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David D Nolte



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Optical scattering and absorption by metal nanoclusters in GaAs

D. D. Nolte

Department of Physics, Purdue University, West Lafayette, Indiana 47907-1396

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Optical extinction by a dilute dispersion of metal nanoclusters in GaAs is calculated using the optical theorem and Maxwell-Garnet theory with complex dielectric functions for Cr, Fe, Ni, Cu, Ag, Au, Er, and As. The large dielectric function of the semiconductor host shifts the surface plasmon resonance frequencies from the ultraviolet to the near infrared. The noble metals have well-defined resonances with significant absorption and Rayleigh scattering at photon energies compatible with diode lasers and semiconductor electro-optic modulators. Interband transitions in metals such as As, Cr, Fe, Ni, and Er strongly damp the surface plasmon modes, quenching the resonant absorption by the particles, but providing significant absorption to wavelengths longer than 1.5 μm . Metal-semiconductor composites may arise during growth or processing of materials, such as GaAs:Er for fiber-optic applications, and GaAs:As in which metallic precipitates of As form in GaAs after low temperature growth of GaAs using molecular beam epitaxy.

I. INTRODUCTION

Metal-semiconductor composites, in which small metal particles are dispersed in a crystalline semiconductor, present a fruitful area of study for a rich variety of solid-state and optical phenomena with potentially interesting applications. These materials have hybrid electronic, dielectric, and optical properties that can be tailored by controlling the volume fraction of metal in the semiconductor. Optical studies of amorphous semiconductors with voids and inclusions have made it possible to measure the void volume in amorphous silicon,¹ as well as optical extinction in amorphous SiAg alloys.² Important recent advances have made it possible to maintain high-quality crystalline semiconductor properties around metal inclusions.³⁻⁵ This has opened the possibility for designing engineered materials for specific applications using known properties of the metal and semiconductor matrix.

The dielectric and optical properties of metal-semiconductor composites share much in common with the dielectric and optical properties of colloidal metal dispersions in solid and liquid insulators. Vast literature exists on this topic,^{6,7} including effective medium models⁸⁻¹² nonlinear optical effects¹³⁻¹⁶, and resonant absorption by plasmon resonances.¹⁷⁻²⁰ In the limit of dilute dispersions of metallic nanoclusters the particles contribute approximately linearly to the composite extinction, but small metal clusters show important deviations from bulk metallic behavior.²¹⁻²⁴ Size-quantized electron states, as well as surface states are expected to contribute to dielectric and electronic properties.^{25,26} In the opposite limit of high metal concentrations, percolation phenomena across connected clusters can have critical effects on the electronic properties of the composite.²⁷ Across this entire range, optical studies provide important diagnostic and spectroscopic tools to study effects in the discrete metal clusters, or as probes of the effective dielectric response of the composite material.

Attention has been focused recently on dilute dispersions of metal particles inside high-quality crystalline semiconductors. This interest has been partly driven by the development

of low-temperature-growth GaAs by molecular beam epitaxy, by which highly nonstoichiometric GaAs is grown with a large excess As concentration up to 1% or 2%.²⁸ Precipitates of As form during annealing after growth.²⁹ The most important feature of this new metal-semiconductor composite is the sensitive control over the physical properties of the metallic dispersion. By controlling the growth temperature, the annealing temperature, and the annealing time, it is possible to accurately control the size and density of arsenic precipitates.³⁰ This unprecedented control is the basis of arsenic-cluster engineering, which has many possible applications.³¹⁻³⁴

In this article, the optical extinction by metal nanoclusters in a semiconductor matrix is calculated using full dielectric functions for the semiconductor host and for As, as well as for the metals Cr, Fe, Ni, Cu, Ag, Au, and Er. These metals have been chosen because of their technological importance in semiconductor physics, as well as the potential ability to form metal-semiconductor composites out of these materials. Precipitates of transition metals in semiconductors can be formed relatively easily.³⁵ Optical studies of these composite materials will play a vital role in the study of their physical properties.

II. OPTICAL EXTINCTION

Optical extinction in inhomogeneous materials is caused by scattering plus absorption. Scattering and absorption both contribute to the forward scattering amplitude $S(0)$, which defines the extinction cross section C_{ext} in the optical theorem

$$C_{\text{ext}} = 4\pi \operatorname{Re} \left(\frac{S(0)}{\bar{k}^2} \right), \quad (1)$$

where Re denotes the real part of the argument, and $\bar{k} = \bar{n}k_{\text{vac}}$ is the complex k value in the medium and \bar{n} is the complex refractive index of the medium

$$\bar{n} = n + i\kappa. \quad (2)$$

If the inhomogeneities in the medium are spheres of arbitrary radius $r = a$, the forward scattering amplitude is given by the Mie scattering formula

$$S(0) = \frac{1}{2} \sum_{j=1}^{\infty} (2j+1)(a_j + b_j), \quad (3)$$

where the lowest-order Mie coefficients are⁷

$$\begin{aligned} a_1 &= \frac{i2x^3 \bar{m}^2 - 1}{3 \bar{m}^2 + 2} - \frac{i2x^5 (\bar{m}^2 - 2)(\bar{m}^2 - 1)}{5 (\bar{m}^2 + 2)^2} \\ &\quad + \frac{4x^6}{9} \left(\frac{\bar{m}^2 - 1}{\bar{m}^2 + 2} \right)^2 + O(x^7), \\ b_1 &= -\frac{ix^5}{45} (\bar{m}^2 - 1) + O(x^7), \\ a_2 &= -\frac{ix^5 \bar{m}^2 - 1}{15 2\bar{m}^2 - 3} + O(x^7), \\ b_2 &= O(x^7), \end{aligned} \quad (4)$$

which have been expanded in terms of $x = nk_{\text{vac}}a$, and

$$\bar{m}^2 = \frac{\bar{\epsilon}_{\text{sph}}}{\bar{\epsilon}_m} \quad (5)$$

is the ratio of the complex dielectric function of the spheres to the complex dielectric function of the medium.

The extinction cross section becomes

$$\begin{aligned} C_{\text{ext}} &= 4\pi a^2 x \operatorname{Im} \left[\frac{n^2(\bar{m}^2 - 1)}{\bar{n}^2(\bar{m}^2 + 2)} \left(1 \right. \right. \\ &\quad \left. \left. + \frac{x^2 (\bar{m}^2 - 1) \bar{m}^4 + 27\bar{m}^2 + 38}{15 (\bar{m}^2 + 2) 2\bar{m}^2 + 3} \right) \right] \\ &\quad + \frac{32\pi}{3} a^2 x^4 \operatorname{Re} \left[\frac{n^2 (\bar{m}^2 - 1)^2}{\bar{n}^2 (\bar{m}^2 + 2)} \right], \end{aligned} \quad (6)$$

where Im denotes the imaginary part of the argument, with the scattering cross sections given by

$$C_{\text{sca}} = \frac{32\pi}{3} a^2 x^4 \left| \frac{\bar{m}^2 - 1}{\bar{m}^2 + 2} \right|^2 \quad (7)$$

which describes elastic Rayleigh scattering. In the limit of a dilute suspension of small metal particles, it is not necessary to use effective medium theories to derive the composite absorption.⁸ Each particle acts independently and contributes approximately linearly to the total extinction for the material. The absorption coefficient α is therefore simply related to the extinction cross section C_{ext} through the density N_{inc} of scattering inclusions

$$\alpha = N_{\text{inc}} C_{\text{ext}}. \quad (8)$$

It is usual to relate the density to the volume fraction of metal in the composite. For scattering from spherical inclusions the volume fraction f is

$$f = \frac{4}{3} \pi a^3 N_{\text{inc}}. \quad (9)$$

For spheres small compared with the wavelength inside the medium, $x \ll 1$ and only the first term in Eq. (6) is significant. In this limit, the absorption in the spheres is much larger than the Rayleigh scattering, and the particulate extinction coefficient for the spheres is

$$\alpha_{\text{ext}} = 3fnk_{\text{vac}} \operatorname{Im} \left(\frac{n^2 \bar{m}^2 - 1}{\bar{n}^2 \bar{m}^2 + 2} \right). \quad (10)$$

The absorption for a fixed volume fraction f is therefore independent of the size of the spheres in the limit of small spheres, and only depends on the total concentration of metal within the medium. On the other hand, if the particles become too small, deviation from bulk behavior can affect the dielectric properties of the particle because of size effects.^{25,26}

The extinction coefficient in Eq. (10) represents absorption of energy out of the electromagnetic wave by the metal particles. There are several processes that contribute to the particle absorption, including Joule heating, interband transitions within the metal, and photoemission of electrons from the metal into the semiconductor.³⁴ However, the most striking feature in the particle absorption is when the denominator in Eq. (10) vanishes for

$$\bar{\epsilon}_{\text{sph}} = -2\bar{\epsilon}_m. \quad (11)$$

This condition represents resonant absorption by surface plasmons, also known as the Fröhlich resonance.⁷ The condition in Eq. (11) can only be satisfied when one of the materials in the composite is a metal with a negative real dielectric function. In general, both dielectric constants are complex and the condition in Eq. (11) can never be satisfied exactly. In addition, nonsphericity of the metal particles can split and shift the resonances.⁷ However, in this analysis it is assumed that the particles are spherical.

The total absorption through the composite material is given by

$$\alpha = \alpha_m + 3fnk_{\text{vac}} \operatorname{Im} \left(\frac{n^2 \bar{m}^2 - 1}{\bar{n}^2 \bar{m}^2 + 2} \right), \quad (12)$$

where α_m is the medium absorption in the absence of the metal spheres. In this expression, the change in the refractive index of the composite medium caused by the metal particles has not been included. This is a good approximation when the volume fraction $f < 1\%$.

For volume fractions larger than 1% it is important to include the changes in the refractive index of the composite medium in a self-consistent manner. This is most often done by defining an average dielectric function for the composite. The Maxwell-Garnet theory approximates the dielectric function of a composite with spherical metal inclusions by

$$\begin{aligned} \bar{\epsilon} &= \bar{\epsilon}_{\text{GaAs}} \frac{1 + 2f(\bar{\epsilon}_{\text{metal}} - \bar{\epsilon}_{\text{GaAs}})/(\bar{\epsilon}_{\text{metal}} + 2\bar{\epsilon}_{\text{GaAs}})}{1 - f(\bar{\epsilon}_{\text{metal}} - \bar{\epsilon}_{\text{GaAs}})/(\bar{\epsilon}_{\text{metal}} + 2\bar{\epsilon}_{\text{GaAs}})} \\ &= \bar{\epsilon}_{\text{GaAs}}(\omega) \bar{G}(\omega), \end{aligned} \quad (13)$$

where the total absorption in the composite materials is

$$\alpha = \frac{k_{\text{vac}}}{n} \text{Im}[\bar{\epsilon}_{\text{GaAs}}(\omega)\bar{G}(\omega)]. \quad (14)$$

For spheroidal inclusions⁸ the expression for $G(\omega)$ contains geometric depolarization factors L_m and is given by

$$\bar{G}(\omega) = \left(1 + f \frac{(\bar{\epsilon}_{\text{metal}} - \bar{\epsilon}_{\text{GaAs}})(1 - L_m)}{L_m \bar{\epsilon}_{\text{metal}} + (1 - L_m) \bar{\epsilon}_{\text{GaAs}}} \right) \Bigg/ \left(1 - f \frac{(\bar{\epsilon}_{\text{metal}} - \bar{\epsilon}_{\text{GaAs}})L_m}{L_m \bar{\epsilon}_{\text{metal}} + (1 - L_m) \bar{\epsilon}_{\text{GaAs}}} \right). \quad (15)$$

For spherical particles, $L_m = 1/3$. For oblate and prolate spheroids L_m takes on values between 0 and 1 depending on the polarization of the electromagnetic wave relative to the major and minor axes of the spheroids. Small deviations from sphericity can have important consequences for absorption of ideal metals like silver. However, nonsphericity has only a small effect on the absorption by weak metals, such as arsenic in GaAs.

In a nonabsorbing medium, the optical theorem and the Maxwell-Garnet results agree for small volume fractions. However, caution is necessary when comparing one composite dielectric model to another, especially in an absorbing medium. For instance, in GaAs for photon energies above the fundamental absorption gap, the optical theorem and Maxwell-Garnet expressions in Eqs. (12) and (14) do not agree, even for small volume fractions. However, they both remain semi-quantitatively correct and are useful as heuristic guides.

To present several of the qualitative features of metal-semiconductor composites, the free electron model (FEM) for a metal is used here. Accurate complex dielectric functions for real metals are used in the next section. The dielectric function for the FEM using the Drude model is

$$\bar{\epsilon}_{\text{sph}} = \epsilon(\infty) \left(1 - \frac{\Omega_p^2}{\omega^2 + i\omega/\tau} \right), \quad (16)$$

where $\epsilon(\infty)$ is the high-frequency dielectric constant, τ is the Drude electron scattering time, and

$$\Omega_p^2 = \frac{4\pi N e^2}{\epsilon(\infty) m_e} \quad (17)$$

is the square of the bulk ionic plasma frequency, where N is the number of lattice atoms per unit cell volume. For $\epsilon(\infty) = 1$ and $N = 4.4 \times 10^{22} \text{ cm}^{-3}$, $\Omega_p = 2.4 \times 10^{16} \text{ s}^{-1}$, corresponding to a vacuum wavelength in the far ultraviolet.

The particle absorption from Eq. (10) for an ideal free-electron-metal is shown in Fig. 1 for a 1% volume fraction of small metal spheres in vacuum, in glass and in a GaAs medium. The complex dielectric function of the bandedge of GaAs is modeled from Ref. 36. The values used in Eq. (16) for the FEM are $\epsilon(\infty) = 2.9$ and $\tau = 5 \text{ fs}$, corresponding to idealized behavior of silver, modeled as a FEM. In vacuum, the high plasma frequency of the FEM places the Fröhlich resonance wavelength at 300 nm, far in the ultraviolet. When imbedded in a glass medium with a dielectric constant of $\epsilon_m = 2.25$, the resonance wavelength moves to a larger value of 365 nm, still in the ultraviolet, and the absorption in-

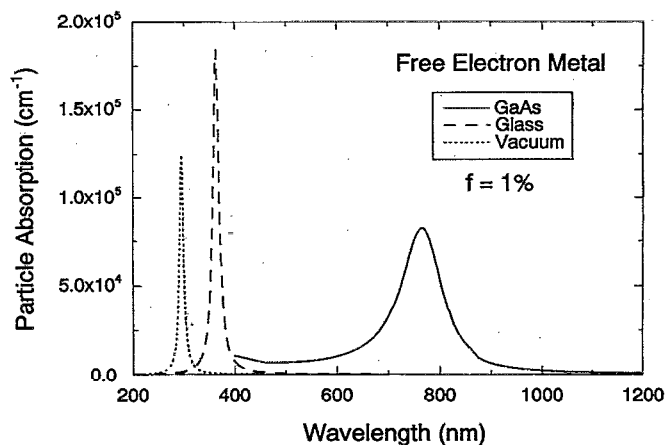


FIG. 1. Particle extinction for a free-electron-metal in vacuum, glass and GaAs. Imbedding a metal sphere in a high-dielectric-constant medium increases the resonance wavelength.

creases. The significantly larger dielectric constant of GaAs dramatically shifts the resonance wavelength to 765 nm.

The large absorption in the GaAs medium contributes an imaginary component to the complex dielectric function of the medium, which significantly broadens the resonance. The integrated absorption for the three cases is shown in Table I. The integrated absorption is proportional to the oscillator strength for absorption by the spheres and is also proportional to the integrated energy absorption out of a broadband electromagnetic wave. The oscillator strength for the three cases are approximately equal, in spite of significantly different qualitative appearances.

The contribution of Rayleigh scattering to the extinction is shown in Fig. 2 for a volume fraction $f = 1\%$ of metal spheres with increasing radii of 3, 10, and 30 nm. Scattering from the 3 nm particles contributes negligibly to the total extinction. The Rayleigh contribution from the 10 nm particles becomes comparable to the particulate absorption. For particles with radii larger than 10 nm, multiple scattering becomes important. For particles larger than 30 nm, the higher terms in the Mie scattering formula Eq. (4) become significant, and Mie resonances will play an important role, which was not discussed here. In the following sections, we assume that the particles have radii smaller than 10 nm and that Rayleigh scattering plays a negligible role in the total extinction coefficient.

A comparison of the total absorption predicted from the optical theorem and the Maxwell-Garnet expression is shown in Fig. 3 for the FEM. With a volume fraction of $f = 1\%$, there is reasonable agreement between the two dielectric models. The interaction of nonisolated particles, ap-

TABLE I. Integrated particulate absorption $\int_0^\infty \alpha(\omega) d\omega$.

Vacuum	$9.5 \times 10^3 \text{ cm}^{-1} \text{ eV}$
Glass	$1.4 \times 10^4 \text{ cm}^{-1} \text{ eV}$
GaAs	$1.2 \times 10^4 \text{ cm}^{-1} \text{ eV}$

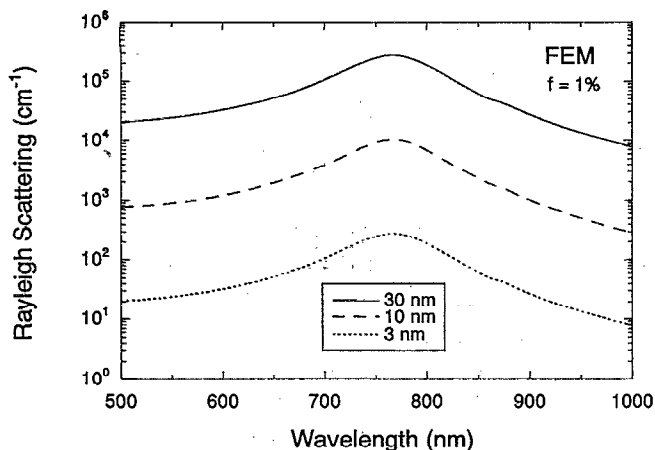


FIG. 2. Rayleigh scattering cross sections for a free-electron metal (FEM) in GaAs. The curves are for increasing radii of 3, 10, and 30 nm at a constant volume fraction $f=1\%$. Particles with radii smaller than 10 nm contribute negligibly to the total extinction.

proximated by the Maxwell-Garnet curve, produces a slight shift of the resonance wavelength, with slight enhancements. These effects become more pronounced as volume fraction increases.

III. METAL CLUSTERS IN GaAs

The parameters $\epsilon(\infty)$ and τ for the Drude model of the FEM in Fig. 1 were chosen to match the dielectric function of silver. For more accurate results, the full dielectric function of specific metals must be used. These have been tabulated in Ref. 37 for a broad range of metals. The metal dielectric functions were parameterized for photon energies between 0.8 and 5 eV. The total absorption of noble metal nanoclusters embedded in GaAs is compared with the absorption of the GaAs medium in Fig. 4 for Cu, Au, and Ag. The Fröhlich resonance in Cu occurs very close to the band edge of the semiconductor. The lower medium absorption at the band edge produces a sharper resonance with a larger

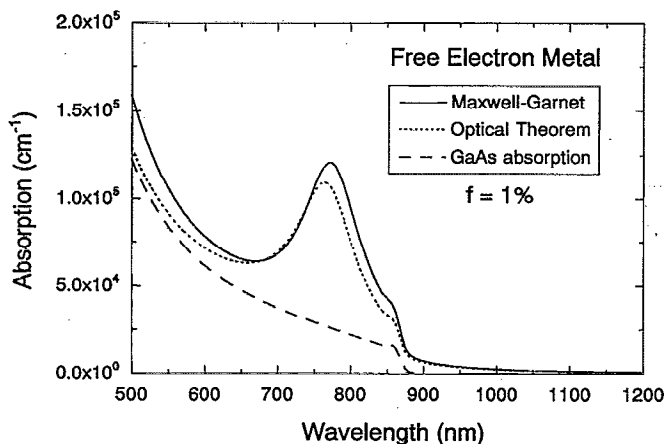


FIG. 3. Comparison of the results from the optical theorem and Maxwell-Garnet for FEM spheres in GaAs for 1% volume fraction of metal. The FEM parameters are $\epsilon(\infty)=2.9$ and $\tau=5$ fs.

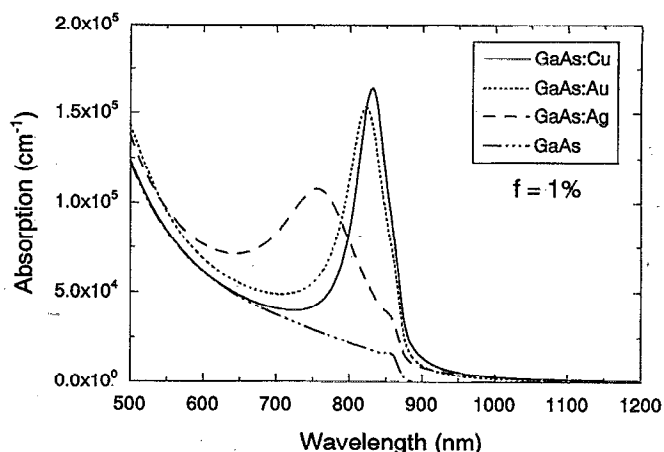


FIG. 4. Total absorption of $f=1\%$ noble metal nanoparticles in GaAs compared with bulk GaAs absorption. The plasmon resonance occurs just above the band edge. Copper and gold have the most pronounced resonances.

value of extinction. In an $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ medium the band edge occurs near 710 nm, above the Fröhlich resonances. The particle extinction becomes sharper and larger, as shown in Fig. 5. It is interesting to note that at the peak of the Fröhlich resonance, the metal/semiconductor composite has an extinction coefficient comparable to that of a metal thin film. This is in spite of the fact that the calculations are carried out for a volume fraction of only $f=1\%$.

The sharp Fröhlich resonances in the noble metals result because of the large negative real dielectric functions and the small imaginary dielectric values. Non-noble metals do not have such pronounced free-electron behavior. Most metals have interband transitions that introduce large imaginary dielectric functions ϵ_2 and add positive contributions to ϵ_1 that prevent condition Eq. (11) from being satisfied. The total extinction near the band edge of GaAs is shown for the transition metals Ni, Fe, Cr, and Er in Fig. 6. The recent interest in Er-doped semiconductors³⁸⁻⁴⁰ has been fueled by Er-

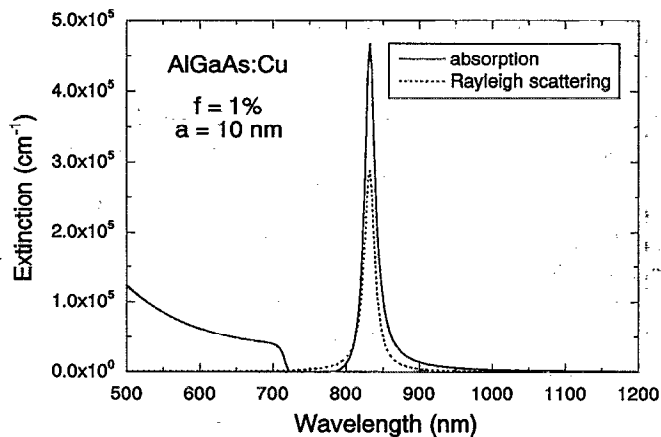


FIG. 5. Total extinction of $f=1\%$ Cu in $\text{Al}_{0.8}\text{Ga}_{0.2}\text{As}$. The plasmon resonance is now below the band edge and is sharper than in Fig. 4. Significant Rayleigh scattering will be possible in this material for radii $a=10$ nm and larger.

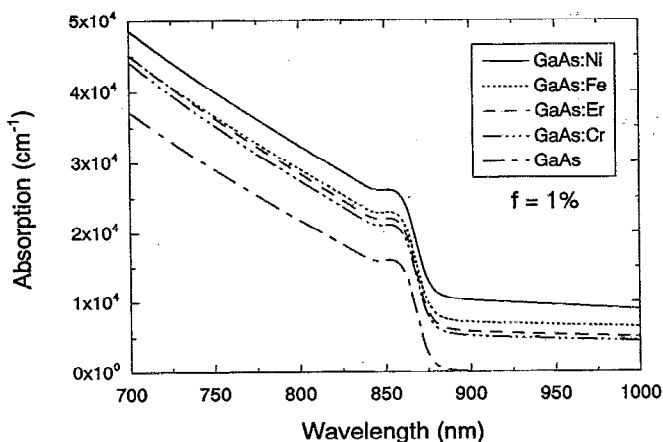


FIG. 6. Total extinction for $f=1\%$ Ni, Fe, Cr, and Er in GaAs is characterized by a weakly wavelength-dependent background absorption added to the bulk GaAs absorption. There is no evidence of a plasmon feature near the band edge.

doped fiber-optic applications. In the case of the transition metals and erbium, the particulate extinction adds a relatively constant background to the semiconductor band edge absorption. Therefore, many of the technologically significant metal species in GaAs do not produce significant resonance features in the optical extinction of metal/semiconductor composites (with spherical metal inclusions).

IV. ARSENIC PRECIPITATES IN GaAs

An important new addition to the class of metal/semiconductor composites is GaAs:As grown using molecular beam epitaxy on substrates at reduced temperatures.⁴¹ The low-temperature-growth (LTG) incorporates up to 2% volume fraction excess arsenic in the GaAs matrix while maintaining excellent crystalline quality.³ After growth, the material is annealed and the arsenic forms precipitates.²⁹ By controlling the growth temperature and the anneal temperature and duration, the size and spacing of the arsenic precipitates can be controlled. This detailed control over the precipitates, in conjunction with the high crystalline quality of the semiconductor matrix, is the basis of "precipitate engineering."

Preliminary studies of the optical properties of GaAs:As have uncovered several interesting aspects. The LTG materials have ultrafast lifetimes below 100 fs, making them attractive for high-speed optoelectronic switches and photodetectors.⁴² The electro-optic properties of the band edge have exhibited unexpected enhancements under dc applied fields.³² Below the band edge absorption, the material shows a significant photoresponse that is attributed to internal photoemission from the metallic clusters,³⁴ which makes the material a prospective far-infrared detector. In view of these optical properties and applications, it is important to understand the role that particulate extinction plays in these materials.

The calculated total absorption of GaAs:As is shown in Fig. 7, compared with the band edge absorption of pure GaAs. The Maxwell-Garnet theory is also included. The ar-

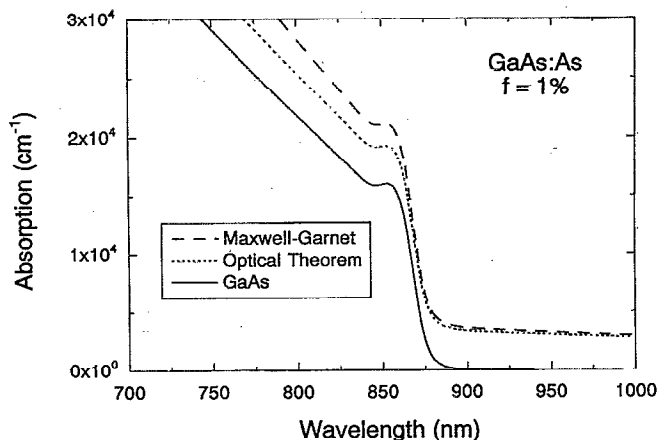


FIG. 7. Extinction of GaAs:As. The qualitative features are the same as for the non-noble metals.

senic clusters behave in a qualitatively similar fashion to the transition metals shown in Fig. 6. Arsenic is a weak metal, with an unusual Fermi surface⁴³ and significant interband transitions that remove the resonance condition in Eq. (11). However, the particulate absorption, shown in Fig. 8, extends significantly below the band edge, with appreciable absorption at 1500 nm, in the range of erbium-doped fiber technology.

V. CONCLUSIONS

In conclusion, small metal spheres imbedded in a semiconductor host medium have resonant absorption that is shifted to the near infrared and is broadened by the absorption in the host medium. The noble metals Au, Ag, and Cu have distinctly sharper resonances than non-noble metals, such as Cr, Fe, Ni, As, and Er. Interband transitions in the non-noble metals introduce positively contributions to the real dielectric function, preventing the excitation of surface plasmon modes in the small metal spheres using near-infrared photon energies. In all the metal-semiconductor

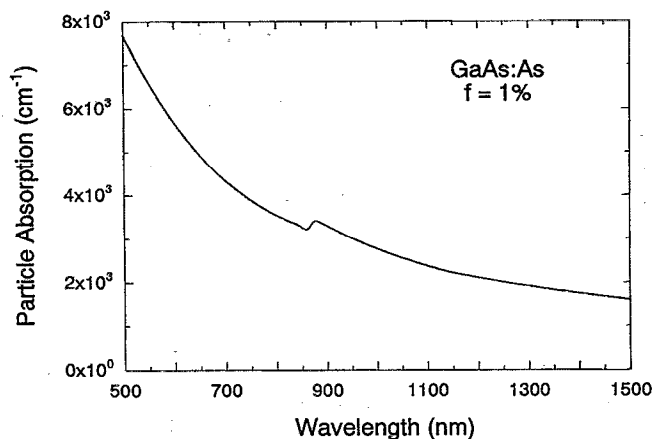


FIG. 8. Particulate absorption for As nanoclusters in GaAs. Significant absorption extends out to $1.5 \mu\text{m}$.

composites discussed here, significant optical extinction is predicted for metal volume fractions as small as 1%.

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