The role of energy and phase relaxation ($T_1$ and $T_2$) in ultrafast laser ablation

Juergen Reif, Florenta Costache, Sebastian Eckert

1 Brandenburgische Technische Universität Cottbus, Konrad-Wachsmann-Allee 1; 03046 Cottbus; Germany
2 IHP/BTU JointLab; Cottbus; Germany

Email: reif@tu-cottbus.de

Abstract. The dynamics of ultrafast laser ablation have been studied by pump-probe experiments, monitoring the ablated ions by time-of-flight mass spectroscopy. For both dielectric and metal target materials, despite their substantial physical difference, a rather similar, general dependence of the ion yield on the pump-probe delay has been observed: for short delays, the typical "coherence" peak occurs, then the signal goes down to zero, and after a longer delay, the signal increases again. This behaviour is discussed in a picture of energy and phase relaxation ($T_1$, $T_2$) mechanisms.

1. Introduction

Though laser ablation has been the subject of intensive research for many years (cf. for instance previous Conferences on Laser Ablation [1]), the investigation of the detailed dynamics still represents an interesting challenge. Driven by the availability of ultrashort laser pulses, experiment and theory try to gain deeper and deeper insight into the fundamental processes, from light-target energy coupling [2] over energy dissipation [3] to particle ejection [4,5] and, finally, target (surface) relaxation [6].

Generally accepted concepts suggest, that there are two principal energy coupling mechanisms: multiphoton absorption and free electron impact heating [7,8], the first being always involved for large bandgap materials, either alone or to provide starting electrons for the second. For the particle ejection, again, two principal mechanisms have been identified: Coulomb explosion preceded by surface ionisation [5,9] and phase explosion as a consequence of superheating [4]. Theoretical simulations [10,11] indicate that the ablation process is associated with the generation of a substantial instability and thermal non-equilibrium at the surface.

In this contribution, we report on femtosecond pump-probe ablation experiments to study the dynamics of energy dissipation in the target.

2. Experimental arrangement

In our experiment, we used pairs of 120-fs laser pulses, separated in time by an adjustable delay, to produce ablation from targets (freshly cleaved BaF$_2$ and CaF$_2$ single crystals in (111) orientation and aluminium foils) placed in an ultra-high-vacuum chamber at a base pressure of $\approx 10^{-10}$ mbar. The pulse pairs were derived in a Michelson-arrangement from the output of a CPA Ti:Sapphire laser ($\lambda$ 800 nm, repetition rate 1 kHz). The two pulses were of fairly equal intensity and hit the target collinearly at an angle of 45°, focussed by a 300-mm lens. The delay between the two pulses could be adjusted by...
controlling the length of one interferometer arm using a translation stage with 0.1 μm resolution. Ablation was detected by monitoring the emitted particles with a time-of-flight mass spectrometer. Taking into account the well-known incubation effect of virgin surfaces [12], characterised by substantial shot-to-shot fluctuations of the ablation yield, the targets were prepared by a number of preconditioning pulses to reach a steady pulse-to-pulse regime. Further, the laser intensity in all experiments was kept well below the (single shot) ablation threshold, i.e. in the desorption range, and was so low that single pulses (at large delays) only generated a very low desorption signal.

3. Experimental results
Typical results of the emitted-particle-yield dependence on the delay between the two pulses in a pair are presented in Figs. 1 - 4.

**Figure 1**: Yield of emitted particles from BaF₂ as a function of delay between pump and probe pulse of equal intensity. The traces are labelled to indicate the respective species.

**Figure 2**: Central peak of BaF⁺ ions desorbed from BaF₂ as a function of delay between pump and probe pulse of equal intensity. The solid line is a Gaussian fit to the data, yielding a width corresponding to the pulse duration.

**Figure 3**: Yield of Ca⁺ ions desorbed from CaF₂ as a function of delay between pump and probe pulse of equal intensity. The solid Gaussian curve inside the central peaks indicates the laser pulse shape. Upper panel: low intensity (0.45×10¹² W/cm²) Lower panel: high intensity (0.9×10¹² W/cm²)

**Figure 4**: Yield of Al₂⁺ ions desorbed from an aluminium foil as a function of delay between pump and probe pulse of equal intensity. The shaded area indicates the central peak, shown in the insert at a widely spread time scale.
As is expected, at the overlap of both pulses the desorption signal is strongly enhanced in all materials. In addition, however, a second desorption range can be observed where the pulses are well separated. For dielectrics, this separation is at the order of 0.5 to 2 ps, for aluminium it is substantially larger and amounts to more than 10 ps. It should be noted here, that on aluminium this effect had already been observed earlier [13]. The central overlap-range corresponds, generally, to about the pulse autocorrelation width of 130 fs. As an exception, the Ba⁺ peak from BaF₂ (Fig. 1) appears to be wider and the Al₂⁺ peak from aluminium (insert in Fig. 2) slightly smaller. However, this might be due to a problem of correctly defining the base line (and thus the total signal height) for the rather strong signals.

A peculiar feature is shown on Fig. 3. The second desorption range only occurs above a certain threshold (lower panel) for the single pulse intensity which coincides with the previously presented transition in ablation mechanism from pure Coulomb-explosion to additional ablation mechanisms, e.g. phase explosion [14]. At lower intensity, desorption enhancement is only observed in the pulse-overlap range.

In Table 1, we present a summary of the delay times for the second desorption range with the materials studied:

| Material | Delay time $T_1$ |
|----------|------------------|
| BaF₂     | 0.9 ps           |
| CaF₂     | 0.3 ps           |
| Al       | 17 ps            |

4. Discussion

In an attempt to understand this behaviour, we start with an idea presented previously for the case of aluminium [13]. There, it was suggested that at large delays the second-pulse ablation may occur from an increased absorption coefficient in a thin liquid film at the surface, prepared by the first pulse. Second, we take into consideration that the ablation/desorption process results in a strong surface instability [10,11,15]. Third, we remember the particular result of Fig. 3.

Putting all these features together, we propose the following scenario: The delayed desorption peak can only be explained by assuming that, for the corresponding pulse separation, the target is changed such that the single-pulse energy coupling is enhanced compared to the unperturbed surface. For instance, the band structure may be completely changed or, at least, exhibit a high density of defect states.

Possibly, this could mean an unstable [15] or even liquid [13] surface area, created by the impact of the first pulse. This is only possible if energy deposited in the target electrons has dissipated to the lattice [3], exciting phonons and even breaking bonds, thus creating a "soft" state with different electronic properties. The decrease of this delayed desorption at still larger delays would, then, correspond to a relaxation of the soft state to normal equilibrium.

For an interpretation, we suggest to consider the situation in a peculiar way. Recalling Anisimov's picture of two distinct regimes, (1) an excited free electron gas at and shortly after excitation and (2) the electron gas coupled to the lattice, we treat the system as a two-level-system with the ground state representing regime (2) and the excited state resembling regime (1). Then, we adopt a formalism which was developed in Quantum Optics to describe such a two-level-system by an optical Bloch vector [16] in analogy to a spin system. In this formalism, we can associate the time for energy dissipation to the lattice with an energy relaxation time of the electron gas, i.e. level (1), classically termed $T_1$ or longitudinal relaxation time. This coupling time between electron gas and lattice could correspond to the electron-phonon relaxation time which, to our knowledge, has not been reliably determined, so far, for the materials investigated in the present study. The result of Fig. 3 indicates that, for this effect to occur, the primary excitation has to be sufficiently strong, i.e., that enough electrons must be created in the first pulse to efficiently couple to the lattice.
Once this picture is established, also the "coherence peak" in the pulse-overlap range can be described in a consistent way. In the Bloch vector picture, another characteristic time has to be considered: the much faster transversal relaxation time $T_2$, denoting a phase relaxation. In analogy, a strong desorption must be observed for delays where the second pulse addresses electrons which still have a "memory" of the first pulse: As long as the electrons excited by the first pulse conserve their phase, the ensemble cannot distinguish between one or multiple pulses arriving, and all pulses act coherently at their combined intensity. Only after the electronic coherence is destroyed, by electron-electron collisions, the two pulses act separately, the total effect being that of their convolution, as in an autocorrelation.

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