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PHOTOTHERMAL IONIZATION SPECTROSCOPY

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Photothermal ionization spectroscopy (PTIS) is one branch of the phenomena of photoconductivity. PTIS was discovered by T. M. Lifshitz and F. Ya Nad when they studied photoconductivity of shallow hydrogenic impurities in germanium.¹ It was found that sharp lines occurred at energies below the threshold of the particular impurity and that their energies corresponded precisely to the energies of the absorption lines produced by the excitation of carriers from the ground state of an impurity to bound excited states.² Theoretical considerations³ showed that the photoconductivity peaks are produced by a two step process involving first excitation from the ground state of an impurity (e.g. donor) to one of the excited states, then subsequent ionization by a phonon into the conduction band, Fig. 1 (or valence band if we deal with acceptors). The free carriers created thereby increase the conductivity of the sample. PTIS is a much more sensitive technique of detecting impurities than IR absorption spectroscopy, mainly because of the sample under investigation serves simultaneously as absorber and detector. This superior sensitivity has made the use of PTIS to spread rapidly for studies

* Work performed under the auspices of the United States Atomic Energy Commission.

of impurities not only in the elemental semiconductors (diamond, silicon and germanium) but also in gallium arsenide, gallium phosphide, cadmium telluride and other semiconductors.

Overlapping of the wave functions of the excited states of the impurities becomes smaller as a material becomes purer; therefore the narrower are the photoconductivity peaks. Making full use of these narrow line widths calls for very high resolution spectroscopy; Fourier Transform Spectroscopy,⁴ which uses interference instead of dispersion as in conventional spectrometers is capable of achieving the required resolution in reasonably short times. The interferogram can be transformed into the spectrum within seconds using a Fast Fourier Transform algorithm in a small computer. While simple PTIS is limited to the majority impurities it was demonstrated that the use of band edge light ($h\nu > E_g$) makes it possible to simultaneously observe both majority and minority impurities.⁵

Using high-purity germanium as an example we would like to demonstrate the wide spectrum of useful applications and also the limitations of PTIS. Not only is the method a useful analytical tool but its use has also led to many interesting discoveries in other fields. We will complement our own results with some of the beautiful results obtained by other groups using PTIS.

THEORETICAL CONSIDERATIONS

W. Kohn presented the first comprehensive theoretical model for shallow impurities in silicon and germanium.⁶ The model is based on the assumption that at low temperatures, where a substitutional donor-impurity in n-type

material is deionized (i.e. neutral), the impurity consists of a singly-charged positive "core" and a single negative-charge moving in the Coulomb field of the fixed impurity ion. The situation is very similar to the one in the hydrogen atom where an electron moves in the vicinity of a proton, but a number of modifications have important consequences. First, the "hydrogenic" impurity is not in a vacuum but in a lattice with a dielectric constant, ϵ , so that all energies emerging from the hydrogen atom are reduced by a factor ϵ^2 and the linear dimensions of the wave functions are increased by a factor ϵ . Furthermore, the electric charge moving in the field of the impurity ion does not have the mass, m , of the free electron but an effective mass m^* which is anisotropic (mass tensor) has to be used. The dielectric constant ϵ and the reduced mass together result in approximately 1000 times smaller energies than in the hydrogen atom, while the orbits of the ground and excited states are extremely large and extend over thousands of crystal cells. The so called "effective mass theory" is very accurate only far away from the impurity where the electric field of the core decreases precisely with a $1/r$ law (r = distance). This is the reason for the high precision with which theory can predict the energies of the excited states. A major problem arises in the immediate vicinity of the impurity ion where the electric field deviates strongly from a Coulomb field, and where the use of the macroscopic dielectric constant ϵ is not valid. For these reasons ground state energies and absorption cross sections cannot be predicted with accuracy. Refined theories have recently been developed for donors⁷ and acceptors^{8,9,10} separately. These give a much better description of the real situation, but the very high resolution results obtained recently with high-purity germanium revealed numerous excited states which are not assignable by theory.

EXPERIMENTAL PARAMETERS

SIGNAL FORMATION

With minor modifications PTIS uses the following experimental set up. A semiconductor sample with ohmic contacts is held at a temperature where practically all its majority impurity atoms are deionized (i.e. neutral). Chopped excitation light from a spectrometer or interferometer is guided through a light pipe to the sample. This causes a change Δn of the free carrier concentration n . If a constant current is maintained in a sample of the area A and the length ℓ we have:

$$\text{Voltage drop } V \text{ without light } \frac{I\ell}{A \mu e n} \quad (1)$$

$$\text{and Voltage drop } (V-\Delta V) \text{ with light } \frac{I\ell}{A \mu e (n+\Delta n)}$$

where μ is the free carrier mobility and e is the charge of the carrier (i.e. 1.6×10^{-19} C). Combining these two equations and assuming that $\Delta V \ll V$ and $\Delta n \ll n$ we have

$$\frac{\Delta V}{V} = \frac{\Delta n}{n} \quad (2)$$

This can also be expressed in the form:

$$\Delta V = (\Delta n/n) \ell |\vec{E}| \quad (3)$$

where $\vec{E}$ is the electric field in the sample.

The upper curve of Fig. 2 shows the dependence of the current upon the electric field in sample 313-0.2 ($N_A - N_D \cong 10^{10} \text{ cm}^{-3}$) held at a temperature of 4.25°K. Space charge effects at contacts cause an increase in the sample impedance at high current levels, but at low levels the sample behaves as a linear resistor of about 10^5 ohms. The lower curve of Fig. 2 shows the variation of the signal ΔV produced by the chopped broad band excitation light ($h\nu < 120 \text{ meV}$) as a function of the electric field. At low levels the behavior $\Delta V \propto |\vec{E}|$ is as predicted by Eq. (3). When the electric field exceeds $\sim 100 \text{ mV/cm}$ a super linear increase in ΔV occurs. Field assisted ionization of holes in excited states close to the valence band is responsible for this effect. At high fields ($> 400 \text{ mV/cm}$) saturation occurs. Although a detailed interpretation of these results is not available, the behaviour is typical of all samples tested.

Sh. M. Kogan derived expressions for the dependence of the signal upon the net-impurity concentration and the degree of compensation.¹¹ Within certain limits the signal does not depend on the net-impurity concentration. This is in contrast to absorption spectroscopy and explains the high sensitivity of PTIS. At very low impurity concentrations the signal begins to decrease linearly with decreasing impurity concentration. In the presence of more than one majority impurity, the ratios of corresponding photoconductivity lines of the different impurities are, however, practically equal to the ratio of their individual concentrations. Hall effect measurements can be used to determine the absolute net-impurity concentration.

NOISE

Noise provides an ultimate limit to the sensitivity of the photothermal ionization technique. At low temperatures noise arises mainly at contacts. We find that p-type germanium can be contacted best with InGa eutectic but no suitable low-noise contact has been developed for n-type material. Contacting n-type material is complicated by the fact that introduction of n-type impurities into the surface layers must be avoided since this would cause false spectra.

The inherent noise produced by the dc-dark current* becomes important when the temperature is increased. This noise source becomes especially important when deep impurities are to be investigated in the presence of a high concentration of shallow impurities. Impact ionization and surface breakdown become sources of noise at higher electric fields.

Using a spectrometer Sh. M. Kogan determined the impurity concentration where the signal to noise equals one to be approximately 10^7 cm^{-3} .¹¹ Our experimental results indicate that the use of an interferometer decreases this limit by a factor of 100.

SIGNAL PROCESSING

As in most optical experiments, light chopping is used to produce a square-wave signal which is amplified by high-Q tuned amplifier and rectified by a synchronous rectifier. A standard "lock-in" amplifier with differential input is used for this purpose. Some improvement in the signal-to-noise ratio can be realized by digital integration.

* Sh. M. Kogan ascribes this noise to the generation-recombination processes.

RESULTS ON HIGH-PURITY GERMANIUM

Of all semiconductors, germanium can be produced with the highest purity and the best crystallography.^{12,13} It is therefore an ideal material to use for high-resolution infrared spectroscopy, and several laboratories are engaged in studies of this type. Our own efforts have been directed mainly at using the technique as an analytical tool to define the impurities in our germanium crystals--particularly acceptors, which are dominant in our case.¹⁴ On the other hand, a M.I.T. Lincoln Laboratory group has concentrated on donor measurements and has achieved resolutions as good as 0.004 meV.¹⁵ A group at Clarendon Laboratory (Oxford, Great Britain) is also working in this area; its recent work has included high-resolution simultaneous detection of donors and acceptors by using band-edge light ($h\nu > E_{\text{gap}}$).¹⁶ The group at the Institute of Radio Engineers of the U.S.S.R. Academy of Sciences in Moscow who originally developed the PTIS technique and also the band-edge light method has a continuing program of work.

SHALLOW HYDROGENIC IMPURITIES

Measurements on shallow impurities such as the common substitutional group III acceptors and group V donors in germanium are relatively simple to perform using PTIS. The cross section for the absorption of a photon by a carrier in the ground state, and the transition probability from the ground to a bound excited state are both high. This makes the technique very sensitive.

The most common residual shallow impurities observed in our studies of high-purity germanium are aluminum (Al) and phosphorous (P). While phosphorous segregates normally, aluminum behaves in an unexpected manner in

crystals grown from a quartz crucible. Since aluminum fails to segregate, a severe problem arises in this case in attempting to remove it from germanium by zone purification. The source for the unusual behaviour of Al and methods of avoiding it are under investigation and results will be published shortly. We are also able to detect boron near the seed end of some crystals. Due to its high segregation coefficient this group III acceptor plays no significant role along most of the crystal length. A spectrum containing lines of boron, aluminum and phosphorous is shown in Fig. 3. The p-type sample was illuminated with band-edge light ($h\nu > E_{\text{gap}}$) which creates free electrons and holes. Some of the electrons deionize a fraction of the minority impurities, in our case phosphorous. In their neutral state they can absorb IR photons and can get photothermally ionized. The free electrons so created recombine, with high probability, with some of the many free holes, reducing the conductivity of the sample. This reduction is expressed by negative going photoconductivity lines. In spite of the wide spread use of InGa eutectic as a contact material, these two acceptors can be detected only rarely in our material and even then in very small concentrations compared to Al. The same is true for group V elements such as Sb, As and also for Li. A number of acceptor and donor spectra of unknown origin were detected. While these play no role in high-purity germanium for detector applications their origin is extremely interesting from a scientific point of view. At least one donor spectrum is strongly dependent on the thermal history of the sample as shown in Fig. 4, recorded at Clarendon Laboratory.* In this case the sample was p-type and band-edge light was used to create the negative going donor lines. Some of these unidentified spectra may be produced by defects or defect-impurity complexes.

* We thank the authors for the kind permission for the reproduction of this spectrum.¹⁶

DEEP, NON-HYDROGENIC IMPURITIES

As discussed earlier, it is not possible to calculate accurately the wave functions of the impurities near its core with the "effective mass theory". While the results are still acceptable for shallow impurities, theory fails completely for deep impurities where the carrier is strongly bound to the core and the potential deviates substantially from the Coulomb type. The results for the excited states, however, are very accurate. Actually the excited state levels for all donors are the same as are those for all acceptors. The wave functions of the excited states extend over very large distances compared with atomic dimensions (many μm) and vanish at the impurity core. Experimental results with acceptors as deep as 90 meV (mercury) demonstrate these facts nicely. It is, however, unnecessary to have a perfect theory to guess that the size of the wave function decreases when the ground state becomes deeper. This means that the optical absorption cross section decreases and the overlapping of the wave functions of the ground state and the excited states become smaller. This results in a reduced transition probability from the ground into the excited states. As a consequence, the sensitivity of PTIS decreases rapidly as the depth of the ground state increases. Despite these difficulties, we have explored higher energies and found several deep acceptors including, in some crystals, surprisingly, beryllium.¹⁴ We assume that this impurity was introduced in the form of particles floating in the air.

Since copper is often mentioned as a serious problem in detector materials and is easily introduced into germanium at relatively low temperatures, we have directed some effort to studying its behavior. Investigations of Cu-doped crystals made by diffusing Cu at 450°C resulted in two acceptors

(A_{Cu}^1 and A_{Cu}^2) at 17.1 and 17.5 meV as shown in Fig. 5. However, we did not detect the substitutional form of Cu (40 meV) often discussed by other authors.^{17,18} The two observed acceptor levels were present in dislocated and dislocation free crystals. There is a strong indication that both A_{Cu}^1 and A_{Cu}^2 are due to an interstitial form of Cu since, on "gettering" in a surface layer of AuGe eutectic at 450°C, the samples returned to their original state. Fast out-diffusion of an interstitial species is the most likely explanation of this result. Control samples (heated without Cu) never showed A_{Cu}^1 and A_{Cu}^2 .

A similar phenomena was observed when Li was diffused into Ge at 400°C. In this experiment the amount of Li was restricted so that the samples did not convert from p- to n-type. Two acceptor levels (A_{Li}^1 and A_{Li}^2) were observed at 20.2 meV and 25.0 meV as shown in Fig. 6. Li is known to combine with deep acceptors to produce shallow acceptor levels.^{19,20} If we extend this observation to interstitial copper (Cu_i) we might expect a similar effect. We therefore assume that $A_{\text{Cu}}^{1,2}$ and $A_{\text{Li}}^{1,2}$ are complexes of a deep acceptor with Cu and Li respectively. The deep acceptor in question might very well be a divacancy (monovacancies are too mobile; also the recombination of Cu with a monovacancy would result in substitutional Cu). The fact that we observe two acceptors in each case, and not one with a ground state split (as it occurs in donors),²¹ is seen from the temperature independence of the ratio of corresponding lines of A_X^1 and A_X^2 . Similar experiments using Ni and probably Na and K are planned.²² Recent observations on dislocation-free germanium grown in pure nitrogen appear to complement the findings with Cu and Li. In this material the acceptor level at ~80 meV which is observed in dislocation-free material grown in pure

hydrogen is completely absent.* Detectors made from N_2 grown material trap strongly, which suggests the presence of a very deep level. We would like to put forward the hypothesis that hydrogen complexes in dislocation-free material with the same deep acceptor as do Cu and Li, producing the 80 meV acceptor (A_H) level. The concentration of A_H is very sensitive to heat treatment, lending further support to this hypothesis. However, we cannot exclude the possibility that oxygen also plays a role in the formation of the semi-deep acceptors.

The limitation of PTIS in regard to its sensitivity to deep acceptors and donors is illustrated by the fact that the deepest spectral lines observed by anyone in germanium by this method, so far as we know, corresponds to substitutional copper (43 meV).²³ Great care must be exercised in interpreting the conductivity spectra obtained at higher energies since phonon IR absorption modes also produce conductivity changes. Figure 7 shows a conductivity spectrum in the deep level range. Note that the broad peak at 80 meV is not the 80 meV level seen in Hall effect measurements on dislocation-free germanium. The peak shown in Fig. 7 is present in both dislocation-free and normally dislocated germanium.

OTHER SEMICONDUCTORS

PTIS has also been successfully applied to silicon technically the most important semiconductor. Figure 8 shows spectra of very pure n- and p-type silicon in which phosphorous and boron are the only impurities.**¹⁶ At these

* Shown with conductivity measurements from 300°K to 5°K.

** We thank the authors for the kind permission for the reproduction of this spectrum.

high purity levels ($N_D - N_A \sim 5 \times 10^{14} \text{ cm}^{-3}$ and $N_A - N_D \sim 10^{13} \text{ cm}^{-3}$) absorption spectroscopy is quite impossible.

A. T. Collins and E. C. Lightowers applied PTIS to natural and synthetic semiconducting diamond.²⁴ They obtained spectra of the neutral acceptor aluminum. Since diamond is not nearly as pure ($n_{\text{Ae}} \approx 10^{17} - 10^{19} \text{ cm}^{-3}$) as the above mentioned semiconductors Ge and Si, complicated features were observed in their spectra which are ascribed to impurity-impurity interactions. In III-V and II-VI compound semiconductors both donors and acceptors have been investigated with PTIS. That the method is extremely valuable for high-purity epitaxial layers was demonstrated in the case of p-type GaAs by R. F. Kirkmann and R. A. Stradling.²⁵ They identified the acceptors carbon and zinc in samples with $N_A - N_D \sim 10^{14} \text{ cm}^{-3}$ and thicknesses of around 20 to 50 μm . In n-type GaAs, spectra of tin and selenium were reported.²⁶ Application of magnetic fields made the observation of Zeemann fine structure possible. Further materials investigated by PTIS included InP and CdTe. The latter is of special interest to the radiation detector community. At least six different donors were reported by P. E. Simmonds, R. A. Stradling, J. R. Birch and C. C. Bradley.²⁷ Magneto-optical experiments also revealed a number of important material parameters. To our knowledge no studies have been made of mercuric iodide, a material of potential interest for radiation detectors.

CONCLUSIONS

Results obtained in a number of laboratories with various semiconductors show that photothermal ionization spectroscopy is particularly well suited to analysis of high-purity materials and of the shallow donors and acceptors.

Conventional IR absorption spectroscopy is only useful in germanium at impurity concentrations greater than 10^{14}cm^{-3} , but PTIS provides unambiguous analysis of all shallow impurities in high-purity germanium down to concentrations below 10^6cm^{-3} . Knowledge of the existence of several unidentified acceptors and donors detected by this method might lead to a better understanding of defects and defect-impurity interactions. The deepest acceptor observed in Ge is substitutional copper with a ground state energy of 43 meV. How much deeper one can go with PTIS cannot be predicted since the optical absorption cross section and the transition probability both decrease rapidly with the depth of the level. PTIS also has sufficient sensitivity for investigation of very pure, thin or small samples such as epitaxially grown layers on semiconductors.

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FIGURE CAPTIONS

- Fig. 1. Schematic presentation of the two processes leading to photothermal ionization of a donor-electron in germanium.
- Fig. 2. Photothermal ionization signal (lower curve $\bullet$) and dc-current (upper curve $\times$) in function of the electric field in sample 313-0.2; temperature $T = 4.25^\circ$; net-acceptor concentration $N_A - N_D \sim 10^{10} \text{ cm}^{-3}$; sample dimensions: $8 \times 8 \times 8 \text{ mm}$.
- Fig. 3. Spectrum of sample 362-5.9 containing the acceptors boron (B) and aluminum (Al). Band-edge light ($h\nu > E_{\text{gap}}$) makes the detection of the minority impurity phosphors (P) possible. Sample Volume $V = 0.4 \text{ cm}^3$, temperature $T = 7.0^\circ \text{K}$. The region above 85 cm^{-1} is magnified by a factor of four.
- Fig. 4. (a) Photoconductivity spectra for p-Ge at 11 K under dark conditions showing aluminum, gallium and an unknown impurity X to be the acceptors present. The bias voltage was 1 V/cm. (b) Same as (a) but at 4 K. (c) Spectrum obtained at 4 K with additional intrinsic illumination revealing Li, P and two unknown impurities S and C to be present as donors. The sample had been heated to 300°C and quickly cooled. (d) Sample annealed at 350°C and cooled slowly (1 hr.). Donor C is now absent and the phosphorus series can be clearly seen.
(Caption was taken from Solid State Comm., 15, 1403 (1974) Ref. 16.)
- Fig. 5. Spectra of sample 342-1.7. Copper was plated and then diffused for 24 hours at 450°C under argon. The two acceptors A_{Cu}^1 and A_{Cu}^2 are due to complexes containing copper. The upper spectrum recorded at 8°K shows also the lines of aluminum. At 10°K most of the aluminum acceptors are thermally ionized as can be seen in the lower spectrum. Sample Volume: 0.15 cm^3 ; $N_A - N_D \approx 2 \times 10^{12} \text{ cm}^{-3}$.
- Fig. 6. Spectrum of sample 235-3.8 recorded at 8°K . A limited amount of lithium was diffused at 400°C for 4 hrs. The two acceptor spectra A_{Li}^1 and A_{Li}^2 are due to complexes containing lithium. Sample Volume: 0.14 cm^3 ; $N_A - N_D \sim 10 \times 10^{10} \text{ cm}^{-3}$.
- Fig. 7. Spectrum of sample 313-0.2; $T = 10^\circ \text{K}$; sample volume: 0.5 cm^3 . The aluminum spectrum is located around 75 cm^{-1} . Phonon absorption is dominant between 200 and 600 cm^{-1} . A strong absorption band due to carbon-hydrogen bonds is visible at 730 cm^{-1} . The minimum of the 1/6 mil thick mylar beam splitter occurs around 840 cm^{-1} .
- Fig. 8. (a) and (c): Photoconductivity spectra for n- and p-Si respectively at 20 K under dark conditions. The bias voltage was 6 V/cm. Phosphorus is the donor in (a) and boron the acceptor in (c). (b) and (d): Same as (a) and (c) but with additional intrinsic illumination, revealing boron and phosphorus as the minority impurities in the n- and p-Si respectively.

(Caption was taken from Solid State Comm., 15, 1403 (1974) Ref. 16.)

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Fig. 1

XBL 7411-8628

Fig. 2

XBL 7411-8633

Fig. 3

XBL 7411-8622

Fig. 4

XBL 7411-8632

Fig. 5

XBL 7411-8631

Fig. 6

XBL 7411-8630

Fig. 7

NBL 7411-8621

Fig. 8

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