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Surface plasmon enhanced second harmonic response from gold clusters embedded in an alumina matrix

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The second order nonlinear response from 4 nm diam gold clusters embedded in an alumina matrix deposited on a pure silica substrate has been recorded as a function of the wavelength of the fundamental incident beam. The spectrum exhibits a narrow resonance band peaked at 520 nm as a result of the coupling of the second harmonic field with the surface plasmon of the particles. The nonlinear second harmonic response of gold clusters is found to be blueshifted compared to the bulk, due to the finite size effects on the cluster optical properties, as already observed with the linear response. Furthermore, this nonlinear response appears to be well described with a simple free electron model where the valence electrons only participate through the screening of the ionic cores, owing to the weakness of the interband transition contribution. *© 1998 American Institute of Physics.* [S0021-8979(98)01820-9]

INTRODUCTION

Embedding gold clusters of nanometer dimensions in a dielectric matrix provides a simple way to study the linear and nonlinear optical properties of these particles.[1] The main feature of the linear optical response of this new material is the collective excitation of the free conduction band electrons, known as the surface plasmon excitation, observed in the visible region of the spectrum for gold clusters. At shorter wavelengths, it has however been shown that the excitation of electrons from the localized 5*d* valence band to the conduction band (interband transitions) strongly affect the spectrum, leading to a steady increase of the optical absorption of the particles.[2] Moreover, in the size range of a few nanometers, it is well known that the optical properties of clusters are strongly affected by finite size. For example, the surface plasmon resonance in the absorption spectra of gold clusters embedded in an alumina matrix is shown to be damped and blueshifted with decreasing cluster size.[2]

Whereas the linear optical properties of noble metal particles have been investigated for a long time, little is known of the nonlinear optical behavior of these systems despite recent growing interest. Beyond the fundamental motivations based on the elucidation of the different contributions to the nonlinear electronic susceptibilities and their evolution as a function of the size of the nanoparticle, potential applications in many fields of research, but more particularly in chemical catalysis, may be forseen. Optical second harmonic generation (SHG) has already been used in the past to monitor catalytic reactions at the surface of metal clusters by the study of metal diffusion into polymer films.[3] Owing to its surface specificity and sensitivity, optical surface SHG (SSHG) is an ideal tool to probe adsorbate–substrate interactions under different environmental conditions where the substrate itself does not generate any contribution to the SH response.[4–6] This case is obtained with centrosymmetric substrates, since in the electric dipole approximation, SHG is forbidden in centrosymmetric media. Furthermore, this nonlinear technique has been proved to be highly sensitive to the surface plasmon excitation of metals.[7,8] Recently, Träger and co-workers[9] have studied the optical second harmonic generation by supported sodium clusters as a function of cluster size during the nucleation. They showed that SH radiation was detectable for particles as small as approximately 1 nm. Thus, the SHG technique seems to be efficient to study nonlinear optical properties from a few nanometer diameter clusters where finite size effects are observed.

In this article, we report on the optical surface second harmonic response from gold clusters with diameter sizes of about 4 nm embedded in an alumina matrix. This work directly follows a previous article reporting on the second harmonic response from gold colloids of about 6 nm in diameter at the air/toluene interface.[10] In the latter work, the observation of a strong narrow resonance in the SH spectrum was reported and discussed in light of a simple free conduction electron model. In this article, we report a similar resonance peak in the SH spectrum for the supported matrix embedded gold clusters but emphasis on the interband transition region is given. Indeed, it is observed that the SH response is free from the interband transition contribution whereas the linear optical spectrum exhibits a strong contribution from those

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transitions. Moreover, the SH resonance is found blueshifted compared to the bulk, due to the small size of the particles and in agreement with the linear response.

EXPERIMENT

The sample preparation and characterization have already been published elsewhere.[2] Briefly, the gold clusters were generated by means of a laser vaporization source, the free cluster size being determined by the conditions in the source chamber. The clusters were then deposited on a pure silica plate by the low energy cluster beam deposition (LECBD) technique.[11] The dielectric matrix of alumina was evaporated with an electron gun and simultaneously deposited on the substrate. Transmission electron microscopy (TEM) micrographs of the gold/alumina composite samples showed a random distribution of nearly spherical clusters, with average sizes between 2 and 4 nm in diameter, with volumic fractions between 1.5% and 6.5% depending on the deposition conditions.[2] In the present study, the samples were characterized and shown to have a mean diameter of 4 nm with a volumic fraction of 6.5%, the thickness of the deposited film being a few nanometers. Linear optical absorption measurements were performed on similar composite films and displayed a broad absorption band lying around 2.36 eV, i.e., 525 nm, as a result of the surface plasmon excitation, and a monotonous increase in the ultraviolet (UV) region of the spectrum due to the interband transitions coming into play; see Fig. 1.

The SHG experiments were carried out at the surface of the gold clusters/alumina composite films in the reflection mode with an angle of incidence of 74° between the incident beam and the surface normal. The source laser used was a nanosecond Nd^{3+}-YAG laser pumping an optical parametric oscillator (Spectra-Physics GCR 170–10 pumping a MOPO 710), the system delivering pulses of 5 ns duration at a repetition rate of 10 Hz in the wavelength range of 900–1200 nm. The unfocused beam typically had an energy of several mJ per pulse. The incident beam was telescoped (with a ratio 3:1) and directed to the composite film. The SH signal generated in the visible range of the spectrum was collected through a lens and a couple of filters to reject any residual fundamental light. The signal was passed through a monochromator and detected with a gated photon counter, each point being recorded for at least 100 s. The wavelength of the fundamental beam was tuned from 900 to 1200 nm (i.e., 1.03–1.38 eV) by small steps of about 4–5 nm. In all these measurements, great care was taken to prevent any residual SH light from the optics and any background light coming from the laser system by the systematic use of filters and noise measurements.

RESULTS AND DISCUSSION

In Fig. 2 is displayed the intensity of the SH response as a function of the SH wavelength for the gold/alumina composite film samples. Silica does not exhibit any significant absorbance in any of the regions of interest of the spectrum, neither between 900 and 1200 nm nor between 400 and 600 nm, and as expected no SH signal was recorded from the pure air/silica substrate interface. In the presence of the composite film, the SH response spectrum, however, displayed a strong resonance peak at about 520 nm (i.e., 2.39 eV), the resonance peak being located at a position close to the peak of the linear absorption spectrum. This resonance peak corresponds to a resonance enhancement of the SH signal with the surface plasmon of the gold clusters. The main feature noticed in Fig. 2 for the SH spectrum is the surface plasmon resonance band which is much narrower than the one observed in the linear absorption spectrum. Indeed, the SH spectrum exhibits a steady decrease in intensity on the blue side of the spectrum whereas the linear absorption spectrum displays a steady increase in absorbance. This latter increase in the linear absorption spectrum is attributed to the interband transitions which dominate in this region of the spectrum. These transitions correspond to the excitation of core electrons from the localized $5d$ valence band to the $6sp$ conduction band of the metal and appear at wavelengths below 640 nm (i.e., above 1.95 eV) in the spectrum of 4 nm diam gold clusters.[12] The appearance of these transitions is well known for noble metal clusters and has also been reported for silver, for example. They are known to strongly affect the absorption spectrum through the broadening of the surface plasmon resonance and the enhanced absorption in the UV range of the spectrum. It therefore appears that the interband transition contribution of the clusters is negligible in front of the conduction band free electron contribution in the SH spectrum whereas the reverse is true for the linear spectrum.

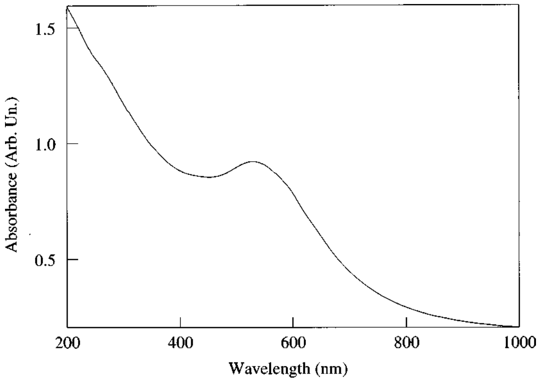

FIG. 1. Optical absorption spectrum in the region of the surface plasmon resonance for 4 nm diam gold clusters embedded in an alumina matrix and deposited onto a pure silica substrate.

The question of the origin of the SH response from metals, and more precisely from metal particles, has already been discussed in the literature.[13–17] The SH electric field originates from a second harmonic polarization consisting of two contributions, one of electric dipole origin and one of electric quadrupole origin. In the electric dipole approximation, no SH generation can occur from media possessing the property of centrosymmetry. Hence the dominant contribution is the next order term in the multiple expansion of the nonlinear polarization, that is, the electric quadrupole contribution. However, at interfaces where the inversion symmetry is broken, the electric dipole contribution is no longer forbidden and must be reinstated in the nonlinear polarization.

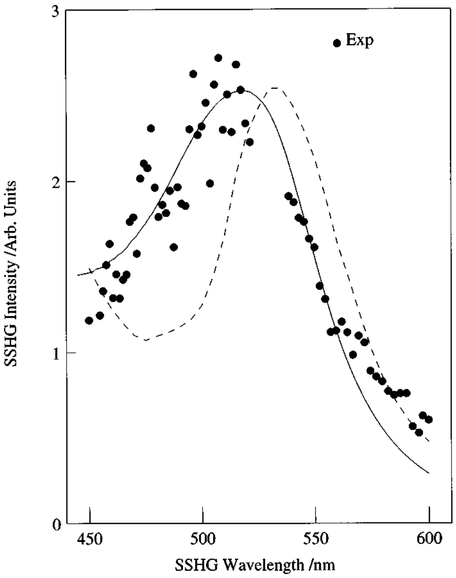

FIG. 2. SHG spectrum for 4 nm diam gold clusters embedded in an alumina matrix and deposited onto a pure silica substrate (shown by dots). The experimental errors are in the range of 15%. The solid line is the free electron gas model. The dotted line is the SH response of the gold clusters if they were retaining a dielectric constant given by the experimental data of Johnson and Christy (see Ref. 22). Both curves are modeled using Eqs. (2) and (3) and the term in brackets in Eq. (4) multiplied by ω^6.

This form of nonlinear polarization is valid at planar metal surfaces, and the electric dipole contribution is usually monitored to study surface effects like adsorption for example. At metal particle surfaces, however, this electric dipole contribution again vanishes for symmetry reasons when the metal particles are spherical and are of a diameter much smaller than the wavelength of the incoming light. In this case, indeed, the particle may act as a centrosymmetric medium for this electric dipole contribution. Any deviation from a centrosymmetric geometry should in principle again allow this contribution. This case may be achieved for nonspherical particles obtained through deposition on a substrate for example, or for spherical particles sitting at the interface between two centrosymmetric media, the two half-spheres forming the colloidal particle becoming distinguishable if in contact with a distinct medium. Although this latter case was indeed obtained in work on gold colloids at the air/toluene interface,[10] this should not be the case here where the particles, about 4 nm in diameter, are completely embedded in a matrix several nanometers thick. Also, TEM micrographs showed that the particles were nearly spherical and therefore we will hereafter assume that the electric dipole contribution to the nonlinear polarization is negligible. Hence, following the work of Bloembergen *et al.*, the nonlinear polarization of electric quadrupole origin is[15]

$$\begin{aligned}\mathbf{P}^{NL}(2\omega) &= (\gamma_{\mathrm{pl}}+\gamma_{\mathrm{val}})\nabla[\mathbf{E}(\omega)\mathbf{E}(\omega)]\\ &\quad+(\beta_{\mathrm{pl}}+\beta_{\mathrm{val}})\mathbf{E}(\omega)[\nabla\mathbf{E}(\omega)],\\ &= \gamma_{\mathrm{eff}}\nabla[\mathbf{E}(\omega)\mathbf{E}(\omega)]+\beta_{\mathrm{eff}}\mathbf{E}(\omega)[\nabla\mathbf{E}(\omega)], \quad (1)\end{aligned}$$

where γ_{pl} and γ_{val} are, respectively, the parameters of the so-called volume contribution from the plasma and the valence electrons and β_{pl} and β_{val} are the corresponding parameters for the so-called surface contribution. Such a denomination for the two terms entering the polarization may indeed be quite misleading, particularly in the case of the surface plasmon resonance since the plasmon is localized at the surface. Bloembergen *et al.* also determined the four parameters as[15]

$$\beta_{\mathrm{pl}}=\frac{e}{2m^*\omega^2}=\frac{4\omega^2}{\omega_P^2}\,\gamma_{\mathrm{pl}}, \qquad (2)$$

for the conduction band electrons where the plasma frequency ω_P is defined as $\omega_P^2=ne^2/\epsilon_0 m^*$ with the plasma electron density n, the charge of the electron e, and the electronic effective mass m^*. The valence electrons also contribute to the total nonlinear polarization even in the limit of long wavelengths through the screening of the ionic cores. In a rather general manner, and in order to account for interband transitions, the deeper-lying valence electrons are introduced with a specific contribution as

$$\beta_{\mathrm{val}}=-2\gamma_{\mathrm{val}}\approx\frac{3}{4en_{\mathrm{core}}}[\chi^{(1)}_{\mathrm{core}}(\omega)]^2, \qquad (3)$$

where n_{core} is the density of the valence electrons and $\chi^{(1)}_{\mathrm{core}}(\omega)$ is the linear susceptibility at frequency ω. In the infrared (IR) range of the exciting light, the valence contribution can be reduced to a screening effect (negligible interband transition) and the parameter $\chi^{(1)}_{\mathrm{core}}(\omega)$ becomes independent of the frequency.

The intensity of the SH signal from gold particles can then been derived from the nonlinear polarization as given in Eq. (1). For small spherical clusters, with diameters smaller than the wavelength of the incoming electromagnetic field, this is achieved with the use of Mie theory where the calculations are performed in spherical coordinates. This work has been carried over by Agarwal and Jha and they have reported the following total SH intensity integrated over the total solid angle:[18]

$$\begin{aligned}S=192\pi^2c|E^{(i)}|^4\left(\frac{2\omega R}{c}\right)^6&\left(\left|\frac{\gamma_{\mathrm{eff}}}{[\epsilon_{\mathrm{eff}}(\omega)+2][\epsilon_{\mathrm{eff}}(2\omega)+2]}\right|^2\right.\\ &\left.+\frac{36}{5}\left|\frac{\beta_{\mathrm{eff}}[\epsilon_{\mathrm{eff}}(\omega)-1]}{[\epsilon_{\mathrm{eff}}(\omega)+2]^2[2\epsilon_{\mathrm{eff}}(2\omega)+3]}\right|^2\right), \qquad (4)\end{aligned}$$

where $E^{(i)}$ is the amplitude of the incident fundamental electric field at the surface of the cluster, R is the radius of the particle, and c is the velocity of light. This form is valid in the limiting case of a vanishing ratio R/λ but other authors have derived the full Mie theory.[19,20] Furthermore, Eq. (4) is valid for particles in vacuum. To take into account the effect of a dielectric medium, the use of the effective dielectric constant $\epsilon_{\mathrm{eff}}=\epsilon/\epsilon_m$ is required. The dielectric constants of the alumina matrix, extracted from ellipsometry measurements, are found to be almost constant with the wavelength, and we took a constant value of 2.6. Note that this value is slightly smaller than the pure alumina one (3.1),[21] as a result of the porosity of the matrix.[2]

The experimental data given in Fig. 2 have been tentatively modeled according to Eqs. (1)–(4) using the experimental dielectric constant data from Johnson and Christy[22] obtained from vacuum-evaporated gold thin film measurements (dotted line). A strong surface plasmon resonance is obtained with a narrower band than the experimental one. Furthermore, the surface plasmon resonance peak is shifted to the red as compared to the experimental data by approximately 15 nm. Note that other experimental values from gold thin films available in the literature[23] lead to a similar behavior. Thus, it appears that the bulk dielectric constant data of gold are not accurate enough to reproduce both the position and the bandwidth of the resonance peak of gold clusters. A similar result has already been observed with the linear response of gold clusters. Indeed, the comparison between the absorption spectrum and the corresponding Maxwell–Garnett calculation (with bulk dielectric function data) showed a blueshift and a damping of the measured resonance compared to the calculated one. This discrepancy has been attributed to finite size effects (limitation of the mean free path of the conduction electrons when the cluster radius becomes smaller), which affect the dielectric function of the clusters. Thus, finite size effects also appear clearly on the nonlinear optical response of gold clusters, and lead to the same effects as already observed with the linear optical response.

However, the nonlinear optical response is markedly different from the linear optical response for those clusters, since the SH response is dominated by the surface plasmon enhancement and not the interband transition. This behavior was already observed for larger gold nanoparticles, ones of about 6 nm diameter, at the air/toluene interface.[10] Thus, in order to find a more suitable description of the experimental data, we used a free electron gas model. The dielectric function of gold clusters as a function of the wavelength is then given by[24]

$$\epsilon(\omega)=1+\chi^{(1)}_{\text{core}}-\frac{\omega_P^2}{\omega^2+i\omega\left(\dfrac{1}{\tau_{\text{bulk}}}+\dfrac{\nu_F}{L_{\text{eff}}}\right)}, \tag{5}$$

where τ_{bulk} is the electron relaxation time in the bulk of the gold metal, v_F is the electron velocity at the Fermi level, and L_{eff} is the effective electronic mean free path. In principle, this value directly scales with the diameter of the particles. In these calculations, the following numerical values were used: $\omega_P=1.36\times 10^{16}\ \text{s}^{-1}$, $\tau_{\text{bulk}}=9.1\times 10^{-15}$ s, $v_F=1.39\times 10^{6}\ \text{m s}^{-1}$, and $L_{\text{eff}}=4$ nm, already used in previous works.[25,26] Using Eq. (5) for the free electron gas dielectric constant, the best agreement with the experimental values was obtained for $\chi^{(1)}_{\text{core}}=8.7$ (solid curve). The value obtained for $\chi^{(1)}_{\text{core}}$ is in good agreement with the values found in the literature, $\chi^{(1)}_{\text{core}}=8.9$ by Innes and Samble[26] and $\chi^{(1)}_{\text{core}}=11.0$ by Johnson and Christy[22] in the limit of long wavelengths where these latter data should follow a free electron gas-like behavior. Note that the position and the bandwidth of the plasmon peak are well reproduced. The bandwidth of the SH resonance band is given by two contributions to the SH response of the samples, the so-called ''volume'' and ''surface'' contributions, [see Eq. (4)]. These contributions have similar magnitude, the larger being the volume contribution. Owing to the vanishing denominator at the surface plasmon resonance, however, the volume contribution becomes a surface contribution again since the surface plasmon is localized at the surface of the particle within a Fermi wavelength. The surface contribution, as may be seen from Eq. (4), gets its resonance for the quadrupole plasmon resonance, whose condition is $2\epsilon(2\omega)+3=0$, and thus has its maximum located at 502 nm, at a different position from that of the volume contribution which is located at 536 nm. As a result, the SH resonance is broadened as compared to what would be obtained with the volume contribution only. This broadening is also clear when compared with the model using Johnson and Christy data for the dielectric constant where the difference in the bulk and surface term is much larger. Hence, the optical nonlinear response of gold clusters appears to be well described with a simple free electron gas model model where the valence electrons only participate through the screening of the ionic cores, owing to the weakness of the interband transition contribution.

CONCLUSION

The observation of the second harmonic response from gold clusters of 4 nm diameter embedded in an alumina matrix and deposited on a silica substrate has been made with the second harmonic wavelength tuned in the vicinity of the surface plasmon resonance, the wavelength analysis of which indicates that the interband transitions do not play a significant role in the total SH response. Rather, the nonlinear optical behavior of the clusters is dominated by the free electron gas-like response of the conduction band, the surface plasmon resonance being much sharper than the interband transition contribution. Also, size effects may be responsible for a small blueshift of the SH resonance peak compared to the location expected from the bulk gold dielectric constant, as already observed with the linear response. These results are of importance in future studies of small clusters since these experimental conditions, whereby the fundamental wavelength lies far away from the interband transition region, look very promising for characterization of the electronic properties of the clusters. Indeed, the surface plasmon, which yields a narrow peaked resonance in the SH spectrum, is very sensitive to the surrounding medium owing to its surface localization. Variations in the position and width of the resonance should then become easily accessible. Application to the study of functionalized clusters for catalysis is one example that may be forseen for future studies.[27–29]

ACKNOWLEDGMENT

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[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995), and references therein.

[2] B. Palpant, B. Prével, J. Lermé, E. Cottancin, M. Pellarin, M. Treilleux, A. Perez, J. L. Vialle, and M. Broyer, Phys. Rev. B **57**, 1963 (1998).

[3] J. Y. Zhang, Y. R. Shen, D. S. Soane, and S. C. Freilich, Appl. Phys. Lett. **59**, 1305 (1995).

[4] Y. R. Shen, Annu. Rev. Phys. Chem. **40**, 273 (1989).

[5] K. B. Eisenthal, Annu. Rev. Phys. Chem. **43**, 627 (1992).

[6] R. M. Corn and D. A. Higgins, Chem. Rev. **94**, 107 (1994).

[7] C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. Lett. **46**, 145 (1981).
[8] A. Wokaun, J. G. Bergman, J. P. Heritage, A. M. Glass, P. F. Liao, and D. H. Olson, Phys. Rev. B **24**, 849 (1981).
[9] T. Götz, M. Buck, C. Dressler, F. Eisert, and F. Träger, Appl. Phys. A: Mater. Sci. Process. **60A**, 607 (1995).
[10] R. Antoine, P. F. Brevet, H. H. Girault, D. Bethell, and D. J. Schiffrin, Chem. Commun., 1901 (1997).
[11] A. Perez, P. Mélinon, V. Dupuis, P. Jensen, B. Prével, J. Tuaillon, L. Bardotti, C. Martet, M. Treilleux, M. Broyer, M. Pellarin, J. L. Vialle, B. Palpant, and J. Lermé, J. Phys. D **30**, 709 (1997).
[12] B. Palpant, B. Prével, J. Lermé, M. Pellarin, E. Cottancin, A. Gagnaire, F. Karolak, M. Treilleux, A. Perez, J. L. Vialle, and M. Broyer (unpublished).
[13] F. Brown and R. E. Parks, Phys. Rev. Lett. **16**, 507 (1966).
[14] G. T. Boyd, Th. Raising, J. R. R. Leite, and Y. R. Shen, Phys. Rev. B **30**, 519 (1984).
[15] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).
[16] S. S. Jha and C. S. Warke, Phys. Rev. **153**, 751 (1967).
[17] F. R. Aussenegg, A. Leitner, and H. Gold, Appl. Phys. A: Mater. Sci. Process. **60A**, 97 (1995).
[18] G. S. Agarwal and S. S. Jha, Solid State Commun. **41**, 499 (1982).
[19] X. M. Hua and J. I. Gersten, Phys. Rev. B **33**, 3756 (1996).
[20] D. Östling, P. Stampfli, and K. H. Bennemenn, Z. Phys. D **28**, 163 (1993).
[21] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, New York, 1985, 1991), Vols. I and II.
[22] P. B. Johnson and R. W. Christy, Phys. Rev. B **8**, 4370 (1972).
[23] M. L. Thèye, Phys. Rev. B **2**, 3060 (1970).
[24] P. Mulvaney, Langmuir **12**, 788 (1996).
[25] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, int. ed. (Holt Saunders, New York, 1976).
[26] R. A. Innes and J. R. Sambles, J. Phys. F **17**, 277 (1987).
[27] M. Brust, J. Fink, D. Bethell, D. J. Schiffrin, and C. Kiely, Chem. Commun., 1655 (1995).
[28] M. J. Hostetler, S. J. Green, J. J. Stokes, and R. W. Murray, J. Am. Chem. Soc. **118**, 4212 (1996).
[29] S. A. Harfenist, Z. L. Wang, M. M. Alvarez, I. Vezmar, and R. L. Whetten, J. Phys. Chem. **100**, 13904 (1996).