Explain covalent bonding in a diatomic molecule.

Essentially, the state of a bond between a pair of atoms can be can be understood by defining the wavefunction for the system as a linear combination of atomic orbitals, and then solving for the expectation value of the electron energy by plugging in the defined LCAO wave function into the expectation equation for the Hamiltonian operator (or using the variational principle to identify the energy minimum in the system). Afterwards, you'll find that there are two symmetrical eigenenergies to the system; one in which the two AOs are in-phase and one in which the two AOs are out-of-phase. The former represents a **bonding state**, in which the energy of the system is lower and the overlap between the two atoms is high. The latter represents the **antibonding state**, in which the energy of the system is higher, and there is no overlap between the two atoms.

A stable diatomic molecule will have a bond order, which the difference between the number of electrons in the antibonding and bonding states, greater than zero. The higher the bond-order, the more stable the diatomic molecule is, as a greater bond order reflects the number of bonding states that are fully occupied. The way that the bond order is able to grow beyond one (which is the limit for atoms like Li or H, which are only comprised of electrons in the s states) is for atoms in groups 13 through 17 to begin bonding, as these atoms have electrons that occupy p-orbitals.

The order at which the orbitals are occupied is determined by **Aufbau principle** (except in certain transition metals), which states that the lower energy orbitals must be fully occupied before the higher energy orbitals begin to be occupied, and **Hund's rule**, which states that the orbitals are occupied as to maximize their total spin.

While s-orbitals are only able to create **sigma** bonding and antibonding molecular orbitals, the electrons in the p-orbitals are able to create both **sigma** bonds, as well as **pi** (between p_y, p_z). This is how single, double, or triple bonds are formed, as the sigma bonding between the s-orbitals of atoms can occur alongside the pi-bonding occurring between p_x or p_z orbitals.

Explain the bonding in covalent diatomic molecules.
Additional questions about LCAO, orbitals, stability and bandgap in larger systems.

ORBITALS:

Very simply, the LCAO is a way to determine the state of a system comprised of multiple overlapping atomic orbitals, that will interact to form molecular orbitals. This molecular orbital can be defined as a linear combination of atomic orbitals (LCAO), while can then be plugged into the equation for the expectation value of the energy of the system. Solving this system with the understanding that the coefficients for the two atomic orbitals in a diatomic system must have equal magnitudes (u_1 = +/- u_2), you can find that two energy states arise as the two atoms are brought closer to one another (these two energy states corresponding to the extrema of the expected energy w.r.t. u_i*).

The first is when $u_1=u_2$, and this is when the **bond integral**, which represents the interaction between the overlapping atomic orbitals, is positive. This will increase the total energy of the system as the two atoms are brought together, and we find that this forms a set of **antibonding MOs**. These MOs represent the presence of a node between the two atoms, in that their atomic orbitals are out-of-phase with one another, and destructively interfere.
     The second energy state occurs when $u_1=-u_2$, in which the bond integral will be negative. This will lower the overall energy of the system and these energy states correspond to a set of **bonding MOs**. These MOs represent the lack of a node between the two atoms, in that their atomic orbitals are in-phase with one another, and constructively interfere. These two states correspond to the electron energy, though, and <u>don't account for the coulombic repulsion between the two atoms</u>. As such, when calculating the total energy by adding in this coulombic repulsion term, you'll find that the antibonding states just go up in energy as the atoms are brought together, while the bonding states present a minimum in energy as the atoms are brought together.

STABILITY AND COVALENT BONDING:

Check the earlier question that pertains to this particular answer. Important to note is that the stability of a diatomic molecule can largely be predicted from the bond order, which finds the difference between the number of occupied bonding and antibonding states. Remember, bonding states have lower energy, while antibonding states have higher energy.

Explain the bonding in covalent diatomic molecules.
Additional questions about LCAO, orbitals, stability and bandgap in larger systems.

BANDGAPS:

Essentially, the introduction of many more atoms into the system will increase the number of potential molecular orbitals that can form. In the LCAO framework, the reason for the slight energy difference that exists between the different MO is given to the fact that different number of antibonding orbitals can arise, corresponding to a positive coefficient in the LCAO. At the atomic density of a crystal, in which the number of atoms in the system approaches one mol, the energy difference between the adjacent MO will be so small, that they can be considered as a continuous **band** of allowed energies.

The reason that band gaps arise is due to the large energy difference between different orbitals. The next unoccupied orbital will form its own energy band that is entirely unfilled. This represents the formation of a conduction band, while the highest energy filled orbitals will form the valence band. This may occur between the bonding/antibonding orbitals, or it may not.

In a more rigorous treatment of the LCAO, we can say that the MO that are formed by the LCAO can be expressed as a **Bloch wavefunction**, which are periodic electron states. These states share with their periodicity with that of the periodic crystal potential. When solving the TISE, using the bloch function as your eigenstate, you will find an equation for the allowed eigenenergies of the electrons in the crystal. Analyzing this expression for the eigenenergies, you can identify that only certain energies are allowed (slide 92), given the nature of the equation (namely, it consists of sines and cosines on one side, and thus can only obtain values between +1 and -1). The energy states that are not allowed will give rise to the formation of **band gaps** between the allowed energy states.

From SCP; these band gaps will often arise at Bragg planes (at which point, the electron wavevector satisfies the Von Laue-Bragg condition). Notably, that these points, the electron wavefunction will be greatly affected by the periodic crystal potential; this makes sense, as when k=npi/a, standing waves will form, and will either be cos(kx) or sin(kx). In the former case, the electron will be in-phase with the minima in the periodic potential, so the eigenenergy will be lower. In the latter case, the electron is fully out-of-phase with the minima in the periodic potential, so the eigenenergy will be higher.

Explain the Effective Mass Approximation

The effective mass approximation essentially allows us to describe the effect of the periodic crystal potential on the energetic dispersion of the electron, most often the conduction electron (or in the case of the valence band, the hole, which itself possesses a corresponding hole effective mass).

This effective mass is particularly important to describing the dynamics of these charged carriers within solids, a fact that is reflected in the classical and semi-classical descriptions of conduction covered later on (usually, you'll see it when applying Newton's equations of motion, F=ma, and in the equations for carrier mobility).

Notably, the hole effective mass is usually much larger than the electron effective mass; this is because the movement of a hole in direct space requires the breaking and formation of bonded electron in the valence band. Electrons in the conduction band, on the other hand, are delocalized, and thus conduct much more easily.

Because a delocalized electron is defined by a continuous spectrum of eigenstates (as it is not bound by an on-site coulombic potential), it is best represented by a linear combination of bloch states (which forms a wave packet). The velocity of this wave packet is defined by the **group velocity**. Understanding this, you can take the time derivative of the expression for the group velocity to find the acceleration, plug this into Newton's second law, and solve for an expression for the effective mass (slide 103). Notably, the effective mass is inversely proportional to the curvature of the band.

The effective mass ina crystal can be best described using an **effective mass tensor**, that is able to more accurately capture the anisotropy of the crystal structure (and thus the effective mass), which often arises in eigenstates that are off-gamma.

What is the effect of strain on mobility?

As is mentioned in the previous question, the effective mass tensor can capture the anisotropy of the effective mass in a crystal system. This anisotropy of the effective mass is itself, a product of the anisotropy of the crystal structure, itself. As such, the effective mass can be altered in along certain axes by introducing strain into the system, which will linearly displace the atoms within the crystal structure (along as the strain remain elastic). An example of this would be the decreasing of the effective mass along the x-axis due to the introduction of tensile stress along the x-axis, which is induced a displacement of the atoms (pulling them further apart), which decreases the spatial frequency of the crystal lattice in that direction.

This increase or decrease in the mobility due to the introduction of strain into the system would then affect the mobility of the carrier, as the mobility is inversely proportional to the effective mass.

More on this in the chapter on high-k at the very end, wowow!

Classical and semi-classical models of conductivity in metals

Preempting the establishment of either of these models is the necessary understanding that electrons, at ambient temperatures, will have some thermal velocity. This thermal velocity should be (more or less) isotropic, meaning that no net charge will be transferred via solely thermal velocity. Instead, the additional of an applied field is necessary to induce a net movement of electrons.

Classical Model

In the classical approach, we just establish a simple equation: the force due to external fields on the electrons will be equal to the frictional forces due to scattering when the electron conduction reaches steady state. In this model, we can essentially state that the electrons are travelling within a "viscous" medium, and are damped as their velocity increases. Notably, when steady state is achieved, the electron should have a **final velocity**, v_f, which is an intrinsic material property.

   Connecting this to Ohm's law, we can then define the total current density of the system as $J = env_f$, which can then be related to Ohm's law ($J = \sigma E$) by defining a new variable, the **mobility**, as the proportionality constant between E and v_f. Finally, we obtain an expression for the conductivity; $\sigma = ne\mu = ne(-v_f/E) = (\tau q/m^*)$. Note, that τ term comes from the solution to the steady-state equation described in the previous paragraph, and is dependent on the drag and electric field applied to the conductor.

Semi-classical Model

This semi-classical approach begins with the **Sommerfeld model**, in which only electrons near the fermi level can participate in conduction, and move with a velocity equal to the fermi velocity, derived from the fermi energy. This can be understood as a shift in the fermi surface of the system, which implies that only electrons near the edge of the fermi surface (representing the electrons at the fermi energy), will have their momentums shifted to previously unoccupied momenta, and will be the electrons that are primarily responsible for conduction. Note; we can assume that these electrons will conduct at the fermi velocity, despite the fact that the energy of the conducting electrons is technically slightly higher. We assume this under the small field assumption.

   We can find an expression for conduction by repeating the steps outlined above. Namely, we start with the expression $J = env_F = eN(E)(dE/dk)$ for the QM case. Afterwards, we just compare this to the expression for Ohm's law, and then derive an expression for the conductivity from there: $\sigma = q^2 N(E)\tau v_F/3$ (slide 26).

One big difference between these models is that in Drude, we assume all electrons shift. In Sommerfeld, only some electrons shift.

KU LEUVEN

Discuss scattering in metallic thin films and polycrystalline materials

In highly **polycrystalline** films:

Electrons are more likely to be scattered by grain boundaries, possibly more than the probability they will be scattered by other mechanisms. As a result, you can define a ratio between the resistivity due to scattering mechanisms that occur within a perfect crystal (phonon, impurity) and the resistivity due to grain boundary scattering. You'll find that the **smaller grain boundaries** include a higher resistivity in the polycrystalline thin film.

If you further include boundary coherence into the theory, you'll find the a more descriptive expression for the ratio between the resistivities, which includes a cofactor **β**, which is proportional to the ratio between the reflection and transmission probabilities (which is dependent on the coherence of the grain boundaries). β is also inversely proportional to the size of the grains. So, if the grains are large, then the ratio between resistivities = 1+3β/2 (similar to what we'd identified by just applying **matthiessen's rule**). If the grains are small, then the ratio of the resistivities = 4β/3 .

In thin films, **surface scattering** can also dominate. This is scattering at the surfaces of the thin film, which start to become dominant as this scattering mechanism has a mean path = D*cos(Ө), where Ө is the angle from the direction perpendicular to the film's longitudinal axis. So the smaller the film thickness, the smaller the mean path length, and thus the more dominant surface scattering becomes. In reality, because the scattering direction are restricted (as the electron cannot just leave the material), and it takes two scattering events (on opposite surfaces of the film) to access the entire range of scattering angles, the **effective path length** is actually = 2*D*cos(Ө). Treating the system using matthiessen's rule again gives rise to another equation for the ration between the thin film resistivity and the bulk crystalline resistivity.

To obtain a more rigorous expression, you can include the **specularity parameter**, which accounts for the elasticity of the surface collision. If P = 1, then the collision is entirely elastic, and no energy is lost; this results in a system that effectively has no resistance from surface scattering. Alternatively, if you have P = 0, then all the energy gained by the external field is lost upon scattering, such that the resistance from the surface scattering events is maximized.

Explain Superconductivity

Oof. As simply as I can muster, superconductors are essentially materials that have a near-zero (or literally just zero) resistivity at temperature below a **critical temperature, T_C**. Simply, electrons that have opposite spins and opposite momenta can create a **Cooper pair**, in which their respective spins cancel eachother out, and the resulting integer-spin particle can be treated as a boson.

This boson is then able to occupy the ground state energy (in part, due to the lack of thermal energy in the system at such low temperatures). It should be noted that the exchange interaction that binds these electrons together, to form the composite boson, is very weak, so even intermediate temperatures can destabilize the Cooper pair. The exchange that brings about the Cooper pair is more accurately described QM, but has a classical analogue; essentially, the exchange occurs via a phonon, as the coulombic attraction between electron 1 and the lattice induces a phonon that can then travel attract electron 2 (up to 100 nm away!). This attraction between the local positive charge density (due to the phonon) induced by electron 1 can overcome the coulombic repulsion between the two electrons, pairing them together. Essentially, the exchange is mediated by the phonon.

Notably, this effect can be disrupted at <u>high temperatures</u>, a <u>large applied magnetic field</u>, or a <u>high current</u>. All three have critical value at which the effect is unable to persist.

Discuss the behaviour of carriers in intrinsic semiconductors.

Free carriers in a SC include holes and electrons. In an intrinsic SC, the only way that free carriers are generated is by exciting an electron up to the conduction band, which can be done via energy transfer from a photon, another electron, or (most often) thermally. The probability that an empty state in the conduction band will be occupied is described by the **Fermi Dirac** distribution; it tells us that the conc of carriers will increase with increasing temperature, a decreasing bandgap, or an increase in the density of states at the CB edge (slide 22 for this last one). In non-degenerate SC, in which the CB edge is over $4k_bT$ away from the fermi level, you can approximate the Fermi-Dirac distribution using the **Maxwell-Boltzmann** distribution, which is easier to solve for.

When an electron is excited up to the conduction band, a hole is also created in the valence band; notably this implies that the number of holes and electrons in the intrinsic system are equal. Both the hole and electron can act as charge carriers (particularly the electrons in the CB, which act as delocalized, quasi-free electrons).

SIDE NOTE:

The impact of temperature on carrier concentration/Fermi level (43-45) and mobility (32-33) are included in slides.

What determines the Schottky barrier height?
What should we do if we want it to be Ohmic contacts?

Forming a Schottky Barrier:

To form a Schottky barrier, the work function of the metal should be larger (smaller) than the work function of the n-type (p-type) SC. This will essentially allow electrons in the CB (holes in the VB) to freely flow into the metal, and thus create a **depletion region**, in which the concentration of the carriers is lower. One way to consider this is that electrons (or holes) will be charging the metal-SC interface, and thus repel the remainder of the carriers from entering the metal (this is observed in the bending of the CB/VB in the SC). I like to think that the depletion region just leaves behind all the dopants, which charge the region and induce an electric field that repulses the carriers. After an EQ is reached, then carriers can still pass through the interface via thermionic transmission.

Notably, the width of depletion region and the height of the barrier can be modulated by the applied voltage. If the voltage on the metal is negative, the electrons are repelled (**reverse bias**) and if the voltage on the metal is positive, then the electrons are attracted (**forward bias**).

Importantly, the height of the Schottky barrier is not only a function of the metal work function, as is predicted by the Shockley-Mott theory; instead, it's a function of the work function and **fermi level pinning**. This latter effect essentially describes the effect of interfacial states can have on the charge transfer between the metal and SC.
- If the fermi level is above the **charge neutrality level**, then the surface states carry a net negative charge. As such, then the SC comes into contact with the metal, electrons occupying states above the charge neutrality level will be transferred to the metal before carriers move from the bulk SC into the metal. So, to achieve EQ, less charge transfer occurs btwn the SC and metal, and so the barrier height is lower (less bending).
- If the fermi level is below the **charge neutrality level**, then the surface states carry a net positive charge. As such, when the SC comes into contact with the metal, electrons will first occupy the surface states up to the CNL before entering the SC. Similarly, this means that less charge transfer needs to occur (usually for p-type) between the SC and metal.
The degree to which fermi pinning determines the barrier height is determined by the **pinning factor**.

Forming an Ohmic Barrier: (Notably, much lower contact resistance than the Schottky barrier, as no thermionic emission is necessary)

Pretty simply, just choose a metal with a work function that is larger than that of the SC. Then electrons will be able to just flow in either direction, as no barrier will have developed to prevent carrier movement. The charge transfer increases linearly with voltage, so it's an Ohmic contact.
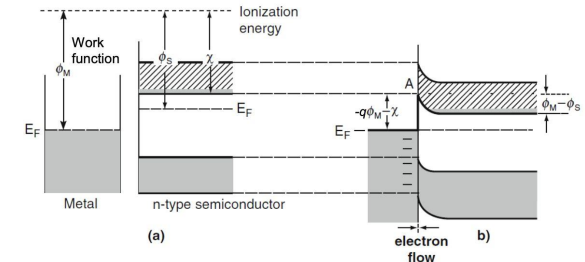
Explain the HEMT
Why we use delta doping?

HEMT stands for **high electron mobility transistor**, and essentially relies on a **2D electron gas** developing in a quantum well that is engineered at the heterojunction interface in the transistor (shown on slide 57). The electrons that arrive at the quantum well are pushed from the adjacent heavily doped later (shown on the left in the figure above). The activation of these electrons over the energetic barrier is driven by a positive bias being applied to the doped region, the E_C of the channel will bend further down, allowing more electrons to fill it. If a negative bias is applied, then the E_C of the channel will not bend as far, removing states that are beneath the fermi level; this will induce electrons to move through the channel to the drain in "one shot" very quickly. The reason they move so quickly is because the 2DEG has no dopants, but a confined path for electrons to move through, so quasi-ballistic transport with little backscattering is possible in the channel.

In order to induce a large energy well, you can increase the bandgap of the substrate and doped layer, while decreasing the bandgap of the channel layer. Further, to increase the current through the channel, you want to increase the dopant density of the doped region, while decreasing the distance between the channel and the gate (so that the gate bias can more effectively induce a change in bending of the E_C of the channel). If the doped region is uniformly doped, then increasing its thickness will further separate the channel and the date, while increasing the number of free carriers that can pass into the channel. So, carrier concentration of the doped layer is inversely proportional to the channel-gate distance. To avoid this, you can use a **delta doped layer**, that is just a layer of dopant atoms implanted (ew?) into the doped region. This will allow for a high dopant concentration in the doped region, without linking the dopant concentration to the thickness of the region.
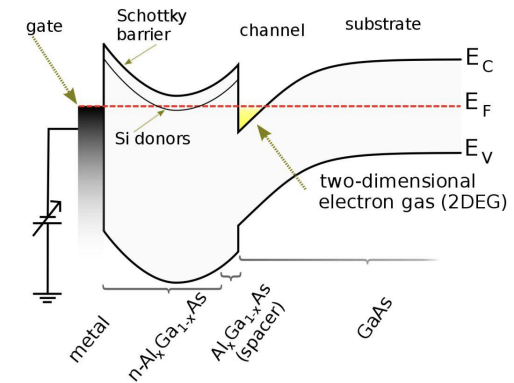
How do we get a certain wavelength for led/diodes
How could you improve its efficiency?

Tuning the Wavelength:

You can tune the bandgap by utilizing **ternary or quaternary compound** semiconductors, in which the size of bandgap is easily modulated by increasing or decreasing the relative concentration of different elements within the compound. Notably, the use of these compounds also allows for the tuning of the lattice parameter, which can be helpful when forming heterojunction diodes with minimal **lattice mismatch** between two compound SCs.

Efficiency:

An increase in the lattice mismatch will lead to the formation of dislocations and other defects at the interface, which may interrupt carrier dynamics (very generally, I guess?). So, by making sure that the heterojunction has low lattice mismatch, you can avoid this. Going further, you can also be sure to utilize a direct-gap SC, as these are the SC that are actually capable of **radiative recombination**; an indirect-gap SC would require the creation or absorption of a phonon to recombine, and would be far less likely to produce a photon. Notably, to obtain certain wavelengths, materials with indirect bandgaps are the only options. In this case, the material can be doped with an **isoelectronic** center, which adds no new carriers (hence, *iso*electronic), but will create states within the bandgap at one dopant energy level. This trap state will have a well-defined position in real space, meaning that it has a poorly defined position in k-space (i.e. the corresponding wavefunction is delocalized in k-space); this means that it spans a large range of k-space, and can thus receive carriers from one momentum and inject them at another.

Fundamentally, the LED works by applying a forward bias to a p-n junction, in which the carriers are able to easily diffuse in the SCR, where they can then recombine (as there would exist a high concentration of both holes and electrons). Usually, the electrons have a much higher mobility, and so can diffuse much further into the p-type region. Understanding this, LEDs are usually designed such that the n-type region is heavily doped, while p-type is less doped. This creates a large depletion width in the p-type, in which electrons can be injected and (because of the large depletion width) are likely to recombine with a hole.

The yield for the LED is measured by the **quantum yield**, which is the ratio between the number of emitted photons and the number of injected electrons. This figure is often limited by the reflections at the interface between the semiconductor and air.

How does a LASER diode work?
What is the main difference between a laser diode and a LED?
How can we improve the efficiency of a LASER?

LASER stands for **Light Amplification by Stimulated Emission of Radiation**, and in this name you can understand the primary difference between the Laser diode and the LED. Namely, the electrons in the LED will release a photon via **spontaneous emission**, whereas in an LED the electrons will release a photon via **stimulated emission**. The former involves no amplification, as a single photon absorption will lead to a single photon emission. The latter, on the other hand, will involve amplification, as the single photon that can interact with electrons (via EM interactions) that have undergone **population inversion** (read the answer to another question on population inversion in the printed notes binder), and induce their decay at an identical energy, wavelength, and phase to the incident photon. Notably, this can cascade, as the emitted photons can then induce decay in other excited electrons. As such, the emission of many photons can be *stimulated* by the injection of a single photon.

Notably, population inversion can occur in a degenerately doped p-n junction under forward bias. In the forward bias is not large enough, then there aren't enough electrons injected into the SCR that can then decay via stimulated emission. This leads to the LASER performing as an LED.

Notably, the efficiency of the LASER can be improved through the use of a **double heterojunction**. As was seen with the HEMT, this can create a quantum well at the junction, which allows for the confinement of carriers (more carriers trapped in the well, contributing to the population inversion), and the confinement of photons (which creates a waveguide with the channel acting as the optical core, keeping the electrons in the same axis as the confined electrons).

For a high efficiency laser, a **resonator** is used to get the most of the photons that are injected and emitted. Namely, a resonator will essentially be formed by two reflective surface at either end of the heterostructure, which will be able to reflect the photons multiple times throughout the LASER structure. This will drastically increase the photon interactions that induce decay for excited electrons (and thus, cause stimulated emission). The application of the **Fabry-Perot resonator (cavity)** is further detailed on slide 105. Great overall picture on slide 112.

How does a VCSEL work?
Why are these structures so interesting?
## And quantum dot lasers?

The VCSEL diode stands for the **Vertical Cavity Surface Emitting Laser** diode. Essentially, the way that this works is similar to the **edge-emitting diodes** described in the previous slide; there is an active region comprised of a double heterojunction that is being biased to induce population inversion (which leads to stimulated emission after photon injection), and there is a reflective surface on either side that builds an optical cavity (resonator). This time, though, the reflective surfaces are **distributed Bragg reflectors** (slide 113), which essentially is a quarter-wave mirror that can reflect several beams of light from one incident beam. The major difference between optical cavities built using DBRs verses those with reflective surfaces that are perpendicular to the active region is that the former can be created from vertical stacks of different thin films. This makes them much easier to build. Plus, the DBR leads to high efficiency, and low power consumption, especially in the VCSEL, as all the light oscillation occurs between them.

The discretization of the DOS in the quantum dot leads to many advantages in the laser power consumption, efficiency, and temperature stability. I'm not writing an explanation, but I'll certainly review it. Generally, just know its on slides 126-129. Generally, seems like the electron can really only enter the ground state of the QD within the CB, which has a extremely high DOS (due to discretization of the allowed energy levels). So, you get just a bunch of electrons all decaying from this one ground state energy at once to the valence band.

KU LEUVEN

# Explain the frequency dependence of the dielectric constant.

The frequency dependence of the dielectric constant arises from four main sources of polarization in the material: electronic, ionic, orientational (dipolar) and space-charge (interfacial) polarization. There exists a particular frequency response associated with each of these sources of polarization that is characterized by the **relaxation time** of the polarization mechanism. Specifically, the list given is ordered from smallest relaxation time to largest relaxation time.

This concept of relaxation time is important, as it defines the frequency response attributable to each of the mechanisms, and to the dielectric permittivity of the material as a whole. Namely, this is because, when the frequency is equal to one of these relaxation constants, then a **resonance condition** is satisfied, and there is large energy dissipation associated with this mechanism (high loss). At frequencies with periods higher than the relaxation time, the mechanism can no longer respond to the voltage signal, and is no longer contributing to the overall permittivity of the material.
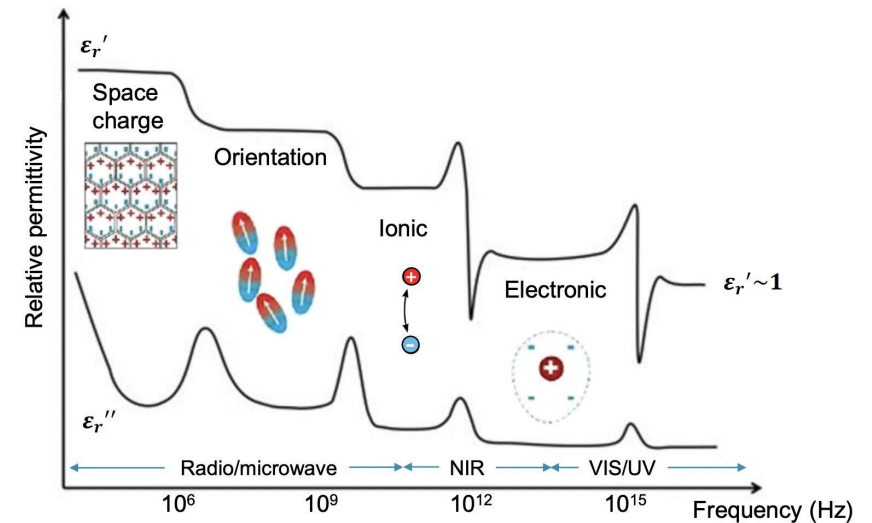
Explain the temperature dependence of a ferroelectric material.
(first and second-order transitions)

First order ($\gamma < 0$)

$T > Tc$

$T = T_c$

$T < T_c$

Second order ($\gamma > 0$)

$T > Tc$

$T = T_c$

$T < T_c$
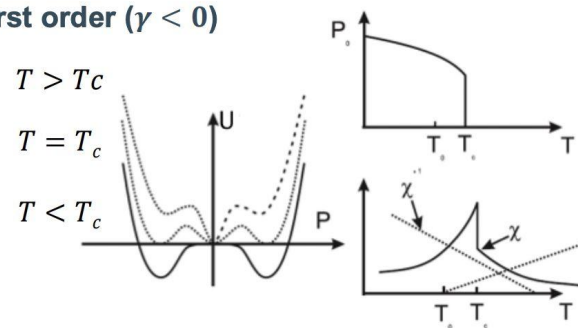
Ferroelectrics have two primary responses to changes in temperature; these are the First and Second order Transitions. Both exhibit different behavior leading up to the Curie temperature, at which point any ferroelectric will have lost its spontaneous polarization. Notably; $P = \varepsilon_0\,(\varepsilon_r - 1)\,E$.

1. <u>The First order Transition</u>: This transition is characterized by a steep decline in the polarization only at the Curie temperature, with very little decline beforehand. This can be explained by the free energy versus polarization plot, in which two minima exist (these represent that displacement of the Ti atom above and below its central position). As the temperature increases, the U of the two minima increase as well, such that they are never eliminated even after $T>T_C$.

   The reason for the sudden decrease is that, when $T=T_C$, the center position now represents an equally energetically favorable state. So while some crystal cells will still be polarized,the average polarization will still be 0, due to thermal fluctuations (notice, the barriers to switching minima has also been decreasing).
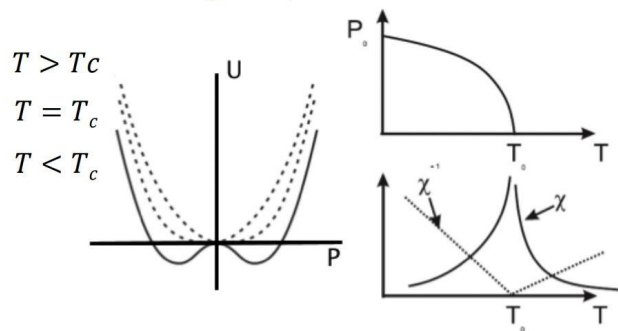
2. In this transition, the decline is more gradually, though it still sharply decreases at the Curie temperature. The free energy vs polarization plot shows that, for the second order transition, the minima are no longer present when $T=T_C$. In fact, the barrier to the two minima slowly decreases until T reaches T_C, which explains why the polarization decreases gradually (hopping between the two states becomes easier, especially with increasing thermal energy, that it becomes difficult to maintain a strong overall polarization).

   This second transition can be explained physically by structural changes gradually occurring as the temperature increases. For example, the thermal expansion of the unit cell may allow for the displace central atom to maintain a central position,thus removing the main mechanism by which polarization of the materials occurred.

What are the advantages and limitations of Si/SiO2 interfaces?

The primary advantage allowed by the use of Si/SiO$_2$ interfaces is the ease by which SiO$_2$ can form. Namely, all that is required is the oxidation of the Silicon to form SiO$_2$. This also means that, while there may exist interfacial defects (which are actually common at an Si/SiO$_2$ interface), there wouldn't be the formation of unwanted phases, as was the case with high-k oxides. Especially with the metallic substance, which was often highly doped SiO$_2$.

From my understanding, the major downside comes from the fact that SiO$_2$ is amorphous. This means that there is no way to form a coherent interface between Si/SiO$_2$, resulting in the inevitable formation of interfacial defects. The primary defect is the **dangling bond**, in which an unbonded silicon present, due to the lack of an adjacent silicon atom. Notably, these dangling bonds can be **passivated** (such that they are charge neutral) by the introduction of hydrogen into the system.

If these interfacial defects are not passivated, then they will form interfacial defect trap states within the band gap, which will either act like a donor or acceptor state. In the former, the trap state is charged when it has an energy higher than Ef, and the latter is charged when the energy is lower than Ef. Ultimately, the presence of the interfacial defects degrades the device performance, as they need to be charged/discharged every time that the MOSFET switches.

Discuss high-k and main material aspects

First off, to understand the reason we care about high-k dielectrics, we need to understand the concept of the **equivalent oxide thickness (EOT)**, which is defined as the thickness of the silicon necessary to obtain a similar capacitive density as the capacitor created using the high-k oxide. Importantly, it relies on the ratio between the silica relative permittivity and the high-k relative permittivity, meaning that a higher high-k permittivity would allow for thinner high-k oxide barriers, while maintaining the EOT.

So we want a high-k material (high permittivity). How did we land on HfO_2? Well, <u>we wanted a dielectric that had ionic bonds</u>, as a high ionic polarizability could increase the permittivity. And because the CMOS frequency doesn't reach the resonance frequency for the ionic bonding, the permittivity wouldn't be decreasing at higher operating frequencies! This is actually why most of the candidates were metal-oxides, as metals have a higher electronegativity than silicon, and thus form more polar bonds with oxygen.

Furthermore, HfO_2 has a sufficiently large VB and CB offset compared to the E_C and E_V of Silicon. This is important, as it can impact the prevalence of Fowler-Nordheim tunneling; the closer the CB and VB edges are, the more likely the potential barrier will be triangular over the oxide barrier (which makes tunneling easier, as the thickness if effectively reduced). BUT it turns out that the band gap is inversely proportional to the relative permittivity, so you need to find a material that can satisfy the two parameters.

Finally, the material must form a thermodynamically stable interface with SiO_2, otherwise interlayers of SiO_2 will form at the interface, full of metal ion defects (yikes!). Because HfO_2 works on all these accounts, and develops fewer structural defects, we primarily use this compound as the oxide of choice in CMOS transistors.

Side note, it's deposited using ALD (<u>slides 35-7</u>). Notably, annealing of the oxide would induce crystallization; often HfO_2 will crystallize into one of three different stable phases, resulting in the formation of grains with varied structures (we DON'T want this, as it may lead to the formation of conductive grain boundaries, which kind of makes the whole oxide barrier useless).

To solve this, people initially looked into adding dopants that would increase the crystallization temperature. Eventually, though, they found that spinodal decomposition would occur, and HfO_2 would precipitate from the solid solution. Eventually, they concluded it was fucked, and couldn't be inthe layers- they just changed the fabrication process instead of the layer.

Significance of metal gates on high-k

So, the gate electrode that was previously used was a heavily doped polysilicon layer. It turns out, that the interface between a metal oxide and the polysilicon results in many interfacial defects due to the formation of M-Si bonds. This would pin the fermi level of the polysilicon, such that the work function of the polysilicon couldn't easily be altered via solely doping (more on pinning on slide 57).

So, instead of using poly-Si, a metal gate electrode was used, as the carrier density of the metals was so high, that it could overcome the fermi level pinning (which was caused by the inability for the heavily-doped poly-Si to fill all of the interfacial defect states up to the original fermi level). So, to form an n-type or p-type MOSFET, different metals would be chosen based on their work function (slide 61).

Notably, the pinning effect can still be an issue, as charge transfer between the metal and surface states would essentially create an interfacial dipole, and screen some of the charge on th metal side that drives band-bending in the SC. This occurs only when the metal-oxide interface was annealed at high temperature, as is done during the source-drain annealing. So, to get around this, researchers just used a dummy gate in place of the metal gate during the annealing. Only after the annealing was completed, was the dummy gate removed and the actual meta gate was added.

How use of high-K dielectrics affect the mobility of electrons?
What are the solutions? How remote phonons couple to electrons in channel?

Notable, the use of high-k oxides instead of silica also resulted in **mobility degradation** in the SC channel, which obviously harms the performance of the CMOS. The many potential sources of this degradation are shown on slide 69.

Now, one of the more prevalent scattering mechanisms that arose from the inclusion of the high-k oxides was **remote phonon scattering**, which describes coupling between the carriers in the SC channel and the phonons within the high-k oxide. The prevalence of this phonon coupling is directly due to the increased bond polarity of the material.

To avoid this issue, an SiO_2 interlayer between the high-k oxide and the SC channel was introduced, which could reduce the coupling between phonons and electrons by increasing the distance between the two materials. As well, this would act as a passivation layer between the oxide and the SC, leading to less surface states in the SC.
	Furthermore, the use of a metal gate could restore the mobility, as the interfacial dipole that develops between the metal and high-k oxide would reduce the coupling interactions via screening (??).

All this leads to the fact that the oxide layer can't be scaled below 0.8nm, as then the SiO_2 interlayer would be too small, and fucking remote phonon scattering would reduce the mobility drastically, once again. Jesus.

How can we improve the Seebeck coefficient?

According to **Mott's Formalism**, the Seebeck coefficient qualifies the contrast in conductivity between the electrons below and above the Fermi level. Putting this into an expression, you find the Seebeck effect is directly proportional to the sum $[n^{-1}(dn/dE) + \mu^{-1}(d\mu/dE)]$.

Understanding this, you can analyze each of these terms separately. The first term is explained on slide 13, and generally accounts for the $S \propto n^{-2/3}$ relationship seen the Pisarenko relation. (Can also increase DOS, which increases $n(E)$ near the E_F via resonant band trick, slide 14).

The second term is can be increased by selectively scattering the electrons with energy lower than the Fermi level, while not scattering the electrons with an energy lower the Fermi level. This is called **energy filtering**, which can be done by utilizing nanoinclusions with an energetic well that only reflects lower energy electrons, while electrons moving at higher velocities (with a higher energy) pass by the nanoinclusion.

Explain the role of thermal conductivity in thermoelectric materials
How do we improve the efficiency of TE materials by changing the thermal conductivity?

To increase zT, you need materials with a <u>high electrical conductivity</u> and a <u>low thermal conductivity</u> (which can difficult, as the two are coupled!). We don't want to lower the thermal conductivity due to electrical conduction, as this will also lower the electrical conductivity. So instead, we look to lower the thermal conductivity due to phonon transport.

We can lower the phonon thermal conductivity contribution by <u>increasing the phonon scattering</u> in the material (remember, we want a perfect crystal or electrons and an amorphous crystal for phonons!). There are three main ways to accomplish this:

- **Umklapp effect**, which involves anharmonic bonding in the material, which is bonding that does not conform to a perfect spring model (parabolic). The degree of anharmonicity is measured by the **Grüneisen parameter**. The more anharmonic the crystal, the more likely the **Umklapp effect** will take place, in which phonon-phonon scattering is very inelastic, and often results in a net loss in momentum that leads to backscattering. Obviously, this decreases the thermal conductivity.
- **Electron-phonon scattering** can be increased by an increase in the carrier concentration. This is a messy way to increase the zT, though, as an increase in the carrier concentration also leads to decreases in the Seebeck coefficient and increases in the electronic contribution to the thermal conductivity.
- **Crystal imperfections**, which can be designed to specifically target certain phonon frequencies (all shown on <u>slide 30</u>).

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How is the domain wall thickness defined in ferromagnetic materials.
Explain underlying principles and formulas of the anisotropy and exchange energy

Wall energy/cross section area

Domain wall energy, σ_{wall}

Anisotropy energy, $\sigma_{anisotropy}$

Exchange energy, $\sigma_{exchange}$

δ

Domain wall thickness, δ
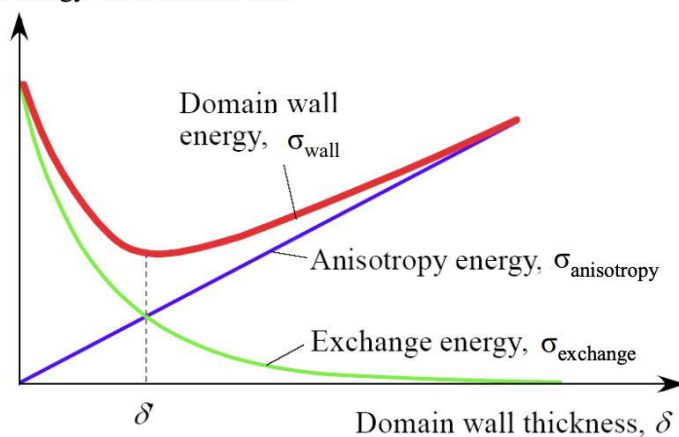
A review of anisotropy and exchange energies in magnetic materials:

1) **Anisotropy energy** is associated with the energy required to maintain the magnetization in certain directions. Often, magnetic materials will be anisotropic, meaning that they posses an "easy axis" that is energetically favorable for the magnetization to be pointed towards. Likewise, they will has a "hard axis" that requires an energetic cost to magnetize along. More on slide 21, 32. The equation that describes the energy is: $U_{ani} = K\sin(\varphi)$

2) **Exchange energy** is associated with the exchange interaction occurring between nearby electrons. In ferroelectric materials, this exchange interaction is characterized by an positive exchange integral, while in antiferromagnetic materials the exchange integral is negative. The energy cost is greater when the spins of the adjacent electrons are not aligned (either parallel or antiparallel). Energy is: $U_{ex} = -2s_i s_j J_{ex}$

The domain wall thickness (which is either a Bloch wall, in which the magnetization points OOP or a Néel wall, which rotates IP) is determined by both the exchange and anisotropy energies, which are both largely reliant on the orientation of the electron spin. Namely, as shown in the figure above, the exchange energy will decrease as the domain wall thickness grows, as this means the difference in magnetization orientation between adjacent spins will be minimized. BUT as the domain wall thickness grows, this mean that more of the spins will not align with the "easy" axis of magnetization, which will ultimately increase the energy cost of the domain wall. So the final thickness is the minimum of the sum of these two energies. :)

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# What is the importance of hybridization? How does it lead to conjugation?

Hybridization is the process of mathematically combining multiple AOs from a single atom to participate in the formation of bonding MOs. Usually, it is only a single AO that interacts with another AO of a different atom to form a bonding MO; in the case of certain atoms (e.g. Carbon, Boron), multiple AOs are hybridized to form a **hybrid AO**.

The importance of hybridization in the context of chemical interaction is that it allows for the formation of hybrid AOs with unique geometry that would be able to form bonds with neighboring atoms that have an overall lower potential energy than if hybridization had not occurred. This is, in part, due to the increased energy of the hybrid AOs, allowing them to move further away from the atom, thus increasing the overlap in the bonding integral that describes the bond. This increased overlap leads to lowered energy of MOs.

Depending on the atom, this framework will result in different degrees of hybridization, and thus different structures. Important, in a graphene, the sp2 hybridized, meaning that the hybrid AO is made up of 2 p-orbitals and 1 s-orbital. This results in sigma-bonding between carbon atoms occurring in-plane, and a second bond occurring between carbon atoms out of plane. This second bond is comprised of the last p-orbital, p_z, which is oriented out-of-plane, and forms pi bonds with other p_z orbitals.

Molecules with this structure of consistent sigma bonding, alongside alternating pi-bonding, are **conjugated** molecules. What this means is that the electrons that are participating in the pi-bonding are delocalized amongst the molecule, and are thus able to easily conduct between atoms. This can also be understood as the formation of **resonance** bonding. These pi-bonds that form the double bond can be present alongside of the three sigma-bonds formed by the sp2 hybridized Carbon atom; all position are energetically equivalent. This indeterminacy of the double bonds position allows for the development of a **resonant bonding** structure, in which the pi-bond is essentially *shared* amongst the sigma bonds.

Discuss electrochromic devices.
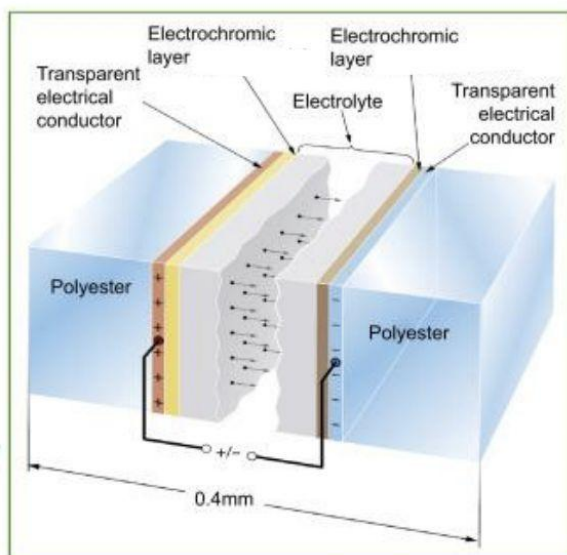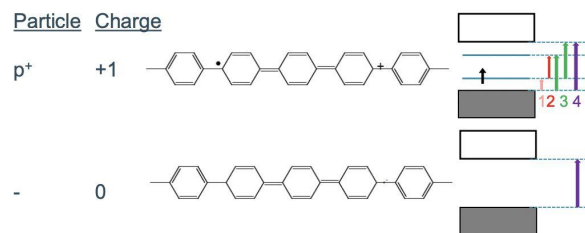
Quick review of quasiparticles that can carry charge/spin in an organic material. NOTE: For all of these quasiparticles, states are added into the bandgap of the system.

1) **Solitons** are neutral quasi-particles that demarcate the border between two different phases (often energetically degenerate phases), and represents a single electron that move off of a double bond. It can be ionized via doping, to carry charge.
2) **Polarons** are made up of two solitons. If they are neutral solitons, the polaron is unstable. If they are ionized in some way, then the polarons are stable + can carry charge.
3) **Bipolarons** are similar to polarons, expect both of the solitons will be charged by dopants. Namely, when the soliton and anti-soliton quasiparticles recombine they can leave behind their additional charge, which will result in a a bipolaron.

You can then dope you system, which is done by diffusing either an oxidizing (p-type)/reducing (n-type) agent into the material. Notably, the material cannot be large, as the direct diffusion of a large molecule may disrupt the morphology of the organic polymer.

Onto the answer; as mentioned, polarons and bipolarons are stable quasiparticles that, when charged positively, are adding in empty states within the bandgap. These empty states are available for excited electrons to fill, **which broadens the range and efficacy of their absorption spectra**. This means that by reversibly doping an organic material, you can increase and decrease the concentration of polarons and bipolarons in the system(as they are comprised of either one or two **charged** solitons). The higher their concentration, the more light they will be able to absorb, and vice versa. Therefore, in an electrochromic device, by applying an external field, you can attract or repulse dopants from the system, thus achieving the reversible doping necessary to control the polaron/bipolaron concentrations. Controlling these concentrations controls the absorptivity.

Why do we use bulk heterojunctions in OPVs
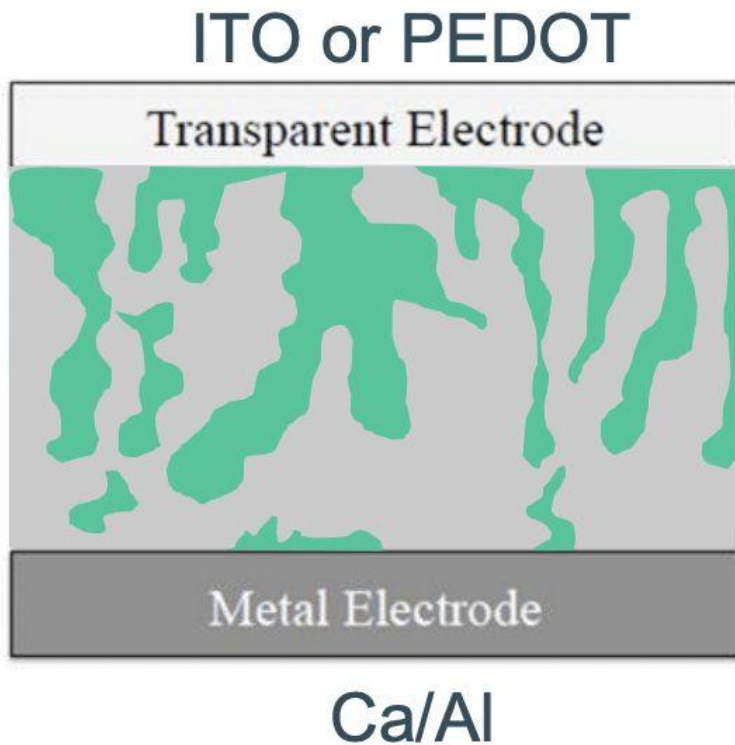
Essentially, the way that OPVs work an exciton pair (comprised of a coupled electron in the CB and hole in the VB) will be generated within the organic electronic material. Importantly, the recombination time for these excitons is relatively short, so the coupling must be broken by the large energy difference that occurs between the donor (teal) and acceptor (gray) materials.

If the split between the donor and acceptor materials was in the middle, then excitons generated in the middle of either of these regions would likely not make it to the interface between them before recombining (the mean path length of the exciton is relatively short). As such, this **bulk heterojunction morphology** is utilized, such that it will be much more likely that the exciton will arrive at an interface (which is now spread throughout the material) before recombining.

Note, the reason the exciton would usually recombine before reaching the middle interface is because the material needed to achieve a certain thickness so that a majority of the incoming EM radiation would be absored.

How can you improve the performance of Organic Thermoelectrics?

So, originally, the **PEDOT** TE, which is doped and stabilized using PSS, has a structure comprised of grains surrounded by PSS shells. This is bad for conductivity, as the PSS is insulating, while the PSS is doped, so is able to conduct charge more easily. Only when a **secondary dopant** (SD) is added is the PSS shell interrupted, and the PEDOT-rich grain "explodes" into a well-percolated nanofibre.

The inclusion of the SD has an effect on the morphology and the transport of the PEDOT. Namely, when SD is added, it will induce the formation of quinoid regions in the PEDOT; these quinoid regions are more planar and rigid, thus promoting pi-pi stacking between conjugated planes. This is good for charge transport along the conjugation axis.

    If the SD is large, then the regions where the SD is bonded, the PEDOT begins to detach from the PSS, which will destabilize the overall structure. Further, it will lead to less dedoping where the PSS detaches, and the reduction of quinoid regions).

You can tell the amount of quinoid in the PEDOT by looking at the XRD; if the **pi-pi stacking arches** are further apart in reciprocal space, then the planes are closer to one another in real space. The planes are closer as they are more rigid (due to increased quinoid presence), so they are able to more easily stack (slide 89).

    You can then find the dopant level by looking at the absorption spectrum at high wavelengths. Because the positive bipolarons will more free states at the lowest energy transition between the VBM and the gap states, it will absorb many high wavelengths. We know the concentration of bipolarons is proportional to the doping level, so if the doping level decreases, bipolaron conc decreases, and the absorption at higher wavelengths will subsequently decrease (slide 90).
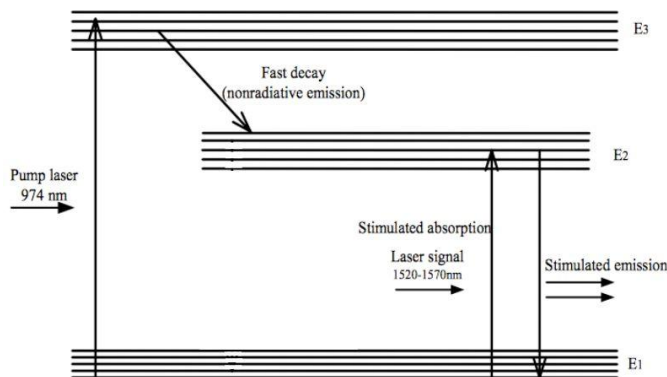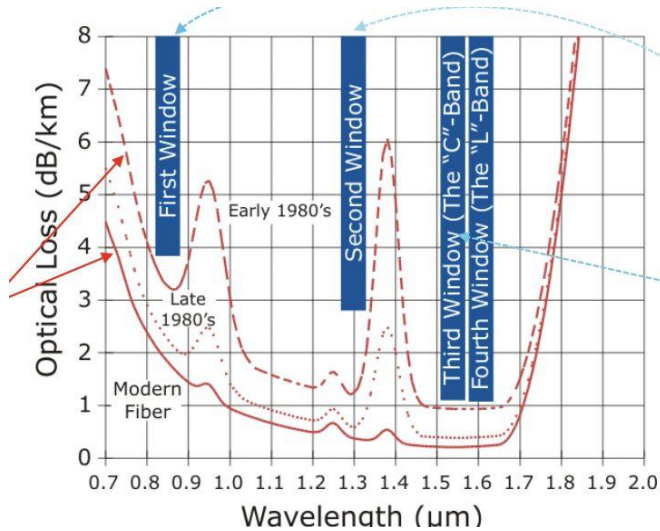
Honestly, everything relevant to the increase in the power factors is well-explained on slide 91.

Also, alignment can help by reducing the phonon mobility while keeping conductivity relatively unaffected.

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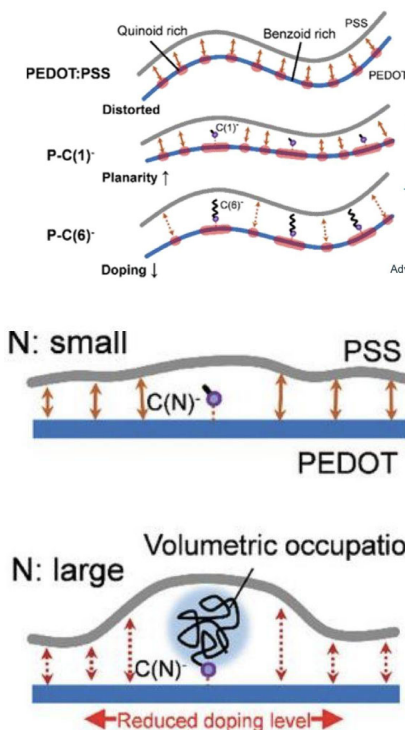
How does an Er-doped fiber optic amplifier work?
(Why is Er used for this?)

First, we should break down the mechanisms behind an optical amplifier itself; it works off of the same principles as LASER technology. Essentially, you have a pump laser excite the VB electrons two states up, allowing them to naturally decay down one state and stabilize as a metastable state.

After the electrons are excited in your Erbium amplifier (i.e. population inversion has occurred), there are three possible outcomes of the EM signal of the waveguide interacting with the amplifier:

1. The signal photon could pass right through. Doesn't degrade the signal at all, but doesn't amplify either.
2. The signal photon is absorbed into the Er, and then immediately reemitted. Doesn't degrade the signal nor amplify it.
3. The signal photon stimulates decay of the inverted e⁻ population. This is great for amplification, as a bunch of identical photons are created !

The reason that Er is used in particular is because the material has a bandgap that corresponds energetically with the most commonly used wavelength windows for optical signals. These windows are used, because they have low optical loss.

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How do we create photonic crystal and what are its application?
What is dispersion graph? What are motivations of slow light?

Photonic Crystals:

Essentially, you create want to create a photonic material with a non-linear dispersion. Uniform mediums effectively only have linear dispersions (slide 24) BUT by creating a structure with a periodic refractive index, you can essentially create **band gaps**! Often, this takes the form of pillars in air, which will only interact with like that is polarized parallel to the figures (**transverse electric**), or holes in the material, which will only interact with light that is polarized perpendicular to the hole axis (**transverse magnetic**). (slide 34).

    The application of a material like this is mainly aimed at creating photonic circuits.

Dispersion:

The creation of band gaps in these materials essentially arises from the fact that at the Bragg condition, total internal reflection is achieved within the material, and this will result in **standing waves** developing in the material at this wave vector. One wave moving left and one wave moving right (both with the same velocity and amplitude) will result in a standing wave. There are two standing waves that are possible; one will have a higher energy than the other, and thus a bandgap will arise.

    Notably, the dispersion is flat near the band gap; this is because a standing wave has developed, which means that the group velocity of the photons at that wave vector is zero, which aligns with the description of the wave as a standing wave.

Slow Light:

As previously mentioned, near the band extrema, the dispersions flatten. This flatter dispersion is indicative of a lower photon velocity, which can give rise to the phenomenon of **slow light**, which can be interesting for sensing, as it increases interaction between light and medium.

    Another note, you can also get a **negative index of refraction**, as the negative dispersion slope is equal to c/n, and because c is a universal constant, n must be negative.

What are the issues in production of graphene FETs?
What are the alternatives to graphene FETs?

For context, the main issue with a graphene FET, in concept, is the fact that there is no bandgap. Without the bandgap, it is very easy to thermally excite carriers, or (I would assume) change the carrier conc. by altering E_F. In any case, this gives the graphene FET a bad on/off ratio. This issue can be ameliorated by using graphene nanoribbons, as the confinement effect in the nanoribbons would be able to discretize the momentum in k-space, in the transverse direction. This would, in term, be able to reduce the continuous band structure of graphene to a series of 2D band structures, which have band gaps as they are off the high-symmetry K and K' points. The issue with this solution is that it is incredibly difficult to actually produce these graphene nanoribbons without harming the carrier mobility through the introduction of disorder, which might otherwise localize the highly delocalized electrons in the system. Generally, **as the band gap is opened, the mobility of the electrons decreases.** The alternative to creating bandgaps in graphene via confinement in the nanoribbon geometry is **twistronics**. As well, the issue of **contact resistance** is also present in graphene FETs, reducing their viability. Finally, there is also the issue of where to apply the gate in the FET. A top-gate would allow for better FET performance (likely lower power consumption?), but would also disrupt pi-conjugation, thus **reducing the mobility of the carriers**.

(As a side note; there are two main ways to fabricate nanoribbons- the top-down and bottom-up approaches. The first one takes a precursor layer, SiC, and then removes the Si via sublimation. The second approach requires the exfoliation of graphene, before transferring it onto a substrate.)

Instead of graphene FETs, one could utilize a CNT FET. Because the pi-conjugation occurs within the tube, you don't have worry that a top gate will reduce the mobility. As well, CNTs that are large enough and of a certain conformoration can also undergo confinement, and maintain a sizeable bandgap. BUT, precise control of the CNT diameter and chirality are still not possible, so evidently, CNT-based FETs have their own host of issues. Though, in theory, they would be able to achieve a better performance.