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ABSTRACT

Recent results obtained from quenching experiments, electron, gamma-ray, neutron and proton irradiation of germanium are reviewed. Major emphasis is given to the introduction of novel techniques for the study of shallow and deep levels. Explicitly introduced are Photothermal Ionization Spectroscopy (also called Photoelectric Spectroscopy), Deep Level Transient Spectroscopy and High-Q Electron Paramagnetic Resonance. Using as examples the recently discovered hydrogen-related centers and the lithium/lithium-oxygen system in germanium it is shown that a combination of techniques can yield information on composition and structure of defects.

1. INTRODUCTION

Many excellent reviews on the subject of radiation effects and defects in germanium have been presented and published in recent years. Special notice should be taken of the detailed and comprehensive articles by Mashovets (1977) and by Saito and Fukuoka (1979). These articles are excellent sources of past and present knowledge for beginners as well as experts in this field.

It is not my intention to present another complete review of the whole subject of defects in germanium. I would rather like to discuss some recent results and mention several novel techniques for the investigation of defects in germanium. I will not restrict myself to induced defects since there are

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far too many interesting connections between native, quenched-in and radiation induced defects.

Germanium is not a semiconductor which enjoys great interest from the point of view of industrial applications. However, there are at least two good reasons why defects in germanium are and should be investigated. One area where further research is vital is radiation damage in nuclear radiation detectors made from either ultra-pure or lithium drifted germanium. Large volume p-i-n junctions are becoming increasingly important for space-born gamma ray astronomy. The highly energetic particles in outer space cause damage and degradation in such detectors. Length and cost of missions are strongly influenced by the rate of degradation and by possible cycles to anneal the damage. But also in earth-bound instruments such as particle telescopes made from stacks of planar germanium detectors (Hubbard and Haller 1979, Riepe and Protic 1979), the useful lifetime is often limited by the radiation damage.

The fundamental knowledge which can be gained from the study of defects in germanium is especially promising. A few examples may be in order.

The purity of germanium single crystals which can be obtained today has made possible the study of the excited-state spectra of shallow acceptors with very high accuracy (Haller and Hansen 1974, Skolnik et al 1974). These experimental results have stimulated theoretical work which has impact on semiconductors other than germanium (Baldereschi and Lipari 1976).

The high purity of germanium has also led to the discovery of a large number of unknown levels in the band gap which have simply been covered up until recently by too many chemical impurities. Several of these centers are under intense investigation and it has already been established that some of them are complexes involving hydrogen (Haller 1978a, b, 1979; Haller and Hubbard 1978). It is expected that much can be learned from hydrogen in germanium and
subsequently be applied to other semiconductors. Hydrogen in amorphous and crystalline silicon seems to affect strongly the number of dangling bonds and electronic transport properties. Hydrogenated amorphous silicon may lead to low-cost solar cells (Pankove et al 1979).

Ultra-pure germanium may be used successfully in radiation damage studies. Most of the experimental information accumulated over the years has been influenced by the presence of impurities. It should now be possible to investigate truly intrinsic defects. There is possible interference from electrically neutral impurities such as hydrogen, oxygen and silicon. They are in general not well characterized and can be present in concentrations around $10^{14}$ cm$^{-3}$. Special care can be taken to reduce them to much lower levels.

These examples demonstrate that a material as old-fashioned as germanium is at present making a comeback.

The novel techniques for defect investigation which were mentioned earlier are photothermal ionization spectroscopy (PTIS; Lifshitz and Ya Nad' 1965; also called: photoelectric spectroscopy), Deep Level Transient Spectroscopy (DLTS; Lang 1974, Kimerling 1976a, Miller et al 1975 and Miller et al 1977) and high-Q electron paramagnetic resonance (high-Q EPR; Haller and Falicov 1978 and 1979). Together with the well established techniques such as Hall effect and conductivity measurements, they can generate detailed quantitative information on concentration, energy level spectrum, structure and composition of defects in a semiconductor. These novel techniques will be described briefly along with typical examples for their application.

2. Quenched-In Defects

Quenching experiments have had a long, often confused history. Interference from fast diffusing interstitial impurities (copper in germanium)
has invalidated many of the early results (Logan 1956). Kamiura and Hashimoto (1978a, b) have performed many quenching experiments in recent years and have clearly characterized the role of copper as fast diffuser and multiple acceptor in germanium. This is an appropriate place to mention another long-standing problem copper has generated. Studies of the drift of interstitial copper at very high temperatures (800-900°C) in an electric field (Fuller and Severiens 1954) have shown copper to be positively ionized. This result has tempted experimenters to assigning donor activity to interstitial copper at low temperatures (Hall and Racette 1964). No experimental evidence exists up to the present time that such a donor level exists. Our own PTIS and DLTS studies of copper doped ultra-pure germanium have not revealed any unknown shallow or deep donor levels (Haller et al 1979). We conclude that interstitial copper is a very "deep" donor with its level inside the valence band analogous to atomic hydrogen where the electron is estimated to be bound with at least one but probably as much as 6 eV (Wang and Kittel 1973; Pickett et al 1979). Besides the clear recognition of the role of copper, Kamiura and Hashimoto have discovered one or more shallow acceptor levels (Figure 1). They eliminate the possibility that the new acceptor is due to interstitial copper or group III impurities. Vacancies or vacancy-clusters with or without chemical impurities seem to be the most likely candidates for the new acceptor level. These results should be reexamined in respect to the role of oxygen and hydrogen in the crystals used for the experiments. In a further group of experiments the same authors have observed a quenched-in acceptor which displays "reverse" annealing in the sense that the fraction of annealed acceptors increases with decreasing annealing temperature. A divacancy model is proposed. Again one should examine the possible role of oxygen and hydrogen.
It also would be useful if one would try to determine the position of the energy level of the particular acceptor with either Hall effect measurements or the deep level transient spectroscopy technique.

In dislocation-free, ultra-pure germanium an acceptor at $E_V + 80$ meV was found which shows "reverse" annealing and is clearly hydrogen related (Haller et al 1977). The proposed divacancy-hydrogen model ($V_2^2H$) recently obtained strong support from gamma-irradiation experiments (Vasilyeva et al 1980). It was found that the $V_2^2H$ level at $E_V + 80$ meV can be produced by irradiation of hydrogen-atmosphere-grown, dislocated, ultra-pure germanium. The extremely small introduction cross-section found is in good agreement with the divacancy model.

It is surprising to see how an old technique such as quenching from high temperature when performed carefully can yield new results.

3. ELECTRON AND GAMMA-RAY DAMAGE

Electrons or gamma-rays are preferred projectiles for the irradiation of semiconductors because they can create point defects only. One would expect a relatively simple spectrum of defects under such circumstances. That this is not the case has been pointed out by many authors and was clearly summarized by Mashovets (1977). A novel technique may in this field bring new results and hopefully better understanding. Kimerling (1976b) and Mooney et al (1979), have used for the first time deep level transient (capacitive transient) spectroscopy to study electron damage in germanium. Commercially available diodes were bombarded at room temperature with 1 MeV electrons from an accelerator. The results are of preliminary nature insofar as the germanium was not very well characterized. Kimerling reports centers at $E_C-0.25$ eV, $E_C-0.30$ eV, $E_C-0.34$ eV, $E_V + 0.25$ eV and $E_V + 0.16$ eV. Mooney et al found levels at $E_C-0.2$ eV, $E_C-0.4$ eV and $E_V + 0.25$ eV.
A typical capacitance transient spectrum is shown in Figure 2. More recently, L. Kimerling together with the author, has performed DLTS spectroscopy of electron damaged p-i-n diodes made from ultra-pure and lightly n-type germanium. None of the levels found in doped germanium were created by e⁻-irradiation at 6 K. Two new electron traps, \( E_1 \) at \( E_C - 0.18 \) eV and \( E_2 \) at \( E_C - 0.28 \) eV with capture cross-sections \( \sigma(E_1) > 2.3 \times 10^{-14} \text{ cm}^2 \) and \( \sigma(E_2) = 9 \times 10^{-15} \text{ cm}^2 \) were observed. The two centers are stable to \( T \sim 450 \) K. The large capture cross-sections together with very small introduction rates indicate large defect complexes involving more than one vacancy.

4. **NEUTRON AND PROTON DAMAGE**

Damage produced by energetic neutrons and protons seems not to be a favorite subject for radiation damage experts. This may be due to the complexity of the defect spectrum. However, from a practical point of view, this kind of damage is very important. Nuclear radiation detectors made from germanium have many applications where their useful lifetime is limited by radiation damage. The p-i-n diode structure of such detectors lends itself ideally to Deep Level Transient Spectroscopy measurements. No reports on such investigations have been published. Another possibility of studying the radiation damage in nuclear radiation detectors lies in the measurement of charge-trapping. Electrons and holes produced by radiation can be trapped at deep levels due to defects. Such trapping leads to a broadening of the lines of a gamma-ray spectrum (Figure 3). There is no straightforward analytical way to derive trap parameters from the spectrum degradation. The measurements performed on a pair of coaxial high-purity detectors with opposite electrode configurations by Pehl et al (1979) brings ample proof that neutrons produce deep acceptor traps. The proton damage studies have not yet yielded such
clear-cut results. Careful observation of the gamma-ray spectrum degradation in function of the operating temperature of detectors may lead to the position of the neutron-produced acceptor traps. Darken et al (1979) have analyzed the data of Pehl et al and propose a model which explains many of the time-dependent features of the gamma-ray spectrum degradation with the charge-state changes of deep acceptors in the depletion layer of p-i-n diodes. Hubbard and Haller (1980) are conducting a search for neutral impurities or other defects in ultra-pure germanium which could influence the neutron damage spectrum. So far differences in spectrum degradation of around 40% between various high-purity germanium single crystals have been found. This work, performed with 5 mm thick planar p-i-n diodes, also confirms the predictions of Darken's et al defect model. In addition to the charge-state dependent trapping phenomena as described by Darken et al, Hubbard and Haller (1980) have been observing changes in trapping which are independent of the bias on the device but depend on the time elapsed after the end of a neutron exposure. This clearly indicates that small defects are mobile at the detector operating temperature of around 80 K. Neutron and proton damage in p-i-n structures are excellent examples for the case where a lot of new information could be gained from the application of a novel technique (i.e., DLTS).

The work on proton damage by Barker and Palmer (1979) is an very interesting contribution. They found that the atomic displacement cross-sections for 25-300 MeV protons are much larger than predicted by a simple binary elastic-collision model. All results were obtained from channeling experiments. These require, due to their low sensitivity, rather high concentrations of defects (> 1% of atoms displaced). No electrical measurements were performed. In view of the strong interaction of hydrogen with amorphous silicon it is not clear if the proton damage results could be affected by Ge-H bonding in some way.
5. GROWN-IN POINT DEFECTS

5.1. THE Li/LiO CONTROVERSY

Lithium is a well-studied interstitial shallow donor (Reiss et al 1956). Together with oxygen it forms a shallow donor complex (Fox 1966). IR-absorption spectroscopy (Aggarwal et al 1965) and more recently PTIS in pure crystals ($n_{A^-} = 10^{12}$ cm$^{-3}$), indicated a donor spectrum consisting of two "hydrogenic" sets of lines (Faulkner 1969). The broad, shallower set was assigned to lithium and the extremely sharp "S"-set to lithium oxide (Secombe and Korn 1972, Skolnik et al 1974 and Hall 1974). This assignment was arbitrary and not understood especially for pure crystals where the lithium concentration can be thousands of times smaller than the oxygen concentration and all lithium is expected to be bound to oxygen at low temperatures.

Bykova et al (1975) proposed a different model claiming that both line series were due to different kinds of lithium complexes. The extreme difference in line width of the two series was never discussed. This feature was understood as soon as the first uniaxial stress experiments with photothermal ionization spectroscopy were performed with germanium samples containing one hundred to one thousand times more oxygen than lithium (Haller and Falicov 1978 and 1979). Whereas all group V impurity donors change their ground state energy in respect to the conduction band, the "S"-donor did not change, i.e., the hydrogenic series of "S"-lines do not change their position in the spectrum under stress (Figure 4). This means that all the "S"-lines are also insensitive to any residual random stresses. A second feature was that the ratio of the broad-line set ascribed to lithium to the "S"-set increased with temperature. This suggests that the two line sets belong to one donor system. A detailed group theoretical treatment shows that a donor
with a symmetry along \langle 111 \rangle which tunnels in between all four equivalent \langle 111 \rangle directions can explain the experimental findings. The spectrum due to the interstitial uncomplexed lithium can be observed when the lithium concentration reaches or exceeds the oxygen concentration or when lithium containing samples are rapidly quenched from temperatures above 300°C (Figure 5).

Confirmation for the model was found in electron paramagnetic resonance measurements. A large cylindrical germanium sample containing \(- 10^{13}\) LiO donors acting as a dielectric cavity with Q-factors up to \(10^6\) was used in a superheterodyne 25 GHz spectrometer (Figure 6). Four lines with varying g-factor were recorded (Figure 7). This result indicates a single valley donor, precisely what one expects if one takes into account that the tunneling frequency of the LiO-donor lies around 2 GHz, much lower than the spectrometer frequency. The high Q-factor of pure semiconductor dielectric cavities increases both sensitivity and stability of EPR spectrometers. It is expected that this technique will find application in many experiments involving pure semiconductors where high sensitivity is essential.

5.2 HYDROGEN RELATED DEFECTS

A large number of hydrogen related centers have been identified in germanium (Haller et al 1977, Haller 1978a, 1979). The results as of one year ago have been summarized by the author at the Nice Conference (Haller 1979). Let me mention here the most important earlier findings and then summarize the more recent results.

In dislocation-free hydrogen-atmosphere grown germanium, one finds a single acceptor at \(E_V + 80\) meV. The concentration of this acceptor can reversibly be changed by heat treatments up to \(- 400^\circ C\). A quantitative model based on a divacancy-hydrogen complex \((V_2H)\) has been proposed (Haller et
The $V_2H$ complex fits into the series of divacancy donor complexes proposed by Mashovers (1977). The $V_2H$-model has obtained further support from the gamma-irradiation experiments by Vasilyeva et al., men earlier.

Other hydrogen related shallow acceptors $A_{1,2}$ and a donor first found by Hall (1975). These levels can be generated by rapid quenching from temperatures around 400°C and annealing of hydrogen-atmosphere-grown germanium. The hydrogen connection was found in an experiment involving hydrogen as well as deuterium-atmosphere-grown single crystals (Haller 1978 a). An isotope shift in the ground state energy of these two centers is direct proof of the presence of hydrogen (Figure 8). Recently uniaxial stress experiments with the acceptors $A_{1,2}$ show that the centers have a symmetry much different from substitutional impurity acceptors (Figure 9). The line series of $A_1$ and $A_2$ in the IR-spectrum do not split under stress. The intensity ratios of the $A_1$ to the $A_2$ lines in function of temperature to low precisely a Boltzmann factor $\exp(\Delta E/kT)$, with $\Delta E = 1.1$ meV, the energy difference between the $A_1$ and $A_2$ ground states (Figure 10). These experimental results have led to the conclusion that $A_1$ and $A_2$ belong to only one center. A model of a hydrogen atom trapped at and tunneling around a substitutional silicon impurity (Figure 11) explains all the experimental data (Haller, Joos and Falicov 1980). The unknown acceptor $A_6$ (Haller 1978b) shows features very similar to $A_{1,2}$. A ground state component $A_6$ lying 1.9 meV above the lowest component has been found. As in the case of $A_{1,2}$, there is no splitting proportional to applied uniaxial stress (Figure 12). There is speculation that the $A_{6,6}$ center is a substitutional carbon atom trapping a hydrogen atom in its vicinity.

Besides the discussed hydrogen-related centers, several multivalent acceptor-hydrogen complexes have been reported (Haller and Hubbard 1978). It appears that hydrogen plays a role very similar to the one of lithium, which
can pair with various electron-deficient sites (i.e., single and multivalent acceptors). Closely related to the hydrogen complexes in germanium are the experiments by Picraux and Vook (1978) and Picraux et al. (1979) in silicon. Using implantation, alpha-backscattering, channeling and nuclear reactions, they did an extensive study on the distribution and position of hydrogen in the silicon lattice (Figures 13 and 14). They conclude that atomic hydrogen sits in an antibonding direction, 1.6 Å away from a Si atom. It is not obvious if these results can be applied to germanium.

**CONCLUSIONS**

Because of space limitations, I have not discussed areas such as muon spin resonance, exciton condensation on defects at low temperatures, electron-hole drop nucleation at defects nor any line-defect studies. To mention these areas must suffice. There is a lot of activity in these fields and new results and/or new techniques may evolve. I hope to have shown that there are now several novel techniques available which promise new results. In particular, I have hopes that the microstructure and composition of some defects can be determined. The role of hydrogen has been discovered in recent years. In pure semiconductors it is much more important than expected. Applications in silicon, crystalline and amorphous, seem to be at hand in the form of solar cells.

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FIGURE CAPTIONS

Figure 1. Temperature dependence of the hole concentration of a specimen quenched from 900°C (from Kamiura and Hashimoto 1978b).

Figure 2. Deep Level Transient Spectrum of electron irradiate germanium diode (from Mooney et al. 1979).

Figure 3. Gamma-ray spectrum degradation in a high-purity germanium p-i-n diode (from Pehl et al. 1979).

Figure 4. The LiO spectrum at zero stress a) and a stress of $1.5 \times 10^9$ dyn cm$^{-2}$ along [111] (from Haller and Falicov 1978).

Figure 5. Stress spectra of two germanium samples containing different concentrations of lithium.

Figure 6. EPR cavity containing the germanium cylinder acting as a dielectric cavity with extremely high-Q factor.

Figure 7. The g-factor of the LiO in germanium (from Haller and Falicov 1979).

Figure 8. Spectra of samples of germanium crystals grown in a hydrogen and a deuterium atmosphere. The isotope shift in the ground-state of D shifts all lines to lower energies in the deuterium sample (from Haller 1978a).

Figure 9. Spectra of acceptors A$_1$, A$_2$ boron and aluminum at three values of stress along [111]. Note that A$_1$, A$_2$ lines do not split under stress. Unit of stress: dyn cm$^{-2}$.

Figure 10. The ratio of the A$_1$ (D) and (C) lines to the A$_2$ (D) and (C) lines (circles and crosses) follow precisely a Boltzmann factor (continuous line). The ratio of the sum of (C) and (D) lines of A$_1$ and A$_2$ to the chemical acceptor aluminum is constant (squares and x's).
Figure 11. The $A_{1,2}$ center consists of a substitutional silicon impurity trapping a hydrogen which tunnels between four equivalent interstitial positions (from Haller et al. 1980).

Figure 12. Spectra of $A_6$ at four different values of stress along 111. The $A_6$ lines do not split. Unit of stress: dyn cm$^{-2}$.

Figure 13. The $\langle 110 \rangle$ axial angular distribution as observed and as calculated for the indicated sites of deuterium. Triangles: D-atom signal; circles: Si-atom signal (from Picraux et al. 1979).

Figure 14. Schematic of the (110) plane in Si showing several identified interstitial impurity centers (reference as in Figure 13).
Figure 1

- 1st level of copper 
  \( (E_V + 0.04 \text{ eV}) \)
- \( E_V + 0.008 \text{ eV level} \)
- \( T_Q = 900^\circ C \) (p-type)
Figure 2
$\text{Stress} = 1.5 \times 10^9 \text{ dyn} \cdot \text{cm}^{-2}$, $\vec{F} \parallel [111]$

Figure 4
STRESS = 1.5 \times 10^9 \text{ dyn cm}^{-2}

\vec{F} \parallel [111]

PHOTOELECTRIC RESPONSE (ARB. UNITS)

65 70 75 80

Figure 5
THIN WALL STAINLESS STEEL TUNING RODS

RG 53/U WAVEGUIDE

1 cm

TUNING PLUNGER

Ge SAMPLE

TE011 CAVITY

STYROFOAM CUSHION

HOLE FOR OPTICAL PUMPING

SLIDING SHORT

Figure 6
Figure 7
Figure 8
Figure 10

Graph showing the relationship between ratio and temperature (T(K)).
Figure 12

GALLIUM
ALUMINIUM
BORON

F II [111]
STRESS=0

STRESS=2.45x10^7

STRESS=4.76x10^7

STRESS=9.74x10^7

ENERGY(cm⁻¹)

PHOTOCONDUCTIVE RESPONSE
Figure 13

- Si-D bond = 1.6 Å
- Antibond direction

- Si-D bond = 0.81 Å (Singh et al. calc)
- Antibond direction

- Bond direction (same as for 1.6 Å)
Figure 14