ELSEVIER

Applied Surface Science 186 (2002) 339–344

applied surface science

www.elsevier.com/locate/apsusc

Femtosecond time-resolved photo-stimulated desorption from ionic crystals

A.G. Joly[a], W.P. Hess[a,*], K.M. Beck[a], J.T. Dickinson[b]

[a]*Pacific Northwest National Laboratory, K8-88, P.O. Box 999, 902 Battelle Blvd., Richland, WA 99352, USA*
[b]*Department of Physics, Washington State University, Pullman, WA 99164, USA*

Abstract

We have used the pump–probe technique to measure the positive ion yield, from ionic crystals, as a function of time delay between two femtosecond laser pulses. The two-pulse technique allows direct observation of solid state and surface dynamics on a femtosecond timescale. We find the ion yield, from 265 nm irradiated MgO and KBr, depends critically on the time delay between pulses. For example, the Mg^+ desorption yield displays three distinct features; a coherence peak followed by a fast rise and decay features. In contrast, the yield of K^+ from KBr displays only the coherence peak and picosecond decay features. The observed ion detection thresholds suggest that, although the nanosecond laser ion desorption mechanism may be dominated by defect photoabsorption, significant electron–hole pair production may contribute to the femtosecond laser desorption mechanism. By determining the ultrafast time-dependence of positive ion emission, we hope to reveal the mechanism of laser ion desorption for both regimes.

Keywords: Laser desorption; Femtosecond time-resolved; Ionic crystals

1. Introduction

Laser ablation and desorption techniques are utilized extensively in a diverse range of disciplines including the production of new materials and extrinsic or in situ chemical analysis [1,2]. Unfortunately, no detailed mechanistic understanding of the processes leading to ion emission has emerged due to the inherent complexity of the laser excitation and subsequent particle emission processes. To date, most laser desorption/ablation processes have utilized nanosecond pulses even though many of the primary processes such as electron/hole recombination [3,4], trapping [5,6], electron–phonon interactions, and exciton relaxation [7,8] occur on a sub-nanosecond timescale. For this reason, femtosecond laser pulses may provide unique insight and serve to clarify the steps involved in the desorption process.

In this paper, we report time-resolved ion desorption yields from MgO and KBr crystals using femtosecond laser pump–probe techniques. The positive ion yield is measured as a function of the temporal delay between two equivalent sub-bandgap UV femtosecond laser pulses impinging upon cleaved MgO or KBr crystals. The ultrafast laser pump–probe technique reveals rapid condensed-phase dynamics that cannot be observed using nanosecond pulses. The high peak intensities of femtosecond pulses open multiphoton absorption pathways to higher excited levels than is possible using nanosecond pulses near the ion emission threshold. Thus, near threshold, the

---

[*] Corresponding author. Tel.: +1-509-376-9907;
zfax: +1-509-376-6066.
E-mail address: wayne.hess@pnl.gov (W.P. Hess).

0169-4332/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0169-4332(01)00670-5

ion desorption mechanism is different for femtosecond and nanosecond laser excitation.

Our previous femtosecond studies of MgO [9,10] and lithium fluoride [11] have shown that the laser pulse width has a significant influence upon the ion mass spectra and that the ion yield varies dramatically with the delay between the sub-threshold pump and probe pulses. Even short delays of a few hundred femtoseconds produce qualitatively distinct ion mass spectra from the single-pulse femtosecond result. The femtosecond laser desorption mechanism proceeds through a multiphoton process while the nanosecond mechanism proceeds through a series of single-photon excitations described as "multiple" photon [12]. In this paper, we present ion desorption results from MgO, obtained with greater time resolution, that reveal interesting new dynamics. Additionally, ultrafast time-resolved measurements of KBr are discussed and compared to previous femto- and nanosecond laser desorption results.

2. Experimental

The experimental apparatus has been described previously [9]. Briefly, the ultrahigh vacuum chamber is fitted with a variable temperature sample manipulator, Wiley–McLaren time-of-flight mass spectrometer, and laser access windows. The base pressure of the vacuum system was maintained at 4×10^{-10} Torr. In a typical experiment, a freshly cleaved (in air) sample of synthetically grown single crystal MgO or KBr is mounted on the sample holder, no attempt is made to select a particular crystallographic orientation with respect to the laser polarization vector.

Femtosecond UV pulses are produced in an amplified titanium–sapphire laser system operating at a fundamental wavelength of 795 nm at a repetition rate of 20 Hz. The amplified output is frequency doubled and tripled in KDP crystals producing 1.5 mJ/pulse at 265 nm. The ultrafast pulse is split into a pair of approximately equivalent pulses. One pulse is directed through a variable distance optical delay line and the pulse pair is recombined, at a small angle, on the sample surface. The pulse energy is adjusted such that each pulse is near, but below, threshold for ion emission/detection. A single mass/charge peak may be integrated and averaged as a function of delay between laser pulses. Using a third-order correlation technique, the correlation width of the UV pulses was found to be about 250 fs. This translates into a 150 fs FWHM pulse width assuming a Gaussian pulse profile. All experiments are performed at room temperature.

3. Results and discussion

Fig. 1 shows the Mg^+ ion signal plotted as a function of delay between femtosecond laser pulses. The figure inset displays an expanded short-time region. Clearly, there are at least three distinct time regions: (i) a narrow coherence peak centered at zero delay with an approximately Gaussian profile; (ii) a fast, picosecond growth and (iii) a slow ~25 ps decay. In addition, a distinct longer decay (>60 ps but not shown) has been reported previously [9]. Fig. 2 shows the short time region of the Mg^+ ion signal when the pulses are polarized parallel and perpendicular to each other. Also shown in Fig. 2 is the third-order correlation of the ultraviolet femtosecond pulses for comparison. The narrow coherence peak is present only if the two laser pulses have parallel polarizations, while the subsequent picosecond duration growth feature exists for cross-polarized pulses as well.

The width of the zero-time feature is significantly shorter than the measured third-order correlation. Therefore, the coherence feature must arise from a high-order nonlinear material response. We have measured the ion yield versus laser power dependence following femtosecond irradiation and found it to be between P^4 and P^5. A similar nonlinear power dependence was reported for MgO under nanosecond pulse excitation and a "multiple" photon model was proposed to explain ion desorption at much lower laser intensities [12]. The coherence feature dominates when both pulses are parallel polarized and overlapped spatially and temporally. The two simultaneous pulses produce a higher intensity pulse (nearly twice the ion emission threshold) that results in an enhanced ion yield due to the high-order nonlinear (multiphoton) material response. Since the ion yield is of a very high-order in the power density, the coherence peak temporal width is significantly narrower than the inherent femtosecond pulse width. If the laser pulse polarizations are perpendicular, the coherence peak is

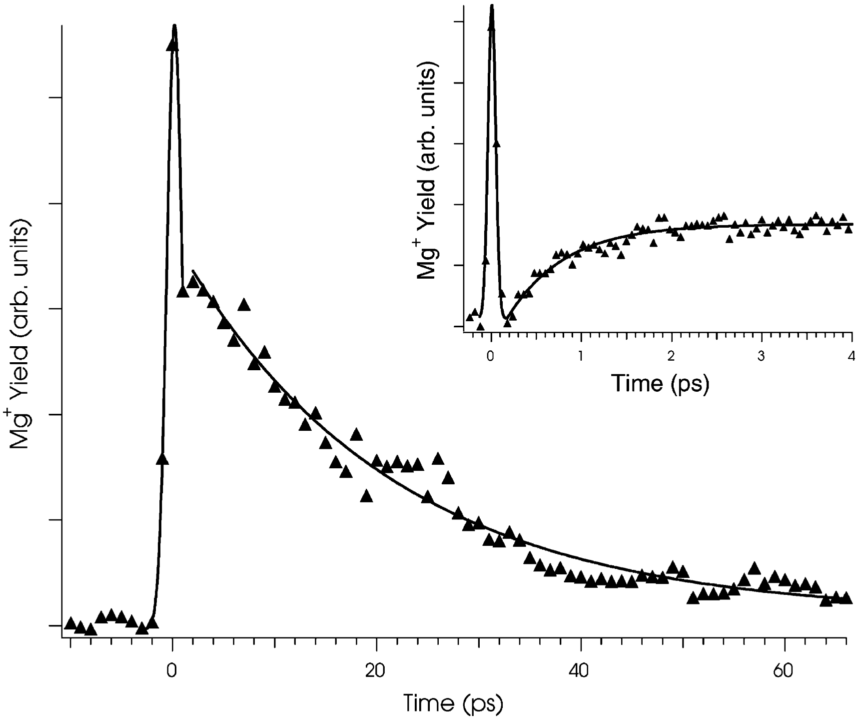

Fig. 1. The desorption yield of Mg^+ from MgO as a function of delay between pump and probe pulses. The inset shows an expanded view of the short-time region. The probe laser beam is blocked for delay times less than −2 ps to obtain a baseline zero.

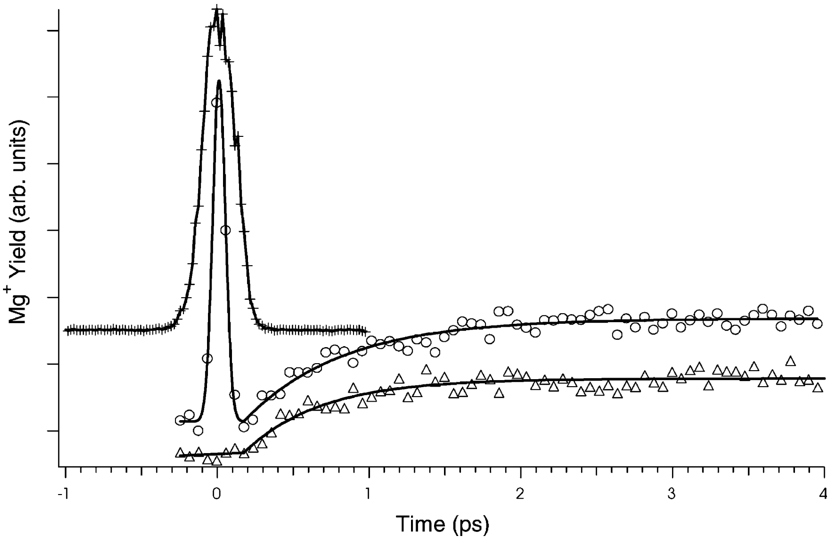

Fig. 2. The desorption yield of Mg^+ from MgO measured as a function of delay between pump and probe pulses for both parallel (circles) and perpendicular (triangles) pump/probe polarization combinations. Also shown is the third-order correlation measurement of the uv pulses (crosses).

absent because the material is responding to each pulse individually and hence the ion emission process is significantly reduced.

There are a number of processes which may lead to desorption of positive ions following either femtosecond or nanosecond excitation. The highly nonlinear power dependence, polarization dependence, and narrowed temporal width of the coherence peak argue strongly that multiphoton absorption is the dominant excitation mechanism resulting in positive ion desorption following ultrashort single-pulse excitation. Such multiphoton excitation would be expected to produce photo-electron emission, hot conduction band electrons, and hot holes in addition to exciting electron traps such as F and F^+ centers. The complex interplay between electrons, holes, and defect states then presumably leads to ion emission. However, the detailed mechanism of femtosecond laser ion desorption from MgO and other ionic crystals remains unclear.

The fast ~1 ps growth feature displayed in Figs. 1 and 2 has not been previously observed. The growth feature lifetime is significantly longer than the pulse duration and is independent of the polarization combinations of the pump and probe pulses. The growth feature represents the evolution of the initially excited state or precursor state through either relaxation or actual reaction to a transient state that may further interact with either photons from the probe pulse or new species directly created by the probe pulse. It is the combined interactions that result in Mg^+ emission in delayed pulse pair excitation. The transient intermediate state then decays on the longer (20 ps and greater) timescale. The transient state lifetime is commensurate with the 50 ps lifetime measured for free carriers by Petite et al. [4] using a femtosecond interferometric technique.

In addition to multiphoton excitation, femtosecond pulse excitation could conceivably be due to single- or multiple single-photon excitation at surface defect sites such as corners, step edges, or kinks. Calculations by Shluger et al. [13,14] demonstrate that such surface defects lower the excitation bandgap by several eV, possibly allowing single-photon excitation at 265 nm (4.7 eV). Similarly, Dickinson and coworkers [12] have suggested a model that requires multiple excitations of F and/or F^+ centers to explain high-order nanosecond power dependences. Such a process involves excitation of electrons that then move to new sites in the lattice. When a significant number of positively charged defects are created near a Mg surface ion, the Mg ion experiences coulomb repulsion and desorbs with high kinetic energy [15]. Multiple electron promotions are required, accounting for the high-order power dependence. We note that this model is related to hole-trapping, which has been proposed to explain desorption of neutral surface adatoms from semiconductors [16,17].

Femtosecond pulses have a variety of excitation mechanisms available. First of all, direct multiphoton excitation (such as is responsible for the coherence peak) may produce hot electron–hole $(e^- - h^+)$ pairs or other energetic species. Also, single-photon excitation of surface defect states (such as steps or kinks) or F or F^+ centers in the lattice may occur. At least one of these species (representing the initial state) must evolve over the picosecond growth lifetime. Whether this evolution involves relaxation of species such as hot holes or excitons, or structural change such as hole- or exciton-trapping, is not known. That the intermediate state then survives for several tens of picoseconds, over which time it may interact with the probe pulse, provides an attractive explanation for the mechanism of nanosecond desorption in the low-fluence regime. Since the formation of this state takes roughly a picosecond and it survives for several tens of picoseconds, a single nanosecond pulse could both create the initial precursor and provide subsequent excitation necessary for ion emission. This view is similar to the model proposed by Dickinson et al. [12,15]. In contrast, femtosecond pulses lead to desorption primarily through a coherent multiphoton absorption process as evidenced by the coherence peak. In essence, although the material excitation (precursor state) exists to produce Mg^+ ions through multiple single-photon events, the pulse duration is too short relative to the intermediate state's formation time to induce such a mechanism.

Potassium bromide (KBr) is also a widely studied insulating crystal [18]. Unlike MgO, however, the KBr crystal is formed by singly instead of doubly charged ions. The differences in electronic structure allow the formation of self-trapped holes in bulk KBr, in contrast to MgO [19]. Fig. 3 shows the results from femtosecond pump–probe experiments performed on single crystal KBr. Fig. 3 shows a large sharp feature at zero-time, and then a slower ~20 ps decay

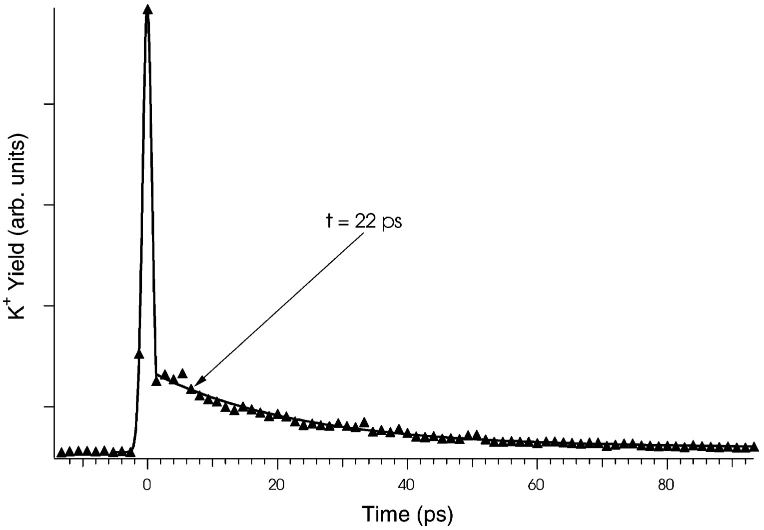

Fig. 3. The desorption yield of K^+ from KBr as a function of delay between pump and probe pulses. In contrast to Mg^+ from MgO, within our signal/noise, there is no observable short-time rise after the coherence feature at zero-time. The probe laser beam is blocked for delay times less than −2 ps to obtain a baseline zero.

in the ion signal. In contrast to MgO, there is no observable prominent rise following the coherence peak at zero delay time within our signal/noise. Once again, KBr allows one to understand the mechanistic differences between femtosecond and nanosecond desorption. The short-time, multi-photon feature is presumably responsible for femtosecond desorption while the longer 20 ps tail allows subsequent single-photon absorption steps for nanosecond pulses.

Petite and coworkers [20] have measured the hole-trapping rate and by extension of the conduction band electron lifetime in KBr and found it to be on the order of 1 ps. While this value is significantly less than our measured decay rate, Shluger and Tanimura [21] have observed that formation of the completely relaxed V_k center requires 10 ps at 80 K. Clearly, further experiments are needed to elucidate the fundamental processes involved in desorption of positive ions from KBr and other wide bandgap ionic crystals.

Acknowledgements

The authors gratefully acknowledge Dr. A.L. Shluger and Dr. P.V. Sushko of University College, London, for insightful discussions. The authors were supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences. Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle under contract No. DE-AC06-76RLO 1830.

References

[1] R.E. Russo, D.B. Geohegan, R.F. Haglund, Jnr., K. Murakami (Eds.), Proceedings of the Fourth International Conference on Laser Ablation (COLA'97), Elsevier, Amsterdam, 1997.
[2] J.S. Horwitz, H.-U. Krebs, K. Murakami, M. Stuke (Eds.), Proceedings of the Fifth International Conference on Laser Ablation (COLA'99), Springer, Heidelberg, 1999.
[3] G. Petite, P. Daguzan, S. Guizard, P. Martin, Nucl. Instrum. Meth. B 107 (1996) 97.
[4] G. Petite, P. Daguzan, S. Guizard, P. Martin, Appl. Surf. Sci. 109/110 (1997) 36.
[5] T. Makimura, K. Tanimura, N. Itoh, T. Tokizaki, A. Nakamura, J. Phys. Condens. Matt. 6 (1994) 4581.
[6] T. Shibata, S. Iwai, T. Tokizaki, K. Tanimura, A. Nakamura, N. Itoh, Phys. Rev. B 49 (1994) 13255.
[7] S. Iwai, T. Tokizaki, A. Nakamura, K. Tanimura, N. Itoh, A. Shluger, Phys. Rev. Lett. 76 (1996) 1691.
[8] T. Sugiyama, H. Fujiwara, T. Suzuki, K. Tanimura, Phys. Rev. B 54 (1996) 15109.
[9] W.P. Hess, A.G. Joly, K.M. Beck, R.M. Williams, J.T. Dickinson, Appl. Phys. A 69 (1999) S389.
[10] K.M. Beck, A.G. Joly, W.P. Hess, Surf. Sci. 451 (2000) 166.
[11] A.G. Joly, K.M. Beck, W.P. Hess, Appl. Phys. A 69 (1999) S153.

[12] D.R. Ermer, J.-J. Shin, S.C. Langford, K.W. Hipps, J.T. Dickinson, J. Appl. Phys. 80 (1996) 6452.

[13] P.V. Sushko, A.L. Shluger, Surf. Sci. 421 (1999) L157.

[14] A.L. Shluger, P.V. Sushko, L.N. Kantorovich, Phys. Rev. B 59 (1999) 2417.

[15] J.T. Dickinson, S.C. Langford, J.J. Shin, D.L. Doering, Phys. Rev. Lett. 73 (1994) 2630.

[16] Y. Nakai, K. Hattori, N. Itoh, Appl. Phys. Lett. 56 (1990) 1980.

[17] K. Hattori, A. Okano, Y. Nakai, N. Itoh, Phys. Rev. B 45 (1992) 8424.

[18] K.M. Beck, A.G. Joly, W.P. Hess, Phys. Rev. B 63 (2001) 125423, references therein.

[19] A.L. Shluger, R.W. Grimes, C.R.A. Catlow, N. Itoh, J. Phys. Condens. Matt. 3 (1991) 8027.

[20] S. Guizard, C. Itoh, P. Martin, P. Meynadier, P. D'Oliveira, M. Perdrix, G. Petite, Nucl. Instrum. Meth. B 141 (1998) 66.

[21] A.L. Shluger, K. Tanimura, Phys. Rev. B 61 (2000) 5392.