Comparative Study of Plasmas Obtained by Femtosecond Laser Pulses Ablation in Si and SiO2

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Electronic density and temperature were measured with temporal resolution on SiO2 and Si samples by using standard fs LIBS imaging spectroscopy. Extinction time of both plasmas is different depending on the kind of sample under irradiation. Lifetime for plasma obtained in dielectric sample is shorter than that of semiconductor. The main reason to explain this behavior is related to the deep defect induced in the dielectric (fused silica) gap by the femtosecond process; these centers act as sink for the free electron promoted by the laser interaction from the valence band to the plasma, so for dielectrics, shorter lifetime plasmas are obtained when femtosecond pulse irradiation is conducted.

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Abstract

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KEYWORDS: silicon, femto LIBS, fused silica, ultra short ablation

INTRODUCTION

Interaction of femtosecond laser pulses with materials is of paramount importance both for fundamental knowledge of basic ionization processes and for laser technology and industrial process.[1-10] It is widely accepted that the ultra-short pulses mater interaction is a multi-step process. In first term, laser energy is deposited over the sample in a region of hundreds of nanometers, frequently called "skin layer"[11] which depends on the laser frequency and the absorption of the material. In metals, the laser

energy is absorbed by the free electron in the material and at end of the laser pulse, only a very hot electron gas and a practically undisturbed lattice are found. In second place, the hot electrons transmit their energy to the lattice. Both processes occur in temporal windows of hundreds of femtoseconds, and the region affected for this interaction is of tens of nanometer in depth. After the electron gas escape from the sample, the Coulomb repulsion among ions parents is the responsible of ablation under femtosecond laser interaction. Lastly, chemical bonds are broken and finally ablation of material and formation of the plasma take place. Those processes occur thanks to the presence of electrons in the conduction band of the material; otherwise they must be firstly promoted. It is worth to mention that laser ablation will be produced if the energy deposited over the sample exceeds the work energy of the lattice and binding energy for the ions remaining in the material.

Dielectrics show a lack of free charge carriers in the conduction band, so the first step in the ablation process is the creation of such electrons. Although the photon energy is less than the band-gap width and one photon is unable to ionize it, the high photon density in the laser radiation allows the ionization of dielectric. A quick estimation can show the feasibility of the multiphoton absorption effect. Let is suppose a pulse light of 100 fs, with energy of 1 mJ focused on a spot of 80 μm of radius. This laser pulse produces a photon flux that in 1 fs on a surface of 1 $Å^2$ is irradiated by nearly two thousands of photons. This quantity is enough to cause a multiphoton absorption and trigger the laser ablation proccess.[12, 13]

Several research works have dealt with laser dielectric and laser semiconductor interaction. Most of them in one way or another suggest that the expected results of such interaction shows no difference between metal and dielectrics plasmas during ultra-short ablation.[11, 14, 15] Those papers suggest that in dielectric and semiconductor once the conduction band is populated by electrons, hereafter the laser mater interaction shows no difference between metals (which have already populated the conduction band), semiconductor or dielectric. So the plasma evolution should be the same regardless the material interacting with the femtosecond laser pulses.

The aim of this paper is to test the above statement. For that reason, we have conducted experiments with samples containing Silicon atoms in two kinds of materials. We explore Si atoms located in different environment such as Si semiconductor and fused silica (SiO_2) dielectric. The experiments allow us to spectroscopically test the ablation plume formed in both kinds of samples after femtosecond laser interaction and follow its dynamics.

Experimental procedure

The experimental setup used in this work is shown in Figure 1. It consists in a Ti: Sapphire femtosecond laser system with a CPA (Chirped Pulse Amplifier). The system delivers laser pulses at $\lambda=$ 780 nm, with a duration of τ = 120 fs, an energy of 700 µJ in single pulse mode. The energy delivered by the laser was measured by a power meter and controlled by a combination of $\lambda/2$ plate plus a polarizer and a set of neutral density filters. The laser pulses were focused on the sample by using a 100 mm focal lens. The working fluence was set in all the experiments at 20 J/cm^2. For inspection and monitoring the impact position of the laser on the samples a white light and a CCD camera were used. The samples were mounted on a X-Y-Z translation stages located perpendicular to the direction of laser incidence, this positioning system allows sub micrometer resolution.

The luminescence of the plasma generated after ablation of the samples was collected by a quartz lens of 10 cm focal length, and directly focused over the entrance slit of an imaging Czwerny-Turner monochromator, which is equipped with a 2400 line/mm holographic grating. For detection, an intensified CCD camera (1024x1024 pixels) with time delay and programmable acquisition gate attached to the monochromator was used. This detection system has an optical dispersion of 0.01 nm/pixel and 11 nm range.

Samples employed were crystals of silicon (semiconductor) and fused silica (dielectric), both kind of samples have a commercially degree of quality.

Results and discussion

Spectroscopic characterization of the femtosecond generated plasmas was done analyzing its emission spectra. Figure 2 shows the emission spectrum corresponding to silicon within the semiconductor sample. It is worth to mention that both spectrum (Si and SiO$_2$) show the same emission lines corresponding to Si but with a remarkable difference of intensity and line width between the two samples.

Femtosecond plasma characterization was made by measuring the electronic temperature and density. Also, these measurements were done with temporal resolution. Electronic temperature determination was conducted under the assumption of local thermodynamic equilibrium (LTE) condition. LTE is said to exist if the life time between collisions of the particles in the plasma is small compared with the duration over which the plasma undergoes any significant change.[16] So, one possible criterion to check if LTE exist in the plasma under observation is as follow:[17]

$$n_e > 1.4 \times 10^{14} \, T_e^{\frac{1}{2}} \left(\nabla E_{mn} \right)^3 cm^{-3} \qquad (1)$$

where T_e is the electronic temperature in eV, ∇E_{mn} is the energy difference between the upper and lower level in eV and n_e is the electronic density in cm⁻³. So, for the transition at 250.7 nm and taken an average temperature of 1 eV, the right side of the eq 1 gives $2,5 \times 10^{16}$ cm⁻³, and the electronic density of the plasmas under study in this paper is never less than 1×10^{17} cm⁻³ (see Figure 5). So the LTE condition is full filed in our experiments.

The compliment of LTE criterion in our experimental condition, allow us to test the electronic temperature of the plasma by using the Boltzmann plot method.[18] In this paper we used the spectroscopic data shown in Table I together with the emission data obtained from the spectroscopic lines observed from the plasmas.

On the other hand, to determine the electronic density we use the Stark broadening method that does not require the fulfillment of the LTE condition. Stark broadening is a consequence of the interactions of the electric fields near the emitter and therefore, it is proportional to the electron number density. To measure the n_e the width of the selected transition and its impact parameter (ω) must be known. The line width is measured from the spectrum and the ω value is obtained from the literature[19, 20], with those data, and applying the following formula, the n_e value can be determined:

$$\Delta \lambda_{1/2} = 2\omega \left(\frac{n_e}{10^{16}} \right) \qquad (2)$$

where n_e is the electronic density in cm⁻³ and $\Delta\lambda_{1/2}$ is the full width at half maximum of the measured transition. Typical Stark broadened line profile is approximately Lorentzian.

The methods described above were employed in this paper to get spectral information on the evolution of the femtosecond generated plasmas. In first place, we measured the spatial plasma evolution by following the intensity of a selected Si emission line identified as "1" in Figure 2 and Table I for both samples. Figure 3 shows the spatial evolution corresponding to these experimental data. It is point out that the maximum emission intensity in both samples it is not immediately near the sample, as it would be expected. On the contrary, the maximum intensity is achieved approximately at 0.5 mm from the sample surface. This behavior was observed and discussed in other research papers.[15, 21, 22] This fact can be interpreted as follow: during femtosecond laser ablation the emission time from excited species is longer than the radiative lifetime of the corresponding atomic transition; this phenomenon is

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explained in terms of re-excitation processes due to collisions present during the plasma expansion. This spectroscopic behavior combined with the expansion velocity of the plasma is a possible explanation of the gap between the maximum intensity emission of the plasma and the sample surface.[15]

In second place, by using eq. 1 and 2 we have measured the temporal dependence of the electronic temperature and density (see Figure 4 and Figure 5, respectively). On those figures, it is shown that the temporal dependence for the density and temperature it is not the same for both samples. The plasma obtained for Si within Silicon semiconductor shows higher temperature and electronic density than the plasma obtained for Si inside the dielectric (SiO$_2$) sample.

Electronic temperature in the semiconductor is higher ($\approx$ 10000 K) and also the time for plasma decay is longer than for the dielectric sample. For semiconductor, a value near 5×10^{-17} cm^{-3} and 750 ns delay time for zero plasma intensity were determined. This is significantly different in the dielectric sample in this case at delay time of 2 ns the value of the electronic density is $\approx 2.5\times10^{-17}$ cm^{-3} and the intensity decays almost 0 at 200 ns. It worth to mention again, that the experimental conditions were the same in both experiments. It means that in both cases we put special attention in keep constant the laser fluence for both experiments.

The results presented above are not in agreement with the theoretical model of the femtosecond laser-matter interaction usually accepted. As it is well known, in dielectric materials there is a lake of charge carrier in the valence band, so the first step in laser mater interaction is to promote some electrons to conduction band. In semiconductors the situation is almost similar, except for the energetic states present in the energy gap. From this point of view, as it is reported in the literature, the laser mater interaction follows as if the material under irradiation were a metal. So, accordingly with this model of laser matter interaction the conclusion is that the quantity of electrons presented in the plasma formed due to the material ablation should be almost the same, regardless of the kind of material under study. As it can be seen from Figures 4 and 5 our results put in doubt this expected result. The behavior of the plasma decay for every of the samples is different depending on whether is a semiconductor or insulator.

It is widely known that dielectric materials are transparent to laser pulses of 800 nm, due to the conduction band is empty and there is not energetic level within the gap. However, as it is well known, in the presence of a laser radiation of high intensity (10^{14} W/cm^2) electrons can be promoted from valence to conduction band through nonlinear absorption processes.[11]

At this laser intensities free-carrier relaxation leads to self-trapped excitons (STE).[23] These STE are usually referred as defects in literature.[24] They mainly corresponds to energetic states situated in the gap of the dielectric material and it is known that are easily produced in fused silica.[23, 25] There are relatively recent experimental results indicating that the relaxation to this energetic levels introduced

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in the gap are the main energy relaxation pathway of the free-electron gas produced by laser excitation. [23] So those energetic levels would act as a sink of the electrons for SiO_2. Up to date no experimental data were reported about the existence of these self-trapped excitons in Si semiconductor, presumably due to smaller band gap.

CONCLUSIONS

In this paper we have shown different plasma characteristics both for semiconductor (Silicon) and dielectric materials (SiO_2) exploring the Silicon emission lines from the femtosecond plasma. Our results have shown a different behavior between both kinds of samples which indicate that the generally accepted model for interaction between laser and mater should be reviewed. As it is expected, the physical situation it is not the same wheatear the sample is a semiconductor or dielectric when interact with femtosecond laser radiation. Follow the temporal evolution of several spectroscopic lines of Silicon by using Imaging LIBS spectroscopy we carried out the measurements presented in this paper.

From the results shown in this paper, we observed an important difference between the plasma evolutions from the semiconductor and dielectric. The shorter plasma decays for dielectric compared with that obtained for semiconductor can be explained taking into account the defects of STE centers that can be created when high intensity (10^{14} W/cm^2) fs laser are used for ablation process. These centers act a sink source that limit the number of free electron that can be promoted to the conduction band by the fs laser interaction.

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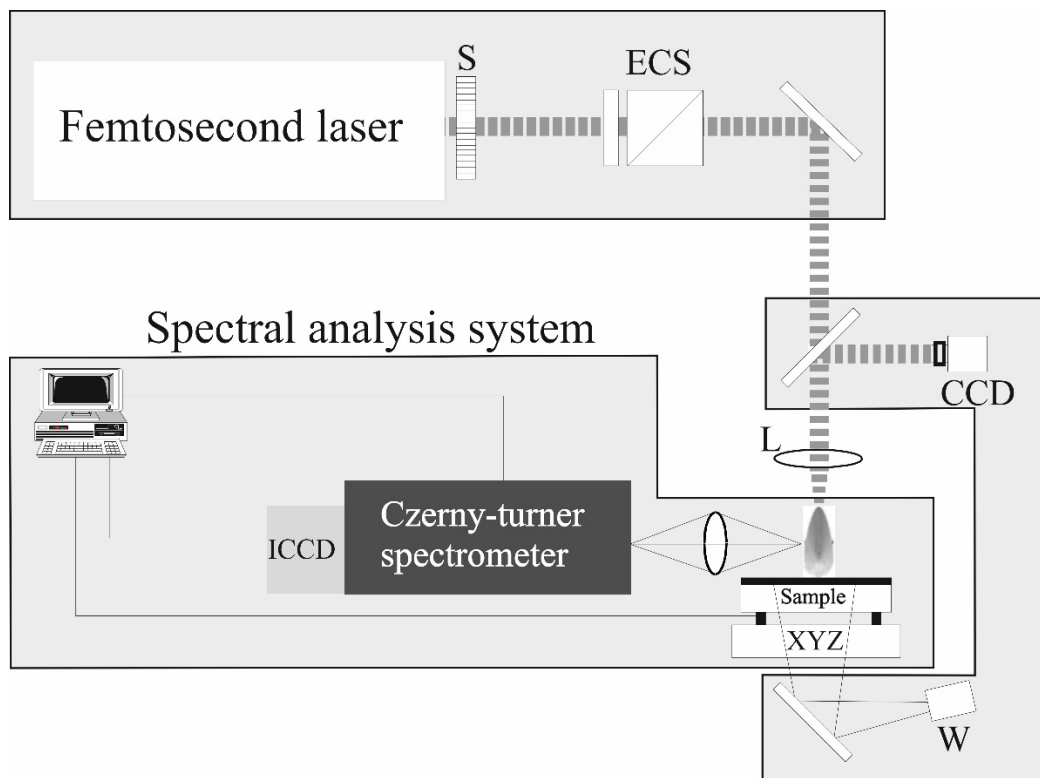
Figure Captions.

Figure 1: Experimental set-up, where S is a laser shutter, ECS is an Electronic Controlled Shutter, CCD is a camera to locate the exact point where the laser is impinging on the sample, L is a focuses lens, W is a white diode to back illuminate the samples and XYZ is a motorized 3 axes translation stage.
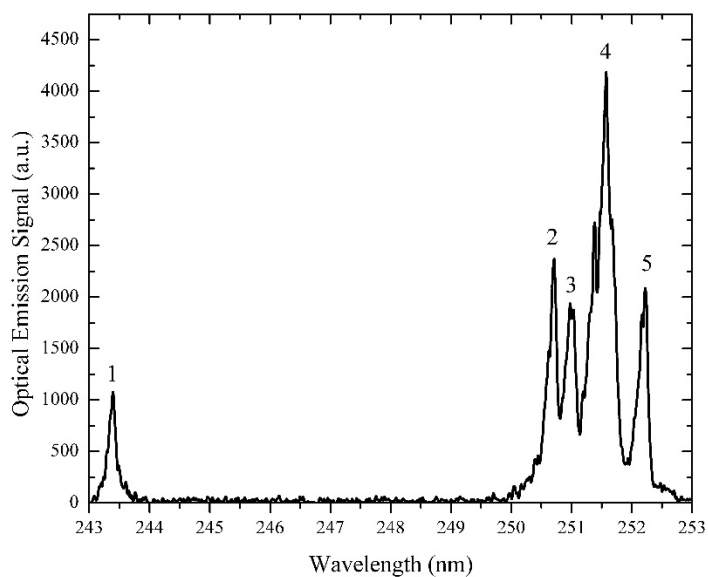

Figure 2: Emission spectra of the femtosecond generated plasma. The identification of each of the numbers in the figure is shown in Table I.
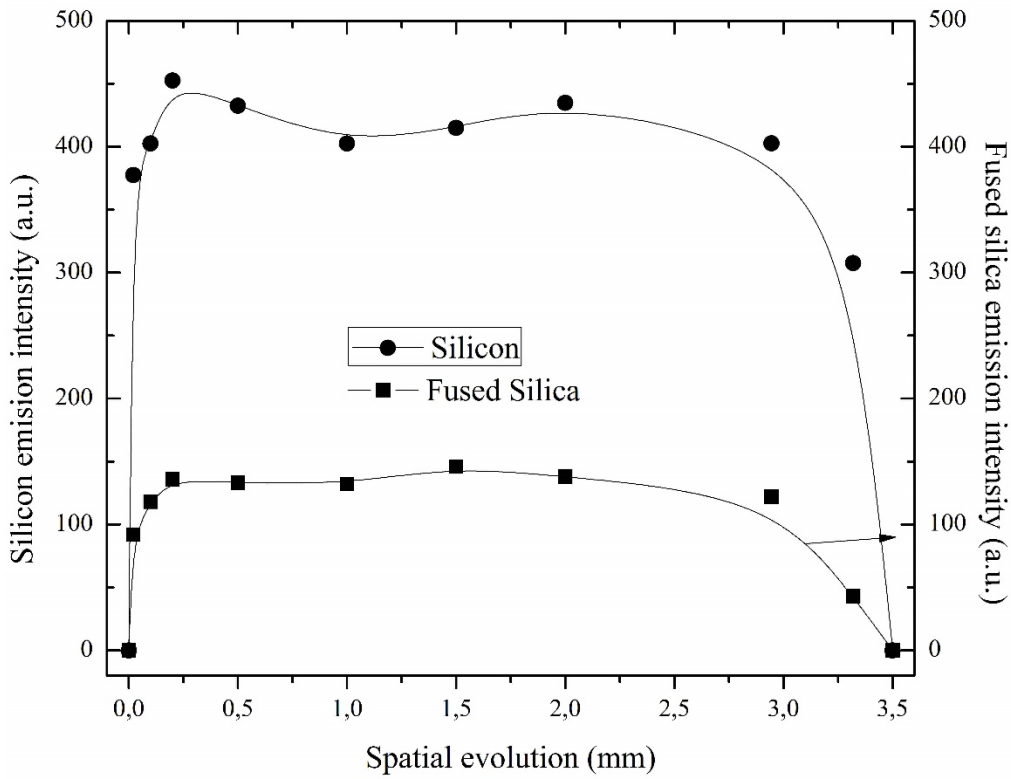
Figure 3: Spatial distribution of the intensity for Si, λ= 243,5 nm. On left axis is shown the intensity for Silicon and in right axis the intensity for SiO_2.
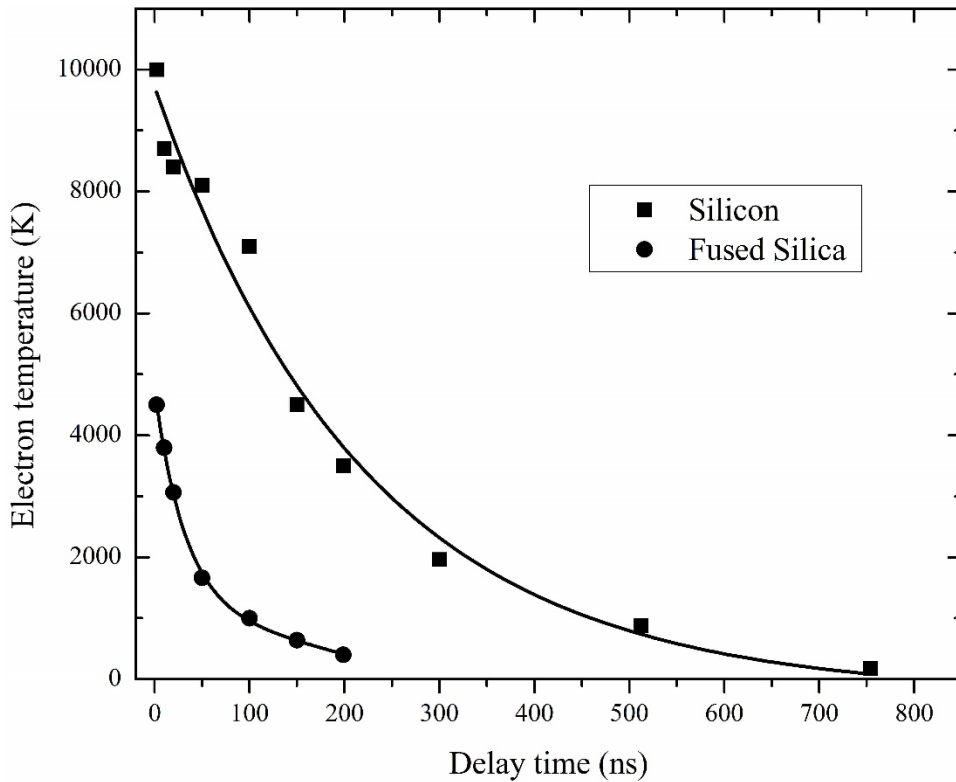

Figure 4: Evolution of the plasma electronic temperature for Si and SiO_2 as a function of the delay time.
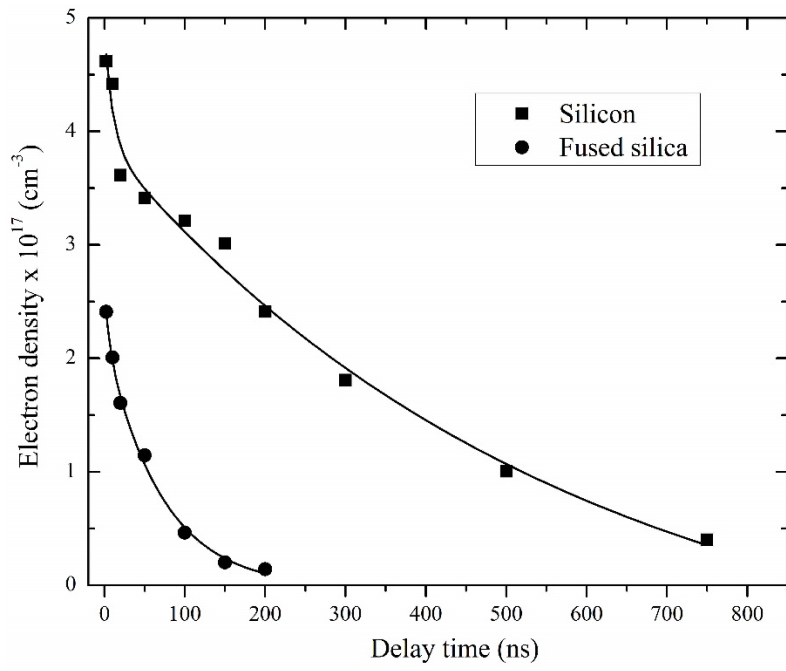
Figure 5: Evolution of the plasma electronic density for Si and SiO2 as a function of the delay time.