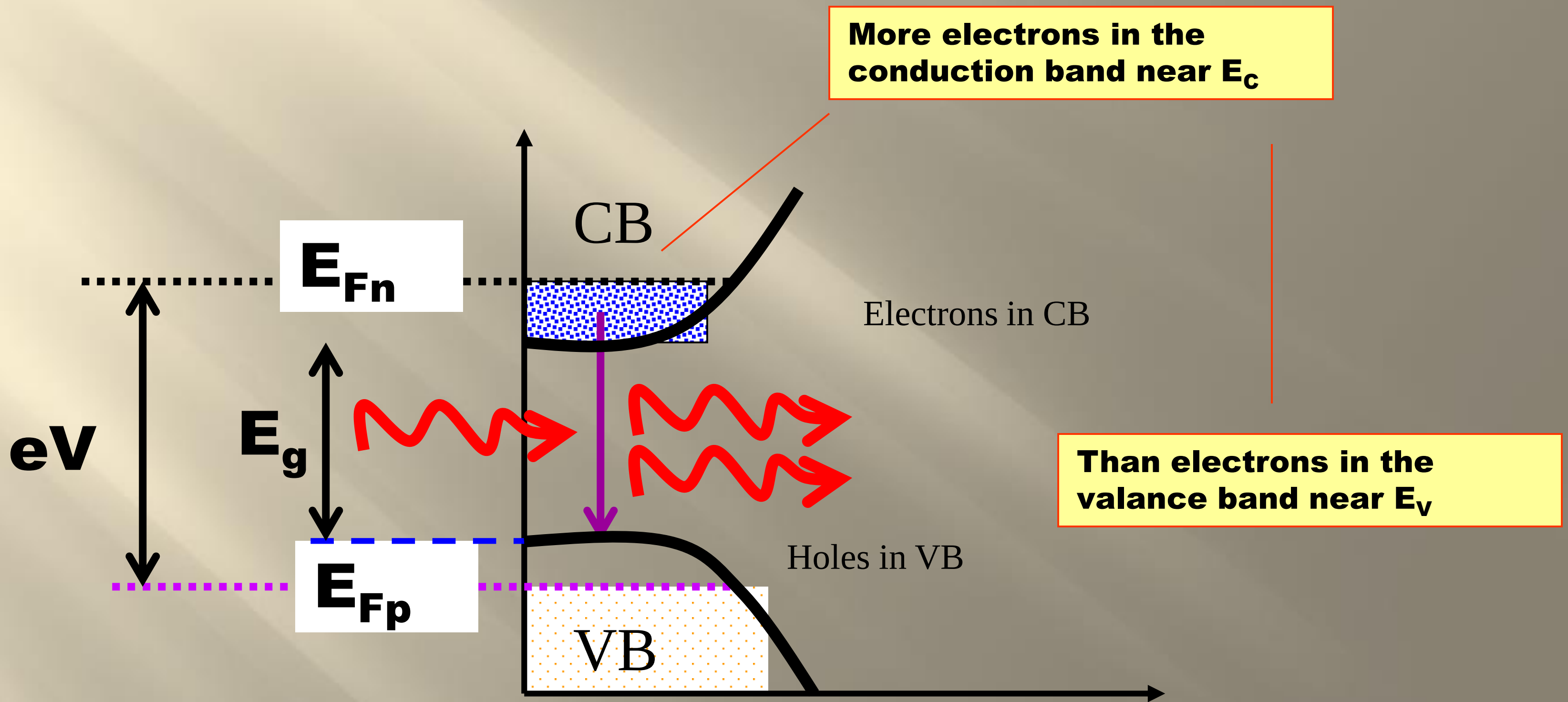
Diode Lasers



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Semiconductor Diode Lasers

Apply a voltage across a semiconductor diode in the forward direction to excite electrons into the conduction band creating hole-electron pairs. When the electrons relax into the valence band energy is released equal to the band-gap energy. $E_g = h\nu$

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Pumping Mechanism in Laser Diode

It is obvious that the population inversion between energies near EC and those near EV occurs by injection of large charge carrier across the junction by forward biasing the junction.

Therefore the pumping mechanism is FORWARD DIODE CURRENT → Injection pumping

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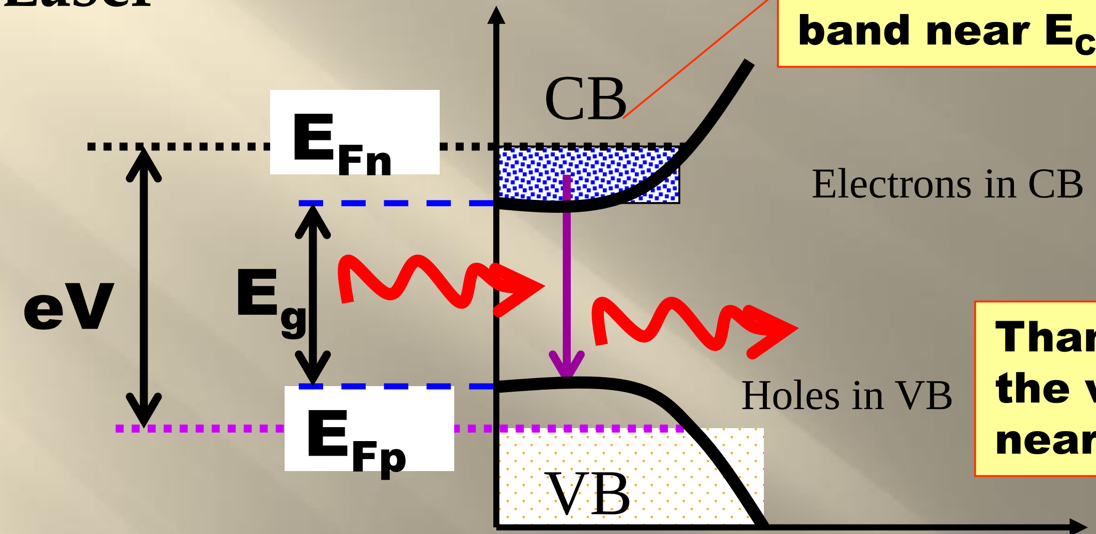
Population Inversion in Diode Laser

More electrons in the conduction band near E_C



Than electrons in the valance band near E_V

$E_{Fn}-E_{fP} = eV$

$eV > E_g$

eV = forward bias voltage

Fwd Diode current pumping → injection pumping

- There is therefore a **population inversion** between energies near E_C and near E_V around the junction.
- This only achieved when degenerately doped p-n junction is forward bias with energy > E_{gap}

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The Lasing Action

The population inversion region is a layer along the junction → also call inversion layer or active region.

Therefore, the incoming photon stimulates emission not absorption.
The active region is then said to have 'optical gain' since the incoming photon has the ability to cause emission rather than being absorbed.

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For Successful Lasing Action:

Optical Gain (not absorb)

- Achieved by population inversion

Optical Feedback

- Achieved by device configuration
- Need to increase the total optical amplification by making photons pass through the gain region multiple times
- Insert 2 mirrors at each end of laser
- This is term an oscillator cavity or Fabry Perot cavity
- Mirrors are partly transmitted and party reflected

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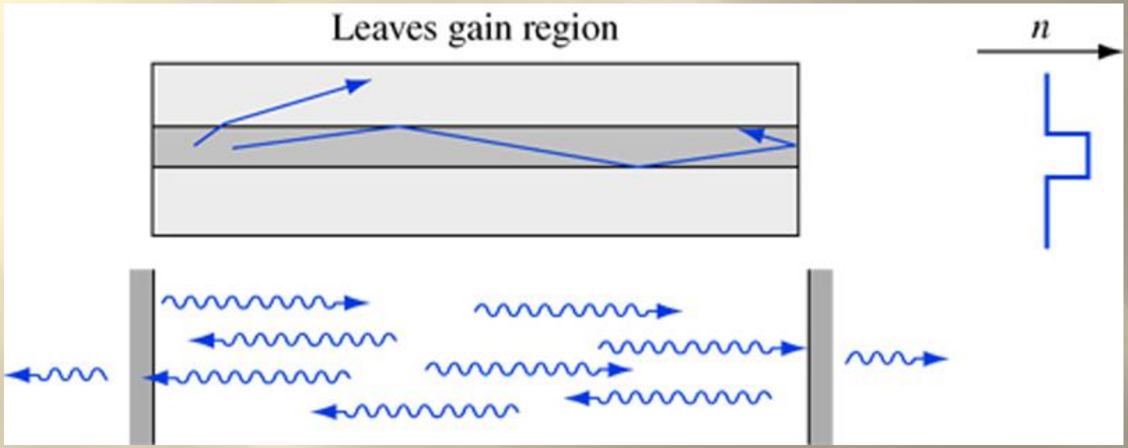
Reflection of Photons Back and Forth, Higher Gain



Fabry-Perot Cavity

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Optical Feedback

In diode laser it is not necessary to use external mirrors to provide positive feedback. The high refractive index normally ensure that the reflectance at the air/material interface is sufficiently high .

The diode is often cleaved at one end and roughened at the other end.

This results in the radiation generated within the active region spread out into the surrounding GaAs, and there is a confinement of the radiation within a small region called the mode volume,

In the mode volume, there are additional carriers present which increases the refractive index of the material as compared to the surrounding material.

This produces a dielectric waveguide similar to the heterojunction LED. However the difference is too small to be an efficient waveguide.

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Optical Feedback

In diode laser it is not necessary to use external mirrors to provide positive feedback. The high refractive index normally ensure that the reflectance at the air/material interface is sufficiently high .

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Threshold Current Density

If the injected carrier concentration become large enough, the stimulated emission can exceed absorption so optical gain can be achieved in the active region. With appropriate configuration to achieve optical feedback, laser oscillation occurs when gain exceeds losses.

For significant gain, a high current density is necessary.
The onset of lasing is characterized by the a specific injection current known as the Threshold Current.

Since the simple homojunction laser has high threshold current, it is considered not efficient.

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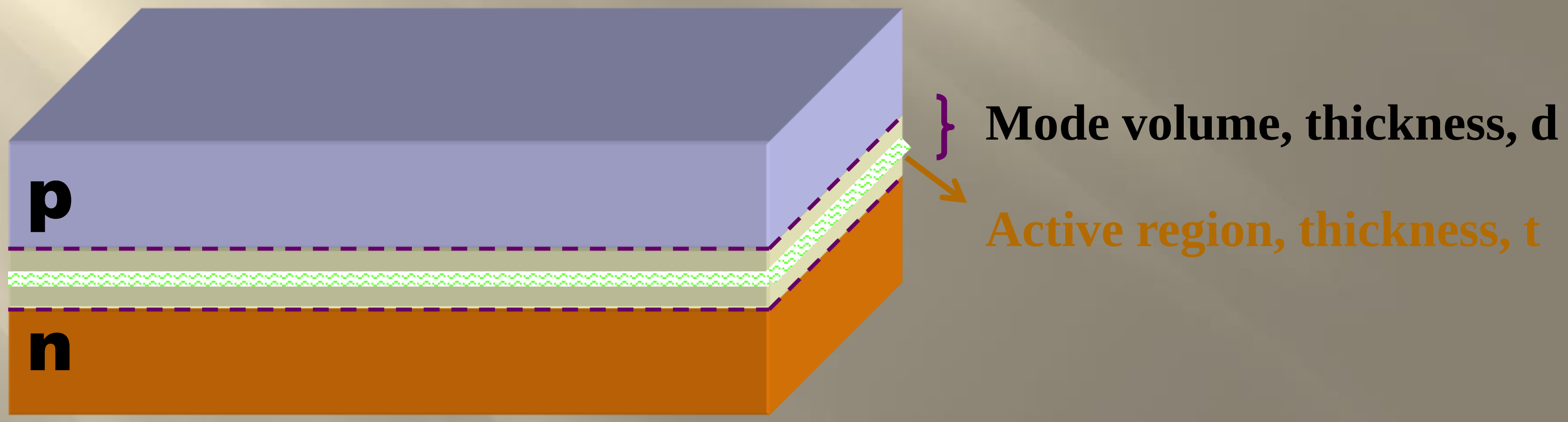
Threshold Current Density

- Recall that when forward biased, with eV > E_g of the material, electrons (from degenerately doped n) and holes (from degenerately doped p) will be injected across the junction to create population inversion.
- The population inversion is created in an active region. Radiative transition may occur resulted in stimulated emission when the photon is absorbed by the electrons in the conduction band.
- The radiation generated will be spread out in the vicinity of the active region and is almost confined in the thin layer (mode volume).

- Consider a diagram showing the active region and mode volume of a semiconducting laser:



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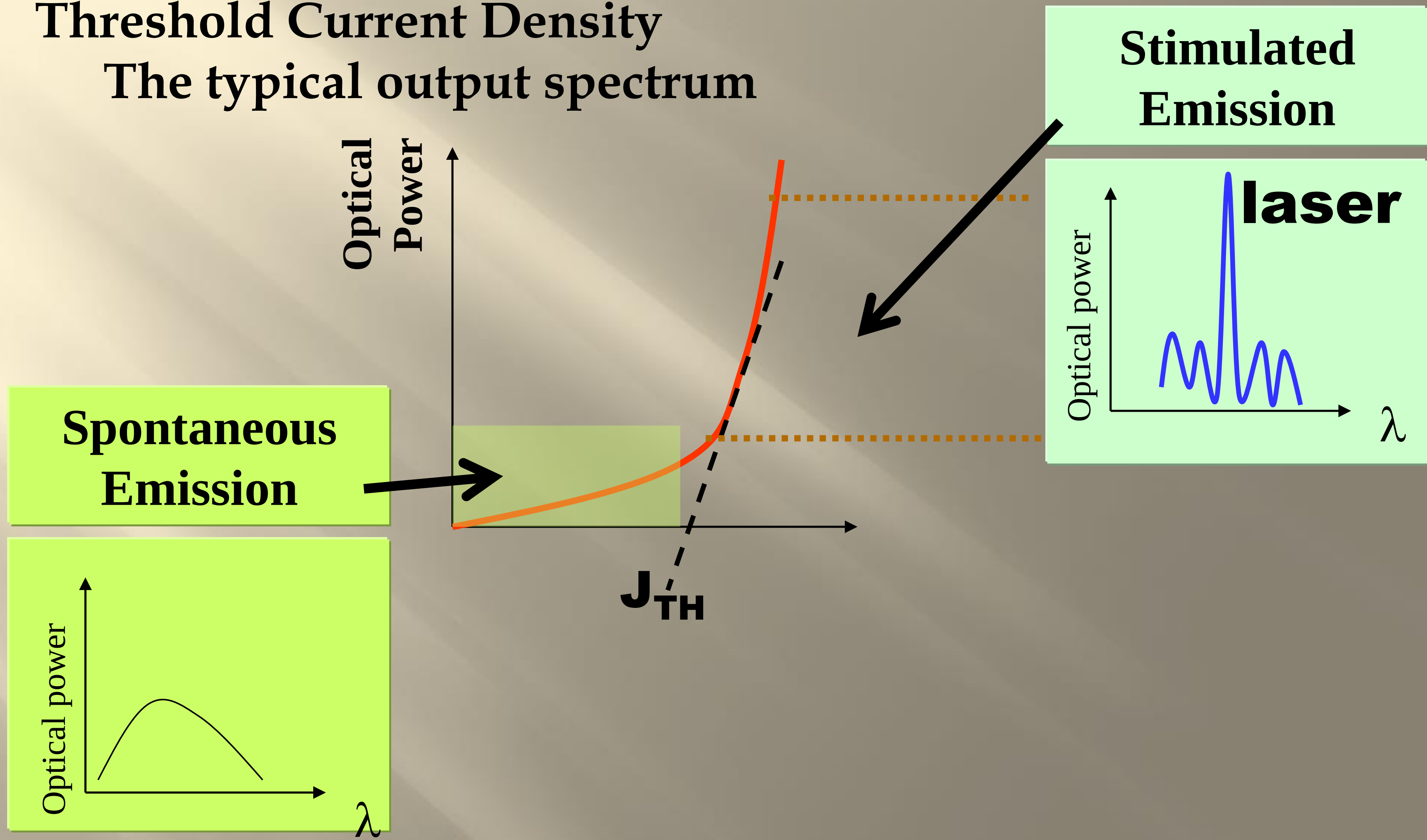
Threshold Current Density

The typical output spectrum



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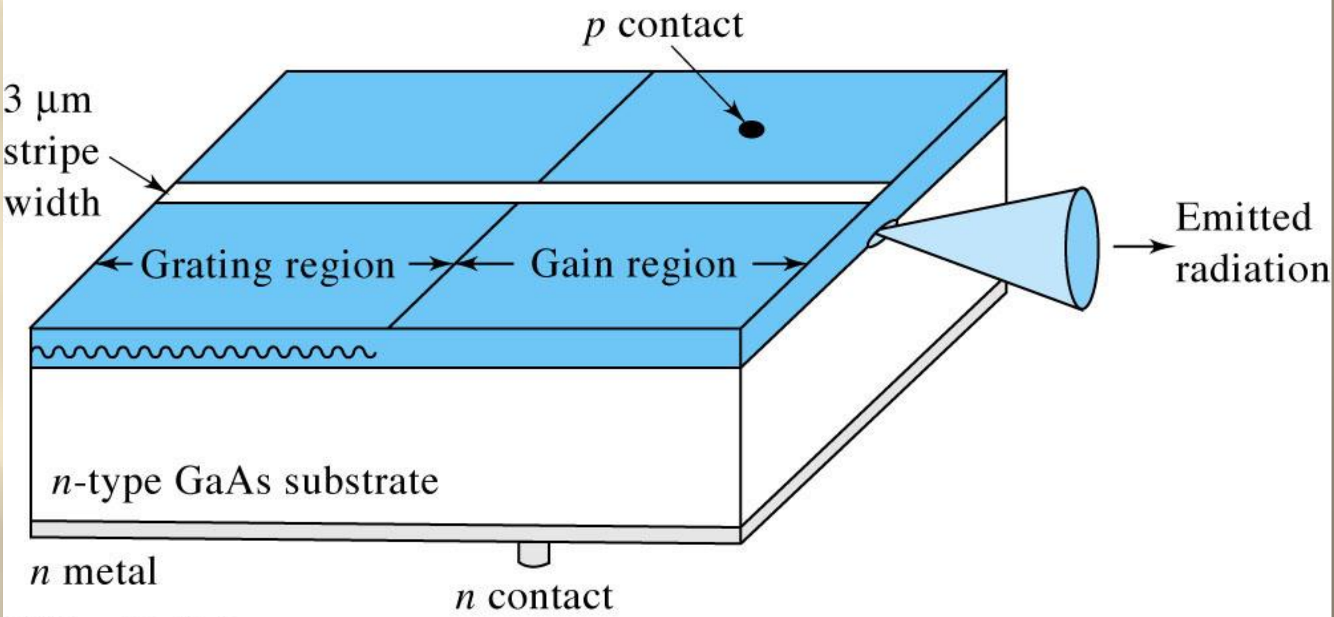
Semiconductor Diode Lasers



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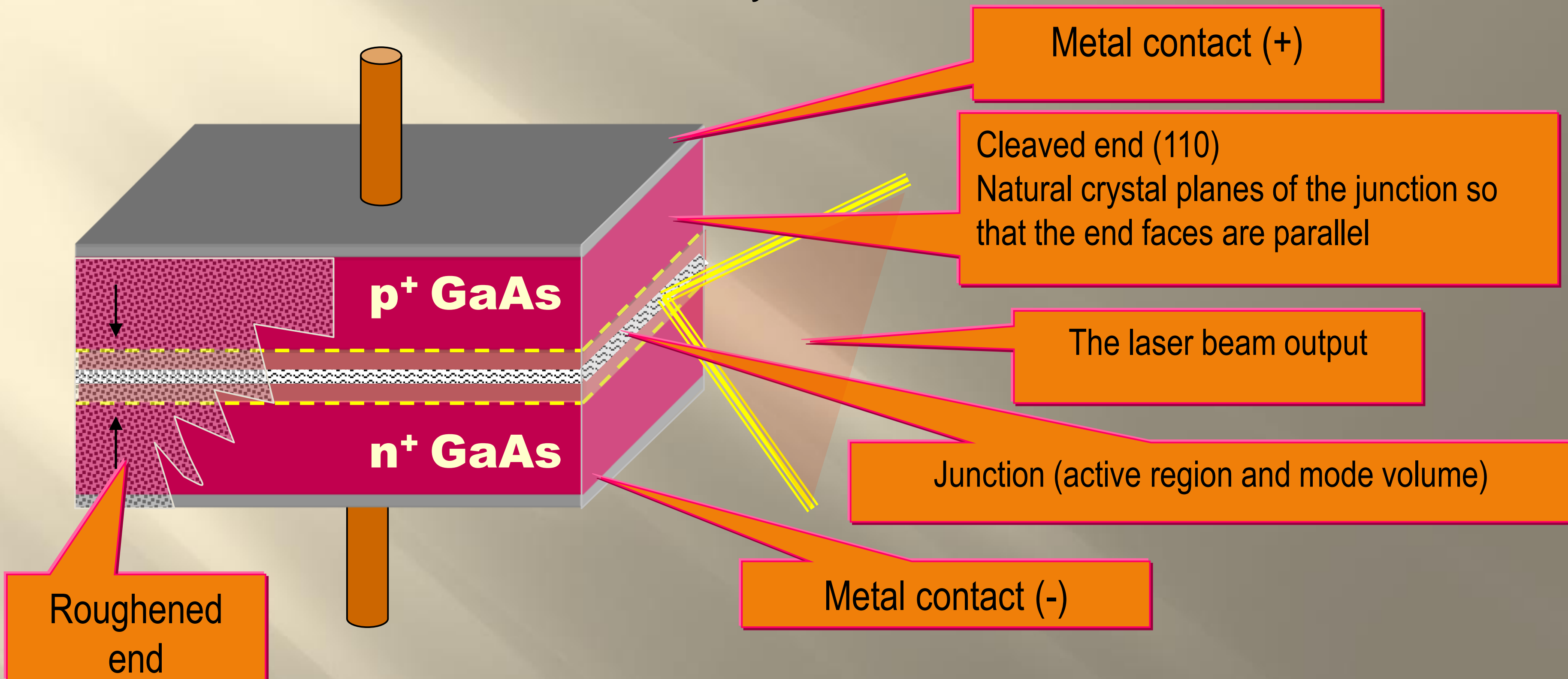
Schematic construction of a homojunction GaAs diode laser.



The carriers in the active region increases refractive index of GaAs
The refractive index increment is only ~0.02, hence is not a good dielectric waveguide
The beam therefore can be spread out to the surrounding region – mode volume
Vigorous pumping is therefore needed to enhance lasing
The threshold current for the pumping action exceeds 400Amm^{-2}

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For the homojunction laser….

The main problem with the homojunction laser diode is that the threshold current density, Jth is far too high for practical applications.

If Jth is low: improve rate of stimulated emission & improve efficiency occurs for optical cavity.

To get low Jth:

Confined carriers in a narrow region → carrier confinement

Build dielectric waveguide around the optical gain region (increase photon concentration hence stimulated emission) → photon confinement

How do we achieve that?

heterostructured laser diodes

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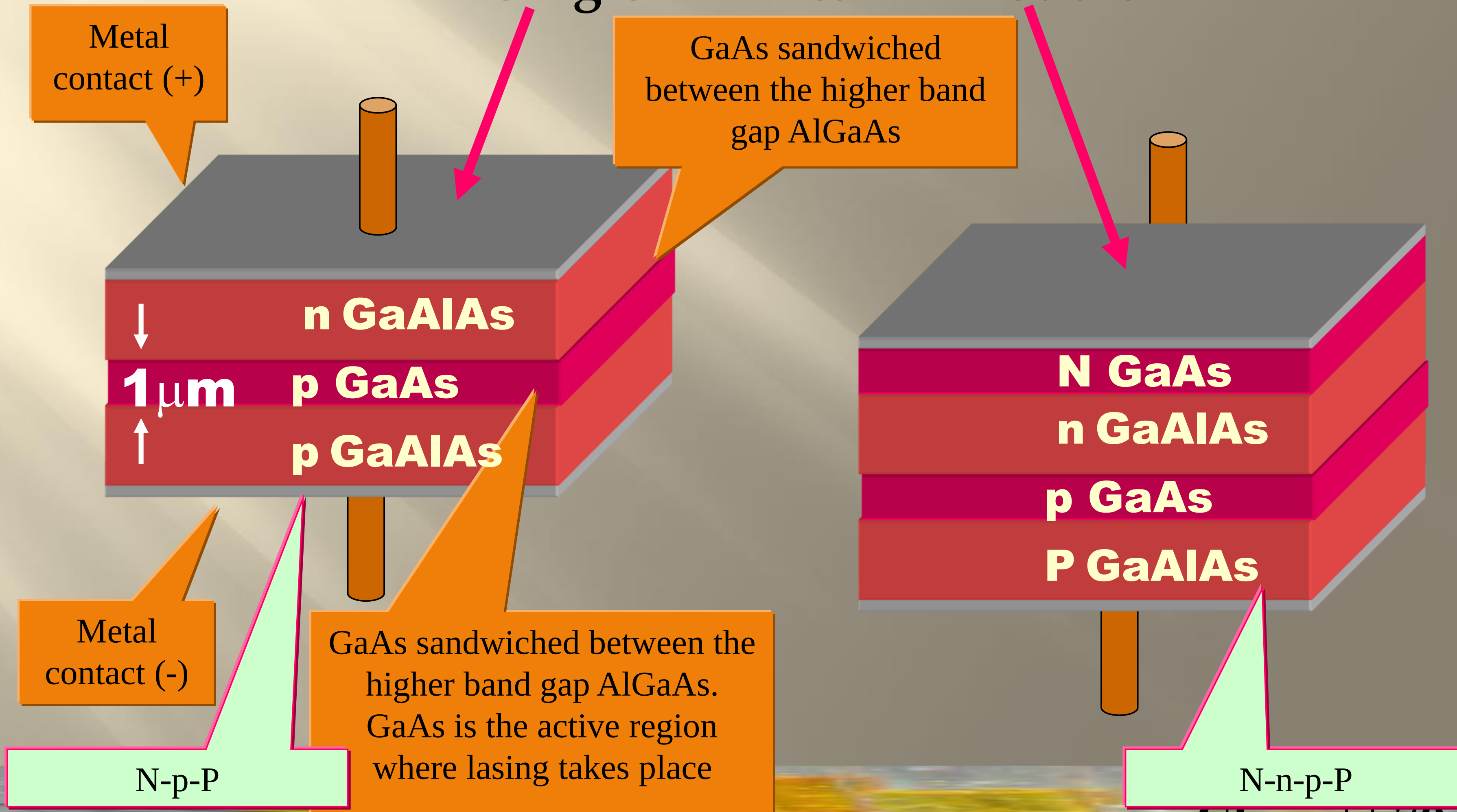
The Heterojunction Laser

Single & Double



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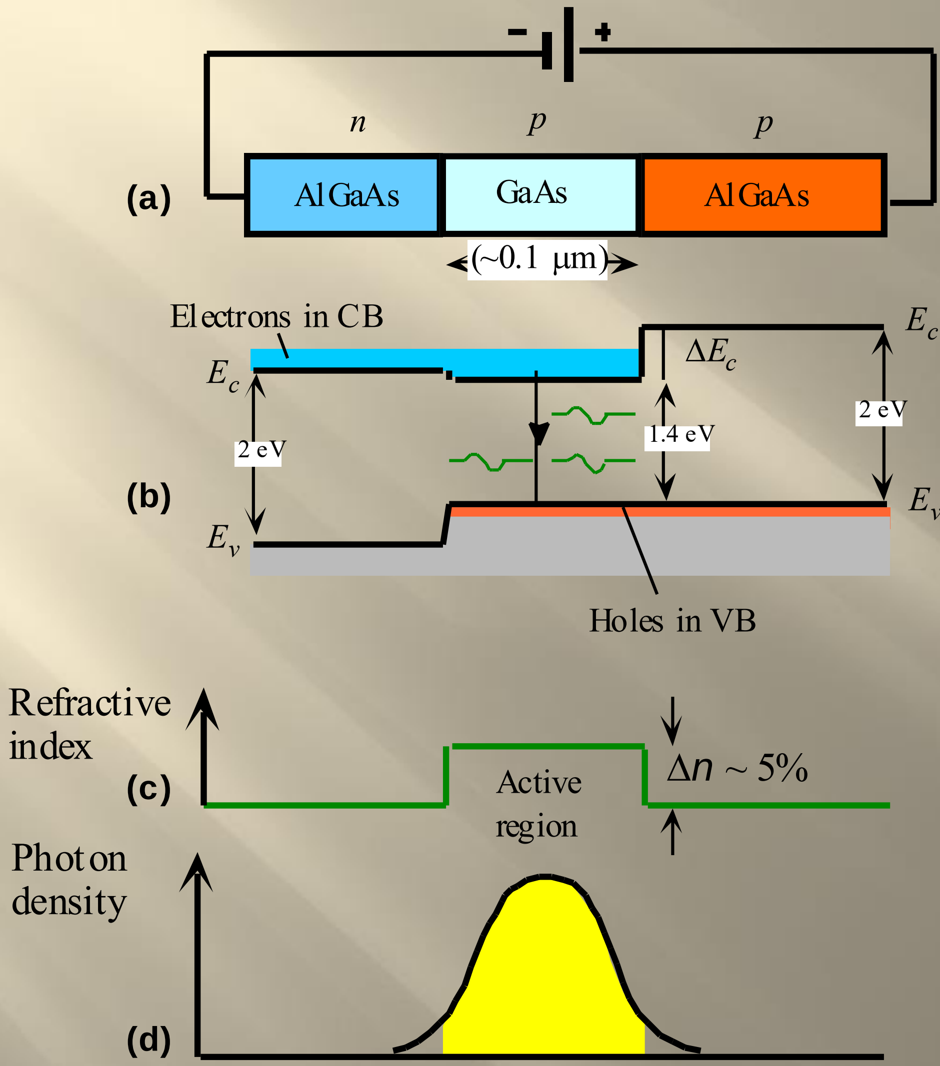

(a) A double heterostructure diode has two junctions which are between two different bandgap semiconductors (GaAs and AlGaAs).

(b) Simplified energy band diagram under a large forward bias. Lasing recombination takes place in the *p*-GaAs layer, the *active layer*

(c) Higher bandgap materials have a lower refractive index

(d) AlGaAs layers provide lateral optical confinement.

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Laser Diode Materials

Basically all of the materials for Lasers are similar to that for LEDs.

UV, Vis and IR Laser can be produced by materials as discussed in the LED lecture.

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Direct Gap Diode Laser

Direct band gap → high probability of electrons-holes recombination → radiatively emission.

The recombination radiation may interact with the holes in the valance band and be absorbed or interact with the electrons in the conduction band thereby stimulating the production of further photons of the same frequency → stimulated emission

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Materials Criteria & Selection

To date GaAs and GaAlAs are largely used.

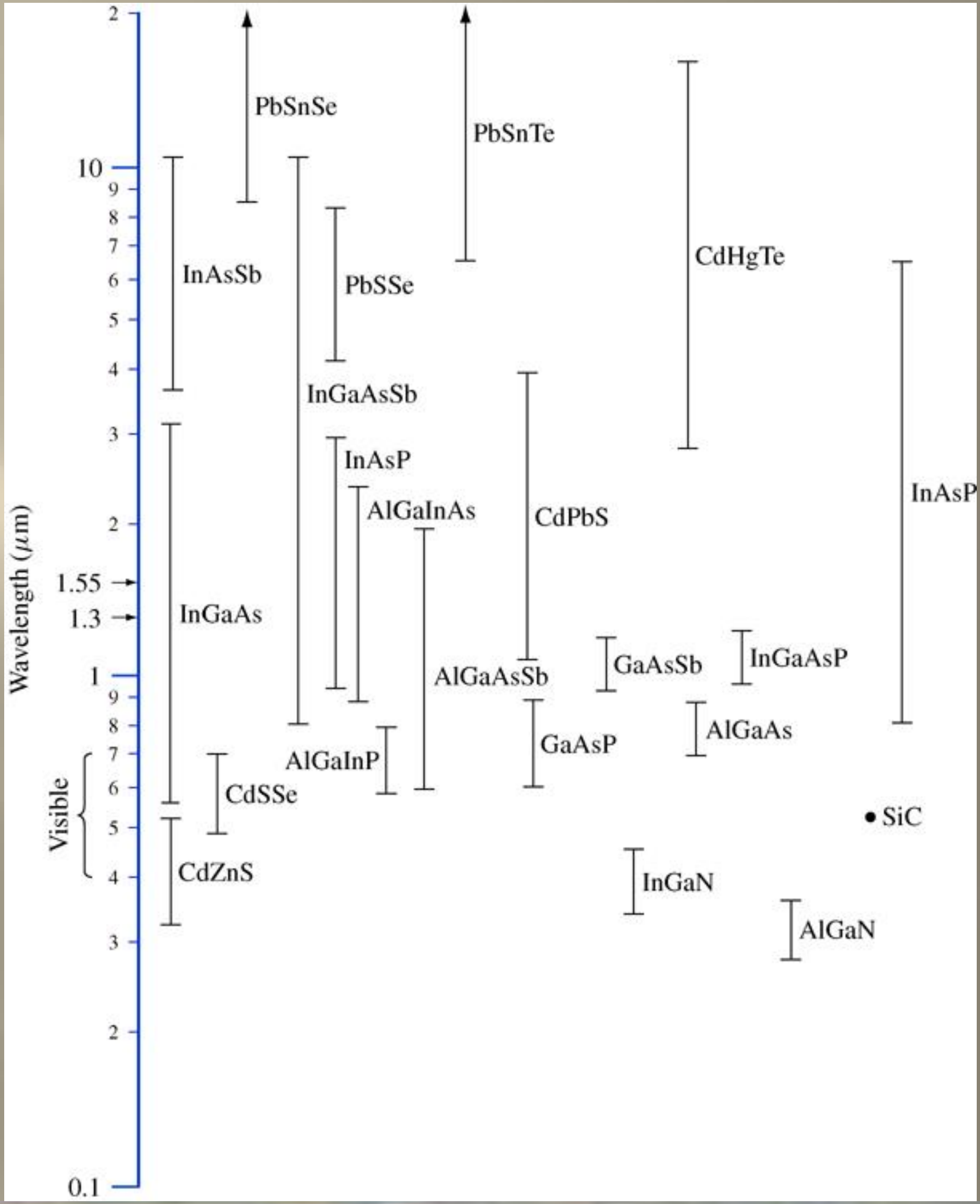
Advantages of AlGaAs/GaAs system is that:
GaAs is direct band gap material
Ga1-xAlxAs is direct when $x < 0.45$

Lattice match between Ga1-xAlxAs & GaAs is very small (0.1%) therefore epitaxial growth can be achieved.

The band gaps of both materials can be manipulated to produce SH or DH junctions lasers for high optical and carrier confinements.

For optical fiber communication, wavelength of 1.1-1.6 um is preferred.

Materials Available



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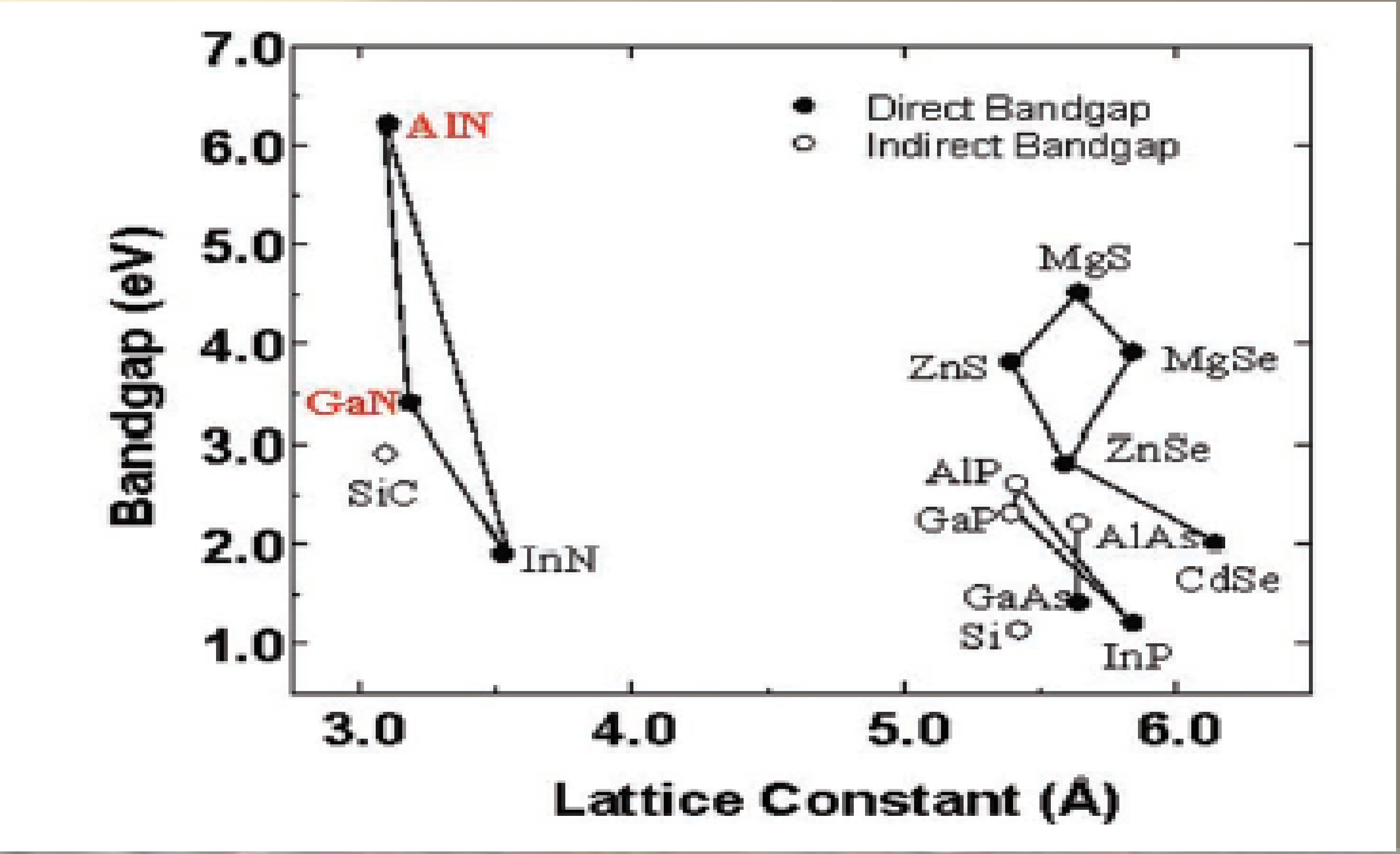
Technologically Important Material for Blue Laser



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InGaN and AlGaN

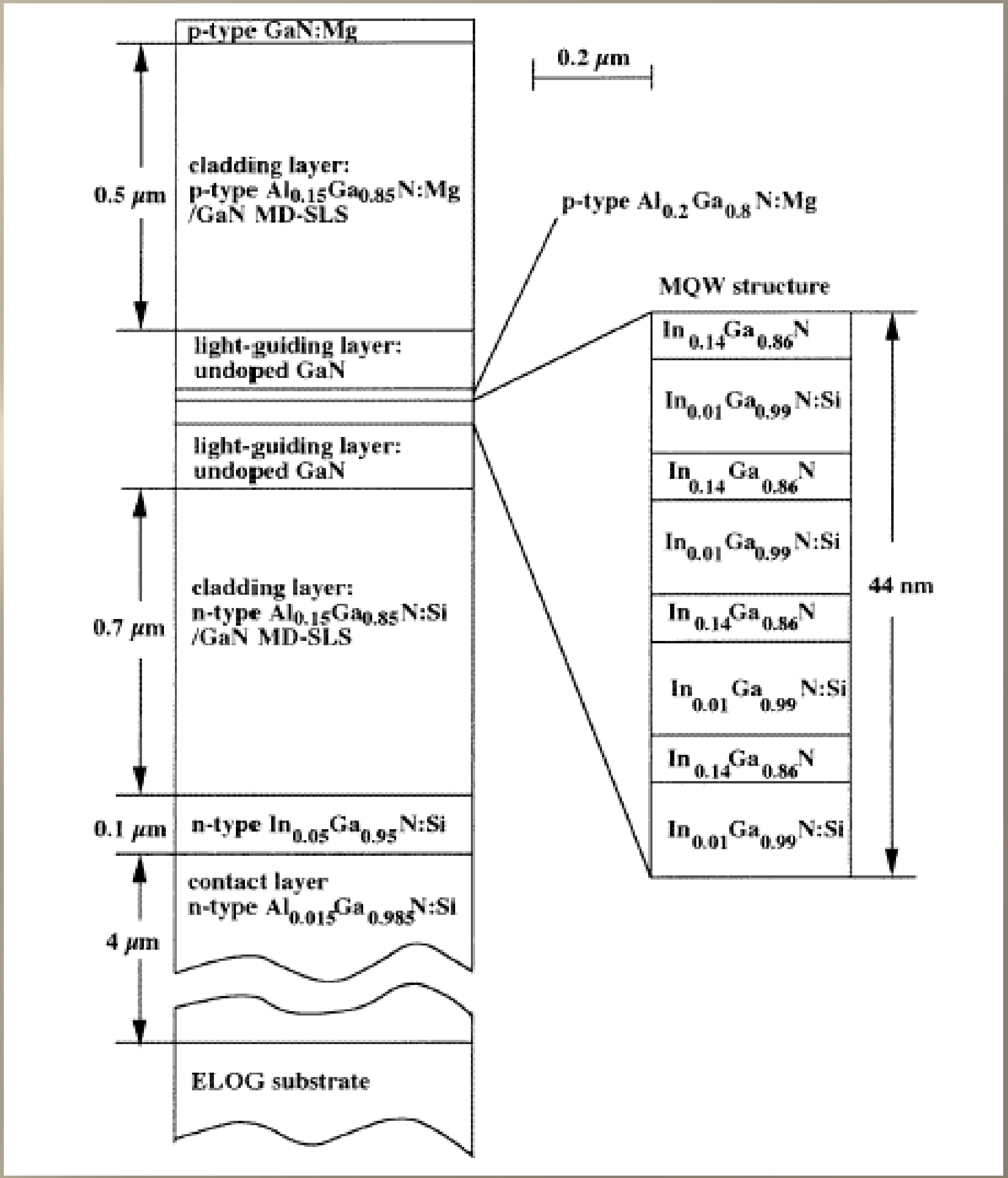
InGaN and AlGaN have been produced over the entire composition range between their component binaries; InN, GaN, AlN.

InAlN is less explored.

GaN and AlN are fairly well lattice-matched to SiC substrates,
SiC has substrate is better as it can be doped (dopability) and high thermal conductivity relative to more commonly used Al2O3 substrates.

AlN and GaN can be used for high temperature application due to wide bandgaps and low intrinsic carrier concentrations.

Blue/Violet Laser



LASERS

Stripe Geometry DHJ Laser

Features:

Oxide layer or high resistive layer (produced by proton bombardment) between metal contact and the semiconductor.

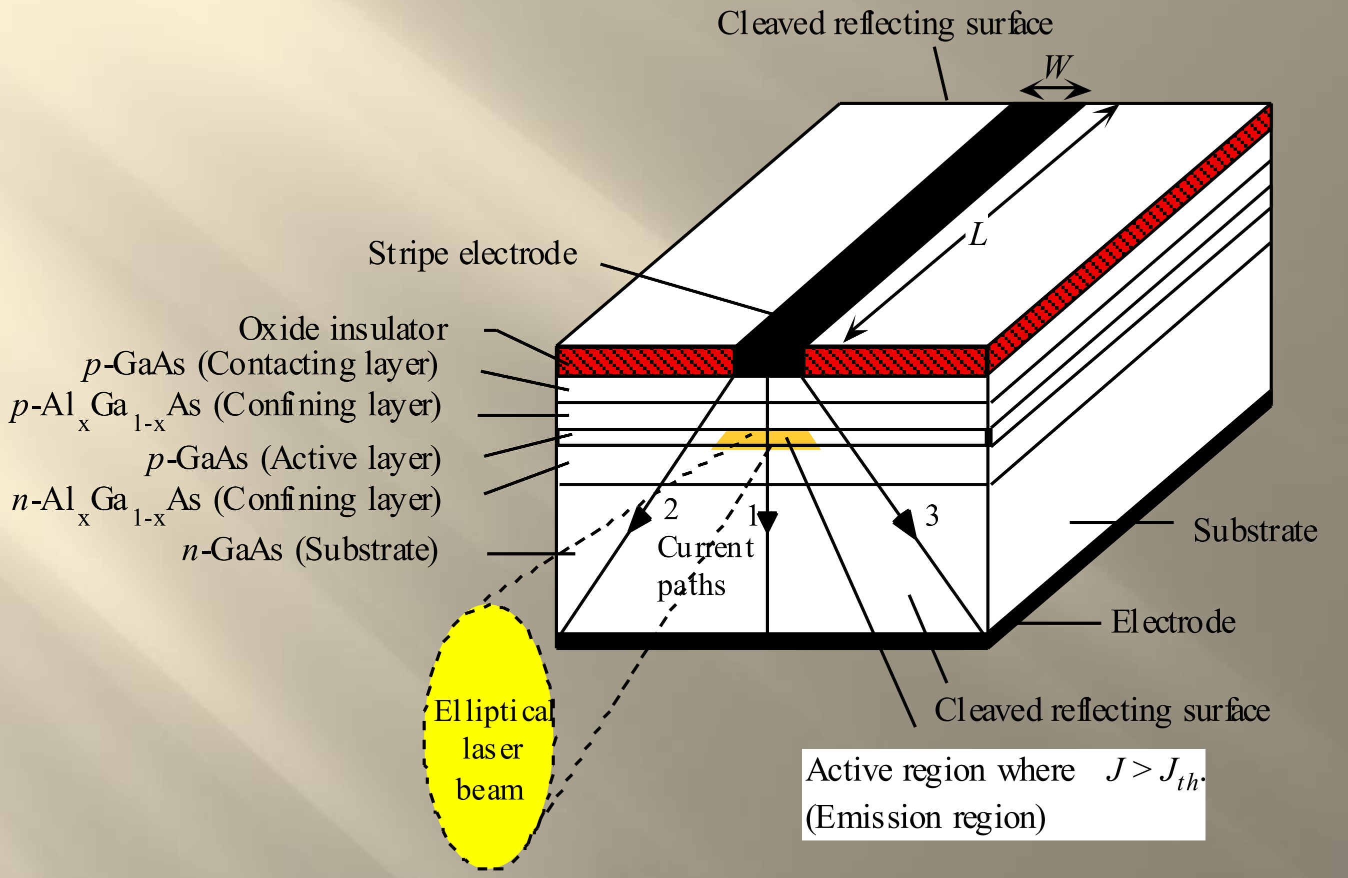
Restrict current along the junction into narrow stripe (few microns)

Small JTH with high Power → continuous operation

Used largely in Optical Fiber Communication

LASERS

Double Heterojunction StripeLaser Diode



Schematic illustration of the the structure of a double heterojunction stripe contact laser diode

LASERS

Quantum Well Lasers

Structure similar to the DH laser except thickness of active layer is very small (10-20nm) - narrow Eg GaAs sandwich between larger band gap GaAlAs.

With this configuration, density of states near the bottom of the conduction band and the top of the valance band increased significantly and hence enhance the population inversion.

Better population inversion, smaller active layer hence JTh is smaller.

LASERS

Quantum Well Lasers

BUT, in single quantum well (SQW) extreme narrowness of the active region created poor optical confinement.

So… Solve by Multiple Quantum Well Structure (MQW)

SQW can be coupled to produce the MQW

Overall active region is now thicker.

Carriers which are not captured in one well can be captured by the second well etc.

MQW has JTH higher than SQW (~ 1mA) but more optical power due to better optical confinement.

Assignment

- Outline of research paper Due 10-12-20