

Quick & Dirty Review of Metals and Dielectrics

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Metals

Metals are characterized as systems where the nature of the bonding between constituent atoms or molecules is by “metallic bonds”. In metallicly bonded systems, the concept of electron pair bonds is not applicable. In these systems, the coordination number, (the number of electrons surrounding a given atom) is frequently much larger than the number of valence electrons (the number of electrons available for bonding).¹ In metallicly bonded systems, the valence electrons become itinerant electrons in the conglomerate, in other words, they are not localized to a given region. In quantum parlance, one would say their wavefunction extends throughout the volume of the metallic system.²

The fact that in metals one has large concentrations of itinerant electrons has profound effects on their materials properties. Their high thermal conductivity (κ) is directly caused by these itinerant electrons, as is the high electrical conductivity (σ) and high reflectivity (R). As a matter of fact, in metals at room temperature where electron scattering is primarily elastic, the thermal conductivity (κ) and electrical conductivity (σ) are related to each other by the Wiedermann-Franz law^{3,4}:

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 T = T \cdot 2.72 \times 10^{-13} \text{ esu/K}^2$$

where T is the absolute temperature in Kelvins, k_B is Boltzmann's constant (1.38×10^{-16} erg/K), and e is the charge on the electron (4.8×10^{-10} esu). The high reflectivity (R) and high electrical conductivity (σ) are related to each other by the Hagen-Rubens law⁵:

$$R = 1 - \sqrt{\frac{2\omega}{\pi\sigma_0}}$$

where σ_0 is the dc electrical conductivity (in cgs units [σ_0]= sec⁻¹), and ω is the angular frequency of the light.

The fabrication of high quality metals by laser processing possess a number of challenges due to the intrinsic nature of metals mentioned above. The reflectivity of the metallic structure being fabricated is high, thus decoupling the laser energy. The thermal conductivity of the metallic structure being fabricated is large, thus drawing heat away from that portion of the structure the laser is trying to heat. Both of these effects can be exacerbated by the properties of the substrate upon which the metallic structure is being fabricated. As appropriate, we will discuss these issues as they applied to the metallic systems covered in this project.

Dielectrics

Dielectrics (insulators) are materials with very low electrical conductivity. A more concise way of stating this is that in terms of their complex conductivity, $\sigma = \sigma_r + i\sigma_i$ (where $i = \sqrt{-1}$), that $\sigma_i \gg \sigma_r$. This is a very broad definition, but is accurate. Dielectrics contain no mobile charges like metals do that can move under the influence of electric fields.^{6,7}

The majority of dielectric materials are covalently bonded insulators. Like metals, where itinerant electrons determine a wide range of physical properties, thus linking those properties, in covalently bonded insulators the strength of the covalent bonds link those same properties. As a result, in covalently bonded insulators many the properties of the materials are determined by the behavior of lattice vibrations and their propagation. This behavior can, in large measure, be reduced to one physical parameter called the Debye Temperature, Θ_D .⁸

A number of properties are determined by the value of Θ_D . The melting temperature is linked by the Lindemann melting criteria⁹ where the melting temperature

$T_m \propto \Theta_D^2$. The specific heat at constant volume¹⁰ (c_v), thermal expansion coefficient¹¹ (α), and thermal conductivity¹² (κ) all are proportional to $\left(\frac{T}{\Theta_D}\right)^3$ at $T \ll \Theta_D$, and become proportional to Θ_D^3 as that limit is left. For materials like diamond, sapphire, and Si, $\Theta_D = 1886\text{K}$, 1035K and 625K respectively, which is why $(T_m, c_v, \alpha, \kappa)_{\text{diamond}} > (T_m, c_v, \alpha, \kappa)_{\text{sapphire}} > (T_m, c_v, \alpha, \kappa)_{\text{Si}}$. The Bulk (K) and Young's (Y) Moduli are also related to Θ_D , with larger (K, Y) going with materials with larger Θ_D .¹³ This linkage of physical properties makes the choice of dielectric materials for the MICE program problematic, as some aspects of a material that are desirable are intrinsically linked with undesirable properties.

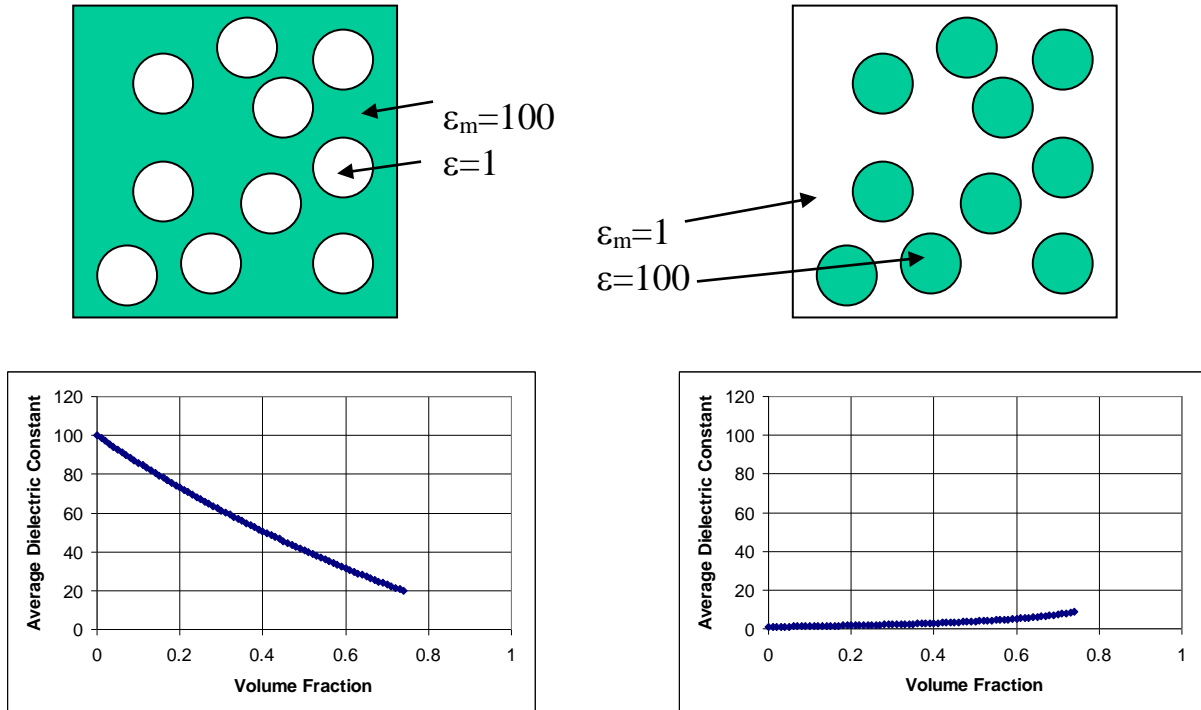
Inhomogeneous dielectric systems, especially ones formed from particles, play a large role in modern electronics. However the behavior of such systems are often non-intuitive.

For a system of spherical particles of dielectric constant ϵ imbedded in a matrix with a dielectric of ϵ_m , the average dielectric constant of the mixture is exactly described by Maxwell-Garnett theory¹⁴

$$\epsilon_{\text{ave}} = \epsilon_m \left(1 + \frac{3f \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right)}{1 - f \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right)} \right)$$

where f is the volume fraction of material the spherical particles of dielectric constant ϵ . As one can see from this equation, the average dielectric constant is dominated primarily by the properties of the matrix over the entire range of f . In the figure below, we show the effects on the average dielectric constant for systems composed of a high dielectric constant matrix with low dielectric constant spherical particles, as well as a low dielectric constant matrix with high dielectric constant spherical particles. In commercial thick film capacitors, the situation is best described by the situation on the left side of the figure below, namely the bulk of the capacitor is high ϵ material with some voids like Swiss cheese. The hit these capacitors take from the voids ($\epsilon=1$) is rather slight as long as their

concentration is rather low. The MICE LTS approach on the other hand, is better represented by the situation on the right side of the figure below. In the MICE approach, the system starts as spherical particles which the LTS procedure is trying to cement or glue together with dielectric.



Spherical dielectric particles ϵ in dielectric matrix ϵ_m . Problem is not symmetric with respect to ϵ & ϵ_m . Maximum volume fraction f possible with single sized spheres is 74% when hexagonal close packed.

As one can see from the above figure, the use of particles does not reduce the burden on the requirement that the precursor convert to a dielectric with an ϵ of the same order as the particles themselves.

¹ S. P. Parker, "Solid-State Physics Source Book", (McGraw Hill, New York, 1987)

² C. Kittel, "Quantum Theory of Solids" (John Wiley & Sons, New York, 1963)

³ C. Kittel, "Introduction to Solid State Physics, 5th Edition" (John Wiley & Sons, New York, 1976), p 178

⁴ Metals will deviate from the Wiedemann-Franz law if inelastic scattering dominates the conduction electron scattering. This only happens if there are extremely large concentrations of impurities in the metal that support isolated magnetic moments. e.g. Mn in Ag

⁵ C. Kittel, "Introduction to Solid State Physics, 5th Edition" (John Wiley & Sons, New York, 1976), p 353, valid when $\omega\tau \ll 1$, where τ is the electron scattering time in the metal.

⁶ P. Lorrain and D. Corson, "Electromagnetic Fields and Waves" (Freeman, New York, 1970), p91

⁷ Strictly speaking, metals and insulators (dielectrics) are only defined by their electrical behavior at absolute zero (0K), and as such semiconductors are dielectrics if nondegenerately doped, and metals if degenerately doped. B.I. Shklovskii and A.L. Efros, "Electronics Properties of Doped Semiconductors", (Springer-Verlag, Berlin, 1984), p 37

⁸ It should be noted that metals also have lattice vibrations (phonons) and can be characterized with a Debye temperature, however the phonons play a negligible role in the metals physical and electrical properties in comparison to the itinerant electrons role, with the exception of superconducting materials in their superconducting state.

⁹ J.M. Ziman, "Principles of the Theory of Solids" (Cambridge University Press, Cambridge, 1972), p65

¹⁰ C. Kittel, "Introduction to Solid State Physics", (John Wiley & Sons, New York, 1976) p 138

¹¹ N.W. Ashcroft and N.D. Mermin, "Solid State Physics" (Holt Rinehart & Winston , New York, 1976) p 493

¹² N.W. Ashcroft and N.D. Mermin, "Solid State Physics" (Holt Rinehart & Winston , New York, 1976) p 504

¹³ W.A. Harrison, "Electronic Structure and the Properties of Solids" (H.W. Freeman and Co., San Fransisco, 1980)

¹⁴ C.J. Maxwell-Garnett , *Philos. Trans. R. Soc.*, **A203**, 385-420 (1904)