PHYSICAL REVIEW A VOLUME 7, NUMBER 2 FEBRUARY 1973

Etched Laser Filament Tracks in Glasses and Polymers

E. E. Uzgiris and R. L. Fleischer
General Electric Research and Development Center, Schenectady, New York 12301

(Received 11 September 1972)

Self-focused laser filament tracks in various glasses and polymers were chemically etched to produce conical voids in a manner similar to the etching of charged-particle tracks in these same materials. The etched filament cones were related to the sharpest Cf^{252} fission-fragment cones by roughly the same ratio of cone angle for all the different materials tested. One interpretation of this observation is that the same damage mechanism operative in the charged-particle-track formation, ionization, is also operative in the formation of filament tracks. The sharper cone angle indicates a higher damage intensity for filament formation than for particle-track formation consistent with the theoretical estimates for energy deposition in the two processes. Annealing studies of the filament tracks show that filament-track fading occurs at much higher temperatures than required for the fading of fission tracks for several of the materials. This is qualitatively in agreement with the observation that higher-energy deposition rates from highly ionizing particles result in tracks which require much higher temperatures for track fading than for tracks formed by less-ionizing particles. Etching reveals an important difference of the filament tracks from charged-particle tracks: The surface of the etched cones is not smooth, but varies periodically in diameter along the track (approximately with cylindrical symmetry). Examination of unetched filament tracks with high magnification and reflected light reveals that the filaments contain a rapidly modulated damage component along the length of the track in all the materials tested. The observed periodicity is quite uniform and seems to be characteristic of the material irradiated. The characteristic period length in fused silica, for example, was measured to be 1.5 μ. This small-scale periodicity in solids seems to be similar to the periodicity observed by Brewer and Townes for filaments formed in liquids.

INTRODUCTION

The formation of filamentary tracks in transparent media by the passage of an intense laser beam has been observed for a number of years.[1] A variety of nonlinear mechanisms can become operative at high light intensity and cause the laser beam to collapse to a small diameter of a few wavelengths. This self-focusing effect is reasonably well understood, and in optical glass a theory based on the electrostrictive effect has been given.[2] In solid transparent dielectrics the very high light intensities which result from self-focusing lead very often to the formation of damage tracks such as have been described by a number of workers.[3] A recent careful study of filamentary damage tracks in various glasses and polymers is described by Steinberg.[4] In that study and in the previous reports, the damage trails were observed visually. In the present work we use the technique of chemical etching to further characterize the filamentary tracks in various materials.

In the presence of an intense light field, several processes may play a role in the formation of permanently damaged regions of material. These include avalanche ionization, stimulated Brillouin scattering, and multiphoton absorption.[2] An explicit identification of the damage mechanism in filamentary tracks has not been made. Recently, Bloembergen[5] has suggested that avalanche ionization limits the maximum power flux density and therefore the minimum diameter of self-focused filaments in liquids and solids. If ionization is indeed important in laser filaments, an interesting analogy can be made between laser damage tracks and the damage tracks observed in solid dielectrics after passage of energetic charged particles. In particular, since the etching of charged-particle tracks has been so successful in identifying and characterizing such particle tracks, it suggests that etching may be a fruitful technique in the study of laser filamentary tracks as well.

We have successfully etched filamentary laser tracks in a variety of glasses and one polymer, polymethyl methacrylate. Cone-shaped voids result from etching. The cone angles were observed to be constant along the track, except for a small periodic variation, and were characteristic of the material. The cone angles of the filamentary tracks were correlated with the observed minimum cone angles from Cf^{252} fission-fragment tracks in the different materials. Since it is believed that ionization is the principal process in charged-particle-track formation in inorganic solids,[6] the similar behavior of filamentary track etching in different materials suggests that intense ionization processes are probably occurring inside the laser filaments. Furthermore, etched laser tracks may be useful in applications requiring long tapered holes of small diameter and constant taper. As an example, a current application of small diameter holes obtained by the etching of fission-fragment tracks is in submicroscopic particle detection by the resistive-pulse technique.[7] Last, we describe

TABLE I. Type of damage and etching conditions for the different materials.

Material	Type of damage	Etching conditions
Stacked microscope slides	Surface damage only	48% HF, 10 min
Fused silica (nonoptical grade)	Gross fractures, no small-scale filaments	48% HF, 10 min
Fused silica (optical grade)	Numerous filamentary tracks	48% HF, 10 min
Phosphate glass	Few filamentary tracks	48% HF, 10 min
Soda lime glass	Numerous filaments and multiple filaments	48% HF, 10 min
Polycarbonate (Lexan)	Burning across beam cross section, no filaments formed	6.25N NaOH
Polymethyl methacrylate (Plexiglas)	Numerous filamentary tracks	Saturated $KMnO_4$ at 85 °C for up to 10 h

the observation of a rapid periodic variation of visible damage along the length of the filamentary tracks formed in these experiments.

IRRADIATION

The output of a Korad K-1Q Q-switched ruby laser was focused into the various samples by a 7-cm focal-length lens. The entrance face of the samples was maintained well away from the focal point in order to prevent surface sparking. The laser used did not oscillate in a single axial mode and therefore the beam shape was not expected to be Gaussian. As a consequence, in addition to single filaments often multiple filaments were also formed after a laser pulse. Therefore, exact quantitative data on power loss in a filament are not possible from the data below. Most laser shots were at a peak power level of 10 MW in 20 nsec. To allow intercomparison of results, laser shots were set to this power level as far as was possible. However, for the fused-quartz experiment an ambiguity in the data recording may in fact have resulted in irradiation with an 18-MW pulse of 20-nsec length instead of the usual 10 MW. Because exact quantitative power data in the filamentary formations are not possible in these experiments, we treat those results as at equivalent power levels. Examination of the burn pattern in a plastic, Lexan, shows a fairly even laser-power distribution across the beam without hot spots.

TRACK-ETCHING RESULTS

Various irradiation experiments are summarized in Table I. Successful track formation in a given material was followed by chemical-etching procedures as indicated in the table. The etchants used were identical to those used for fission-fragment tracks. The most difficult material to etch, both for fission fragments and for laser filaments, was polymethyl methacrylate. The small resulting cone angle and the accompanying surface discoloration due to the etchant $KMnO_4$ made observation of the tracks difficult, and the long etching times required made this material tedious to study. The etching of the inorganic glasses was, however, quite straightforward.

Briefly, the etchant dissolves material along the damage trail more rapidly than along undamaged regions. As a result, after the etch a conical void is produced. The observed cone angle θ, defined as the angle between the axis of symmetry and the cone surface, is given by $\arcsin(V_g/V_t)$, where V_g is the general attack rate and V_t is the attack rate along the track.[8] For the same material and the same etchant, the cone angle has been shown to decrease with increasing ionization density by a charged particle.[9] Indeed, for energetic particles the cone angle changes along the length of the track as the particle slows down and stops, being larger at the entrance and decreasing to a minimum value near the stopping point of the track (as has been observed for heavy-ion-irradiation experiments).[9]

For the laser filaments we would expect a nearly constant energy loss per unit length along a short (1 mm or shorter) section of the track, and therefore a nearly constant cone angle. This is indeed observed in our experiments. The fused silica in Fig. 1 shows an etched cone which has a well-defined cone angle. However, a modulation of the damage along the track is evident, as is indicated and amplified by the etching. This effect will be described in more detail below. Hole boring by a long etch of soda lime glass is illustrated by Fig. 2. Here the etchant has broken through from both sides to form a clearly visible hole in this head-

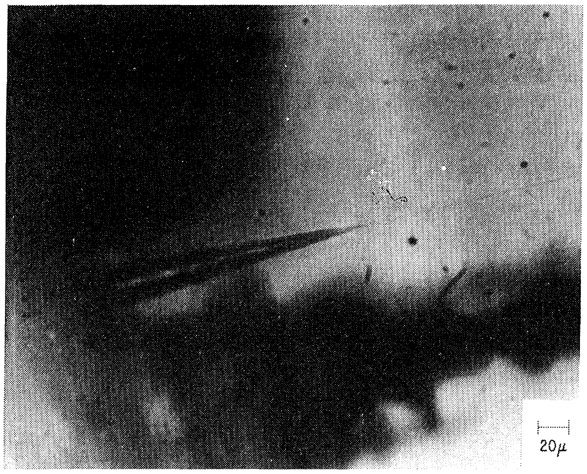

FIG. 1. Filamentary track in fused silica after etching with 48% HF for 20 min. A portion of the original track has etched into a conical shape; the remainder is unetched.

on view of the track. The results indicate that it is possible to produce holes of nearly constant taper by this etching technique. The cone angle depends on the choice of material and (presumably) on the etchant used. In principle, the minimum hole size could be that of the filament track itself from $\frac{1}{2}$ to 1 μ in diameter.

The geometrical results of etching of laser filament tracks are summarized in Table II and compared to the etching geometry of fission-fragment tracks in these same materials using the identical etchants. We note that the cone-angle relationship between filament tracks and the fission tracks is nearly identical for the different materials. Fused quartz may be an exception from the general trend exhibited by the other materials or may merely reflect the variation of the laser pulse reproducibility mentioned above.

ANNEALING OF TRACKS

By exposing fission-fragment irradiated materials to a high enough temperature for an appropriate duration of time it is possible to cause the tracks to fade partially or to disappear altogether. When tracks have partially faded, etching produces larger cone angles; and when they have fully faded, no preferential etching takes place. Also, it has been found that the annealing character changes with the degree of damage caused by the charged particle. Tracks from more highly ionizing particles require higher temperature and longer exposure times to fade to the same degree than do those from less-ionizing particles.[10,11]

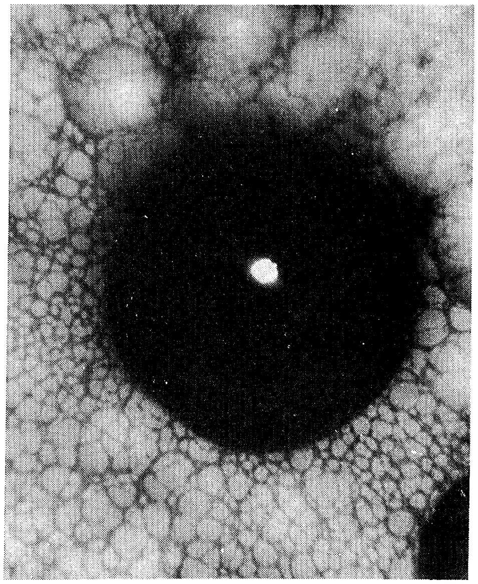

FIG. 2. End-on view of a tapered etched laser track through a 0.13-cm soda lime glass plate etched for 1.94 $\times 10^5$ sec in 5.7% HF. The mouth diameter is 510 μ; the constriction diameter is 39 μ.

Table III presents annealing results for three materials and compares these data with known fission-track results. For both fused quartz and soda lime glass, filamentary tracks are retained to considerably higher temperatures than are fission tracks. In the plastic, filament tracks persist all the way to the softening point of the material, as was the case for fission-fragment tracks in Lexan,[8] a slightly less sensitive polymer.

After 1 h at 1300 °C the fused-quartz samples were etched again. Many of the tracks failed to etch further, some etched with a much larger cone angle, and some persisted to etch through but in a

TABLE II. Comparison of cone angles for etched tracks in laser-irradiated and Cf^{252}-fission-fragment-irradiated materials.

Material	Minimum filament cone angle, θ_f	Minimum fission-fragment cone angle, θ_{ff}	θ_f/θ_{ff}
Polymethyl methacrylate	0.75°	1.5°	0.5
Phosphate glass	1.4°	3.3°	0.42
Fused quartz	6.0°	19°	0.32
Soda lime glass	15°	30°	0.5

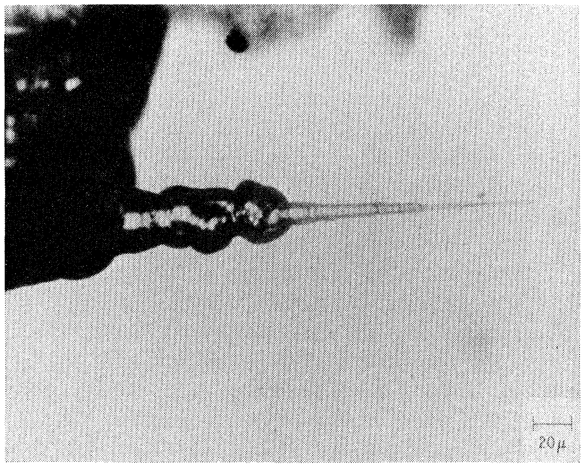

FIG. 3. View of track etched in fused silica after the laser-irradiated silica glass was subjected to 1300 °C for 1 h.

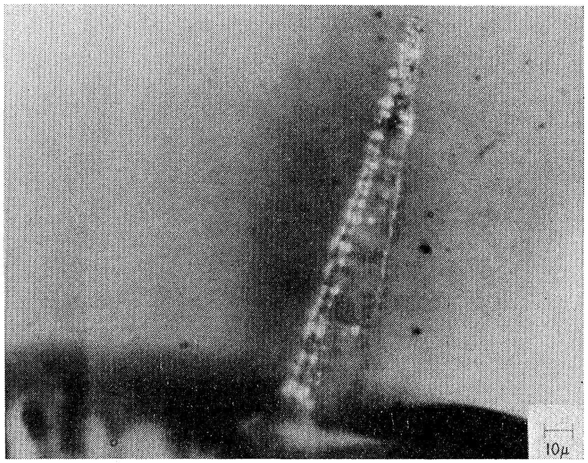

FIG. 4. Replica of etched filament track in fused silica. Track was etched for 20 min in 48% HF.

nonuniform channeling way. The hypodermic-needle shape in Fig. 3 shows the latter behavior. Evidently the annealing process partially repairs damage intermittently along the track, causing a temporary stopping of the track etching. With continuing etching this repaired region is broken through by the general chemical attack, whereupon preferential etching proceeds to the next repaired point along the track. The etched tracks which show a larger cone angle indicate that in those cases the annealing has taken place on a finer scale. The blocked tracks, on the other hand, are indicative that in those cases rather extensive annealing of the damage in a particular region had taken place.

DAMAGE MODULATION

Although most filaments in these materials look like long uniform lines of altered material, under high magnification and with reflected light it is possible to see small-scale periodic variations along the filamentary track. The variations in reflected light along the track are the easiest to see under these conditions, but in some cases it is possible to see the track vary periodically in diameter, comparable to linked sausages on a string. The remarkable feature is the regularity of the variations and the small dimension of the periodicity—on the order of a few microns.

The chemical etching of the filaments magnifies the varying structure that can be observed microscopically. Figure 4 shows a replica of an etched track in fused silica. (Replication[12] is for the convenience of observation and is performed by letting silicone rubber flow into the conical void, allowing the rubber to cure, and then withdrawing and gold plating the resulting track replica.) It differs markedly in appearance from a charged-particle track such as that shown in Fig. 5; there are cylindrical variations of track diameter along the etched filament, whereas the surface of the charged-particle track is quite smooth. This is indicative that filamentary formation involves periodic damage modulation along the filament, at least in the cases studied here.

The regularity of the longitudinal fine-scale structure of the filaments is shown for Plexiglas and fused quartz in Fig. 6. A histogram of the intervals between successive variations in observed light intensity for the various materials shown in Fig. 7 indicates two principal observations: (a) There is remarkable regularity in the variations

TABLE III. Comparison of the effects of heating on fission tracks and laser-filament tracks.

Material	Laser filaments Partial fading	 Complete fading	Fission-fragment tracks Complete fading
Fused silica[a]	1 h at 1300 °C	3 h at 1400 °C	1 h at 700 °C
Soda lime glass[a]	2 h at 600 °C		1 h at 370 °C
Polymethyl methacrylate	>200 °C		
Polycarbonate[b]			>185 °C

[a] Fission-fragment data in R. L. Fleischer and P. B. Price, J. Appl. Phys. 34, 2903 (1963).

[b] Reference 8.

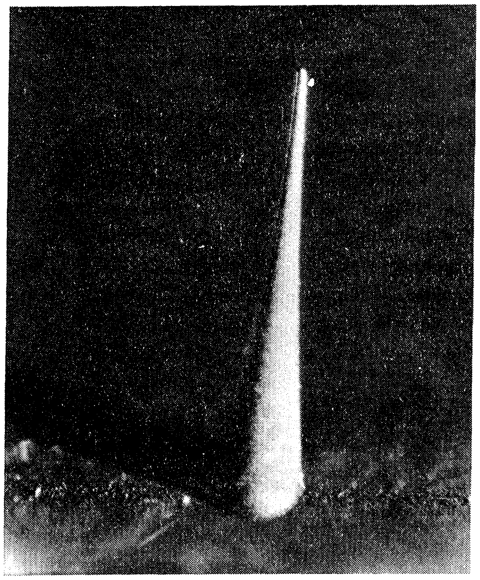

FIG. 5. Replica of a 700-μ-long etched track made in an Apollo space helmet by a cosmic-ray zinc ion. The track was etched for 196 h in 1 part 6.25*N* NaOH to 1 part ethanol (Ref. 12).

along the track; (b) the periodicity is on a very small scale. In fused quartz, for example, the average interval between successive modulated portions of the filament is 1.5 μ. The regularity, the small-scale aspect, and the fact that etched particle tracks do not show the modulation establish that the observed structure is not due to material variability but rather arises in the process of filament formation itself.

Brewer and Townes[13] have previously observed small-scale regular structure in filaments formed in liquids. The periodic structure in that case was shown to be due to the generation of strong Raman-frequency components together with the generation of standing waves with a period determined by the Raman frequency shift. The period length of the observed filament structures was 4.1 μ in CS_2 and 2.4 μ in a mixture of CS_2 and nitrobenzene. The generation of standing waves and strong stimulated Raman light shifted from the laser line by 656 cm^{-1} for CS_2 and 1344 cm^{-1} for the nitrobenzene mixture, explained well the filamentary structure.

We may conjecture that in the present case the periodicity may also arise from the generation of new frequency components which beat with the laser light. It is, however, difficult to prove without direct measurement of the spectrum within a filament because there are numerous Raman lines in these solids and it is difficult to know which

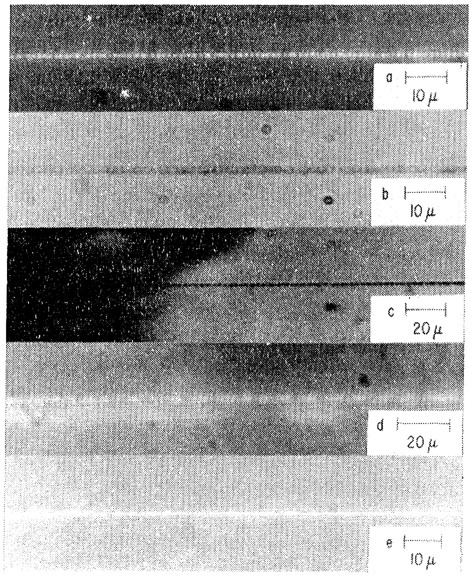

FIG. 6. Highly magnified views of small-scale structure along laser filaments. (a) and (b) Fused silica with strong modulation; (c) Plexiglas with strong modulation; (d) Plexiglas, a different track with a longer modulation spacing; (e) Plexiglas track which shows small-scale weak modulation along the length of track.

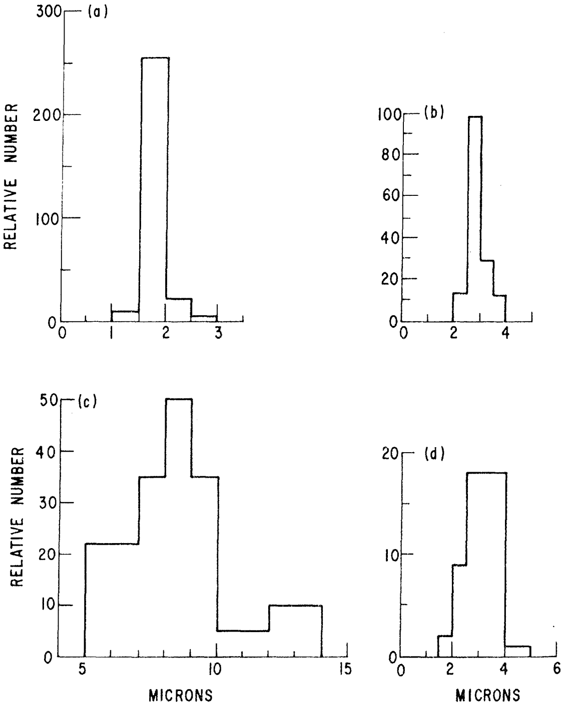

FIG. 7. Examination of the relative spacing between filamentary structural components along the filament length. (a) Fused quartz; (b) small-scale component in Plexiglas; (c) larger-scale modulation which sometimes is quite visible in Plexiglas and is also shown in Fig. 6(d); (d) soda lime glass.

Raman line will dominate in the stimulated Raman process during filament formation. Polymethyl methacrylate has a strong Raman line at 1161 cm^{-1}.[14] If we assume an index of refraction $n + \delta n$ of about 1.6 within the filament, then the spatial beat period of this light with the laser light is about 2.6 μ, in agreement with the results shown in Fig. 7(b). Light flint glasses similar to the soda lime glass used in this experiment have a strong Raman line at about 800 cm^{-1}.[15] Light of this frequency shift would result in a spatial beat period of 3.8 μ for $n + \delta n \approx 1.6$, again in agreement with the results shown in Fig. 7(d). On the other hand, fused quartz has strong Raman lines at ~ 800 and ~ 1200 cm^{-1}, but only weak lines were observed for larger Raman shifts (1400–1600 cm^{-1}).[16] There is evidently no strong Stokes line which could be directly implicated in the formation of the short-spatial-period structure of fused-quartz filaments.

The temporal modulation of the incident laser pulse must next be considered as a possible cause of the observed filament structure. Giuliano and Marburger[17] have observed discrete damage regions along a filament near the focal point when the incident pulse consisted of several modes spaced 7.5×10^8 Hz apart. The spatial distance between the discrete damage regions did not appear to be uniform, but on the average was about 500 μ. In the experiments reported here, we did not measure directly the spectral width of the laser pulses. However, the laser configuration used (consisting of two etalons for output coupling) was previously known to have a spectral width of about 0.1 Å or better. Therefore, by analogy to the results of Giuliano and Marburger, we may expect that such a spectral width could lead to temporal modulation producing spatially periodic damage regions of 60-μ-period length. In fact we see period lengths of 1.5–2 μ for fused quartz, 2.5–3.0 μ for Plexiglas, and 3–4 μ for soda lime glass. For these reasons, in addition to the strong dependence of the observed period on material, it is quite unlikely that temporal modulation of the incident pulse had caused the filament structures.

ANALOGY BETWEEN LIGHT TRACKS AND PARTICLE TRACKS

It is appropriate to ask whether the damage mechanism of coherent self-focused laser beams is a unique one or merely a variant on some other mechanism, such as is responsible for charged-particle tracks in solids. Unfortunately, we cannot test either possibility with rigor using only the presently known experimental facts. We can, however, point out qualitative similarities between filamentary tracks and particle tracks which make tenable the position that the quantitative differences which exist are the result of the greater intensity and extent of damage in the case of laser tracks.

We can intercompare three properties of laser filamentary tracks and a particular type of intense charged-particle tracks—caused by fission fragments. The properties are size, intensity of damage (measured by etching rate), and ease of repair (measured by response to heating). Laser filaments are ~ 10^{-4} cm in diameter and fission tracks ~ 10^{-6} cm,[18,19] a ratio of 10^4 in the volumes of affected material per unit length. The comparative etching-rate data given in Table II show that light tracks consist of somewhat more intensely damaged material than do fission tracks—the observed ratio of the etching rates of fission tracks relative to light tracks being given for all four detectors by 0.42 ± 0.10, a remarkably constant value. Here the cone angle θ decreases as the extent of the damage (and hence the chemical reactivity) increases.[20]

For the annealing data of Table III the results are consistent in each material with the light tracks being similar to the particle tracks, but being larger and more intense. The property of the etching rate increasing with damage intensity is extensively documented,[20] as is the fact that less-intense tracks anneal out at lower temperatures—tracks of recoil nuclei at lower temperatures than fission tracks,[10] and iron-group cosmic-ray nuclei at lower temperatures than fission tracks.[11] Laser tracks, since they are both more intense and greater in extent, would therefore be expected to persist to higher temperatures than do fission tracks. Without a successful explicit theory of annealing, it is not possible to explain quantitatively the observed magnitudes of the track annealing temperature differences between filamentary tracks and fission tracks. In particular, the damage intensity increase with ionization, as judged by the resulting etching rate, may vary greatly from one material and one etchant to another,[20] thereby complicating the quantitative interpretation of the results given in Table III. It should be noted, however, that the intermittent nature of the partially annealed light tracks (as displayed in Fig. 3) is similar to the behavior of annealed fission tracks in mica.[21]

An estimate of the minimum energy deposit needed to produce a light track is derivable from the paper by Steinberg[4] which gives an energy loss of ~ 5×10^{24} eV/cm^3 for fused silica. For comparison, a full-energy-light fission fragment deposits ~ 4×10^4 Mev/cm or 5×10^{22} eV/cm^3 in a diameter of 70 Å,[19] assuming that about half of the energy loss is within that diameter. Thus, light tracks result in greater specific energy deposit over the etched region, and also occupy a larger diameter. With fields estimated to be 10^7–10^8 V/cm, an electron, if loosened, could be accelerated to 10^3–10^4 eV within the track region, reaching peak energies comparable with those of the δ rays produced by a fission fragment.

One alternative mechanism that might be suggested is that the filament is simply a region that has been heated to a high temperature and then rapidly cooled by conduction and radiation into the adjacent unheated material. The energy deposit just quoted implies transient temperatures in excess of 10^4 °K, and the subsequent rapid cooling of the glass would be expected to quench in structures corresponding to a high-specific-volume high-temperature glass. The observed temperatures of 600 and 1300 °C for removing laser filaments from soda lime glass and silica glass are in fact very close to the temperatures required[22] to lower the glass viscosity to the $\sim 10^{13}$ poise needed for stress relief—which would allow the filaments to revert to their normal low-temperature lower-specific-volume form. By the oblique-illumination method,[23] the filament tracks are inferred to be of lower index of refraction than the surrounding glass[24] both for fused quartz and for soda lime glass, the two glasses so examined. These observations, therefore, do not exclude the above model but neither do they contradict the ionization model.

CONCLUSION

It is now most generally believed that the variation of cone angle in different materials after etching of charged-particle tracks is best explained by an ionization-damage process (or, for organic solids, an excitation plus ionization[6]). Because of the correlations between etched laser tracks and fission-fragment tracks in the different materials, it is tempting to conclude that ionization is implicated as an important damage mechanism in the propagation of self-focused laser light in a solid dielectric. Although, as noted earlier, we cannot rule out as yet unspecified alternatives, the experimental facts of which we are aware are consistent with light tracks and particle tracks being of the same type of solid-state damage, differing only in intensity.

ACKNOWLEDGMENTS

The authors are indebted to L. M. Goldman for the use of his ruby laser and help in the initial stages of the experiment. They also thank R. C. DeVries, H. R. Hart, Jr., and W. R. Giard for their experimental assistance on several occasions.

---

[1] M. Hercher, J. Opt. Soc. Am. **54**, 563 (1964); and R. Y. Chiao, E. Garmire, and C. H. Townes, Phys. Rev. Lett. **13**, 479 (1964).

[2] E. L. Kerr, Phys. Rev. A **4**, 1195 (1971).

[3] *Damage in Laser Materials*, edited by A. J. Glass and A. H. Guenther, Natl. Bur. Std. Spec. Publ. No. 341 (U. S. GPO, Washington, D. C., 1970); and Natl. Bur. Std. Spec. Publ. No. 356 (U. S. GPO, Washington, D. C., 1971).

[4] G. N. Steinberg, Phys. Rev. A **4**, 1182 (1971).

[5] N. Bloembergen, Bull. Am. Phys. Soc. 17, 677 (1972); and E. Yablonovitch and N. Bloembergen, Phys. Rev. Lett. 29, 907 (1972).

[6] R. L. Fleischer, P. B. Price, and R. W. Walker, J. Appl. Phys. **36**, 3645 (1965).

[7] R. W. DeBlois and C. P. Bean, Rev. Sci. Instrum. **41**, 909 (1970).

[8] R. L. Fleischer and P. B. Price, Science **140**, 1221 (1963).

[9] P. B. Price, R. L. Fleischer, D. D. Peterson, C. O'Ceallaigh, D. O'Sullivan, and A. Thompson, Phys. Rev. **164**, 1618 (1967).

[10] M. Maurette, Proceedings of the Clermont–Ferrand Conference on Nuclear Track Registration, 1969, p. IV-40; and Radiation Effects **5**, 15 (1970).

[11] P. B. Price, I. D. Hutcheon, D. Lal, and V. P. Perelygin, Lunar Science Institute Contribution No. 88, 1972, p. 619 (extended abstract).

[12] R. L. Fleischer, H. R. Hart, Jr., and W. R. Giard, Science **170**, 1189 (1970).

[13] R. G. Brewer and C. H. Townes, Phys. Rev. Lett. **18**, 196 (1967).

[14] J. H. Hibben, J. Chem. Phys. **5**, 706 (1937).

[15] J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold, New York, 1939), p. 412.

[16] T. G. Kujumzelis, Z. Phys. **100**, 221 (1936).

[17] C. R. Giuliano and J. H. Marburger, Phys. Rev. Lett. **27**, 905 (1971).

[18] P. B. Price and R. M. Walker, J. Appl. Phys. **33**, 3407 (1962).

[19] C. P. Bean, M. V. Doyle, and G. Entine, J. Appl. Phys. **41**, 1454 (1970).

[20] P. B. Price and R. L. Fleischer, Annu. Rev. Nucl. Sci. **21**, 295 (1971).

[21] R. L. Fleischer, P. B. Price, E. M. Symes, and D. S. Miller, Science **143**, 394 (1964).

[22] G. W. Morey, *The Properties of Glass*, 2nd ed. (Reinhold, New York, 1954).

[23] See for example F. D. Bloss, *An Introduction to the Methods of Optical Crystallography* (Holt, Reinhart, and Winston, New York, 1961), p. 52.

[24] R. C. DeVries (private communication).

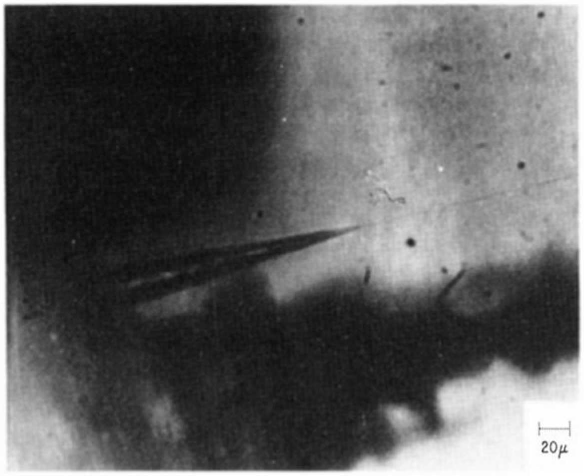

FIG. 1. Filamentary track in fused silica after etching with 48% HF for 20 min. A portion of the original track has etched into a conical shape; the remainder is unetched.

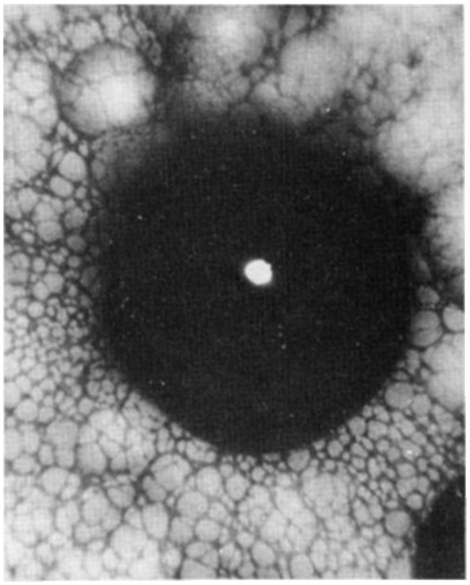

FIG. 2. End-on view of a tapered etched laser track through a 0.13-cm soda lime glass plate etched for 1.94×10^5 sec in 5.7% HF. The mouth diameter is 510 μ; the constriction diameter is 39 μ.

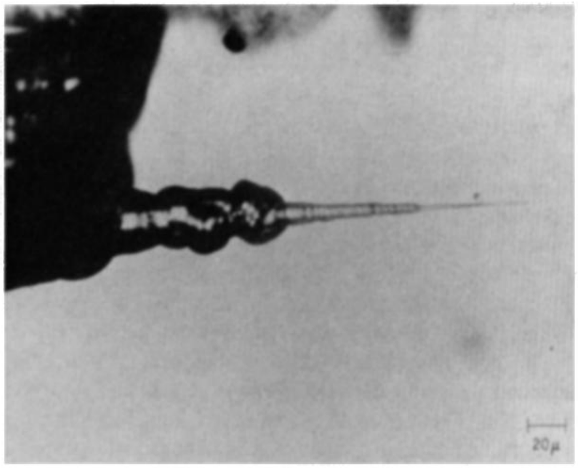

FIG. 3. View of track etched in fused silica after the laser-irradiated silica glass was subjected to 1300 °C for 1 h.

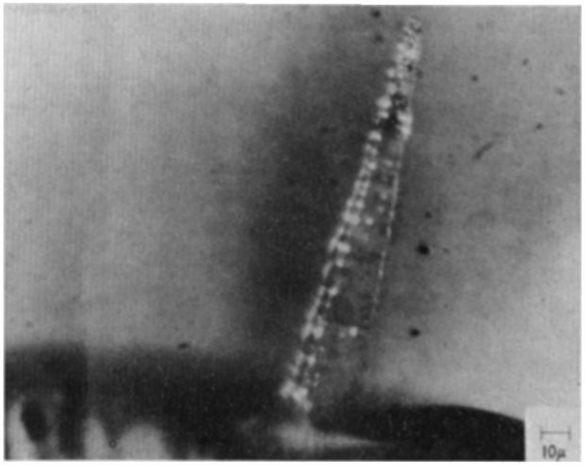

FIG. 4. Replica of etched filament track in fused silica. Track was etched for 20 min in 48% HF.

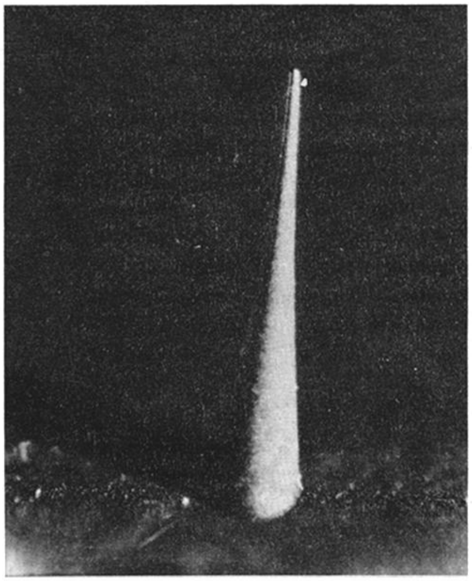

FIG. 5. Replica of a 700-μ-long etched track made in an Apollo space helmet by a cosmic-ray zinc ion. The track was etched for 196 h in 1 part 6.25N NaOH to 1 part ethanol (Ref. 12).

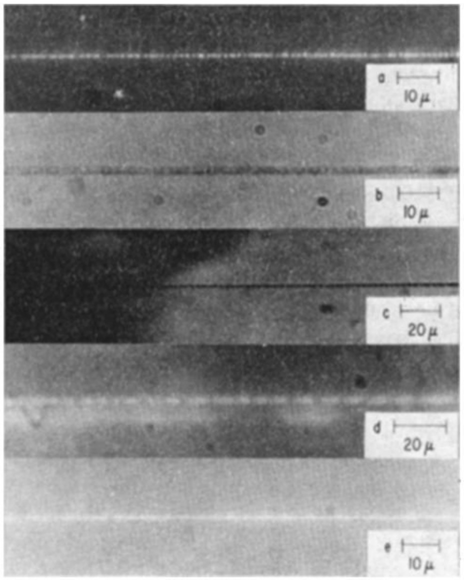

FIG. 6. Highly magnified views of small-scale structure along laser filaments. (a) and (b) Fused silica with strong modulation; (c) Plexiglas with strong modulation; (d) Plexiglas, a different track with a longer modulation spacing; (e) Plexiglas track which shows small-scale weak modulation along the length of track.