Ultrafast processes on semiconductor surfaces irradiated by temporally shaped FS Laser Pulses: Tuning & Controlling surface Micro/Nano-Structures

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Abstract- The application of temporally shaped femtosecond laser pulses in the micro/nano-structuring of semiconductor surfaces is demonstrated. As an initial step towards full pulse shaping, sequences of double pulses with variable temporal spacing in the picosecond time domain with equal intensity have been used. Craters decorated with nm-sized ripples are formed following the laser-surface interaction depending on the irradiation conditions. The area, depth and strikingly the ripple periodicity show a dependence on the temporal delay between the double pulses. Our analysis and explanation for the dependence of the micro and nano-morphological features on the pulse delay is based on a combination of mechanisms including laser-triggered ultrafast excitation and relaxation on a semiconductor surface such as carrier excitation, ultrafast carrier-lattice energy exchanges and energy transport along with the slower phenomena of melting, the corresponding hydrodynamics and re-solidification that follow until the final surface morphology is established. Our investigations on laser-irradiated Si and ZnO surfaces are discussed.

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1. INTRODUCTION

The pioneering work of Eric Mazur’s group [Her et al. (1998)] has shown the way to create quasi-periodic nanostructures using laser irradiation. This work has triggered a lot of research on laser-matter interaction with the aim of nanostructure formation due to the wide range of applications involved that could benefit from the generated structures. These include opto-electronic, mechanical, thermo-chemical and biological applications. The materials involved can be metals, semiconductors, dielectrics and polymers. Therefore, there exists a great demand for continuing experimental and theoretical research aiming at controlling the generated structures. Researchers frequently use fs laser pulses which present a clean and precise method to create nanostructures on surfaces using light.

The type of the nanostructures produced depends on the level of irradiation. As Varlamova et al. have shown [Varlamova, Bounhalli et al., 2013], following irradiation by only a few laser pulses one forms ripples with their direction perpendicular to the polarization of the electric field. With an increasing number of incidents pulses the ripples start to break up and at greater levels of irradiation they observe the formation of craters decorated by characteristic microstructures with a conical shape. In this work we are going to focus on the first level of irradiation (i.e. few laser pulses) which leads to the formation of ripples.

Ripples on semiconductor surfaces were first observed by Birnbaum [Birnbaum (1965)] and their formation was attributed to the optical diffraction of the laser beam with itself at the focal position. Later on, other groups have given explanations on the ripple formation such as Emmony et al. [Emmony et al., (1973)] where they ascribed the ripple formation on Ge surfaces to the interference of the incident laser with surface scattered waves. Lastly the dominant explanation was presented by Sipe et al. [Sipe et al., (1983)] where they explained the formation of ripples on Si surfaces by the generation of surface plasmon waves and their interaction, i.e. their interference with the incident laser wave. Still, after several decades, there is ongoing experimental and theoretical work in order to form nanostructures beyond the diffraction limit, to explore the fundamental mechanisms in the formation of the nanostructures and to control the underlying processes and therefore engineer and tune the characteristics of the nanostructure formed in order maximize the efficiency of the base material for the sake of a given application.

The ripples have been observed on the surfaces of metals, semiconductors and dielectrics [Vorobyev and Guo, (2013)]. Also, different periodicities have been observed. Depending on the relation of the ripple wavelength with the laser wavelength we can
distinguish between low spatial frequency ripples which have wavelengths near and below the laser wavelength and high-spatial-frequency ripples which have wavelengths which are much lower than the laser wavelength [Bonse et al. (2005)].

In our work we aim to demonstrate control and tuning of the ripples that are induced on semiconductor surfaces by application of temporally shaped laser pulses in order to exhibit control and tuning of the periodicity of the formed rippled that is important for application where the optical properties of the structured surfaces are crucial. At the same time, we pursue the fundamental understanding of the physical processes that are involved during the interaction of the laser beam with the surface and leads to the formation of ripples from the ultrafast to the ns temporal domain.

1. EXPERIMENTAL DETAILS

Experiments were performed with a femtosecond Ti:Sapphire laser system operating at a wavelength of 800 nm and a repetition rate of 1 kHz. The pulse duration was set to 80-430 fs and measured by means of a cross-correlation technique. A 4f pulse shaping configuration using a Spatial Light Modulator (SLM) was used to filter the Fourier spectrum of the laser pulses and create double pulse sequences with pulse separations varying from 0 to 7 ps. A primitive form of pulse shaping was performed by splitting the initial pulse into two equal components and varying the temporal pulse separation to some few picoseconds time range, thus attempting to manipulate the ultra-fast electron interaction and cooling processes that take place in this temporal range for many solids in general and in silicon in particular.

A Pockels cell controlled the repetition rate and the number of the pulses that irradiated the silicon and ZnO surfaces. The beam was perpendicular to the silicon substrate giving a spot diameter of 15-30 µm located inside a vacuum chamber evacuated down to a residual pressure of 10−2 mbar. The number of laser pulses and fluences used ranged from 15 – 1000 and 0.55 – 4.5 J/cm², respectively. Field emission scanning electron microscopy (FE-SEM) was used for the morphological characterization of the irradiated areas. ZnO thick films with thickness up to 4 µm were deposited onto Corning glass (1737F) in an Alcatel D.C. magnetron system using a 99.999 % pure metallic zinc target of 15 cm diameter. The base pressure of the ultra-high vacuum (UHV) chamber was below 5×10−7 mbar while during the deposition the pressure was 8×10−3 mbar and the substrate temperature at 27 °C. All the films were grown at a constant plasma current of 0.45 A. In order to avoid thickness non-uniformities, the distance between the target and substrate was set to 20 cm. The ZnO films thicknesses were measured using an AlphaStep profilometer.

More details on the experiments performed can be found in our previous work [Tsibidis, Barberoglou et al. (2012); Barberoglou, Gray et al. (2013); Barberoglou, Tsibidis et al. (2013); Tsibidis, Stratakis et al. (2014)].
2. THEORETICAL DETAILS

To account for ripple formation, we have elaborated both optical and capillarity driven effects assuming that the applied conditions are sufficient to induce minimal ablation. The proposed theoretical model comprises: (i) an electromagnetic component that describes the surface plasmon interference with the incident beam that leads to a periodic energy deposition (ii) a heat transfer component that accounts for carrier-lattice thermalization through particle dynamics and heat conduction (iii) a hydrodynamics component that describes the molten material dynamics and re-solidification process.

Simulations were performed with a p-polarised laser pulse with a Gaussian (both spatially and temporally) distribution of fluence. A systematic analysis of the fundamental mechanism reveals that mass removal due to the fact that excessive temperatures are reached (larger than ~ 0.90 $T_c$, $T_c$=3540 K) and inhomogeneous (i.e. periodic) deposition of the laser energy leads to a recoil pressure, surface tension variance and temperature gradients. These effects induce a Marangoni-driven flow and capillary waves that eventually leads upon resolidification to the formation of a crater and a rippled profile while mass conservation and surface tension forces produce a protrusion near the periphery of the spot.

Fig. 3. Surface profile and flow pattern of the irradiated Si surface at 0.1 ns after laser excitation.
Due to the anticipated small vertical surface modification with respect to the size of the laser beam, a finite difference method to solve the equations that describe the heat transfer and hydrodynamics equations suffices to produce accurate results. For time-dependent flows, a common technique was employed to solve the Navier-Stokes equations which is the projection method where the velocity and pressure fields are calculated on a staggered grid using fully implicit formulations. An explicit solution method is employed to solve heat transfer and compute temperature values at subsequent time points.

More details on the simulation details of the theoretical results produced can be found in our previous work [Tsibidis et al. (2012); Barberoglou et al. (2013); Tsibidis et al. (2014)].

3. RESULTS AND DISCUSSION I: Si

We parametrize our experiments by varying the level of irradiation, i.e. the number of incident pulses and the inter-pulse delay, i.e. the temporal delay between the double fs laser pulses. FESEM pictures of the irradiated spots are shown in Fig. 1. These illustrate the dependence of the morphology of the irradiated spots on both the number of incident pulses as well as the inter-pulse delay. In order to examine the evolution of the irradiated spot morphology with increasing irradiation level, we first examine the result of irradiation of the Si surface by just one laser shot. This is shown in Fig. 2. We observe the formation of a shallow crater which is confirmed by the intensity cross section obtained from the SEM images. Additionally, as observed by Atomic Force Microscopy, the shallow crater is surrounded by a rim which is formed at the periphery of the crater.

In order to understand and explain the morphology of the crater that is experimentally observed, we make the following basic considerations described in the following basic steps:

1. Firstly, we consider energy absorption and dissipation which includes electron transport and electron cooling by electron-phonon interaction. These processes are described theoretically by the so called two-temperature model by Anisimov et al. [Anisimov and Luk'yanchuk (2002)].
2. Then, we consider lattice heating, then melting and evaporation of some part of the irradiated surface which exceeds the critical temperature for lattice evaporation.
3. Then, we introduce hydrodynamics in order to describe particle flow and capillary wave formation. The fluid is considered to be an incompressible Newtonian fluid.
4. Lastly, we consider lattice cooling that leads to resolidification leaving a surface which is modified and has micro- and nanostructures.

These basic steps have been previously considered by research groups in the theoretical description of the processes following laser excitation of the Si surface [ (Zhou et al. (1982); Sipe et al. (1983); Bonse et al. (2005); Tan and Venkatakrishnan (2006); Costache et al. (2008); Huang et al. (2009); Han and Qu (2010)]. Our distinct contribution here is the introduction and the consideration of the
particle flow and the hydrodynamics that follow the laser irradiation and the ultrafast processes involved as described in detail in [Tsibidis et al. (2012)]. The simulated crater profile calculated is shown in Fig. 3 and is in very close qualitative and quantitative agreement with the crater profile as measured by the SEM and AFM pictures. This demonstrates that we have developed a theoretical model that is in a position to describe well the experimental data concerning the crater formation on the Si surface. Therefore, the next step will be to introduce the irradiation by multiple and single (i.e. non-temporally shaped) laser pulses.

A characteristic SEM image of the Si surface irradiated by 4 laser pulses is shown in Fig. 4. Ripples are clearly observed with the orientation vertical to the polarization of the electric field of the laser pulses. In order to explain the formation of this periodic nanostructure, we introduce as a first step in our theoretical model the mechanism that was first proposed by Sipe et al. [Sipe, Young et al. (1983)], i.e. the generation of surface plasmons and the interference of the incident laser field with the surface plasmon. This

Fig. 5. Calculated crater profile and flow pattern for the irradiated by 4 pulses Si surface at 1 ns delay time.

Fig. 6. SEM and AFM images of the Si surface irradiated by temporally shaped (double) fs laser pulses. a,b,c shows SEM images for 0, 0.5 and 2 ps respectively. d,e are AFM images of the crater profile for 0 and 2 ps respectively. g,h show the intensity profile of the craters for the same interpulse delays as in d and e.
interference leads to spatially periodic distributions of energy deposition, surface temperature, carrier densities and hydrodynamic quantities. The generation of surface plasmons on Si (i.e. a semiconductor) is possible due to the fact that the produced carrier density number is sufficient to allow validity of the condition that is necessary for plasmon excitation (i.e. real part of the dielectric constant smaller than \(-1\)). After the introduction of wave interference, the calculated crater profile is modified and is shown in Fig. 5. The calculated profile is in very good qualitative agreement with the rippled nanostructures observed by SEM and AFM pictures. Moreover, the predicted, by the theoretical simulations, periodicity of the ripples is very close to the experimental value, i.e. 738 nm.

Since now we have demonstrated the development of a working theoretical model for the prediction of the crater characteristics and the ripple periodicity we move on, by introducing temporal pulse shaping in its most basic form i.e. sequences of double fs laser pulses where we can control the inter-pulse delay. We irradiated the Si surfaces with laser pulses and the results are evaluated by SEM and AFM images as shown in Fig. 6. It is evident, by the instances of zero inter-pulse delay time (i.e. single pulse with the same total energy as the sum of the energies of the double pulses), 0.5 ps and 2 ps interpulse delay time, the crater size is reduced when the interpulse delay time is increased. This in confirmed by the cross sections obtained by the corresponding AFM images. The results are summarized for all the irradiation levels used (i.e. number of incident laser pulse sequences) in Fig. 8. Thereby, we deduce that the crater spot area as measured by the SEM images is monotonically reduced with an increasing interpulse delay time for values from 0 to 2 ps and remains stable thereafter (not shown).

![Fig. 6. Measured crater area on the Si surfaces as irradiated by 12, 50, 200, 500 and 1000 double pulses.](image)

![Fig. 7. Ripple wavelength as measured by the SEM images vs. interpulse delay time.](image)
In order to evaluate the ripple periodicity, we obtain intensity cross sections from the SEM images. The results for the ripple periodicity vs inter-pulse delay time shown in Fig. 7 show that there is a sharp decrease in the ripple periodicity within the first few ps on inter-pulse delay time followed by a smaller slope of decrease with further increasing inter-pulse delay time. The decrease in the ripple periodicity within the first few ps is roughly 20 nm, i.e. from 742 nm for 0 ps to about 723 nm for 14 ps which is the largest value of inter-pulse delay that could be achieved in our experiments.

Let us look at how our theoretical simulations can interpret these experimental findings. The actual real time temporal profile of the simulated laser pulse is shown in the inset of Fig. 9 and the temperature profile as a result of such an irradiation is shown in the main part of the same figure. It is very interesting to examine the maximum carrier and lattice temperatures that can be achieved using our theoretical model as a function of the inter-pulse delay time. This is shown in Fig. 10. The maximum carrier temperature falls monotonously, while the maximum lattice temperature exhibits a non-monotonous behavior: first it increases and it reaches its maximum value at an inter-pulse delay of about 2.2 ps which is roughly 4-5 pulse durations apart and then it drops monotonically with increasing inter-pulse delay time. The monotonous drop of the maximum electronic temperature is consistent with the decreasing value of heat conductivity $k(T)$. The maximum electron temperature is achieved when the two pulses overlap in time. When we introduce a delay between the two pulse components the maximum electron temperature on the surface that is achieved is dropping, as expected.
On the other hand, the optimum lattice temperature at a non-zero interpulse delay is a result of the competing mechanisms of electron transport vs. electron-phonon scattering. Due to efficient electron transport at zero inter-pulse delay time (due to the highest values of heat conductivity) the electrons move very efficiently away from the surface region and therefore they do not interact a lot with the surface and the energy is lost by transport into the bulk. Energy is transferred to the lattice by electron-phonon coupling which tends to take over only after some time where the heat conductivity drops due to the now decreased electron maximum temperature and therefore the decrease of the electron heat conductivity. Therefore, the electrons stay for more time at the vicinity of the surface and therefore there is more time available for transfer of the energy towards the lattice, i.e. greater values of the maximum lattice temperature that is finally reached. This optimum could be potentially used as a feedback to genetic algorithms and feedback loops in pulse shaping optimization applications.

When looking at the experimental results of the crater area and the crater depth vs. inter-pulse delay time in Fig. 11 we observe a monotonous decay for both graphs in a very good agreement with the predictions of our theoretical model shown with the solid line. Moreover, we observe that the evolution of the crater area and the crater depth is qualitatively similar to the evolution of the maximum electron temperature dynamics with interpulse delay time, shown in Fig. 10. This observation confirms the electron dynamics related ablation like mechanisms as is also previously reported and analyzed by previous experimental and theoretical works [Bulgakova et al. (2004)].
In Fig. 12 we plot the evolution of the ripple periodicity with inter-pulse delay time comparing our experimental results with the predictions of our theoretical model. Again, the agreement is very good, and this helps us to conclude that we may assign the decreasing ripple period with inter-pulse delay time to the decreasing maximum electron temperature with inter-pulse delay time and to the wavelength of the surface plasmon which follows the dynamics of the maximum electron temperature and the number of excited carriers. Therefore, a decreasing number of carriers and a decreasing maximum electron temperature with inter-pulse delay time leads to a decreasing surface plasmon wavelength and therefore to a decreasing ripple period, since we have attributed the ripple emergence to the interference of the laser wave with the surface plasmon wave. The theoretical values become even closer to the experimental ones if we include in our model the recoil pressure that is induced by the ejected species during the ablation process and is described in more detail in our previous work [Barberoglou et al. (2013)].

Here, we would like to mention that although the ripple wavelength could be tuned, and in particular could be decreased by increasing the level of irradiation of the surface, i.e. by increasing the number of incident laser pulses as was shown in our previous
experimental work [Tsibidis et al. (2012)] (see also Fig. 13) this may prove to be undesirable in many applications since a increased number of incident pulses leads inevitably to an increased level of damage effects which is of course undesirable for applications that demand fine interaction of the laser beams with optical materials and the creation of fine nanostructures on these materials. Therefore, we demonstrate a unique way of creating these nanostructures by exploiting the temporal regulation of the energy of the laser beam on a material’s surface.

4. RESULTS AND DISCUSSION II: ZnO

Next, we will explore laser induced formation of nanostructures on ZnO, which was selected as a representative material of semiconductors with high band gaps that belongs to a class of photonic materials important for use in light-related applications. For the case of ZnO, similarly to Si, we parametrize our experiments with respect to incident number of laser pulses and increasing interpulse delay times. As shown in Fig. 14 we obtain various SEM images for varying the previously mentioned parameters as well as the fluence of the incident pulses. If we examine more carefully a SEM image at a higher magnification as in Fig. 15a,b we observe three distinct classes of ripples with different periodicities. Firstly, at the center of the laser irradiated spot we find the low-frequency ripples with a period of 640 nm. When zooming closer to the periphery of the irradiated spots we find with close inspection two more ripple periodicities: one with a period of about 260 nm and one with even higher periodicity of about 170 nm. The ripple periodicities are summarized in Fig. 15c as a function of the incident laser fluence.

We attribute the formation of the lowest periodicity ripples on the ZnO surface to the generation of a surface plasmon wave and the interaction with the incident laser radiation as in the case of the Si surface. As for the medium and high periodicity ripples, we argue that these are created by the generation of a surface wave at the second harmonic frequency. The second harmonic wave then in turn excites a surface plasmon wave and the medium and periodicity ripples are the result of the interference of these two waves, as was previously analyzed and explained by the work of Duft et al. [Duft et al. (2009)].

By inspection of Fig. 15c we find that the low frequency ripples disappear when we increase the incident laser fluence beyond 1 J/cm² and we attribute this observation to melting effects at the surface which we consider responsible for washing out of the low frequency ripples. Further investigations are required to obtain further insights for this particular effect.
When we turn on the dependence of the ripple periodicities on the temporal shape of the laser pulses i.e. the inter-pulse delay time, we observe a remarkable effect, as shown in Fig. 16: For inter-pulse delay times from 0 to about 0.5 ps we find the three different ripple periodicities co-existing at the ZnO film surface. However, when we increase the inter-pulse delay time further than 0.5 ps, the low-spatial frequency ripples immediately disappear leaving only the medium and high frequency ripples at the surface. Even at the central part of the crater where the low-frequency ripples existed, now for larger than 0.5 ps interpulse delays we observe the crater surface being dominated by the medium and the high frequency ripples. This is also corroborated in Fig. 18 where we examine the area coverage of each of the ripple classes for various inter-pulse delay times. Again, we find that all three different ripple periodicities co-exist at the crater surface for low interpulse delay times but when we increase the inter-pulse delay time we find that the coverage by the low frequency ripples is rapidly decreasing and drops to practically zero coverage for inter-pulse delays above 0.5 ps. On the other hand, the coverage by the medium and high frequency ripples increases for delays up to 0.5 ps at the expense of the coverage by the low frequency ripples. Then for larger inter-pulse delay times the coverage is decreasing overall as the total area of the crater decreases, similarly in the case of the Si surfaces analyzed previously in this manuscript.

We wish to emphasize at this point the significance of the aforementioned observations for applications in the nanostructuring of photonic materials. And we do this by demonstrating the printing of gratings at larger scale on ZnO surfaces. We scan the surface below the laser beam with a constant velocity and let the interaction of the laser beam with the surface print large surfaces which in principle can be infinitely large. In Fig. 17a we observe the SEM image of a printed surface with 0 inter-pulse delay time and the result is a grating with a periodicity of about 650 nm as was observed in the central part of the SEM images of Fig. 17a. On the other hand, in Fig. 17b we have switched the temporal shape of the laser pulses and we have introduced an interpulse delay time of 1 ps. Remarkably, the grating has switched now to a larger periodicity measured to be ~220 nm which is in accordance with the results previously presented in Fig. 16. Thus, we demonstrate the ability to drastically control the morphology of a nanostructure that we imprint on the surface of a photonic material by changing nothing else in the laser pulse but the shape of its temporal profile. This way, weLoukakos et al. (2014), Ultrafast processes on semiconductor surfaces irradiated by temporally shaped FS Laser Pulses: Tuning & Controlling surface Micro/Nano-Structures, *J. Modern Trends in Phys.* R., Vol. 14 pp. 42-54

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interfere with the way that the laser energy is regulated and on how this energy is deposited on the materials surface, thus controlling the interaction of the laser beam with the material, thus finally controlling its macroscopic properties.

5. CONCLUSIONS

To summarize, we would like to point out that we have developed an experimental approach employing temporal pulse shaping and a unified theoretical model in order to describe the crater formation and the ripple formation on semiconductor surfaces following interaction with sequences of double fs laser pulses with varying inter-pulse delay. We have shown that it is possible to control and fine tune the morphological characteristics of the craters i.e. the crater size as well as the morphology of the nanostructures formed i.e. the ripples. These were attributed to the interference of the incident laser pulses with a surface scattered wave, the surface plasmon. The inter-pulse delay results in the control of the maximum achieved electron temperature and carrier density at the surface which in turn results in fine tuning of the plasmon wavelength and thus the nanostructure periodicity. This effect was also observed on ZnO surfaces where additionally we demonstrated the striking change in the morphology with a vast change of the periodicity of the printed gratings. Our next investigations involve the extension of our studies to more complex nanostructures such as grooves and micro cones, and the effect of combining temporal shape and polarization. Also, different materials such as metals, ceramics, polymers important for solar applications are planned to be investigated. Lastly, more complex pulse shapes and feedback and genetic algorithms are planned to be developed and employed to allow for the nano-gratings to self-evolve and self-optimize their optical properties.

![Fig. 18. Measured area coverage by the different ripple classes on the ZnO surface vs. interpulse delay time.](image)

![Fig. 17. Formed gratings on the ZnO surface by scanning it under the incident laser beam with the interpulse delay at a) 0 and b) 1 ps.](image)
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