Optical and Photonic Glasses

Lecture 38:
Non-Linear Optical Glasses II – Semiconductor Doped Nano-Glasses

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Semiconductor-doped glasses

Glasses doped with semiconductor (SC) nanocrystals are candidates for **resonant NLO** materials. They show rapid response times of a few tens of ps. One such glass has been available for many years as a sharp cut color filter; it contains a very fine (diameter ~ 10 nm) CdS_xSe_{1-x} microcrystalline phase dispersed in the glass matrix.

When an electron is excited from the top of the valence band (VB) to the bottom of the conduction band (CB) of a SC through the absorption of a photon with an energy ~ E_G, a *free electron-hole pair* is formed. If the excitation energy is < E_G, an electron-hole pair may form, in close proximity and relatively immobile and Coulomb attraction may keep them in a stable orbit as a *bound electron-hole pair*, called *exciton*. Low T may be needed to prevent the thermal dissociation of the excitons with lower binding energies, E_B.

Exciton energy level diagram

(adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)
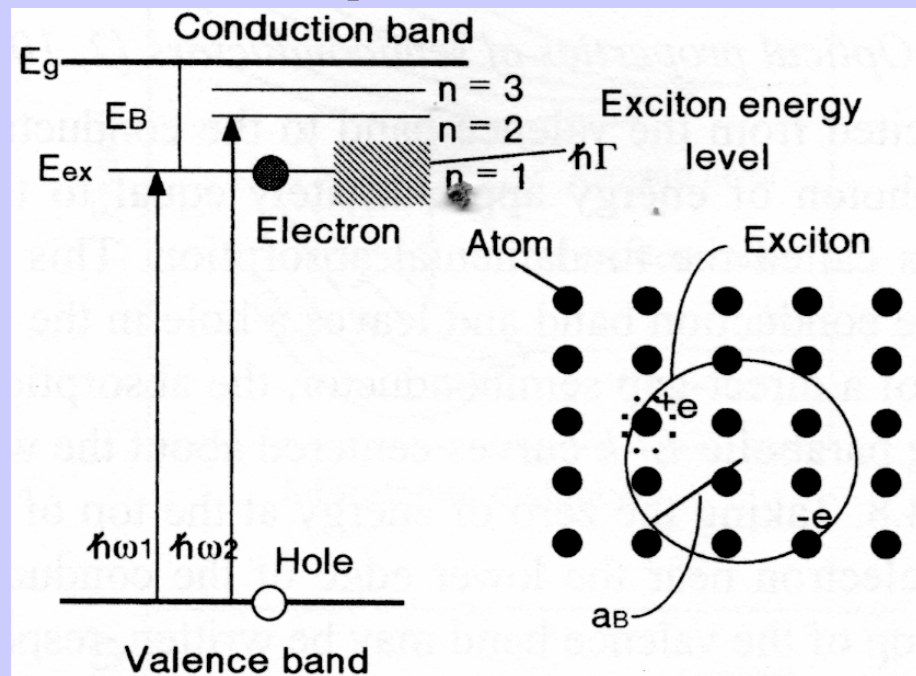
The experimental evidence for excitons usually comes from the optical absorption curves, where small peaks can be found red-shifted from the main absorption edge of the glass.
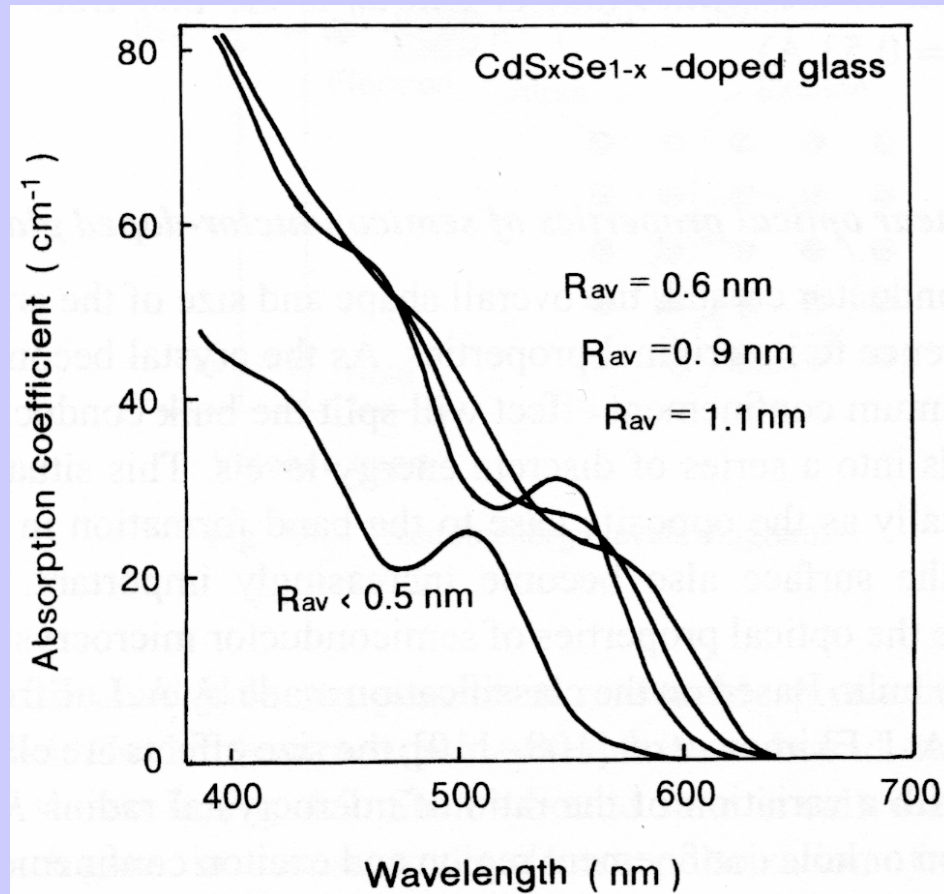
Absorption spectra of the glasses doped with CdS_xSe_{1-x} microcrystallites with various average radii. [Reprinted from H. Shinojima, J. Yumoto, N. Uesugi, S. Ohmi and Y. Asahara, *Appl. Phys. Lett.* **55** (1989) 1519, copyright (1989) with permission from the American Institute of Physics.]

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

The average separation between the electron and hole in an exciton, or effective radius, for the lowest exciton state, is called the exciton Bohr radius, estimated by:

$$a_B = h^2 \, \varepsilon \, / \, (4 \, \pi^2 \, m^* \, e^2) = m_e \, \varepsilon \, a_o \, / \, m^*$$

where ε is the static dielectric constant of the semi-conductor, m^* is the exciton reduced mass ($m_e \, / \, m^* = 1 + m_e \, / \, m_h$) and a_o is the Bohr orbit of hydrogen (0.053 nm).

In a SC, as its size becomes progressively smaller, the *quantum confinement* effect splits the bulk CB and VB into a series of discrete energy levels. For this reason, the SC nanoparticles are often called *quantum dots*.

If the SC microcrystallite radius, R, is much smaller than a_B, the electron and hole are individually confined (weakly bound exciton, of small E_B) and the microcrystallite excitons and absorption edge are blue-shifted relative to the bulk SC. This is called the *strong confinement* limit, observed in SC's like CdS and CdSe ($E_G \sim 600$ nm), with large a_B (the bulk exciton Bohr radius of CdSe is 3 nm). The effect becomes larger as R decreases, as observed in the previous figure.

It may be pointed out, however, that quantum confinement effects are not present in commercial filter glasses, since the CdS_xSe_{1-x} crystals present are too large (~ 10 nm).

The other limiting case, where R >> a_B (tightly bound exciton, of large E_B), is called the *weak confinement* case and occurs in glasses containing microcrystals such as CuCl (E_G ~ 400 nm), with a relatively small a_B (~ 0.6 nm) . A blue shift of the exciton absorption relative to the bulk CuCl is also observed in this case.

The main mechanism leading to the blue shift in the absorption edge has been proposed to be a "band filling" effect, particularly in the strong confinement case, due to the formation of a large number of electron-hole pairs when the SC is pumped near the bandgap and the filling of the states near the bottom of the CB with electrons. This saturates absorption near the band edge, shifting the band edge to higher energies with increasing laser intensity.

The changes in absorption of the SC crystallites relative to the bulk SC lead to refractive index changes, through the Kramers-Kronig transformation. The value of $\chi^{(3)}$ will be proportional to the reciprocal of the confinement volume and will normally increase with decreasing R. Therefore, larger non-linearities are obtained for glasses containing smaller particles and larger volume fractions of SC particles.
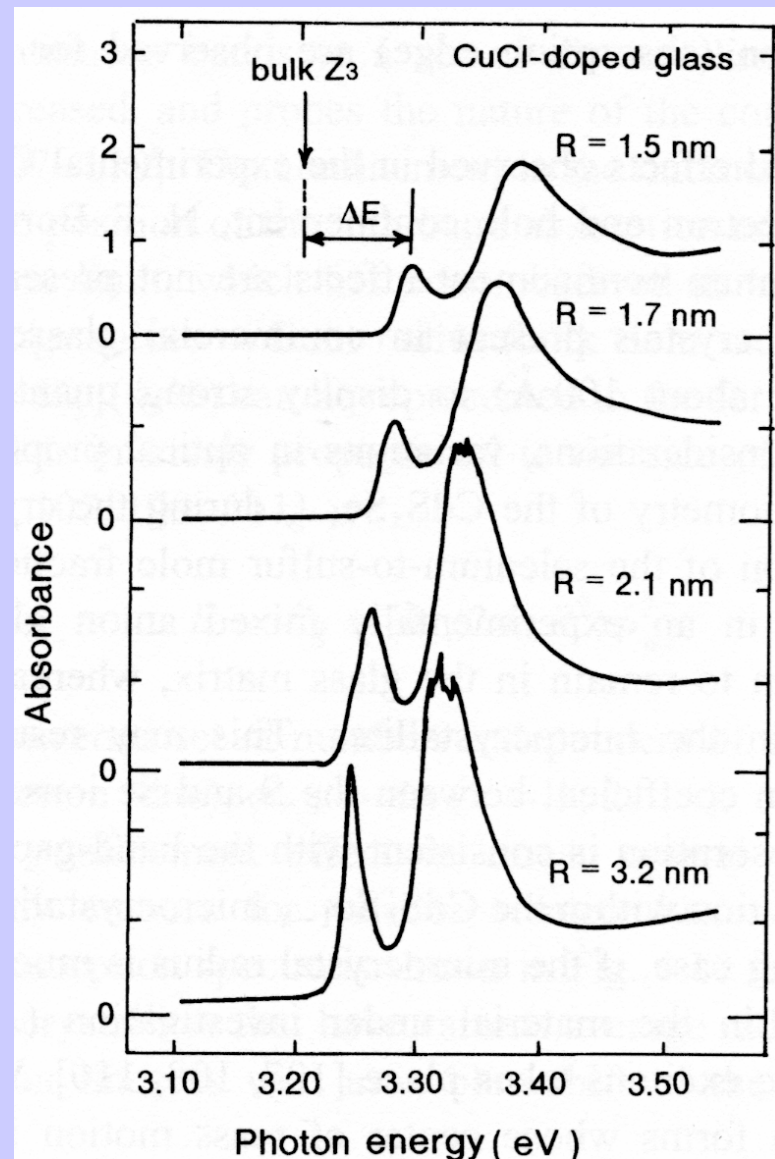
Absorption spectra of CuCl-doped glasses

(high E_B excitons in weak confinement)

Here, the two states of the excitonic absorption of CuCl nanocrystals are blue-shifted relative to the exciton energies of bulk CuCl.

The value of $\chi^{(3)}$ under resonant pumping @ the exciton energy was actually found in this case to reach a maximum of 3.4×10^{-6} esu for R ~ 5.5 nm.

(Adapted from: *Glasses for photonics,* M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)


A typical example of absorption spectra around an exciton in CuCl doped glasses at 77 K. The arrow indicates the Z_3 exciton energy of the bulk crystal. [Reprinted from T. Tokizaki, T. Kataoka, A. Nakamura, N. Sugimoto and T. Manabe, *Jpn. J. Appl. Phys.* **32** (1993) L782, copyright (1993) with permission from Publication Office, Japan Journal of Applied Physics.]

Response time

The photo-excited carriers in SC-doped glasses have both fast and slow relaxation mechanisms. The fast decay processes are assigned to the relaxation of free carriers down to the valence band, or to non-radiative relaxation, whereas the slow decay processes are thought to be related to the slow relaxation of carriers trapped in defects, predominantly in the nanocrystallites, including the surface states.

The figure shows the typically very broad PL spectrum of a CdSe-doped glass. The narrow band near the absorption edge is due to direct carrier recombination to the VB, whereas the broad band in the NIR is due to radiative recombination via the trap levels.
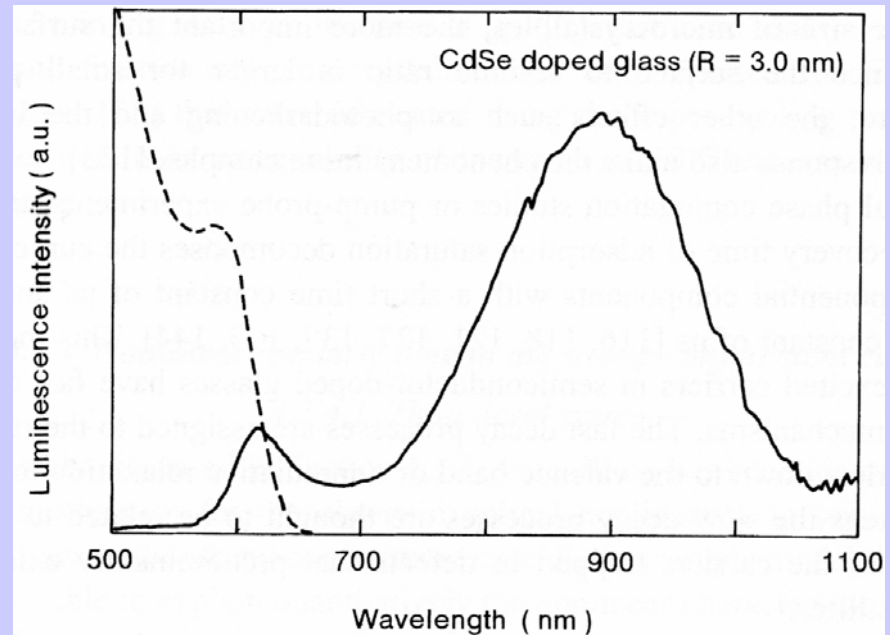
(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

Photoluminescence spectrum of CdSe-doped glass. ($R = 3.0$ nm) (50ZnO-50P$_2$O$_5$ + 4CdSe (mol %)). [Reprinted from Y. Asahara, *Advances in Science and Technology* **4**,

The long radiative recombination times of SC-doped glasses in the strong confinement case still restricts their use in high-speed applications such as fast optical switching.

The *photo-darkening* effect, a permanent red shift in the absorption after a long period of intense laser irradiation, is associated with a decrease in the optical response time. Such changes are permanent at room temperature, but a darkened glass may be bleached at high temperatures close to T_g. Together with the photo-darkening, a significant reduction in the lifetime and efficiency of the direct recombination PL process has been observed, together with a reduction of the broad luminescence of the deeply trapped carriers. Since neither the undoped glass nor the bulk SC shows such effects, the photo-darkening must be related to the particular structure of the microcrystallites, or to the SC particle / glass interface.

Fabrication methods

The commercial SC-doped filter glasses are prepared by melt quenching, followed by a heat treatment slightly above T_g to precipitate the SC nanoparticles. Other methods have been tried for films, such as vapor deposition, the sol-gel process, or ion implantation. The following table summarizes the NLO properties of SC-doped glasses prepared by different methods.

Dopant	Diam. d (A)	Matrix	Process	Measurement	Absorption Coeff. $\alpha(cm^{-1})$	Wavelength λ (nm)	$|\chi^{(3)}|$ (esu)	n_2'' (cm^2/W)	τ (ps)
CdS	$35 \sim 60$	S	SG	TBSD	~ 1715	460	$\sim 6.3 \times 10^{-7}$		
CdS$_x$Se$_{1-x}$	$20 \sim 200$	BS	MQH	TBSD		$580 \sim 620$			$4 \sim 90$
CdS$_x$Se$_{1-x}$	$440 \sim 2400$	P	MQH	Z		1064		2.5×10^{-13}	
CdS$_x$Se$_{1-x}$		FP	MQH	DFWM		584	1×10^{-7}		14000
CdS$_x$Se$_{1-x}$ ($x = 0.41$)		FP		FWM		587	$\sim 10^{-7}$		
CdS$_x$Se$_{1-x}$ ($x = 0.73$)		FP		FWM		532	$\sim 2.9 \times 10^{-9}$		
CdSe	15	S	SPT	DFWM	1270 (600 nm)	532	1.3×10^{-8}		$10 \sim 60$
CdSe	~ 25			DFWM		546	$0.3 \sim 2 \times 10^{-9}$		
CdSe	$25 \sim 40$	P	MQH	TBSD	526		$\sim 1 \times 10^{-6}$		
CdSe	~ 70	S	IBS	TBSD		$445 \sim 510$	1×10^{-8}		
CdTe	30	P	MQH	TBSD			5×10^{-7}		
CdTe	$35 \sim 80$	S	LE	DFWM	6000	580	4.2×10^{-7}		~ 10
	35	S	LE&CVD	DFWM	~ 800	580	$\sim 6 \times 10^{-7}$		
InP	40	S	PP	Z		1064		$\sim -7 \times 10^{-11}$	
CuCl	$30 \sim 160$	BS	MQH	TBSD (80 K)			$\sim 1 \times 10^{-6}$		~ 100
CuCl	$30 \sim 160$	BS	MQH	TBSD (80 K)			$\sim 1 \times 10^{-6}$		
CuCl	$44 \sim 68$	BS	MQH	PP (77 K)				$\sim 3 \times 10^{-7}$	
CuCl	$30 \sim 60$	S	SG	TBSD (77 K)			1.1×10^{-8}		
CuCl	$\sim 40, \sim 400$	SAS	MQH	TBSD (77 K)		$381 \sim 383$	$\sim 4 \times 10^{-8}$		
CuCl	81	BS	MQH	TBSD (77 K)		384	3×10^{-6}		
CuCl	80	–	MQH	KS (77 K)	94	–	2×10^{-7}		< 4
CuBr	182	BS	MQH	TBSD (77 K)		413	$\sim 1 \times 10^{-7}$		
CuBr	~ 84	BS	MQH	TBSD (77 K)		–	$\sim 2.6 \times 10^{-7}$		30
Cu$_x$S	~ 80			PP			$\sim 10^{-7}$		
Cu$_x$S				Z			1.3×10^{-9}		
CuBr$_{0.26}$Cl$_{0.73}$	$106 \sim 230$	BS	MQH	TBSD (77 K)			1.1×10^{-8}		43
PbSe	$32 \sim 146$	PBS	MQH	Z		1060	$\sim 1.14 \times 10^{-9}$		

BS, borosilicate; P, phosphate; S, silica, SAS, sodium-almino-silicate; FP, fluoro-phosphate; MQH, melt-quench and heat treatme porous process; SPT, spattering process; IBS, ion beam sputtering; LE, laser evaporation; SG, sol-gel process; CVD, chemical deposition; PP, pump-probe technique; DFWM, degenerate four wave mixing; KS, *Kerr shutter technique; TBSD, two-beam* diffraction; FWM, four wave mixing; Z, z-scan.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

Metal-doped glasses

In noble metals like Cu, Ag and Au, the d-band overlaps the s-p CB, which makes possible *intraband* transitions in the CB and *interband* transitions between the d-bands and the CB.
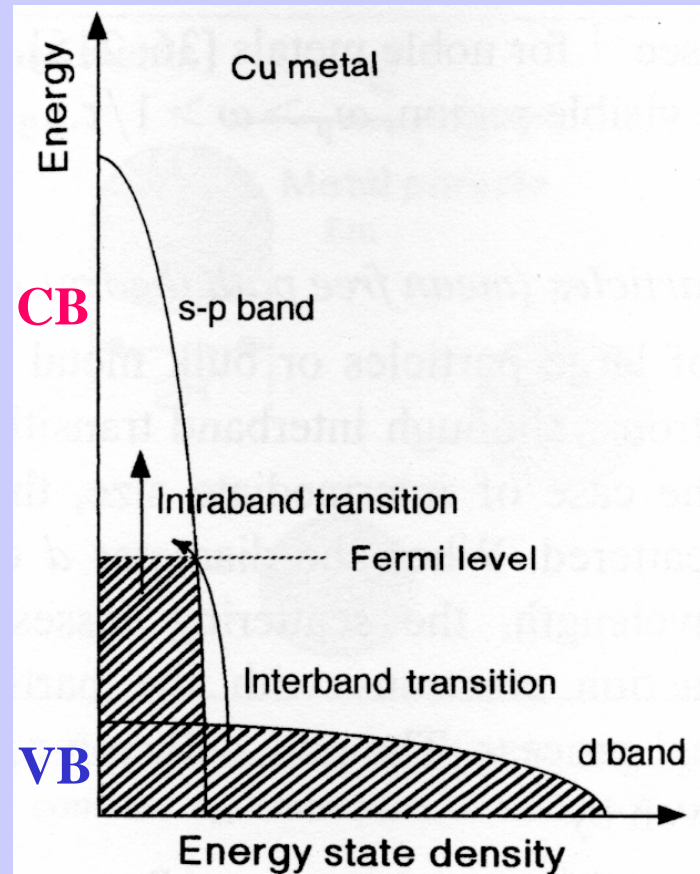
Schematic expression of electron state density and band structure of Cu metal.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

The dielectric constant of the metal particles is given by:

$$\varepsilon_m = \varepsilon_m' - i\,\varepsilon_m'' = 1 - \omega_p^2 / [\omega\,(\omega - i/\tau)]$$

where ω_p is the *plasma frequency* of the *bulk metal* ($\omega_p = (4\,\pi\,N\,e^2 / m^*)^{1/2}$ and m^* is the effective mass of the $N \sim 10^{22}$ cm^{-3} conduction electrons per unit volume) and τ is the time between collisions among electrons. Therefore:

$$\varepsilon_m' = n^2 - k^2 = 1 - \omega_p^2\,\tau^2 / [1 + (\omega\tau)^2]$$

$$\varepsilon_m'' = 2\,n\,k = \omega_p^2\,\tau / \{\omega\,[1 + (\omega\tau)^2]\}$$

For a metal like Cu or Ag, the mean free path of the conduction electrons is ~ 50 nm and τ (= 50 nm / v_F) $\sim 5 \times 10^{-14}$ s. Thus, at visible or NIR frequencies ($\omega \sim 10^{15}$ s^{-1}) , one has $(\omega\tau)^2 \gg 1$ and the simplified form of the equations:

$$\varepsilon_m' = 1 - \omega_p^2 / \omega^2$$

$$\varepsilon_m'' = \omega_p^2 / \omega^3\,\tau$$

For noble metals, $\omega_p \sim 10^{16}$ s^{-1}. Therefore, for Ag or Cu in the visible region, one has $\omega_p > \omega > 1/\tau$. (At ω_p, $\varepsilon_m = 0$; below ω_p, $\varepsilon_m < 0$ and n^* is imaginary and % R ~ 1).

When the diameter (d = 2R) of spherical metal particles is $\ll \lambda$, scattering of the incident light beam is negligible. Also, collisions of the conduction electrons with the particle surfaces become important and the new collision relaxation time, τ_{eff}, is given by:

$$1 / \tau_{eff} = 1 / \tau_b + v_F / R$$

where τ_b is the bulk value and v_F is the Fermi velocity (= 1.4 x 10^6 m/s for Ag) and the mean free path is ($v_F \tau_b$) ~ 50 nm. If 2R $\ll$ 50 nm, then the mean free path in the nanoparticle is ~ 2R and it is entirely limited by particle boundary scattering:

$$1 / \tau_{eff} = v_F / R$$

Glass / metal particle nanocomposites

Composites formed by spherical metal nanoparticles embedded in a dielectric glass with a real dielectric constant ε_d have rather interesting NLO properties. If 2R $\ll \lambda$ and the volume fraction of spheres is p $\ll$ 1, the effective dielectric constant of the composite will be:

$$\varepsilon_{eff} = \varepsilon_d + 3 \, p \, \varepsilon_d \, [(\varepsilon_m - \varepsilon_d) / (\varepsilon_m + 2\varepsilon_d)]$$

The *absorption coefficient* of the *composite* ($\alpha = 2 \, \omega \, k / c$) has a *maximum* at the "surface plasma resonance" frequency, ω_s: ε_{eff}'' maximum <=> ε_m'(ω_s)+2ε_d = 0. This corresponds to collective electronic excitations at the metal/glass interface.