Project Notes

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Abstract

Abstract.. abstract.

1 PLASMONS

Notes from Justin White http://large.stanford.edu/courses/2007/ap272/white1/

Surface Plasmon Polaritons

- Surface Plasmon polaritons are collective longitudinal oscillations of electrons near a material surface, strongly coupled to an electromagnetic wave.

- Both bulk and surface plasmons have associated EM-waves, and can consequently be described by Maxwell's equations.

- the coherent oscillations of electron motion can be encapsulated in the dielectric constant of the material.

- The basic form of the bulk and surface plasmon solutions are shown below:

$$E_{bulk} = E_0 e^{k_x x - \omega t} \tag{1.1}$$

$$E_{spp} = E_0 e^{-\kappa|z|} e^{k_x x - \omega t} \tag{1.2}$$

  The bulk plasmons are associated with purely transverse EM waves ($E \perp k$ and $B \perp k$) and can only exist for $\omega < \omega_p$. For $\omega > \omega_p$: the wave-vector for bulk plasmons becomes imaginary, giving an exponentially decaying wave, instead of a propagating wave. It is for this reason that most metals are highly reflective for visible light ($\omega < \omega_p$), but transparent for ultraviolet light ($\omega > \omega_p$)

- Surface plasmons have an associated EM wave with both transverse and longitudinal field components. Such waves can only be excited at the interface between a conductor and dielectric, and aretightly bound to the surface. The field reach their maximum at the interface ($z = 0$), and exponentially decay away from the surface.

- The wave-vector of the surface plasmon mode k_{spp} always lies to the right of the free space wave-vector k_0 (in the dispersion diagram/relation), such that $\lambda_{spp} < \lambda_0$. this makes it impossible to directly launch a surface plasmon wave by illumination with free-space radiation, because the free-space photons simply do not have enough momentum to excite the surface plasmon.

  As ω increases, k_{spp} gets larger and larger, moving further away from k_0 (textit??making it harder and harder for light to excite the surface plasmons??)d. As k_{spp} increases, the surface plasmon wave is more tightly bound to the surface. This process has an upper limit of ω_{sp}, the surface plasmon resonant frequency, which occurs when the dielectric constant of the metal and the dielectric have the same magnitude but opposite signs.

- **Excitation of Surface Plasmons**
  High energy electrons that bombard a thin metalic film can launch surface plasmons and a surface plasmons of a whole range of wavelengths can be excited. However, only plasmons far along the dispersion curve, where k_{spp} is largest are generally excited.

  As mentioned previously, direct excitation of surface plasmons by free-space photons is not achievable because k_{spp} is always greater than k_0; this can be seen from the dispersion relation, where the surface plasmon dispersion relation always lies to the right of the free space dispersion curve.

  This can be overcome by back-side illumination through a material with a higher index of refraction n, where the far field radiation has a larger wave-vector ($k = nk_0$) (like done in a Kretschmann-Raether coupler) [5]. A surface plasmon will be efficiently excited when

$$k_{\parallel} = nk_0 \sin\theta = k_{spp} \tag{1.3}$$

  A mor egeneral approach to launch surface plasmons with light is the use of structured surfaces that are able to impart momentum on the photon, enabling it to couple to the surface plasmon mode. Anything from a single sub-wavelength disk or slit, to rectangular or sinusoidal diffraction gratings are used for this type of coupling. **A thorough overview of surface plasmon coupling and patterned and rough surfaces is given by Raether[6]**

- Appendix: Derivation of Bulk and Surface Plasmons (see article).

Other Nice sources:

- Really nice article on Plasmons:
  http://nanocomposix.com/pages/plasmonics

- Article:
  http://cdn.intechopen.com/pdfs-wm/44351.pdf

- Surface Plasmon Theory(book?):
  https://www.physik.hu-berlin.de/de/nano/lehre/Gastvorlesung

- Chemistry-blog:
  http://www.chemistry-blog.com/2007/03/19/plasmonics-part-ii/

- Mie theory:
  http://www.orc.soton.ac.uk/publications/theses/1460T_lnn/1460T_lnn_03.pdf

From Wikipedia

- **What are Plasmons?**
  A plasmon is a quantum of plasma oscillation (quasiparticle from the quantization of plasma oscillations). Plasmons are collective (a discrete number) oscillations of the free elctron gas density. Plasmons can also couple with a photon to create another quasiparticle called a plasma polariton (electromagnetic wave - electric/magnetic dipole-carrying exitation - coupling.

  Plasmons can be described as oscillations of free elctron density with respect to fixed positive ions in a metal. Imagine a cube of metal placed in an external electric field pointing to the right. Electrons will move the the left side and uncover positive ions on the right side. The electrons will continue moving left until they cancel the field inside the metal. Removing the field will make the electrons move back by their mutual repulsion and attraction to the ions, leaving the electrons to oscillate back and forth, at the **plasma frequency**, in a so called plasma oscillation.

- **Plasma Oscillation, aka "Langmuir waves"**
  Rapid oscillations of electron density in conducting media such as plasmas or metals. The oscillations can be described as an instability in the dielectric function of a free electron gas. The frequency depends weakly on the wavelength of the oscillation.

  'Cold' electrons (plasma oscillations)
  If the thermal motion of the electrons is ignored and assuming infinite ion mass, the charge density oscillates at the plasma frequency

$$\omega_{pe} = \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}}, \text{[rad/s] (SI-units)} \tag{1.4}$$

$$\omega_{pe} = \sqrt{\frac{4\pi n_e e^2}{m^*}}, \text{(cgs-units)}, \tag{1.5}$$

where n_e is the number density of electrons, e is the electric charge, m^* is the effective mass of the electron and ε_0 is the permittivity of free space. Since the frequency is independent of the wavelength, these oscillations have an infinite phase velocity and zero group velocity. Note in addition that, if m^* is the electron mass m_e, the plasma frequency ω_{pe} depends only on the physical constants and concentration of electrons n_e. The numeric expression is:

$$f_{pe} = \frac{\omega_{pe}}{2\pi} \approx 8980\sqrt{n_e}, \text{[Hz]} \tag{1.6}$$

with n_e in [cm^{-3}]

'Warm' electrons (plasma oscillations)
When the effects of the electron thermal speed $v_{e,th} = \sqrt{\frac{k_B T_e}{m_e}}$ are taken into account, the electron pressure acts as an additional restoring force and the oscillations propagate with frequency and wavenumber related by the longitudinal Langmuir wave:

$$\omega^2 = \omega_{pe}^2 + \frac{3 k_B T_e}{m_e} k^2 = \omega_{pe}^2 + 3 k^2 v_{e,th}^2 \tag{1.7}$$

called the 'Bohm-Gross dispersion relation'. If the spatial scale is large compared to the Debye length (measure of a charge carrier's net electrostatic effect in solution, and how far those electrostatic effects persist), the oscillations are only weakly modified by the pressure term, but at small scales the pressure term dominates and the waves become dispersionless with a speed of $\sqrt{3}v_{e,th}$. For such waves, however, the electron thermal speed is comparable to the phase velocity, i.e.

$$v \sim v_{p,th} \equiv \frac{\omega}{k}, \tag{1.8}$$

so the plasma waves can accelerate electrons that are moving with speed nearly equal to the phase velocity of the wave. This process often leads to a form of collisionless damping called Landau damping. Consequently, the large-k portion in the dispersion relation is difficult to observe and seldom of consequence.

In metal of semiconductor, the effect of the ions periodic potential must be taken into account. This is usually done by using the electrons effective mass in place of m.

- **Role of Plasmons**
  Plasmons play a large role in the optical properties of metals. Light of frequencies below the plasma frequency is reflected, because the electrons in the metal screen the electric field of the light. Light of frequencies above the plasma frequency is transmitted, because the electrons cannot respond fast eneough to screen it. In mot metals, the plasma frequency is in the unltraviolet, making them shiny (reflective) in the visible range. In semiconductors, the valence electron plasma frquency is usually in the deep ultraviolet, which is why they are reflective.
  The plasmon energy can often be estimated in the free electron model as

$$E = \hbar \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}} = \hbar \omega_p \tag{1.9}$$

- **Surface Plasmons (SPs)**
  Surface plasmons (plasmons at the interface of two materials) interact strongly with light, resulting in a polariton (usually occurs at metal or doped dielectric interface, which both have small $\text{Im}(\varepsilon) > 0$ and big $\text{Re}(\varepsilon) < 0$). These surface electron oscillations can exist at the interface between any two materials where the real part of the dielectric function changes sign across the interface (e.g. a metal-dielectric interface like metal sheet in air).
  SPs have lower energy than **bulk (or volume)** plasmons, which quantise the longitudinal electron oscillations about positive ion cores within the bulk of an electron gas (or plasma).

  The charge motion in a surface plasmon always create electromagnetic fields outside (as well as inside) the metal. The total excitation, including both the charge motion and associated electromagnetic field, is called either a **surface plasmon polariton** at a planar interface, or a **localized surface plasmon** for the closed surface of a small particle.

  Surface Plasmon polaritons can be excited by electrons or photons. In the case of photons, it cannot be done directly, but requires a prism, or a grating, or a defect on the metal surface. *??? Or like trunctated spheres on granular films???.*

  At low frequency an SPP approaches the dispersionrelation in free space $\omega = ck$. At high frequency, the dispersion relation reaches an asymptotic limit called the "sufrace plasma frequency".

  As an SPP propagates along the surface, it loses energy to the metal due to absorption and due to scattering into free-space or into other directions. The electric field falls off evanescently perpendicular to the metal surface. At low frequencies, the SPP penetration depth into the metal is commonly approximated using the 'skin depth formula'. In the dielectric, the field will fall off far more slowly. SPPs are very sensitive to slight perturbations within the skin depth and because of this, SPPs, are often sed to probe inhomogeneities of a surface

  Surface plasmons have been used to control colors of materials and is possible since controlling the particle's shape and size determines the types of surface plasmons that can couple to it and propagate across it. This in turn controls the interaction of light with the surface. These effects are illustrated by the historic *stained glass* wich adorn medieval cathedrals. In this case, the color is given by metal nanoparticles of a fixed size which interact with the optical field to give the glass its vibrant color. To produce optical range surface plasmons effects involves producing surfaces wich have features < 400nm.

  Surface plasmons are very sensitive to the properties of the materials on which they propagate.

- **Surface Plasmons Resonance (SPR)**
  Surface plasmon resonance is the resonant oscillation of conduction electrons at the interface between a negative and positive permittivity meterial stimulated by incident light. The resonance condition is estalished when the frequency of incident photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei.

Surface plasmon polaritons are surface electromegnetic waves that propagate in a direction parallel to the metal/dielectric (or metal/valcuum) interface. Since the wave is on the boundary of the metal and the external medium, these oscillations are very sensitive to any change of this boundary, such as adsoption of molecules to the metal surface.

To describe the existence and properties of surface plasmon polaritons, one can choose from various models, e.g. the **Drude Model**. The simplest way to approach the problem is to treat each material as a homogeneous continuum, described by a frequency-dependent relative permittivity between the external medium and the surface (this is a complex dielectric function). In order for the terms that describe the electronic surface plasmons to exist, the real part of the dielectric constant of the metal must be negative and its magnitude must be greater than that of the dielectric. This condition is met in the infrared-visible wavelength region for air/metal and water/metal interfaces (where the real dielectric constant of a metal is negative and that of air or water is possitive).

Localized SPRs (LSPRs) are collective charge oscillations in metallic nanoparticles that are excited by light. They exhibit enhanced near-field amplitude at the resonance wavelength. This field is highly localiced at the nanoparticle and decays rapidly away from the nanoparticle/dielectric interface into the dielectric background, though far-field scattering by the particle is also enhanced by the resonance. Light intensity enhancement is a very important aspect of LSPRs and and localization means the LSPR has very high spatial resolution (subwavelength), lmited only by the size of nanoparticles. Because of the enhanced field amplitude, effects that depend on the amplitude such as magneto-optical effect are also enhanced by LSPRs.

In order to excite surface plasmoms in a resonant manner, one can use an electron or light beam (visible and infrared are typical). The incoming beam has to match its momentum to that of the plasmon.
With p-polarization this is possible by assing the light through a block of glass to increase the wavenumber (and the momentum) and achieve the resonance at a given wavelength and angle.
s-polarized light however cannot excite electronic surface plasmons.

When the surface plasmon wave interacts with a local particle or irregularity, such as a rough surface, part of the energy can be re-emmited as light. This emitted light can be detected behind the metal film from various diretions.

- **The Drude Model**
  Treats the behavior of electrons in a solid like a pinball machine. The electrons are small light balls in a sea of static, positively charged ions. The only form of action instantaneous collisions.

- **Mie Scattering**
  Mie theory is sometimes used for the collection of methods and solutions to Maxwell's equations for scattering, by e.g. using geometries where one can write separate equations for the radial and angular dependence of solutions. More broadly, "Mie scattering" suggests situations where the size of the scattering particles is comparable to the wavelength of the light, rather than much smaller or much larger.

REFERENCES

[1]

2 ARTICLE NOTES

2.1 THERMOCHROMISM

[2] **Intelligent Themochromic Windows**
The use of air-conditioning systems to maintain comfortable working and living environments has become more common [1]. This leads to an increase in hte use of electricity and a concurrent increase in carbon dioxide emissions and other atmospheric pollutants formed in the electricity generation process. A self-propagating cucle results, in which blobal warming due to increases in these greenhouse gases necessitates the increased use of air conditioning systems. Technology is thus required that can reduce the use of air conditioning commercial and residential buildings to help break this cycle.

(...) window coatings can reduce cooling costs or heating requirements [2]. Using thermochromic coatings as intelligent window coatings[1-7], which change their optical properties with temperature; usually related to a structural pase change on passing through a critical temperature T_c. Thermochromic coatings would be applicable to climates where there are extreme changes in temperature over the year, for example, central and northern Europe, Japan, the United States, and Canada, which have hot summers and cold winters.

Vanadium(IV) oxide; transition temperature $Tc = 68°C$; visually and infrared trasnparent belov $T_c \rightarrow$ solar radiation passes through, keeping the interior warm. Below T_c it becomes infrared reflective and preventing excessive heating, while remaining visually transparent.

Critical temperature for vanadium is too high, but this can be lowered to 25°C uing dopants ([9]), most efficiently with tungsten(loading of only 2 atom percent required), in thin films prepared by physical vapor deposition methods [10] and sol-gel spin or dip coating [11].

problem: low luminous transmittance of the glazing VO_2 film [10-13]. (could be solved with doping[4] or anti-reflective coating ([12])). Also one needs a method where the thin films of the material can be applied cheaply and efficiently to the glass ([17]).

(p.394) Discussion of MST(metal-to-semiconductor transition) of VO_2 and structure changes through the MST. Discussion involves structure figures.

Goodenough proposes antiferroelectric transition being the drivings force for the MST in VO_2. $\rightarrow$ two transition temperatures: one due to antiferroelectric distortion and one due to the crystallographic distortion.

The next paragraph explains how doping of various elements varies the MST temperature. The most effective dopant in reducing the temperature is Tungsten (additional info about tungsten and after that it considers other dopants).

Thinner thickness, stress and strain can also reduce the thermchromic transition temperature.

A little bit on VO_2 thin film durability?
Methods of preparing Pure and doped Vanadium(IV) Oxide Films:
Sol-Gel Method: forming thin films by dip- or spin-coating substrates with solutions of metal alkoxides.
PVD Method: energetically removing atoms/molecules under reduced pressure conditions, then to react with seed gas.
CVD method: chemical vapor deposition, in particular atmospheric pressure CVD (APCVD).
APCVD: deposit tin solid films from gaseous precursors onto a suitable substrate. (+Pictorial representation) (and more on APCVD).

Comparison of the above methods.

3 atom percent tungsten(VI) $\rightarrow$ transition temperature reduced to 5°C.
1.9 percent $\rightarrow$ 29°C.
transition temperature decreases linearly with tungsten atom percent incorporation(Figure).

Summary: intelligent TC glass with desired switch temperature($25 - 30^{circ}$C, obtainable using APCVD. Mst of the problems regarding commercial use are solvable. Market in household, offices, factories and space exploration.

[3] **Thermochromism in Commercial Products**

- Thermochromic liquid crystals: Periodicity between layers, PITCH, and constructive interference!. TC liquid crystals can have a versatile range of colors and useful color changes bewteen -30 and 120°C, often with very high temperature sensitivity. TC liquid crystals are only useful when they are in the liquid crystalline phase, which is a meso-phase (an intermediate phase of matter) between an isotropic liquid (high temperature) and crystalline solid (low temperature), which restricts the temperature range of theur applicability.

- **Microencapsulation**: Defined as the coating of small solid particles, liquid droplets, or gas bubbles with a thin film or coating or shell material, and typical particle sizes are 1 to 1000 μm ([20] Kirk-Othmer Encycloped. of chem. Tech. 4thEd). For three component organic mixtures, particle sizes are < 50 μm. **Micro encapsulation allows the additional advantage of combinations of several narrow color ranges**, and very sharp color changes, as well as protection of the coloring agent from the environment ([16] Nakasuji med flere. Chem.Abs.). **complex coacervation** and **interfacial polymerization** → processes to microencapsulate thermochromic materials! Also described! Nice to include if I use thin layer on my granular film!

- Smart window candidates: Fe_3O_4, $FeSi_4$, NbO_2, NiS, Ti_2O_3 and VO_2, which owe their temperature change to a semiconductor-to-metallic state transition (aka **Mott transition temperature**)

[4] **A Qualitative Description of Thermochromism in Color Measurements**

- Wyszecki and Stiles stated ([2] color science), for TC transmitting filters, that the spectral transmittance curve at a given wavelength with a large positive slope usually dereases with increasing temperature. As a rule: steeper(positive) slope → greater temperature effect!
The curve with negative slope is of minor importance, but often causes transmittance increase for increasing temperature (if it is important).

  Neutral samples (gray, white, black) did not exhibit TC, because their spectral reflectance curves have a small or no slope.

- Assuming nonfluorescent, linear material which is "nice" with respect to polarization effects, then

$$1 = R_\lambda + A_\lambda + T_\lambda$$

where, R_λ is the reflectance, A_λ is the absorbance and T_λ is the transmittance of the sample.
Considering **transmitting samples**, the intensity I_λ transmitted through a sample of thickness d is given by

$$I_\lambda = I_{0\lambda} e^{-\mu_\lambda d}$$

where μ_λ is the absorption coefficient of the sample at wavelength λ. The optical density D is then given by:

$$D = -\log(T_\lambda) = -\log(\frac{I_\lambda}{I_{0\lambda}}) = \mu_\lambda d \log e = \frac{\mu_\lambda}{\ln 10}$$

For **opaque samples** there is no transmittance, but the optical density can be calculated from the reflected intensity $I_{R\lambda}$:

$$D_\lambda = -\log(\frac{I_{R\lambda}}{I_{0\lambda}}).$$

The light reflected from the material is also exponentially attenuated, for opaque materials. Thus, $D = \frac{\mu_\lambda}{\ln 10}$ holds for reflected light if d is the distance the reflected light has passed in the material.

[?] A Qualitative Description of Thermochromism in Color Measurements

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[?] Performance, materials and coating technologies of thermochromic thin films on smart windows

- A significant amount of energy is consumed to maintain thermal comfort in buildings, a huge portion which is lost through windows. smart windows obtained by thin films is the solution. The touchstone of performance is the change in visible and infra-red transmission and reflectance!

- A significant amount of the energy consumption in buildings are mainly due to HVAC (heating, ventilation and air conditioning) devices, used to obtain thermal comfort, The building energy consumption in developed contries accounts for 20-40% of the total energy use. (including further details of US and China energy consumption). The building energy consumption is even more dominant in hot and humid regions, using one-third to half of the elextricity produced in some contries. Energy related carbon dioxide emmision. Motivates energy saving measures to reduce building energy losses and CO_2 emissions.

- Two approaches to increase energy efficieny (7-10)
  - Active stratergies: improving HVAC systems and building lighting.
  - Passive stratergies: improving the thermal properties of the building envelope (elementss separating the indoor from outdoor), i.e. thermal insulation to wall, cool coatings on roofs and coated window glazings.

- Windows are known as one of the most energy inefficient components of buildings.(11)
  Improving the thermal performance of windows will result in reduced electricity costs and less greenhouse gas emmissions.
  In addition to controlling transmitted IR radiation an ideal window should be capable of sufficient transmission of visible light(12).
  Improving glazing characteristics of windows such as thermal transmittance and solar parameters is the most important criterion to be considered in building winows standards (14).

- International and local standards related to energy and lighting performance of windows TABLE.

- **Smart windows** defined as the type of windows that partially block the unwanted solar radiation. The energy performance can be improved by increasing heat gain in cold weather and decreasing it in hot weather by adopting windows radiative and thermal properties dynamically (25). Adding a controllable absorbig layer on teh surface of hte glass can change the optical properties of the glass by controlling the incident solar heat flux(26). Therefore, smart windows lead to reduced HVAC.energy consumption, size and elecric demand of the building (11,27,28).

- (Low emissivity (low-E) coatings are spectrally selective films that are aimed to let the visible light pass through and block the IR and UV-wavelengths which generally create heating(10). Typically, there are two types of these coatings: the tin oxide based hard coating and the silver based soft coating with higher IR reflectance and lower transmittance. The visible transmittance of hard coatings can be boosted with anti-reflecting silicon dioxide (29).)

- **The switchable reflective devices** (also called dynamic tintable windows) are categorized into **passive-** and **active systems**:
  - Passive devices: the switching process is activated automatically in accordance with the environmental conditions, e.g. temperature and heat in thermochromic windows.
  - Actice systems: Require an external triggering mechanism to perform the modulation. For instance, electricity is the actuating signal in electrochromic windows. The active switchable glazing systems offer supplementary options compared to the passive systems whereas their dependenvy on power supply and wiring should be reckoned with as a drawback.

- Chromic material, liquid crystals and suspended particle windows are the three most common active controlled intelligent windows (11). (Chromic materials = electrochromic(active), gasochromic(active), photochromic and thermochromic.

- Providing a see-through mode is a must in any application.

- (p.356) The technology using liquid crystals in intelligent windows is called Polymer. Dispersed liquid crystals (PDLC).

- Electrochromic windows and thermochromic windows demand the lowest cooling energy, where the former require less energy for lighting than the latter (69). **Figure 1 (24) (nice figure comparing TC to the other chromic glazings together with clear glass, tinted glass and reflective glass)** .

- **Thermochromic Windows**: **ALSO NOTE PAGE 357! ALOT OF NICE FIGURES!!!**
  Word originates from the Greek roots: "thermos" meaning warm or hot; and "Chroma" which means color. Generally TC materials change color in response to temperature variations.
  The TC thin film is initially in its monoclinic state(cold state) at lower temperatures (usually room temperature). Monoclinic materials behave as semiconductors, less reflective especially in the near-IR (NIR) radiation. As the temperature becomes higher than a certain point, the TC material changes its nature from monoclinic to rutile state(hot state), where the material acts like a semi-metal, reflecting a wide range of solar radiation (76). **FIGURE 3** The transition is called **metal to semiconductor transition (MST)**.

- **Figure 4**, The majority of the heat gain in solar spectrum takes place at NIR range (800-1200 nm) (78-80). The red line(line 1) indicates the transmittance of a perfect TCW in cold state. Visible light should be transmitted and NIR should be reflected. Long wave radiation is also reflected back to indoor. This transmittance approach leads to reduction of solar heat gain and is apt in nearly all climates.
  The blue line(line 2) indicates the tranmittance of a perfect TCW in its hot state. Visible and near infrared radiation are transmitted, while long-wave infrared is reflected to inside. This transmittance mode is suitable in low temperature climates where solar heat gain is desired. Therefore, in high temperatures, TCW reduce NIR and far-IR transmittance, while in low temperatures they allow these parts of solar adiation to pass (82), (Figure 5).
  The MST is fully reversible, co-occurred with large variations in electrical and optical properties in NIR range (83). The MST temperature should decrease to near the ambient temperature. Doping metal ions into the lattice of TC materials can alter the transition temp(84,85). The size and charge (84,86,87) of dopant ion, film's strain (88,89) as well as the variations in electron carrier density are the determinant factors prevailing on the fall or rise of the transition temperature (90).

- The **Ideal spectral behavior of TCW** is presented in **Table 3**. The visible transmission and reflectance should be equal on both sides of transition, while the infra-red variations are from 0% to 65%. The change in transmittance (ΔT%) and reflectance (ΔR%) can be formulated as (92):

$$\Delta T\% = (T_{hot} - T_{cold}) \cdot 100$$
$$\Delta R\% = (R_{hot} - R_{cold}) \cdot 100$$

  where hot and cold denotes transmittance/reflectance at the hot and cold state respectively.

- The most common TC material in TCWs is pure **vanadium dioxide**, with a transition temperature of 68°C which shoud be decreased to ambient temperature for practical use.
  The most critical weakness of VO_2 coatings is their low transmittance in the visible range. Many studies have reported values between 40% and 50%, which is well below the acceptable value of 60% (93, 94). **Table 4** shows the reported values of transmittance and reflectance in the visible and IR range for VO_2.

- Low energy-saving efficiency also limits the application of VO_2 coatings. The change in transmittance before and after the transmittion temperature T_t, at 2500nm, is known as the **switching efficiency η_T** and is the benchmark of energy-saving efficiency. (?why? because of lighting?). This value is inciuenced by doping(107,108), microstructure(80,95,109-111), **and film thickness (80,88)**. The most paramount factor among them is film thickness that affects the switching efficiency most significantly. However, increasing the film thickness has an adverse effect on T_{vis}. As observed from table 4, **the ideal film thickness is between 40 and 80 nm**.

- Crucial Steps to overcome the limited application of TWCs:

  - Suitable doping(reducing T_t and improving T_{vis})
  - Appropriate Coating Technology
  - Adding efficient anti-reflecting coating(to increase T_{vis}) (read next title in article)
  - Reducing coating costs

thermochromic
coating

glass

solar radiation

thermal radiation
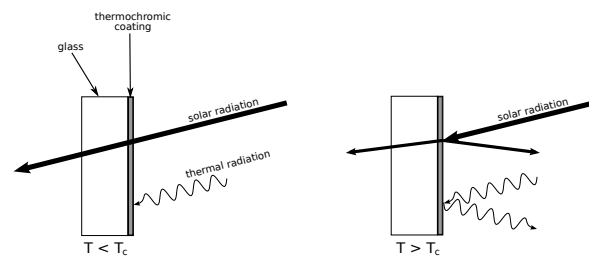
T < T$_c$

solar radiation

T > T$_c$

Figure 2.1: Schematic demonstration of the application of thermochromic materials to advanced window glazing [8]. In the article it is used as a pictorial representation of how vanadium(IV) oxide thin film will work as an intelligent window.

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[1] D. Bedeaux, J. Vlieger, *Optical Properties of Surfaces*, Imperial College Press, London, 2001

[2] Parkin IP, Manning TD. *Intelligent thermochromic windows*, Journal of Chemical Education, London 2006;83(3):393. ?I DON'T KNOW WHAT 393 is!? what is it?

[3] White MA, LeBlanc M. *Thermochromism in Commercial Products*, Journal of Chemical Education, Canada, September 1999;76(9) ?IS THIS RIGHT? IS SOMETHING WRONG? DO I MISS SOMETHING?!

[4] Hiltunen J, Silfsten P, Jaaskelainen T, Parkkinen JPS, *A Qualitative Description of Thermochromism in Color Measurements*, ???????????????, ???????????????

3   BOOK NOTES

4   HANDBOOK OF OPTIAL CONSTANTS OF SOLIDS; EDWARD D. PALIK

Institute for physical Science and Technology, University of Maryland
Academic Press 1998, 1985.

4.1   BULK AND THIN-FILM EFFECTS; EFFECTIVE-MEDIUM THEORY; P.104

- p. 105:
  In this discussion, we assume that the characteristic dimensions of the microstructure are large enough ($> / \sim 10 - 20$Å) so that the individual regions retain essentially their bulk dielectric responses, but small ($> / \sim$ 0.1-0.2 λ) compared to the wavelength of light. Then, the macroscopic E and H fields of Maxwell's equations will not vary appreciably over any single region, and quasistatic theory can be used. This avoids complications due to scattering and retardation effects that are dominant in macroscopiccally inhomogeneous systems [1].

  The dielectric functions is obtained from the macroscopic average electric field E and polarization P according to

$$D = \varepsilon E = E + 4\pi P \tag{4.1}$$

$$P = \frac{1}{V} \sum q_i \Delta x_i, \tag{4.2}$$

  where Δx_i is the displacement of the charge q_i under the action of the local field at q_i. It is the apperance of the volume normalizing factor in the latter equation that is responsible for the sensitivity of ε to density.

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REFERENCES

[1] Beckmann P. The depolarization of electromagnetic waves. Golem, Boulder, Colorado, 1968.

4.2   JENSEN B: THE QUANTUM EXTENSION OF THE DRUDE-ZENER THEORY IN POLAR SEMICONDUCTORS; P.169-188

p.169-170:
Introduction
The classical Drude model for the complex dielectric constant of a semi-conductor can be used to extract the mobility and the free-carrier density n_e from an analysis of the reflectivity and transmittance data in the far infrared (1-4)= [1, 2, 3, 4, 5]. The dielectric constant ε is the square of the complex refractive index, which determines the optical properties of a given material. One has

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = N^2, \tag{4.3}$$

were the real and imaginary parts of the complex parts of the complex dielectric constant ε_1 and ε_2 are functions of the complex refractive index N as

$$N = n - ik \tag{4.4}$$

$$\varepsilon = n^2 - k^2 \tag{4.5}$$

$$\varepsilon = 2nk = \frac{4\pi\sigma}{\omega} \tag{4.6}$$

The choice of $n - ik$ rather than $n + ik$ is determiend by the original use of $\exp i(\omega t - \boldsymbol{q} \cdot \boldsymbol{r})$ in the assumed plane-wave solution of Maxwell's equations. In Eqs (4.3)-(4.6), n is the real part of the complex refractive index, k the imaginary part or extinction coefficient, and σ the optical conductivity. The absorption coefficient α is proportional to σ, to ε_2, and to k:

$$n\alpha = \frac{4\pi\sigma}{c} = \frac{\omega}{c}\varepsilon_2 \tag{4.7}$$

$$\frac{\alpha}{2} == \frac{\omega}{c}k = \frac{1}{\delta} \tag{4.8}$$

The extinction coefficient k is essentially the ratio of the free-space wavelength of light of frequency ω to the skin depth δ.

The Drude theory gives the free-carrier contribution to ε_1 and ε_2 in terms of the plasma frequency $\bar{\omega}_p$ and the electron scattering time τ as

$$\varepsilon_1 = \varepsilon_\infty \frac{1 - \bar{\omega}_p^2}{\omega^2 \eta} \tag{4.9}$$

$$\tag{4.10}$$

$$\varepsilon_2 = \frac{\omega_p^2}{\omega^2 \eta} \frac{1}{\omega\tau} \tag{4.11}$$

where ε_∞ is the high-frequency lattice dielectric constant. The real and imaginary parts of the complex refractive index are obtained from ε_1 and ε_2. One has

$$\varepsilon = \sqrt{\varepsilon_1^2 + \varepsilon_2^2} = n^2 + k^2, \tag{4.12}$$

$$n = \sqrt{\frac{\varepsilon + \varepsilon_1}{2}}, \tag{4.13}$$

$$k = \frac{\epsilon_2}{2n} = \sqrt{\frac{\varepsilon - \varepsilon_1}{2}}. \tag{4.14}$$

Experimentally, n and k are found from measurements of the reflectivity R of a bulk, opaque sample and the transmittance T of a slab, which are given in terms of n and k as

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{4.15}$$

$$T = \frac{(1-R)^2 e^{-2\omega kd/c}}{1 - R^2 e^{-4\omega kd/c}}, \tag{4.16}$$

where d is the sample thickness. For the slab multiple-reflection effects are averaged, so that interface fringes are not resolved.

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In the far infrared, for photon energies small compared with $k_0 T$ (k_0 boltzmanns const.) and with the energy $\hbar\omega_Q$ of the phonon involved in the scatteering, the quantum result reduces to the λ^2 dependenve given by the Drude Theory, and the quasi classical Boltzmann transport equation (1-3). The departurs from the Drude theory at high frequencies are associated mainly with k rather than n, and hence, the transmission is affected more than the reflectivity. The latter depends on k in the region of the reflectivity minimum, where $n \simeq 1$, but is determined essentially by n over the region of the absorption spectrum for which $n > k$, which is the region where departures from the Drude theory would occur.

(...)

The response of electrons to a driving field may be followed from the quasi-classical limit of small ω to the quantum limit that occurs when $\hbar\omega$ is no longer small compared with characteristic energies of the system. In this case, a generalized Boltzmann equation is obtained that reduces to the quasi-classical Boltzmann transmport equation when the electron wave vector q tends to zero and ω is small (14-17)= [6, 7, 8, 9] . When ω is appreciable,

one obtaines, under certain conditions, a solution of the Boltzmann equation in terms of a frequency-dependent relaxation time. This relaxation rate, which has been tabulated as a function of frequency and carrier concentration for various materials (18-20)= [10, 11, 12] , can be used in the usual expression of the classical Drude theory to obtain the quantum result. In particular, the low- frequency $\hbar\omega \simeq k_0 T$ limit gives a good estimate for the dc mobility as a function of carrier concentration. At high frequencies, in lightly doped materials in which polar scattering dominates, $n\alpha$ is proportional to λ^3 and ε_2 and k are proportional to λ^4 rather than λ^3. The real part of the dielectric constant is given approximately by the Drude-theory expression and $n \simeq \sqrt{\varepsilon_\infty}$ for $\bar\omega_p \ll \omega \ll G/\hbar$, where $G/\hbar$ is the frequency of the fundamental absorption edge and G is the direct-band-gap energy of the semiconductor. As ω approaches $G/\hbar$ there is a small quantum-mechanical correction to ε_1 and hence to n. A summary of the results of the quantum theory is given in Section II.

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Comparison with experimental data

A calculation of ε_1 appropriate to electrons in polar semiconductors with the band structure of the Kane theory and based on the quantum density-matrix equation of motion yields a high frequency modification to Eq.(4.10) . For $\omega\tau \gg 1$ and $X < 0.1$, ($X = \hbar\omega/G$) one obtains (18,22)

$$\varepsilon_1 = \left[\frac{\varepsilon_\infty}{1-X}\right]\left[1 - (X/\varepsilon_\infty) - \bar\omega_p^2/\omega^2\right] \tag{4.17}$$

$$= \left[\frac{\varepsilon_\infty}{1-X}\right]\left[1 - \bar\omega_p^2/\omega^2\right] \tag{4.18}$$

$$= \varepsilon_\infty(1 - \bar\omega_p^2/\omega^2), \quad X \ll 1 \tag{4.19}$$

We note that $1/\varepsilon_\infty < \sim 0.1$ and hence $X/\varepsilon \ll 1$, for compounds we consider, and this term can be neglected. In the limit $X \ll 1$, the quasi-classical high-frequency Drude result is recovered, as required. For $X \sim 0.1$, there is a high-frequency correction given by Eq.(some equation), which is used to calculate the numerical values of $\varepsilon_1 = n^2 - k^2$. The major modification of the classical result is dispersion in n as one approaches the fundamental absorption edge [13].

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4.3   SHASHANKA S. MITRA

OPTICAL PROPERTIES OF NONMETALLIC SOLIDS FOR PHOTON ENERGIES BELOW THE FUNDAMENTAL BAND GAP

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Infrared Dispersion by plasmons

In the preceeding discussion of absorption of infrared radiation by phonons in a solid, it was tacitly assumed that the solid was an insulator. This assumption does not hold well for a narrow–gap semiconductor at ordinary temperatures or for a doped semiconductor with a partially filled conduction or valence band. The collective excitation of this free-carrier electron gas(plasma) in such a crystal will modify the infrared absorption by phonons, as discussed earlier. The dispersion mechanism through which electromagnetic radiation interacts with a solid should include the contribution of free-charge carriers in solids for which their numbers are significant, in addition to contributions from bound electrons and phonons. The dielectric response function of such a solid can now be written as

$$\varepsilon = 1 + 4\pi(\chi_{BE} + \chi_L + \chi_{FC}), \tag{4.20}$$

where χ_{BE}, χ_L and χ_{FC}, respectively represent the bound electron,lattice,and free-carrier contributions to the electrical susceptibility. For the spectral region of interest, we are not concerned with teh bound-electron dispersion; thus this term, as usual, will be represented by a dispersion-free, high-frequency dielectric-constant term

$$\varepsilon_\infty = 1 + 4\pi\chi_{BE}. \tag{4.21}$$

An approximate expression for the dielectric response function for a free-electron gas in a solid can be obtained from the classical Drude model in which a free electron of effective mass $m*$ and charge e is displaced by an amound $\boldsymbol{x}$ as a result of interaction with the electric field $\boldsymbol{E}$, with the equation of motion

$$m^*\ddot{\boldsymbol{x}} + m^*\gamma\dot{\boldsymbol{x}} = e\boldsymbol{E}_0 e^{-i\omega t} \tag{4.22}$$

The damping term proportional to the velocity obviously represents the electron-phonon scattering in a phenomenological manner. Solving for $\boldsymbol{x}$, one obtains

$$\boldsymbol{x} = -e\boldsymbol{E}/m^*\omega(\omega + i\gamma) \tag{4.23}$$

The polarization, defined as the electric-dipole moment per unit volume, is given by

$$\boldsymbol{P} = Ne\boldsymbol{x}, \tag{4.24}$$

where N is the carrier concentration. Recalling that

$$\boldsymbol{P} = \left[(\varepsilon - 1)/4\pi\right]\boldsymbol{E}, \tag{4.25}$$

one readily obtains

$$\varepsilon_{FC} = \varepsilon_\infty - \frac{4\pi Ne^2}{m*\omega(\omega + i\gamma)} \tag{4.26}$$

for the dielectric response function due to a single-component plasma. In terms of the plasma frequency defined as

$$\omega_p = \sqrt{\frac{4\pi Ne^2}{\varepsilon_\infty m^*}} \tag{4.27}$$

ε_{FC} becomes

$$\varepsilon_{FC} = \varepsilon_\infty\left[1 - \left(\omega_p^2/\omega(\omega + i\gamma)\right)\right]. \tag{4.28}$$

For a number of semiconductors there exists a region of the infrared spectrum in which the free-carrier contributions dominates, and both the bound electron and lattice contributions to dielectric response function are negligible. For a semiconductor, such a situation prevails in a region of the infrared spectrum in which $\omega_g \gg \omega_p \gg \omega_{TO}$,

where $\hbar\omega_g$ is the electronic band gap. The analysis of optical response is also smpler in a region in which the reflection coefficient is independent of carrier scattering. For such a situation to prevail, one usually finds $\gamma \ll \omega$ and $\varepsilon_1 \gg \varepsilon_2$. In a few semiconductors for which all these condition are met, the reflectivity spectrum in the appropriate ($\sim \omega_p$) infrared region becomes a function of carrier concentration. Here PbTe satisfies the preceding specified consditions, and its infrared reflection spectrum (117) as a function of hole carrier concentration is shown in Fig.(some figure). Since this case satisfies the preceding outlined conditions, the reflectivity minimum is a measure of the effective mass

$$m^* \simeq \frac{1}{(\varepsilon_\infty - 1)} \frac{Ne^2}{\pi c^2} \lambda^2_{min}, \tag{4.29}$$

and the real and imaginary part of ε are given by

$$\varepsilon_1 = \varepsilon_\infty - \frac{e^2}{\pi c^2}\left(\frac{N}{m^*}\right)\lambda^2 \quad \text{and} \quad \varepsilon_2 = \frac{e^2}{2\pi c^3}\left(\frac{N}{m^*}\right)\gamma\lambda^3. \tag{4.30}$$

The λ^2 dependence of ε_1 is confirmed eperimentally (117).

For most polar semiconductors, however,lattice dispersion contributes significantly. For such cases,

$$\varepsilon(\omega) = \varepsilon_\infty\left[1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}\right] + \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_0^2}{\omega_0^2 - \omega^2} \tag{4.31}$$

where the last term represents a sinle undamped oscillator representing the long-wavelength optical phonons. It may be recalled from Subsection B that $\omega_{TO} = \omega_0$ was identified with the maximum in ε, whereas ω_{LO} with its zero. Because of the first term, the second condition is now altered: ie, ω_{TO} can still be identified with the maximum in ε but not ω_{LO} with its minimum. Thus for a polar semiconductor with an appreciable carrier concentration, the resonance corresponding to the long-wavelength LO frequency will no longer correcpond to the real LO phonon frequency. In the limit of negligible damping for both electrons and phonons, the solution of Eq.(4.31) is given by

$$\omega_\pm^2 = \frac{1}{2}(\omega_{LO}^2 + \omega_p^2) \pm \frac{1}{2}\sqrt{(\omega_{LO}^2 + \omega_p^2) - 4\omega_p^2\omega_{TO}^2} \tag{4.32}$$

where ω_+ and ω_- represent new resonances above and below ω_{LO}.

The plasmon-phonon interaction obviously will be modified by the inclusion of both plasmon and phonon damping terms. (...)

(?Jeg tror LO=longitudinal oscillator og TO=tranversal oscillator?)

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