

**Course Name- Nanophotonics, Plasmonics and Metamaterials**

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**Week-11**

**Lecture -33**

Hello students, welcome to lecture 33 of the online course on Nanophotonics, Plasmonics and Materials. Today's lecture will be on alternative plasmonic materials. So, here is the lecture outline, we will quickly give a overview of this topic, then we will discuss about the limitations of conventional plasmonic materials. We will discuss some elusive lossless materials which are basically difficult to find. Then semiconductors to metals, we will look for metals to dilute metals how they are relevant as alternative plasmonic materials. We will also discuss some 2D plasmonic materials and then we will conclude.

## Lecture Outline

- Overview
- Limitations of Conventional Plasmonic Materials
- Elusive Lossless Metals
- Semiconductors to Metals
- Metals to Dilute Metals
- 2D Plasmonic Materials
- Summary



So, here is the overview. Materials technology has played a significant role in human history across different areas which enabled creation of novel applications that in turn contribute to the exploration of new scientific knowledge. Advancement in scientific concepts often drive the development of more advanced material technologies. This has been exemplified by the transition from bronze age to iron age and this has basically marked the progress in metallurgy.

The relationship between science and technology they form a positive feedback loop with materials playing a critical role in this mutually reinforcing process. Two

significant examples that we can cite from the first century are basically the semiconductor technologies and optical communication. Both of which have had a transformative impact on our ability to handle information. So it is the blessings from semiconductor technology that we are able to do the computation very fast and the optical communication that allows the transfer of data at a lightning speed. So, these two has actually impacted a lot.

## Overview

- Materials technology has played a significant role in human history across different eras, enabling the creation of novel applications that, in turn, contribute to the exploration of new scientific knowledge.
- Advancements in scientific concepts often drive the development of more advanced materials technologies.
- This had been exemplified by the transition from the Bronze Age to the Iron Age, which marked progress in metallurgy.
- The relationship between science and technology forms a positive feedback loop, with materials playing a crucial role in this mutually reinforcing process.
- Two significant examples from the past century are semiconductor technologies and optical communications, both of which have had a transformative impact on our ability to handle information.
- In recent decades, the processing speeds for handling information have experienced exponential growth, primarily driven by the scaling of semiconductor electronic components.



In recent decades the processing speeds for handling information have experienced exponential growth and that is primarily driven by the scaling of semiconductor electronic components. So, if you think of this trend, this trend was predicted by Moore's law, this particular scaling trend that the number of transistors in a chip will double every 1.5 years or 2 years. So this advancement in semiconductor technology and optical communication they have basically revolutionized the way we process information, we transfer information in this modern digital age. So, we have seen transistors scaling down from 200 nanometer to 35 to 1.8 micron even nanometer.

## Overview

- This scaling trend was originally predicted by Moore's Law.
- These advancements in semiconductor technology and optical communications have revolutionized information processing capabilities and have been instrumental in shaping the modern digital era.
- Transistors, have undergone significant scaling down from approximately 200 nm to 35 nm in the past decade, resulting in considerably higher operational speeds.
- Further extensive scaling faces substantial challenges, including issues like short-channel effects, gate leakage, and a dramatic increase in power density.
- These difficulties highlight the complexities and limitations associated with pushing the boundaries of transistor miniaturization in semiconductor technology.
- Plasmonics, as an alternative technology, has garnered significant interest as a potential solution to overcome the challenges in increasing information processing speeds.

So that has actually gone down to very very tiny channel length size and that has allowed amazing miniaturization and it has also given very high operational speed. Now when you think of further extensive scaling, so till 35 nanometer or bit that was achieved in the last decade, till then those effects like short channel effect, gate leakage and dramatic increase in power density they were not that significant but then with further extensive scaling you will be starting to see all these effects coming into picture. Now these difficulties highlight the complexities and limitation associated with pushing the boundary of the semiconductor transistor miniaturization. So, this is where you will find a problem with the miniaturization.

## Overview

- Plasmonics, together with related fields like metamaterials and transformation optics, has experienced significant expansion, showcasing novel physical phenomena and application prototypes.
- To translate these innovative concepts and prototypes into practical technologies, **materials technology plays a crucial role.**
- Achieving desirable properties in plasmonics and metamaterials heavily relies on the engineering of the constituent materials.
- This highlights the **importance of materials science** in these domains.
- Plasmonics has gained significant recent attention, despite its ancient applications, such as the Lycurgus Cup and stained glass in medieval cathedrals.

And we have also already discussed as plasmonic can be an alternative technology which already has gathered a lot of interest as a potential solution to overcome some of these challenges by increasing the information processing speed.

## Overview

- Plasmonics can play a vital role in information processing as it offers a pathway to miniaturize optical components for on-chip integration
- This is done by overcoming the limitations of diffraction in conventional optical systems.
- Optical communication, being the fastest means of information processing, faces challenges in compact packing due to diffraction limits, which plasmonics can help overcome.
- In conventional optical systems, diffraction limits the minimum size of optical components.
- It is then plasmonics which allows for size reduction below the diffraction limit.

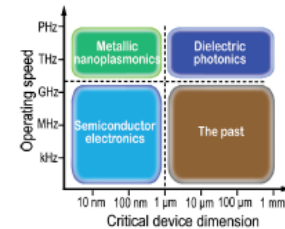


Figure: Operating speeds vs. critical dimensions of current chip-scale devices

And plasmonics when you combine this with the fields like metamaterials and transformation optics they have significant expansion over the last couple of years or last one decade you can say and they have given the hope that lot of new exciting physical or optical phenomena can be realized using these technologies and people have demonstrated different application prototype. They are not commercially available but they are still in the research laboratories and people are able to demonstrate different capabilities of these technologies and they are really really promising. Now to translate these innovative concepts and prototypes into practical technologies this is where material technology will be playing a crucial role. So, you want to achieve desired properties in plasmonics and metamaterials and they actually rely heavily on the engineering of the constituent materials.

## Overview

- In plasmonics, Light interacting with metals can generate a surface plasmon wave.
- This is characterized by charge density fluctuations on the metal's surface, enabling advanced applications.
- Surface plasmons strongly couple light to metal surfaces, allowing for confinement of light in areas smaller than the diffraction limit.
- This enables amplification of local electromagnetic field intensity by many orders of magnitude.

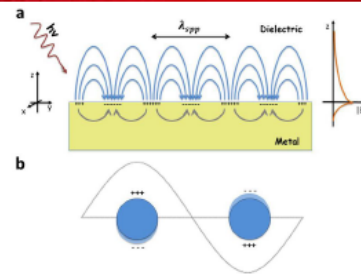


Figure: Schematic representation of Surface plasmon polariton

So that brings in the importance of the material science in these domains or in these areas. Now plasmonics has gained significant recent attention, okay. Though the initial the first demonstration of plasmonic effects were like age old so if you can remember the Lycurgus cup or the stained glasses those are seen in the medieval cathedrals, okay. Those were the first instances where plasmonic effect could be seen, okay. Still people are exploring plasmonics in this new digital era because that can actually help you in overcoming the limitations of both semiconductor electronics as well as dielectric photonics and can give you the best of the both worlds something like you can get the critical dimension of the device tip almost below 10 nanometer and you can still target speeds operating speed above 1 terahertz.

So this can be done by breaking the limitation of the diffraction of the conventional optical system that is what dielectric photonics faces the challenge. This is the typical diffraction limit of light. So optical communication being the first instruments of information processing, okay they are having this problem of miniaturization and this is where plasmonics can help, okay. So plasmonics can get you the size below the diffraction limit. So, we have seen this already this is an this is a example of how you can excite surface plasmon polariton propagating along a metal dielectric interface when some light is falling, okay.

But one thing is not shown here is that there this it cannot be directly excited by simply shining light on the interface you have to have a arrangement of phase matching either using a prism or a grating, okay. So we have seen this and this is the example of localized surface plasmonics which can work without anything you can simply shine light on it and you can excite localized surface plasmonics on this, okay. So we have

already seen this and they actually allows amplification of local electromagnetic field intensity by several orders and they have found applications in sensing and scattering or absorption enhanced absorption or enhanced scattering kind of phenomena. So we have also seen that metamaterials are basically engineered artificial materials that can give you new optical properties and we know that the meta atoms or meta molecules are designed to be much much sub wavelength that is much smaller than the wavelength of light. Now metamaterials have enabled noble functionalities something like optical magnetism, sub diffraction resolution or negative refractive index and all these things are possible by the materials themselves like if you take metals they exhibit a negative real permittivity at optical frequencies whereas at optical frequencies dielectrics have a positive permittivity, right.

## Overview

- Metamaterials are engineered artificial materials used to achieve optical characteristics, with meta-molecules much smaller than the wavelength.
- Metamaterials have enabled novel functionalities, including optical magnetism, sub-diffraction resolution, and a negative refractive index.
- Metals exhibit a negative real permittivity at optical frequencies, while dielectrics have a positive one.
- However, metals also introduce optical losses due to electronic transitions, limiting the performance of optical devices
- This presents **challenges in the design and integration of plasmonic and metamaterial devices.**



And metals they introduce optical loss due to their electronic transitions and that creates a problem at optical frequencies because that will limit the performance of the device. So if there is loss the device will heat up and you are losing energy because it is simply getting absorbed, okay. Now this presents challenge in the design integration of plasmonic and metamaterial devices. So if you use the metals the conventional metals you are facing issues because of this high loss at the optical frequencies. Now let us discuss these limitations of conventional plasmonic materials in more details.

So when you think about plasmonic materials gold and silver should come to your mind immediately. They are the popular choice for plasmonic and optical metamaterial devices due to their low ohmic loss and high DC conductivity. However, when you think at optical frequencies this metal they exhibit inter-band transitions which introduce significant losses, okay. And these losses are in the form of valence electrons absorbing those photons to jump to a higher energy level. These inter-band transitions are basically

responsible for the distinct colors of the metals like copper, gold, okay and they come from electron energy level shifts.

The imaginary part of the gold, so if you remember the gold permittivity that we saw a couple of lectures back there is a real and there is an imaginary part. And the imaginary part of the permittivity reveals basically two types of losses. One you can call intraband or Drude loss and the other one is interband loss, okay. And in this particular diagram you can actually see that the imaginary part of the permittivity is being plotted, okay. And the finely dotted ones that shows the inter-band transition and this one shows the intra-band transition and what you can see that the Drude losses, okay the intra-band transitions they are more prominent in the near infrared regime but they decrease at shorter wavelength.

## Limitations of Conventional Plasmonic Materials

- Gold and silver are popular choices in plasmonic and optical metamaterial devices due to their low ohmic losses and high DC conductivity.
- However, at optical frequencies, these metals exhibit interband transitions, introducing significant losses
- These losses are in the form of valence electrons absorbing photons to jump energy levels.
- Interband transitions are responsible for the distinct colors of metals like copper and gold, stemming from electron energy-level shifts.
- The imaginary part of permittivity for gold in the optical range reveals two primary loss components: intraband (Drude) and interband losses.
- Drude losses in gold are prominent in the near-infrared (NIR) region but decrease at shorter wavelengths.

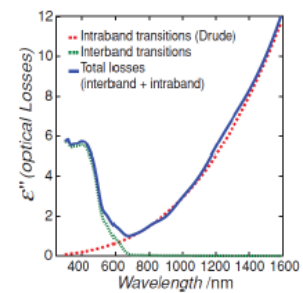


Figure: Imaginary permittivity or optical losses in gold:

And at shorter wavelength you can see that interband transitions they actually dominate and they become the main reason for optical losses, okay. So these are the, this particular interband transitions or the losses at short wavelength for metals like gold and silver they make those metals less suitable for plasmonic and metamaterial applications. So people are looking for, scientists are looking for materials which can have reduced inter-band losses, okay so that you can overcome this limitation and enhance the performance of the optical devices which operate in this region. So for applications like transformation optics it is crucial for metals imaginary function to have low values indicating minimal loss that we have seen, right. If you want to match the permittivities, okay of the metal and the dielectric part and dielectric is more or less lossless, okay.

So you want metal which should have negligible amount of loss then only you should be able to match the permittivity between metal and dielectric and that should help you in

transformation optic devices like cloaks or other ones, okay. Now we understand that the imaginary part of the permittivity is basically influenced by three loss mechanism. So one is the inter-band transition, the other one is intraband or the drude and the third one is the scattering loss that comes from the defect within solid structure. So we can actually look into that also in more details. So here is the real and imaginary part of permittivity for silver, okay.

## Limitations of Conventional Plasmonic Materials

- In contrast, interband losses in gold are most significant at shorter wavelengths in the visible range, exacerbating the limitations of these metals for optical devices.
- These interband losses at optical frequencies make metals like gold and silver less suitable for numerous plasmonic and metamaterial applications.
- **Alternative materials with reduced interband losses are required** to overcome these limitations and enhance the performance of optical devices.
- For applications like transformation-optics devices, it's crucial for a metal's imaginary dielectric function to have low values, indicating minimal loss.
- The imaginary part of permittivity is influenced by three main loss mechanisms: *interband transitions*, *intraband transitions*, and *scattering losses* resulting from defects within the solid structure.

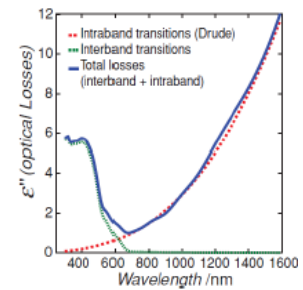


Figure: Imaginary permittivity or optical losses in gold:

Now if the interband transitions are absent in a metal then the intraband and scattering losses from the defects they will contribute to the significant overall loss, okay and they will pose a challenge to the device performance, okay. So here we can see how the electrons are behaving in metal, okay. So it has been, you have used a drude model to explain the behaviour of the electrons in this metal. So here we have considered silver. So, the permittivity is written as real and the imaginary part and then there are two components here.

So one is the real part, this is the imaginary part and in the real part you actually can see there is  $\epsilon_b$  which is frequency independent and this is called as the polarization response from the core electrons or you can simply call it as background permittivity. Here  $\omega_p$  is the plasma frequency and  $\gamma$  is the drude relaxation rate. So when you plot this you see this is how the dots show you how exactly that these are the real values, okay, the dots one, the experimental measured values and the curved line over here that comes from this particular equation. On the other side this is basically the imaginary part that is  $\epsilon''$  and you can see that also closely follows the experimental data till a particular wavelength or energy range, okay. Now what is important here to note that now the drude relaxation rate that is the  $\gamma$  it actually plays a role in the scattering or ohmic loss, okay, because it directly affecting the imaginary part of the permittivity which is

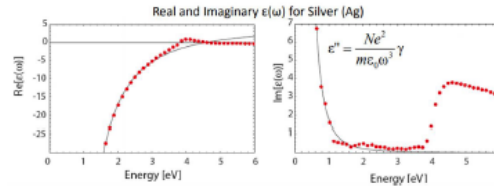


$\epsilon''$ ,

right.

## Limitations of Conventional Plasmonic Materials

- Even if interband transitions are absent in a metal, intraband transitions and scattering losses from defects often contribute to significant overall losses, posing challenges in device performance optimization.
- To better understand this issue, let's take a closer look at how electrons behave in metals.
- We can describe this behaviour using a model known as the Drude model, shown in Equation below.



$$\epsilon(\omega) = \epsilon' + i\epsilon'' = \epsilon_b - \frac{\omega_p^2}{(\omega^2 + \gamma^2)} + i \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)\omega}$$

$\epsilon_b$  is the polarization response from the core electrons (background permittivity)  
 $\omega_p$  is the plasma frequency and  $\gamma$  is the Drude relaxation rate.



Source: Stefan Maier, Plasmonic Fundamentals and Applications p.17 (Drude model fit) [2007]

Now if you want  $\epsilon''$  to be really small, if you want this part to be really small, okay, then you should reduce gamma, okay and that means you have to decrease the carrier concentration  $n$  or ideally both, okay. So if you are able to do that, that will bring down your imaginary part. Now the efforts to reduce gamma which is basically the relaxation rate, okay, in conventional plasmonic materials like the noble metals, gold or silver that can be achieved through cryogenic cooling but that has not yielded sufficient amount of loss reduction for practical devices. So that did not work out, okay. So once again what is the method of making this imaginary part small? You can reduce gamma by decreasing the carrier concentration, okay.

These are the two methods, okay. So either you decrease this or this or both simultaneously, okay. So here what has been seen that for noble metals or materials they have very high carrier concentration and that is why, and this further increases  $\epsilon''$  in the NIR and visible range. So, lowering the concentration in this metal would be very beneficial for reducing this  $\epsilon''$  magnitude, okay. So what we are planning? We are planning to actually reduce the carrier concentration in the metal.

That should give you lower imaginary part of the permittivity. Now because the conventional plasmonic materials like gold, silver they suffer from high loss, okay. They have significant issues in applications in plasmonics, then optical metamaterials and transformation optics. It is understood because if you design a waveguide using this kind of plasmonic materials because of the loss the propagation length will be very short, okay.

So that will not help you. Although you are able to confine energy in a very tiny space you will not be able to take that energy further because of this kind of material loss which are intrinsic, okay. And another challenge will arise from this kind of real part, okay. Challenge in magnitude of this material will be in the transformation optic devices. So transformation optic devices you have seen that metal dielectric, okay you should not have very large singular values, okay. Now if you actually make your  $\epsilon$  very low,  $\epsilon''$  very small, okay, in that case another challenge will come from this exceptionally large magnitude of the real part of the permittivity, okay.

## Limitations of Conventional Plasmonic Materials

- The Drude relaxation rate ( $\gamma$ ) plays a crucial role in scattering or ohmic losses, directly affecting the imaginary part of the dielectric function,  $\epsilon''$ , in materials used for plasmonic applications.
- Achieving a small  $\epsilon''$  is essential, and this can be accomplished by reducing  $\gamma$ , decreasing carrier concentration ( $n$ ), or ideally, both factors simultaneously.
- Efforts to reduce  $\gamma$  in conventional plasmonic materials like noble metals through cryogenic cooling have not yielded sufficient loss reduction for practical devices.
- These materials typically have a high carrier concentration, further increasing  $\epsilon''$  in the near-infrared (NIR) and visible spectral regions.
- Lowering the carrier concentration in these metals would be highly beneficial in reducing  $\epsilon''$  magnitude.



So usually in this particular materials, okay in this material like gold and silver the real part of the permittivity is very high and that will make your life difficult when you want to realize a transformation optics device. And the challenge arises from the exceptionally large magnitude of the real part of permittivity in this metals making it difficult to design transformation optics device. When the real parts of the permittivity of the metal and dielectric are of the same magnitude it is easier to tune for the geometric field fraction to design some required specification. But if because dielectric does not have this imaginary part in the permittivity, so if the metal has got that it makes it very difficult to obtain the correct geometric filling factor. On the other hand if the metals real part is significantly larger than that of the dielectric it requires using very small metal inclusion within the metamaterials, okay or metamolecules in a metamaterial design and that because this kind of very very small metal inclusions makes it very difficult for the nanofabrication, okay.

## Limitations of Conventional Plasmonic Materials

- Conventional plasmonic materials like gold and silver suffer from high losses, which is a significant drawback for applications in plasmonics, optical metamaterials, and Transformation Optics (TO).
- Another challenge arises from the exceptionally large magnitude of the real part of permittivity in these metals, making it difficult to design transformation optics (TO) device.
- When the real parts of permittivity of metal and dielectric are of similar magnitude, it allows for easier tuning of geometric fill fractions to meet design specifications.
- Conversely, if the metal's real part of permittivity is significantly larger than that of the dielectric, it requires using very small metal inclusions within the meta-molecule, which presents challenges in nanofabrication processes.
- Therefore, having plasmonic materials with smaller magnitudes of  $\epsilon'$  (real part of permittivity) would offer distinct advantages in numerous applications, simplifying design and fabrication processes.



So there will be fabrication challenges in this case. Therefore, having plasmonic materials with smaller magnitude of  $\epsilon'$  that is a real part of permittivity would offer distinct advantages in numerous application while simplifying the design of your structure also it will simplify the fabrication processes. So we understood that noble metals pose a significant technical challenge and they are not compatible with the standard silicon manufacturing processes. So these limitations actually hinders the utilization of plasmonic and metamaterial devices in conjunction with the common nanofabrication technologies. So, the incompatibility limits the potential integration of the plasmonic and metamaterial components with the nanoelectronic devices and that restricts the development of advanced hybrid technologies.

## Limitations of Conventional Plasmonic Materials

- Noble metals pose a significant technological challenge as they are **not compatible** with standard silicon manufacturing processes.
- This limitation hinders the utilization of plasmonic and metamaterial devices in conjunction with common nanofabrication technologies.
- Also the incompatibility limits the potential integration of plasmonic and metamaterial components with nanoelectronic devices, restricting the development of advanced hybrid technologies.
- The incompatibility issue with noble metals arises from their tendency to diffuse into silicon, forming deep traps.
- This diffusion negatively impacts the performance of nanoelectronic devices.

So, you can understand that the issue is with the material which show this plasmonic properties. The incompatibility issue with the noble metals arises from their tendency to diffuse into electron sorry into silicon forming dip traps and this diffusion negatively impacts the performance of nanoelectronic devices. So that is a problem. So integrating noble metals into silicon manufacturing process becomes a very complex task due to the diffusion issue and it makes it very difficult to achieve without specialized processing steps. So, you have to incorporate some extra care into the fabrication process to handle this.

## Limitations of Conventional Plasmonic Materials

- Integrating noble metals into silicon manufacturing processes is a complex task due to the diffusion issue, making it difficult to achieve without specialized processing steps.
- While copper has been incorporated into silicon processes, it requires additional steps to establish diffusion barriers between silicon and copper, limiting the ease of integration.
- Despite advancements, gold and silver still remain impractical for integration into silicon manufacturing processes, further highlighting the challenges associated with noble metals in these technologies.
- With all the shortcomings of conventional plasmonic materials, **researchers have been motivated to search for better alternatives.**
- Many alternatives to metals have been proposed that overcome one or more of the drawbacks mentioned.
- The significance of choosing an alternative plasmonic material depends on the end application, but general criteria can be derived from the issues discussed earlier.

While copper has been incorporated into silicon processes it still requires additional

steps to establish diffusion barriers between silicon and copper which actually limits the ease of integration. Now despite all these advancements gold and silver still remain impractical for integration into silicon manufacturing processes and these are due to the challenges associated with these noble metals in these technologies. So with all these shortcomings of the conventional plasmonic materials researchers have been motivated to search for better alternatives. So many alternatives to metal have been proposed that can overcome one or more of the drawbacks that have been mentioned till now. The significance of choosing an alternative plasmonic material depends on the end application.

So this is very important. So you need to know what application you are looking for that is no one size fits all kind of thing. So depending on the application you can choose the right alternative material and we will discuss the general criteria on how to choose materials in this lecture. So we have been looking for an alternative to metals in a lossless metal which is a bit elusive difficult to find but that is an ideal candidate that can replace the metals in plasmonic and metamaterial devices. So what are we looking for? We are looking for purely real and negative permittivity that is your  $\epsilon'' = 0$  and the real part is negative. So, this is the best kind of metal you can think of which will give you a metallic response but no loss.

## Elusive Lossless Metals

- An ideal candidate to replace metals in plasmonic and metamaterial devices would have purely real and negative permittivity ( $\epsilon'' = 0$  and  $\epsilon' < 0$ ), offering a metallic response to light without any losses.
- Such a material would produce metallic behaviour while maintaining zero losses, making it highly desirable for various applications.
- However, achieving zero losses and negative permittivity simultaneously for all frequencies in any dispersive material is **impossible** due to the causality condition, limiting the feasibility of such an ideal material.

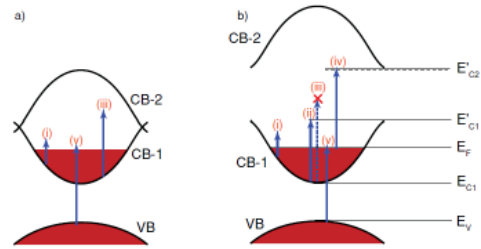
But such a metal is like although this kind of metal material would be like highly desirable for various applications but achieving this kind of thing that your 0 loss and negative permittivity simultaneously for all the frequencies in any dispersive material is impossible due to the causality condition and that basically limits the feasibility of such an ideal material. So the real and the imaginary part of the permittivity are related by the Kramers-Kronig relationship which we are not discussing here in detail but I just

wanted to tell you that this relation tells you that this two components are tied together ok. So if one is made too small the other one will become very large ok like that. So let us now think of this material ok without loss how things will look like ok. So here this particular figure shows two possible electronic band structure for a metal.

## Elusive Lossless Metals

- **Figure** shows two possible electronic band structures for a metal.
- Figure (a) resembles the typical band structure of many common metals.
- Figure (b) represents a hypothetical band structure of a unique metal.
- Figure (b) depicts three energy bands of the metal:
  - a completely filled valence band (VB),
  - an incompletely filled conduction band (CB-1), and
  - a completely empty conduction band (CB-2)

with their respective energy levels as indicated.



**Figure:** A schematic showing band structures of  
 a) metal with losses  
 b) metal with no losses in a specific wavelength range.

The arrows (labeled (i) through (v)) show the electronic transitions upon absorption of a photon of the corresponding energy.

So, this one has got loss and this one is lossless for a specific wavelength range ok. So this figure a resembles the typical band structure of many common metals and figure b is basically a hypothetical band structure of unique metal and this is typically a lossless metal ok. So here in this particular figure you are able to see three things first you can see a completely filled valence band then you can see a incompletely filled conduction band 1 and then you can also see a completely empty conduction band 2 ok. So, what happens when photons with energy less than  $E'_{c1} - E_{c1}$  this gap ok that can cause inter band transitions and that is leveled as 1 ok in CB1 is leading to significant optical loss ok which is very similar to the droop metals at low frequencies. Now if you see that when the photon energy slightly exceeds this  $E'_{c1} - E_{c1}$  ok if the photon energy is slightly larger than these ok they will end up going here and this is not allowed ok.

So that is the case where you do not have any transition ok and this situation is very unique and this does not happen here ok because here you will find a within the conduction band there are empty levels but here because you are able to have this gap there these are not allowed levels ok. So, the lossless regime actually persist as long as the photon energy is less than the lower of  $E'_{c2} - E_f$  so this gap and  $E_f - E_v$  okay. So as long as the photon energy is less than the minimum of these two you will end up having this kind of a transition which is not allowed so the photon energy is not basically absorbed. So, this is happening because there are no allowed electronic transitions and

that is because of the unavailability of the energy states and this results in a zero optical losses. So, you can understand this can happen over a specific wavelength range.

## Elusive Lossless Metals

- Photons with energy less than  $(E'_{c1} - E_{c1})$  can cause intraband transitions, labeled as (i), in CB-1, leading to significant optical loss similar to Drude metals at low frequencies.
- A metal depicted by Figure b becomes lossless when the photon energy slightly exceeds  $(E'_{c1} - E_{c1})$  since there are no allowed electronic transitions.
- This unique situation does not occur in Figure (a).
- The lossless regime persists as long as the photon energy is less than the lower of  $(E'_{c2} - E_f)$  and  $(E_f - E_v)$ ,

where no allowed electronic transitions occur due to the unavailability of energy states, resulting in zero optical losses ( $\epsilon'' = 0$ ).

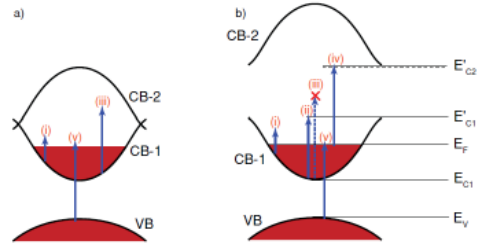


Figure: A schematic showing band structures of  
a) metal with losses  
b) metal with no losses in a specific wavelength range.

The arrows (labeled (i) through (v)) show the electronic transitions upon absorption of a photon of the corresponding energy.

So depending on your application or the required application range you can think of materials which can have this kind of band structure but again this is a hypothetical one ok. Now the optical losses will return for energies larger than  $E'_{c2} - E_f$  okay and  $E_f - E_v$  due to interband transitions from CB1 to CB2 that is your this number 4. So this one shows interband transition ok from CB1 to CB2 ok and also you can have this transition which is from  $E_v$  to CB1 that is leveled as 5. So intraband transitions at low photon energies produce a polarization response that typically generate a negative real permittivity while the unit band structure here can lead to zero loss within a specific range of photon energies ok and this is the range over which there will be no allowed transition. So, the described scenario here tells you that theoretically there could be a possibility of metal where it is completely lossless over a specified range ok and this allows you to think of new possibilities for advanced material design.

# Elusive Lossless Metals

- Optical losses return for photon energies greater than  $(E'_{C2} - E_F)$  and  $(E_F - E_V)$  due to interband transitions from CB-1 to CB-2 (labeled as (iv)) and from VB to CB-1 (labeled as (v)).
- Intraband transitions at low photon energies produce a polarization response that can generate a negative real permittivity, while the unique band structure can lead to zero losses within a specific range of photon energies.
- The described scenario theoretically allows for the existence of a metal that is entirely lossless within a desired frequency range - offering intriguing possibilities for advanced material design.

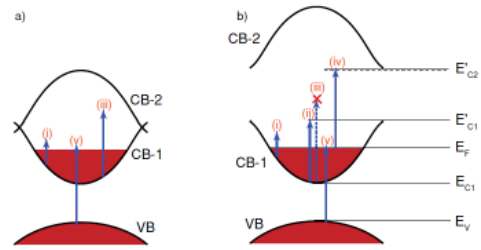


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b) metal with no losses in a specific wavelength range.

The arrows (labeled (i) through (v)) show the electronic transitions upon absorption of a photon of the corresponding energy.

So the absence of naturally found metals with the required band structure we have just seen ok, explains why metal in nature always exhibit inherent losses ok. So in metal you will have this the natural metal will look like this so here all these bands will get accepted and then you will have those losses ok. So Khurgin and Sun proposed in this particular paper they proposed the stretching of the lattice of a sodium metal by nearly a factor of 2 could achieve metallic behaviour that is real part of permittivity to be negative and lossless in a particular spectrum that is in mid IR 1.8 micron to 2.4 micron ok although the practicality of this concept remains uncertain.

So they have proposed but then they could not show it ok. The paper also suggest techniques to stretch metal lattices for including foreign atoms for example, aluminium oxide is mentioned as a metallic material with increased inter aluminium spacing due to the inclusion of oxygen atoms. But such modifications will require careful consideration of their effects on the band structure and also free electron cloud. The addition of foreign atoms can alter the electronic band structures that we all know and also the conduction band electron distribution. So, in the case of this aluminium oxide oxygen nuclei bonding with aluminium electrons they reduce the concentration of the free electrons in aluminium.



## Elusive Lossless Metals

- The absence of naturally found metals with the required band structure (mentioned earlier) explains why metals in nature always exhibit inherent losses.
- Khurgin and Sun proposed that stretching the lattice of sodium metal by nearly a factor of two could achieve metallic behavior ( $\epsilon' < 0$ ) and losslessness in the mid-IR spectrum (1.8  $\mu\text{m}$  to 2.4  $\mu\text{m}$ ), although the practicality of this concept remains uncertain.
- The paper also suggests techniques to stretch metal lattices, including the incorporation of foreign atoms.
- For example, AlO is mentioned as a metallic material with increased inter-Al spacing due to the addition of oxygen atoms, but such modifications require careful consideration of their effects on the band structure and free-electron cloud.
- The addition of foreign atoms can alter electronic band structures and conduction-band electron distributions. In the case of AlO, oxygen nuclei bonding with aluminum electrons reduces the concentration of free electrons in aluminum.



Sources: Khurgin, Jacob B., and Greg Sun. "In search of the elusive lossless metal." *Applied Physics Letters* 96.18 (2010).

Now despite theoretical proposals and potential lattice modifications the absence of naturally occurring lossless metals underscores the ongoing challenge of realizing materials with simultaneous losslessness and negative real permittivity ok in practical applications. So there are two possibilities in producing alternative materials based on the Drude description. One you can think of heavy doping of semiconductor so you are basically doping a semiconductor such that it starts behaving like a metal. So that will introduce a significant number of free carriers in that case and this process can shift the optical properties of semiconductor towards metallic behaviour within a desired wavelength range and that could enable the plasmonic applications.

## Elusive Lossless Metals

- Despite theoretical proposals and potential lattice modifications, the absence of naturally occurring lossless metals underscores the ongoing challenge of realizing materials with simultaneous losslessness and negative real permittivity in practical applications.
- There are two possibilities in producing alternative plasmonic materials based on the Drude description:
  - Heavy Doping of Semiconductors:
    - Doping semiconductors heavily with appropriate impurities to introduce a significant number of free carriers.
    - This process can shift the optical properties of the semiconductor towards metallic behavior within the desired wavelength range, enabling plasmonic applications.
  - Carrier Reduction in Metals:
    - Reducing the excess free carriers in metallic materials through various techniques.
    - By controlling and reducing the carrier concentration, it becomes possible to tailor the plasmonic properties of metals for specific applications or desired wavelength ranges.



And the other approach is carrier reduction in metal. So you have to reduce the excess

free carriers in metallic materials through various techniques and by controlling and reducing the carrier concentration it will then become possible to tailor the plasmonic properties of metals for specific application over a desired wavelength range. So there are a few other techniques that can produce low loss metal. One of these techniques is to use or design a material with nearly zero loss that results from electromagnetically induced transparency EIT. So what happens in EIT? EIT effect can make materials nearly lossless to specific laser radiation there the transmission suddenly improves because of a resonance effect and EIT relies on a non-linear optical phenomena where one resonance frequency reduces losses when a strong field is applied at another resonance. We will not go into the details of EIT effect but you can always look for the electromagnetically induced transparency effect in material and there you can see that it actually becomes lossless at a particular laser radiation.

## Elusive Lossless Metals

- There are a few other techniques that can produce low-loss metals.
- One of these techniques is to use or design a material with nearly zero loss resulting from electromagnetically induced transparency (EIT).
- Electromagnetically Induced Transparency (EIT) can make materials nearly lossless to specific laser radiation.
- EIT relies on a nonlinear optical phenomenon where one resonance frequency reduces losses when a strong field is applied at another resonance.
- This effect causes the real permittivity of the material to switch from negative to positive near the resonance frequency with minimal losses.
- However, EIT has limitations, including its narrowband nature, dependence on specific material properties, electronic structures, and the need for high-intensity optical excitation.



This is a narrow band effect. So this effect causes the real permittivity of the material to switch from negative to positive near the resonance frequency with minimal loss. However, as you can see that EIT has limitations they are inherently narrow band in nature and that depend on specific material properties and electronic structures and they also require high intensity optical excitation. Various other techniques also exist to reduce losses in metals but most technically significant ones are those implementable in devices. So another approach would be to alter the plasma frequency of the Drude models, Drude metals and that could be a promising and accessible approach without major technical barriers or challenges. So how you can do that? Two prominent strategies of tailoring metals can be one you can convert a semiconductor into a metal through heavy doping and the second one is to reduce the carrier concentration in metal to decrease this metallic behavior.

## Elusive Lossless Metals

- Various techniques exist to reduce losses in metals, but the most technologically significant ones are those easily implementable in devices.
- Altering the plasma frequencies of Drude metals is a promising and accessible approach without major technological barriers.
- Two prominent strategies for tailoring metals include:
  - converting a semiconductor into a metal through heavy doping &
  - reducing carrier concentration in a metal to decrease its metallic behavior.
- Subsequent sections will provide in-depth reviews of these two techniques and their applications.



So we have actually discussed briefly these two methods. So we will now look into each of these ideas in details and see what are their applications. So let us begin with semiconductor to metal. So we understand that heavy doping of semiconductors can be a method of increasing the carrier concentration and make the semiconductors behave like metals but they are also actually less metallic metals. To achieve metal like optical properties that is you require the real part of the permittivity to be negative in a specific spectral range. There is a minimum required carrier concentration that can be estimated from the Drude model.

## Semiconductors to Metals

- Heavy doping of semiconductors is a method to increase carrier concentration, making them behave like metals.
- To achieve metal-like optical properties ( $\epsilon' < 0$ ) in a specific spectral range, there is a minimum required carrier concentration, estimated using the Drude model.
- The lower limit on carrier concentration ( $n$ ) needed for  $\epsilon' < 0$  at frequencies below the plasma frequency ( $\omega < \omega_c$ ) can be determined using Equation.

$$\omega_p^2 > \epsilon_b(\omega_c^2 + \gamma^2)$$
$$n > \frac{\epsilon_0 m^*}{e^2} \epsilon_b(\omega_c^2 + \gamma^2)$$

where  $\epsilon_0$  is the vacuum permittivity,  $e$  is the electron charge, and  $m^*$  is the effective mass of the carrier

- Doping is a crucial technique for tailoring materials to exhibit desired optical properties and plasmonic behavior.



So you have to make sure that you reach that level. So the lower limit on  $n$  for achieving negative permittivity at frequencies below plasma frequency can be taken

from this equation. So  $\omega_p^2 > \epsilon_b(\omega_c^2 + \gamma^2)$ . So you have got a limitation. So, this has a lower limit that will give you a negative real part of the permittivity at frequencies below the plasma frequency.

## Semiconductors to Metals

- Common semiconductors like silicon need a minimum carrier concentration of around  $10^{21} \text{ cm}^{-3}$  to exhibit metal-like optical properties in the Near-Infrared (NIR) spectrum.
- Achieving such high carrier densities requires ultrahigh doping densities, which can present substantial technological challenges and limitations.
- Another issue to be considered when choosing a semiconductor for creating metal-like behavior is the mobility of the carriers.
- The mobility ( $\mu$ ) of charge carriers is a critical consideration when selecting semiconductors for achieving metal-like behavior, as expressed by Equation :  $\gamma = e/\mu m^*$ .
- To reduce damping losses, it is essential to maximize the product of carrier mobility and effective mass.



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So you are looking for  $\omega$  less than  $\omega_c$ . So, this is basically the crossover frequency  $\omega_c$ . And here what are the other things you are using  $\epsilon_0$  that is the vacuum permittivity,  $e$  is the electron charge and  $m^*$  is the effective mass of the carrier that is electron here. So doping is a crucial technique for tailoring materials to exhibit desired optical properties and plasmonic behavior. Now common semiconductors like silicon need a minimum carrier concentration of around  $10^{21} \text{ cm}^{-3}$  to exhibit metal like optical properties in the near infrared regime. Achieving such high carrier densities require ultra high doping densities which can present substantial technical challenges and limitations.

## Semiconductors to Metals: Silicon

- Transitioning to silicon plasmonics is a possibility, but heavily doping silicon for metallic behavior at telecommunication wavelengths presents significant challenges.
- Silicon can be doped as n-type using Group V elements like phosphorous, arsenic, and antimony, or as p-type using Group III elements like boron, aluminum, and gallium.
- The solid-solubility curves for some of the more soluble dopants in silicon are shown in figure.
- Although the solid solubility is high, the doping efficiency decreases when the doping concentration approaches the solubility limit
- Despite the lower effective mass of conduction electrons in silicon compared to holes, achieving the necessary high n-type doping for silicon to become metallic at telecommunication frequencies remains a significant challenge,
  - necessitating research into solid-solubility limits and doping efficiency for various dopants.

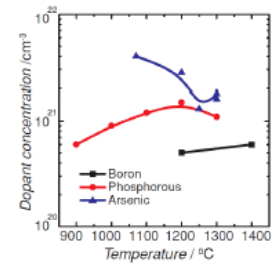


Figure. Solid solubility curves for three different dopants in silicon as a function of doping temperature

Another issue to be considered when choosing a semiconductor for creating a metal like behavior will be the mobility of the carriers. Now the mobility  $\mu$  of charge carriers is a critical consideration when you want to select semiconductors for achieving metal like behavior. This is the equation that correlates mobility with the other parameters. So you can see that  $\gamma$  equals  $e$  over  $\mu m^*$ . So, to reduce the damping loss it is important to maximize the mobility and effective mass product.

So the denominator should be as high as possible if you want to reduce the damping loss. So if you want to transition to silicon plasmonics that is a possibility but as we discussed it will require heavy doping of silicon so that silicon can exhibit metallic behavior at telecom wavelengths. But then this high doping presents some challenges. Silicon can be doped as n-type using group 5 elements such as phosphorus, arsenic and bony and it can also be doped as p-type with group 3 like boron, aluminum and gallium. And the solid solubility curve for some of these soluble dopants are shown here.

## Semiconductors to Metals: Germanium

- Germanium, commonly used alongside silicon in electronic devices, offers higher electron mobility and a smaller optical bandgap, making it suitable for telecommunication frequency photodetectors.
- However, germanium faces absorption issues at telecommunication frequencies due to interband transitions, making it challenging for plasmonic applications.
- The higher dielectric constant ( $\epsilon_b$ ) of germanium compared to silicon requires even higher doping levels for achieving metallic properties at a given wavelength.
- Figure shows the solid solubility curves for highly soluble dopants in Ge.
- Gallium has the highest solubility in germanium, followed by aluminum and arsenic.
- However, the numbers are nearly an order of magnitude smaller than those of silicon. Hence, it is even more challenging to heavily dope germanium to turn it plasmonic in the optical range.

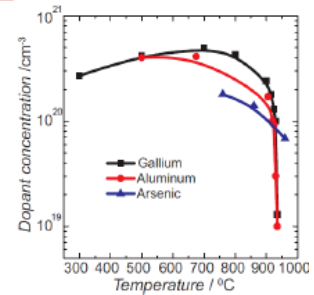


Figure. Solid solubility curves for three different dopants in germanium as function of processing temperature



Source: Naik, Gururaj V., Vladimir M. Shalaev, and Alexandra Boltasseva. "Alternative plasmonic materials: beyond gold and silver." *Advanced Materials* 25.24 (2013): 3264-3294.

So here the dopant concentration is shown as a function of temperature and what you can see here is that the solid solubility although it is high the doping efficiency decreases when the doping concentration approaches the solubility limit. Although the lower effective mass of the conduction electrons in silicon compared to the holes okay achieving the necessary high n-type doping for silicon to become metallic at telecom wavelengths will be difficult and that requires research in this solid solubility limits and also the doping efficiency for various dopants. So here we have seen the group 3 kind of so it is mixed actually you have got boron, aluminum you have got phosphorus and arsenic. So, it shows different doping concentration and solid solubility for each of this.

The next thing we can try with germanium. So germanium commonly used alongside silicon in electronic devices it offers high electron mobility and it has also got a smaller optical band gap. So it makes it suitable for use as detectors right. So you have seen germanium based detectors in telecommunication wavelengths. However germanium faces absorption issues at telecom frequencies due to inter band transitions and that means it is lossy and that is challenging for plasmonic applications again. So, the higher dielectric constant  $\epsilon_b$  that you see for germanium when you compare with silicon that will tell you that it will require even higher doping levels for achieving metallic properties at given wavelength okay.

## Semiconductors to Metals: III–V Semiconductors

- III–V semiconductors have played a pivotal role in various technologies, including high-speed switching, power electronics, and optoelectronics, owing to their wide tunability in optical bandgap through ternary and quaternary compound variations.
- Integrating plasmonics and metamaterial devices into optoelectronic platforms is a crucial development, making the exploration of plasmonic properties in III–V semiconductor systems highly relevant for achieving this objective.
  - **Arsenides and Phosphides:**
    - III–V semiconductors, including GaAs and InP, offer optical bandgaps in the Near-Infrared (NIR), making them potential candidates for plasmonic applications.
    - These materials have a dielectric constant ( $\epsilon_b$ ) comparable to silicon, and their high electron mobility reduces the carrier concentration requirement for plasmonic behavior in the NIR.
    - However, achieving the necessary high doping levels in III–V semiconductors for plasmonic properties is challenging due to lower solid solubilities of dopants and poor doping efficiency.



So the solid solubility curve for highly soluble dopants in germanium is shown here and you can see that germanium has highest solubility in germanium followed by aluminum and arsenic. So if you go back and compare this with silicon here arsenic had the highest solubility and boron has the lowest one. However the numbers are nearly an order of magnitude smaller than those of silicon. So you can actually see the dopant concentration and compare. Hence it is more challenging to heavily dope germanium to turn it into plasmonic.

So if they are getting saturated okay so you cannot dope beyond that right. So it means it is difficult to dope germanium to that level you can do for silicon. So it is difficult to turn it into plasmonic in the optical range. Now you can also think about 3-5 semiconductors. These 3-5 semiconductors have played an important role in various technologies something like high-speed switching, power electronics, optoelectronics and that is due to their wide tunability of the band gap through ternary and quaternary compound variations right. So, if you think of integrating plasmonics and metamaterial devices into optoelectronic platform okay that is a very crucial development and that will make the exploration of plasmonic properties in 3-5 semiconductors highly relevant okay for achieving this objective.

So you can think of arsenides and phosphides okay. So 3-5 semiconductors including say gallium arsenide and indium phosphide they offer optical band gaps near infrared okay. So they are also potential candidates for plasmonic applications. They have background dielectric constant which is comparable to silicon and their high electron mobility reduces the carrier concentration requirement for the plasmonic behavior in the near infrared range. However, achieving the necessary high level of doping in these 3-5

semiconductors are challenging due to the lower solid solubilities of dopants and poor doping efficiency.

## Semiconductors to Metals: III–V Semiconductors

- In some III–V materials like GaAs, achieving n-type doping beyond  $10^{19} \text{ cm}^{-3}$  is difficult due to effects like doping compensation.
- P-doping can lead to carrier concentrations above  $10^{20} \text{ cm}^{-3}$  in materials like p-GaAs, but holes have a higher effective mass and poor carrier mobility.
- While heavily doped InAs has shown promise for plasmonic behavior in longer wavelengths, further increasing carrier concentration in these materials is challenging, limiting plasmonic applications to the mid-infrared (MIR) range.
  - **III-Nitrides:**
    - Gallium Nitride (GaN) is an emerging platform for optoelectronics, capable of operation across the entire visible spectrum.
    - InGaN ternary systems offer large bandgap tunability, attracting researchers for visible optoelectronics applications.



So though there are some good factors there are also some challenges. In some 3-5 semiconductors like gallium arsenide achieving n-type doping beyond  $10^{19} \text{ cm}^{-3}$  is difficult due to the effects like doping compensation and p-type doping can actually lead to something above  $10^{20}$  okay in materials like p-type gallium arsenide but  $\mu$  will be larger in this case right because  $\mu$  has higher effective mass and poor carrier mobility. So that will also not help. So while we heavily doped in indium arsenide you can actually see good promise for plasmonic behavior in longer wavelengths. So this is a good option. However further increasing the carrier concentration in these materials look challenging and that limits the application of these materials for plasmonic applications in mid infrared range.

## Semiconductors to Metals: Transparent Conducting Oxides

- Oxide semiconductors like zinc oxide (ZnO), cadmium oxide (CdO), and indium oxide ( $\text{In}_2\text{O}_3$ ) can be heavily doped to create transparent conducting oxides (TCOs).
- TCOs, known for their large bandgap, are transparent in the visible range and serve as electrical contacts in display panels.
- TCOs can exhibit metal-like optical properties in the Near-Infrared (NIR) due to their high DC conductivity as shown in figure.
- The optical properties of TCOs can be tuned by adjusting carrier concentration/doping levels.

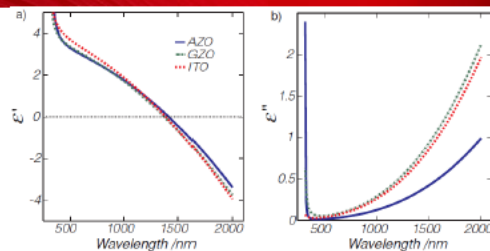


Figure. a) Real and b) imaginary parts of dielectric function of TCO films: Al:ZnO (2 wt%), Ga:ZnO (4 wt%) and ITO (10 wt%) deposited using pulsed laser deposition.





You can think of nitrides, gallium nitride is an emerging platform for optoelectronics and these are capable of operation across the entire visible spectrum. So indium gallium arsenide this ternary system can offer large band gap tunability and that is why it has attracted researchers for various optoelectronic applications. So we can also look for transparent conducting oxides or TCOs. These are basically oxide semiconductors like zinc oxide, cadmium oxide, indium oxide they can be heavily doped to create transparent conducting oxides and TCOs are known for their large band gap and they are transparent in the visible range and they typically serve as electrical contacts in display panels.

## Semiconductors to Metals: Transparent Conducting Oxides

- TCO nanoparticles and nanostructures exhibit Localized Surface Plasmon Resonance (LSPR) behavior, with tunability based on doping levels.
- A thin film of ITO deposited on a prism was able to support SPPs when infrared light was incident in the Kretschmann geometry (schematic shown in Figure a).
- Figure b–d shows the reflectivity measurements from prism coupling measurements.
- TCOs can be incorporated into metamaterial designs, offering low-loss alternatives for negative refraction, and they can be used in tunable plasmonic devices like modulators and switches in the NIR wavelength range.

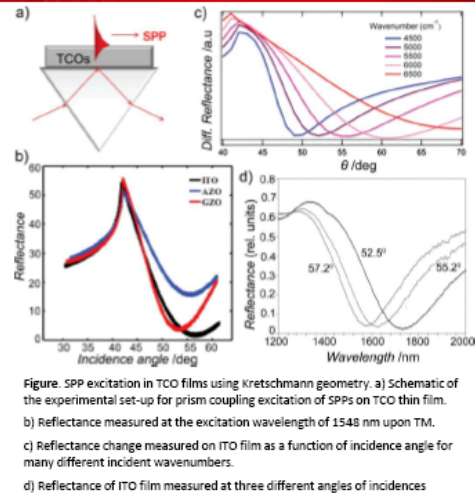


Figure. SPP excitation in TCO films using Kretschmann geometry. a) Schematic of the experimental set-up for prism coupling excitation of SPPs on TCO thin film. b) Reflectance measured at the excitation wavelength of 1548 nm upon TM. c) Reflectance change measured on ITO film as a function of incidence angle for many different incident wavenumbers. d) Reflectance of ITO film measured at three different angles of incidences

Even every smart phone has got TCOs. TCOs can exhibit metal like optical properties in the near infrared regime due to high DC conductivity as can be shown in the figure. So here the real part and here the imaginary part of the TCO films are shown. So this one is aluminum doped zinc oxide, this is gallium doped zinc oxide and this is ITO indium doped tin oxide. The optical properties of the TCOs can be tuned by adjusting the carrier concentration of the doping levels. Now TCO nanoparticles or nanostructures they can exhibit localized surface placement and resonance behavior which you can tune based on the doping levels.

So you can also deposit a thin film of TCOs on a glass prism and this can support SPP waves at the TCO air interface when infrared light is incident from the prism side in the Kretschmann geometry. Figure b to d actually shows the reflectivity measurement from the prism coupling. So here you can see that and what is important here is that the TCOs can be incorporated into metamaterial design because they are low loss alternatives for negative diffraction and they can be used in tunable plasmonic devices like modulators, switches in near infrared range. So the other method is metals to dilute metals. So, this is an alternative approach to reduce the optical losses in metal by exploring dilute metals

or metallic compounds with lower carrier concentration.

## Metals to Dilute Metals

- An alternative approach to reduce optical losses in metals is to explore "dilute metals" or metallic compounds with lower carrier concentrations.
- Introducing non-metallic elements into a metal lattice can effectively reduce the carrier concentration but may result in altered electronic band structures and potential drawbacks like increased interband absorption losses.
- Research on dilute metals has been limited, but these materials offer advantages such as tunability, ease of fabrication, and integration that can outweigh the disadvantages.
- Various classes of less-metallic materials, including metal silicides, germanides, ceramics (oxides, carbides, borides, and nitrides), and intermetallics, have been studied for their optical properties, with many exhibiting negative real permittivities in different optical spectra regions.
- Specific focus is given to materials like silicides, germanides, and metal nitrides that have relevance in silicon CMOS technology.



So introducing non-metallic elements into a metal lattice can effectively reduce the carrier concentration but may also result in altered electronic band structures and there are potential drawbacks like increased interband absorption losses. So, the research on dilute metals has been limited but these materials can also offer advantages such as tunability, ease of fabrication and integration that can outweigh the disadvantages that we mentioned here.

So various classes of less metallic materials such as metals, silicates, germanides, ceramics like oxides, carbides, borides, nitrides and intermetallic they have also been studied for their optical properties and many of them has exhibited negative real permittivities in different optical spectral regime. So specific focus is actually given to materials like silicates, germanides and metal nitrides because they have relevance also in silicon CMOS technology.

So let us look further into silicates and germanides. Germanates and germanides these are compounds of metals with silicon and germanium. They can exhibit metallic properties across the mid infrared and near infrared ranges. So that is pretty wide range. These materials possess high DC conductivities due to large free carrier densities but their optical losses are significant due to the inter band transitions and high carrier relaxation rates. Despite these losses silicates and germanides that can offer advantages for technological applications as they are commonly used in silicon CMOS integrated ICs and they can grow epitaxially on silicon substrates.

## Metals to Dilute Metals: Silicides and Germanides

- Silicides and germanides, compounds of metals with silicon and germanium, exhibit metallic optical properties across the MIR (mid-infrared) and NIR (near-infrared) ranges.
- These materials possess high DC conductivities due to large free carrier densities, but their optical losses are significant due to interband transitions and high carrier relaxation rates.
- Despite their losses, silicides and germanides offer advantages for technological applications as they are commonly used in silicon CMOS integrated circuits and can grow epitaxially on silicon substrates.
- Various deposition techniques, including co-deposition, chemical vapor deposition, and physical vapor deposition, are employed to fabricate silicides and germanides.
- Etching techniques, both wet and dry, can be used for patterning, and lift-off processes with hard masks like silicon oxide or nitride are common in their fabrication.
- While silicides exhibit metallic behavior in the MIR, NIR, and visible ranges, their high losses limit their applicability in shorter wavelengths. However, they hold promise for infrared plasmonics applications.



So that way fabrication wise it is much easier. Various deposition techniques such as co-deposition, chemical vapour deposition, physical vapour deposition we will be looking into these techniques in the next lectures ok. They can be applied for fabrication of silicides and germanides. Etching techniques both wet and dry can be used for patterning and lift off processes with hard masks like silicon oxide or nitride are common in their fabrication. So do not worry we will cover briefly all these different methods of nanofabrication in the next two lectures. While silicides exhibit metallic behaviour in mid infrared and NIR range and also visible ranges their high loss limit their applicability in shorter wavelength ok.

## Metals to Dilute Metals: Interstitial Metal Nitrides

- Metal nitrides such as titanium nitride (TiN), zirconium nitride (ZrN), tantalum nitride (TaN), and hafnium nitride (HfN) exhibit metallic properties in the visible and longer wavelengths (figure 1) and
  - are non-stoichiometric, interstitial compounds with large free-carrier concentrations.
- Figure 2 shows the optical image of thin films of metal nitrides deposited on glass substrates.
- The films were deposited by DC reactive sputtering.
- The thickness of films is in the range of 100 to 120 nm.
- The metallic luster indicates the possibility of plasmonic behavior in the visible spectrum.
- The color of the films correlates with the plasma frequency or carrier concentration in these films.

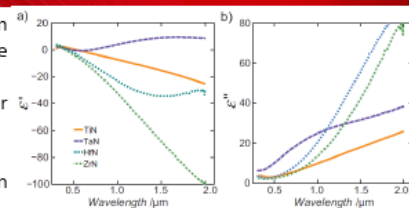


Figure 1. The real (a) and imaginary (b) parts of dielectric functions of metal nitride plasmonic materials

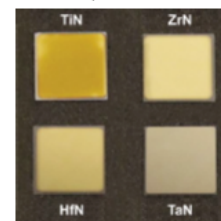


Figure 2. Optical image of thin films of metal nitrides deposited on glass substrates



Source: Naik, Gururaj V., Vladimir M. Shalaev, and Alexandra Boltasseva. "Alternative plasmonic materials: beyond gold and silver." *Advanced Materials* 25.24 (2013): 3264-3294.

However for infrared plasmonics they have good potential. So next will be the metal

nitrides. So you can think of different metal nitrides like titanium nitride, zirconium nitride, tantalum nitride ok, hafnium nitride. They also exhibit metallic properties in the visible and long visible and longer wavelengths you can see here yeah they are metallic in the visible and longer wavelengths. So that is good and this kind of nitrides are non-stoichiometric they are interstitial compounds with large free carrier concentrations. Here you can see the different optical images of the thin films of metal nitrides which are deposited on glass substrate and this films are basically deposited by DC reactive sputtering. The thickness of the films is in the range of 100 to 120 nanometre and you can see metallic luster ok from the films and that is showing the possibility of the plasmonic behaviour from this films in the visible spectrum.

## 2D Plasmonic Materials

- Plasmonics with 2D materials, often referred to as flatland plasmonics, has gained substantial attention, particularly following the demonstration of plasmons in graphene.
- Two-dimensional materials like graphene offer advantages over bulk 3D materials in both scientific research and technological applications.
- The optical properties of 2D materials differ significantly from those of 3D materials, leading to distinct plasmon dispersion relationships.
- 2D materials are valuable in various applications, including electronics, and offer the advantage of dynamic tuning of their properties through methods like electrical, chemical, and electrochemical means.
- However, challenges in synthesizing large-area single-crystalline 2D materials are being actively addressed.
- 2D electron gas (2DEG) systems have been observed in various materials, including semiconductor inversion layers, semiconductor heterostructures, polar interfaces of oxides, and 2D sheet materials like graphene, chalcogenides, perovskites, and oxide nanosheets.

The colour of the films correlate with the plasma frequency or the carrier concentration in this films. Now with that we understood the different methods of creating alternative materials that can be beneficial for plasmonic applications in different frequency range. We can also look for different 2D plasmonic materials ok. So, this is the process with 2D materials which is also referred to as flat land plasmonics and it has gained a substantial attention after demonstration of plasmonics in graphene. Two dimensional materials like graphene over they offer advantages over the bulk 3D materials and that is why lot of scientific research and applications have been demonstrated using graphins and the 2D material properties the optical properties they significantly differ from the 3D materials and that leads to distinct plasmon dispersion relations.

## 2D Plasmonic Materials

- Plasmons have been experimentally observed in 2DEG systems such as semiconductor inversion layers, semiconductor heterostructures, and graphene.
- However, in most cases, these observations were limited to low-temperature conditions due to high losses (low carrier mobility or high carrier scattering rates) at room temperature.
- Plasmons in 2DEG systems were primarily observed in the mid-infrared (MIR) or longer wavelength ranges.
- Plasmons in the visible or near-infrared (NIR) ranges are not observed in these 2D materials due to insufficient carrier densities.
- The behavior of plasmons in 2DEG systems can be understood through the dispersion relation described in equation:

$$\frac{n_s e^2}{\epsilon_0 \epsilon_s m^*} q_p = \omega^2 \left( 1 + \frac{i\gamma}{\omega} \right) \longrightarrow \text{Eqn (A)}$$

Here  $n_s$  is the surface charge density,  $\epsilon_s$  is the permittivity of the surrounding medium,  $m^*$  is the carrier effective mass,  $\gamma$  is the carrier relaxation rate, and  $q_p$  is the plasmon wavevector.



Now this 2D materials are valuable in different applications including electronics and they offer advantage of dynamic tuning of their properties through methods like electrical, chemical or electrochemical means. So, that is something which is really groundbreaking if you can dynamically tune the properties of a device after fabrication that makes it very very cool thing else you have to make a new device for all different applications, but if you are able to tune say the voltage and change the spectral response of a particular device that has got a graphene. So, that will be very useful one right. So, however all this not good here as well because there are challenges in synthesizing large area single crystalline 2D materials right. So, 2D electron gas system these are 2D electron gas systems and they are also observed in other materials not only in graphene.

So, you can think of semiconductor inversion layers, semiconductor heterostructures, polar interfaces of oxides and other 2D sheet materials like graphene, chalcogenides, perovskites and oxide nanosheets. Now, plasmons have been experimentally observed in this 2D electron gas systems such as semiconductor inversion layer, semiconductor heterostructure and graphene. However, in most cases these observations are limited to low temperature conditions due to high losses and here the high loss is because of the low carrier mobility or high carrier scattering rate at room temperature. If you think of plasmons in 2D electron gas systems they are primarily observed in mid infrared or longer wavelength range. So, plasmons in visible and NIR are not observed using this 2D plasmonic materials due to insufficient carrier densities.

## 2D Plasmonic Materials

- In the case of graphene, the carriers behave as if massless, and hence the dispersion relation is different.
- Equation (B) describes the plasmon dispersion relation in graphene at low temperatures:

$$\frac{e^2 E_F}{\pi \hbar^2 \epsilon_0 \epsilon_s} q_p = \omega^2 \left( 1 + \frac{i\gamma}{\omega} \right) \longrightarrow \text{Eqn (B)}$$

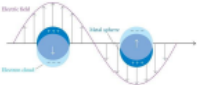
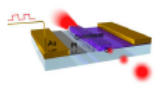
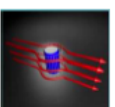
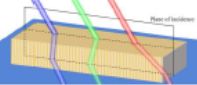
$E_F$  is the Fermi energy of single-sheet graphene

- Equations A, B allow us to quantitatively examine the characteristics of plasmons in 2D plasmonic materials.
- Plasmons can theoretically exist in 2DEGs at all wavelengths, but practical limitations may prevent their excitation or observation when the plasmon wavelength becomes too short.



So, the behavior of plasmons in 2D electron gas can be understood through the dispersion relation which are mentioned here ok. So, here you can see  $n_s$  is the surface charge density,  $\epsilon_s$  is the permittivity of the surrounding medium,  $m^*$  is the carrier effective mass,  $\gamma$  is the carrier relaxation rate that you see here and  $q_p$  is the plasmon wave vector. So, in case of graphene the carriers behave as if they are massless and hence the dispersion relation is different ok. So, this is the this plasmon dispersion relation in graphene at low temperature.

## Comparative Study

	2000	2005	2010	2013
	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Alkali</b> IR   NIR   VIS   UV	<b>ITO, AZO, GZO</b> IR   NIR   VIS   UV
	<b>Si</b> IR   NIR   VIS   UV	<b>Ge, III-V</b> IR   NIR   VIS   UV	<b>Graphene</b> IR   NIR   VIS   UV	<b>ITO, AZO, GZO</b> IR   NIR   VIS   UV
	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Nitrides, ITO, AZO, GZO</b> IR   NIR   VIS   UV	<b>Silicides, Germanides</b> IR   NIR   VIS   UV
	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Au, Ag</b> IR   NIR   VIS   UV	<b>Alkali</b> IR   NIR   VIS   UV	<b>Alkali</b> IR   NIR   VIS   UV



So, here  $E_f$  stands for the Fermi energy of single sheet graphene. So, if you take equation A that was shown here A and B this one ok this to allow us to quantitatively examine the characteristics of plasmon in 2D plasmonic materials. So, plasmon can

theoretically exist in 2D electron gas at all wavelengths, but practical limitations may prevent their excitation and observation when the plasmonic wavelength becomes too short. So, let us do a comparative study. So, you can see that LSPR localized surface plus 1 resonance was seen initially only for gold and silver in the visible spectral range and by 2010 alkali metals also showed this properties in visible and UV and now with ITO, AZO and GZO included in the list they can also show localized surface plasmon resonance this kind of nanostructures can show this in UV visible and NIR. So, new materials are allowing people to explore the same plasmonic properties at different wavelength range which was not explored before using conventional plasmonic materials.

## Summary

	LSPR	SPPs & Waveguides	NIMs	TO	ENZ	Switchable MMs
Noble Metals	✓	✓	✓	×	×	×
Metal Nitrides	×	✓	×	✓	×	×
TCOs	✓	×	×	✓	✓	✓
Noble Alkali Alloys	×	×	×	✓	✓	×
Alkali Metals	✓	✓	✓	×	×	×
Other Metals	×	×	×	×	×	×
Graphene <sup>2)</sup>	✓	✓	×	✓	×	✓
Conventional semiconductors <sup>3)</sup>	✓	×	×	✓	✓	✓

**Table.** Summary of comparative study of various alternative plasmonic materials for different metamaterial and plasmonic applications in the visible and NIR ranges. ✓ represents suitable; × represents not suitable.

<sup>2)</sup> Current considerations are only in the mid-IR.

Similarly, if you think of tunable materials silicon gave tunability in NIR and visible germanium and 3,5 semiconductor also in the same range with graphene you can explore infrared ok and with ITO, SZO and GZO also you can explore tunability in this range ok. For transformation optics gold and silver if you use you can only cater to the visible range, but with nitrides ITO, AZO, GZO you can look after the NIR range and with silicates and germanides you can also look for visible NIR and MIR mid-IR range. For negative index metamaterials materials you can see gold and silver again only invisible with alkali you can get it in the UV ok and that is how different materials gave you options to explore the similar kind of feature or phenomena in different wavelength range. So, here is a summary of the things we have discussed today. So, noble metal you can use for LSPR, SPP and waveguides, negative index metamaterial, but they are not good for transformation optics and  $\epsilon$  near zero effect and they are not allowing you to have switchable metamaterials.

## Summary

- Plasmonic materials play a crucial role in nanophotonics and metamaterials, enabling the manipulation of light at the nanoscale.
- Noble metals like gold and silver have been traditionally used in plasmonic applications due to their strong and tunable plasmonic resonances in the visible and near-infrared (NIR) spectral ranges.
- However, noble metals suffer from high optical losses, limiting their applicability in certain devices and at shorter wavelengths.
- Alternative plasmonic materials, including transition metal nitrides, transparent conducting oxides (TCOs), and 2D materials like graphene, have gained attention for overcoming the limitations of noble metals.
- Transition metal nitrides, such as titanium nitride (TiN), zirconium nitride (ZrN), and tantalum nitride (TaN), exhibit metallic properties in the visible and longer wavelengths.



Whereas metal nitrides they can be good for SPP and waveguides and transformation optics, TCOs are good for LSPR and transformation optics ENZ and switchable, but they are not good for negative index and SPP waveguiding ok and so on. So, you can actually go into this list and find out that which metal material is good for which particular application and then in what particular frequency range or wavelength range. So, let us conclude what we have discussed in this particular lecture. So, plasmonic materials play a crucial role in nanophotonics and metamaterials because they enable manipulation of lighted nanoscale and we have seen that noble metals like gold and silver are traditionally used in plasmonic applications due to their strong and tunable plasmonic resonance in the visible and near infrared range. However, these metals they suffer from high optical losses that limits their applicability in certain devices at shorter wavelengths.

So, researchers have been looking for alternative plasmonic materials such as transition metal nitride, transfer and conducting oxide, 2D materials like graphene all these things are gaining more attention to overcome the limitation of the noble metals. Transition metal nitrides like titanium nitrides, zirconium nitride they also exhibit metallic property in visible and longer wavelength. TCOs like ITO, AZO they provide low optical losses and they are good for transfer and plasmonic applications ok. Graphene a 2D material also allows dynamic tunability of the plasmonic properties via electric field effect methods. So, you can bias the graphene sheet and change its chemical potential and that can give you a different optical property and that is very cool.



## Summary

- TCOs, like indium tin oxide (ITO) and aluminum-doped zinc oxide (AZO), provide low optical losses and are useful in transparent plasmonic applications.
- Graphene, a 2D material, allows for dynamic tuning of its plasmonic properties via electrical field-effect methods.
- Plasmons in alternative materials can be harnessed for various applications, including sensors, waveguides, superlenses, and negative index metamaterials.
- Resonant and non-resonant plasmonic applications differ in their reliance on localized plasmon resonance and material properties, with noble metals excelling in resonant devices.
- While there is no single ideal material for all plasmonic and metamaterial applications, alternative plasmonic materials are better suited for specific applications and wavelength ranges, offering promising alternatives to noble metals.



Plasmas in alternative materials can be harnessed for different applications such as sensors, waveguide, super lenses and negative index materials. Resonant and non resonant plasmonic applications will differ in their reliance on the plasmon localized surface plasmon resonance and the material properties while noble metals excelling in resonant devices. So, while there is no single ideal material for all plasmonic and metamaterial application that you have seen there is no one superhero kind of material, but you can look keep looking for alternative plasmonic materials for a particular application and a wavelength range and they can actually offer you promising alternative to the noble metals like gold and silver. So, with that we will conclude today and in the next lecture we will look into the nanofabrication techniques. So, if you have got any query on this lecture drop an email to me mentioning MOOC on the subject line. Thank you.