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Self-organisation of single-crystals as ripple patterns through laser ablation of ionic salt solutions

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ABSTRACT

Relatively thin (d = 2.5 μm), diluted (c = 0.001–0.1%wt.) aqueous liquid films of ionic salts (NaCl, K_2CrO_4) were each irradiated with a single infrared laser pulse (wavelength, λ = 10.59 μm, fluence J –100 J/cm^2, spot diameter D = 3 mm, irradiation time t = 100 μs). This approach has induced the formation of hierarchically arranged single crystal ripples near the edge of the laser impact zone. Depending on the ionic salt concentration and β angle of incidence in respect to the surface, the number of ripples varied between 5 and 100 and their interspacing between a few micrometres and hundreds of micrometres. In addition to ripples, K_2CrO_4 salts form beside ripples, parallel, long and thin single crystals, which orthogonally intersect the ripples to form a rectangular crystal grid. In addition to the theoretical gain, crystals have potential applications in optoelectronics and sensors.

1. Introduction

The formation of superficial coherent features, such as ripples, also denoted as laser-induced periodic surface structures (LIPSS), is an interesting phenomenon based on the interaction of a laser beam under certain conditions with various materials. LIPSS were observed during femtosecond pulsed laser ablation with a high repetition laser source. Ripple formation was first observed by Birnbaum [1] after ruby-laser irradiation of various semiconductors. Since then, it has been observed on many different materials, using lasers with wavelengths ranging from 0.193 to 10.6 μm and pulses from micro- to femtosecond regimes. Metals [2], semiconductors [3] and insulators [4] have been shown to form periodic ripples after laser irradiation. The common characteristics observed on all of these solid materials as well as on liquids [5] led some authors to conclude that “laser-induced periodic surface structure (LIPSS) by single laser beams is a universal phenomenon that can occur on any material that absorbs radiation, regardless of its dielectric constant” [6].

Starting with a liquid relative thin film and a high fluence laser, which irradiates as in LIPSS, but with a film of different nature than the solid substrate, the liquid (salt solution) undergoes local explosive boiling and total expulsion, whereas an adjacent limited zone seems to suffer a periodic ordered fragmentation as hierarchically liquid solution droplet arrays, which subsequently lose mass by natural evaporation accompanied by the solute crystallisation. Thus, the initial liquid passes into a solid not through solidification from melting but through a first-order transition phase (crystallisation), resulting in the formation of single crystal ripples, which can be considered to be similar to LIPSS.

However, ripples also form when a liquid thick film (of different nature than the solid substrate) is locally dewetted by dipping a Teflon tip at the centre of the film [7]. A liquid rim appears at the edge of the dewetted zone [7], which induces an exponentially decaying harmonic oscillation that relaxes into the prepared film thickness [8–10].

In LIPSS experiments, it was found that the orientation and period of the ripples depend on the following laser parameters: polarisation, angle of incidence, fluence, wavelength and number of pulses. The interference patterns are predicted with a ripple period of $\lambda/(1 \pm \sin\beta)$ (λ, laser wavelength in vacuum; β angle of incidence with respect to the surface normal) [11], but also with $\lambda/\cos\beta$, for p-polarised light [12], or with $\lambda/n_{\mathrm{environment}}$ when the irradiated sample is immersed in a liquid [13].

In the aim of explaining ripple formation, some mechanisms, such as interference of the incident beam with microscopic fields

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scattered by a surface roughness [14], resonant absorption of photons by plasmons at the surface of critically sized metallic droplets [15] or, boson condensation in very high carrier density regions [16], are proposed. These mechanisms are in good agreement with the experimental data when low fluence lasers are used. When a high-fluence regime is performed, laser-induced capillary wave mechanisms seem to be more appropriate [6]. Young et al. showed that, “at higher fluences, periodic structures are also formed even through the material/air interface melts uniformly. This occurs through the excitation of capillary waves at the liquid/air interface, which then freezes as the material resolidifies” [6].

In this work, we show for the first time how periodic ripples can occur if a liquid film of aqueous NaCl deposited on a solid (glass) is single pulse irradiated with an IR laser ($\lambda = 10.59\ \mu m$). We aimed to determine the laser has only the role of producing a shock dewetting or it has a more subtle influence. Laser-induced periodic surface structures may now refer to single crystals in addition to metal semiconductors and insulators. A new research domain has been added, in which single crystallisation phenomenon [17–19] could be connected with laser liquid ablation [20] and LIPSS if we presume that the driving force in crystal ripple formation is laser-induced capillary waves mechanism. In addition to the theoretical gain, crystals have potential applications in optoelectronics and sensors.

2. Experiment

An aqueous NaCl or K_2CrO_4 diluted liquid film ($c = 0.01 – 1\%$ wt.) was produced by dipping and vertically extracting a microscope glass slide from aqueous solution. It completely covered the substrate surface (2.5×5.0 cm) and has a thickness d, (determined by weighing) of $d – 2.\ 5\ \mu m$. The horisontally held liquid film was single pulse laser irradiated at a β angle of incidence with respect to the horisontal surface. The laser characteristics were: wavelength, $\lambda = 10.5\ \mu m$, fluence $J – 100\ J/cm^2$, spot diameter $D = 3$ mm, irradiation time $t = 100\ \mu s$. After the natural drying of the film, its laser-irradiated surface was investigated through optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM)

3. Results and discussion

Laser irradiation of solids can melt their surface and induce ripple formation when the melted surface solidifies. To the best of our knowledge, laser irradiation of colloidal liquid films does not organise these nanoparticles as ripples. Experiments using inorganic Fe_2O_3, TiO_2 and C nanoparticles as aqueous colloidal films showed the formation of solid non-homogeneous agglomerates with or without a nanoparticle coffee ring [21]. Ionic salt solution thin films form crystal ripples, which can be considered to be related to the classical LIPSS, as both methods form parallel elongated tridimensional fine structures. We found that highly diluted aqueous NaCl ($c < 1\%$ wt.) films deposited onto glass substrate and irradiated with an IR laser single shot($100\ J/cm^2$ in fluence) form crystal ripples (Fig. 1). The ripples are placed at the edge of the laser impact zone, surrounding it (Fig. 1a), and their measured interspacing is in the micrometres or tens of micrometres range. The ripples are not influenced by the propagation of glass surface cracks (Fig. 1a), and they did not form when pure water films were used.

The number of ripples varied between 5 and 100 and increased with decreased NaCl concentration. Optical microscopy observations performed a short time after laser irradiation (tens of seconds) reveal that, at the beginning, the ripples consist of small droplets (Fig. 2a), which in time evaporate to form NaCl single crystals (Fig. 2b). The surface density of the ripples seems to periodically vary (Fig. 2b). AFM images (Fig. 2c) show a high surface density of rather flat (hundreds of nanometres in height) single crystals when comparing their lateral sizes (micrometres), which can be seen in SEM images (Fig. 2d). Both investigation methods show how the NaCl single crystals increase their sizes (in radial direction) across each ripple forming a “saw tooth”-like distribution.

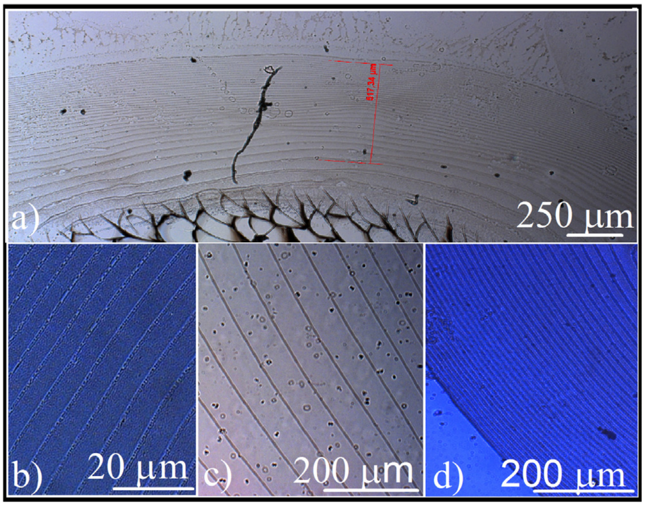

Fig. 1. Optical microscopy images of NaCl crystal ripples.

K_2CrO_4 also forms ripples through laser irradiation. When dissolved in water and recrystallized from a drop or film on a substrate through solvent evaporation in normal conditions, it forms separated 3D single crystals (Fig. 3a). If a highly diluted solution deposited as film on a hot plate ($T = 300–500\ ^\circ C$) is rapidly evaporated, it forms a crystal grid consisting of long and parallel K_2CrO_4 single crystals interspaced every few micrometres (Fig. 3b) [22]. We assumed that the growing mechanism is related to the geometrical constraint of the film (high aspect ratio of its thickness and its lateral size).

If the same aqueous film is laser irradiated (one shot, $\lambda = 10.5\ \mu m$, $100\ J/cm^2$) in normal conditions, it forms ripples (Fig. 3c). A closer observation using optical microscopy shows that the crystalline grid forms and intersects the ripples in a rectangular net (Fig. 3d). This net forms only in the laser presence and again, the geometrical constraint (thickness) of the film may play an important role in the ripple formation mechanism, namely laser-induced capillary waves, which appear only when their wavelength is much higher than liquid film thickness [6].

Optical microscopy image analysis performed on NaCl ripples showed that:

a) the interspacing (period) of ripple decreases non-linearly toward a constant value, which is closer to the laser wavelength, from the laser impact zone edge to the exterior (Fig. 4a).
b) the ripple interspacing mean size decreases with the decreasing of NaCl concentration (Fig. 4a).
c) the ripple interspacing variation decreases with increasing aqueous NaCl dilution (Fig. 4a) down to 20% of the largest period.
d) the number of ripples on the unit length measured radially across the ripples increases with decreases of the aqeous NaCl concentration (Fig. 4b).
e) the ripple size increases with increases of the β-angle of the laser incidence (Fig. 4c) as in classical LIPSS, yet not sin β or cos β dependence was observed.

Regarding the size and distribution of NaCl single crystals inside the ripple, AFM and SEM image analysis shows a “saw tooth”-like

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