

Modification of the Optical Properties of Glass by Sequential Ion Implantation

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Abstract

The linear and nonlinear optical properties of a series of samples formed by the sequential implantation of Ti, O and Au are examined. Energies of implantation for each ion were chosen using TRIM calculations to insure overlap of the ion distributions. The Ti was implanted with nominal doses of 1.2 and 2×10^{17} ions/cm². The samples were implanted with oxygen to the same nominal dose as the Ti. Au was then implanted with a nominal dose of 6×10^{16} ions/cm². The samples were subsequently annealed in oxygen at 900 °C for two hours. The Ti and O are incorporated into the host network, while the Au forms nanosize colloids. The presence of the Ti in the substrate causes a shift in the surface plasmon resonance frequency of the Au metal colloids as well as an increase in the nonlinear response of the composites. The results are interpreted in terms of effective medium theory.

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Introduction

Ion implantation offers a unique method of forming nanometer dimension metal particles in glass. In particular it offers the ability to form metastable phases of the colloids, increased volume fraction of metal and well defined depth control compared with conventional processing. Sequential implantation of different metal species can be used to significantly alter the composition of the nanometer dimension metal particles formed and/or to alter the substrate composition before formation of the metal particles.¹

Effective medium theory can be used to describe the optical response of nanometer dimension metal particles embedded in a dielectric medium.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 Mie scattering theory in the electric dipole approximation,³ 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 peak 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, $\chi_{\text{eff}}^{(3)}$, of small non interacting particles in a dielectric also can be expressed using effective medium theory as²

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

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where $f_c(\omega)$ is the local field factor and $\chi_m^{(3)}$ is the nonlinear susceptibility of the metal colloids. There is a potentially large enhancement of the effective nonlinear susceptibility due to local field effects at the surface plasmon resonance frequency. The index of refraction and the intensity dependent term are related to the above quantities by⁴

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

where n_0 is the linear index of refraction and n_2 is the intensity dependent component.

Neeves and Birnboim⁵ extend the effective medium theory to include particles in a nonlinear medium. Their extension indicates a significant enhancement of the nonlinear response of the colloids is possible. The addition of polarizable ions to silica can increase its the nonlinear response.⁶ Using sequential implantation of suitable polarizable ions and colloid forming ions it may be possible to alter the host medium and enhance the nonlinear response of the colloids both on and off the surface plasmon resonance. Here we report the effects of sequentially implanting Ti, O and Au ions in silica.

Experimental

Samples were implanted with Ti⁺⁺ at 320 keV at a current density of 5 $\mu\text{amps}/\text{cm}^2$ to doses of 1.2 and 2.0×10^{17} ions/ cm^2 . The samples were implanted with oxygen at 120 keV with the same dose as the Ti. A group of the different dose Ti and O implanted samples was sequentially implanted with Au⁺ ions at 1.1 MeV and current density of ~ 1 $\mu\text{amps}/\text{cm}^2$ to a dose of 6×10^{16} ions/ cm^2 and a group of the different Ti+O implanted samples were not implanted with Au. One sample was implanted only with Au⁺ ions at 1.1 MeV to a dose of 6×10^{16} ions/ cm^2 . All the samples were annealed in oxygen at 900 °C for 2 hours. Implantation energies were chosen using TRIM 89 calculations to overlay the depth distributions of the implanted ions. Ion backscattering techniques with 2 MeV He⁺ ions were used to measure the ion depth profiles.

Optical measurements were made at room temperature in air from 900 to 200 nm using a Cary 5 dual beam spectrometer. All samples were measured using an unimplanted sample in the reference beam. The spectra are reported as optical density. The absorption spectra were measured at three different positions on each sample. The scatter in the absorption due to these different positions was less than 2%.

The nonlinear index of refraction was measured for the samples using the Z-scan method.⁷ Z-scan measures the normalized transmission as a function of laser intensity as the sample is moved through the focal plane of a long focal length lens (150 mm in these experiments). The laser used for these experiments was a cavity dumped tunable dye laser with a ~ 6 picosecond pulse duration. The laser was operated at 3.8 MHz. The average power was 200 mW in the TEM₀₀ mode. The peak irradiance for a focal spot of 25 μ m in radius was ~ 4.4x10⁸ W/cm².

Results

Figure 1 shows the backscattering measurements for the samples implanted with 2.0x10¹⁷ Ti ions/cm², 2.0x10¹⁷ O ions/cm² and 6x10¹⁶ Au ions/cm² and annealed at 900 °C for 2 hours. The RBS measurements show a gaussian profile for the Ti and Au implants. Profiles were similar and the concentrations were within 85 % of the nominal dose implanted for all samples.

The optical spectra for the sample implanted with 6x10¹⁶ Au, the sample implanted with 2x10¹⁷ Ti and 2x10¹⁷ O and the sample implanted sequentially with 2x10¹⁷ Ti, 2x10¹⁷ O and 6x10¹⁶ Au are shown in figure 2. The sample implanted with Ti and oxygen has minimal absorption in the 350-900 nm region but has strongly increasing absorption with decreasing wavelength in the 350 to 200 nm region. The sample implanted with Au only exhibits a peak at ~ 530 nm and increasing absorption with decreasing wavelength. The sample implanted with Ti-O-Au exhibits a peak at ~ 560 nm and increasing absorption

with decreasing wavelength. Figure 3 shows the optical density in the 350 nm - 900 nm region for samples sequentially implanted with Au and with the different doses of Ti+O as well as the sample implanted with only Au. The increasing Ti concentration causes a increase in the absorption in the ~ 560 nm peak region of the spectra.

In the z-scan measurements 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 reference 7. The values for n_2 increase with increasing Ti dose. All samples were also measured using an open aperture. Only one sample showed detectable two photon absorption, β . Table 1 lists the values calculated for n_2 and β at 592 nm.

Discussion:

The RBS spectra indicate that the ion distributions of Au while not ideally centered were overlapped by the Ti implantations. The spectra for the Ti+O samples show no indication of particle formation but do show strong absorption in the 200- 300 nm region where the charge transfer bands of Ti^{3+} , Ti^{4+} would absorb and where defects induced by the implantation process would exhibit absorption.^{8,9} Annealing at 900 °C is expected to remove most defects associated with absorption in this region. The sample implanted with Au has the characteristic surface plasmon resonance absorption for Au nanosize particles at ~ 530 nm.¹⁰ From these results we conclude that the Ti is incorporated in the network and the Au forms nanosize metal colloids.

A similar process in the Ti, O and Au implanted samples where the Ti is incorporated into the network and the Au forms nanometer dimension particles during annealing can explain both the observed linear and nonlinear results. The incorporation of the Ti gives rise to the change in the index of refraction of the host substrate resulting in the observed shift in the wavelength of the surface plasmon resonance of the Au colloids to ~

560 nm (figure 3) as suggested by equation 1. Accompanying this shift is a change in the magnitude of the surface plasmon resonance absorption. This increase in magnitude is indicative of increasing particle size.¹¹ We estimate based on the optical spectra particle sizes to range from 5 to 10 nm.^{10,11}

The amount of Au implanted was constant resulting in a constant volume fraction of Au present in all the samples and hence can not account for the increase in n_2 observed. Prior work has shown that changes in Au particle size from 5 to 12 nm resulted ~ 15 % changes in n_2 while we observe here a factor of 2 increase with the implantation of Ti.¹¹ We conclude the observed increases in n_2 are too large to be accounted for by particle size differences only. However, an enhancement of the nonlinear response of the Au colloids can be expected both on and of the surface plasmon resonance in the more nonlinear medium formed as the Ti is incorporated into the silica.⁵ Consequently we attribute the increase in n_2 to the formation of a more polarizable medium in the silica with increasing Ti concentration resulting in the enhanced n_2 response.

For small apertures, the Z-scan method measures contributions to n_2 from both electronic and thermal mechanisms.⁷ The calculations reported do not distinguish between the contributions from thermal and electronic components to the nonlinear index hence the values for n_2 may have contributions from both mechanisms. However, based on similar thermal loading of the samples, the speed of the laser pulses (6ps), the low rep rate of the laser (3.8MHz) and low two photon absorption, we suggest that the nonlinear response is mostly electronic.¹²

Conclusion

Using sequential implantation of polarizable ions and metal colloid forming ions we have demonstrated that it is possible to shift the frequency of the surface plasmon resonance of the metal colloids and significantly increase their nonlinear response.

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Table I

Linear and Nonlinear Optical Coefficients Measured at 592 nm

Sample	n_2 (cm ² /W)	β (cm/W)
2x10 ¹⁷ Ti+ O 6x10 ¹⁶ Au	1.2x10 ⁻⁹	5.3x10 ⁻⁶
12x10 ¹⁷ Ti+ O 6x10 ¹⁶ Au	0.9x10 ⁻⁹	N.D.
2x10 ¹⁷ Ti+ O	N.D.	N.D.
6x10 ¹⁶ Au	0.6x10 ⁻⁹	N.D.

N.D. not detected

Figure Captions

Figure 1

Ion distribution as a function of distance from the surface for sample implanted with 2×10^{17} Ti, 2×10^{17} O and 6×10^{16} Au.

Figure 2

Optical density as a function of wavelength for a samples with 6×10^{16} Au, with 2×10^{17} Ti+ 2×10^{17} O and with 2×10^{17} Ti+ 2×10^{17} O+ 6×10^{16} Au.

Figure 3

Optical density as a function of wavelength for samples A) 2×10^{17} Ti+ 2×10^{17} O+ 6×10^{16} Au, B) 1.2×10^{17} Ti+ 1.2×10^{17} O and C) 6×10^{16} Au.

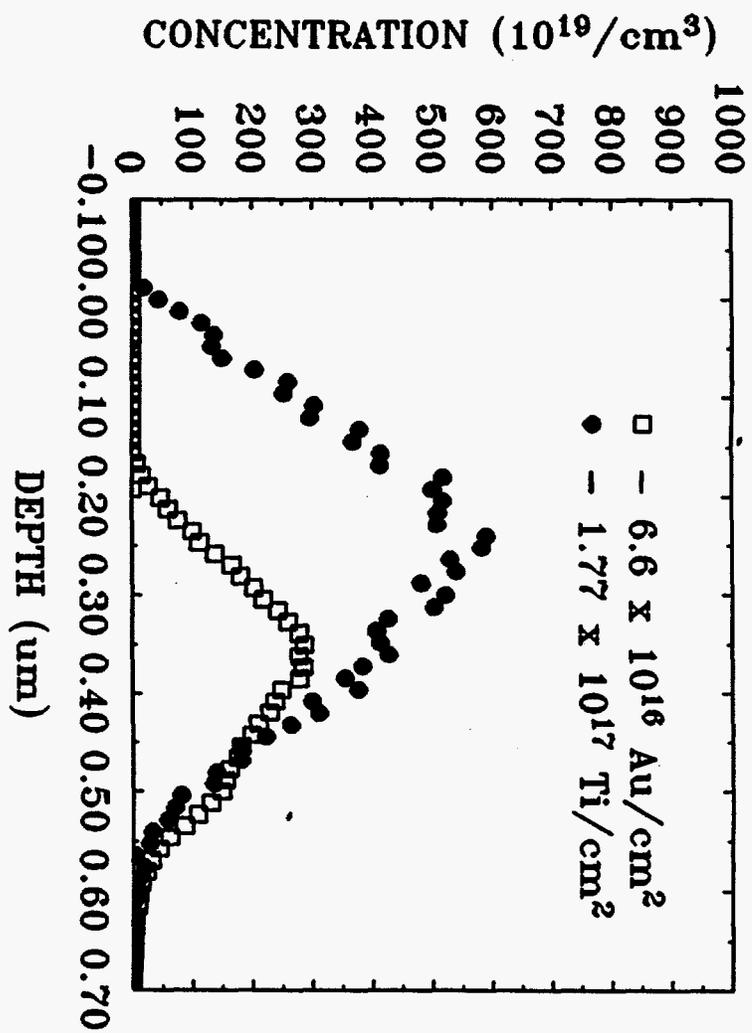


Figure 1
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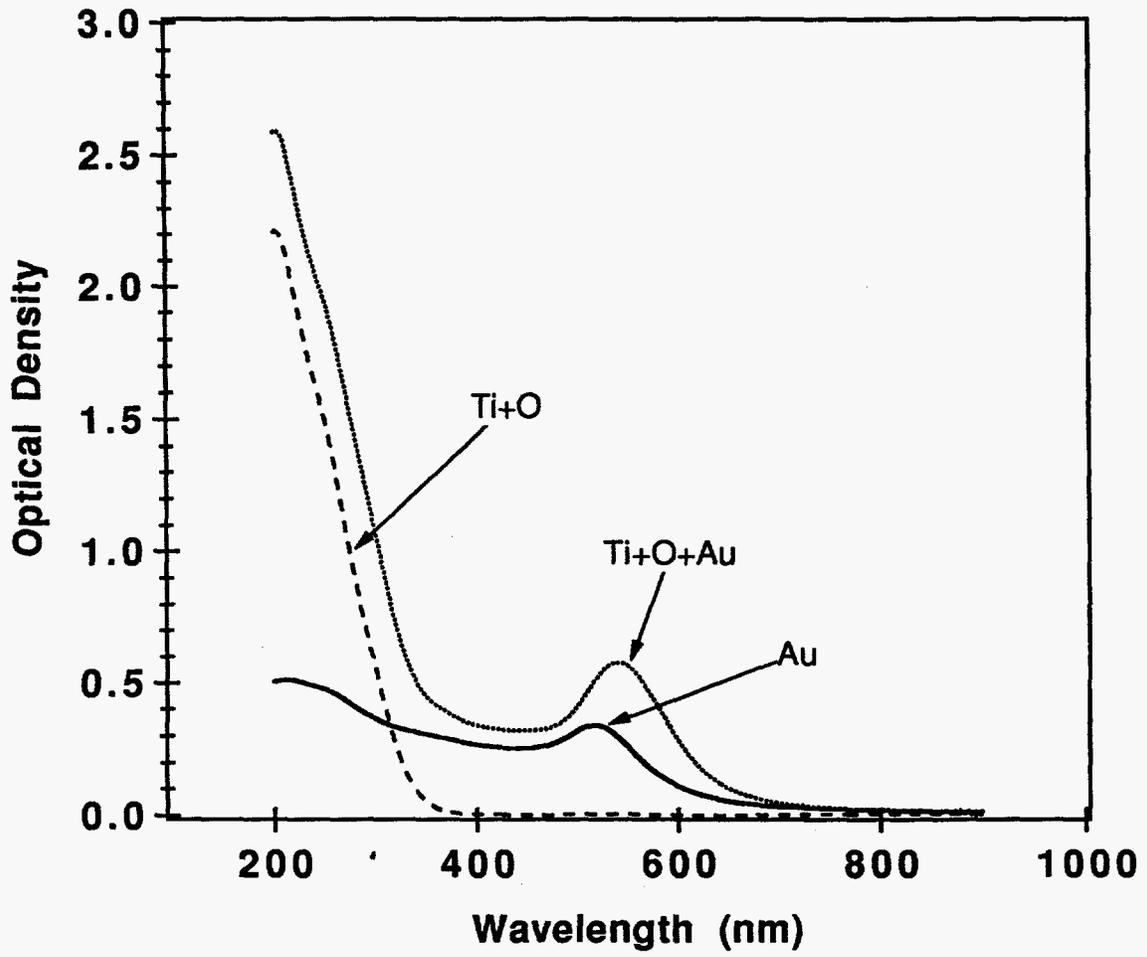


Figure 2
Magnifying glass

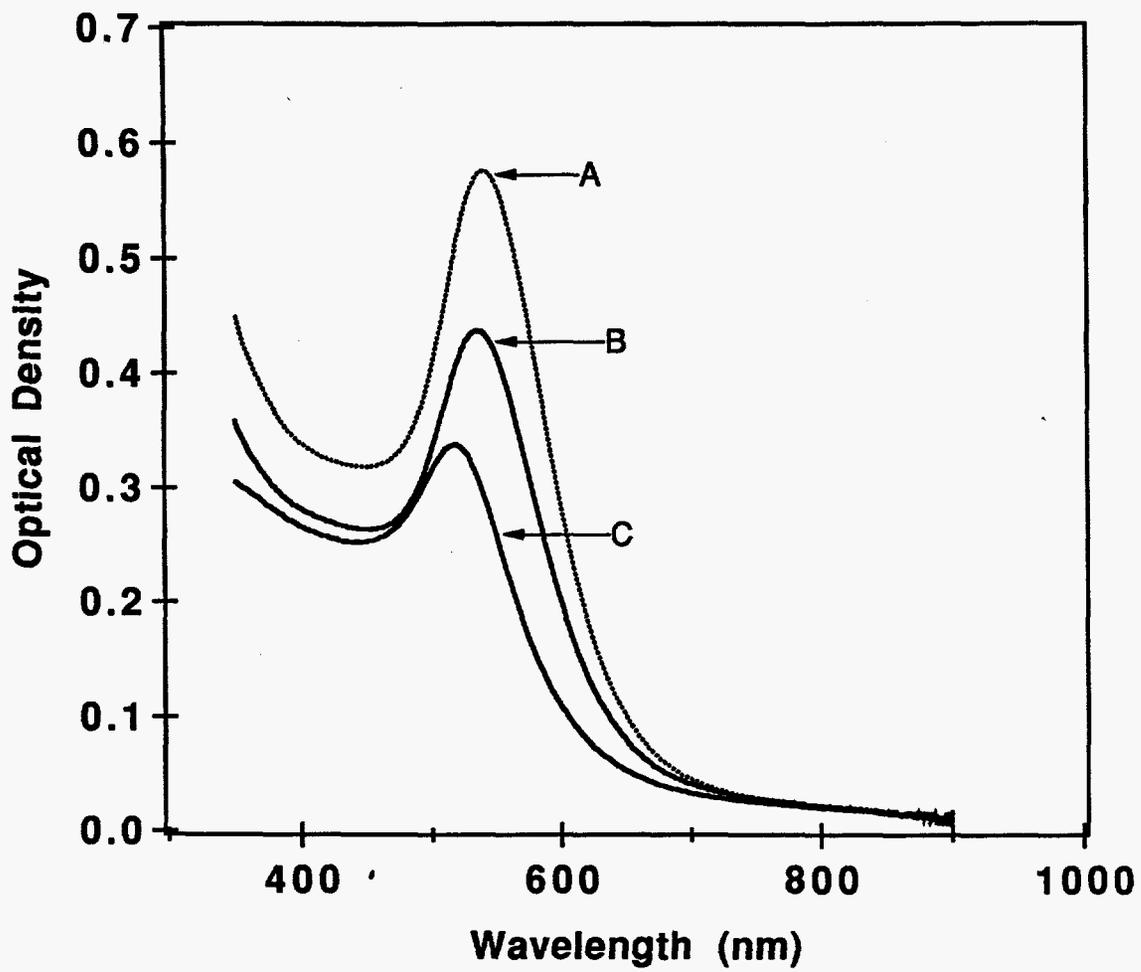


Figure 3
Magnesia