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OPTICAL PROPERTIES OF MULTI-COMPONENT CADMIUM-SILVER NANOCLUSTER COMPOSITES FORMED IN SILICA BY SEQUENTIAL ION IMPLANTATION

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ABSTRACT

The formation and optical properties of nanometer dimension metal colloid composites formed by the sequential implantation of Cd then Ag and by single element implantations of Cd and Ag in silica were characterized by transmission electron microscopy (TEM) and optical spectroscopy. A nominal dose of 6×10^{16} ions/cm^2 as determined by current integration was used for both ion species . The doses used for the sequential implantations were a 1 to 1 ratio of Cd to Ag. Sequential implantations of Cd and Ag led to the formation of both multi-component metal nanoclusters and elemental nanoclusters. The electron diffraction measurements indicated that the polycrystalline particles of Ag_5Cd_8 and elemental Ag were formed. The optical response was consistent with results expected from effective medium theory.

INTRODUCTION

Nanometer-size metallic particles have been used for millennia to color melt-glasses for decorative purposes and for passive optical elements such as filters. Particle sizes and size distributions as well as glass coloration can be controlled across a broad region of the visible spectrum by thermal annealing.[1] Metal nanocluster composites can also be fabricated by ion implantation, a technique which permits control of depth, concentration and, to some extent, chemical state of the implanted ions.

Ion beam fabrication of nanocluster glass composites for optical devices is of recent interest because of its ability to form thin films in dielectrics containing a high volume fraction (> 1%) of metal colloids with well defined vertical and horizontal dimensional control.[2] A significant problem with metal nanocluster-glass composites for device applications is that both linear and nonlinear absorption, in general, increase near the surface plasmon resonance frequency (SPR) and with increasing volume fraction of metal. This increase in absorption has deleterious effects on the relative figure of merit for potential devices operating near the SPR frequencies in these materials.[3] Even away from the SPR frequencies, linear and nonlinear absorption can limit device performance. The ability to form unique metal colloid-glass composites with larger volume fractions of metal that exhibit smaller linear and nonlinear absorption losses could significantly improve the feasibility of these materials for optical devices.

Using sequential ion implantation we can modify the composition and structure of the nanoclusters to form multi-component and coated nanoclusters.[4-6] In this work we report the modification of the optical response of nanometer dimension metal colloids formed by sequential implantation of Cd and Ag with a 1 to 1 ratio of ions. This ratio for implantation was chosen because Cd and Ag form a stable compound, AgCd.

EXPERIMENT

Cd and Ag ions were sequentially implanted in Corning 7940 high purity silica substrates. The implantation energies were chosen from calculations using TRIM 89 [7] to target energies that would overlay the depths of implantation for each metal. The sequentially implanted samples were made by implanting Cd followed by implantation of Ag. For all samples the Cd ions were implanted at 320 keV at a substrate temperature of ~ 0° C and a current density of ~ 2 μamps/cm^2.

The Ag ions were implanted at 305 keV at the same substrate temperature and a current density. Substrates were held at 0° C to maintain a uniform substrate temperature during implantation and to minimize the effects of beam heating. Doses used were 6 x10^{16} ions/cm^2 for both Cd and Ag implantations. For the sequentially implanted sample the total nominal dose as determined by current integration was 12x10^{16} ions/cm^2. Single element implantations for each ion species at the same dose were made for comparison.

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 the TEM sample preparation have been reported elsewhere.[4] Standard bright field (BF) imaging in the plan view 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. The scatter in the absorption coefficient at these different positions was less than 2%. The nonlinear index of refraction was measured at 596 nm using the Z-scan method described in reference [8]. 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 in the TEM$_{00}$ mode and the peak irradiance for a focal spot of 25 mm radius was ~5x10^8 W/cm^2. The error in these measurements in all cases was less than 20%.

RESULTS

The RBS spectra for the samples with Cd, Ag and Cd/Ag show that for the single element implantations the distributions as a function of depth from the surface are gaussian in shape with the peaks at ~ 0.14 microns. The Cd implanted sample has a slightly broader distribution of the implanted ions than the Ag implanted sample, while the Ag is more sharply peaked than the Cd. The full width at half maximum (FWHM) is ~ 0.1 microns for the Cd implanted sample and ~0.09 microns for the Ag implanted sample . The RBS spectrum for the sequentially implanted sample is a slightly skewed gaussian with the peak at ~ 0.15 microns. Its FWHM is the same as for the Cd implanted sample. The dose as measured by RBS for the single element implantations is 5.0 and 4.7x10^{17} ions/cm^2 for the Cd and Ag samples respectively. The total dose as measured by RBS for the Cd/Ag sample is 1.0x10^{17} ions/cm^2 which agrees within error with the expected dose based on the single element implantations. We attribute differences between nominal doses and RBS measured doses to sputtering.

Bright field images obtained for the Cd, Ag, and Cd/Ag samples are shown in Figure 1.

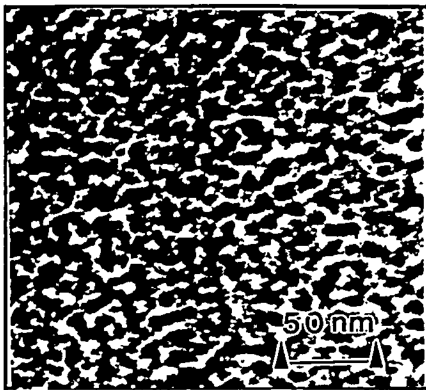

Figure 1a Electron transmission micrographs for 6Cd sample

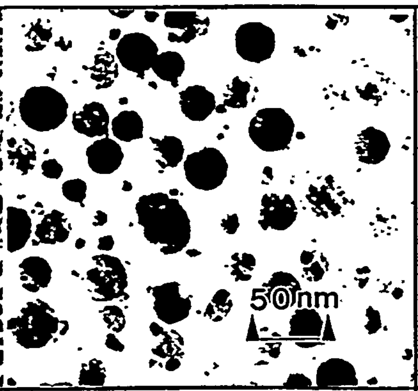

Figure 1b Electron transmission micrographs for 6Ag sample

Figure 1c Electron transmission micrographs for 6Cd/6Ag sample

The microstructure of the Cd sample displays approximately spherical colloids with a narrow particle size distribution and no particles > 15 nm in diameter. Mean particle size for the Cd sample is 7.2 ± 1.8 nm with a standard deviation of 2.2 nm. Selected area diffraction patterns reveal that the colloids are polycrystalline Cd. The microstructure of the Ag sample also displays approximately spherical colloids. Mean particle size is 13.5 ± 1.8 nm with a standard deviation of 8.8 nm. A significant number of the Ag particles are larger than 25 nm. Selected area diffraction patterns reveal that the colloids are polycrystalline FCC Ag. The microstructure of the Cd/Ag sample displays a high density of approximately spherical colloids with a narrow particle size distribution and no particles > 25 nm in diameter. Mean particle size for the Cd/Ag sample is 8.6 ± 1.8 nm with a standard deviation of 3.0 nm. Selected area diffraction patterns reveal that the colloids are polycrystalline. The d-spacings obtained from the ring pattern for the Cd/Ag sample are most consistent with a composition consisting of Ag_5Cd_8 and elemental Ag. Due to measurement uncertainty unambiguous identification of the composition of the multi-component phase of Ag-Cd is not possible.

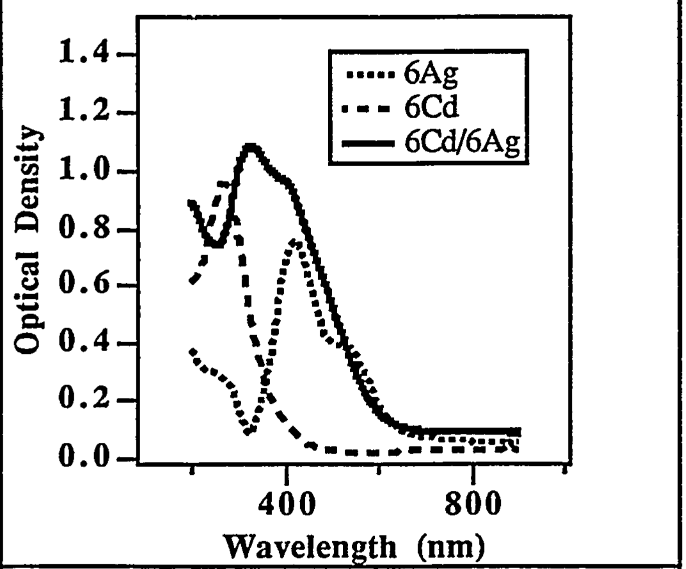

Figure 2: Optical density as a function of wavelength for 6Cd, 6Ag and 6Cd/6Ag samples.

Figure 2 shows the optical density as a function of wavelength for samples implanted with 6Ag, 6Cd and 6Cd/6Ag.The absorption spectrum for the 6Cd sample has a peak at ~ 271 nm with decreasing absorption for increasing wavelengths. The sequentially implanted sample has two superimposed peaks at ~ 321 nm and ~ 412 nm. Table I gives the linear absorption, α, the nonlinear index of refraction, n_2, and the nonlinear absorption, β, for the samples at 596 nm. The nonlinear coefficients were calculated using the formalism from reference [8]. At 596 nm the values for n_2 are largest in the 6Cd/6Ag sample even though it has ~ 20 % less linear absorption than the 6Ag sample.

While the 6Ag sample shows a saturation of the nonlinear absorption, β, as indicated by the negative sign in Table I, the sequentially implanted sample did not have detectable nonlinear absorption for the laser intensity levels used here. The 6Cd sample has the lowest n_2 but also the lowest linear absorption with no detectable nonlinear absorption.

Table I
Linear and Nonlinear Optical Coefficients Measured at 596 nm

Sample	α (cm^{-1})	n_2 (cm^2/W)	β (cm/W)
6Cd/6Ag	$2.58x10^4$	$1.4x10^{-9}$	N.D.
6Cd	0.31	0.5	N.D.
6Ag	3.13	0.9	$-0.2x10^{-4}$

DISCUSSION

The single element implantations lead to the formation of polycrystalline nanoclusters with different microstructures. The Cd nanoclusters have a significantly smaller size distribution and the mean nanocluster size is less than for the Ag nanoclusters. The largest Ag particles observed are ~ 40 nm in diameter while for Cd the largest particles are ~ 14 nm. We attribute these differences to the difference in diffusion rates for the two ions in silica. Ag is known to be a fast diffusing ion in silica. Particle size in the Cd/Ag sample is smaller than in the Ag sample and more like that for the Cd implanted sample. We suggest that the Cd nanoclusters formed in the first part of the sequential implantation are forming nucleation sites for the Ag ions resulting in the smaller Cd/Ag clusters.

There are two possible mechanisms responsible for the optical absorption in the metal nanocluster -silica composites. The first source of absorption is defects created during ion implantation. While part of the absorption in the ultraviolet may be attributed to these defect centers, based on prior work we expect that the absorption due to this mechanism will be dominated by the presence of the metal colloids.[4,5]

The second absorption mechanism is the interaction of the metal particles with the incident radiation. Effective medium theory can be used to describe the optical response of nanometer dimension metal particles embedded in a dielectric medium as a function of the properties of the metal colloids and the host dielectric.[1-3] The linear response for colloids with diameters less than 20 nm is reasonably described by Mie scattering theory in the electric dipole approximation[9, 10] and is given by

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

where α is the absorption coefficient, $\varepsilon(\lambda) = \varepsilon_1 + i\,\varepsilon_2$ is the dielectric function of the metal, p is the volume fraction of the metal colloids, 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 where the condition $\varepsilon_1 + 2n_d^2 = 0$ is satisfied as a function of photon wavelength. The surface plasmon resonance frequency depends explicitly on the electronic properties of the metal colloids through $\varepsilon(\lambda)$ and on the index of refraction of the host dielectric, n_d, while depending implicitly on particle size through $\varepsilon(\lambda)$.[19, 20] Assuming that n_d remains constant for the host dielectric, we will not consider it further and will instead focus on the metal particle contributions to the absorption. For particles greater than 20 nm in diameter higher order terms than the dipole term may be needed to account for the absorption.[19, 20] We expect that changes in the dielectric function due to composition changes will give rise to alterations in the optical absorption in accordance with equation (1).[11]

The third order nonlinear susceptibility, $\chi_{eff}^{(3)}$, can be expressed as[1]

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

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[12]

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

where n_o 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 surface plasmon resonance frequency is possible due to local field effects. We also expect changes in $\chi_m^{(3)}$ with changes in the electronic structure of the nanoclusters.

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 nanoclusters are noticeably larger for the 6Ag implanted sample than for the 6Cd/6Ag and the 6Cd samples. From electron diffraction measurements the single implantations of Cd and Ag result in the formation of randomly oriented polycrystalline metallic nanoclusters of Cd and Ag respectively. For the sequentially implanted sample the electron diffraction pattern is that of a phase of Ag/Cd and elemental Ag. From the phase diagram of Ag and Cd there are two possible stable compounds with compositions AgCd and Ag_5Cd_8. Electron diffraction results are most consistent with the formation of a multi-component nanocluster of Ag_5Cd_8 and elemental Ag being formed. Because of the formation of a compound phase we do expect changes in the optical absorption of the composite in accordance with equation (1) and this is observed in the optical spectra.

The optical spectra of the Ag only implanted glasses exhibit the characteristic absorption due to the surface plasmon resonance of nanometer dimension Ag colloids. We attribute the peak at 403 nm in the Ag implanted sample to Ag colloids < 25 nm in diameter. The absorption shoulder at 530 we attribute to an additional higher order absorption term in Mie theory, i.e., the quadrupole term. The optical spectrum for the Cd implanted sample exhibits a peak at 271 nm. We attribute this peak to the SPR of small metallic nanoclusters of Cd observed in the TEM micrographs. All nanoclusters were less than 20 nm in diameter and we expect only a dipole absorption term.

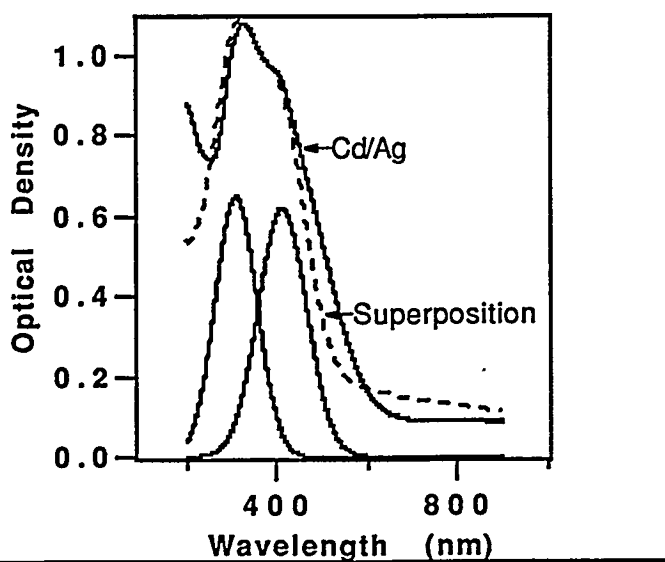

Figure 3: Optical density as a function of wavelength for 6Cd/6Ag and the superposition of peaks at 310 and 412 nm

The optical spectra in Figure 2 suggest the presence of two peaks. We attribute the absorption in the 6Cd/6Ag sample to the superposition of a peak at 310 nm due the formation of Ag_5Cd_8 and the peak at 412 nm due to elemental Ag. These assignments are consistent with electron diffraction observations. A curve fit of a superposition of a peak at 310 nm and 412 nm with background absorption gives a reasonable fit to the data as seen in Figure 3.

The nonlinear index of refraction, n_2, at 596 nm increases with the sequential implantation of Ag with Cd. The value of n_2 for the 6Cd/6Ag sample is ~ 3 times greater than the n_2 for the 6Cd sample and 55 % greater than that for the 6Ag sample. Nonlinear absorption is no longer detectable and most importantly this increase in n_2 occurs with a decrease in total absorption, ~ 20%, compared to the 6Ag sample which is significantly lower than the absorption of a superposition of the 6Ag and 6Cd samples. While the volume fraction of metal ions has increased, it cannot account for the changes in the nonlinear response observed. In particular, nonlinear absorption is no longer detected in the 6Cd/6Ag sample. This is opposite to what would be expected if the volume fraction of metal ions was the dominant factor. These results indicate that the electronic structure of the multi-component colloids formed has resulted in significant changes in $\varepsilon(\lambda)$ and $\chi_m^{(3)}$ of the colloids. This is consistent with a change in the composition of the nanoclusters.

CONCLUSIONS

Sequential ion implantation can be used to form stable multi-component metal compound phases. The linear and nonlinear optical properties of these multi-component nanoclusters are modified from that of their single element counterparts. This technique may open vistas for the fabrication of unique composites whose nonlinear responses are enhanced while the linear and nonlinear absorption are simultaneously reduced. Such composites would have improved figures of merit in device applications.

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