Instability at the melting threshold of laser-irradiated silicon

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Symmetry breaking at the silicon melting threshold is demonstrated to result from an increase of reflectivity associated with a strong decrease of the laser penetration depth. One shows analytically that starting with a uniform irradiation, one can produce periodic solid and liquid stripes with the average surface temperature at the melting value and liquid regions slightly hotter than solid ones in contradiction with the previous idea of an undercooled liquid. The pattern size has to be smaller than a critical value of the order of the laser penetration depth.

In recent studies on laser annealing, various patterns[1–4] of coexisting liquid and solid regions have been observed close to the melting threshold of the irradiated silicon. These patterns often take the appearance of spontaneous periodic surface structures, or ripples, with spatial periodicity L related to the optical wavelength of the formula[3] $L=\lambda/(1\pm\sin\theta)$, where θ is the angle of incidence measured from the normal to the surface. These facts strongly suggest that the pattern period L is due to the interference of the incident laser beam with one or two waves traveling along the surface in two opposite directions.[3] The surface waves can be produced by scattering of the incident wave by various perturbations such as scratches, defects, plasmons, etc. To produce the observed ripples, this initial perturbance with spacing L must grow, so that we must find an amplifying mechanism.

The purpose of this paper is to show that such an instability exists near the melting temperature and that it can lead to the observed ripples. Once the melting temperature T_m is reached on the surface, an increase of laser intensity should produce melting. But, as liquid silicon is metallic, its reflectivity is twice as large as the solid one. Consequently, the absorbed laser energy decreases by a factor of 2 when the surface becomes liquid; its temperature should go below T_m and the surface should solidify again. So the increase of reflectivity implies a nonuniform surface phase even with a uniform irradiation[5] as first noticed by Hawkins and Biegelsen.[2] But, in order to explain the observed liquid and solid stripes, they argued that the liquid stays in fact undercooled. This undercooling is explained as a surface-tension effect, the pattern size resulting from a balance between the lateral thermal gradient and the high surface energy coming from the liquid-solid interfaces. But this interpretation implies an overpressure in the liquid, i.e., a curvature of the liquid-solid interface according to Laplace's law which is not present in the observed stripe geometry.

In this Rapid Communication, we want to present a new theoretical model which explains how starting from a *spatially uniform laser irradiation,* one produces a *spontaneous symmetry breaking* which could lead to a regular set of liquid and solid stripes, but *with liquid temperature slightly above* T_m and the solid one slightly below, in contradiction with the previous idea of an undercooled liquid.

Besides the reflectivity increase, there is another very important consequence of melting, unnoticed up to now in this ripples problem, which is the strong decrease of the laser penetration depth (which goes from $\sim 1\ \mu$m in the solid to ~ 100 Å in the liquid for wavelength $\sim 0.4\ \mu$m). It is true that less heat enters a liquid region but as this heat is deposited in a region much thinner than in the solid, the liquid surface should finally be hotter than the solid one, the important physical quantity in fact being the heat deposition per unit volume rather than the heat deposition per unit surface. In order to compensate for the decrease of absorbed energy in the liquid, a lateral heat flow is necessary from the solid region to the back of the liquid one, leading to a heat-flow pattern shown on Fig. 1(a) in a two-dimensional situation (liquid stripes). Such a compensation is only possible if the widths of the liquid and solid stripes are not too large compared with the laser penetration depth in the solid. This would lead to an upper boundary for the pattern period L, as for any instability, the observed pattern being given by external boundary conditions. Finally, as liquid and solid coexist at the surface, one expects an average surface temperature close to the melting one, and, consequently, a ratio liquid-to-solid area such that the resulting mean reflectivity leads to T_m at the surface.

In order to emphasize the importance of the decrease of laser penetration depth compared to reflectivity change, we now consider a simple situation where the temperature distribution can be calculated exactly. This model is two dimensional and contains all the main physical features of the problem, i.e., different reflectivities $R_s<R_L$ and different penetration depths $d_s>d_L$ for the solid and liquid phases. We give a complete analytical solution, assuming for simplicity that $d_L=0$ (as $d_L\sim 10^{-2}d_s$) and that all the heat conduction coefficients K are equal: from Fig. 1(a), it is clear that most of the heat flows through the solid phase. The introduction of a different conductivity in the liquid would just add unnecessary complications in the analytical calculation, without new physical insight. Let us consider a silicon sample of thickness D, the back surface of which is kept at a constant temperature (chosen as the zero for T), irradiated with a laser power P having spatial uniformity. What happens to the irradiated surface when P increases? In order to get simpler results, we will restrict to the case

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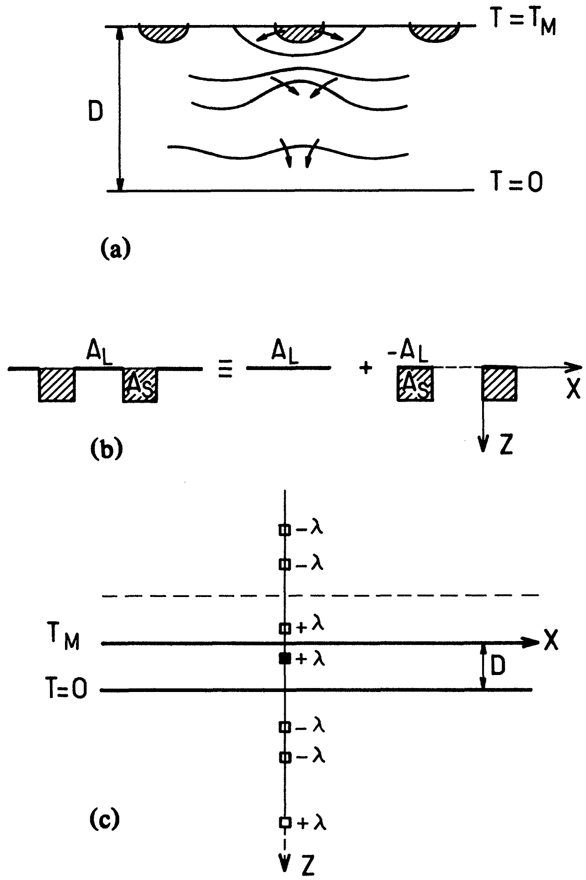

FIG. 1. (a) Two-dimensional heat flow pattern for liquid stripes on the surface. (b) Spatial distribution of heating elements used in the calculation. (c) Electrical images analog for a heating line at depth z.

$D \gg d_s$. If the whole surface is solid, the equilibrium surface temperature is $T_s = A_s PD/K$ where $A_s = 1 - R_s$. Similarly, if the whole surface is liquid, the surface temperature is $T_L = A_L PD/K$. Let us call P_s and P_L the laser powers such that T_s and T_L equal T_m. As $A_L < A_s$, $P_L > P_s$, and for a laser power $P_s < P < P_L$, the silicon surface cannot be homogeneously liquid or solid. One can introduce an absorptance A such that for an intermediate value of P

$$T_m = \frac{AP}{K} D, \quad A = \alpha A_s + (1-\alpha) A_L \ . \tag{1}$$

α represents the percentage of solid area for a surface partially molten which would produce, for a specific P, an average surface temperature equal to T_m.

As the Si surface cannot stay homogeneous, we have to look for an inhomogeneous solution. In order to prove that there is *at least* one solution exhibiting a symmetry breaking, we choose arbitrarily to consider a specific one—a periodic system of liquid and solid stripes. We calculate the surface temperature in this case and show that it is indeed a possible steady-state situation. For that purpose it is convenient, as the heat equation is linear, to replace the real solid-liquid heating pattern [see Fig. 1(b)] by a uniform heating as if the whole surface were liquid, plus a regular set of "heating" elements ($A_s P$ over depth d_s, and $-A_L P$ on the surface). The surface temperature is $T = T_L + \Delta T$. The problem is to calculate the modulation ΔT corresponding to heating elements $(A_s P, -A_L P)$ located at $nL < X < nL + a$ [see Fig. 1(b)], where a and b are the widths of the solid and liquid stripes, respectively, and $L = a + b$, n being an integer from $-\infty$ to $+\infty$. For that we first cut a heating element in infinitely small heating lines, having a section $dx\,dz$, located at a distance z from the irradiated surface. Noting that in steady state the heat equation is analogous to Poisson's equation in electricity, we are led to solve the equivalent problem in electrostatics. There are two boundary conditions: (i) as the heat flow at the irradiated surface is zero, we introduce a mirror system with respect to that surface; (ii) then we are left with the boundary conditions $T=0$ at $z = \pm D$ (equivalent to the electrostatic potential $V=0$). To take into account these boundary conditions, we use the trick of electrical images, which finally transforms one heating line into a double infinity of lines, images of the initial line with respect to the planes $z = \pm D$ (see Fig. 1). Using this method, one finds that a heating line of intensity $(A_s P/d_s) e^{-z/d_s}$, produces on the surface, at the distance X away from it, a temperature increase

$$\delta T(X,z) = 2 \frac{A_s P}{K d_s} e^{-z/d_s} dx\, dz \frac{1}{4\pi} \ln \left| \frac{e^{2\bar{X}} + 1 + 2e^{\bar{X}} \cos\bar{z}}{e^{2\bar{X}} + 1 - 2e^{\bar{X}} \cos\bar{z}} \right| , \tag{2}$$

where $\bar{X} = \pi X/2D$. Integrating Eq. (2) over z, the temperature increase produced by a solid heating element of width dx, reads for $d_s \ll D$

$$\delta T(X) \simeq dx \frac{A_s P}{2\pi K} \ln \left| \frac{(e^{\bar{X}}+1)^2}{(e^{\bar{X}}-1)^2 + \bar{d}_s^2} \right| = A_s f(X, d_s)\, dx \ . \tag{3}$$

The temperature increase for a liquid element is obtained by setting $d_s = 0$ and replacing A_s by A_L in Eq. (3). (It is pleasant to check that extending this heat from $-\infty$ to ∞, one finds again T_L.)

Using Eq. (3) for an infinite number of "heating" elements, one gets the surface temperature modulation

$$\Delta T(X) = \sum_{n=-\infty}^{+\infty} \int_{nL-X}^{nL+a-X} [A_s f(x,d_s) - A_L f(x,0] dx \ . \tag{4}$$

An explicit calculation shows that ΔT is composed of a constant term

$$\Delta T_0 = \frac{PD}{K} \frac{a}{L} (A_s - A_L) \tag{5}$$

independent of the position X on the surface, and a modulation depending on X

$$\Delta T_1(X) = \frac{PD}{K\pi^2} \sum_{-N+1}^{N-1} [\phi(nL - X + a) - \phi(nL - X)] \ , \tag{6}$$

with

$$\phi(X) = X(A_L \ln \bar{X}^2 - A_s \ln(\bar{X}^2 + \bar{d}^2))$$

and $N = 1/\bar{L} = 2D/\pi L$. The modulation comes essentially from the neighboring stripes and will be found small, of order $\bar{L}$ (see below).

From Eqs. (1) and (5) one finds that in order to have a temperature close to the melting one on the surface a/L should be equal to α, to lowest order in L/D. This means that the ratio of solid to liquid area is such that it corresponds to an average absorption coefficient giving T_m at the surface, as expected.

Let us turn to the temperature modulation and verify that it is indeed very small and mostly of the correct sign, i.e., liquid areas slightly hotter than solid ones. At the center of a solid stripe, Eq. (6) gives for the temperature variation

$$\Delta T_1(a/2) \simeq \bar{a}\left[(A_s - A_L)\ln 4 - A_s \ln\frac{a^2+4d_s^2}{a^2+d_s^2} + \tfrac{3}{4}\alpha^2\left(A_L - A_s\frac{L^2}{L^2+d_s^2}\right)\right]\frac{PD}{K\pi^2} . \quad (7)$$

One easily checks that for $L \ll d_s$, $\Delta T_1(a/2)$ is always negative, i.e., the solid temperature is below T_m while a similar calculation done at the center of the liquid stripe will give a temperature above T_m. On the other hand, for $L > d_s$, $\Delta T_1(a/2)$ will be negative only if a is smaller than a critical value

$$a^* \sim d_s\left(\frac{4-\mathscr{A}}{\mathscr{A}-1}\right)^{1/2}, \quad \ln\mathscr{A} = \left(1-\frac{A_L}{A_s}\right)\left(\ln 4 - \frac{3}{4}\alpha^2\right) . \quad (8)$$

Similarly, one finds ΔT_1 positive at the center of the liquid only if b is smaller than a critical value b^*, obtained from Eq. (8) by changing α to $(1-\alpha)$. This implies an *upper limit* for the pattern period, $L^* = \inf[a^*/\alpha,\ b^*/(1-\alpha)]$, which for silicon is $L^* \sim 3.5 d_s \sim 3.5\ \mu$m (i.e., of the order of the lamellae size observed experimentally[2]). Our calculation allows also an estimate of the temperature difference ΔT_{max} between the liquid and solid regions. Taking an average laser intensity of 2.5×10^5 W/cm^2 and the thermal conductivity of silicon at 1410 °C to be $K = 0.25$ W/cm K, as used in Ref. 2, we find that $D = 25\ \mu$m and $\Delta T_{max} = 0.6$ K.

In conclusion, the new results of this Rapid Communication show that, although the increase of reflectivity at melting is the main physical reason for producing an inhomogeneous phase surface starting with an homogeneous excitation, it is crucial to include the decrease of penetration depth in order to restore the fact that liquid regions have to be hotter than solid ones, in agreement with common sense. We have also determined the range of possible pattern sizes for this instability.

As for any instability, the pattern effectively observed results from external boundary conditions which have to be added to the basic mechanism. In the present case, this additional effect comes from the interaction between the incident beam and diffracted waves traveling along the surface: the resulting interference and diffraction effects can select a critical pattern if the laser wavelength is compatible with the possible values of the pattern size; this is actually what happens in most experiments as shown by the fact that the observed ripples spacing is of the order of λ and the pattern shape changes with the laser polarization. Consequently, a complete interpretation of the experiments on ripples should include interference and diffraction effects as well as changes in the optical properties at melting. But this complete calculation is far beyond the scope of this paper, which is only devoted to the elucidation of the physical mechanism inducing a spontaneous symmetry breaking at the silicon surface when irradiated by a uniform laser beam.

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[5]Note that if the reflectivity decreases at melting, one gets a bistable system, both a uniform liquid surface and a uniform solid surface being stable solutions, while if the reflectivity increases neither uniform solution is possible.