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Materials response to glancing incidence femtosecond laser ablation

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A femtosecond Ti:sapphire laser was used to ablate samples of copper, strontium titanate (STO), a nickel alloy René 88DT (R88), {111}-oriented single crystal silicon, and gallium nitride (GaN) *in situ* in a focused ion beam scanning electron microscope (FIB-SEM). The laser beam was scanned parallel to the specimen surface, which resulted in laser ablation using the tail of the Gaussian beam distribution, near the ablation threshold for each of the materials. Transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD) were utilized to investigate damage in the bulk and at the surface of the laser ablated samples in cross-sections that were extracted by FIB-SEM. In contrast to normal incidence, post-ablation damage in the glancing incidence configuration was extremely limited across a wide range of laser pulse energies. Elevated dislocation densities were observed within 150–200 nm of the ablated surface in the Cu, STO, and R88 samples. An amorphized Si layer as thin as 30–50 nm was observed with no dislocations near the surface or in the bulk. Gallium nitride exhibited exceptional damage resistance to femtosecond laser irradiation, whereby no laser-induced dislocations or amorphization near the ablated surface was observed. For materials where there is surface damage following laser ablation, we show that a subsequent machining step with a Ga^+ FIB beam located in the same chamber can remove this damage in a short period of time.

1. Introduction

Femtosecond lasers have enabled new pathways for surface texturing and rapid material removal across many materials systems [1–8]. Femtosecond laser induced material removal also allows for chemical analysis of the ablating species via light induced breakdown spectroscopy [9,10]. For specific experimental geometries, the resulting low-fluence femtosecond laser pulses used to ablate material result in very low damage surfaces that are amenable for direct imaging for emerging tomography techniques. This enables 3D mesoscale materials characterization with nm-scale resolution and multiple chemical, structural, and crystallographic imaging modalities [11,12].

The unique low damage nature of ultrashort pulsed laser-material interactions are a result of the large impulse of energy (mJ pulse energies) tightly focused onto the sample surface over time periods often substantially less than 500 fs. Kinetic transport and the ablation processes do not begin to occur until long after (> 100 ps) the laser pulse has been deposited [13–15]. The large amount of energy deposited into the structure over such short time scales suppresses large scale structural damage and melting in crystalline and amorphous materials because the interaction is mostly confined within the electronic structure of the material [16,17]. The difference in thermalization time between the electronic structure and the lattice significantly reduces the extent of thermal damage surrounding the ablation event [4,13].

The mechanisms by which material is removed during femtosecond laser ablation and the resulting forms of damage are dependent on the absorbed fluence on the target and the material

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properties. Under beam-normal to surface incidence conditions, distinct transitions in the type of damage and laser ablation rates are observed across fluence thresholds in many materials. Transitions in damage type occur as the ablation threshold is crossed [2,18,19] and with the crossing from low fluence to high fluence threshold [6,20]. The values of these discrete thresholds depend on the optical penetration depth and the electronic heat conduction within the irradiated material, which have been studied in detail for some metals [19]. For instance, laser ablated metals may experience dislocation injection [5,21,22], phase changes [23], or recrystallization [24] during laser ablation. However, semiconductors are observed to amorphize [2], recrystallize [25], exhibit phase changes [26], and generate dislocations [27] under certain laser processing conditions. Dielectrics respond differently by not exhibiting discrete changes in the rate of material removal during ablation [8,28] - likely due to their low thermal conductivity.

Femtosecond laser ablated surfaces have been studied using a range of analytical techniques. These include optical microscopy [29], scanning electron microscopy (SEM) [5,20], electron backscatter diffraction (EBSD) [21,22], and transmission electron microscopy (TEM) [5,30–33] imaging of the ablation region resulting from single laser pulses impinging with normal incidence to the sample surface. For most materials, melting occurs at very high fluences, often near the peak of the Gaussian beam with regions of high dislocation densities or amorphization radially surrounding the high fluence region of the pulse. In contrast, laser ablation at glancing incidence to the sample surface limits laser pulse energy deposited at the material removal interface to low fluences near the ablation threshold. This results in low levels of damage [5,31,33], though damage resulting from glancing incidence irradiation has not yet been studied in detail. In this research, results of damage studies performed on a series of laser ablated materials, including metals, semiconductors, and ceramics with glancing incidence ablation are presented. These different materials classes were methodically examined using consistent experimental methodologies and characterization approaches.

2. Experimental

Samples of annealed oxygen-free high conductivity (OFHC) Cu, strontium titanate (STO), a Ni-based superalloy René 88DT (R88), Si, and GaN were irradiated using the TriBeam [12], which is a FIB-SEM microscope with *in-situ* femtosecond laser capability. A Ti:sapphire gain medium femtosecond laser operating at 780 nm wavelength, 1 kHz repetition rate, and 150 fs pulse width was used to ablate sample surfaces in the TriBeam FIB-SEM vacuum chamber at a pressure of 4×10^{-6} mbar. The laser beam propagation direction was aligned parallel with the sample surfaces and then scanned laterally, as shown schematically in Fig. 1. The stage on which the sample is mounted is composed of piezoelectric driven nm-resolution actuators (X, Y, Z, tilt) that permit material removal by incrementally moving the sample surface into the scanning beam path, shown in Fig. 1a. The TriBeam system and the femtosecond ablation process is described in more detail elsewhere [34].

The sample surfaces were incrementally laser machined with a scanned beam by raising the specimen using the z-positioner of the piezo substage at micron to sub-micron step sizes. The femtosecond laser beam is tightly focused into a spot diameter of 15–35 μm with a Gaussian profile. The beam is scanned horizontally, as shown in Fig. 1a and b, with 75% spot overlap in the beam scanning direction. The beam is scanned across the surface with a width up to 1.2 mm for 100–200 lateral passes in order to remove all material within the focused and scanned beam region that is above the ablation threshold (θ_{th}), the point at which vaporization occurs [35]. The location of the ablation threshold along the radial edge of the Gaussian beam is shown schematically in Fig. 1b. As a result, the tail of the Gaussian beam profile that has fluence at or very near the ablation threshold of the material, is the only part of the beam interacting with the final sample surface. The removal rate as a function of beam fluence is shown in Fig. 1c for laser pulses across a wide range of fluences in a nickel base superalloy [20]. Laser machining with the beam parallel results in irradiation fluences at or near the ablation threshold, which is a property unique to each material [36]. The focusing optics have a depth of focus of 0.98 mm. The sample surface was incrementally raised with the piezo stage z-positioner with 1 μm steps into the tail of the Gaussian beam between laser beam scanning operations. The sample surfaces were milled at least 50–100 μm (50–100 slices) in depth. The laser machining procedure used in this study is in contrast to other single pulse type laser machining studies or hole drilling, where the laser beam propagation direction is orthogonal to the sample surface that experiences the full Gaussian distribution of the beam energy.

Measurements of the light induced periodic surface structure (LIPSS) wavelength were made from secondary electron SEM images collected from the laser machined sample surfaces. The LIPSS structures form with their long axis oriented orthogonal to the linear polarization vector of the laser light [2,37–39], which has been chosen such that the long axis of the LIPSS structures is also orthogonal to the propagation direction of the laser beam. The amplitude of the LIPSS structures were additionally measured in the TEM lamellae extracted from the laser machined sample surface. The long axis of the lamellae was oriented to be orthogonal to the prevailing LIPSS structure orientation, therefore capturing a cross-section of the LIPSS wavelength where the damage is observed to vary somewhat between the maximum and minimum amplitude. A summary of the LIPSS wavelength and amplitude measurements, using SEM and TEM, are given in Table 1.

Electron backscatter diffraction (EBSD) maps were collected from the laser machined surfaces surrounding the lift-out areas using a FEI Quanta 3D FIB-SEM equipped with an EDAX Hikari XP EBSD in order to determine the crystallographic orientations of the grains contained in the TEM foils. Grain orientation information was collected directly from the laser ablated surfaces with a 0.5 μm resolution at 70° tilt relative to the 25 keV electron beam operating at a 3–30 nA beam current.

TEM analysis was carried out on lamellae extracted from the laser ablated surfaces in each sample to determine the extent of subsurface damage. TEM specimens were extracted from the samples using a FEI dual-beam Helios Nanolab 600 FIB-SEM equipped with a tungsten Omniprobe needle for lamella extraction. In order to ensure that ion damage or implantation did not occur on the specimen surface, the TEM lamellae were protected with approximately 500 nm of electron beam deposited Pt, followed by an additional 1.5 μm of ion-beam deposited Pt. The TEM lamella were investigated using a FEI T20 TEM operated at 200 keV in both conventional bright-field and dark-field imaging modes.

EBSD information was also collected from the Cu TEM lamella to quantitatively determine misorientation gradients that can result from laser irradiation. These scans were performed with the samples tilted to 70° relative to the 30 keV electron beam operating at a 0.5–5 nA beam currents and collected with 0.5 μm in plane resolution.

In order to investigate methods to remove small-scale material damage from near-surface regions the STO, nickel alloy, and Si specimens were also milled after laser ablation using a near glancing angle Ga^+ focused ion beam at the accelerating voltages and beam currents shown in Table 2. TEM lamellae were extracted from the laser ablated and ion milled regions using the same protocol as detailed for the laser ablated surfaces. Detailed analysis of