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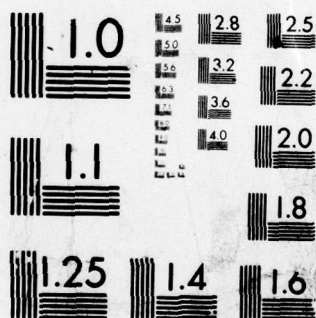
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→ Doping effects and photoconductivity were studied for single crystal films of lead tin telluride ($Pb_{0.8}Sn_{0.2}Te$) grown by vapor phase epitaxy. Growth of films was carried out by an evaporation condensation process in which the alloy was evaporated from a polycrystalline source and the vapor was condensed on a barium fluoride substrate. Interesting doping effects were obtained with indium which produces a deep level in the gap with unusual properties. Extensive galvanomagnetic measurements suggest that indium enters as a self-compensating impurity and pins the Fermi level near midgap, in →			

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TRANSPORT AND RECOMBINATION PROPERTIES OF
LEAD TIN TELLURIDE ALLOYS

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A. Abstract

AFOSR-78-3509

Doping effects and photoconductivity were studied for single crystal films of lead tin telluride ($\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$) grown by vapor phase epitaxy. Growth of films was carried out by an evaporation condensation process in which the alloy was evaporated from a polycrystalline source and the vapor was condensed on a barium fluoride substrate. Interesting doping effect were obtained with indium which produces a deep level in the gap with unusual properties. Extensive galvanomagnetic measurements suggest that indium enters as a self-compensating impurity and pins the Fermi level near midgap, in contrast to other Group III elements such as gallium and thallium which dope the material n-type and p-type, respectively.

An investigation of the kinetics of photoconductive revealed that around the "device temperature" of 77°K, the recombination of excess carriers is thermally activated, but becomes approximately temperature independent below 50°K. These results and the magnitude of the photoconductive lifetime lead to the surprising conclusion that contrary to prevailing opinion, Auger recombination is not the dominant recombination mechanism for samples with carrier concentration in the $1-10 \times 10^{16} \text{ cm}^{-3}$ range.

B. Objectives, Status of Research Effort and Significance of Achievements

1. Objectives: The objectives set out in the research proposals can be summarized as follows:

- a) Optimization of preparation techniques of lead tin telluride (Pb/Sn ratio 5/1) by vapor phase epitaxy.
- b) Control over carrier type and concentration either by changing the stoichiometry of the films or by introducing impurities.
- c) Study of the electrical properties of doped crystals.
- d) Study of photoconductivity with emphasis on studying the kinetics of the photoconductive decay for the purpose of gaining information about the recombination process.
- e) Study of properties of alloys with higher tin content, corresponding to a bandgap of about 0.05 eV.

2. Status of Research Efforts: We have concentrated on the first four of these objectives, but did not address ourselves to objective "e" since the first four objectives used up the entire time allotted to the project. We summarize our activities as follows: 1) With respect to objectives a and b, we have mastered the techniques for obtaining single crystal films in the concentration range $2 \times 10^{16} \text{ cm}^{-3}$ (n-type) to $4 \times 10^{18} \text{ cm}^{-3}$ (p-type) using the "hot wall" evaporation-condensation process with BaF_2 as the substrate material; 2) With respect to objective c, we have studied the behavior of indium in considerable detail and made preliminary studies of doping with Ga and Bi; 3) With respect to objective d, we have studied the temperature dependence of the photoconductive decay time between 100°K and 14°K, during which interval the decay time increases from tens of nanoseconds to several microseconds.

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3. Significance of Achievements:

a) State-of-the-art quality of vapor phase epitaxial crystals of lead tin telluride was achieved.

b) Interesting effects concerning the electrical behavior of In in lead tin telluride were studied which lead to the conclusion that In produces a deep level in the gap with amphoteric properties. We have attempted to develop a theoretical model which contrasts this behavior with that of other Column III elements such as Ga and Tl which dope the material n-type and p-type, respectively.

c) Measurements of the photoconductive decay time as a function of temperature have led to the surprising conclusion that the commonly held belief of the dominance of Auger recombination at the device temperature of 77°K is not valid. Apparently, a non-intrinsic process, possibly recombination at a surface inversion layer, dominates the recombination.

C. Extended Summary of Activities and Achievements

1. Preparation of Samples and Control of Stoichiometry: A large part of the effort throughout the contract was devoted to a study of the optimum preparation conditions and effective control of stoichiometry. Samples were prepared by a simple evaporation-condensation technique in which a source material of desired composition (typically 0.80 PbTe-0.20 SnTe) was evaporated at about 500°C and condensed on a cleaved BaF₂ substrate held typically at 400°C. The "hot wall" evaporation chamber⁽¹⁾ was contained within an oil-free vacuum system maintained at about 10⁻⁶ during evacuation. Further details about the evaporation procedure can be found in the report covering the first period of the contract.

Routine evaluation of samples was based on Hall effect and resistivity measurements at 77°K and room temperature from which carrier concentration and mobility could be calculated. From time to time, X-ray measurements were also carried out in order to ascertain that the films were single crystals and that the composition as determined from the lattice constant agreed with that of the source material. In varying the parameters of the evaporation procedure, namely temperature of source and substrate, stoichiometry of source and evaporation rate, the goal was to produce samples with carrier concentration of less than 10¹⁷ cm⁻³ and of high mobility in a reproducible fashion. By "high" mobility we mean a mobility at liquid helium temperature of at least 10⁵ cm²/Vsec which is comparable to that of bulk material.⁽¹⁾ Since it was not practical to make liquid He measurements on each sample, a satisfactory criterion for high mobility was about 20,000 cm²/Vsec at 77°K.

After an extensive period of trial and error, it was found that between broad limits neither the substrate temperature (350° to 450°K) nor the rate of evaporation (1 to 20 microns/hr.), which was determined by the source temperature and geometrical factors, had any reproducible effect on crystal quality as measured by the mobility at 77°K . Most likely, the initial nucleation process on BaF_2 is the most important factor in producing high quality crystals, but time did not permit us to investigate this hypothesis. Instead, we selected a number of high mobility, low carrier concentration samples for studies of photoconductivity (Section 3) and also devoted considerable time to a study of doping effects of Column III elements (Section 2).

As for obtaining samples with low carrier concentration (10^{16} to 10^{17} cm^{-3}) we first endeavored to achieve this aim by using a co-evaporation technique⁽¹⁾. In this technique, one aims at a proper balance between the flux emanating from a metal rich source which by itself would give heavily doped n-type material and the flux from a Te reservoir which is supposed to neutralize the excess metal content of the vapor coming from the source. We only had limited success with this technique and we, therefore, turned to a more reliable method; namely, that of adjusting the stoichiometry of the source. Nominally stoichiometric material yielded p-type material with carrier concentration of typically $4 \times 10^{18} \text{ cm}^{-3}$ while strongly metal rich sources (e.g., excess metal concentration of 1.5 percent) yielded n-type material in the 10^{18} cm^{-3} range. However, by adjusting the excess metal concentration to one percent, it was possible to obtain n-type material with a typical concentration of $4 \times 10^{16} \text{ cm}^{-3}$, and by further reducing the excess metal in the source to 0.4% p-type material in the concentration range of typically $2 \times 10^{17} \text{ cm}^{-3}$ was obtained quite reproducibly.

2. Doping Effects: In the report covering the first period of this contract, some interesting electrical properties of indium doped lead tin telluride were described and the results have since then been published.⁽²⁾ Briefly, it appears upon superficial examination that In produces a deep acceptor level in the gap which renders the material essentially intrinsic. However, a careful study of the Hall constant as a function of temperature and indium concentration suggests that indium is not an ordinary deep acceptor; as a result of a negative correlation energy⁽³⁾ two neutral In atoms "react" to produce one positive and one negative ion with the Fermi level slightly below the middle of the gap.⁽⁴⁾ During the second period of the contract, doping experiments with gallium were carried out to gain further insight into the behavior of Column III elements as dopants. (Because of the low vapor pressure of Ga, considerable difficulty was encountered in incorporating Ga into the films using the co-evaporation techniques employed for In but eventually the proper flux ratio between Ga and LTT was found and a clear doping effect was achieved). It was established that Ga acts as a donor level without evidence of freeze-out at low temperatures. Thus, the sequence of Ga, In, Tl (in descending order of Column III) produces a donor for Ga, a deep level self-compensating level for In and an acceptor for Tl,⁽⁵⁾ again without freeze-out effects.

We suggest the following qualitative explanation for this phenomenon. We assume that the band structure of LTT for $x = 0.2$ is still essentially that of lead telluride⁽⁶⁾ which means that the top of the valence band is formed by an L_6^+ band. In the spirit of Dimmock's et al's explanation for the behavior of the bandgap as a function of Sn content⁽⁶⁾ we suggest that the change-over from the p-type behavior of Tl to the n-type behavior of Ga can be traced to a relativistic effect. Since the L_6^+ band is believed to

have appreciable s-like character around the metal atom⁽⁷⁾ the substitution of the sequence Tl, In, Ga for Pb corresponds to an increasingly repulsive electron potential compared to that of Pb as the relativistic correction for the binding energy decreases.⁽⁸⁾ The effect is negligible for Tl (Z=81) which is adjacent to Pb (Z=82) and, therefore, Tl becomes an ordinary acceptor since it has one electron less than Pb. At the other extreme, the effect for Ga (Z=31) is apparently large enough to push a level out of the L_6^+ band into the conduction band. The 3p Ga electron which would ordinarily go into the L_6^+ band would then occupy a conduction band level and render the material n-type. For In (Z=49), with a relativistic correction intermediate between that of Tl and Ga, the perturbation on the L_6^+ band is sufficiently strong to produce a level in the gap but not strong enough to push a level out of the valence band into the conduction band. Clearly, these ideas can only be regarded as a qualitative explanation of these doping effects. It is hoped that they can serve as a guide for serious calculations for the perturbations produced by Column III impurities on the energy levels of the lead telluride-tin telluride system.

3. Measurements of Photoconductivity and the Recombination Mechanism in Lead Tin Telluride: In the report covering the first period of the contract some preliminary measurements of photoconductive decay times as a function of temperature were reported and the experimental details were described.* During the second period of the contract, these measurements were extended to other samples and considerable effort was devoted to an

*Photoconductivity was excited by electro-optically modulated pulses from a CO₂ laser. The pulses had a decay time of about 15 nanoseconds and the measuring circuit of the samples had a similar response time so that photoconductive decay times of the order of 20 nanoseconds were measurable. Data were collected on samples with carrier concentrations between about 2 and $10 \times 10^{16} \text{ cm}^{-3}$ since more heavily doped samples had decay times which were too short to be measured by our apparatus.

attempt to interpret the results of these measurements in terms of various recombination mechanisms.

Briefly, the experimental results can be described as follows.

Starting with temperatures of about 100°K, the photoconductive decay time τ_{pc} first increases with decreasing temperatures but eventually flattens out below about 50°K. Typical values of τ_{pc} obtained from a plot of photoconductivity vs. time after cessation of the light pulse, were 30 nanoseconds at 77°K and microseconds at 14°K, the lowest temperature reached. (In the course of this investigation, it was discovered that similar results were recently obtained by a research group in Germany.⁽⁹⁾ In arriving at our conclusions, we could therefore combine both experimental findings.

Prior to our investigations and that of the German group,⁽⁹⁾ data for τ_{pc} were available only at temperatures around 77°K.⁽¹⁰⁾ On the basis of the concentration dependence of the τ_{pc} 's at these temperatures, it had been concluded that Auger recombination was the dominant mechanism for the decay of photocarriers.⁽¹⁰⁾ The scatter in the available experimental data, however, was very considerable and hence this conclusion was based on rather scanty evidence. One might add that most theoretical device analysis of photovoltaic lead salt detectors is also based on the premise that Auger mechanism dominates the recombination process at 77°K for material with a carrier concentration in the $1-10 \times 10^{16} \text{ cm}^{-3}$ range.^(11,12) Our analysis of the magnitude of τ_{pc} and of its temperature dependence sheds considerable doubt on the validity of these conclusions. Briefly, the following picture emerges from our analysis of the data: Emtage's theory⁽¹¹⁾ for the Auger process in the lead chalcogenides gives order of magnitude agreement with

the measured τ_{pc} 's at 77°K. However, the temperature dependence of τ_{pc} around 77°K ($\tau \propto \exp E/kT$) yields an activation energy E of about .075ev which is an order of magnitude greater than that expected from the theory. Since the activation energy can be predicted quite reliably from the theory while an estimate of the absolute value of the recombination constant relies on details of the band structure, we conclude that the approximate agreement between theory and experiment at 77°K is fortuitous. In the temperature independent regime below about 50°K and where τ_{pc} is in the range of microseconds for samples with carrier concentrations in the 10^{16} cm^{-3} concentration range, most of the data can be accounted for by assuming that the dominant recombination process is radiative. In order to reconcile the fact that τ_{pc} is actually longer than the decay time τ_r calculated for interband radiative recombination process (always the slowest recombination process), one must make a correction for the small probability of a photon leaving the crystal upon being created by electron-hole recombination.⁽¹³⁾ Since photons can create an electron-hole pair as long as it remains within the semiconductor $\tau_{pc} > \tau_r$.

In summary, our analysis concludes that Auger processes are not important in the concentration range $1-10 \times 10^{16} \text{ cm}^{-3}$ in the temperature range from about 14°K to 100°K. This conclusion leaves open the question of the nature of the thermally activated process at the "device temperature" of 77°K. From the magnitude of the activation energy, we speculate that we are dealing with recombination at an inversion layer at the surface⁽¹⁴⁾ though recombination at internal inversion layers caused, for example, by small grain boundaries or dislocations not observable by ordinary x-ray techniques, cannot be ruled out.

Publications:

1. Electrical Properties of In Doped Lead Tin Telluride, K. Weiser, A. Klein, M. Ainhorn, Applied Physics Letters, 34, 607 (1979).
2. Electrical Behavior of Group III Impurities in Lead Tin Telluride, Manuscript in preparation.
3. Recombination of Excess Carriers in Lead Tin Telluride, Manuscript in preparation.

Presentations:

1. Properties of Lead Tin Telluride, presented at Spring Meeting of the Israeli Physical Society, April 1979.
2. Status Report on Contract, Seminar at Wright-Patterson Air Force Base, June 1979.
3. Electrical Properties of In Doped Lead Tin Telluride - Seminar at Naval Research Laboratory, Washington DC, June 1979.

Personnel Associated with Contract:

Professor K. Weiser, Project Leader, 1/3 salary support by grant.
Mr A. Klein, Engineer, full time; not supported by grant
Mr M. Ainhorn, Engineer, full time support by grant for 15 months
Mr E. Rieback, Engineer, 1/3 support for 15 months

Coupling Activity: Material grown under the grant was used by Miss D. Shumyatski to produce diodes as part of an M.Sc. thesis in the Department of Engineering, Technion Institute of Technology, and by Mr Y. Kleinman for etching studies as part of his M.Sc. degree in the same Department.

Patent Applications: None.

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