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Composites Formed by Implantation of Sb in High Purity Silica**

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF METAL NANOCUSTER-SILICA COMPOSITES FORMED BY IMPLANTATION OF SB IN HIGH PURITY SILICA

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ABSTRACT

The linear and nonlinear optical properties of a series of Sb nanometer dimension metal colloids in silica were measured. The colloids were fabricated by the implantation of Sb in silica with nominal doses of 3, 6 and 9×10^{16} ions/cm² at 320 keV. The linear optical response was measured from 200 to 900 nm. The nonlinear optical properties were measured using the z-scan technique at wavelengths of 596 and 617 nm. The results are compared to linear and nonlinear properties of a sample implanted with 6×10^{16} Ag ions/cm². Both absorption and the nonlinear index of refraction increase with increasing volume fraction for the Sb implanted samples. The lower linear absorption and comparable nonlinear index of refraction for the Sb colloid-glass composites may be better for devices than composites using metal colloids that have a surface plasmon resonance.

INTRODUCTION

Effective medium theory for small non interacting particles in a dielectric [1, 2] predicts substantial enhancements of the nonlinear response of the composite for optical frequencies near the surface plasmon resonance (SPR) frequency. This enhancement is due to local field effects and results from dielectric confinement. A significant problem with metal colloid-glass composites for device applications is that both the linear and nonlinear absorption in general increase near the surface plasmon resonance frequency. This increase in absorption has deleterious effects on the relative figures of merit for devices operating near these SPR frequencies using these materials.[3, 4] Even away from the SPR frequencies, linear and nonlinear absorption can limit device possibilities. The ability to form metal colloid-glass composites with large nonlinear responses while exhibiting smaller absorption losses could significantly improve the feasibility of these materials for optical devices.

Here we report the modification of the optical response of nanometer dimension metal colloids formed by the implantation of Sb. Sb was chosen because its electronic structure does not give rise to a surface plasmon resonance in the 200 to 900 nm wavelength region.[5, 6] We compare the results for the Sb metal colloids to those for Ag colloids.

EXPERIMENTAL

Sb ions were sequentially implanted in Corning 7940 high purity silica substrates. The Sb ions were implanted at 320 keV with a substrate temperature of $\sim 270^\circ$ K and a current density of ~ 2 μ amps/cm². Nominal doses of 3, 6 and 9×10^{16} ions/cm² were used. For comparison an Ag implanted sample with a nominal dose of 6×10^{16} ions/cm² was fabricated. The Ag ions were implanted at 305 keV with substrate temperatures of $\sim 270^\circ$ K and a current density of ~ 2 μ amps/cm². The implantation energy for the Ag was chosen from calculations using TRIM 89[7] to target an energy that would have the same depth of implantation as the Sb.

Rutherford backscattering (RBS) measurements with 2.3 MeV He⁺⁺ ions were used to measure the depth profiles of implanted species. Transmission electron microscopy was done on all samples. Details of sample preparation are reported elsewhere.[8] Standard bright field (BF)

imaging was used to observe the implanted layer and selected area electron diffraction was used to analyze the metal colloids formed in the silica wafers.

Linear optical absorption measurements were made at room temperature in air from 900 to 200 nm using a dual beam spectrometer (Cary 5). All samples were measured using an unimplanted sample in the reference beam. The absorption spectra were measured at three different positions on each sample and are reported as optical density (OD). The scatter in these measurements at these different positions was less than 1%. The nonlinear index of refraction was measured at 596 and 617 nm for the samples using the Z-scan method.[9] The laser used for these experiments was a cavity dumped tunable dye laser with a 6 ps pulse duration. The laser was operated at 3.8 MHz. The average power was 250 mW for 596 nm and 200 mW for 617 nm in the TEM₀₀ mode and the peak irradiance for a focal spot of 25 mm radius was 5×10^8 W/cm² for 596 nm and 4×10^8 W/cm² for 617 nm. The error in these measurements was less than 20 %.

RESULTS

The distributions of ions as a function of depth from the surface are gaussian in shape with a peak at 0.14 microns for the Sb samples. The full width at half maximum (FWHM) for the Sb implanted sample is 0.14 microns. This value, 0.14 microns, was used to calculate values for n_2 and α . For the Ag implanted sample the distributions of ions as a function of depth from the surface is also gaussian in shape with a peak at 0.13 microns and FWHM of 0.09 microns.

Figure 1 and 2 show the bright field transmission electron micrographs for the 6×10^{16} Sb implanted sample and the 6×10^{16} Ag implanted sample respectively. Approximately spherical colloids are formed in both implantations.

Figure 1: Electron transmission micrographs for sample implanted with 6×10^{16} Sb sample. Mean particles size is 5.7 ± 1.8 nm with a standard deviation of 1.6 nm.

Figure 2: Electron transmission micrographs for sample implanted with 6×10^{16} Ag sample. Mean particles size is 13.5 ± 1.8 nm with a standard deviation of 8.8 nm.

Figure 3 shows the optical spectra as a function of photon wavelength for the samples implanted with Sb and Ag. The absorption in all the samples increases with decreasing wavelength with an approximate $1/\lambda$ dependence and exhibits no distinguishing features. The total absorption throughout the spectral region increases with increasing dose. Figure 3 also compares the 6 Sb and 6 Ag implanted samples. The absorption spectra for the Ag implanted sample is dominated by an absorption peak at ~ 400 nm and a shoulder at ~ 520 nm.

Figure 3: Optical density as a function of wavelength for samples implanted with $3, 6$ and 9×10^{16} Sb and a sample implanted with 6×10^{16} Ag.

Table I lists the linear and nonlinear optical coefficients for the samples at 596 nm for all three Sb samples and the 6Ag sample. Table I also lists the linear and nonlinear optical coefficients for the samples at 617 nm for the 6Sb and 6Ag implanted samples. The nonlinear coefficients were calculated using the formalism from reference [8].

Table I

Linear and Nonlinear Optical Coefficients @ 596 nm and 617 nm

Sample 10^{16} ions/cm ²	α (cm ⁻¹) $\times 10^4$ (596 nm/617 nm)	n_2 (cm ² /W) $\times 10^{-9}$ (596 nm/617 nm)	β (cm/W) $\times 10^{-4}$ (596 nm/617 nm)
3 Sb	0.13	N.D.	N.D.
6 Sb	0.55 / 0.51	0.4 / 0.4	N.D. / N.D.
9 Sb	1.36	0.9	N.D.
6 Ag	3.17 / 2.20	0.9 / 0.4	-0.2 / N.D.

At 596 nm the linear absorption coefficient, α , and the nonlinear index of refraction, n_2 , increase with increasing Sb concentration. In comparison, the 6Ag sample has the same n_2 as the 9Sb sample however the 6Ag sample has more than twice the linear absorption. Nonlinear absorption was not detected in any of the Sb implanted samples, while the 6Ag sample shows a saturation of the nonlinear absorption, β , as indicated by the negative sign in Table I. At 617 nm n_2 for the 6Ag sample has decreased a factor of ~ 2 while its linear absorption decreased $\sim 30\%$ compared to that at 596 nm. The n_2 for the 6Sb sample remains constant though α decreases by $\sim 10\%$ from the values measured at 596 nm.

Discussion:

The optical properties of these metal colloid -glass composites can be described using effective medium theory for small non interacting particles in a dielectric.[1,2] The linear response for colloids with diameters less than $\lambda/20$, where λ is the wavelength of the incident radiation, is reasonably described by effective medium theory in the electric dipole approximation [1,10] and is given by

$$\alpha = \frac{18\pi n_d^3}{\lambda} \cdot \frac{p\epsilon_2}{[\epsilon_1 + 2n_d^2]^2 + \epsilon_2^2} \quad (1)$$

where α is the absorption coefficient, $\epsilon(\lambda) = \epsilon_1 + i\epsilon_2$ is the dielectric constant of the metal, p is the volume fraction of the metal particles and n_d is the index of refraction of the dielectric host. The absorption is expected to exhibit a maximum at the surface plasmon resonance frequency for which the condition $\epsilon_1 + 2n_d^2 = 0$ is met. The surface plasmon resonance frequency depends on the electronic properties of the metal colloids and on the index of refraction of the host dielectric, n_d . The third order nonlinear susceptibility, $\chi_{\text{eff}}^{(3)}$, can be expressed as[1]

$$\chi_{\text{eff}}^{(3)} = pf_c^2(\omega)|f_2(\omega)|^2\chi_m^{(3)} \quad \text{with} \quad f_c(\omega) = \frac{3n_d^2}{\epsilon_1 + 2n_d^2} \quad (2)$$

where $f_c(\omega)$ is the local field factor and $\chi_m^{(3)}$ is the nonlinear susceptibility of the metal colloids. The index of refraction and the intensity dependent term are related to the above quantities by[11]

$$n = n_0 + n_2 I \quad \text{and} \quad n_2 = \frac{12\pi}{n_0} \text{Re}[\chi_{\text{eff}}^{(3)}] \quad (3)$$

where n_0 is the linear index of refraction and n_2 is the intensity dependent component. From equation (2) a potentially large enhancement of the effective nonlinear susceptibility and in turn n_2 near or at the surface plasmon resonance frequency is possible due to local field effects.

While part of the linear absorption in the ultraviolet may be attributed to defect centers, based on prior work we expect that the absorption will be dominated by the presence of the metal colloids.[10]

From equation (1) the optical properties depend explicitly on the electronic properties of the metal colloids through $\epsilon(\lambda)$ and on the index of refraction of the host dielectric, n_d , while depending implicitly on particle size through $\epsilon(\lambda)$. Assuming that n_d remains constant for the host

dielectric, we will not consider it further and will instead consider the metal particle contributions to the absorption.

From Figure 1 the TEM measurements reveal that the particles are approximately spherical in shape for all samples. Because the shape is similar for all implants we do not expect any changes in the optical spectra based on particle shape differences. However the colloids are larger for the 6Ag implanted sample than for the Sb implanted samples.

For Sb implanted samples there is no indication of a surface plasmon resonance absorption in the optical absorption spectra. We attribute the increasing absorption with decreasing photon wavelength in these samples to the formation of Sb nanometer dimension colloids. The dielectric properties of the Sb clusters are such that the condition $\epsilon_1 + 2n_2^2 = 0$ is not satisfied[5] and therefore these samples do not exhibit a distinct surface plasmon resonance absorption feature. However the spectra does exhibit an approximate $1/\lambda$ dependence behavior expected from equation (1) for nanometer dimension colloids. We attribute the increasing absorption with dose to the increase in volume fraction of metal colloids formed with increasing dose.

The optical spectra of the 6Ag sample exhibits the characteristic absorption due to the surface plasmon resonance of nanometer dimension Ag colloids.[7,10,12] We attribute the peak at 400 nm in the 6Ag sample to Ag colloids < 25 nm in diameter.[10,12] With an increase in particle size additional higher order terms than the dipole term from Mie theory are required to describe the absorption observed. We attribute the shoulder at 520 nm in the 6Ag sample to the quadrupole term from Mie theory.[7,10,12]

The optical properties of the Sb implanted samples are clearly different than those of the Ag sample. From equation (1) the volume fraction of the metal present and the dielectric function, $\epsilon(\lambda) = \epsilon_1 + i\epsilon_2$, of the metal clusters are expected to effect the absorption. We readily observe the effect of the volume fraction of metal colloids by the increase in absorption with dose in the Sb implanted samples. Colloid size and volume fraction increase with dose. For increasing dose more ions are found in colloid form. While some of the ions may be in colloids too small to be observed (< 2 nm in diameter) in the lower doses the increase in dose reduces the presence of these smaller colloids.[8] This reduction is thought to occur from the additional heating with the longer implantation time of the larger doses. The total concentration of metal ions in the 6Sb and 6Ag samples is the same. The difference in the optical properties are then the result of a different electronic structure.

The nonlinear index of refraction, n_2 , at 596 nm increases with the dose in the Sb implanted samples. Both the linear absorption and n_2 increase approximately at the same rate with dose. These changes are in reasonable agreement with equation 1 and 2 that show that α and n_2 increase with volume fraction of the metal ions. Nonlinear absorption is not detected in the Sb implanted samples. The n_2 for the Ag implanted sample has the same value as for the 9Sb implanted sample but with larger linear absorption and a saturated nonlinear absorption.

The value for n_2 at 617 nm has not changed for the 6Sb compared to that at 596 nm. The value for n_2 at 617 nm for the 6Ag sample decreases 60 %. While the n_2 's for the 6Sb and 6Ag samples are the same at 617 nm the 6Ag sample has ~ 4 times the linear absorption. The lack of change in n_2 for the 6Sb sample and the rapid decrease in n_2 for the 6Ag with wavelength suggest that different mechanisms may dominate the nonlinear responses for these elemental colloids.

Reference 1 gives a review of the various mechanisms. Using n_2/α as a figure of merit (FOM), at 596 nm the 6Sb, 9Sb and 6Ag samples have FOM of 0.7, 0.6 and 0.3. As the Sb samples do not have a surface plasmon resonance and we are far off the surface plasmon resonance frequency for the Ag colloids we anticipate only minimal enhancements of the nonlinear response due to local field effects. We conclude the behavior of the values of n_2 as a function of λ arise from

differences in the $\chi_m^{(3)}$ of the metal colloids. These results suggest there are metal nanometer dimension colloids, that while not showing a SPR enhancement at wavelengths away from the SPR, can have better figures of merit.

The z-scan technique measures both the thermal and electronic contributions to the nonlinear index. Previous nonlinear measurements on Cu colloids with similar absorption formed by ion implantation have been reported.[8] Using similar wavelength, power, repetition rate and pulse width of the laser the thermal loading of the sample was found not to dominant the response

because of the relatively long interpulse spacing (263 ns) even though the 6 ps pulse duration is comparable to the electron thermalization times of the Cu colloids.[8] Based on the above discussion we conclude that the nonlinear response is either dominated by or has a significant contribution from electronic mechanisms.

CONCLUSIONS

From these results we suggest that some metallic colloids even though they do not exhibit a surface plasmon resonance frequency may be better for devices because of lower linear absorption yielding substantially better figures of merit for device applications.

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