Dynamics of Electronic Excitations Involved in Laser-Induced Damage in HfO_2 and SiO_2 Films

K. R. P. Kafka, B. N. Hoffman, A. A. Kozlov, and S. G. Demos

Laboratory for Laser Energetics, University of Rochester

Progress toward the development of thin-film–based optical components to meet the increasing demand for higher peak or average-power short-pulse laser systems requires improvements in their resistance to laser-induced damage. Understanding the dynamics of electron excitations associated with the initiation of laser-induced damage and the role of defects is of fundamental interest. The presence of native defects in a thin film is largely dependent on the manufacturing process.[1] Recent work has demonstrated that different defect species are responsible for damage initiation depending on the laser pulse length.[2] This suggests that the excitation and relaxation parameters of the precursor defects are directly expressed by the fluence where these defects can initiate damage for a given set of laser parameters. Pump–probe time-resolved experiments are a standard method being used to study the dynamics of electronic excitations. Such damage-testing experiments previously performed have provided important information (such as the relaxation time of the conduction band electrons and the presence of a delayed return to pre-exposure conditions).[3]

The present work aims to reveal information on the dynamics of the electronic excitation at the onset of damage initiation in plasma ion–assisted deposition silica and hafnia monolayers. The experiments employ a pump–probe damage-testing configuration using 1053-nm, 0.6-ps laser pulses. Special attention was given to the determination of damage-initiation conditions, which are defined by any observable material modification using differential-interference contrast (DIC) microscopy. In each set of data, the pump pulse intensity/fluence is kept constant and below that of the single-pulse laser-induced–damage threshold ($LIDT_1$), while the temporally delayed probe pulse fluence is independently adjusted to the onset of damage initiation. By analyzing the probe beam's damage threshold ($LIDT_{probe}$) as a function of delay, combined with detailed study of the resulting morphology, we aim to characterize the relaxation dynamics of defects that are involved in the damage process.

The measured $LIDT_{probe}$ values (markers) are shown in Fig. 1 for both hafnia and silica samples for the indicated pump fluence levels. The $LIDT_{probe}$ values increase with increasing delay toward the respective $LIDT_1$ values (horizontal lines). This behavior provides insight into the dynamics of the relaxation of electronic excitations associated with the damage initiation process that are activated by the pump pulse. The experimental results in hafnia show that the effective relaxation time of the pump-induced excitation depends on the pump fluence. For the lowest pump fluence, the $LIDT_{probe}$ returns to the single-pulse value by a 100-ps delay, while for the highest pump fluence, the $LIDT_{probe}$ value does not fully return within the 1-ns delay range of this experiment.

The morphology of the damage sites was studied using DIC and SEM microscopies. DIC microscopy images (not shown) demonstrate that when the pump and probe fluences are held constant, the density (severity) of damage significantly decreases as the delay increases for both materials. SEM analysis reveals that all damage sites of both materials (generated at damage threshold conditions) are composed of nanoscale pits, including sites formed by a single pulse. Characteristic images are shown in Fig. 2 for the case of silica. The SEM image of damage formed by a single pulse with fluence at $LIDT_1$ [Fig. 2(a)] demonstrates a nanopit damage density $>10^8$ cm^{-2}.

The series of SEM images at different delay times shown in Fig. 2 indicates that the morphology of the silica damage sites changes with pump–probe delay time, with their size being the most-characteristic attribute of this effect. There are two general types of pits, which for simplicity we will refer to as "smaller" (having a diameter <100 nm) and "larger" (having a diameter

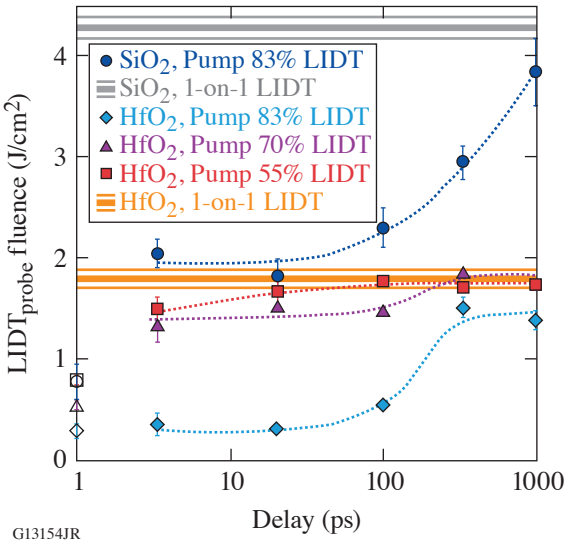

Figure 1
Double-pulse damage thresholds as a function of delay for indicated pump fluences. Horizontal lines indicate the one-pulse LIDT and uncertainty values for hafnia (orange lines) and silica (gray lines). Open markers represent the theoretical minimum value. Dotted lines are drawn to guide the eye.

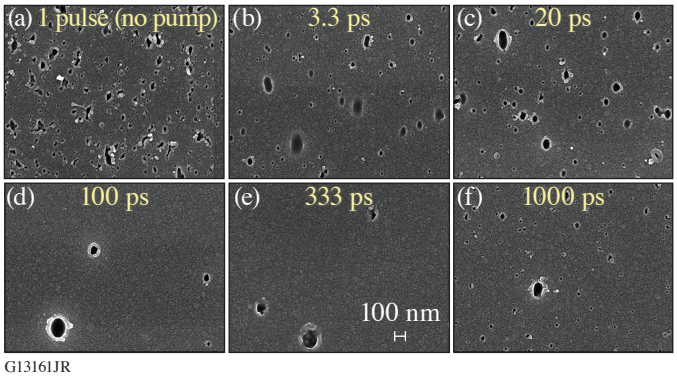

Figure 2
SEM images of damage sites on SiO_2 tested in vacuum at near-threshold fluences and indicated delay times. Fluences: (a) $\phi_{pump} = 0$, $\phi_{probe} = 4.5$ J/cm^2, [(b)–(f)] $\phi_{pump} = 83\%$ $LIDT_1$ with ϕ_{probe} values as follows: (b) 2.2 J/cm^2, (c) 2.0 J/cm^2, (d) 2.5 J/cm^2, (e) 3.2 J/cm^2, and (f) 3.8 J/cm^2.

>100 nm). Damage with a single pulse exclusively contains the smaller pits at very high damage density. These smaller pits are also observed for short delay times (3.3 ps and 20 ps) and reappear at 1000 ps, when the $LIDT_{probe}$ has returned to single-pulse damage behavior. In contrast, the larger pits were generated with much lower damage density and observed at all tested double-pulse delays (>3 ps) but not under single-pulse damage. Therefore, both types of pits were observed to coexist only at delays of 3.3 ps, 20 ps, and 1000 ps, as manifested in Fig. 2. SEM analysis of hafnia damage sites also shows the nanopit morphology but lacks any evidence suggesting a change in the damage morphologies as a function of the delay time.

Previous observations demonstrated that damage in silica/hafnia multilayer dielectric coatings is initiated by two different mechanisms as a function of the pulse duration, where the change in mechanism occurs at about 2.5 ps (Ref. 2). It was suggested that this may arise from defect populations having different properties, either physical (such as size) or stoichiometric/electronic. Following this line of reasoning, we postulate that the morphology behavior observed for silica in this work is due to two types of defects that have different relaxation times. This hypothesis requires further investigation that is outside the scope of this work.

Finally, it must be noted that the SEM images clearly show that damage initiates at distinct locations, even though some adjacent pits do merge together. Due to this high areal density of nanopits at damage initiation conditions with a single pulse, of the order of 10^8 cm^{-2}, it is not surprising that damage appears to be uniform at lower magnifications for subpicosecond laser pulses, giving rise to the widely adopted assumption that damage is "intrinsic." This perception becomes dominant in optical components employing multilayer dielectric coatings, when damage initiates below the top layer of the multilayer coating.

In conclusion, the results indicate that the relaxation time of electronic excitations associated with laser-induced–damage initiation depends on the pump fluence and extends up to about 1 ns. Furthermore, the damage morphology near $LIDT_1$ in all cases was observed to be a collection of nanopits. The results for silica show two different types of nanopit morphologies, arguably suggesting two types of defects, that manifest on different time scales: (1) <100 ps and (2) >3 ps, while observations for hafnia were unable to distinguish multiple morphologies. Future work identifying these defect structures could potentially enable subsequent material optimization for damage performance with subpicosecond lasers.

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