PbTe Quantum Dots - SiO$_2$ multilayers for optical devices produced by laser ablation

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ABSTRACT

Thin films of glass doped with PbTe quantum dots were successfully fabricated. The semiconducting quantum dots were grown by laser ablation of a PbTe target (99.99%) using the second harmonic of a Q-Switched Quantel Nd:YAG laser under high purity argon atmosphere. The glass matrix was fabricated by a plasma chemical vapor deposition method using vapor of tetramethoxysilane (TMOS) as precursor. The QD`s and the glass matrix were alternately deposited onto a Si (100) wafer for 60 cycles. Cross-section TEM image clearly showed QD`s layer well separated from each other with glass matrix layers. The influence of the ablation time on the size distribution of the quantum dots is studied. HRTEM revealed anisotropy in the size of the QD´s: they were about 9nm in the high and 3-5 in diameter. Furthermore HRTEM studies revealed that the QD´s basically growth in the (200) and (220) directions. The thickness of the glass matrix layer was about 20 nm. Absorption, photo luminescence and relaxation time of the multilayer were also measured.

KEYWORDS

Laser Ablation, PECVD, Quantum Dots, Multilayer, Optical Device

1- INTRODUCTION

Semiconductor quantum dots (QD) have attracted attention because they exhibit large optical nonlinearities as well as fast response times (less than 1 ps) potentially useful for optical devices [1,2,3,4]. It is well known that semiconductor QD materials consisting of clusters or crystal of nanometric dimensions embedded in dielectric host exhibit properties that differ from those of the corresponding bulk material[5]. These materials have opened many possibilities for their use in various technological applications because of their optical, electrical and magnetic properties [6]. The study of semiconductor nanocrystals embedded in glasses has attracted great attention because their non-linear optical properties making them promising material for the development o integrated "all-optical" devices. However, their use has in many cases been hindered bay the lack of appropriate depositions techniques with the capability to control the dimensions, shape, and size distribution of the nanocrystals.

Pulsed-laser deposition (PLD) is a thin film deposition technique that has high potential for development of structured materials. This technique has the advantage of not requiring any pos-processing steps allowing a high degree of control over the distributions of the nanocrystals.

PbTe quantum dots exhibit band absorptions in the region of interest for optical communications 1.3-1.5μm making this material an excellent candidate for development of optical devices[7,8]. In the present work is reported the fabrication and characterization of PbTe nanocrystals embedded in a dielectric host (SiO$_2$).

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2- EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental set-up used for the fabrications of the nanostructures. It consists of a vacuum chamber pumped to a base pressure of ~1 x 10^{-7} mbar by a turbo molecular pump. Laser ablation of a PbTe target (99.99%) was performed using the second harmonic of a Q-Switched Quantel Nd:YAG laser.
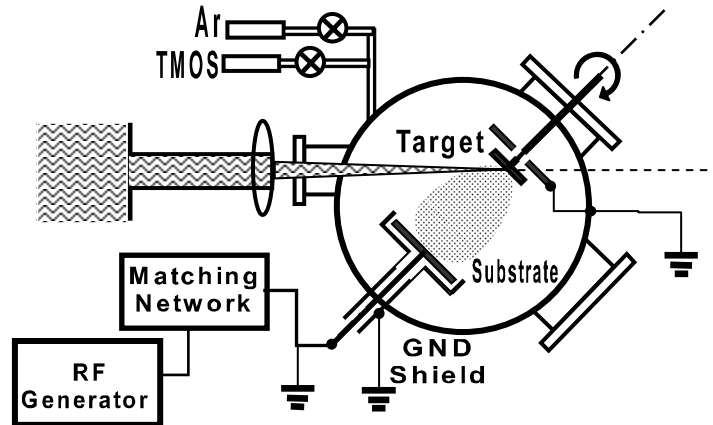

Figure 1 Experimental Set up used for the fabrications of PbTe QD/ SiO$_2$ multilayer**.**

The pulse duration is 4 ns and the laser repetition rate is 20 Hz. The energy per pulse measured at the target surface was 70 mJ, which yields to a fluency of 20 J/cm^2. The pulsed laser beam is focused on an incidence angle of 45° on a target, using a 30 cm lens. The target holder can be rotated around the target normal, which reduces target degradation by multiple irradiation of a single spot.

The source for the glass matrix is a silicon-alkoxide, tetrametoxysylane (TMOS). Vapor of TMOS evaporated in a vessel floated in a heath bath (30°C) was introduced into the chamber. Flow rate of TMOS an Ar were independent controlled with needle valves LV10K. Si (100) wafers or BK7 glass plates were used as substrates for HRTEM measurements and optical characterizations respectively. Substrate was maintained at room temperature. Multilayer was fabricated by alternatively PLD of the PbTe target during a time t$_{LASER}$ and PECVD of TMOS during a time t$_{RF}$. A computer controlled interface switched properly RF and Laser Q-Switch. HRTEM was performed using a Jeol JEM 3010 microscope, 300kV and 1.7 Å point-to-point resolution. For optical characterization (absorption and photoluminescence) a lock in based experimental set up was used. For the relaxation time measurements the pumping and prove technique was used.

3- RESULTS AND DISCUSSION

3.1 High Resolution Transmission Electron Microscopy (HRTEM) measurements.

For the HRTEM measurements on the multilayer, a Si (100) wafer was used as the substrate. Figure 1(a) shows the low magnification cross-section image of the 11 layers structure obtained while (b) shows a high resolution image of the Si substrate (right bottom corner), and the first QD layer. This micrograph shows 9 nm thick QD layers separated by 20 nm thick SiO$_2$ layers. The total thickness agrees well with the SiO$_2$ deposition rate of 0.58 nm/sec previously determined by refractive index measurements. The bright 5 nm amorphous layer just over the substrate is composed of native oxide of silicon as shown by an Energy Dispersive Spectroscopy (EDS) measurement. The equidistance between the 11 layers shows the good repetitiveness of the whole process. The Fourier Transform shown at insert (i) agrees with the 0.31 nm spacing of the [200] planes of the FCC PbTe structure. Inset (ii) is the Fourier Transform of the Si(100) substrate.
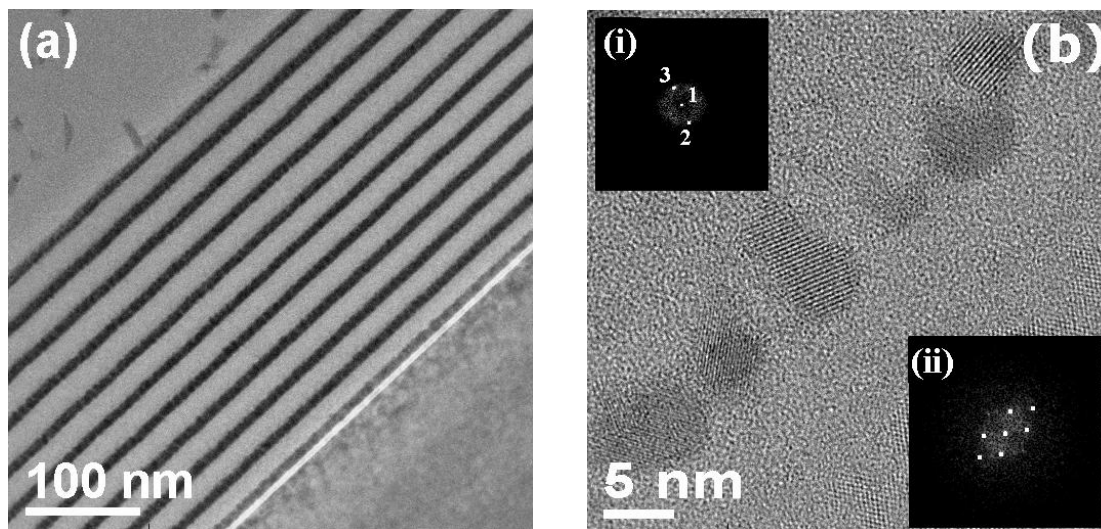
Figure 2 (a) Low magnification cross-section image of a multilayer PbTe/SiO$_2$ growth on a Si (100) substrate. (b) HRTEM image of the multilayer showing the quantum dots embedded in the dielectric host. The insets (i) and (ii) are the Fourier transform of a PbTe nanoparticle and Si(100) substrate respectively.

3.2 Absorption measurements

For optical characterization a BK7 Corning glass was used as substrate. The two-steps deposition process (PbTe/SiO$_2$) was repeated 60 times until the amount of nanoparticles is enough to be measured. The total sample thickness can be controlled by changing both the PbTe ablation time (t_{LASER}) and the SiO$_2$ deposition time (t_{RF}). Three multilayers were fabricated where the PbTe ablation time was varied (t_{LASER}=20, 40 and 60 seg) an the glass matrix deposition time was held constant (t_{RF}=50 seg). The total thickness for all the three multilayers was about 1.5-2.0 µm.

Results for the absorption measurements are in Figure 3 (a). Measurements were carried out in the central region of the sample (Figure 3 (b)) where the highest diameter of the quantum dots is expected. Even with the 60 bilayers the absorption was too weak to be detected with a single pass through the film, therefore we used a total internal reflection multiple pass arrangement for this measurement as shown in Figure 3(c). The experimental setup consisted of a 150 Watt halogen xenophot lamp mechanically chopped, a Kratos GM 252 monochromator and a SR830 DSP lock-in amplifier. For the 400-1100 nm band a 818-BB-40 Newport silicon detector was used while for the 1100-2200 nm band a liquid nitrogen cooled J12 EG&G-Judson InAs detector was used. The background spectrum was obtained with a SiO$_2$ film grown on the same substrate and with the same SiO$_2$ content as in the multilayer structure for each sample.

For sample 1, where the lowest PbTe deposition time was used, an absorption band near 650-700 nm is observed. For samples 2 and 3, with greater number of pulses (consequently higher particle diameter) two or more absorptions bands are observed. Absorption bands below 450 nm are artifacts, probably related to the low spectral irradiance of the halogen lamp in this region of the spectrum.

Figure 3(b) shows schematic isothickness contours (dashed rings) corresponding to the in-plane distribution of the amount of PbTe deposited. The deposit has a central maximum and then decays with the distance from the target normal. This distribution of deposited material is typical for films grown by PLD when a spherical lens is used to focus the laser beam on the target and no steps are taken to homogenize the thickness of the deposited film[9,10]. Moreover, Barnes et al.[9] found that the in-plane size of the QD increased approximately linear with the amount of deposited material. For

those reasons dots with equal sizes will be distributed along concentric rings. Because the dimensions of the contour lines are comparable with the sample length used to measure the absorption (~2.5 cm), the absorption for QD of different sizes were measured, because dots with equal sizes will be distributed along concentric rings and not lines. For that reason, the different absorption bands observed for each sample are most probably related to the absorption bands of different quantum dots populations due to the multiple reflection geometry used for these measurements.
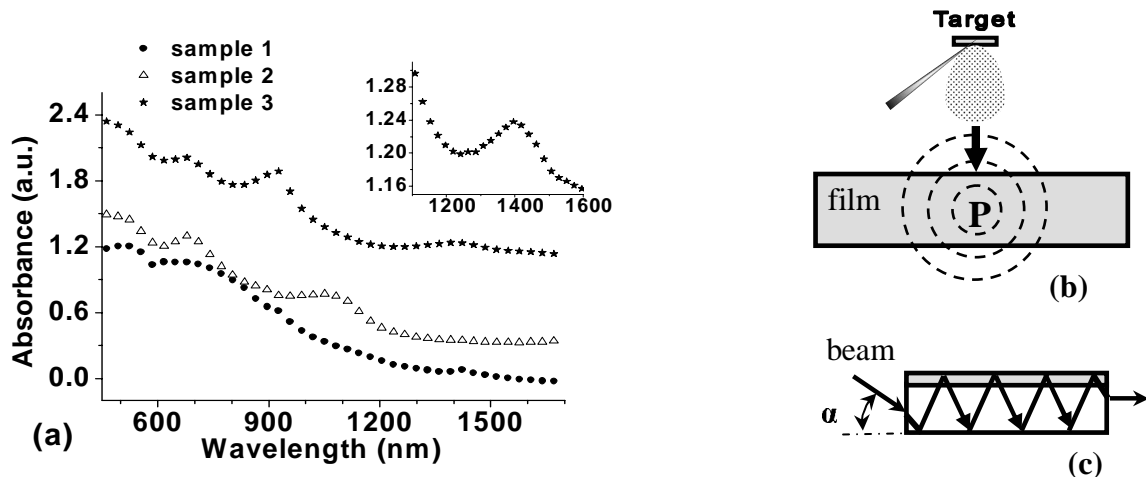

Figure 3: (a) Absorption spectra of a SiO$_2$/PbTe quantum dots multilayer grown by alternately PLD of PbTe nanoparticles and PECVD of SiO$_2$. The samples were fabricated with different PbTe ablation time sample 1(•) t$_{LASER}$= 20 seg; sample 2 (Δ)t$_{LASER}$=40 seg and sample 3 (✱)t$_{LASER}$=60 seg. The deposition time for the glass matrix was held constant for all three samples. (B) The measurements were carried out at the central position of the sample (position P). where the quantum dots with the greatest size are expected. (C) Schematic representation of the multiple pass total internal reflection geometry used for these measurements.

Especially interesting was the result of sample 3. This sample was grown with t$_{LASER}$ of 60 seg (1200 laser pulses) and exhibit an absorption band around 1400nm, just inside the region of remarkable interest for optical communications. The mean breath for the NCs and its dispersion in this sample were 7.2 nm and 2.1 nm, respectively. This multilayer could be used for the development of optical devices like

Although the absorption band agrees with the region of interest for optical communications, options have to be studied to obtain a lower size dispersion, which increases the device efficiency. For applications where it is necessary a low dispersion in the quantum dots size, its mandatory to use a lower ablation time for the semiconductor, this meaning that a higher evaporation rate per pulse must be achieved in order to fabricate quantum dots of the same size.

3.3 Size distribution

In order to study the in plane morphology of the nanoparticles, samples with simple sandwich structure of SiO2/PbTe/SiO$_2$ were grown. For TEM observations, the nanoparticles were deposited on copper grids with previously deposited carbon film. Carbon film was deposited by sputtering on mica substrate and then floated off in deionized water. Finally, the floating carbon film was picked up on TEM grids. Size distribution studies were carried out by manually outlining the nanoparticles from several dozens of low and high resolution TEM images. Once digitized and saved in proper format the image was processed using the Gatan Digital Micrograph program which provided data on the size, area and separation of the nanoparticles.

To understand the behavior obtained in the absorption measurements a series of three sample were fabricated with different ablation time (t$_{LASER}$= 20 seg, 40 seg and 60 seg). The ablation times for the semiconductor were the same used for the fabrication of the multilayers. The glass matrix deposition time was held constant for all three samples (t$_{RF}$ = 50seg). HRTEM measurements for size distributions studies were carried out at the same position P (Figure 3(b)) where

absorption was measured. Figure 4 shows the results of these measurements for three samples grown with different PbTe ablation time and keeping constant all other growing parameters.
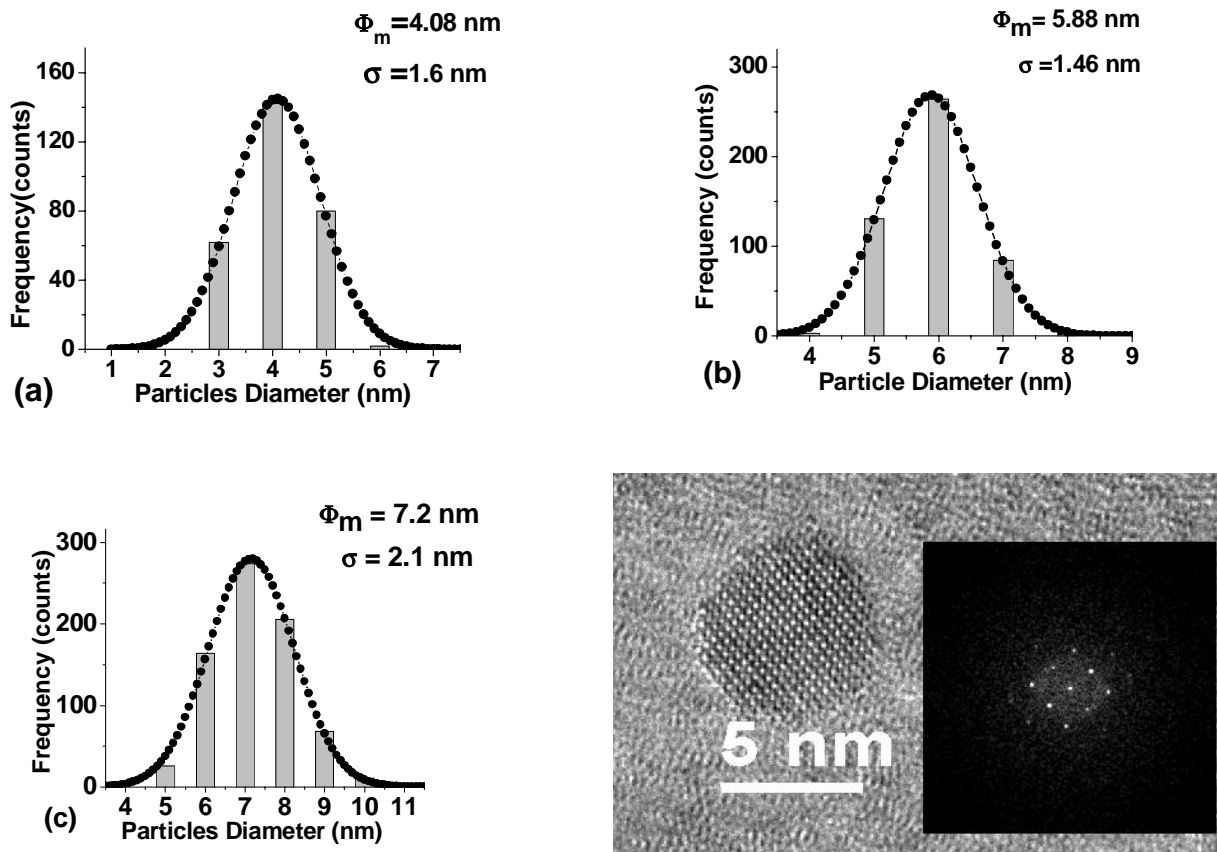

Figure 4: Size distribution for samples grown with different ablation time (a) t_{LASER} = 20 seg; (b) t_{LASER} = 40 seg and (c) t_{LASER} =60 seg. (d) HRTEM image of a PbTe particle grown by PLD inside of a PbTe/SiO$_2$ multilayer. The inset showing the Fourier Transform of this image.

Studies on the size distributions of the nanoparticles exhibit an approximately linear increase of the particle mean diameter as function of the amount of material deposited. The mean dispersion also increases by increasing the ablation time.

Using the calibration curve previously obtained [11,12] we can estimate the absorption peak wavelength by using the relation $E_o = a + br^{-1} + cr^{-2}$, where *a, b*, and *c* are fitting constants with values a = 0.3512, b = 0.4786 and c = 5.1367, E_0 is the ground state energy and *r* is the particle radius. Using the experimental mean diameter obtained from Figure 4(a, b and c) for the three samples $\Phi_m(a)$ = 4.08 nm, $\Phi_m(b)$ =5.88 nm and $\Phi_m(c)$ =7.02 nm, we can estimate the wavelength for the absorption peak as λ(a) ≈ 680 nm, λ(b)≈ 1120 nm and λ(c) ≈ 1400 nm, respectively. These wavelengths are in excellent agreement with the peak values observed in Figure 3(a) for the absorption spectra in of samples 1, sample 2 and sample 3 respectively.

3.3 Photoluminescence measurements

For these measurements a lock in based experimental set up was used. For the excitation was used a Ti-sapphire laser operatin in 800-900 nm. The laser power was varied from 900 mW to 1.2 W. The laser beam was focused with e cylindrical convergent lens producing a 4mm-long spot over the sample at the lens focus. The photoluminescence of the sample was observed perpendicular to the excitation beam. A N_2-cooled InGaAs detector was used to detect the luminescence in the 1000-1600 nm region. Preliminary results of these measurements are shown in Figure 5
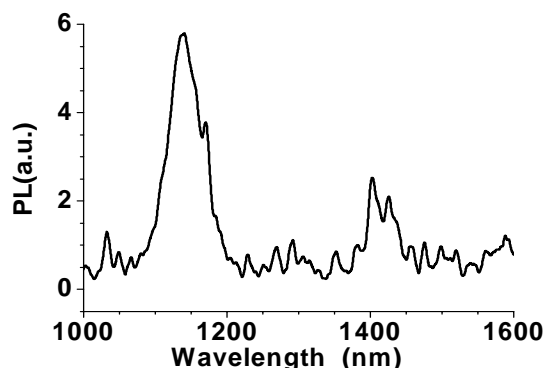

Figure 5 Photoluminescence of the multilayer at the central position of the sample

Although it is a small signal, emission around 1140 nm is observed which could be associated to the absorption band for this sample around 930 nm. A still lower emission around 14 40 nm is also observed which could be associated to the absorption band of the sample 1400 nm. Other studies are needed in order to obtain a better understanding of this photoluminescence spectrum.

3.4 Relaxation Time measurements.

For the relaxation time measurements, the samples were also fabricated on BK7 Corning glass. The two-steps deposition process ($PbTe/SiO_2$) was repeated 300 times until the amount of nanoparticles is enough to produce certain absorption of the multilayer. For the ablation time of the semiconductor t_{LASER} 25 seg was chosen in order to produce nanoparticles with absorption band around 800 nm where the Ti:sapphire operates. The glass matrix deposition time was t_{RF} = 20 seg.

We used a three-beam pump and probe set-up to observe response differences between the sample when it is excited by one pump pulse or two pump pulses. Translation stages for the probe and one pump pulse control the delays between the three pulses. The pulses were generated from a tunable femtosecond Ti:sapphire laser operating at 80 MHz pumped by an Argon laser. The two pumps and the probe pulses were split from the Ti:sapphire laser output in the ratio $I_{pump1}:I_{pump2}:I_{probe}$ = 20:20:1. The two pump and the probe pulses are polarized perpendicularly to each other to avoid coherent artifacts, and chopped at different frequencies, f_{pump} and f_{probe}. The lock-in was synchronized at $f_{pump}+f_{probe}$ to guarantee that the signal detected was generated only by a joint pump and probe effect. The three beams were focused on the same spot in the sample with a spot size of approximately 10 □m by a 5 cm focal length lens. The transmitted probe passes through a polarizer to block light scattered from the pump beams and collected with a PIN detector connected to a lock-in amplifier. The temporal FWHM of the pulses was 80 fs with 8 nm spectral line width. All measurements were performed at room temperature.
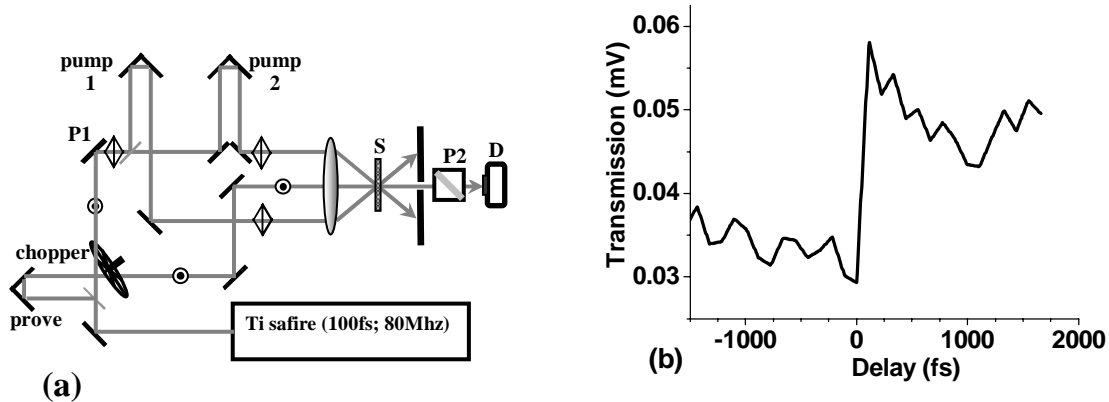
Figure 6 (a) experimental set up used for the ralaxation time measurements. (b) Relaxation time measured in a SiO$_2$/PbTe quantum dots multilayer.

The signal for the transmission variation obtained presented a noise component, which does not enabled an adequate evaluation of the relaxation time. From the obtained result, even only preliminary ones, the following conclusions can be drawn:

1. - The presence of the step and tail in the measured signal, demonstrates that the transmission of the prove being modified by the pump beam. When both arrive simultaneously, the step is produced. For higher times, where the shift between pump and prove increases, the measured signal (i.e. the variation of the transmission) decreases. This fact was proven experimentally: when one of the signals (pump or prove) was blocked, the resultant signal in the *lock in* became null.
2.- The relaxation is expected in the picoseconds scale.
Both conclusions turn this material in an excellent candidate for developing of optical devices.

4- CONCLUSIONS

Multilayer of PbTe/SiO$_2$ was successfully fabricated using alternatively PLD a PECVD techniques. The absorption bands related to the quantum dots were measured for three samples with different quantum dot size. For a sample, the absorption band was found around 1400 nm, which is a region of interest for optical communications. Photoluminescence and relaxation time measurements were also carried out.

5- ACKNOWLEDGEMENTS

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