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ELEMENTS IN VULCANIZED LEAD (LEAD SULFIDE)

by

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Investigation into the Laser Damage of the Photo-Sensitive Elements in Vulcanized Lead (Lead Sulfide)

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ABSTRACT

This paper reports on the experimental
results of laser damage of photosensitive
detectors in vulcanized lead. We have studied
the factors in the laser damage threshold and
the threshold effect on the PbS photo-
sensitive detectors. The lasers utilized
all have a wavelength of 1.06 microns, but
their pulse widths and power densities vary
by several orders of magnitude.

I. Introduction

There have been many studies performed on the interaction
between lasers and various materials, especially metals [1].
In particular, a variety of analytical models have been
proposed for damage handling [3 - 9]. However, there have
been comparatively few studies performed for laser damage
on semi-conductors and detectors. Only in the last few years
have more systematic studies been made on these materials
[10-15].

In order to understand the interaction between lasers and
semiconductors, we have selected the photo-sensitive PbS
detector for studying laser damage. First we observe PbS under
an irradiation from 1.06 micron lasers with various pulse
widths. The signal-to-noise ratio varies with the rules on
light density. We observe its laser damage threshold, and
compare it to that of metals, etc. The result of our ex-
periments shows that the PbS damage threshold value is much
lower than that of metals, and that our findings basically

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coincide with those obtained by Kruer [16].

II. Requirements of the Experiment

We used a 1.06 micron solid laser device in the experi-
ment on PbS photo-sensitive detectors and studied the related
laser damage elements. We tried to obtain a laser pulse
width with varying threshold of 8 - 10 orders of magnitude
(from tens of seconds to tens of nanoseconds). We selected
separately several kinds of solid laser devices. We used the
YAG:Nd^{3+} laser device (with an attached time-synchronized
turntable valve) to experiment on the damage, in time
intervals from 1 to tens of seconds. We also used neodymium
glass laser devices to obtain experimental data with
2 millisecond and 0.2 millisecond duration. We also used
a photocurrent, Q-switched neodymium glass laser device to
conduct damage experiments using a laser with a pulse width
of 50 nanoseconds. The experimental arrangement is shown
in Figure 1.

In order to obtain the variation threshold on 10-12 orders
of magnitude (10^{-4} - 10^{8} W/cm^{2}), we passed the laser
irradiation energy density and power density of the PbS in
a semiconductor, photosensitive detector through an increment/
decrement light filter (to pass through some pre-selected,
varying focal length of the lens, and the distance between the
PbS element and the lens). This was done to vary the laser
pulse width and the output energy in order to achieve the
above threshold.

In order to calculate accurately the irradiation energy
density of the PbS detectors, we set a standard for the
energy-measuring instrument before the experiment, and we

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measured the dimensions of the light bands. In every experiment we measured the output energy with care, and we used a gas laser to fix the position of irradiation on the detector.

We used a PbS photosensitive detector of differing structures to conduct the damage experiments. We also at the same time used semiconductor or germanium segments, and ZnS with coated semiconductor germanium membrane to undergo laser damage experiments.

The kinds of PbS detectors used in the experiments have the following structures:

(1) PbS photosensitive surface (the optical segment) receives direct laser illumination. There are two kinds of optical segments of this type: one with combined ammonia treatment, and one that has undergone high temperature treatment. The structure is shown in Figure 2.

(2) The PbS photosensitive receiving detector has a quartz window (for passing through the light). The quartz window (sliding cover) is tightly bonded to the photosensitive surface of the PbS. This is shown in Figure 3.

(3) Its structure is basically the same as (2). However, the windows are quartz or germanium, and there is a fixed gap from the PbS photosensitive surface.

(4) The window is a PbS photosensitive detector in the doped germanium lens, as shown in Figure 4.
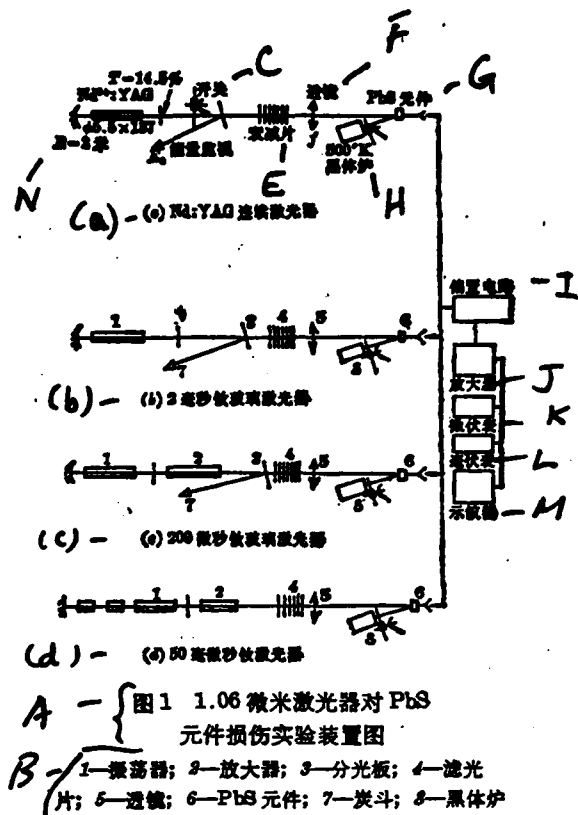
Figure 1. A. The set up for experiment of damage on PbS element by 1.06 micron laser device. B. 1 - oscillator, 2 - amplifier/ magnifier, 3 - beam-splitter plate, 4 - light filter, 5 - lens, 6 - PbS detector, 7 - carbon tank, 8 - black body stove. C. valve, D. energy monitor, E. attenuator, F. lens, G. PbS detector, H. black body stove, I. bias circuit, J. magnifier/ amplifier, K. microvolt meter, L. millivoltmeter, M. oscillometer, N-R-2m, (a) - (a) Nd:YAG continuous laser device, (b) - (b) 2 millisecond Nd glass laser device, (c) - (c) 200 micro Nd glass laser device, (d) (d) 50 nanosecond Nd laser device.
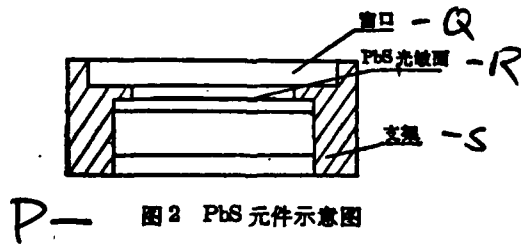
P. Figure 2. PbS detector diagram, Q. window; R. PbS photo-sensitive surface, S. support rack.
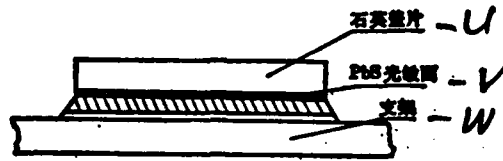
图3 有石英盖片的 PbS 元件示意图

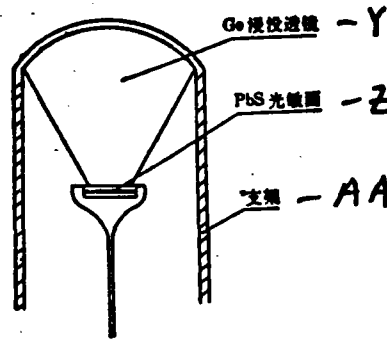T. Figure 3. Diagram of PbS detector with quartz slip cover;
V. PbS photo-sensitive surface, U. quartz slip cover; W. support
rack

图4 Ge 浸没透镜 PbS 元件示意图

X. Figure 4. Diagram of PbS Ge-immersed lens, Y. Ge-doped lens.
Z. PbS photo-sensitive surface, AA - support rack

III.   Results of the experiments and their analyses

1.   The effect of laser irradiation on the performance
of the PbS photo-sensitive detectors.

During the laser irradiation experiments, for short
pulsewidth laser (τ < 2 milliseconds), we measured the PbS
signal-to-noise ratio V_s/V_n (V_s being signal and V_n being noise)
before and after irradiation and the changes in resistance
R. For experiments with laser of long pulsewidth not only we
can measure the change in performance of PbS before and after
radiation, but also the change of V_s during the radiation pro-
cess. The results of the measurements have been summarized as
            curves between signal-to-noise ratio and the radiation

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energy density, in Figure 5, and　　　　　curves between
resistance and radiation energy density, as in Figure 6.
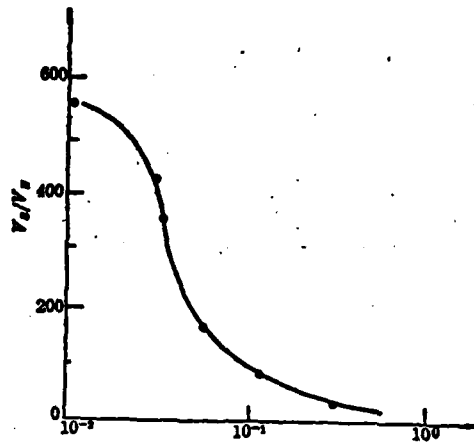
图5　PbS 元件的 $V_s/V_n \sim E$ 曲线

波长 1.06 微米; 脉宽 50 毫微秒; $E_0 \sim 4.5 \times 10^{-2}$ 焦耳/厘米²; $E_s \sim 4 \times 10^{-1}$ 焦耳/厘米²

Figure 5. 1. Figure 5 PbS detector $V_s/V_n \sim$ E curve, 2. E (Joule/cm²), 3. wavelength = 1.06 micron; pulsewidth = 50 nanoseconds; $E_0 \sim 4.5 \times 10^{-2}$ Joule/cm²; $E_s \sim 4 \times 10^{-1}$ Joule/cm².
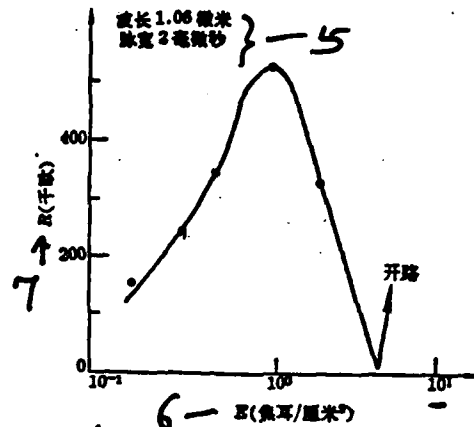
图 6 PbS 元件的 R～E 曲线（典型例子）

Figure 6. 4. Figure 6 PbS detector R~ E curve (typical
example, 5. Wavelength - 1.06 micron, pulse width= 2 nanoseconds,
6. E (joule/cm^2), 7. R(K Ω).

From analyses on the aforementioned curve with respect to signal-
to-noise ratio (V_s/V_n), the relationship between resistance (R)
and laser irradiation energy density (E), and the corresponding
surface damage situations, we can draw the following three con-
clusions:

(1) As E increases, changes in V_s/V_n and R vary from
moderately slow to rapid changes. In the region of changes,
V_s/V_n begins with a moderately slow change(the typical procession
is a slow decrease, but for some other elements the curve will
slowly rise and then fall), then pass through a stage before
a quick fall. In this process, there are two clear characteris-
tics. One of them is that at a certain time interval after the
laser irradiation, V_s/V_n will increase to a higher value. The
other characteristic is that the surface of the element will
not show observable damage (even under a 40x microscope). We
may conclude that decrease in V_s/V_n is a temporary deterioration.
Its material composition, structure, and (electric) conductivity
have not undergone any basic changes. Clearly, the above two
characteristics are related. As for the corresponding R ~ E

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curve in this region, as E increases, R will first change slowly, then it will rapidly rise.

(2) When E continues to have small changes in quantity, V_s/V_n falls rapidly. After irradiation is ended, even after some time lapse the value of V_s/V_n cannot return to any higher value. At this time, the surface of the detector will have begun to show flight damage. In this region, when we decrease V_s/V_n to 50% of the initial value of the energy density, we have this value, E_o, the onset damage threshold value. Actually, under this condition, we say that the detector is damaged. As for the corresponding $R \sim E$ curve in this region, when R reaches its maximum value, its corresponding E value is basically that of E_o. Since the detector surface has begun showing damage, and its performance characteristics cannot recover, this clearly shows that the detector's material composition has begun to change, and the damage has become permanent. We assess the situation by analytically computing the temperature (about 600°C) that can be achieved by the surface of the element at the time the onset damage threshold value is reached; the PbS material is not yet damaged because the temperature is still lower than the melting and vaporizing temperature (respectively at 1114°C and 1281°C). Note that in the sensitization of the PbS manufacturing process it is possible that some oxide and halide compounds of Pb are introduced, thereby lowering the melting temperature. For example PbO_2, Pb_2O_3, and Pb_3O_4 have the respective melting temperatures of 290°c, 370°C and 500°C. We can deduce from this, that with the damage onset threshold value of E_o, after the material has undergone laser irradiation, the apparent damage on the surface of PbS and the change in performance characteristics may be caused by the heat dissociation by one or many lead oxides.

(3) As the value of E continues to rise, V_s/V_n falls to the minimum value. We decrease V_s/V_n to 1% of

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the initial value or to the value of E when the absolute value approaches 1, this is regarded as the critical damage threshold value E_s. Under this condition most of the PbS material will be lost through vaporization (this applies to the situation where the PbS optical segment is being irradiated by short pulse laser). As for the $R \sim E$ curve, when E is increased more, R will quickly fall to a very small value (corresponding to E_s). Now if E is further increased, the value of R will suddenly increase to infinity, leading to the open circuit, as shown in Figure 6. When R falls to a very small value (near the short circuit path), i.e., as the conductivity rapidly increases, this is possible in the PbS gas, some of the PbS will revert to metal. At this time we may observe, under a microscope, thin layers of glittering metal granules. As R reaches points of infinity, an open circuit path is formed, usually the following three phenomena appear: (1) the PbS on the detector will completely vaporize, leaving behind only quartz substrates and electrodes; (2) quartz substrate in pieces, or (3) severed electrode (welding) pads or severed electrodes.

Synthesizing the above analyses we may see that: under laser irradiation with continuously increasing energy density the PbS detector will degenerate from excellent material to a thoroughly damaged one, beginning with surface damage. Also, during this process, the characteristics of the PbS detector undergo some very complex changes in both quantity and quality, resulting from a multitude of processes.

2. The effect of laser pulsewidth on the damage threshold of PbS.

We will first describe the damage threshold values E_o and E_s (their respective power density damage thresholds being P_o and P_s) determined by $V_s/V_n \sim E$ and $R \sim E$ curves. We use

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different pulsewidths to draw the curves, i.e., to obtain energy
damage threshold values (or power density damage threshold
values) and the relational curves of the irradiating laser
pulsewidth (E_o, $E_s \sim \tau$, P_o $P_s \sim \tau$) as shown in Figure 7. In
this region, as the pulsewidth undergoes change of 8 orders of
magnitude, the damage threshold values will change by 4 orders of
magnitude. Looking at the entire curve, the damage threshold
values E_o, E_s increase as τ does (P_o and P_s will decrease as τ
increases). In the region of short pulsewidths, the change in
E_s is slower. In the continuous long pulsewidth region, E_o and
τ have a linear relationship.
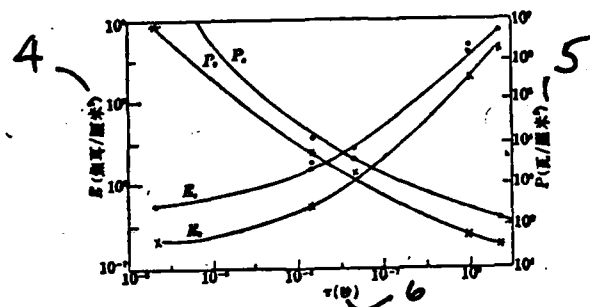
图7 PbS 元件的损伤阈值与激光
辐照时间的关系

P_o, E_o—开始损伤的功率密度和能量密度;
P_s, E_s—严重损伤的功率密度和能量密度

Figure 7. 1. Figure 7. The relationship between the damage
threshold values of the PbS detector and the duration of laser
irradiation, 2. $P_o E_o$ - the respective onset damage power
density and energy density, 3. P_s, E_s - the respective severe
decomposition power density and energy density, 4. E (joule/cm^2);
5. P (w/cm^2), 6. τ (seconds).

For the damage handling of PbS under laser irradiation,
it is generally of the nature of dealing with effect of heat.
Therefore, in the case of PbS optical segments we may use a
thermal model of "uniform irradiating semi-infinite solids,"

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and for the PbS detector with slip cover, we use model of "thin absorption layer sandwiched between two uniform irradiating plates." However, with lasers of different pulsewidth and different energy density, the changes in the characteristics of PbS detector with different structures and the mode of damage are rather complex. PbS has strong absorption ability for the 1.06 micron laser (the absorptivity is 2 x $10^4 cm^{-1}$), and it has comparatively higher spectral sensitivity. Therefore, under the 1.06 micron laser irradiation PbS produces photocurrent, and its output signal is directly proportional to the irradiation intensity, i.e., $V_s \propto nh\nu$, While observing the change in V_s of the PbS detector undergoing irradiation by lasers of long pulsewidth, we find that there exist a signal with its V_s value being scores of times the irradiation of a black body. Clearly, this is the irradiation signal of a 1.06 micron laser. It is caused by the direct transition of PbS absorbing photons of the 1.06 micron laser, thereby producing a large quantity of carrier rheotons [Translator's Note: I am at loss to translate this term: 载流子 . Apparently this is purely the author's own, original, invention. It could very well been translated as carrier stray particle or carrier fluid particle, any of these will be appropriate in Chinese]. Furthermore, through the indirect transition (with corresponding 10^{-3} ev) and due to the induced PbS temperature rise, a large quantity of acoustic particles. [Translator's Note: This again appears to be the author's own invented term]. Under the uniform irradiation of lasers with long pulsewidth , the heat in PbS has sufficient time to conduct its (heat) energy to quartz substrate (the thermal conductivity of PbS and molten quartz are respectively 0.024 and 0.014 w/cmK and the heating time constant of PbS thin film is approximately in the range of micro-to-milliseconds). This reaches the frame holding the detector and, it then irradiates to influence the existing damage caused by the convection energy . Therefore, the longer the pulsewidth (of laser used),

the higher will be the damage threshold. Under this situation, we may attribute the following as principal cause of damage; material decomposition through heat, thereby severing the welded component of the electrode, which causes melting of PbS material and partial vaporization. For lasers of short pulsewidth, the damage caused by heat conduction, etc. is negligible. With lower energy density ($E < E_o$), the damage is apparently done by melting, decomposition, and partial vaporization. We can observe, under microscope, molten material in the melting pit or in the vapor. When the irradiation energy density reaches the severe decomposition threshold ($E > E_s$), PbS will primarily or completely vaporize. As for lasers of medium pulsewidth, the extent of material damage will be somewhere between that of the long and short pulsewidths.

3. The structure of PbS and the effect of experimental conditions on the damage threshold.

(1) The PbS detector with quartz window

Since the 1.06 micron laser has a permeability on molten quartz, then its damage threshold value does not differ basically from the windowless PbS detector. As for the PbS treated with high temperature as well as PbS manufactured with ammonia, the laser damage threshold values show significant differences.

(2) The PbS detector with quartz cover

The damage threshold value of PbS with this kind of structure is slightly lower than the windowless PbS. Even when its irradiation energy density reaches the severe decomposition threshold value E_s its surface will still not show observable, clear damage. Even at this time some vaporization may take place, but due to its being bonded tightly by quartz slip cover

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and with condensation, the vaporized material will just solidify
again. If we further raise the irradiation energy density,
then, finally, the PbS material will be completely along the edges
of the bonding material. A PbS detector with this kind of struc-
ture has a threshold value four to five times higher than the
aforementioned material, for complete vaporization.

(3) PbS detector with immersed Ge lens and PbS with
Ge window.

For continuous pulse (laser), the damage threshold value
of PbS detector with doped lens is ten times higher than that of
PbS detectors with quartz slip cover. The PbS detector with Ge
window has a damage threshold value 40 times higher than that of
PbS detectors with quartz slip cover. During the irradiation pro-
cess (time = 30 seconds) we always discovered that the
V_s signal rapidly increased by scores of times, this being simi-
lar to the V_s rise induced by the direct irradiation by a 1.06
micron laser. At this time, the PbS damage is mainly caused by
the material on Ge lens and on Ge window having been irradiated by the
laser; this induced higher temperatures resulting in heat conduc-
tion and heat radiation, and this caused rising temperatures in
PbS adhesion and solder. When the irradiation energy density
is lower, it causes V_s to fall, and if E is then raised, it will
finally cause the decomposition of adhesive material and solder;
the solder joint is loosened and an open circuit results If we
replace the Ge window with a piece of Ge, and set it apart from
the photosensitive surface of PbS, then even when the irradia-
tion energy density reaches 4 to 5 times higher than that which
caused an open circuit in the PbS element of a Ge lens, evidence of
severe damage will still fail to appear.

For lasers with short pulses, the onset damage threshold
value of PbS detector with Ge lens and Ge window is 10 to 30

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times higher than that with quartz slip covers. Furthermore, for PbS elements with Ge window, the irradiation energy density can even reach 160 joule/cm^2; it will still not reach the stage of severe decomposition. Similar to the condition of long pulse with Ge elements and PbS being separated, at this time the fall of V_s, of the PbS signals, is usually caused by the lowered permeability of the blackbody radiation; this is induced by damage (crack lines, concavity, etc.) on the Ge surface material while under laser irradiation. Whether we have long or short pulse irradiation, the damage threshold value of PbS elements with Ge lens will always be lower than that with Ge window. This is probably due to the condensed coking of the Ge lens heat radiation and further direct heating on PbS.

(4) Effect of partial vaporization of the PbS material on the performance properties and damage threshold value.

We use a laser bundle of 2 mm diameter to irradiate a 6 x 6 mm^2 PbS photo-sensitive surface and vaporization will not cause severe decomposition of PbS detector. It is not related to either the effect on the properties of the element or the position of damage on the photo-sensitive surface, but it is related to the total damage area and the sequence of irradiation. After the first irradiation, 3.22 mm^2 of the photo-sensitive material is vaporized; at this time V_s falls by 50%. This shows that 10% of the photo-sensitive area suffered damage and vaproization; therefore the damage on the detector has begun (i.e., E_o is reached). V_s continues to fall after the second and third irradiations. The stage of severe decomposition is reached after the fourth irradiation.

If the element is pressed while the laser is irradiating, the damage threshold value is about 30% when it is not.

4. The laser damage threshold value of a Ge segment and a Ge segment with a film of ZnS.

Different laser pulse widths have significantly differing damage threshold values on Ge and the Ge with Z_nS film on its surface. Under a continuous laser irradiation of 18 watts for 1 to 50 seconds, the surface of Ge shows almost no damage. Only when the irradiation energy density is greater than 2×10^4 joule/cm^2 we find some shallow trace of damage in the Z_nS film. For short pulse lasers, at 2 milliseconds of irradiation the damage threshold value is 5 joule/mm^2 for ZnS film, and 20 joule/mm^2 for Ge (its surface shows molten groves and hairline cracks. For irradiation of 50 nanoseconds, Z_nS film has damage threshold values of 0.4 joule/mm^2, and for Ge, 80 joule/mm^2).

IV. Conclusions

The study of the reaction between laser and semiconductor material has just begun. We have selected PbS for our study, i.e., to investigate the damage threshold value of PbS under irradiation of a 1.06 micorn laser. This value varies according to the pulsewidth of the irradiating laser: E_o and E_s increase as τ increases ; when τ is longer, they increase linearly. For PbS of different structure, the threshold value of the laser damage will be different. For the different PbS detectors that we have selected, their threshold values can differ by 30 to 40 times. The difference in the amount of partial vaporization of the PbS detector will influence the properties of the elements as well as the values of damage thresholds.

Consider Ge, which is used for windows in the PbS detector, and Z_nS film with respect to their thresholds of laser damage; we find through observation, clear evidence of dependence between damage threshold and pulsewidth.

Whether we have PbS of different structures or the material with Ge windows, their laser damage thresholds are much

lower than those of metals or dielectric material.

Furthermore, we have observed during the experiments that long before the initiation of damage by laser irradiation, the PbS element signal V_s displays the phenomenon of saturation and the ability of the 1.06 micron laser to penetrate the Ge segment. The experimental arrangement and procedures await further study. Under the influence of strong lasers, especially under the influence of lasers with super-short pulses, a semiconductor displays a non-linear optical phenomenon. In particular, for non-elastic light scattering experiments and theory, we need to study the interaction of photons with electrons, sound particles, laser particles, polarons, magnetized oscillations, and ions. We must clarify the energy band structure of semiconductors, electrical conductivity, and light generation. Based on this, we can expand the range of applications for lasers and semiconductors, and explore the important implications for developments in solid state physics.

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