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Structural changes and crystallization of amorphous hydrogenated silicon generated by laser irradiation

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Structural instabilities at nucleation and crystallization of hydrogenated amorphous silicon (*a*-Si:H) induced by continuous laser irradiation are investigated by means of Raman scattering. The temporal evolution shows four stages, which depend on the laser intensity as follows. (a) For relatively low intensities, the amorphous Raman spectrum exhibits quasiperiodic changes. (b) At intermediate laser levels, traces of crystalline structure appear and disappear quasiperiodically. (c) For somewhat higher irradiation levels, but below the crystallization threshold, the Raman crystallinelike peak has an oscillatory behavior for some time and after that its intensity increases and saturates. (d) For irradiation levels above the threshold, the Raman crystalline peak intensity increases monotonically and rapidly. We propose the following model, that the optical field pumps the material athermally from the amorphous disordered states towards more ordered states. This is achieved through the formation of energetically favorable small wurtzite and somewhat larger diamond submicrocrystalline clusters, whose average size depends on the pumping rate. The formation of these clusters is opposed by a restoring force from the stressed surrounding material, which accounts for the oscillations observed.

I. INTRODUCTION

The structural transformations induced by lasers in amorphous materials has been of considerable interest in the last decade, due to the technological importance of recrystallization by intense laser beams.[1–3] This can be divided mainly into two types of laser irradiations: pulsed and cw irradiations. With regard to the first type, there is a strong debate on the nature of the microscopic mechanisms involved in laser annealing. Some advocate laser melting, while others suggest athermal mechanisms.[4,5] However, when the radiation is higher than a given intensity, the sample temperature rises rapidly and the annealing is mainly thermal. The question is which mechanisms contribute to the annealing process, when the intensity is so low that heating is negligible. Since the suggestions of van Vechten and co-workers[4] that pulsed laser annealing is due to the existence of very dense plasma of electrons and holes created by the photon flux, much work has been done on the subject.[1,2] On the other hand, cw laser annealing was thought to be essentially a thermal process because there is no dense plasma as created in the case of nanosecond pulses.

Various experimental techniques[1–3] have been utilized to probe the cw laser-induced crystallization of *a*-Si. An important result is the existence of a threshold intensity for crystallization above which drastic changes occur in the physical properties of the irradiated material.[1–3] More recently the question of athermal annealing by cw lasers has been raised by Griffiths *et al.*[6] The Raman-scattering experiments on the $GeSe_2$ glass system under cw laser irradiation by Balkanski *et al.*[7] explored three significant effects depending on the incident laser power and they describe the progressive transformations of the material structure under irradiation. They showed that for intensities below the threshold, clusters are created which can increase in number and size, attaining microcrystallite size depending on the power level. Up to this stage the system is reversible, that is, without further input of radiation energy the clusters can relax back to the glassy state. After the threshold is reached, the clusters can coalesce and form polycrystallites which then remain stable.

In a previous paper[8] we reported on the new instability effect on glassy As_2Se_3. Through the evolution process of the irradiated material from the glassy state toward the crystalline state, we found that crystalline Raman peaks appear and disappear quasiperiodically during the irradiation time. Our interpretation was based on the proposition that submicrocrystalline clusters are created and annihilated quasiperiodically with the irradiation time, when the laser power was just below the threshold for crystallization. For low enough intensities, we found no significant changes in the Raman spectrum, except for small changes in the scattered intensity due to photodarkening. On the other hand, by doing the same experiments on *a*-Si:H we found[9,10] quasiperiodic oscillation in the shape, position, and width of the TO Raman line, together with quasiperiodic changes in the transmittance. The proposed model was based on the assumption that atomic transitions take place under the influence of the laser beam through the formation of hot mobile electrons trapping and their energy release.

In the present work we extend this study with laser intensities close to the threshold intensity, and we follow the time evolution of the Raman spectra for different laser powers at room and liquid-nitrogen temperatures. We shall concentrate more on the nature of the metastable states in *a*-Si between which the transitions take place, on the pumping mechanisms, the mechanism for oscillations, and on the kinetics of crystallization.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The 0.5-μ m-thick hydrogenated amorphous-silicon samples were prepared using the glow-discharge method on different substrates: quartz, sapphire, and crystalline silicon. We present the results on quartz substrate. The substrate temperatures are about 250 °C. Under these conditions the hydrogen content was determined to be about 8%.

For the Raman measurements we used a standard Spex double monochromator. The spectral resolution of the system is about 4 cm^{-1}. The HH (incident and scattered polarizations parallel) spectrum taken in the backscattering geometry[11] between 300 and 700 cm^{-1} was measured both at room temperature and at liquid-nitrogen temperature using a focused beam of spot diameter about 140 μm, in the single-line operation, 5145 or 4880 Å, of the Ar^+-ion argon laser. We have not measured the VH spectrum. The measurements were performed as a function of the irradiation time for different laser powers as measured near the sample surface. The irradiation laser beam is also used as the probe beam. The measurements at room temperature were done in part in open air and in part inside a cryostat in a vacuum of 10^{-6} torr. We have not found any significant difference between the two sets of measurements, indicating that oxidation in open air does not occur or at least it does not influence the Raman spectrum. Since laser irradiation influences for a long time the structure of the irradiative volume, we take care that for each power level our starting point is the amorphous state by using a virgin spot on the sample surface.

The typical Stokes Raman spectra in the range 300–700 cm^{-1} are shown in Fig. 1 for *a*-Si:H on quartz in the case of low irradiation level for different irradiation times. The spectrum in this range consists mainly of the broad peak centered at around 480 cm^{-1} which corresponds to the TO zone-edge phonon. From Fig. 1, one can easily see the changes in the peak position, width, and shape as a function of the irradiation time. Changes in width and position are inversely correlated; the higher peak width, the lower the peak position. These oscillations are not perfectly periodic, and an average quasiperiod t_1 was defined. (The relatively high noise background is due to the limited collection time which had to be short relative to t_1.) They were correlated with transmittance measurements reported recently[9,10] and a kinetic many-body semiquantitative model was developed[12,13] to explain the dependence of the quasiperiod on the photon energy and flux. No drastic differences have been observed between samples on different substrates. Changes in the peak shape exhibit the appearance and disappearance of a hump on the low-energy side at about 430 cm^{-1} and the existence of two close peaks separated by about 10 cm^{-1} centered at 470 cm^{-1}. The peak at 430 cm^{-1} was interpreted recently by Okada *et al.*[14] as a surface mode by doing Raman measurements on small silicon particles. They observe that it appears only for particles of size less than 250 Å and its intensity increases as the particle size decreases.

By increasing further the laser intensity, a small crystalline peak at 508 cm^{-1} starts to appear as shown in Fig. 2. It appears and disappears quasiperiodically with the irradiation time. The evolution process of the spectrum shows that in the early stages (the second and third spectra in Fig. 2) of irradiation the TO peak becomes structured. This pattern is reproducible at these power levels. The average quasiperiod in this power range will be called t_2. Our explanation for this interesting phenomenon is given in Sec. III B.

For higher laser powers but still below the threshold for crystallization (Fig. 3), the small crystalline peak exhibits the oscillatory behavior for some time t_3 which depends on the power level and after that the intensity of the peak grows gradually and saturates after long enough time t_4 of irradiation, where the peak height, width, and position achieve a saturation value which depends on the power level. The laser-intensity interval where the time t_3 is finite is very small. In our case it is between 4.35 and 4.68 kW/cm^2. Above this intensity, the crystalline peak grows rapidly (Fig. 4) without the oscillatory behavior and achieves a saturation level appropriate to the incident laser intensity. The saturation time t_4 becomes very small as the intensity increases. The definition of the threshold intensity will be the intensity at which t_4 vanishes. In Fig. 5 we plot the crystalline-peak height measured with respect to the amorphous background against the irradiation time for different laser intensities showing

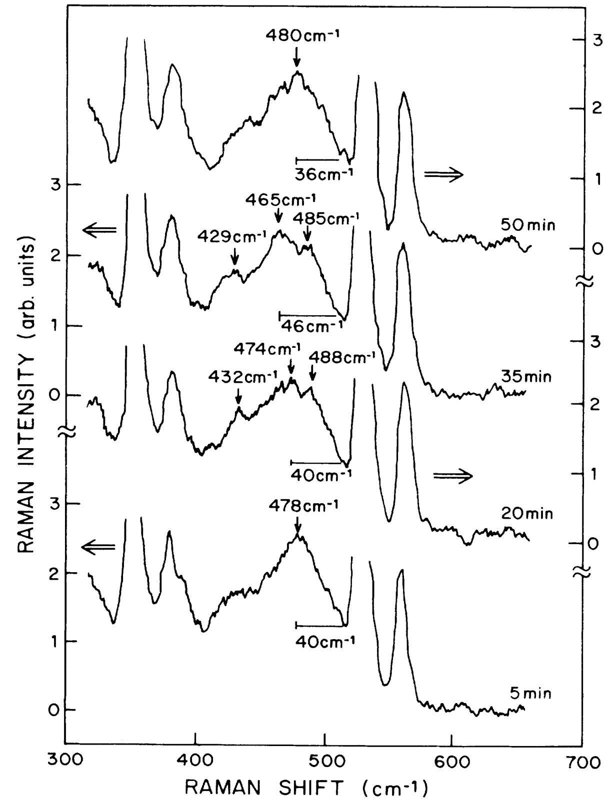

FIG. 1. Raman spectra in the range 300–700 cm^{-1} for *a*-Si:H on quartz substrate taken at low irradiation level of $I \simeq 3.25\ \text{kW/cm}^2$ and for different irradiation times. Excitation wavelength $\lambda = 4880$ Å line of the Ar^+ ion laser. The fluorescence lines of the laser were used for calibration.

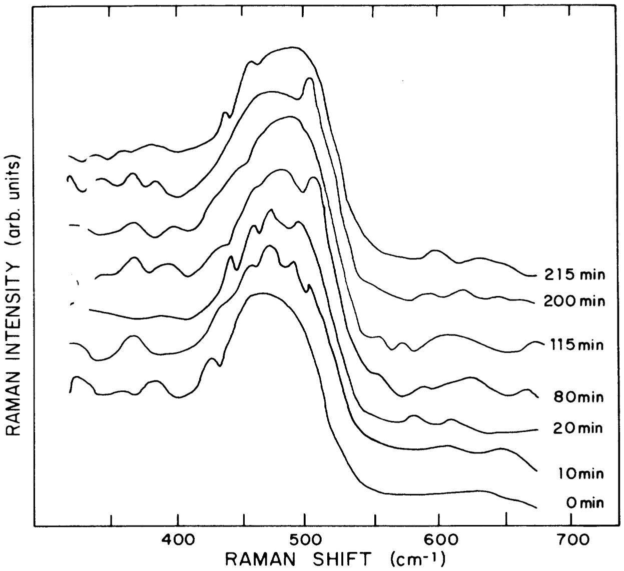

FIG. 2. Raman spectra of *a*-Si:H on quartz taken with intermediate power level of $I = 4.22$ kW/cm^2 and excitation wavelength $\lambda = 5145$ Å for different irradiation times. Here one can see the appearance and disappearance of the small crystalline peak around 508 cm^{-1}. The complex structure of the TO peak seen in the second and third spectra is reproducible and indicates the existence of a distribution of submicrocrystalline clusters at this stage.

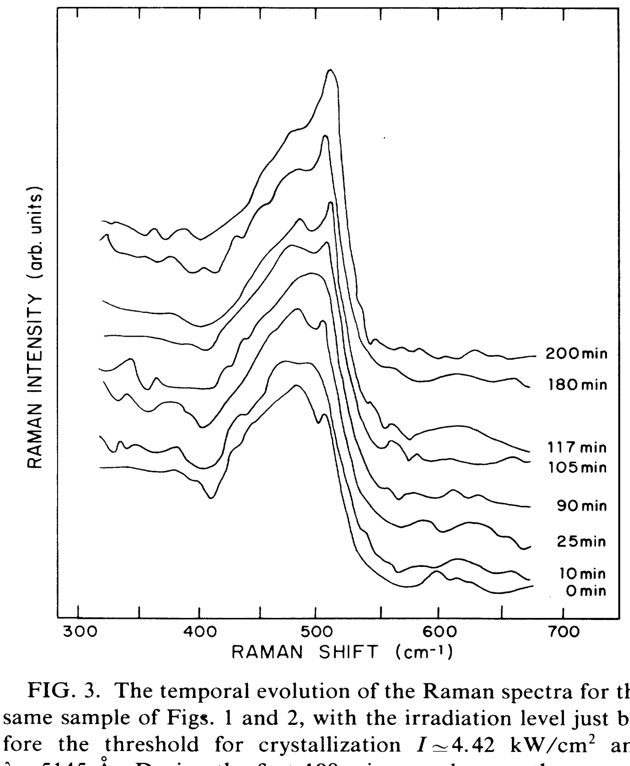

FIG. 3. The temporal evolution of the Raman spectra for the same sample of Figs. 1 and 2, with the irradiation level just before the threshold for crystallization $I \simeq 4.42$ kW/cm^2 and $\lambda = 5145$ Å. During the first 100 min one observes the appearance and disappearance of the small crystalline peak. After that this peak increases without any oscillatory behavior attaining a saturation value after sufficient time of irradiation. During the first 100 min the system is reversible.

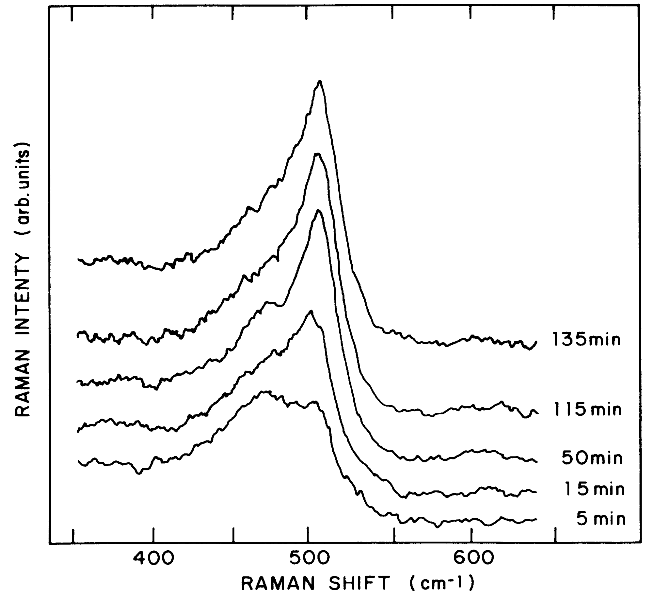

FIG. 4. The same as Fig. 3 except with irradiation level above threshold $I = 5.2$ kW/cm^2. No oscillatory changes occur in this case. The crystalline peak rises rapidly, while the amorphous part transforms into a tail with a decreasing area.

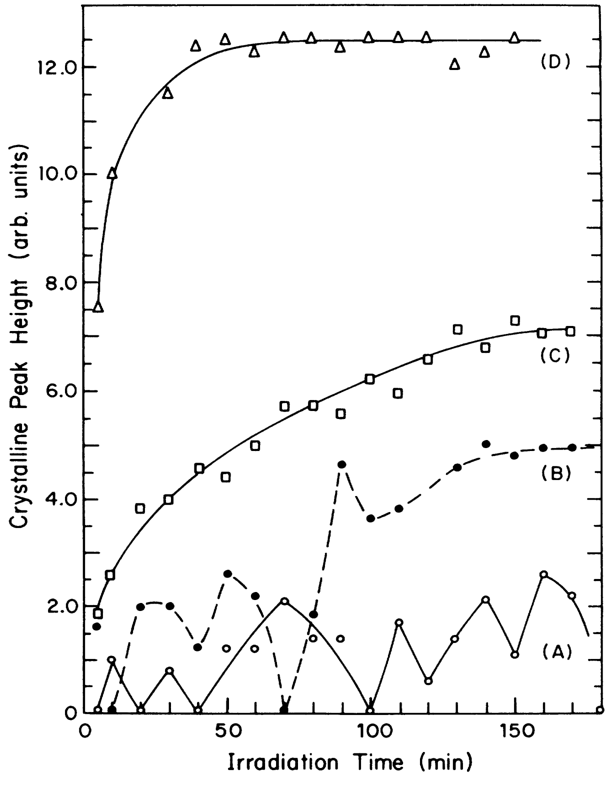

FIG. 5. A plot of the crystalline-peak height as measured with respect to the amorphous background from Figs. 2–4 as a function of the irradiation time for different irradiation levels: (a) 4.22 kW/cm^2; (b) 4.48 kW/cm^2; (c) 4.74 kW/cm^2; (d) 4.94 kW/cm^2.

the main properties of the evolution process as described in Figs. 1–4.

The amorphous part of the spectrum is the main component for intensities below the threshold. It decreases with the irradiation time depending on the irradiation level. The fraction of crystallinity can be measured by the crystalline-peak height. The surface mode at 430 cm^{-1} also decreases with the increase of the crystalline peak, indicating that the contribution of the surface is higher as the crystalline size decreases, as expected.

In Fig. 6 we show the first Raman spectrum taken at different laser intensities, from different spots on the sample surface, in order to determine the threshold intensity. One can see that the amorphous part is still well defined up to $I=5.52$ kW/cm^2, while its position is difficult to determine for higher intensities. It transforms into a tail with a decreasing area as a function of laser power or irradiation time. Hence, there are two ways to obtain crystallization; either by increasing the intensity well above the threshold, or at intensity just above threshold, by irradiation for a sufficient time. For intensities less than the threshold, the amorphous peak persists together with a small crystallinelike peak which reaches its saturation height after a very long time of irradiation. The threshold intensity is determined from Fig. 7, where the crystalline-peak height is plotted against the intensity. It shows a sharp increase above a certain intensity and it saturates when the intensity is high enough. The threshold intensity is 5.07 kW/cm^2, which is the value obtained if one plots the saturation time t_4 as a function of intensity and extrapolates at time zero. We should mention here that the threshold intensity obtained both at 300 and 77 K is the same and no significant difference was observed. These experimental results are summarized in Table I.

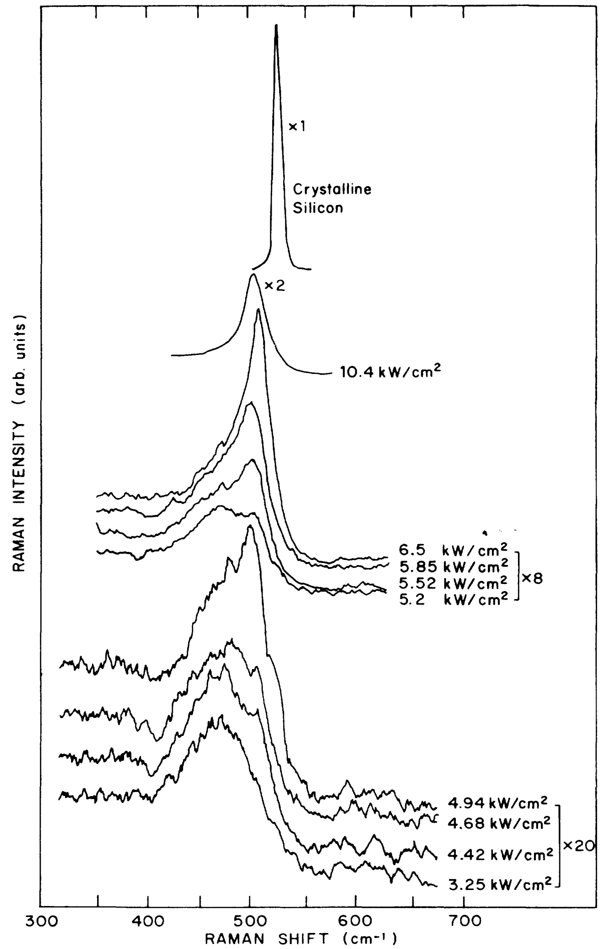

FIG. 6. The evolution of the Raman spectra with increasing irradiation level. Starting from an amorphous state at $I=3.25$ kW/cm^2 up to the polycrystalline state at $I=10.4$ kW/cm^2. The single crystalline peak was plotted for comparison. Every spectrum in this figure was taken on different virgin spots on the sample surface in order to ensure that the starting point is always from the amorphous state.

Changes in the crystalline-peak position and width for intensities above threshold are very small. Saturation occurs after sufficient exposure time as is seen in Fig. 8. It starts from about 505 cm^{-1} and saturates at about 512 cm^{-1}. Similar behavior exists for the peak width. It becomes narrower with the illumination time starting from about 35 cm^{-1} and saturates at 25 cm^{-1}. The saturation values of the position (width) decreases (increases) with the irradiation level. For $I=13$ kW/cm^2 the peak position saturates at 503 cm^{-1} and the width at 28 cm^{-1}. The shift of about 20 cm^{-1} from the single crystalline peak which is at 552.5 cm^{-1} was attributed both in pulsed[15,16] and cw laser annealing[17] to residual stresses inside the annealed region. This is actually expected,

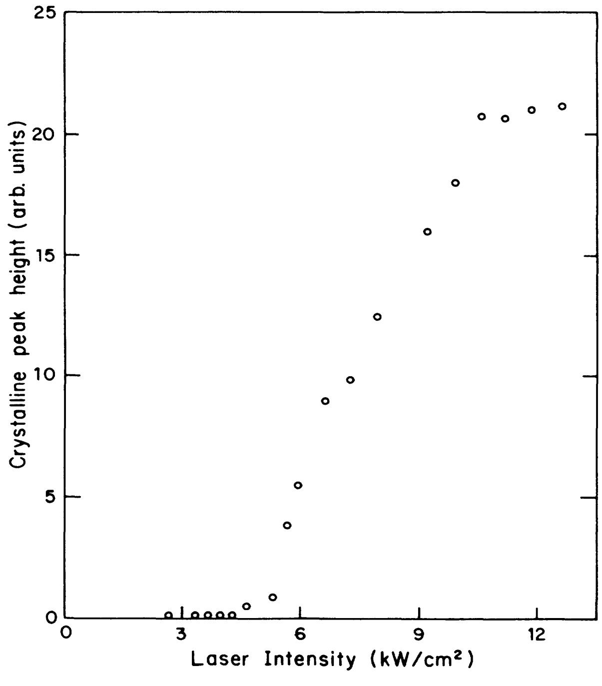

FIG. 7. The crystalline-peak height plotted as a function of the laser intensity as taken from Fig. 6. The threshold intensity for crystallization was determined from this figure to be 5.07 kW/cm^2 by extrapolation.

since the crystallized material in the irradiated volume has a density larger than its amorphous surrounding. Furthermore, one may expect that some heating exists. Therefore, the annealed region will be under tensile stress, which will cause some down shift of the TO phonon frequency. However, if the stress is to be invoked, it would have to be more than[16] 25 Kbar which is beyond the yield point for silicon. On the other hand, if heating is responsible for the down-shift and broadening, the temperature[18] would have had to be about 1000 K for laser intensity of 6.5 kW/cm^2, which is too high to be achieved with the intensities used in our experiment.[19] (The question of heating is discussed shortly in Sec. III A based on measurements of the Stokes to anti-Stokes ratio.) Furthermore, our measurements at temperature 77 K exhibit similar behavior, although the background temperature is lower by 200 K. In order to get more insight into this problem, we measured the Raman spectra at different laser intensities after the sample was irradiated by an intensity well above threshold for sufficient time, so that crystallization was assured. In Fig. 9(a) the amorphous peak was taken first at a low irradiation level of 2.6 kW/cm^2, then the intensity was increased to 5.85 kW/cm^2 until the saturation was reached, as in Fig. 9(b), and then the intensity was decreased gradually. It is seen that as the intensity is decreased, the peak frequency is up-shifted and becomes narrower, achieving the single-crystalline-peak position at 522.5 cm^{-1} with 0.65 kW/cm^2. The peak position and width are plotted in Fig. 10 as a function of the intensity. The width at 0.65 kW/cm^2 is 15 cm^{-1}, that is, about 10 cm^{-1} wider than the single-crystalline-peak width. These results are reproducible, and after the spectrum at 0.65 kW/cm^2 was taken, the same previously mentioned down shift and widening will come back at high irradiation levels. Furthermore, the same behavior has been observed at liquid-nitrogen temperature.

All of the facts mentioned in this section lead us to suggest that the amorphous material transformations under the influence of cw laser irradiation are not due to laser heating. In the next sections we shall give additional explanations to the observed phenomena.

III. DISCUSSION

Our results lead us to propose that the laser radiation pumps the atoms inside the irradiated volume between different metastable states having different degrees of disorder. The pumping mechanism is mainly athermal. For high powers some heating may take place, but the main mechanism is still athermal. Through the evolution process of the system from the amorphous state towards the crystalline state, a distribution of atomic clusters undergoes several changes until the minimum size for microcrystalline material is reached above the threshold power for sufficient irradiation time. In order to clarify these predictions we divide our discussion into four subsections.

TABLE I. The behavior of the amorphous material under CW laser irradiation in the four power ranges as seen by the changes in the Raman spectra with the characteristic times t_1-t_4.

Name	Irradiation level (kW/cm^2)	Behavior of the Raman spectrum	Characteristic time
Low	$I<4.22$	Quasiperiodic changes in TO peak position, width, and shape.	t_1—the average quasiperiod $\simeq 1$ h with dependence on photons energy and flux.
Intermediate	$4.22 \leq I < 4.35$	Appearance and disappearance of a small crystalline peak.	t_2—the average quasiperiod $\simeq 0.5$ h.
Just before threshold	$4.35 \simeq I < 4.68$	Same behavior as before for some time and after that a saturation achieved.	t_3—the time at which the oscillations stopped and a saturation achieved ($t_3 \simeq 1.5$ h approaches zero at 4.68 kW/cm^2).
Close to and above threshold	$I>4.68$	A rapid increase of the crystalline peak until final polycrystalline state is achieved after enough time of irradiation while the amorphous part decreases and transforms into a tail with decreasing area.	t_4—the time at which the crystalline peak approaches its saturation—it depends strongly on the laser intensities and goes to zero for high enough intensities.

A. Mechanisms of laser pumping

The injected photons have an energy of about 0.7 eV above the absorption edge. The estimated concentration of photoelectrons is about 10^{15} cm^{-3}, if one takes a relaxation time $\tau \sim 10^{-12}$ s.[9-11] Therefore, the energy transfer from the hot electrons to the lattice is negligible at these power levels, that is, no appreciable heating takes place. The presented results support this conclusion as follows.

(1) The Stokes to anti-Stokes ratio does not reveal any appreciable heating for power levels less than the threshold. The maximum temperature estimated is about 350 K. For intensities higher than the threshold ($\sim$9.75 kW/cm^2), and after a very long time of irradiation, the maximum temperature estimated from the Stokes to anti-Stokes ratio was about 500 K. These results agree with the theoretical[20] and experimental results[18] reported so far by different authors on the cw laser heating of silicon.

(2) The changes in Raman TO peak position and width for low power levels are about 15 and 30 cm^{-1}, respectively. If heating would be involved, this would correspond a change of temperature from 300 to 800 K, which is beyond the crystallization temperatures of *a*-Si:H.

(3) In the early stages of the formation of submicrocrystalline clusters (the appearance of the crystalline peak) the system is reversible. That is, if the light was blocked off for enough time, the material relaxed back to its initial, disordered, state. As shown in Fig. 11, the material was exposed to a laser intensity of 4.74 kW/cm^2 for about half an hour so that it is just below the final saturation state. The small crystalline peak appears at this power level without oscillations as shown in Fig. 5. After that, the light was blocked off for 3 h and the Raman spectrum was taken again with a low intensity of 2.6 kW/cm^2, which cannot induce any crystallization. One can see that the small crystalline peak disappeared. This reversibility effect occurs whenever the final saturation state is not reached. If crystallization was to occur due to heating, this reversibility effect would not be observed because the crystalline state is thermodynamically more stable.

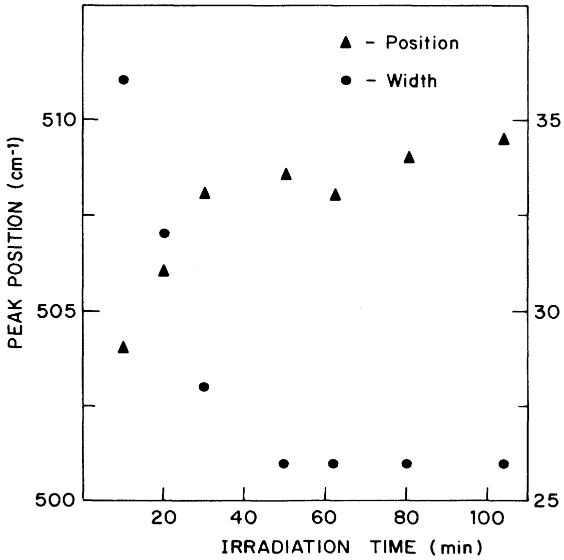

FIG. 8. The crystalline-peak position and width against the irradiation time for irradiation level above threshold $I = 5.85$ kW/cm^2.

(4) The threshold intensity measured both at 300 and 77 K is the same. If laser heating would be responsible for the existence of a threshold intensity, then a decrease of 220 K in the substrate temperature would require a higher value of the threshold power.

Nevertheless, these reasons do not give a final answer to whether the cw laser annealing is either a thermal or an athermal process. They simply provide support for the possibility of nonthermal annealing. The question that arises is what is the alternative mechanism which could cause atoms to rearrange themselves in a more ordered configuration. In cw lasers with intensities used in our experiments, the free-carrier concentration (10^{15}

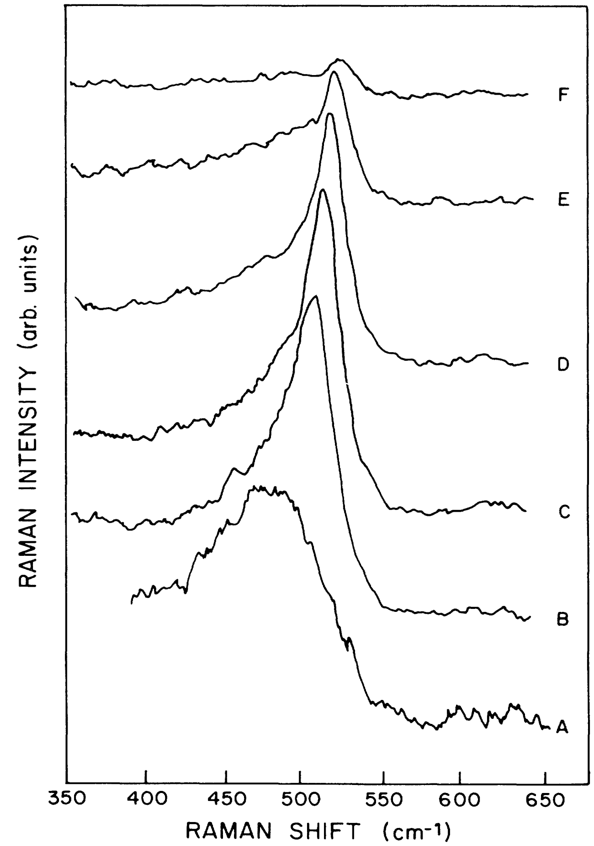

FIG. 9. Raman spectra taken with different laser intensities after the sample was irradiated long enough with intensity above threshold $I = 5.85$ kW/cm^2 so that the final crystalline state was reached as in (b). In (a), the amorphous spectrum is taken initially with $I = 2.6$ kW/cm^2 in order to ascertain that the initial state is amorphous and for comparison. (c) Measured after the final crystalline state was achieved; $I = 4.55$ kW/cm^2. (d) The same as (c), but $I = 3.25$ kW/cm^2. (e) The same as (d), but $I = 1.95$ kW/cm^2, and (f) the same as (e), but with $I = 0.65$ kW/cm^2. One observes the up-shift and narrowing of the peak when measured with low intensities attaining the single-crystalline-peak position in (f).

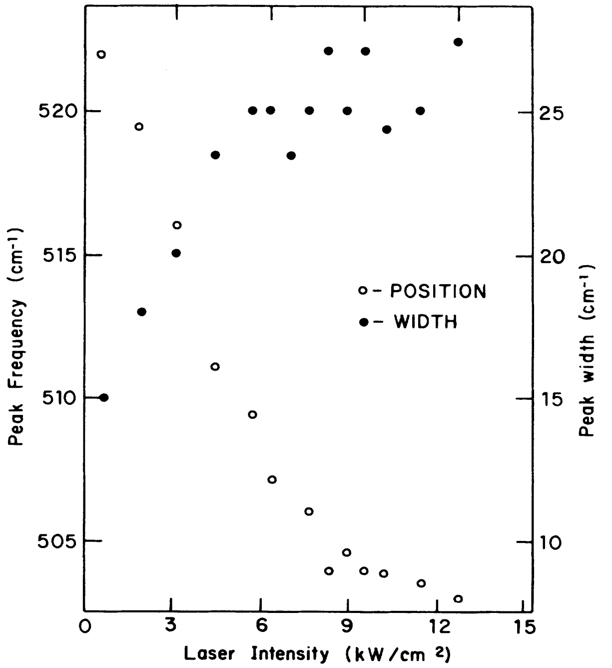

FIG. 10. The crystalline-peak position and width against the laser intensity at which the spectrum is measured after the final crystalline state was achieved. Taken from spectra as in Fig. 9.

cm^{-3}) is much less than the critical concentration for complete screening, and some ordering may be achieved by sufficiently weakening the covalent bond-bending forces so that the atoms will rearrange themselves in response to the stresses imposed by the surrounding nonirradiated material.

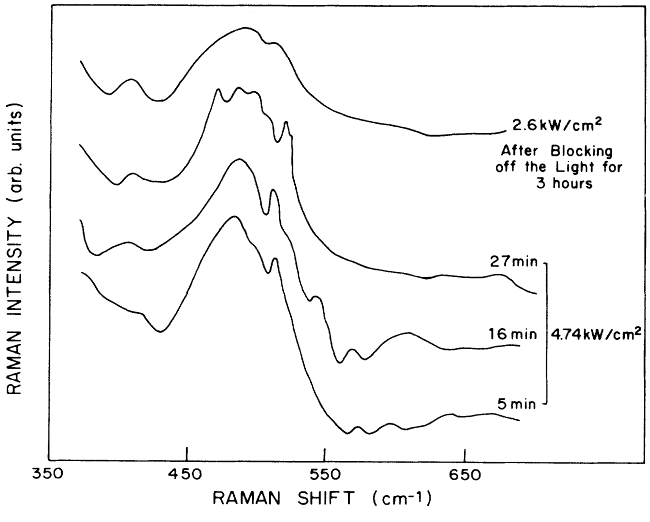

FIG. 11. Three Raman spectra taken with $I = 4.74$ kW/cm^2 during irradiation of half an hour. The small crystalline peak increases gradually, but does not reach its saturation value yet. The fourth spectrum taken with $I = 2.6$ kW/cm^2 after the light was blocked off for about 3 h. One can see that the crystalline peak disappears. This is the reversibility effect, which exists whenever the system is before the final saturation state.

We proposed a microscopic mechanism recently.[8-10] It consists in the generation of hot mobile electrons by the laser for a time of $\tau_R \simeq 10^{-12}$ s. We propose the existence of short-lived large-energy fluctuations[12,13] (SLEF's) of atoms inside the solid. When these fluctuating atoms jump from one metastable state to another, they stretch and cut off bonds with neighbors. This leads to the formation of transient local electronic levels of lifetime $\Delta\tau_e$ of the same order of magnitude as the fluctuation lifetime $\Delta\tau \simeq 10^{-13}-10^{-12}$ s. The trapped electrons release their energy in the immediate vicinity of the hopping particles and increase the probability of the transition between the two metastable states through the energy barrier. These transitions of the atoms, assisted by the interaction with the hot mobile electrons, change the material structure and cause the changes in the Raman width and position of the absorption edge and other related parameters.[21,22] This is the sense of "chemical pumping." The material is pumped athermally from one metastable state to another more ordered one with a pumping rate, which depends on the incident photons flux, and other characteristic parameters of the material (electronic effective mass and charge, relaxation times, quantum efficiency, etc.). The pumping rate determines both the final saturation state achieved after sufficient irradiation time and the way the system evolves to reach this state.

The estimated characteristic time of the atomic transitions was shown[9,10] to play a crucial role in determining the quasiperiod of the oscillations in the case of powers less than the threshold. When crystallization occurs, however, the calculation does not hold, because this is a cooperative phenomenon where the interaction between clusters of different sizes takes place under the influence of laser pumping. We believe that the approach to this problem should include the physics of clusters via percolation calculations.

B. Nature of the metastable states in *a*-Si and their relation to Raman scattering

The structure of amorphous materials has been studied extensively by means of different structural models. One can divide these studies into two main categories. The first is a continuous random network (CRN) as was proposed by Zachariasen[23] and Polk.[24] The second deals with submicrocrystalline (SMC) structures of the amorphous materials.[25-29] Within the two categories, the structure of covalent amorphous semiconductors was shown to exhibit various possible metastable states, which are in our opinion strongly related to the changes observed in the Raman spectra.[30-32]

In CRN there exist different metastable states. Here we mention the most important for our purpose, which could be related to the quasiperiodic changes in the Raman spectra.

(1) The tetrahedral angle distortions: The rms value of the bond angle, $\langle \Delta\theta^2 \rangle^{1/2}$, plays an important role in estimating the degree of disorder.[22,33,34] The values of the tetrahedral angle distortions are model dependent and are in the range[35] $\langle \Delta\theta^2 \rangle^{1/2} \sim 7°-15°$. Therefore, changes in the Raman width could be related to changes in $\langle \Delta\theta^2 \rangle^{1/2}$

induced by laser irradiation in the low-powers region.

(2) Bond-length distortions: The distortions in the bond angle are accompanied with bond-length deviations.[36] The relative rms values $\langle \Delta r^2 \rangle^{1/2}/r$ are also model dependent and are in the range 0.8–4.5 %. These distortions influence the vibrational frequencies as is expected at least from the harmonic approximation.

(3) Topological structure: Fivefold, sixfold, and sevenfold rings are likely to exist in CRN model. In the case of fivefold rings, the statistics is between 0.38 and 0.48 rings per atom, while in the case of sixfold rings it is between 0.85 and 1.07 rings per atom. It was shown by Meek[36] that the shape of the TO peak is strongly influenced both by topology and by bond-angle distribution of the network. A distribution of even-membered rings would result in a lower peak frequency than for the odd-membered ones, and when the structure contains both even- and odd-membered rings, the TO peak would exhibit splitting, such as appears frequently in our spectra (Fig. 1). The recent calculations of Beeman *et al.*[34] support this last prediction.

Within the SMC structure model the amorphous material is composed of clusters of atoms having a size less than 30 Å—the critical size at which a microcrystalline Si in the diamond structure becomes thermodynamically unstable with respect to the amorphous state.[37,38] The structure of these small clusters could be different depending on their size and the preparation conditions. Among these structures we mention the following which are related in our opinion to the changes in Raman spectrum.

(i) Clusters of wurtzitelike structure: These clusters, having a size of about 14 Å, have been frequently reported to occur in *a*-Si from electron-microscopy measurements.[25–28] The Raman spectra of *a*-Si composed of wurtzite clusters of size $\simeq 14$ Å have been calculated by Alben *et al.*[39] The TO peak frequency is at ~ 500 cm^{-1} and its width is ~ 20 cm^{-1}. The splitting, which we observe in the second spectrum of Fig. 1, which shows two peaks at 474 and 488 cm^{-1} and the third spectrum at 465 and 485 cm^{-1}, could also be due to the existence of wurtzite clusters of size less than 30 Å in an amorphous matrix or created by the laser-induced nucleation. Such small clusters could also contribute to the scattered intensity around 500 cm^{-1}, broadening and shifting the amorphous peak. This model is consistent with the ellipsometry experiments, which measure the initial stage of the growth of microcrystalline Si.[40]

(ii) Clusters in the Si III phase structure: The high-pressure phase called Si III has a bcc structure of eight atoms per unit cell. The Raman spectrum of the Si III phase[41] consists of five peaks at 478, 433, 403, 397, and 181 cm^{-1} as computed by Kobliska *et al.*[42] Their reported spectra show peaks at 463, 433, 416, and 384 cm^{-1}. There are no reports in the literature that clusters of Si III could exist in an amorphous matrix. Here we propose this possibility due to the similarity of this phase with the amorphous phase both from a structural point of view and from the similarity of its highest two Raman peaks at 478 and 433 cm^{-1} to the TO peak at ~ 480 cm^{-1} and the proposed surface mode at 430 cm^{-1} in *a*-Si.

(iii) Other typical examples of structures of small clusters containing 10–30 atoms are the icosahedron and the pentagonal dodecahedron as suggested by Grigorivici.[43] The recent calculations by Barojas and Levesque[44] have shown the growth sequence of 10–32 silicon-atom clusters. Up to $N=11$ atoms the clusters are unstable and the tetrahedral bonding starts to build up, for the 15-atom cluster. The binding energy per atom and the coordination number of the clusters grows with the cluster size exhibiting some oscillations and saturation after a certain cluster size of about $N=20$ atoms. Internal transformations between the different metastable structures of small clusters could be induced by laser- or electron-beam irradiations as was already confirmed for gold particles.[45] Finally, the calculations of the diffraction and radial distribution functions by Weinstein and Davis[26] and their comparison to experiments suggest that a statistical microcrystallite model should reveal quite acceptable agreement between theory and experiment. Thus one can see that the metastable states could be justified either by the CRN or the SMC models.

C. Mechanisms for structural oscillations

Transitions of the atoms inside the irradiated volume between the various metastable states occur due to photon absorption in the amorphous matrix in the low-power region, as mentioned in the last section. At these power levels, the Raman spectrum is still that of an amorphous material as seen in Fig. 1. Therefore, the transitions are between these metastable states characteristic of the material. The mechanism of the laser pumping was explained in Sec. III A. Here we give an explanation for the quasiperiodic oscillations both at low power levels, where the material still has an amorphous peak, and at intermediate power levels, where a small crystalline peak exhibits the oscillatory behavior up to powers close to the threshold and above it, where a polycrystalline material is formed.

1. In the low-intensity range

Assume that the atoms make jumps $A_j \leftrightarrow A_{j+1}$ between the different metastable states $A_1, A_2, \ldots, A_j, A_{j+1}, \ldots, A_n$, as described in Sec. III B. These transitions of single atoms or small groups of atoms are due to the pumping via a nonthermal mechanism described in Sec. III A. For more details the reader is referred to our previous paper,[9,10] where we estimated the quasiperiod and its dependence on the photon energy and flux. The question now is what causes the observed oscillatory changes in the Raman spectra and the transmittance. Here we introduce the effect of the surrounding nonirradiated material. It provides a restoring force, which opposes the forward structural transitions and promotes the backward transitions. The metastable states, as explained, are of different degrees of disorder, a fact which manifests itself in changes in the Raman TO peak position and width. These were correlated with the energy gap[22] and therefore the transmittance and other parameters of the material are related to each other. The quasiperiod increases and the amplitudes of oscillation decreases with the irradiation time due to an increase of the fraction of the material coming into the final, less disordered state A_n, different from the initial one A_1. These oscillations are similar to the kinetic oscillations in various rate processes known for a long time.[46,47]

The other possible mechanism for the oscillatory behavior is based on the laser-induced formation of submicrocrystalline clusters of size up to 30 Å at these pumping rates. Whether the material is a CRN or SMC structure, the injected photons flux pumps the material through the different metastable states up to the formation of submicrocrystalline clusters. When the size of these clusters is about 14 Å their preferred structure is wurtzite. They could contribute to the scattered Raman intensity around 500 cm^{-1}, which results in the broadening and shift of the TO peak. When the size of these clusters approaches 30 Å, minimum surface energy prefers a diamondlike structure and the transformation of wurtzite to diamond occurs. However, diamondlike clusters of this size are thermodynamically unstable and could transform back to wurtzite under the high pressure of the surrounding. Furthermore, the melting temperature of small clusters is very small compared to that of the bulk.[48] Therefore a slight heating will influence their structure strongly. The lattice expansion will reach the critical one estimated by Veprek *et al.*[38] $\Delta d/d_0 \simeq 0.01-0.02$ and they become unstable resulting in the backward critical transformation of diamond to wurtzite.

After sufficient irradiation time, a part of the opposing pressure from the surrounding nonirradiated material is released and the fraction of the clusters of diamond type increases causing the quasiperiod to increase, and a saturation behavior after a very long time of irradiation. Actually we were led to this interpretation, because we can go a step further and consider the appearance and disappearance of the small crystalline peak at intermediate irradiation levels.

2. *In the intermediate-intensity range*

Here the pumping rate drives the material to nucleate in microcrystalline clusters of maximum size slightly larger than the critical size of 30 Å. A small crystalline peak appears and disappears quasiperiodically. The maximum size must be only slightly larger than 30 Å in order for the reverse transition to occur. The fact that this intermediate-intensity region is a very small region between 4.22 and 4.35 $\mathrm{kW/cm^2}$ in our case indicates that the maximum size of the microcrystalline clusters up to which the oscillatory structural instabilities occur would be close to the critical size of 30 Å. The small-crystalline-peak position is at about 510 cm^{-1}, which corresponds to a microcrystalline size of 35 Å, when compared to the experimental results of Iqbal and Veprek[31] or to the theoretical calculations of Richter *et al.*[49] The transformation of wurtzite to diamond seems to us the most probable transformation. The phenomenon seems quite general in amorphous materials and different transformations may occur in different materials. For instance, in the chalcogenide glass $\mathrm{As_2Se_3}$ we have found a transformation between two metastable clusters:[8] a small cluster with internal crystalline topology, but with a large surface area that has a large number of reconstructed bonds, and a stable cluster, which is a microcrystallite, that exhibits the crystalline Raman peaks.

3. *Higher irradiation levels*

When the pumping rate is so high, clusters of size above 35 Å formed. They are now far from the critical instability size and can grow and coalesce to form large clusters attaining a microcrystallite size after sufficient irradiation time. However, the oscillatory behavior is observed in the early stages of irradiation. The small peak appears and disappears for some time t_3 ($t_3 \simeq 100$ min in Fig. 3) and after that the peak grows up to its saturation value which corresponds to the pumping rate present. The effect of the pressure applied by the surrounding and the slight heating are very small compared to the case where the cluster's size is in the neighborhood of the critical size. After a certain power level, the time t_3 vanishes, that is, no more oscillations occur. The crystalline peak grows very rapidly, reaching its saturation value after a time t_4 which goes to zero as the threshold intensity is reached.

D. The final polycrystalline state

After sufficient irradiation time with laser intensities above the threshold, the amorphous part of the TO peak vanishes, while the crystalline peak becomes very sharp. Its position and width have been shown in Fig. 9 to depend on the power at which the spectrum is measured. When we irradiated the sample with intensity well above threshold ($\simeq 13$ $\mathrm{kW/cm^2}$) and for sufficient time, the peak position and width saturated at 503 and 28 cm^{-1}, respectively. By taking the spectrum with lower intensities on the same irradiated spot, we observe that the peak is up-shifted and becomes narrower. It reaches the single-crystalline-peak frequency of 522 cm^{-1} at an intensity of 0.65 $\mathrm{kW/cm^2}$. Its width, however, is still higher than the expected width of single-crystalline silicon. This latter fact is probably due to residual internal strains. The down shift due to increasing the power could not be a result of laser heating, because this would correspond to a temperature of about 1100 K, which is far from the measured Stokes to anti-Stokes ratio. Furthermore, we obtained the same frequency shift at low temperature of 77 K.

We should note here that Nakashima *et al.*[17] obtained a down shift of $\simeq 5$ cm^{-1}, which was attributed to internal residual strains. Their proposition was based on the fact that when they thermally treated the sample, this strain was released and the down shift was canceled. Our results show no down shift when the Raman spectrum is measured with low intensities (Fig. 9). We have pointed out that the Raman shift and width are inversely correlated to the size of the microcrystallites. Then two explanations follow of the observations illustrated by Fig. 9.

(1) The Gaussian distribution of the laser beam has different heights for the different output laser intensities. One expects that in the interior of the irradiated spot

there is a more ordered material than in the periphery. Therefore, when the measurement was taken with a high intensity, some scattering from the periphery was detected, which contributed to the scattered intensity at lower frequencies causing the down shift and the broadening of the overall measured peak. On the other hand, with lower intensities only scattering from the more ordered internal regions is detected and the peak exhibits upshifting and narrowing. This point could be cleared further by performing a double-beam experiment with a high-power laser used to irradiate a larger spot and a probe beam with different wavelength to scan the area.

(2) The depth of the annealed layer is of the order of the penetration depth. Therefore, higher power will cause a contribution to the scattered intensity from less annealed regions deeper than the penetration depth.

IV. CONCLUSIONS

Structural instabilities of amorphous materials driven by cw lasers were investigated by means of Raman spectroscopy as a function of the irradiation time for different irradiation levels. In the case of *a*-Si:H these instabilities are expressed by quasiperiodic changes in the Stokes TO Raman peak against the irradiation time. The temporal evolution of the system from the amorphous disordered state towards the ordered crystalline state could be divided into four stages with respect to the irradiation level.

(1) At low irradiation levels the Raman TO peak positions, width, and shape undergo quasiperiodic oscillations. The average quasiperiod depends on the photons energy and flux. It decreases for higher irradiation levels and increases for higher photon energies.

(2) For intermediate irradiation levels a small crystalline peak appears and disappears quasiperiodically. Its position, width, and its ratio to the amorphous part indicate that it is due to existence of submicrocrystalline clusters of size up to 30 Å. That is the critical size for which a diamond structure becomes unstable with respect to the amorphous phase.

(3) For higher irradiation levels just below threshold, the small crystalline peak appears and disappears for some time interval which depends on the power level. After that it increases, attaining its saturation height after sufficient irradiation time. As long as the peak does not reach its saturation height, the system is reversible. That is, if there is no further input of the radiation energy, the system can relax back to its initial amorphous state after a time interval, which depends on the amount of energy injected into the irradiated volume.

(4) For irradiation levels above a threshold, the crystalline peak grows rapidly without any oscillatory behavior, reaching its saturation value after a time interval, which decreases significantly with increasing irradiation level.

The final polycrystalline state shows a peak position and width, which depends on the intensity at which the spectrum is measured. We found that the peak position approaches that of single-crystalline silicon with low-intensity power of 0.65 kW/cm^2.

Our explanations are based on the proposition that the radiation field pumps the illuminated material mainly athermally between different metastable states of the material at low irradiation levels. The nature of these metastable states and their relation to the changes in the Raman spectra were considered both within the framework of the CRN and SMC models. The SMC model seems to us the most reasonable for these irradiation-induced metastable states, since, based on it, the behavior at low intensity, and the explanations for the appearance and disappearance of the crystalline peak at intermediate powers, are straightforward. Within this approach the transformation of wurtzite to diamond seems to us the most probable intermediate process. At low irradiation levels, the forward transformation takes place due to the laser pumping. The backward transformation occurs due to the influence of a restoring force applied by the surrounding, nonirradiated material, and due to some heating, which could influence strongly small metastable clusters of the diamond type. These are a size near the critical size of the transition from "amorphous" to microcrystalline states and, as Phillips[50] wrote, "As the material hesitates on the knife edge between metastable phases, clamping due to strain produces oscillations." When the cluster's size is above the critical size of instability ($\simeq$30 Å) it grows, attaining microcrystallite size at higher irradiation levels and for enough time of irradiation.

These observations are, in our opinion, of importance toward a full understanding of the microstructure of amorphous materials. Correlation of the oscillations we have observed in these measurements with other types of experiments, such as electron diffraction, electron-spin resonance, photoconductivity, and photoluminescence, should yield much information on the nature of the metastable states in an amorphous matrix. It would also be of interest to follow the Raman-spectra oscillations at different higher temperatures inside a furnace. This will yield more information on the kinetics of crystallization and help to distinguish between thermal and athermal annealing mechanisms.

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