IS LASER-INDUCED NUCLEATION DUE TO A BULK LONG-WAVELENGTH INSTABILITY ?

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Abstract.-The speculative suggestion is made that laser-Induced Nucleation of single crystals from amorphous thin films is due to an instability of the system against certain long-wavelength fluctuations, analogous to spinodal decomposition of binary mixtures.

It is the purpose of this note to discuss laser annealing of thin amorphous semiconductor films /1,2/ and the mechanisms which have been suggested to explain it /1,3,4/, applying the view point of nucleation theory /5-7/. As a result, a mechanism of recrystallization is suggested which slightly differs from the other approaches /3,4/.

In the standard approach /3/ one assumes that the whole amorphous layer (and eventually part of the single crystal substrate) is molten into a more or less ordinary liquid during the duration of the laser pulse ; when the molten layer afterwards cools down it finally crystallizes by epitaxial growth from the substrate (i.e., quick motion of the liquid-crystal interface when the liquid is strongly enough supercooled, in order to enable a recrystallization completed during a time of about 10^{-9} s.). Many arguments have been given /4/ which shed doubt on this hypothesis. A particular convincing counterargument is the observation /2/, that fairly large simple crystalline domains can also be produced without having a single crystalline substrate of the same material. The standard explanation of such an observation would be that the single crystals originated from presumably heterogeneous) nucleation. This explanation will be examined below.

Van Vechten /4/ suggested another mechanism, where the system experiences nonthermal "melting" in a second-order phase transition. Rather than producing melting by enhancing the temperature of the system, he suggested that the laser energy produces a (suitably long-lived) dense electron-hole plasma, which weakens the interatomic bonds strongly enough that all transverse acoustic phonon frequencies and associated elastic constants vanish at this transition.

Here, of course, the question arises : how can there exist a second-order phase transition between a solid and a "cold liquid"? After all, thermal solid-liquid transitions for all kinds of materials always are first order in three-dimensional systems (and symmetry arguments suggest this to be the case, too /8/). Rescaling the forces means rescaling the melting temperature, but it is not clear how this could change the qualitative character of the transition. The Lindemann criterion predicts that a solid melts when the root mean square displacement of atoms becomes of the order of 10% of the interatomic distance. A second order liquid-solid transition would imply that on the solid side of the transition the root mean square displacement continuously goes to infinity (i.e., there would be a regime of the solid with displacements large in comparison with interatomic distances).

I am now going to point out that there may be also a bulk long-wavelength instability associated with first-order rather than second-order transitions. In mixtures, this phenomenon is well-known as "spinodal decomposition" /9/ (see also /5,6/). Let us consider the energy barrier $\frac{\Delta F}{k_B T}$ which has to be overcome by nucleation of the new phase at a first order transition /5,6/ (figure 1). For sufficiently large undercooling ΔT the formation energy ΔF of a critical "cluster" (microdomain of the new phase) is no longer large in comparison with thermal energy $k_B T$, and through a so-called spinodal regime (which in the simplest

6

version of the theory is a well-defined
sharp line /9/) one enters a regime of gene-
ral instability of the system with respect
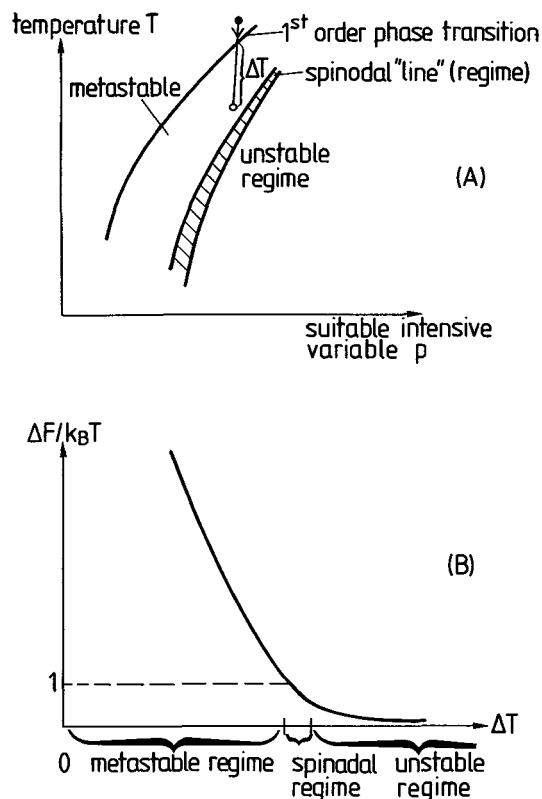to fluctuations.

Fig.1.- Schematic description of metastable and uns-
table regimes at first order phase transitions (A)
and the associated variation of the nucleation energy
barrier with undercooling ΔT.

While in the metastable regime the energy
barrier determines the rate at which the pha-
se transformation proceeds via nucleation
events, occuring independently of each other
with a rate

$$J = \nu_a \exp(-\Delta F/k_B T) , \qquad (1)$$

where ν_a is the "attempt frequency", this
picture breaks down in the unstable regime:
Here the density of unstable clusters or flu-
ctuations (which grow instead of decreasing
with time) is so large that they strongly
interact with each other, and ΔF is no
longer a very meaningful parameter.

It is convenient to analyze what happens
in the unstable regime by introducing a coar-
se-grained free energy F_{cg}, i.e. the free
energy of a finite subvolume of the system
large enough that it is meaningful to define

an " order parameter" $\psi/8/$ of the transi-
tion for the subvolume. In a binary mixture,
this order parameter ψ is a concentration
difference ; for liquid-solid transitions,
an order parameter component might be the
amplitude of a density wave exp $(i\vec{\tau}\vec{r}+i\psi)$,
where $\vec{\tau}$ is a reciprocal lattice vector of
the solid to be formed and ψ a phase factor.
Figure 2 shows then the schematic structure
of F_{cg} as a function of ψ if the initial
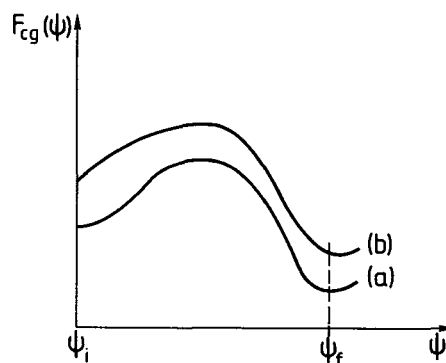state ψ_i is metastable (a) or unstable (b).

Fig.2.- Schematic description of the coarese-grained
free energy as a function of the order parameter in
the case where the initial state (ψ_i) is metastable
(a) or unstable (b). ψ_f is the order parameter of
the resulting final new equilibrium state.

In case (a) we have $\partial^2 F_{cg}(\psi)/\partial\psi^2|_{\psi_i} >0$, while
in case b) $\partial^2 F_{cg}(\psi)/\partial\psi^2|_{\psi_i} <0$. Since the free
energy of the total system wants to become
a minimum, one can derive the following
equation for the time evolution of long-
wavelength $(\lambda = 2\pi/k)$ order parameter fluc-
tuations $\delta\psi(\vec{k},t)$, in linearized approxima-
tions /9-12/

$$\frac{d}{dt} \delta\psi(\vec{k},t) = -\Gamma(k)\left[\frac{\partial^2 F_{cg}}{\partial\psi^2}\bigg|_{\psi_i} +Kk^2\right] \delta\psi$$

$$+ \eta(kt) ; \qquad (2)$$

here $\Gamma(k)$ is a kinetic factor, $\frac{1}{2} K(\nabla\psi)^2$
describes a static gradient energy (K >0),
and $\eta(\vec{k},t)$ a random noise term due to
short-wavelength fluctuations. In the uns-
table regime for small enough k the square
bracket in equation (2) is negative, and
fluctuations increase exponentially fast.
Of course, this invalidates the use of the
linearization approximation for the descri-
ption of the later stages of the phase

transformation (and the treatment of the non-linear case in fact is still a formidable problem /6,10,11./)/

In equation (2) there is an important difference between the case where the order parameter $\psi(0,t)$ is a "conserved" quantity [i.e. $d/dt\ \psi\ (0,t)\equiv 0$], where $\Gamma(k) = Mk^2$, M being some mobility factor, and the case where it is not conserved, where $\Gamma(k\to 0)\to$ const. Although fluctuations increase in both cases, the <u>rate of increase</u> is very small in the conserved case for long wavelengths, while in the nonconserved case the rate of increase is basically a microscopic frequency. As a result, only in the conserved case [like in binary mixtures where the order parameter, a concentration difference, is conserved because the chemical composition of the total system is held constant] there so far has been a chance of observing this "spinodal decomposition" mechanism, as one calls this growth of unstable modes /9/. In the non-conserved case, this hardly could be observed because in an experiment the desired undercooling ΔT can never be reached instantaneously, but only with a finite rate $\Delta T/dt$. Since in equation (1) v_a is sufficiently large and ΔF sufficiently small (at least close to certain defects, impurities or surfaces), nucleation will occur in the metastable regime already. Since in typical experiments (see Ref./7/) the final undercooling ΔT is reached during a time of 10^{-3} to 1 s, and one is interested in a completion of the phase transformation during a similar time-scale, there is no chance at all to see a phase transformation on the basis of this mechanism where long-wave-length-fluctuations grow, since it is superceded by nucleation during the cooling. It is speculated here that in "laser-induced nucleation", where the characteristic times are of order 10^{-9} s, the situation might be different : going through the metastable regime on such a quick time-scale there is more chance that ordinary nucleation does not come into play, and hence one might reach the spinodal or unstable regime. The concept of such a bulk long-wavelength instability would account for the observation

that fairly large coherent single-crystalline domains are formed. The nonlinear terms neglected in equation (2) together with the effect of boundary conditions should lead to a selection of the most favorable mode out of the band of unstable modes, which then survives in a particular case. One does in fact expect, that the coarse-grained free energy of the amorphous film before the laser pulse is qualitatively similar as in figure 2, case (a), with $\psi_1= 0$ (no periodic arrangement present). The hypothesis hence is that even for this phenomenon far from thermal equilibrium one can introduce a functional which would play the role of a coarse-grained free energy in thermal equilibrium, and that this functional immediately before crystallization has the shape of figure 2(b). With less laser power, on the other hand, one would expect that one would get an intermediate case, where F_{cg} before crystallization looks qualitatively as in figure 2 (a), but the energy barrier ΔF is strongly reduced. In such a case where the phase transformation still starts well inside the metastable regime one would expect nucleation and growth, but with a comparatively high density of critical nuclei. This should lead to a polycrystal.

With the present information, one can hardly make these speculations more quantitative and hence prove or disprove them. The present arguments say not much about the physical nature of the initial state before crystallization, and hence presumably are consistent with both the " hot liquid" or "cold -liquid" picture.Microscopic theories for the nonlinear transport phenomena occuring due to the irradiation /13/ are certainly an important first step for a more quantitative analysis.

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