Subwavelength ripple formation on the surfaces of compound semiconductors irradiated with femtosecond laser pulses

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High-spatial-frequency periodic structures on the surfaces of InP, GaP, and GaAs have been observed after multiple-pulse femtosecond laser irradiation at wavelengths in the transparency regions of the respective solids. The periods of the structures are substantially shorter than the wavelengths of the incident laser fields in the bulk materials. In contrast, high-frequency structures were not observed for laser photon energies above the band gaps of the target materials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1586457]

Coherent surface structuring after laser irradiation of solids, also termed ripple formation, was first observed by Birnbaum[1] on various semiconductor surfaces. Since then, laser-induced periodic surface structures (LIPSS) have been reported on virtually all materials.[2–12] In many cases, after irradiation at normal incidence, the period of the observed structures is close to the wavelength of the incident radiation, with ripples oriented perpendicular to the direction of the electric field. However, reports of periodic structure formation with spatial period much smaller than the laser wavelength have recently been published.[13–15] Varel *et al.*[13] presented images of ablation craters produced on sapphire under multiple-pulse irradiation conditions (200-fs, 790-nm pulses) where patterns resembling higher spatial frequency ripples can be seen in the annular region see Fig. 1(c) in Ref. 13). Ozkan *et al.*[14] found ripples with periods ~50–100 nm resulting from 248-nm femtosecond laser irradiation of thin diamond films. Yasumaru *et al.*[15] reported formation of ripple patterns with mean periods of 100–125 and 30–40 nm on TiN and diamond-like carbon after irradiation with 800- and 267-nm femtosecond pulses, respectively.

We have extended the scope of these investigations to other materials and laser wavelengths. Our laser-irradiation studies were performed on (100) InAs, InP, GaP, and Si with femtosecond pulses at wavelengths of 2100, 1300, and 800 nm, and selected experiments were also conducted on (111) Ge, (100) and (110) GaAs, and sapphire samples (cut perpendicular to the *c*-axis). Under specific conditions, we observed the formation of high-spatial-frequency LIPSS (HSFL) on InP, GaP, GaAs, and sapphire, where the period of the LIPSS is significantly smaller than the wavelength of the incident light. Classic low-spatial-frequency LIPSS (LSFL), with a spatial period close to the wavelength of the excitation pulse, were observed on all materials studied after irradiation with all three wavelengths.

A commercial 130-fs Ti:sapphire regenerative amplifier was used to produce pulses at 800 nm, while pulses in the near infrared were obtained from an optical parametric amplifier pumped by another commercial 50-fs Ti:sapphire regenerative amplifier. Signal and idler beams at center wavelengths of 1300 and 2100 nm, respectively, and having pulse durations of 50–100 fs, were used. The samples were placed inside a small vacuum chamber (~0.1 mbar base pressure) mounted on a precision, computer-controlled *xyz* translation stage. A manual rotation stage allowed positioning of the sample around an axis normal to the sample surface in studies of the dependence of LIPSS formation on the crystal orientation. In this work, the number of pulses delivered to the samples is limited to rather low values, typically 1–100. This was achieved via a fast mechanical shutter synchronized with the laser operating at 10 Hz. The linearly polarized laser beam was focused on the sample at normal incidence by a 5× microscope objective, yielding spot sizes (beam radius at $1/e^2$) on the sample surfaces of ≈5 μm at 800 nm and ≈7–10 μm at 1300 and 2100 nm. After irradiation, the surface morphology was examined under a scanning electron microscope (SEM).

Single-femtosecond pulses with fluence exceeding the ablation threshold were found to leave smooth craters on the surfaces, exhibiting a characteristic rim marking the ablated area, with no evidence of LIPSS. The periodic surface structuring appeared only after several consecutive pulses and was found to depend on the material, the laser pulse fluence, the total accumulated fluence, and the wavelength. As in previous studies,[1–12] LSFL were most pronounced after multishot irradiation with single pulse fluences in the vicinity of the ablation threshold. In our experiments, HSFL were also observed, as illustrated for InP in Fig. 1. The figure shows the morphology of two ablation craters after irradiation with 20 pulses at a laser wavelength of 2100 nm, for single-pulse energies of 390 and 1100 nJ. The spatial period of HSFL is ≈430 nm. The formation of HSFL on InP was observed only after irradiation with 1300- and 2100-nm pulses, wavelengths corresponding to photon energies below the bandgap energy of InP, and with pulse fluence below the single-pulse ablation threshold. At fluences above the single-pulse ablation threshold, following multiple-pulse irradiation, the dominant features were the LSFL [Fig. 1(b)], with spatial periods close to the free space wavelength of the excitation pulse.

Figure 2 presents HSFL and commonly observed LSFL

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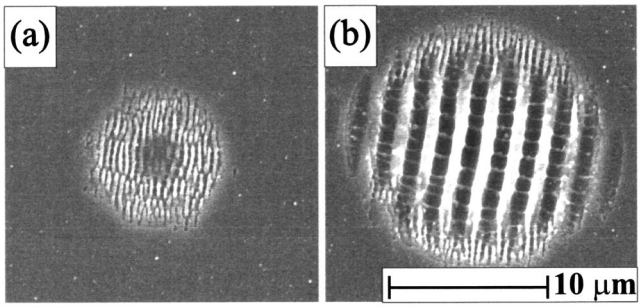

FIG. 1. Surface morphology of (100) InP after irradiation with 20 pulses at 2100 nm and pulse energies of (a) $E_p = 390$ nJ and (b) $E_p = 1100$ nJ. Ripples are perpendicular to the direction of the electric field. Some residual HSFL can still be seen on the outer perimeter of the larger feature, where the local fluence is below the single-pulse ablation threshold.

formed on GaP after irradiation with 800-, 1300-, and 2100-nm pulses. All three wavelengths are in the transparent region of GaP. The images were taken from central areas of the irradiated regions and were achieved under fluence conditions where respectively the HSFL and LSFL are the dominant structures. Figure 3 shows images of GaP, InP, InAs, and Si after irradiation with a 2100-nm beam, 20 consecutive pulses, and pulse fluences near the respective ablation thresholds. HSFL form rapidly in GaP and InP, appearing after a few consecutive laser pulses. In contrast with GaP and InP, which are both transparent at 2100 nm, no trace of HSFL was found on the surface of InAs, which is opaque at 2100 nm. Furthermore, no HSFL were revealed via SEM on Si (Fig. 3) under these conditions, nor at 2100 nm on a (111) Ge crystal, despite the fact that both are transparent at that wavelength. The spatial periods of LIPSS were determined by taking the Fourier transforms of the images. All results are summarized in Table I, where the error in the period measurement is ~10%, which includes the calibration uncertainty of the SEM.

As can be seen in Table I, the period of LSFL does not precisely correspond to the laser wavelength. Departures of the LSFL period from the incident wavelength have been observed previously. For example, Dumitru *et al.*[8] found ripples with a period of 600–630 nm with 150 fs, 800-nm pulse ablation of ultrahard materials. In addition, 650–750-nm LIPSS periods were observed in 800-nm, femtosecond ablation of Si.[16] The period of our HSFL on III-V semiconductors is 4.2–5.1 times smaller than the laser wavelength. These values are somewhat greater than $\lambda/2n$ (the second harmonics of the incident wavelengths (λ) in the unirradiated materials with indices of refraction n). For example, under 2100-nm laser irradiation, the second harmonic wavelength in GaP would be 345 nm, compared to a 410-nm ripple period measured experimentally. Similarly, the period of HSFL on sapphire was ≈260 nm, close to the second harmonic wavelength of 800-nm light in the solid (226 nm).

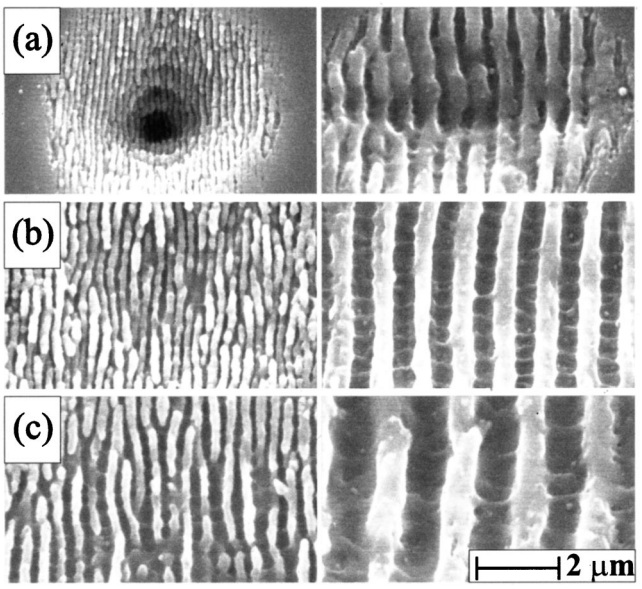

FIG. 2. HSFL (left) and LSFL (right) formed on the surface of (100) GaP after irradiation with (a) 800-nm, (b) 1300-nm and (c) 2100-nm femtosecond pulses.

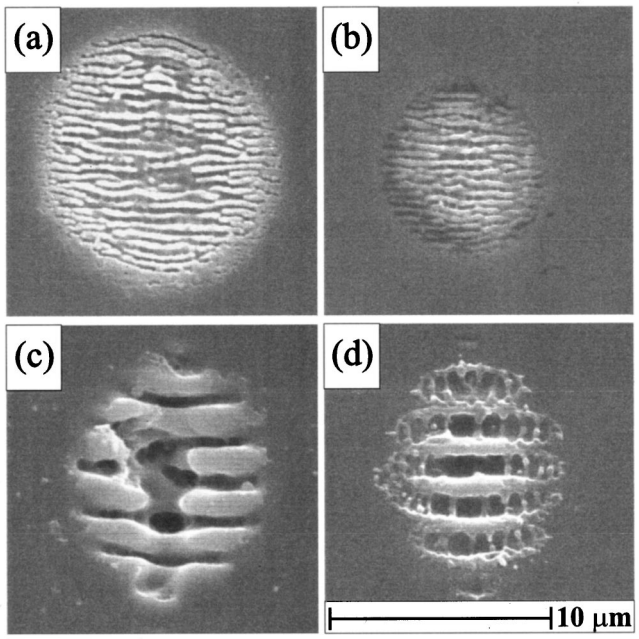

FIG. 3. SEM images of (100) (a) GaP, (b) InP, (c) InAs, and (d) Si surface after irradiation with 20 consecutive pulses at 2100 nm near the respective ablation thresholds.

TABLE I. Periods of HSFL and LSFL formed on various materials at laser wavelengths of 800, 1300, and 2100 nm. The results are given for similar multiple-pulse irradiation conditions for the respective samples. For a particular material, the values of spatial periods are averages of a number of individual measurements. Symbols: (-) no high-frequency structure observed; (/) no experiment attempted.

		Spatial period of LIPSS at given wavelength λ					
		λ = 800 nm (1.55 eV)		λ = 1300 nm (0.96 eV)		λ = 2100 nm (0.59 eV)	
Material	Band gap (eV)	HSFL	LSFL	HSFL	LSFL	HSFL	LSFL
Si	1.11	-	650	-	1050	-	1600
InAs	0.35	-	700	-	1100	-	1800
InP	1.35	-	680	310	1150	430	1750
GaP	2.26	170	680	300	1050	410	1900
GaAs	1.43	/	/	/	/	470	1650
Ge	0.67	/	/	/	/	-	1800
Sapphire	8.7	260	730	/	/	/	/

We also conducted preliminary experiments on the crystal orientation dependence of HSFL formation on (100) and (110) GaAs for a laser wavelength of 2100 nm. Within the set of parameters investigated, the formation of HSFL was found to be independent of the crystal orientation relative to the polarization of the incident beam, as in the formation of LSFL.[2] However, the null result should be considered in the context that the present SEM measurements do not characterize the amplitude of the observed features. Additional experiments are planned in order to confirm this conclusion.

The insensitivity of HSFL to crystal orientation of the III-V semiconductor targets suggests that second-harmonic generation in the bulk of undamaged semiconductors does not play a key role, despite the approximate correspondence of some of the HSFL periods and laser second-harmonic wavelengths. However, the compound materials are expected to undergo rapid modification during multiple-pulse irradiation. Thus the near-surface region in the modified materials might facilitate harmonic generation and explain an orientation insensitivity. Initial defects or subsequent laser-induced modification possibly also explain recent observations in the literature on single component diamond-like systems.[14,15] Ozkan *et al.*[14] reported subwavelength laser writing on diamond crystals and microclusters under multiple-pulse irradiation with a higher number of pulses than utilized here. Yasumaru *et al.*[15] investigated HSFL formation on diamond-like carbon and obtained structures very analogous to those described in the present work. The sample quality (defect density, surface roughness) and specific processing conditions (pulse fluence, number of pulses) might represent key differences between observations on diamond-like systems versus our preliminary investigations on the centrosymmetric crystals Si and Ge. The extent of material segregation or preferential loss of the more volatile element for compounds and the role of material imperfections for single-component samples should be examined in follow-up studies. Furthermore, high-intensity femtosecond light pulses propagating in media are subject to a number of nonlinear effects,[17] complicating arguments based on the initial optical properties of the sample. Detailed analysis should include behavior of the dielectric function of the materials under intense excitation.[18]

In summary, we have observed rapid formation of high-spatial-frequency laser-induced periodic surface structures on the surfaces of crystalline compound semiconductors (InP, GaP, and GaAs) and sapphire. HSFL were formed after femtosecond pulse irradiation in the transparency region. A requirement of one-photon transparency has been established. In addition, the present work has elucidated a difference between Si and Ge versus selected III-V semiconductors under the multiple-pulse irradiation range explored here. Our study complements the observations of Refs. 13–15 by extending the target materials to technologically important semiconductors. The exact mechanism of formation of these patterns is still very much an open question, requiring a detailed theoretical analysis and more experimental studies. Experimental extensions encompassing for example, non-normal incidence, characterization of the ripple amplitudes and stoichiometry, and using a much broader range of laser parameters, should lead to a better understanding of the underlying physics. In addition to purely fundamental interest, the appreciation of high-frequency ripple formation is potentially important for a number of emerging applications in nanotechnology.

Note added in proof. The authors very recently became aware of additional studies on wide band-gap dielectrics which are complementary to our present work on compound semiconductors. The reader is referred to Q. Wu *et al.*, Appl. Phys. Lett. **82**, 1703 (2003), and F. Costache *et al.*, Appl. Surf. Sci. **208–209**, 486 (2003), and references therein.

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