HORIBA

Raman

Penetration Depth in Raman Microscopy

Technical Note RA TN-20

Introduction

In Raman microscopy, understanding how deeply the laser light penetrates a sample, known as the optical penetration depth, is crucial for interpreting the origin of the Raman signal. Penetration depth determines whether a measurement probes only a thin surface layer or captures information from within the bulk. This is especially important when analyzing layered materials, thin films, biological tissues, or particles suspended in liquid. The depth of penetration depends primarily on the wavelength of the light, and the material's optical properties, which dictate how light is reflected, absorbed, transmitted, or scattered.

Materials and Methods

When light interacts with a sample, several processes can occur simultaneously—reflection, absorption, transmission, and scattering (Figure 1). Together, these govern how deeply the excitation laser can probe into a material.

- **Reflection:** A portion of the incident light is redirected at the surface due to the change in refractive index (*n*) between air and the sample.
- **Absorption:** The light energy is converted into electronic or vibrational energy, resulting in a reduction in transmitted intensity.
- **Transmission:** Light that is not reflected or absorbed continues to propagate through the material.
- **Scattering:** Light is redirected in various directions due to irregularities, particles, or inhomogeneities in the medium.

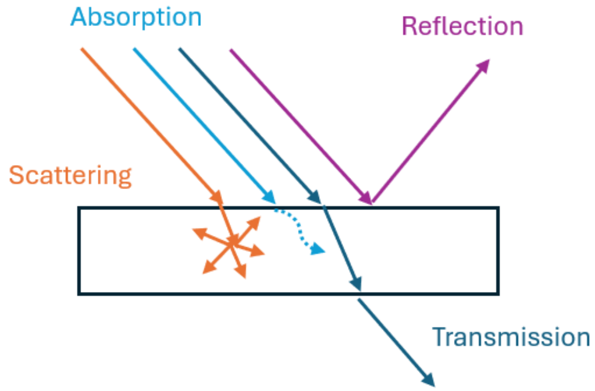

Figure 1. Illustration of light–matter interactions at a sample surface. Incident light can be reflected, transmitted, absorbed, or scattered. Absorption and scattering together determine how deeply the laser penetrates.

These behaviors are described by the complex refractive index:

$$\tilde{n} = n + ik$$

where *n* (refractive index) defines how much the light slows and bends inside the medium, and *k* (extinction coefficient) defines how strongly it is absorbed.

The absorption coefficient (α) relates to *k* through

$$\alpha = \frac{4\pi k}{\lambda}$$

with λ as the wavelength of light. A large *k* means rapid attenuation of light intensity with depth. This exponential decay follows Beer's Law:

$$I(z) = I_0 e^{-\alpha z}$$

where I_0 is the intensity at the surface and $I(z)$ is the remaining intensity at depth *z*. The penetration depth (δ) is the distance where the intensity falls to 1/e (≈ 37%) of its surface value:

$$\delta = \frac{1}{\alpha} = \frac{\lambda}{4\pi k}$$

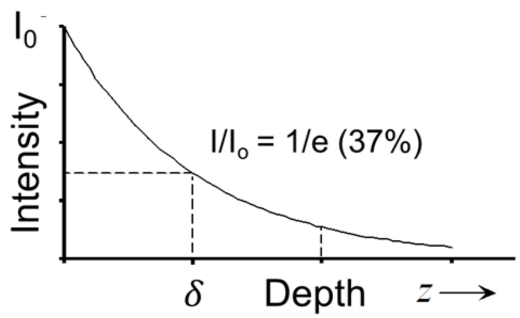

Figure 2. Exponential decay of light intensity with depth, showing penetration depth (δ), where intensity drops to 37% of the surface value.

Material Classes and Band Gap Dependence

The optical constants *n* and *k* depend on a material's band gap (E_g), the energy difference between its valence and conduction bands, as shown in Figures 3 (a) and (b). The relationship between the photon energy (*hv*) and E_g dictates how much of the light is absorbed or transmitted.

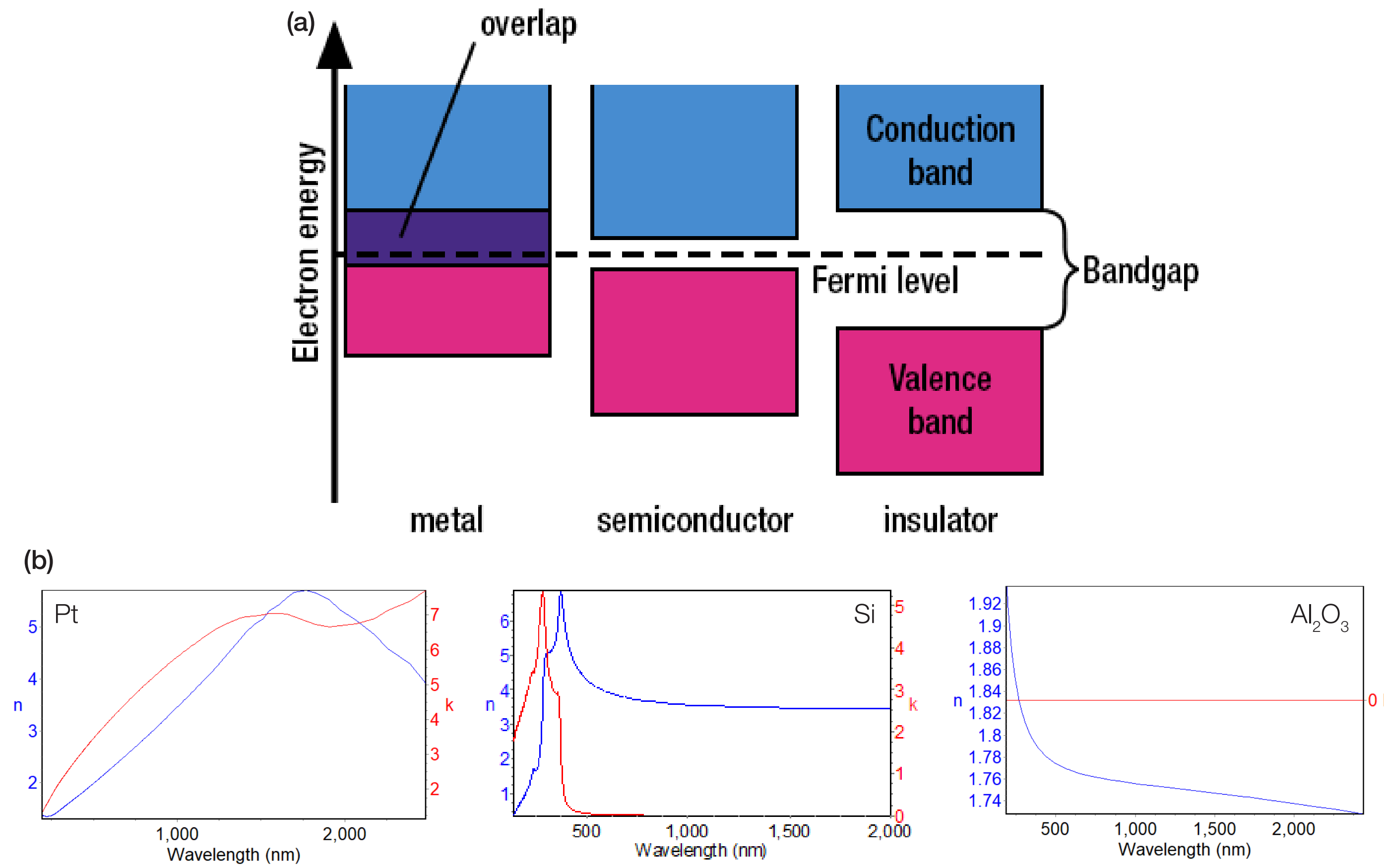

Figure 3. (a) Simplified band diagrams for metals, semiconductors, and dielectrics/insulators and (b) corresponding example optical constant (n and k) dispersions for platinum (metal), silicon (semiconductor) and Al2O3 (dielectric).

Metals

Metals have overlapping valence and conduction bands ($E_g \approx 0$ *eV*). Free electrons dominate the optical response, producing very large *k* values. Light is mostly reflected, and any transmitted intensity decays within tens of nanometers—the optical skin depth. Because free electrons screen the electric field, metals do not exhibit intrinsic Raman scattering. However, metal oxides that form on the surface can produce strong Raman signals, with their penetration depth depending on whether the oxide behaves as a semiconductor (moderate absorption) or dielectric (low absorption).

Semiconductors

Semiconductors have intermediate band gaps (0.5–6 eV), as shown in Table 1 below. When the photon energy (*hv*) exceeds E_g, electrons are excited across the band gap, resulting in a sharp increase in *k* and reduced penetration. Thus, higher energy lasers (shorter wavelengths), such as 405 nm or 532 nm, penetrate less deeply because they are absorbed more strongly. Lower energy lasers (longer wavelengths) like 785 nm or 1064 nm, are often below the band gap, minimizing absorption and probing deeper into the bulk.

Material	Band Gap (E_g)
Silicon (Si)	1.17 eV
Germanium (Ge)	0.66 eV
Silicon Carbide (SiC)	3.26 eV
Diamond	5.47 eV
GaAs	1.52 eV
GaP	2.32 eV
InP	1.42 eV
InAs	0.43 eV
ZnO	3.44 eV

Table 1. Band Gaps for Some Common Semiconducting Materials

Dielectrics

Dielectrics (insulators) have wide band gaps (> 6 eV), which are much larger than the energies of visible photons. Here, $k \approx 0$ is at wavelengths below E_g, meaning negligible absorption, and *n* remains relatively stable across the visible–NIR range. Light can penetrate hundreds of micrometers to millimeters, with Raman depth limited primarily by focusing geometry or scattering rather than absorption.

Some typical optical penetration depths for metals, semiconductors, and dielectrics are shown below in Table 2.

Material Type	Example Material	Band Gap (eV)	Penetration Depth 532 nm	Penetration Depth 633 nm	Penetration Depth 785 nm	Notes
Metal	Aluminum (Al)	~0	10 - 20 nm	12 - 25 nm	15 - 30nm	Strong reflection and absorption; no intrinsic Raman signal
Semiconductor	Silicon (Si)	1.1	800 nm	2.6 µm	8.3 µm	Shorter wavelengths absorbs more strongly; longer wavelengths probes deeper
Semiconductor	Germanium (Ge)	0.66	18 nm	65 nm	186 nm	Penetration is strongly wavelength-dependent; longer wavelengths penetrate further
Dielectric	Fused Silica (SiO_2)	> 8	> 100 µm	> 100 µm	> 100µm	Highly transparent; penetration limited by scattering and optics, not absorption

Table 2. Example Optical Penetration Depths Across Material Classes

Scattering and Complex Samples

In real-world samples, scattering can strongly influence penetration. Even when a material is weakly absorbing, multiple scattering events can redirect light, confining the effective Raman sampling depth to near-surface regions.

- **Powders and Rough Surfaces:** Multiple scattering and reflection cause light to diffuse within a shallow layer.
- **Colloids, Supensions, and Emulsions:** Interfaces between particles and liquid media scatter light strongly, limiting the depth to which both excitation and scattered photons can travel.
- **Biological and Turbid Samples:** Cells, fibers, and organelles scatter light in complex ways, while absorption by pigments (e.g., hemoglobin, melanin) further limits the depth of penetration. Using longer wavelengths (red/NIR) reduces scattering, allowing for deeper probing.

Scattering therefore modifies the simple exponential attenuation predicted by Beer's Law, especially in heterogeneous or multiphase systems. In such samples, penetration depth becomes an effective optical depth, dependent not only on absorption, but also on scattering strength and geometry.

Summary

The depth of Raman signal generation and collection depend on how light interacts with the material's optical and electronic structure. The complex refractive index ($n + ik$) determines how much light is refracted and absorbed, while the absorption coefficient (α) and penetration depth ($\delta = \lambda / 4\pi k$) describe how rapidly light intensity decreases with depth.

The band gap (E_g) determines which wavelengths of light the material absorbs. Metals, with high k values, confine light to nanometer depths and do not produce intrinsic Raman signals. Metal oxides can generate Raman signals, acting optically like semiconductors or dielectrics depending on their composition. In semiconductors, higher-energy (shorter-wavelength) lasers are absorbed more strongly, reducing penetration, while longer wavelengths can probe deeper. Dielectrics transmit light efficiently, so penetration depth is often limited by focusing optics or scattering rather than absorption. Scattering from particles, grains, or biological structures further reduces the effective depth in heterogeneous samples.

Understanding these optical properties and their interactions allows researchers to select the most suitable excitation wavelength, distinguish between surface and bulk Raman signals, and design experiments that target specific regions of interest within a sample.

Note that the discussion here focuses only on penetration depth and does not consider Raman sampling volume, which is a separate topic. Note also that wavelength is inversely related to energy by the following equation:

$$E(eV) = \frac{hc}{\lambda} \approx 1240eV \bullet nm/\lambda(nm)$$

info.sci@horiba.com

www.horiba.com/raman

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606
France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 80 41273637
Brazil: +55 (0)11 2923 5400
Germany: +49 (0) 6172 1396 0
Japan: +81(75)313-8121
Singapore: +65 (0)6 745 8300
Other: +33 (0)1 69 74 72 00