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Crystalline orientation effects on conical structure formation in femtosecond laser irradiation of silicon and germanium

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ABSTRACT

Irradiation of Si(1 0 0), Si(1 1 1), Si(1 1 0), Ge(1 0 0), and Ge(1 1 1) is compared for 150 fs, 800 nm wavelength pulses in a rough vacuum atmosphere. The surface crystalline orientation of the material is found to affect the final morphology, with (1 1 1)- and (1 1 0)-surface orientations exhibiting a much higher tendency for conical structure formation under multiple-pulse irradiation. Using cross-sectional transmission electron microscopy, the structures on Si(1 1 1) are found to have primarily crystalline cores with the same crystalline orientation as the substrate. The results show that the crystalline orientation of the target should be considered in laser machining applications.

1. Introduction

Laser-based processing of materials has been an active area of research, both from the desire to better understand laser-material interaction, and because of the possibility of developing improved manufacturing techniques in industrial applications [1]. The use of femtosecond laser pulses for material irradiation can provide better precision than that obtained using longer pulse lasers, due to a generally reduced plasma shielding effect and heat affected zone [1]. Study of the final state of materials, such as the resultant crystallinity and surface morphology, can be used to understand the material modification processes during intense irradiation. On semiconductors a variety of laser-induced modifications have been observed, such as annular rings and rims [2–4], amorphization [4–9] and periodic 'ripples' [10–14]. Cone-like structures have been previously reported on silicon after femtosecond laser irradiation [3,14–17], with the irradiation atmosphere affecting the morphology [16,17]. Structure formation may be detrimental in some applications, possibly limiting the precision or smoothness with which surfaces can be prepared. However, surface roughening can be beneficial in other applications, for instance when an increased surface area is desired. Such is the case for improving adhesion of other materials [16] and applications where high optical absorption is desired [15,18]. Pointed structures can be used as field-emission sources [16,18]. Texturing can change the hydrophobic properties of surfaces [19], and affect cell attachment in biomedical applications [20]. Femtosecond laser milling can provide various advantages in prototyping and material manufacturing, and as an alternative to photolithography [3].

We present surface structuring of silicon and germanium irradiated by various pulse fluences and numbers of femtosecond pulses, with particular attention paid to the effects of different target crystal orientations. These effects are important to consider when comparing the results from different experiments in the literature, since the optical properties and chemical composition of the target and atmosphere are not the only factors which can influence the final morphology. The choice of substrate orientation

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could affect the applicability of laser structuring for certain applications. Silicon and germanium are compared to investigate the generality of the behaviour.

2. Experimental

Unless otherwise specified, the laser source used for material irradiation was a regeneratively amplified Ti:sapphire-based laser system producing linearly polarized $\sim$150 fs pulses, operating at a peak wavelength of 800 nm and a pulse repetition rate of 1 kHz. The Ge(1 0 0) and Ge(1 1 1) samples were undoped with a thickness of approximately 300 μm each. Samples of Si(1 0 0) and Si(1 1 1) (phosphorous-doped with 2$-$6 Ω-cm resistivity, and boron-doped with 7$-$13 Ω-cm resistivity respectively) were used, each approximately 300-μm thick. The boron-doped Si(1 1 0) samples with resistivity of 75$-$100 Ω-cm in this study were approximately 1000-μm thick. All irradiation targets had a polished front surface and a rough back surface, and were irradiated under similar conditions to allow straightforward comparison between targets. Irradiation proceeded in a fashion similar to that used in reference [11], and a brief summary is given here. Pulses were focussed using a 12.5 cm or 15.0 cm focal length BK7 plano-convex singlet lens through a 1-mm thick fused silica window onto targets placed in a small sample chamber, evacuated to a rough vacuum atmosphere (less than $\sim$100 mTorr). A grid of irradiation sites was produced on each sample, with various numbers of pulses N along one axis and pulse energy E along the other axis. After initial attenuation to 10–15 μJ per pulse using a half-wave plate and thin film polarizer, metallic neutral density filters in increments of 0.1 OD (transmission =10^{-OD}) allowed the variation of pulse energy, decreasing in steps to well below the sample modification threshold. The numbers of pulses included 1, 5, 10, 25, 50, 100, 200, 350, 500, 650, 750, 850, 1000, 2000, 5000, and 10,000, set by a computer-controlled mechanical shutter. When fewer than 50 pulses were desired, a mechanical chopper placed in the beam reduced the effective pulse repetition rate to 50 Hz. Certain experiments were repeated with the two different lenses, or with a separate $\sim$50 fs Ti:sapphire laser system, to check for the possibility that the results were due to an anomaly with a particular lens or laser.

Optical microscopy was used to image single-pulse irradiation sites, using both bright-field mode and Nomarski differential interference contrast (DIC) mode to enhance visibility of shallow surface features. No cleaning of the samples was performed between irradiation and imaging. As described previously (e.g. references [2,11]), measurements to the outside of the prominent ring on single-pulse sites were used with a D^2 method to determine the on-sample spot size $\omega_\circ$. Peak incident fluences ($2E/\pi\omega_\circ^2$) are reported here, not considering the reflectivity of the target surfaces. Scanning electron microscopy (SEM), which has a much greater depth of field than optical microscopy, was used to image multiple-pulse sites. Selected sites were processed using focussed ion beam (FIB) milling employing gallium ions, enabling subsequent cross-sectional transmission electron microscopy (TEM) analysis as done in previous works [7,9,13]. This allowed investigation of the final crystalline state of the material using bright-field and dark-field TEM imaging modes and selected-area electron diffraction. Energy-dispersive X-ray spectroscopy (EDXS) was performed in the TEM for elemental analysis.

3. Results

3.1. Surface analysis

On each of the five targets single-pulse irradiation sites were produced, possessing a thin irregular ring which was prominently visible under Nomarski DIC optical microscopy. For a given pulse energy, the diameter of the ring did not depend significantly on the crystalline orientation of the target. However, the ring diameters on germanium targets were larger than those on silicon for the same pulse energy, indicating a lower modification threshold on germanium. On Si(1 1 1) there was a region of higher optical reflectivity both within the thin ring and extending outside a short distance. On the other orientations of silicon, and on both germanium samples, the reflectivity of material within the ring did not significantly differ from the material outside the ring or from non-irradiated material.

Fig. 1 shows the three crystal orientations of silicon and the two orientations of germanium, with each site irradiated by 100 pulses at various pulse energies. Fig. 2 shows the five samples irradiated by various numbers of pulses, at a per-pulse fluence of approximately 810 mJ/cm^2. As in previous studies on semiconductors under similar conditions (e.g. references [9–14]), 'classic' low spatial frequency laser-induced periodic surface structures (LIPSS) could be formed on all samples. These run perpendicular to the polarization of the incident laser light and have periods $\sim$70–90% of the in-air irradiation wavelength. LIPSS are present in Figs. 1 and 2, and cover a large portion of the lowest fluence silicon sites, though the low magnification used in these images makes LIPSS difficult to resolve. When pulse energies near the material modification fluence were used, LIPSS gradually formed with increasing number of pulses over most of the laser-irradiated site. For higher energies and after higher numbers of pulses, they were eroded away in the central area of sites but were still often present in a ring around the site, where the local fluence was low. A coarse somewhat-periodic modulation can be seen on the walls of deeper sites, but this structure appears qualitatively different than the LIPSS which formed on the relatively flat surfaces in the lower fluence areas. The material composition (silicon or germanium) did not seem to affect the LIPSS period or direction, nor were the period and direction noticeably affected by the target crystalline orientation. The three crystallographic orientations of silicon did not show significant differences in their tendency to form these periodic structures. Germanium showed much lower tendency than silicon to form such LIPSS, although the two crystallographic orientations of germanium did not differ substantially in LIPSS formation. No periodic structures were observed after irradiation by only a single pulse. In an additional experiment performed on the silicon samples using 50 fs pulses and the 15.0 cm focal length lens, a half-wave plate was placed in the laser beam to rotate the laser polarization $\sim$45°. As in the experiments without the wave plate, the LIPSS formed running perpendicular to the incident laser polarization, independent of the surface crystallographic orientation.

Blunt cone-like structures with diameters of a few to several micrometres can form in the central region of the irradiation sites where the fluence is high enough that the ripples are eroded away. These had a much stronger tendency to form on the materials with (1 1 1)-surface orientation than on the materials with (1 0 0)-surface orientation. On the (1 0 0)-surface orientation, they were particularly lacking in the centers of the irradiation sites where the local fluence was highest. Instead of the blunt cones, the central areas of sites on (1 0 0) surfaces showed some roughness but minimal large-scale variation in depth. For silicon with a (1 1 0)-surface orientation, the cone formation tendency was similar to or slightly less than for (1 1 1). Experiments on Ge(1 1 0) were not performed in this study. For the Si(1 1 1), Si(1 1 0), and Ge(1 1 1), larger but more widely separated cones resulted from higher numbers of incident pulses. The dependence of conical structure formation on surface crystallographic orientation can be clearly seen in Figs. 1 and 2. For silicon, the differences in the formation