Enhancement of the optical Kerr effect exhibited by an integrated configuration of silicon quantum dots and silver nanoparticles.

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Abstract. We present nonlinear refractive results for three different systems produced by ion implantation: high purity silica substrates with silicon quantum dots (Si-QDs), silver nanoparticles (Ag-NPs), and one sample containing both. We used a femtosecond optical Kerr gate (OKG) with 80 fs pulses at 830 nm to investigate the magnitude and response time of their nonlinear response. The Ag-NPs samples were prepared implanting 2 MeV Ag$^+$ ions at different fluencies. A sample with $1 \times 10^{17}$ ions/cm$^2$ showed no discernible Kerr signal, while for one with $2.4 \times 10^{17}$ ions/cm$^2$ we measured $|\chi^{(3)}_{1111}| = 5.1 \times 10^{-11}$ esu. The Si-QDs sample required irradiation with 1.5 MeV Si$^{2+}$ ions, at a $2.5 \times 10^{17}$ ions/cm$^2$ fluence in order that the OKG results for this sample yielded a similar $|\chi^{(3)}_{1111}|$ value. The sample containing the Si-QDs was then irradiated by 1 MeV Ag$^{2+}$ ions at a $4.44 \times 10^{16}$ ions/cm$^2$ fluence and thermally treated, for which afterward we measured $|\chi^{(3)}_{1111}| = 1.7 \times 10^{-10}$ esu. In all cases the response time was quasi-instantaneous. These results imply that the inclusion of Ag-NPs at low fluence, enhances the nonlinearity of the composite by a factor of around three, and that this is purely electronic in nature. Pump-probe results show that there is not any nonlinear absorption present. We estimate that the confinement effect of the Si-QDs in the sample plays an important role for the excitation of the Surface Plasmon Resonance (SPR) related to the Ag-NPs. A theoretical model that describes the modification of the third order nonlinearity is also presented.

1. Introduction

The nonlinear optical properties of metallic and semiconductor nanocrystals embedded in glassy matrices have been the subject of very active research, due mainly for their potential application in optical information processing systems. The systems studied include nanoparticles (NPs) with different morphologies: nanorods, nanoshells, particles capped with organic materials, to name a few. However, there are few reports of the effect of the interaction of particles of different materials on the nonlinear properties of the composite.
Strong modification in the nonlinear optical response of NPs can be obtained by changing different parameters like size [1], shape [2], environment [3], the processing route of preparation of the sample [4] and the selectivity of the physical mechanism that originates the optical nonlinearity [5]. Moreover, studies related with the participation of the NPs in the optical response, clearly show that the third order susceptibility significantly changes with density of NPs, as it has been visibly reported for the case of Ag [6] and Si [7]. In addition, the polarization and pulse duration can also determine the nonlinear optical response in a NPs system. Completely different results can be observed for experiments performed at different time regimes. A third order nonlinearity that is forbidden for a picosecond excitation can be perfectly appreciable with nanosecond pulses [8]. In agreement with this property, it has been reported that for femtosecond pulses, anisotropic Ag-NPs seem to exhibit their nonlinearity only in specific geometric orientations and polarization [9]. The femtosecond nonlinear response of Ag-NPs in a silica matrix has been related only to the local electric field inside the nanoparticle induced by an external electric field [10], however, enhancement of the nonlinear refraction in Ag-NPs can be also explained by the electromagnetic field near and out of the surface of the NPs [11]. The mechanisms of nonlinear absorption and refraction in metallic Ag-NPs are still under discussion [12]. Sapphire doped by Ag-NPs presents self-focusing properties [13], while it is interesting to observe that Ag-NPs ablated in water present thermal induced self-defocusing in the case of picosecond pulses with high pulse repetition rate, as well as in the case of nanosecond pulses; but in the case of low repetition rate, self-focusing and saturated absorption of pico- and femto-second irradiation have been obtained [14].

On the other hand, a combination of different metallic NPs, like Cu with Ag in the same media, exhibits a stronger nonlinear response in comparison to the response of only one kind of metallic NPs [15], and recent advances in the use of NPs in nanomedicine incorporate researches about different combinations of metallic NPs of Au and Ag with promises of applications associated with scattering and absorption controlled by tuning the SPR of the NPs [16,17].

The improvement of the optical nonlinearities in nanostructured materials is the most important motivation for this work. Measurements of the optical nonlinear parameters in Ag-NPs [18] and Si-QDs [19] seem to point out that these nanostructures behave with quite similar self-focusing effects even though their respective plasmonic and confinement mechanisms, which are responsible for the nonlinearity, are entirely different. We estimated that the combination of these materials can bring potential applications for development of all-optical photonic devices.

The importance of the work here presented is given by the experimental evidences of an enhancement of the third order nonlinearity exhibited by a nanostructured sample with Ag-NPs and Si-QDs. An attempt to describe the observation of the Kerr transmittance behavior is made considering a theoretical model associated with a two-level system.

2. Theory

Considering the dipole approximation in a system of N two-level atoms per unit volume, the Hamiltonian can be written as,

\[ H = \hbar[\omega_1 \sigma_{11} + \omega_2 \sigma_{22} + \Omega(t)\sigma_{12} + \Omega^*(t)\sigma_{21}] \]

where \( \sigma_{ij} = c_i^\dagger c_j \) and \( \Omega(t) \) is the Rabi frequency expressed by,

\[ \Omega(t) = -m \frac{E(t)}{\hbar} \]

\( m \) represents the atomic dipole moment and \( E(t) \) is the externally applied vectorial electric field. In the Markovian approximation, the differential equations which describe the dynamics of the two-level system can be derived from the master equation of Lindbladian [20,21],

\[ \frac{d\rho_{21}}{dt} = -\left(i\omega_{21} + \frac{1}{T_2}\right)\rho_{21} + i\Omega(t)(\rho_{22} - \rho_{11}). \]
\[
\frac{d(\rho_{22}-\rho_{11})}{dt} = -\frac{(\rho_{21}-\rho_{12})+1}{T_1} - 2i(\Omega(t)\rho_{12} - \Omega^*(t)\rho_{21}),
\]

where \(\rho\) represents the density matrix, \(\omega_{21} = \omega_2 - \omega_1\), \(1/T_1\) represents the population loss through radiative and non-radiative processes of the upper level, and \(1/T_2\) represents the rate of polarization loss for the off-diagonal matrix elements [20]. By solving Equation (3) and (4) it can be demonstrated that the Kerr susceptibility can be written as [20],

\[
\chi^{(3)} = \frac{4Nn^4|\tau_1\tau_2^2(\Delta\tau_2-i)|^2}{3h^4[1+n^2\tau_2^2]^2}.
\]

where \(\Delta = \omega - \omega_{21}\) is the detuning of the frequency \(\omega\) of the incident radiation. In the limit of large detunings, i.e. \(\Delta T_2 >\rangle > I\), the real part of equation (5) can be written as [22],

\[
\text{Re} \chi^{(3)} \approx \frac{4}{3} 4Nn^4 \left[ \frac{1}{\lambda^3} \right] \tau_1 \tau_2^2.
\]

For an isotropic material, that the Kerr susceptibility can be calculated with [23],

\[
\chi^{(3)}_{1111} = \chi^{(3)}_{1122} + \chi^{(3)}_{1212} = 2\chi^{(3)}_{1122} + \chi^{(3)}_{1221}.
\]

In a multi-wave mixing experiment, the evolution of the amplitudes of the different fields involved can be expressed as [24]:

\[
E_{11}(z) = \left[ E_{11}^0 J_0(\Psi^{(i)}) + iE_{21}^0 - iE_{12}^0 \right] J_1(\Psi^{(i)}) - E_{22}^0 J_2(\Psi^{(i)}) \exp \left( -i\Psi^{(i)} - \frac{\alpha(I)z}{2} \right),
\]

\[
E_{12}(z) = \left[ E_{12}^0 J_0(\Psi^{(i)}) + iE_{12}^0 J_1(\Psi^{(i)}) - E_{12}^0 J_2(\Psi^{(i)}) \right] \exp \left( -i\Psi^{(i)} - \frac{\alpha(I)z}{2} \right),
\]

\[
E_{13}(z) = \left[ E_{13}^0 J_0(\Psi^{(i)}) - iE_{13}^0 J_1(\Psi^{(i)}) - E_{13}^0 J_2(\Psi^{(i)}) \right] \exp \left( -i\Psi^{(i)} - \frac{\alpha(I)z}{2} \right),
\]

\[
E_{14}(z) = \left[ E_{14}^0 J_0(\Psi^{(i)}) - iE_{14}^0 J_1(\Psi^{(i)}) + E_{14}^0 J_2(\Psi^{(i)}) \right] \exp \left( -i\Psi^{(i)} - \frac{\alpha(I)z}{2} \right),
\]

where \(E_{11}(z)\) and \(E_{22}(z)\) are the complex amplitudes of the circular components of the transmitted waves beams; \(E_{13}(z)\) and \(E_{14}(z)\) are the amplitudes of the self-diffracted waves, while \(E_{11}^0, E_{22}^0, E_{13}^0\) and \(E_{14}^0\) are the amplitudes of the incident and self-diffracted waves at the surface of the sample; \(\alpha(I)\) is the irradiance dependent absorption coefficient, \(I\) is the total irradiance of the incident beams, \(J_m(\Psi^{(i)})\) stands for the Bessel function of order \(m\), \(z\) is the thickness of the nonlinear media, and the phase changes experienced by the waves can be expressed [24],

\[
\Psi^{(i)} = \frac{4\pi^2z}{n_d \lambda} \left[ A + \frac{n_d \beta}{2\pi} \sum_{j=1}^{4} E_{j,i} \right] + \left( A + B + \frac{n_d \beta}{2\pi} \right) \sum_{j=1}^{4} \left| E_{j,i} \right|^2 ,
\]

\[
\Psi^{(o)} = \frac{4\pi^2z}{n_d \lambda} \left[ A + \frac{n_d \beta}{2\pi} \sum_{j=1}^{4} E_{j,i} E_{j,i}^* \right] + \left( A + B + \frac{n_d \beta}{2\pi} \right) \sum_{j=1}^{4} \sum_{j=1}^{4} E_{j,i} E_{j,i}^* ,
\]

with \(A = 6\chi^{(3)}_{1122} = 3\chi^{(3)}_{1122} + 3\chi^{(3)}_{1212}, B = 6\chi^{(3)}_{1221}\), and \(B/A = l\) [25] for the case that a pure electronic response is induced with ultra-short pulses in nanostructures [8].
3. Experimental set-up

3.1 Sample preparation
For the preparation of the NPs two high purity silica glass plates (16×16×1 mm³) with OH content less than 1 ppm and impurity content less than 20 parts per million (ppm), with no individual impurity content greater than 1 ppm, were implanted at room temperature (RT) with 2 MeV Ag²⁻ ions. For the first sample a fluence around $1\times10^{17}$ ions/cm² was used, while for the other one the fluence was $2.4\times10^{17}$ ions/cm². After implantation, the samples were cut into identical small pieces (35 mm²) and thermally annealed in a reducing atmosphere for 1 hr at 600 ºC. The metal distribution and fluences were determined by Rutherford Backscattering Spectrometry (RBS) measurements using an $^4$He⁺ beam in the 2-4 MeV energy range. Ion implantation and RBS analysis were performed at the 3 MV Tandem accelerator NEC 9SDH-2 Pelletron at the Instituto de Física, UNAM.

3.2 Femtosecond nonlinear optical response
Optical Kerr effect measurements were performed using the standard configuration for the time resolved Kerr gate technique [25]. The femtosecond pulse source was a Ti:sapphire laser with $\lambda$=830 nm, 80 fs pulses, 3 nJ maximum pulse energy and a repetition rate of 94 MHz. Figure 1 shows the experimental setup for our Kerr gate experiments. BS is a beam splitter, M1-5 are mirrors. A half wave plate, $\lambda/2$, with a polarizer, PA, are used for controlling the plane of polarization of the probe beam. L represents the focusing system. Pump and probe beams, with an irradiance relation of 15:1 and their linear polarizations making an angle of 45°, are focused on the sample with a spot size of 80 μm. An analyzer, PB, with its transmission axis crossed respect to the initial polarization of the probe beam, is placed before the photodetector D. The probe beam energy is captured using a lock-in amplifier. By delaying the probe beam with respect to the pump beam, we can observe a change in the transmittance of the system and measure the decay of the induced birefringence in the sample.

4. Results
In order to determine the Ag depth profile as well as the concentration, the RBS spectra were simulated using the SIMNRA code [26]. Figure 2 shows the 3 MeV $^4$He⁺ experimental RBS spectrum of the of the samples containing Si QDs and Si QDs + Ag NPs after being annealed in a
reducing atmosphere at 1100°C and 600°C, respectively. The energy of the \(^{4}\text{He}^{+2}\) ions backscattered by the Ag atoms can be observed from 2300 keV to 2570 keV, with a maximum at 2400 keV. This means that Ag ions are implanted from surface to 0.8 microns inside the silica matrix, with the maximum at 0.44 microns. The Si signal coming from the Si QDs is veiled by the silicon signal due to the matrix, because the RBS technique does not allow to difference between the silicon of the matrix and the one implanted at 1.5 MeV. The SIMNRA code also allows calculate the Ag fluence of the sample, whose result is \(4.44 \times 10^{16} \text{Ag/cm}^2\).

![Normalized Yield vs. Energy (keV)](image_url)

**Figure 2.** Experimental RBS spectrum of the Si-QDs and the Si QDs + Ag NPs.

The linear absorption spectra of the samples are presented in Figure 3. One can clearly observe the Surface Plasmon Resonance band (400nm) associated with the Ag-NPs in the silica sample. The absorption spectrum related with the sample with Si-QDs shows a well defined absorption edge around 400 nm. From these data is possible to observe that when the samples contain Ag NPs and Si-Qds, it is obtained a uniform red shift in the absorption peaks associated with the SPR in the spectrum. An important absorption is presented at 830 nm but we can consider that this excitation is far from resonance for the samples.
We used the experimental setup illustrated in Figure 1 to determine the third order nonlinearity for the samples in the femtosecond regime. The fs pulses allow us to induce a pure electronic Kerr response in the samples without the concurrent effect of a thermal process. The first nonlinear optical measurement was made for the samples with Ag-NPs; secondly, the sample with Si-QDs was measured; and finally, the measurement related with the sample containing Ag-NPs and Si-QDs was performed. Figure 4 shows the data obtained from the resulting transmittance Kerr gate experiments.

Since the Kerr gate signal arises from $|\chi^{(3)}|$, we conducted standard pump-probe experiments to quantify the possible contribution from nonlinear absorption to the response. From the results, we did not observe TPA even with the highest energies ($3nJ$) available from our laser system.

We used the experimental data and equations (7-13) in order to calculate the nonlinear optical parameters associated with the samples. From the performed experiments, we found that the Ag-NPs
sample with \(1 \times 10^{17} \text{ ions/cm}^2\) showed no discernible Kerr signal, while for the other samples, table 1 presents the summary of the resulting parameters obtained. The error bar is approximately ±10%.

### Table 1. Optical nonlinearity exhibited by the samples.

| Sample                  | \(\chi^{(3)}\) [esu] |
|-------------------------|----------------------|
| Ag-NPs \((2\text{MeV}, 1\times10^{17} \text{ ions/cm}^2)\) | -                     |
| Ag-NPs \((2\text{MeV}, 2.4\times10^{17} \text{ ions/cm}^2)\) | \(5.1 \times 10^{-11}\) |
| Si-QDs \((1.5\text{MeV}, 2.5\times10^{17} \text{ ions/cm}^2)\) | \(5.1 \times 10^{-11}\) |
| Si-QDs \((1.5\text{MeV}, 2.5\times10^{17} \text{ ions/cm}^2)\) \(+\) Ag-NPs \((1\text{MeV}, 4.44\times10^{16} \text{ ions/cm}^2)\) | \(1.7 \times 10^{-10}\) |

The ultrafast optical response (<100fs) exhibited by all the samples, together with the absence of TPA in our measurements, allow us to say that the obtained optical nonlinearity are purely electronic in nature. These results imply that the integrated configuration of Si-QDs with Ag-NPs at low fluence, enhances the pure electronic nonlinearity of the composite by a factor of around three.

### 5. Discussion

The nonlinear parameters extracted from the femtosecond experimental results remain approximately constant within the experimental error level. In all cases the response time for the samples was quasi-instantaneous. The Si-QDs sample exhibits an important Kerr nonlinearity and it seems that the processing route gives not only a better mechanical and optical stability in comparison with other samples with nc-Si [7,19], but additionally the interference effect given by the typical Fabry-Perot interferometer associated with thin films is completely avoided. The results associated with the Ag implanted samples allow us to see that the distribution density of Nps in the sample plays an important role in the Kerr nonlinearity. But the inclusion of Ag-Nps in the sample with Si-QDs exceptionally shows an extraordinary enhancement of the Kerr nonlinearity. This important enhancement of the optical nonlinearity is clearly observed in Figure 4 with the results for the sample containing Ag-Nps and Si-QDs. Although the OKG technique only gives information about the magnitude of the nonlinear refractive index of the sample, we assume that this enhancement could possibly be given not by the reinforcement of the Nps density in the matrix but by the modification of the surrounding related with the Nps response. Apparently, if a collection of independent two-level atoms is embedded within an environment with suppressed reservoir of modes, the optical nonlinearities could be enhanced due to the quenching of the atomic spontaneous emission [20]. Through equations (3-6), we take into account this consideration in order to explain our experimental results. We argue that the quenching of the atom decay can be reached as a purely surface phenomenon of the NPs, in contribution of enhancement of the optical nonlinearity. Given the well defined SPR absorptive band of the Ag-Nps surrounded by the QDs-Si, it can be expected a stronger enhancement for resonant excitations. Under these conditions probably the non-radiative spontaneous emission of the atoms would be much smaller than both the radiative spontaneous emission and the decay due to phonons. Currently we are performing resonant picoseconds experiments in order to
clarify this aspect. The high nonlinear refraction coefficient exhibited by the sample with Ag-NPs and Si-QDs, together with a negligible two-photon absorption in the fs regime, noticeably indicates the importance of the combination of plasmonic and quantum effects in order to look for numerous photonic applications.

6. Conclusion
We present results for three different systems produced by ion implantation: high purity silica substrates with Si-QDs, Ag-NPs, and one sample containing both. We used a femtosecond optical Kerr gate with 80 fs pulses at 830 nm to investigate the magnitude and response time of their nonlinear response. The experimental results allow us to identify that as well as the distribution density of Ag-NPs is a very important parameter for the enhancement of the third order nonlinearity, also the addition of Si-QDs in a sample can give a strong reinforcement associated with the modification of the matrix in which the Ag-Nps are embedded too. Pump-probe results show that there is not any nonlinear absorption present in the resulting samples. The response time for the nanocomposites was quasi-instantaneous and we claim that a pure electronic response was exhibited by the samples. We estimate that the confinement effect of the Si-QDs in the sample can play an important role for the excitation of the SPR related to the Ag-NPs. A theoretical model that describes the modification of the third order nonlinearity was also considered for the explanation of the observed effects.

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