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Lifetime of Carriers in Lead Sulfide Crystals

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The relationship of carrier lifetime in lead sulfide crystals to the density of dislocations and crystal resistivity is studied experimentally. Dislocation density is obtained by etch pit counting. Two groups of crystals are analyzed: in one group the density of dislocations is approximately the same but the resistivity varies; in the other the resistivity is approximately the same but the density of dislocations varies. The carrier lifetime was found to be independent of the resistivity for a high dislocation density, ruling out the Auger process as an important recombination mechanism. Carrier lifetime was found to be inversely proportional to the density of dislocations, which suggests that the Shockley-Reed recombination mechanism is an important one.

INTRODUCTION

THE decay back to equilibrium of an excess number of electrons or holes in a semiconductor may occur through a number of recombination mechanisms. First there is the possibility of a one-step process in which an electron in the conduction band combines directly with a hole in the valence band. The energy liberated in the process is given out as radiation. This recombination process is characterized by a radiative time constant τ_r. One can calculate τ_r from optical absorption data, and the value for PbS is estimated to be about 40 microseconds with a probable error of a factor of five.[1]

The second recombination process is through a three-body collision mechanism called the Auger process. An electron in the conduction band combines with a hole in the valence band, giving up the energy to a third carrier. In this process the lifetime is inversely proportional to the square of the carrier density. Moss[2] reported data which suggest that the Auger process may be present in lead sulfide.

The third important recombination process is a two-step process in which an electron falls into an energy level due to a crystal imperfection, where a hole recombines with it. According to the Shockley-Reed theory,[3] when recombination takes place at lattice dislocations, the lifetime is independent of resistivity in strongly n- or p-type material. This lifetime, however, is dependent upon the density of dislocations in the crystal.

The resultant lifetime in a crystal when all these mechanisms are present simultaneously is obtained from the sum of reciprocals of the component lifetimes. Thus the process of shortest lifetime dominates the resultant lifetime.

The importance of lattice dislocations on the lifetime of carriers in lead sulfide is the subject of this paper.

Method for Estimating Dislocation Densities

There are two methods used today for estimating the density of dislocations in crystals. One is to count etch pits on the crystal surface[4] and the other is to measure the half-width of x-ray diffraction lines which is then related to the defect density.[5]

The etch-pit-counting technique has some advantages over the x-ray method in simplicity; furthermore, it shows the distribution of dislocations in a crystal. For high densities of dislocations, it is frequently difficult to count all the pits or else all dislocations do not produce pits and in such cases the x-ray line-width method is thought to be best. At the present time we have only etch-pit data on PbS.

Chemical Etch for PbS

The first problem in such studies is to find a suitable etch. The requirements are that it be mild in its action and, in the case of compound semiconductors, that it form soluble or volatile products of the elements of the compound. With PbS, many of the conventional etches lead to undesirable insoluble side-products. An etch was found that has produced excellent results with PbS.[6] It is a 3:1 mixture of a 100 g/l thiourea solution and concentrated HCl used at a temperature of 60°–80°C for a few minutes. The functions of the two ingredients are believed to be as follows:

Thiourea tends to form complexes with metal ions which in this case tie up the lead in a soluble form and permit more lead from the PbS to go into the solution. The sulfide ion reacts with the hydrogen ion from the acid to form HS^- and H_2S.

With this etch has come a new approach to some of the problems of properties of PbS crystals. Among these are lifetime and mobility of carriers as related to density of dislocations. In this paper, the results of some of the studies of lifetime will be discussed.

Method for Measuring Lifetime

The principal method used in these studies for measuring the carrier lifetime is based upon the ratio of the photoelectromagnetic (PEM) and photoconductive

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[1] I. M. Mackintosh, Proc. Phys. Soc. (London) **B69**, 115 (1956).

[2] T. S. Moss, Physica **20**, 989 (1954).

[3] W. Shockley and W. T. Reed, Phys. Rev. **87**, 835 (1952).

[4] Vogel, Pfann, Corey, and Thomas, Phys. Rev. **90**, 489 (1953).

[5] Gay, Kirsch, and Kelley, Acta Metallurgica **1**, 315 (1953); Kurtz, Kulin, and Averbach, Phys. Rev. **101**, 1285 (1956).

[6] R. F. Brebrick and W. W. Scanlon (to be published).

(PC) signals described by Moss,[7] Aigrain,[8] and others. This method is not subject to the effects of surface adsorbed layers which seriously alter the values of lifetime for PbS as obtained from other methods such as the moving line of light method.[9] If the PbS crystal is cleaved and the lifetime measured by the moving-line-of-light method while the crystal is protected by an atmosphere of pure argon, the values of lifetime so obtained agree with the values obtained from the PEM-PC method.

Thin sections of crystals about 0.2 to 0.5 mm thick were used for the PEM-PC measurements. The ends of the crystals are electroplated with rhodium and leads are soldered on. By masking certain areas of the crystal surface, regions could be found which had a negligible photovoltaic effect. For these regions, the photoelectromagnetic signal and the photoconductive signal were measured by using 90-cycle/sec chopped radiation from an incandescent lamp. From the ratio, the lifetime was calculated by using the formula derived by Moss.[7]

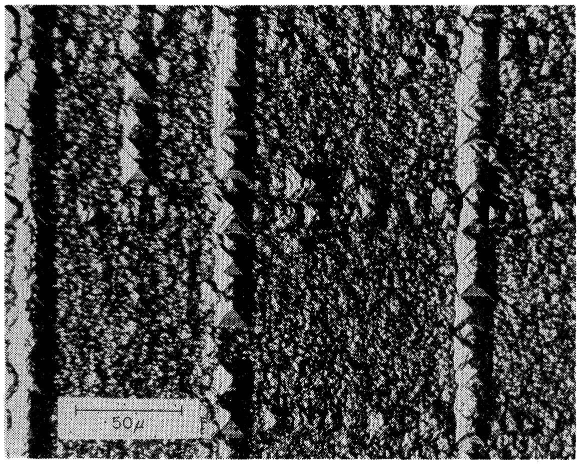

FIG. 1. Etch pattern on a natural PbS crystal.

EXPERIMENTAL RESULTS

Etch Patterns

We shall first indicate a few general results which were revealed by the etch patterns of PbS crystals. Following this, we shall illustrate the dependence of lifetime on the density of etch pits in PbS.

Figure 1 is the etch pattern obtained on a typical natural crystal. On every natural crystal there is a plaid network of lines of etch pits. The alignment is parallel to cleavage planes and the density varies from almost complete coverage to fewer lines than shown in illustration.

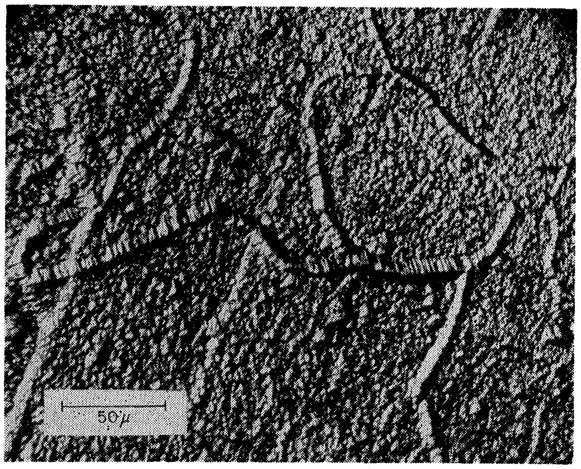

FIG. 2. Etch pattern on a synthetic PbS crystal.

One crystal, which had only parallel lines, was studied for Hall effect and resistivity when the current was parallel and perpendicular to these lines. The Hall effect was essentially independent of the orientation but the resistivity and mobility varied with orientation. The mobility for this sample was 30% greater with current parallel to the lines of etch pit than across them.

Figure 2 gives a typical etch pattern on a synthetic PbS crystal grown from the melt. Both this crystal and the one of Fig. 1 gave mirror-like cleavage planes. The density of pits on this crystal is high.

Figure 3 is the etch pattern of a typical natural crystal in which we altered the composition by the vapor-diffusion process.[10] This process requires heating the crystal to 500°C for 20 hours and quickly cooling to room temperature to freeze-in the equilibrium composition. The lines of pits are gone and the density of pits is increased by a factor of 20 to 50.

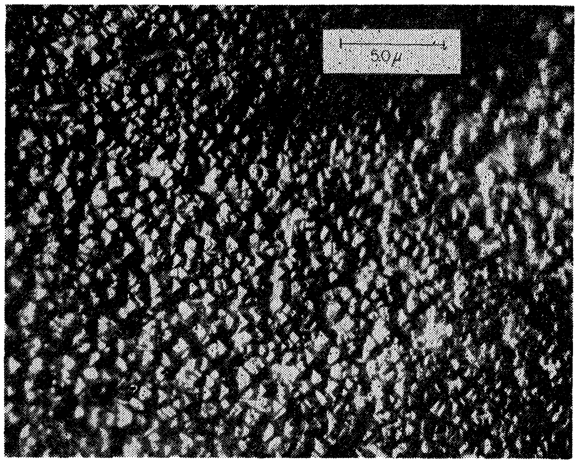

FIG. 3. Etch pattern on a natural PbS crystal after heat treatment.

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[7] Moss, Pincherle, and Woodword, Proc. Phys. Soc. (London) **B66**, 743 (1953).

[8] P. Aigrain and H. Bulliard, Acad. Sci. Paris **236**, 595, 672 (1953).

[9] W. W. Scanlon, in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, 1957), p. 238.

[10] R. F. Brebrick and W. W. Scanlon, Phys. Rev. **96**, 598 (1954).

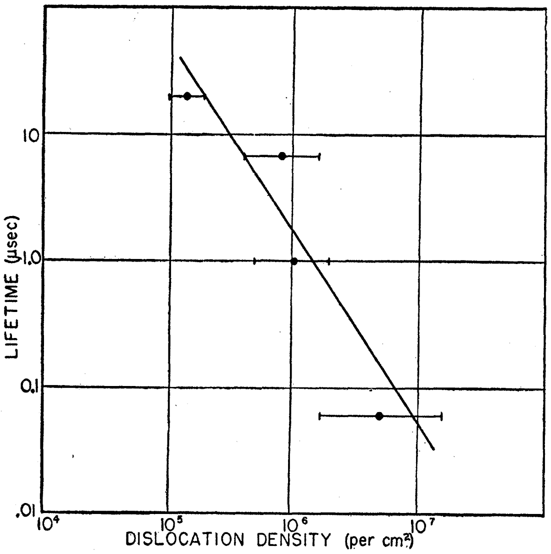

FIG. 4. Carrier lifetime as a function of dislocation density.

Lifetime as a Function of Etch-Pit Density

We have a group of crystals prepared by the vapor diffusion process which have a range of resistivity from a few hundredths of an ohm-cm to over an ohm-cm. All these crystals had a high density of pits, 10^6 to 10^7/cm^2. If we assume that each pit represents the penetration of a dislocation line through the surface, the dislocation density is then given by the pit density. Lifetime of carriers in this group of crystals was not related to resistivity. In general the lifetimes were all very short, from a tenth to one microsecond.

In the case of PbS we do not have the wide selection of crystals that were available for studies relating lifetime to dislocation densities in germanium and silicon. However, we have a few crystals within the small resistivity range of from 0.2 to 0.4 ohm-cm which varied considerably in their dislocation densities. Carrier lifetime varied from 20 microseconds in the crystal of lowest dislocation density, 10^5/cm^2, to about 0.1 microsecond in the crystal of highest dislocation density, 10^7/cm^2. The relation of carrier lifetime in these crystals to dislocation density is shown in Fig. 4. The estimated uncertainty in pit counting is indicated for the points.

CONCLUSIONS

These experiments show that the lifetime of carriers in lead sulfide is determined largely by the density of dislocations in the crystal; the higher the density the shorter the lifetime.

In a group of crystals having about the same high density of dislocations but varying greatly in resistivity, the lifetime is independent of the crystal resistivity. This suggests that the Auger mechanism is not an important recombination process in these lead sulfide crystals. The results suggest that recombination occurs principally at dislocations by the Shockley-Reed mechanism.

The maximum lifetime observed, 20 microseconds, was in a crystal of relatively low density of dislocations, 10^5/cm^2. Presumably better crystals would lead to higher values of lifetime approaching the radiative limit.

PbS crystals are easily deformed by thermal or other stresses with the result that the lifetime is reduced. Synthetic crystals generally have very short lifetimes, possibly because of a high density of dislocations introduced when the crystal is grown from the melt (1150°C) or else when the crystal is being cooled to room temperature.

ACKNOWLEDGMENTS

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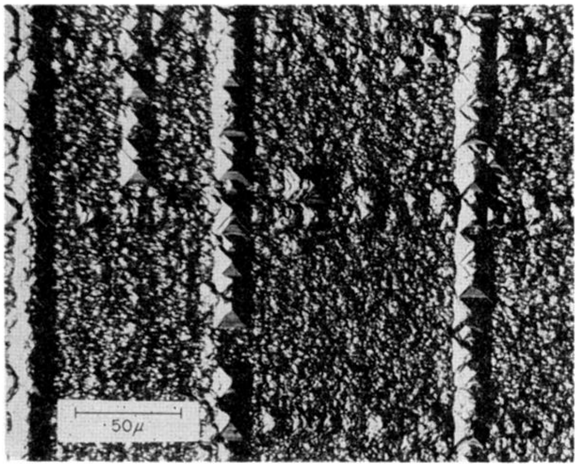

FIG. 1. Etch pattern on a natural PbS crystal.

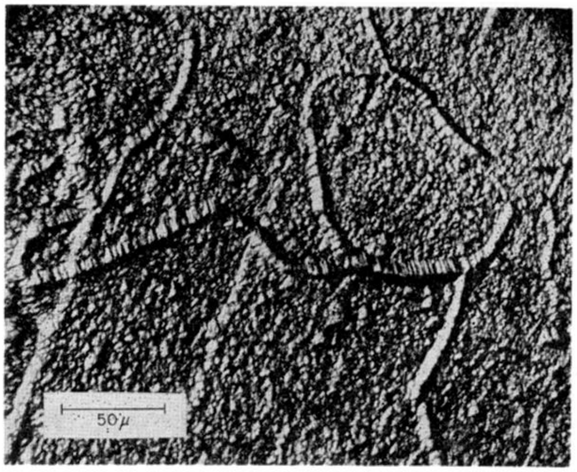

FIG. 2. Etch pattern on a synthetic PbS crystal.

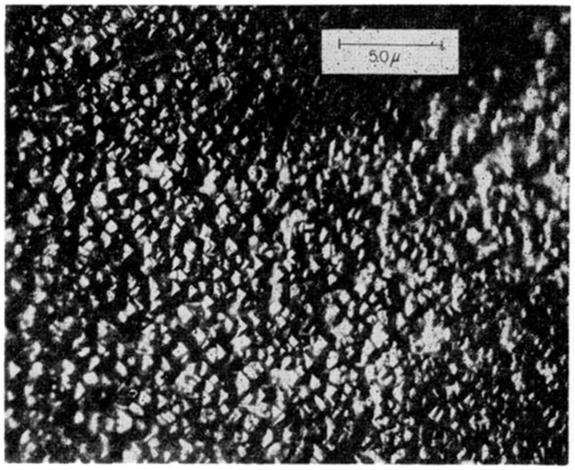

FIG. 3. Etch pattern on a natural PbS crystal after heat treatment.