Structures with 'dead zones' on Si crystal surfaces after ultraviolet excimer laser irradiation

1992 J. Phys.: Condens. Matter 4 1699

(http://iopscience.iop.org/0953-8984/4/7/008)

J. Phys.: Condens. Matter 4 (1992) 1699–1705. Printed in the UK

Structures with 'dead zones' on Si crystal surfaces after ultraviolet excimer laser irradiation

A Je Semjonow, K Lenz and A Lau

Institute of Optics and Spectroscopy, Rudower Chaussee 6, 1199 O-Berlin, Federal Republic of Germany

Received 14 May 1990, in final form 8 October 1991

Abstract. This paper is devoted to problems of self-organization of surface periodic structures on a Si crystal under the action of nanosecond excimer laser radiation. One kind of structure, the so-called 'dead zones', on Si crystal surfaces after UV excimer laser irradiation is discussed in detail. A possible mechanism of the formation of regions lacking indulation ('dead zones') is due to an interaction between the capillary waves (grad $T_x \neq 0$, along the surface) and the thermocapillary waves (grad $T_z \neq 0$, towards the interior of the liquid silicon).

1. Introduction

The phenomenon of laser-induced periodic surface structures (LIPSS), i.e. grating-like patterns on the surface of materials due to incident laser radiation, has been observed in many studies [1–7].

LIPSS by a single laser pulse is a universal phenomenon [7] that can occur on any material that absorbs radiation, regardless of its dielectric constant, and by laser wavelengths from 249 nm [3, 7] to 10600 nm [1, 4, 5]. Substantial progress in the understanding and the classification of LIPSS after excimer laser irradiation was made in [7]. The basis of the currently accepted theory of LIPSS, i.e. the interference of the incident light and some form of 'surface scattered wave', was suggested by Emmony *et al* [1].

The first type of LIPSS contains strictly periodic gratings which arise on the surface of solids under the action of radiation whose intensity is insufficient for uniform melting of the surface. The characteristic parameters of these structures (the period and the direction of the reciprocal grating vector of the structure) and their relation to the characteristics of the laser radiation (the angle of incidence of the laser and the incident light wavelength) are accounted for in non-uniform-interference heating models by melting which occurs only at the maxima of the interference field formed by the incident radiation and the wave scattering by the surface.

The other type of LIPSS is a structure generated on the surface of a liquid in the case of uniform melting of the surface in the irradiation zone [5].

At fluences higher than the minimum required to form a LIPSS but not necessarily high enough to wash out the LIPSS patterns, variably spaced wave-like structures propagating radially outwards from the centre of the impact zone were observed. The spacing of these patterns, which was between 1 and 3 μm near the centre and

0953-8984/92/071699+07$04.50

well below 1 μm towards the edge of the impact zone, showed *no dependence* on either the angle of incidence or the polarization of the incident light. For reasons primarily based on the lack of angular dependence of the ripple spacing these patterns are attributed to induced capillary waves (ICW)(when the forces of surface tension are dominated) which are frozen into the surface upon resolidification [7].

At the highest fluences used, the patterns are again independent of the laser polarization and the incident angle, but LIPSS show a much larger spacing and have been labelled anomalous laser-induced periodic surface structures (ALIPSS) [7]. At these high fluences the interaction of the laser radiation with the target produced a large volume of plasma (many times that seen at lower fluences) accompanied by an audible cracking sound. The results under these conditions were poor impact sites with a variety of complex structures of various orientations and spacings varying from less than 1 μm to more than 20 μm [7].

At the same time, experiments on the generation of ICW on the surface of semiconductors subjected to melting by nanosecond excimer laser pulses show that the possible structures of the surface relief are not limited to the categories of the conventional classification.

Excimer laser–material interaction leads to results which in many cases differ strongly from the features of infrared laser irradiation known previously [1–8]. These differences are connected with the absorption and reflection coefficients for UV, visible and infrared light (table 1).

Table 1. The dependence of absorption α and reflection R coefficients on light wavelength for crystalline Si (c-Si), amorphous silicon (a-Si), liquid silicon (Si(l)) and SiO_2 [9].

	$\lambda = 250$ nm		$\lambda = 500$ nm		$\lambda = 1060$ nm	
	$1/\alpha$	R	$1/\alpha$	R	$1/\alpha$	R
c-Si	6 nm	0.61	500 nm	0.36	200 μm	0.33
a-Si	10 nm	0.75	100 nm	0.48	1 μm	0.35
Si (l)	—	0.90	8 mm	0.72	13 μm	0.72
SiO_2	> 1 cm	0.06	> 1 cm	0.04	1 μm	0.04

The structures on the Si crystal surface after irradiation with an excimer laser show the following pecularities. The structures have different directions not connected with the crystallographic axes. They are not parallel to the crystallographic axes a, b and c; the structures have periods from 0.1 to 50 μm and have elements of chaotic behaviour, e.g. bifurcations. Some of these structures are presented in figure 1 and can be identified with ALIPSS. Structures with 'dead zones' (DZ) (figure 2), produced by spatially inhomogeneous melting (the edge of the impact zone for example), showed no dependence on either the angle of incidence ($\theta < 70°$) or the number of shots incident on the target. They destroyed and re-formed after each single shot. They have spatial periods between 1 and 3 μm and are attributed to capillary waves (CW). However, the DZ of these CW structures are not described with the aid of the above classification and still remain unclear. It seems that interpretation of the results with DZ must involve the consideration of thermocapillary waves (TCW), when grad $T_z \neq 0$, towards the interior of the Si(l). A possible mechanism of the formation of regions with DZ is due to an interaction between CW (grad $T_x \neq 0$ along the surface and the forces of surface tension $f_x \neq 0$) and TCW.

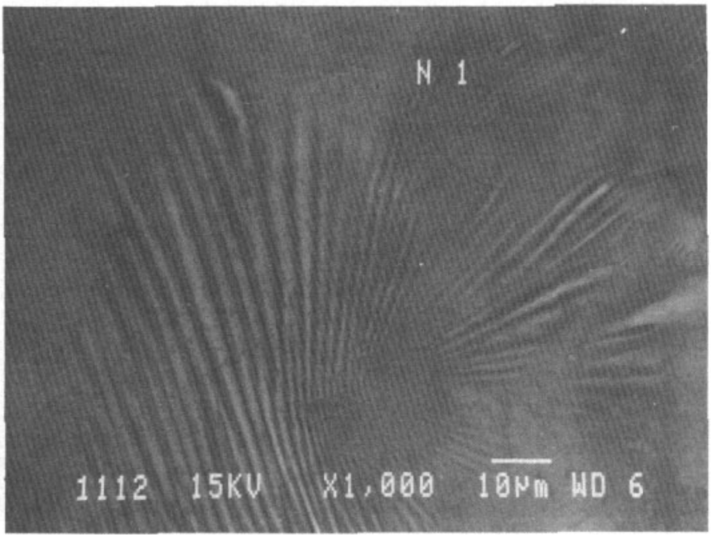

Figure 1. Examples of the structures on the Si crystal (n-type) surface after irradiation by an excimer laser ($\lambda = 248$ nm, non-polarized light incident at 0°; normal incidence). (Magnification, × 1000.)

2. Experimental technique

In the experiments reported here laser radiation at a wavelength of 248 nm (KrF excimer laser (Lambda Physik model 1003i) with pulse energies of 20–40 mJ and a pulse duration of 20 ns were applied). Experiments were performed in atmospheric and fore-vacuum environments and under normal incidence of the laser beam with respect to the Si (111) surface (n-type crystals). Laser energy fluxes higher than the threshold for surface melting ($\rho_{sm} \simeq 0.2$ J cm^{-2} [9]) were applied: 0.2 J cm^{-2} $< \rho <$ 1.2 J cm^{-2}. To reach the required fluences a 10 cm quartz lens was used to focus the beam such that the full widths at the 1/e^2 points in each direction were approximately 2 mm and 0.5 mm. The laser light was unpolarized. After the Si samples had been polished and cleaned, the exposures were performed in air which was dust-free.

3. Experimental results

This paper will consider only one type of structure, the so-called structures with DZ (figure 2), for which patterns have plots without linear structures. These structures, as a rule, are situated close to the boundary of melting where an extremely high temperature gradient exists. Structures with DZ have the following characteristic properties:

(i) There is a threshold effect for the appearance of structures with DZ: $\rho_{thr} \geqslant$ 0.3 J cm^{-2}.

(ii) The structures arise not at the edge of the melted zone but within the region of a non-uniformly heated liquid.

(iii) The structures can be induced by UV lasers with wavelengths of both 248 and 193 nm.

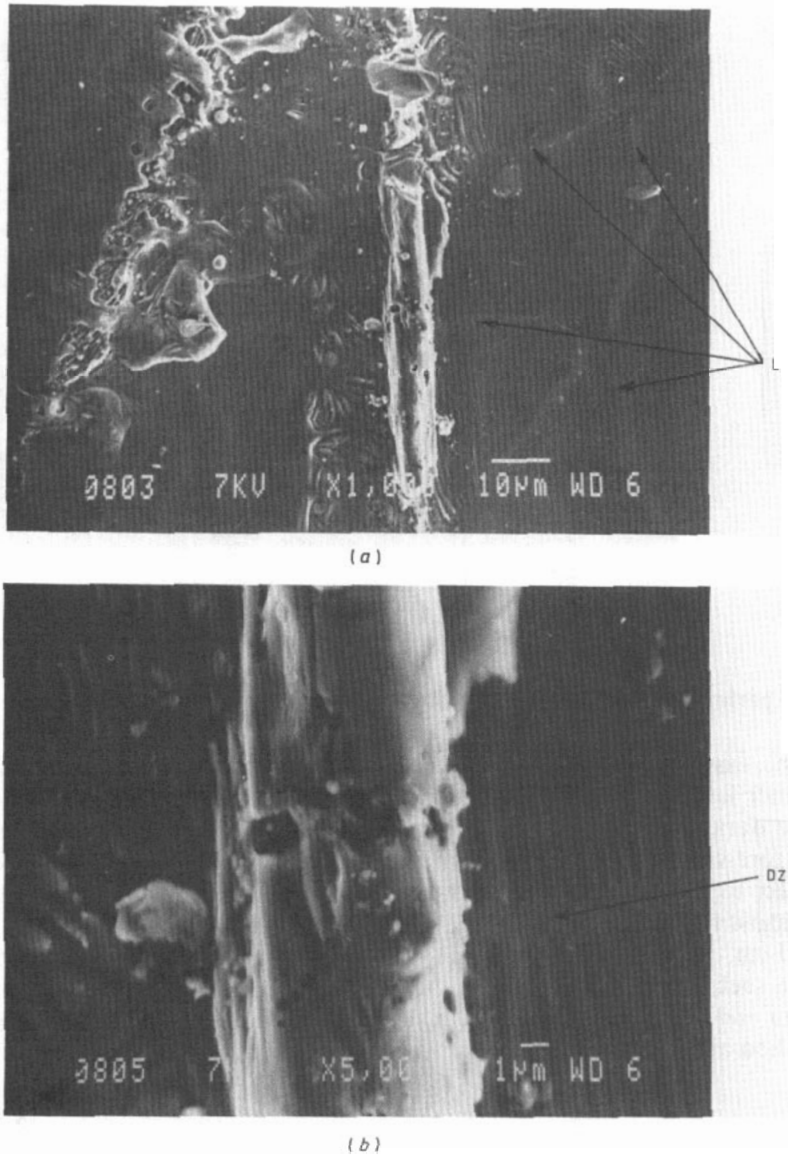

Figure 2. Examples of the structures with DZ on the Si crystal surface. These micrographs show that DZ have a lighter hue than the ripples of CW. The number of pulses is always one. The micrographs were obtained with a JEOL JSM-940 A electron microscope.

(iv) The structures showed no dependence on either small angles of incidence or the number of shots incident on the target. However, the flattening, randomization and disappearance can be observed for $\theta > 70°$ (nearly oblique).

(v) UV irradiation on samples in vacuum do not produce the structures.

(vi) DZ are always perpendicular to the directions of the CW structures.

(vii) The CW structures have a kind of 'memory' for directions when they pass over DZ.

(viii) Space periods of these structures are always smaller than 3 μm; the width of DZ is $d_{DZ} = 1.5$–$3\ \mu$m.

(ix) DZ always have a lighter hue (figure 2(*a*)).

4. Interpretation of experimental results

Consider the effect of a laser beam of constant intensity on the surface of a semi-infinite body occupying the half-space $z < 0$ (figure 3(*a*)). We make our interpretation of the experimental results according to scheme of Bugaev *et al* [4].

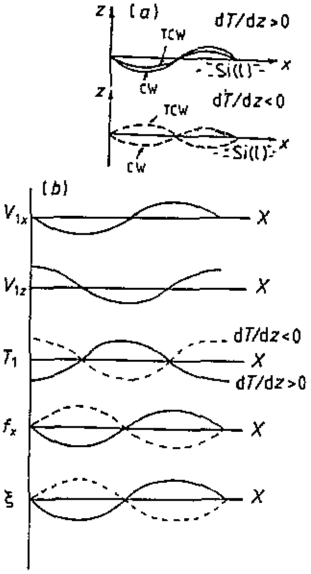

Figure 3. (*a*) Orientation of the crystal surface. The z axis of the Cartesian coordinate system is directed perpendicular to the unperturbed surface of the Si(l) ($z = 0$); the horizontal vector k_T of the perturbations is directed along the x axis. (*b*) Schematic diagram of the formation of the DZ as the result of the interaction between CW and TCW where V_{1x} and V_{1z} are the tangential and normal velocity components, T_1 is the change in temperature on the surface of the Si(l), $f_x = -\partial\bar{\alpha}/\partial x$ is the tangential force of surface tension and ξ is the displacement of the surface of the liquid along the z axis as function of the tangential coordinate x in an unstable CW: ----, $\mathrm{d}T/\mathrm{d}z < 0$ (the formation of DZ, TCW and CW have a phase shift of $-\pi$, hotter material will be carried out of the interior; ——, $\mathrm{d}T_1/\mathrm{d}z > 0$ (for $T_1(x)$, $f_x, \xi(x)$, the amplitude of capillary waves increases), colder material will be carried out of the interior, and the TCW and CW are in phase.

Let us clarify the mechanism of excitation of CW with the aid of figure 3. Suppose that at the initial time a slow motion along the x axis has arisen in the liquid, with a velocity V_{1x} that depends sinusoidally on x. By virtue of the incompressibility of the liquid, this motion will give rise to flow in the z direction with velocity V_{1z}, which will be phase shifted by $-\pi/2$. In a non-uniformly heated liquid the motion in the z direction will cause hotter or colder material (depending on the sign of $\mathrm{d}T/\mathrm{d}z$) to be carried out of the interior. Suppose, for definiteness, that $\mathrm{d}T/\mathrm{d}z > 0$, i.e. the subsurface is colder. Then in regions where $V_{1z} > 0$, colder material will be carried out of the interior and the surface temperature will decrease. Contrarily, in regions with $V_{1z} < 0$ the surface temperature will increase. Thus small temperature perturbations T_1 arise which depend sinusoidally on x. The surface tension depends on the temperature; it is larger in cold regions than in hot regions. Therefore a tangential force $f_x = \partial\bar{\alpha}/\partial x$ ($\bar{\alpha}$ is the coefficient of surface tension) appears, directed from the hot regions to the cold regions. Under this force the initial motions along the x axis are amplified, i.e. the amplitude of the oscillations increases, signifying the presence of an instability.

The proposed mechanism for the instability of CW as the result of the existence of the TCW may be responsible for the formation of DZ. When $\mathrm{d}T/\mathrm{d}z < 0$ (hotter material is carried out of the interior; broken curve in figure 3), the surface temperature will increase. The tangential force will be shifted by $-\pi$. Under this force the initial motions along the x axis are damped, i.e. the amplitude of the oscillations decreases; we have the DZ.

According to [4], TCW exist only for $\Lambda_T \leqslant \Lambda_c$ (Λ_T and Λ_c are the wavelengths of TCW and CW). We have in our experiments $\Lambda_T = \Lambda_c$ with the phase shift $(-\pi)$ for TCW and CW. The wavevectors of the TCW and CW are parallel ($K_{TCW} \| K_{CW}$); therefore the DZ are always perpendicular to the directions of the CW structures. The reason why there is a 'memory' concerning the directions of CW structures when the DZ passes over the structure is also clear; the interaction between the CW and the TCW with the formation of DZ takes place only in the regions of the surface where $\mathrm{d}T/\mathrm{d}z < 0$ and other parts of the CW remain without changes.

The absence of structures with DZ after UV irradiation in vacuum can be explained by expulsion of material out of the crater. The lighter hue of DZ confirms our results about the nature of DZ, because hotter ($\mathrm{d}T/\mathrm{d}Z < 0$) material is carried out of the interior and the time of resolidification is extended. The resolidification occurs in a time scale of tens of nanoseconds, thus providing an interface velocity slow enough for the lattice to be reconstructed [10]. The resolidification time will be slightly different for the regions with DZ and CW structures; therefore these regions have different colours. The lighter hue of DZ corresponds to more disordered material [5]. Raman scattering measurements were performed using a microprobe with an exciting laser beam focused on a spot 1 μm in diameter for examination of the disorder in the regions of DZ and CW structures. c-Si exhibits one Raman-active peak related to the interaction of a photon-induced electron–hole pair with the zone-centre optical phonon whose frequency is 521 cm^{-1}. The full width at half-maximum of this Raman peak is about 3 cm^{-1}.

We observed in our Raman spectra a broadening of the line (to 5 cm^{-1} for CW structures and to 5.7 cm^{-1} for the regions with DZ), an increase in peak intensity, but no difference in frequency. This shows that there is more disordered material in DZ but no true amorphization. The Raman scattering signal had no lines of SiO and SiO_2 vibrations or a-Si.

5. Conclusions

The CW instability discussed here develops owing to thermocapillary effects in a non-uniformly heated liquid and has an entirely different nature from that of the instability of laser-induced CW [5], which are driven by the electric field of the laser radiation.

A possible mechanism for the formation of structures with DZ represents the interaction between the CW ($\mathrm{d}T/\mathrm{d}x \neq 0$) and the TCW ($\mathrm{d}T/\mathrm{d}z < 0$) with the phase shift $(-\pi)$ for CW and TCW.

In conclusion we should like to remark that structures with DZ on Si crystal surfaces after UV excimer laser irradiation is novel effect and DS are *not* dead in spite of being in Si(l). Structures with DZ are frozen into the surface upon resolidification. They have a number of unusual features which still remain peculiar; so the width of the DZ is not changed (i.e. TCW do not diverge) and the width of the DZ is less than 3 μm (the space period of CW). A more convincing description of the proposed mechanism of the interaction between CW and TCW will require detailed calculations of the growth of capillary perturbations in the non-linear regimes with allowance for the finite thickness of the liquid film and its evolution during solidification.

Acknowledgment

We should like to thank Dr Rechenberg for help with electron microscopy measurements.

References

[1] Emmony D C, Howson R P and Willis L J 1973 *Appl. Phys. Lett.* **23** 598–600
[2] Young J F, Sipe J E and Van Driel H M 1984 *Phys. Rev.* B **30** 2001–15
[3] Clark S E, Kerr N C and Emmony D C 1989 *J. Phys. D: Appl. Phys.* **22** 527–34
[4] Bugaev A A, Lukoshkin V A, Urpin V A and Yakovler D G 1988 *J. Technol. Phys.* **58** 908–14
[5] Akhmanow S A, Emelyanow V I, Koroteev N I and Seminogov V N 1985 *Usp. Fiz. Nauk* **147** 675–749
[6] Preston J S, van Driel H M and Sipe J E 1987 *Phys. Rev. Lett.* **58** 69–72
[7] Clark S E and Emmony D C 1989 *Phys. Rev.* B **40** 2031–41
[8] Semjonow A Je, Lau A, Lenz K, Pfeiffer M and Werncke W 1988 *Proc. 13th Int. Conf. on Coherent and Nonlinear Optics (Minsk, 1988)* P-1 pp 42–43; *Proc. 11th Int. Conf. on RS (London, 1988)* pp 248–9
[9] von Allmen M 1987 *Laser-Beam Interaction with Materials* ed A Mooradian (Berlin: Springer)
[10] Nissim Y I, Spriel J and Oudar J L 1983 *Appl. Phys. Lett.* **42** 504–6