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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF METAL NANOCLUSTER-SILICA COMPOSITES FORMED BY SEQUENTIAL IMPLANTATION OF AG AND CU

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ABSTRACT

Nanometer dimension metal colloids were formed in silica by sequential implantation of Ag and Cu ions. The Ag and Cu were implanted with relative ratios of Ag to Cu of 9:3, 6:6, and 3:9. The total nominal dose was $12x10^{16}$ ions/cm^2. TEM techniques were used to examine colloid size and size distributions. The linear optical response was measured from 200 to 900 nm. The nonlinear optical properties were measured using the z-scan technique at a wavelength of 570 nm. The linear and nonlinear optical properties were found to be dependent upon the relative ratio of sequentially implanted Ag to Cu. The results are consistent with effective medium theory.

INTRODUCTION

Sequential ion implantation offers a unique method of forming nanometer dimension metal particles in glass.[1,2,3] It has been demonstrated to significantly alter the composition of the metal particles formed, and hence the electronic structure of the colloids, by forming nanometer dimension "alloy" colloids. As both linear and nonlinear optical properties are a function of the electronic structure of the colloids, sequential implantation can significantly affect the optical response of these composites.[4,5,6] The ability to form these "alloy" metal-glass composites could significantly improve the feasibility of these materials as optical devices by enhancing the nonlinear response and by changing the character of that response.[7] In this paper we report the effects of the relative ratio of sequentially implanted Ag to Cu on the formation of the nanosize particles and on the optical response of the composites formed.

EXPERIMENTAL

Ag and Cu ions were sequentially implanted in Corning 7940 high purity silica substrates. The implantation energies were chosen from calculations using TRIM 89[8] to target energies that would overlay the depths of implantation for each metal. The Ag ions were implanted first at 305 keV with substrate temperatures of ~ 270° K and a current density of ~ 1.3 μamps/cm^2. The Cu ions were implanted sequentially at 160 keV with substrate temperatures of ~ 270° K and a current density of ~ 3 μamps/cm^2. The doses used were in ratios, Ag to Cu, of 9:3, 6:6, and 3:9. Nominal total doses as determined by current integration for the three samples were $12x10^{16}$ (Ag + Cu) ions/cm^2. Rutherford backscattering (RBS) measurements with 2.3 MeV He^{++} ions were used to measure the depth profiles of implanted species. Planar view samples for transmission electron microscopy (TEM) were prepared by conventional techniques reported elsewhere.

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. The scatter in the absorption coefficient at these different positions was less than 5%.

The nonlinear index of refraction was measured at 540 nm for the samples using the Z-scan method described previously. 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

patterns from the samples reveal that two distinct metallic crystal structures exist in the implanted layer. The predominant features of the polycrystalline ring patterns were representative of the face centered cubic (FCC) Ag lattice and FCC metallic Cu lattice. The average particle size increases with increasing Cu dose. The mean size is 14.4, 15.2, and 17.5 nm respectively for samples with Ag/Cu ratios of 9/3, 6/6, and 3/9. The 9/3 sample exhibits a bimodal distribution with the smallest distribution centered at ~ 12 nm and the largest at ~ 60 nm. The 6/6 Ag/Cu sample exhibits a bimodal distribution with the smallest particles centered at a depth of ~ 15 nm and the largest at ~45 nm. The frequency of occurrence of particles in these two samples drops by a factor of ~ 9 for particle sizes in the part of the distribution containing the largest particles. The 3/9 ratio Ag/Cu sample exhibits more of a skewed distribution centered at ~ 17 nm than a bimodal distribution as observed in the other two samples. However, while small in number, the largest individual particles are in the sample with the 9/3 ratio of Ag/Cu. The 6/6 ratio sample has the next largest individual particles, and the 3/9 sample the smallest individual particles.

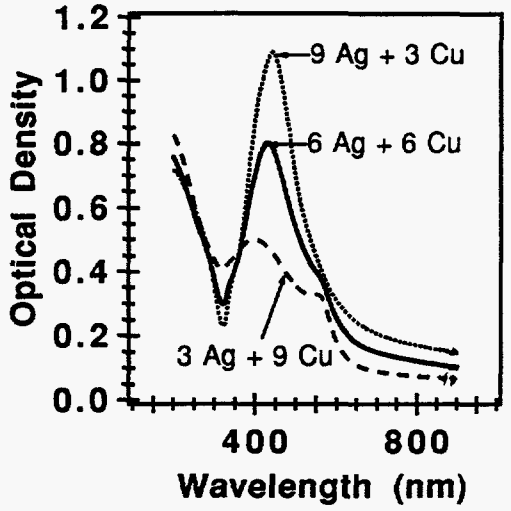

Figure 3. Optical Density as a function of wavelength for different ratios of Ag to Cu.

The optical density for the three samples is shown in figure 3 as a function of wavelength. The dominant peak is at ~ 410 nm and shifts to longer wavelengths, ~ 440 nm with increasing Ag concentration. A second peak at ~ 575 nm grows with increasing Cu concentration. This peak appears as a shoulder in the lowest Cu dose sample, but is clearly discernible for the highest Cu dose. The values for the absorption coefficient, α, at 570 nm are given in Table I. The normalized far field transmission for a small aperture as a function of sample position relative to the focal plane of the lens shows a decreasing then increasing intensity while moving through the focal plane indicating a positive intensity dependent index of refraction, n_2. All samples displayed similar behavior. The z-scan results can be related to n_2 using the formalism of references.[9,10] The values for n_2 were calculated for a wavelength of 570 nm assuming an effective thickness of 0.15 microns. The values for n_2 increase with Cu dose and are given in Table I.

Table I Linear and Nonlinear Optical Coefficients Measured at 570 nm

Sample	α (cm^{-1})	n_2 (cm^2/W)	β (cm/W)
9 Ag to 3 Cu	5.9×10^4	1.0×10^{-9}	3.8×10^{-5}
6 Ag to 6 Cu	5.4×10^4	1.3×10^{-9}	-0.9×10^{-5}
3 Ag to 9 Cu	4.6×10^4	1.6×10^{-9}	-1.4×10^{-5}

The samples were also measured using an open aperture. The open aperture measurements saturate for Ag doses > 6×10^{16} Ag ions/cm^2. From the open aperture results the two photon absorption coefficient, β, can be determined. Table I gives the values calculated for β at 570 nm.

DISCUSSION

Effective medium theory can be used to describe the optical response of nanometer dimension metal particles embedded in a dielectric medium. The linear response for colloids with diameters

less than $\lambda/20$, where λ is the wavelength of the incident radiation, is reasonably described by Mie scattering theory in the electric dipole approximation,[11,12] and is given by

$$\alpha = \frac{18\pi n_d^3}{\lambda} \cdot \frac{p\varepsilon_2}{[\varepsilon_1 + 2n_d^2]^2 + \varepsilon_2^2} \tag{1}$$

where α is the absorption coefficient, $\varepsilon(\lambda) = \varepsilon_1 + i\,\varepsilon_2$ 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 peak at the surface plasmon resonance frequency for which the condition $\varepsilon_1 + 2n_d^2 = 0$ is met. The surface plasmon resonance frequency depends explicitly on the electronic properties of the metal colloids and on the index of refraction of the host dielectric, n_d, while depending implicitly on particle size.

The third order nonlinear susceptibility, $\chi_{eff}^{(3)}$, of small non interacting particles in a dielectric can also be expressed using effective medium theory as [13]

$$\chi_{eff}^{(3)} = p f_c^2(\omega) |f_2(\omega)|^2 \chi_m^{(3)} \quad \text{and} \quad f_c(\omega) = \frac{3n_d^2}{\varepsilon_1 + 2n_d^2} \tag{2}$$

where $f_c(\omega)$ is the local field factor and $\chi_m^{(3)}$ is the nonlinear susceptibility of the metal clusters. There is a potentially large enhancement of the effective nonlinear susceptibility due to local field effects at surface plasmon resonance frequency. The index of refraction and the intensity dependent term are related to the above quantities by[14]

$$n = n_o + n_2 I \qquad \text{and} \qquad n_2 = \frac{12\pi}{n_o} \mathrm{Re}[\chi_{eff}^{(3)}] \tag{3}$$

where n_o is the linear index of refraction and n_2 is the intensity dependent component.

Previously we explained the optical absorption of sequentially implanted Ag and Cu samples with the same nominal dose by the formation of small alloy particles of Ag-Cu < 30 nm in mean diameter. We reported a shift in the surface plasmon resonance compared to samples implanted separately with Ag or Cu ions. This shift was attributed to the formation of a metastable Ag-Cu alloy when the ions were sequentially implanted. Here we observe a small increasing blue shift and decreasing intensity with increasing Cu concentration for the peak at ~440 nm.. For the sample implanted with the highest dose of Cu ions a second peak is clearly discernible. A simple superposition of the absorption in samples with single element implantations at the same doses of Ag and Cu under the same conditions does not yield the absorption observed in the sequentially implanted samples. While the peak at ~ 440 nm is similar to that due to Ag particles formed by single element Ag implantation into silica, the shifts to longer wavelengths and the changes in intensity and shape of the peak suggest that the Ag and Cu interact with each other. The peak at ~575 nm is similar to that in Cu implanted samples for similar doses, but is clearly affected by the presence of the Ag. While some of the broad absorption exhibited by the 9/3 Ag/Cu sample on the long wavelength side of the spectrum may be due to the small number of larger particles formed, all the absorption spectra appear to be dominated by the more numerous small particles whose sizes are more nearly represented by the mean particle size.[6] We conclude, based on the small differences in average particle size and the similar frequency of occurrence of the dominant particle sizes in all samples, that the changes observed in the linear optical spectra are due for the most part to interaction of the sequentially implanted ions to form metastable phases of varying concentrations of Ag and Cu. The compositions formed depend on the relative amounts of Ag and Cu sequentially implanted.

The values calculated for n_2 increase with increasing Cu dose and decreasing optical absorption as seen in Table I. Enhancements of the nonlinear susceptibility of the composite are expected on or near the surface plasmon resonance of the metal colloids. The measurements of n_2 at 570 nm are

closer to the surface plasmon resonance for Cu particles than they are to the surface plasmon resonance of Ag particles(~ 400 nm). We suggest that this increase in n_2 is due to the presence of increasingly Cu rich particles with increasing Cu dose. However the presence of the Ag has a substantial impact on the nonlinear response of these composites. For a sample implanted with Cu to a dose of $6x10^{16}$ ions/cm^2 under similar conditions, we obtain a value of $3.4x10^{-10}$ cm^2/W for n_2. This is a factor of ~ 5 smaller than the sequentially implanted sample with the same Cu dose. While there is twice the nominal dose of metal ions present in the sequentially implanted sample, this factor of ~ 5 difference is too large to be accounted for by concentration differences alone, as n_2 increases linearly with volume fraction, p (equation 1). We suggest the increase in n_2 is due to changes in the composition of the metal colloids with changing relative concentrations of implanted Ag to Cu. The presence of the Ag ions appears to enhance the nonlinear response of the Cu near its surface plasmon resonance frequency.

The values for n_2 increase by ~ 60 % while the absorptivity decreases by ~ 25 % for the change in relative concentrations of Ag to Cu used in this work. We would expect the opposite behavior for an n_2 dominated by a thermal mechanisms, i.e., the values for n_2 would increase with increasing absorptivity due to increased thermal loading of the sample. As the electronic structure of the colloids and hence the optical response will be determined by the metal species,[7,15] the observation that n_2 increases with Cu to Ag ratio while α decreases indicates that the nonlinear response is related to the electronic structure of the colloids. Nonlinear measurements on Cu colloids formed by ion implantation have been reported previously.[6] Using similar wavelength, power, rep rate, and pulse width of the laser, the thermal loading of the sample was found not to dominate 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. Based on the above discussion we conclude that the nonlinear response observed for these sequentially implanted samples is dominated by an electronic mechanism. With increasing Ag dose β saturates indicating a change in the nature of the two photon response. The role of the relative ratio of Ag to Cu in the two photon absorption processes is currently being studied.

In summary the presence of the Ag has a significant impact on the linear and nonlinear optical properties. These results suggest that it may be possible to significantly alter and enhance the optical responses of one metal colloid near its surface plasmon resonance frequency by the addition of a second element.

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