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Interaction of an intense laser field with a dielectric containing metallic nanoparticles

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ABSTRACT In order to understand the role played by nanodefects in optical breakdown of dielectrics, the interaction of an intense laser field with model dielectric samples containing metallic nanoparticles is studied both theoretically and experimentally. A theoretical study of the metal conduction electrons dynamics in the laser field predicts an efficient injection of carriers from the metallic inclusion to the conduction band of the dielectric, which leads to a strong local increase of the optical absorption in the initially transparent matrix. This prediction is tested experimentally by using time-resolved spectral interferometry to measure excitation densities as a function of the laser intensity in silica samples doped with gold nanoparticles, which are compared with similar measurements in pure silica.

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1 Introduction

In the large laser facilities dedicated to inertial fusion, dielectric materials used for the optical elements will be subjected to high laser fluences (e.g. 10 J/cm^2 at 351 nm). Although these fluences are below the threshold for intrinsic optical breakdown of these materials, in practice such intense laser beams are found to induce unpredictable local damage on large-aperture optics. There is increasing evidence that this damage is due to the unavoidable presence of nanometric defects (micro-fractures, impurity clusters, etc.) in the dielectric matrix [1, 2]. These defects are difficult to detect and to characterize, which makes it all the more difficult to determine by which processes they initiate optical damage.

In order to understand these mechanisms for damage initiation, we are studying a model system, which consists of nanometric metallic inclusions embedded in a dielectric matrix [3, 4]. The purpose is to understand the influence of these nanometric defects on the interaction with the laser field.

To determine the laser energy deposition in such systems, we have developed a theoretical model, including the description of thermionic and photoelectric effects in the metallic inclusions[5]. A strong injection of electrons by metal nanoparticles in the surrounding dielectric matrix is predicted, which leads to the creation of a plasma around the inclusion, and hence to an increase in the optical absorption of the medium. This model is briefly presented in Sect. 2. To test these predictions experimentally, we are using time-resolved spectral-phase interferometry to study the interaction of an intense femtosecond laser pulse with a 1-micron-thick SiO_2 film containing gold nanoparticles. This technique provides the instantaneous change in refractive index induced in the sample by the pump pulse, and thus gives access to the excitation density in the target. Comparison with pure dielectric targets indicates a strong effect of the gold nanoparticles. The principle of this technique and some of the results it has provided on pure dielectrics [6] are presented in Sect. 3. The experimental results on silica samples doped with gold nanoinclusions are presented in Sect. 4. We discuss a possible interpretation of the observed effects in Sect. 5.

2 Theoretical study

A two-temperature description of the metallic nanoparticle is inadequate for a strong electron excitation in the femtosecond regime. Firstly, because at such time scale the electron-distribution function differs from the Fermi–Dirac one and, secondly, the electron-ejection processes do not necessarily conserve the electron number inside the nanoparticle. Hence, we have developed a kinetic theory for the interaction of laser radiation with metal nanoparticles embedded in a wide-band-gap dielectric [5]. The formalism is based on the integration of the Boltzmann equation for electrons of an open system (varying number of particles). This enables us to describe electron exchanges between the nanoparticles and the silica matrix, in particular through thermionic and photoelectric emission. Such a kinetic theory is required to properly evaluate these exchanges, which are determined by the tail of the electron-energy distribution. The model also includes nanoparticle–matrix energy transfer by thermal conduction.

This kinetic model has been used to calculate the laser energy deposition and redistribution inside a gold nanoparticle towards the silica matrix. An important part of the gold electron population is found to be driven beyond a typical 10-eV energy. Thus, an efficient excitation of electrons from the valence to the conduction band of silica might occur around a gold nanoparticle, thanks to the following mechan-

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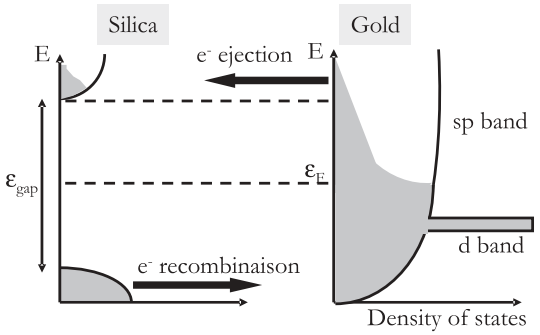

FIGURE 1 Schematic of the electron-ejection process from a metallic nanoinclusion to the surrounding silica matrix

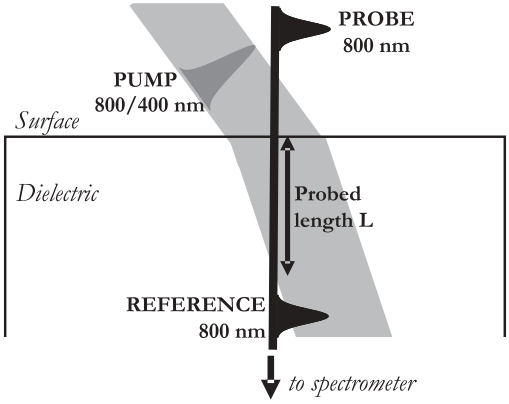

FIGURE 2 Configuration of the pump and probe beams impinging on the silica sample

ism (Fig. 1): (i) conduction electrons in gold are heated by the laser field, (ii) once a gold conduction electron has enough energy, it can access the conduction band of silica and thus escape the nanoparticle by thermionic or photoelectric effects, (iii) this electron is assumed to be instantaneously replaced by a silica valence electron, which can again be heated by the laser field and access the silica conduction band. The metallic nanoparticle would thus act as a 'shortcut' between the valence and the conduction bands of silica.

Numerical calculations [5] show that this process could result in the ejection of many more electrons than initially present in the nanoparticle, leading to the creation of a plasma around the particle. These conduction electrons in silica then absorb laser energy through electron–photon–phonon collisions, leading to an energy deposition much higher than for an isolated gold nanoparticle interacting with the same laser field.

3 Principle of spectral interferometry and experimental results on pure dielectrics

To validate this model experimentally, we are using time-resolved spectral interferometry, a technique well suited to the study of laser–dielectric interaction [6, 7].

Two identical 60-fs pulses, separated by a fixed delay Δt of the order of a few ps, are used to probe the refractive-index changes induced in a dielectric by an intense pump pulse (Fig. 2). The spectrum of this twin-pulse signal presents fringes, because of the interference between the spectra of the two pulses: these spectra indeed have the same amplitudes, but differ by a frequency-dependent phase factor $e^{i\omega\Delta t}$. The pump pulse excites the solid between the first pulse (reference) and the second (probe). It results in a change $\Delta n = n - n_1$ in refractive index of the dielectric (n_1 being the refractive index of the non-excited solid), which leads to a change $\Delta\Phi$ in the relative phase of the reference and the probe, and thus to a measurable shift of the spectral fringes. This phase shift $\Delta\Phi$ is given by $\Delta\Phi(t) = 2\pi\,\Delta n(t)L/\lambda$, where t is the pump–probe delay, λ is the probe wavelength in vacuum, and L is the probed length (Fig. 2).

For this study, we are using a 800-nm reference/probe beam and either a 400-nm or a 800-nm pump beam (fundamental and second harmonic of a 20-Hz, TW Ti–Sa laser). These two beams were spatially superimposed at the surface of the solid, and made an angle of about 30° inside the dielectric. The probed length L depends on the pump diameter (Fig. 2) and is about 10 μm in the present case.

This technique has been successfully used to study the ultra-fast dynamics of conduction electrons in dielectrics [6]. In silica, the change in refractive index $\Delta n(t)$ induced by the pump pulse varies in time in the following way (Fig. 3a): (i) the optical Kerr effect induced by the pump pulse first leads to a positive Δn, (ii) when the pump intensity gets high enough, electrons are excited into the conduction band, leading to a negative Δn as predicted by the Drude model, (iii) all these electrons then evolve with a time constant $\tau = 150$ fs into localized electronic states through the formation of self-trapped excitons (STEs), which leads to a positive Δn according to the Lorentz model [6].

The important point for the present work is that, for large enough delays after the pump pulse (such as those indicated

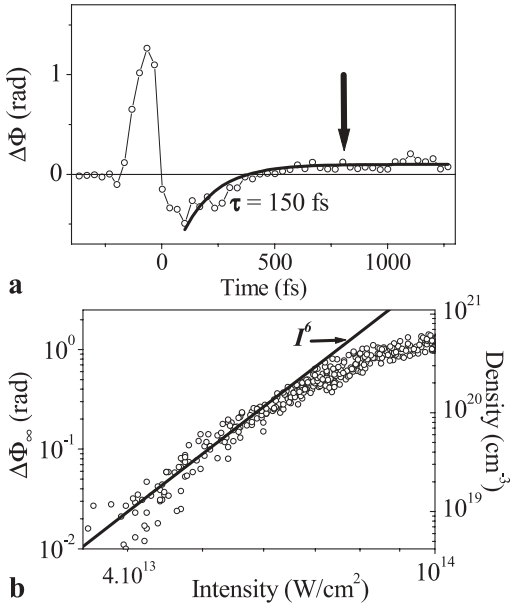

FIGURE 3 Typical experimental results on bulk silica. **a** shows the temporal evolution of $\Delta\Phi$. **b** shows the positive phase shift at long delays (*arrow* in **a**) as a function of the peak intensity of a 800-nm, 60-fs pump pulse. The *right-hand axis* gives the correspondence between the measured phase shift and the excitation density, assuming that the medium is homogeneously excited along the probed length

by the vertical arrow in Fig. 3a), $\Delta\Phi(t) = \Delta\Phi_\infty$ is directly proportional to the density N_{STE} of STEs created by the pump. Thus, measuring the probe phase shift a few hundreds of fs after the pump pulse gives access to the STE population. The evolution of this population with the pump intensity provides insight into the non-linear excitation mechanisms by the laser field.

This approach has already been successfully used to evidence multiphoton absorption of infrared light in pure dielectrics [7]. This is illustrated in Fig. 3b, which shows a measurement of $\Delta\Phi_\infty$ in silica as a function of the peak intensity I of a 800-nm ($\hbar\omega = 1.55$ eV), 60-fs pump pulse.

This phase shift is observed to vary as I^6: the exponent of this power law corresponds to the minimum number of photons that valence electrons have to absorb to be injected into the conduction band of SiO_2 ($6\hbar\omega = 9.42\,\mathrm{eV} > \varepsilon_{\mathrm{gap}} \approx 9\,\mathrm{eV}$). This proves that the dominant excitation process in this intensity range is perturbative multiphoton absorption by valence electrons. At higher intensities, a saturation of $\Delta\Phi_\infty(I)$ is observed compared to this power law. It is due to the absorption of the pump beam over the probed length by the laser-excited conduction electrons, which becomes efficient at high excitation densities.

We note that by measuring the negative phase shift $\Delta\Phi(t_e)$ at the appropriate time t_e just after the pump pulse, the evolution of the conduction-electron density with the pump intensity can also in principle be obtained. However, in this case, the situation is not as simple as for $\Delta\Phi_\infty$, since the Kerr effect, and the STEs that have already formed, might also contribute to the phase shift measured in this delay range.

4 Experimental results: effect of gold nanoparticles

We have compared the intensity dependences of $\Delta\Phi_\infty$ for a 400-nm pump in three samples: a bulk silica substrate covered with a thin layer of gold-doped vapor-deposited silica, a similar sample without any gold (i.e. covered with a pure vapor-deposited silica layer), and a pure bulk silica sample.

The first two samples have been elaborated at the Laboratoire de Spectroscopie Ionique et Moleculaire (LASIM) at the University of Lyon I (France) [8]. The experimental set-up enables to obtain a maximum layer thickness of about 1 μm: as a consequence, our probe beam not only probes the deposited layer, but also, and mostly, bulk silica corresponding to the substrate. The two LASIM samples used in this study were covered with a 1-μm layer of silica. For the gold-doped sample, this layer contained 10^{17} cm^{-3} gold nanoparticles of 2-nm diameter, corresponding to a 20-nm distance between the inclusions.

The temporal behavior of $\Delta\Phi(t) = 2\pi\Delta n(t)L/\lambda$ was found to be qualitatively the same in the three samples: a positive phase shift occurs when the pump and probe temporally overlap, followed by a negative phase shift due to free electrons, which relaxes to a positive value in about 150 fs. However, the behavior of the three samples differs quantitatively. This can be seen by comparing the intensity dependences of $\Delta\Phi_\infty$ in the three samples (Fig. 4) for a 400-nm pump.

In pure bulk silica, this phase shift is observed to evolve as I^n with $n = 5$. This dependence is stronger than the $n = 3$ power law that would be expected for multiphoton excitation of silica at 400 nm. This might be due to the absorption by the valence electrons of more photons than the minimum number required to cross the band gap [9].

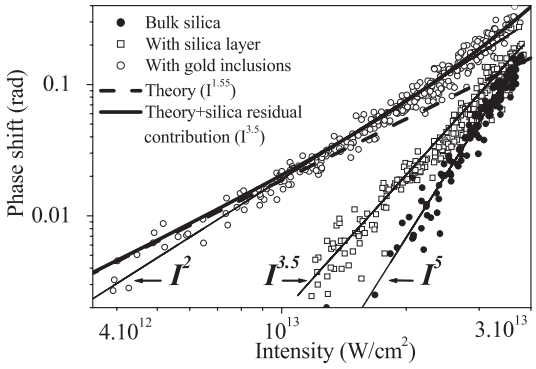

FIGURE 4 Evolution of $\Delta\Phi_\infty$ with the intensity of a ≈ 60-fs, 400-nm pump pulse, in three silica samples (silica substrate covered with a 1-μm gold-doped silica layer, similar sample without gold inclusions, pure bulk silica). The *dashed line* shows the prediction of the kinetic model for the long-delay phase shift induced solely through the effect of gold nanoparticles. When the residual contribution of the silica matrix ($I^{3.5}$ curve) is added to this calculated curve, a very good agreement with the experimental data is obtained (*thick full line*)

In the presence of a pure vapor-deposited silica layer, a slight shift of the $\Delta\Phi_\infty(I)$ curve towards lower intensities is observed, as well as a small change in the exponent ($n \approx 3.5$). This is probably due to the more perturbed structure of this deposited silica and to the presence of defects, which might lead to a reduction of the band gap and hence to a higher excitation probability and to a smaller non-linearity of the excitation process.

When gold nanoparticles are added, a very strong shift of the $\Delta\Phi_\infty(I)$ curve towards lower intensities is observed. This curve follows a power law with an exponent of $n = 2$. Such a strong shift is remarkable, since gold nanoparticles are only present in the 1-μm-thick layer, which is about 10 times thinner than the total probed length L of silica.

5 Discussion

At first sight, these measurements appear to confirm the theoretical predictions of Sect. 2: electrons would be injected from the gold nanoparticles to the silica matrix, where they would then trap and form STEs, leading to the observed positive phase shift. This mechanism would require lower intensities than n-photon ($n \geq 3$) absorption in pure silica, thus leading to the observed shift of $\Delta\Phi_\infty(I)$ towards lower intensities in the presence of gold inclusions. However, our theoretical results seem to suggest another, less direct, interpretation.

The kinetic model described in Sect. 2 has recently been extended to describe the dynamics of the electrons once they have escaped from the nanoparticles. We have assumed that excited carriers follow an ambipolar diffusion mechanism. This approach remains essentially phenomenological and will require some improvements. The model also takes into account laser energy deposition on free electrons, their trapping as STEs in 150 fs, and energy transfer from the carriers to the lattice.

The first results of this model suggest that the positive phase shift $\Delta\Phi_\infty$ observed in the presence of gold inclusions might not have the same origin as in pure silica. This would forbid a direct comparison of the measurements with and without gold.

In pure silica, we have seen that this phase shift is due to the contribution of STEs to the refractive index. In the presence of gold nanoparticles, our calculations show that this contribution of STEs to Δn might be dominated by the following mechanism: as electrons escape from the nanoparticles, a dense plasma is created around the inclusion, and this plasma strongly absorbs the laser energy. This leads to a strong local temperature increase of the silica matrix, and thus to a local increase in refractive index [10].

The $\Delta\Phi_\infty(I)$ curve calculated by taking this effect into account is shown in Fig. 4 (dashed curve). It is obtained by calculating the effective dielectric constant of this inhomogeneous medium. When adding to this curve the residual contribution of the silica layer and substrate to the positive phase shift ($I^{3.5}$ curve), a very good agreement with the experimental data is obtained. The exact position of the curve was adjusted by varying the nanoinclusion density. The best fit was obtained for 0.85×10^{17} cm^{-3}, in very good agreement with the experimental estimation of 10^{17} cm^{-3}.

We emphasize that this temperature increase is caused by the high local density of excited carriers, and is therefore significant only at very high intensities and excitation densities in pure silica.

Spectral interferometry can also be used to obtain the change in absorption induced by the pump pulse, by exploiting the fringe contrast. We have not focused on this quantity during the first set of measurements. However, some data have been obtained which indeed indicate that the absorption of the probe beam after the pump beam is much higher in the presence of gold nanoparticles. This effect is consistent with the previous interpretation, and will be investigated in more detail in future measurements.

6 Conclusion

A model has been developed for the interaction of an intense laser field with a silica matrix containing gold nanoparticles. Spectral interferometry experiments in the fs regime have been carried out to test this model, and have revealed strong effects due to the presence of gold nanoparticles. These effects suggest that a strong absorption of the laser energy occurs around the gold nanoparticles, leading to a local temperature increase that produces a noticeable change in the refractive index of silica, detectable with spectral interferometry. More experiments will be required to get a full understanding of these first results. This approach should lead to a better insight into the mechanisms of optical breakdown initiation by nanodefects in dielectrics, a major technical issue for high-energy lasers.

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