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RECENT ADVANCES IN COMMON SEMICONDUCTOR MATERIALS

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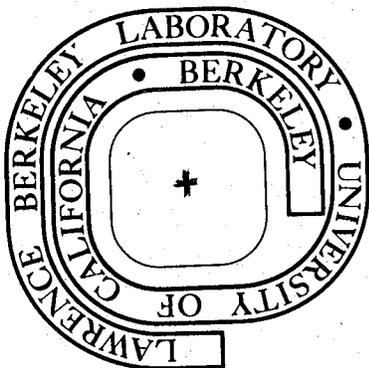
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### Introduction

Semiconductor crystals have been used for more than 30 years in the production of nuclear radiation detectors. From the very narrow depletion layers of diffused p-n-junctions of the very early days, we have come to large volume high-purity germanium detectors. A great effort in research and development of semiconductor materials and methods was necessary to arrive at the present results. It is not possible to honor the numerous contributions, inventions, and discoveries in this lecture. The reader is referred to books of Dearnaley and Northrop<sup>1</sup> and Bertolini and Coche<sup>2</sup> which give a lively description of work done up to about ten years ago.

Around that time, Hall at General Electric predicted<sup>3</sup> that it maybe possible to develop germanium pure enough that no lithium drift process was needed to produce large volume radiation detectors. Today, we are in a position to fully appreciate Hall's good judgment. Detectors made from high-purity germanium are commercially available. A large part of this lecture will deal with the recent exciting results obtained with ultra-pure germanium.

Silicon purification and crystal growth for detector applications have not experienced as rapid a progress as germanium. This in part is due to the much larger difficulties encountered in the silicon processes and to the rather limited interest on the part of commercial places in the problem. It can be rather difficult at times to obtain detector grade silicon.

Rather than spending time on the Si-problem, I will try to summarize recent results obtained from studies of solid phase epitaxy, of ion-implantation and of regrowth of amorphous layers. Many of these new results have been applied to detector making.

With the limited time and space available, I have to assume that the basic physical concepts of a semiconductor are known.

### Novel Techniques

#### 1) Solid Phase Epitaxy (SPE)

Mayer's group at the California Institute of Technology has worked for several years on SPE.<sup>4,5</sup> They have shown that a metal in contact with silicon or germanium single crystals can dissolve up to several percent Si or Ge at temperatures far below the eutectic point. Upon cooling, the dissolved Si or Ge regrows epitaxially on the bulk semiconductor, moves to the other metal surface and/or precipitates depending on temperature, cooling rate, etc. (Figs. 1 and 2). The regrown layer incorporates metal atoms up to the solubility concentration.

SPE can be used to produce thin doped layers. The aluminum-germanium system has already been successfully applied in high-purity germanium detector fabrication.<sup>6</sup> A very important condition has to be met in order to achieve uniform regrowth layers with the SPE technique. The interface between metal and semiconductor has to be as free of any oxides or contaminants as possible.

#### 2) Silicides and Germanides

If very large amounts of semiconductor material are dissolved in a metal layer (more than ~30%), one talks about silicides<sup>7,8</sup> or germanides.<sup>9</sup> Figure 3 shows that such compounds have metallic character and form Schottky barriers. The big advantage over evaporated or otherwise deposited Schottky barrier contacts is the intimate contact between semiconductor and metal without any interface layer. The physics of such Schottky barrier devices is well understood and does not depend on ill defined oxides and ions at the interface. Silicides and germanides form at very low temperatures (e.g., Pd<sub>2</sub>Si:200°C).

They have found commercial application in power-rectifiers and fast diodes. We have obtained some experience with palladium and platinum silicides and also palladium germanides used in nuclear detectors. They have several distinct advantages such as high ruggedness and stability. A problem concerning the uniformity of the dead layers produced by such metal-semiconductor compounds can arise. We have observed that one can obtain very inhomogeneous windows with large variations over small distance which we attribute to a formation of many little silicide/germanide fingers reaching relatively deep into the semiconductor bulk. We are convinced that this phenomenon can be avoided by proper choice of parameters such as crystal orientation and temperature.

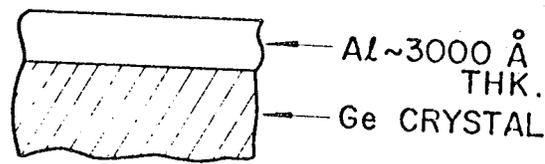
#### 3) Ion Implantation and Annealing of Amorphous Layers

Ion implantation has found wide application in semiconductor device production. Still this technique has found very little use in nuclear detector fabrication. This may be in part due to the high cost of an ion-implantation facility. On the other hand, it is clear that the results from early work of on ion-implantation were not very encouraging to detector makers. In spite of elaborate annealing cycles, it seemed impossible to remove all the damage produced by the energetic ions colliding with the semiconductor single crystal.

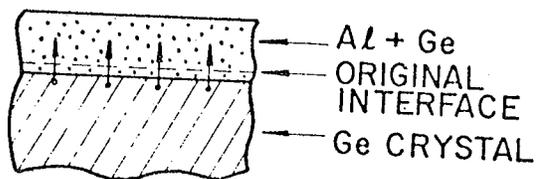
The history of ion-implantation in germanium is especially interesting and typical. The early work Herzer and Kalbitzer<sup>10</sup> and Ponpon, et.al.,<sup>11</sup> demonstrated that implanted boron ions were already electrically active "as-implanted." Little annealing at temperatures around 200°C was sufficient to activate nearly 100% of the ions. Phosphorous ion-implantation on the other hand did not lead so easily to strongly doped layers. The damage produced could not be annealed out fully and only a small percentage of the ions became substitutional donors. These results were accepted as final for a long time.

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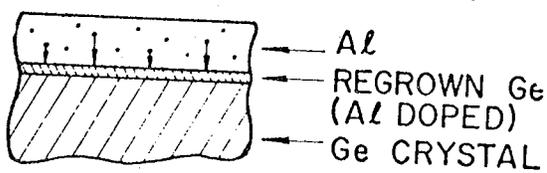
(a) Al EVAPORATION



(b) 300°C HEAT FOR 20 MIN.



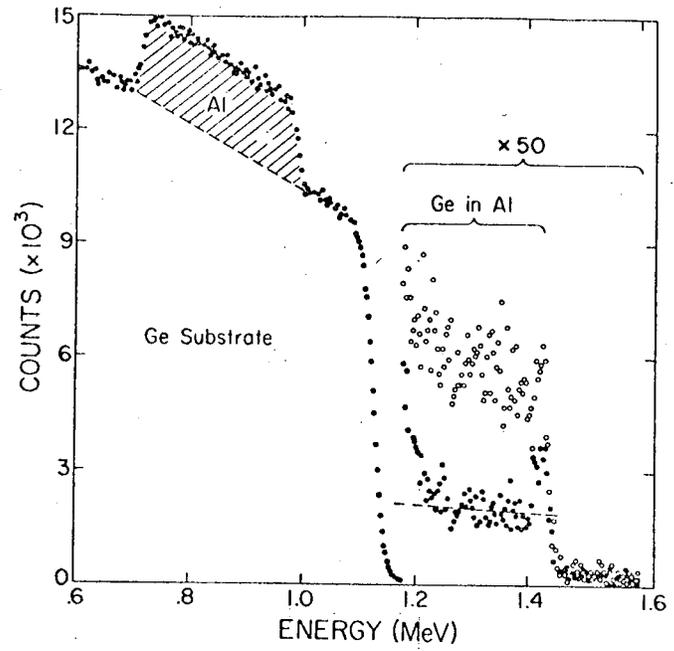
(c) SLOW COOLING (~3°C/MIN.)



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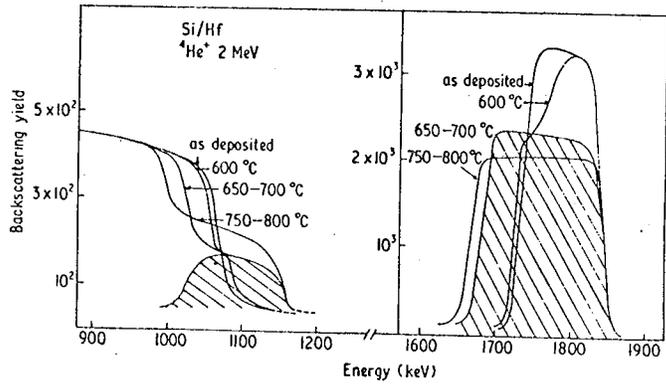
Fig. 1 Schematic diagram illustrating the concept of solid-phase regrowth from a 3000 Å Al film on Ge. At 300°C, Ge diffuses into the Al until the solubility limit of Ge in Al is reached. During slow cooling, the Ge regrows epitaxially on the Ge substrate. Reprinted with courtesy of Ref. 6.

Only the intensive search for a solution of the thin  $n^+$ - contact problem on high-purity germanium detectors brought ion implantation back into focus. Careful work done by Hubbard, et.al.,<sup>12</sup> showed that four parameters were strongly affecting the end results of ion implantation. The surface to be implanted must be free of any oxides in order to minimize damage deep in the semiconductor by light "knock-on" ions (i.e., oxygen). The second parameter is the temperature of the crystal to be implanted, the third, not too important parameter, is the crystal orientation during implantation, and the fourth is the temperature-time relationship of the annealing cycle. The importance of these parameters was pointed out in recent work. Glowinski, K. N. et.al.,<sup>13</sup> found that at room temperature interactions between ion created defects take place which can lead to unannealable complexes. Sigmon<sup>14</sup> suggested that implantation into a cold crystal, (i.e., 77°K) may avoid this problem. The regrowth of silicon crystal surface layers, which were yielded amorphous by silicon ion implantation, was studied by Csepregi, et.al.<sup>15</sup> (Fig. 4). They found that every crystal direction regrows with a typical rate at a certain temperature and with its own degree of crystal perfection. [100] planes regrow fastest and most perfectly. A preannealing stage at only lightly elevated temperatures (e.g., 150°C) prepares the interface between the single crystal bulk and the amorphous layer to obtain a more perfect regrowth.



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Fig. 2 Backscattering spectrum of 1.8 MeV  $He^+$  on specimen of Ge + 6400 Å of Al. The spectrum below 1.20 MeV is independent of heat treatment. Open circles: after 350°C treatment for 15 mins. Filled circles: after subsequent treatment at 250°C for one hour. For comparison purposes, the dashed line shows [Ge] in similar specimen which was only treated at 250°C. Reprinted with courtesy of Ref. 25.



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Fig. 3 Backscattering spectra (of 2 MeV  $He^+$ ) on Hf-Si devices after heating at various temperatures showing the formation of HfSi and HfSi<sub>2</sub> compounds. Reprinted with courtesy of Ref. 26.

Hubbard, et.al.,<sup>12</sup> showed that when all these parameters were chosen carefully, it was impossible to produce thin  $n^+$ - layers which were excellent blocking contacts up to electric fields of several thousands  $V\ cm^{-2}$  (Figs. 5 and 6).

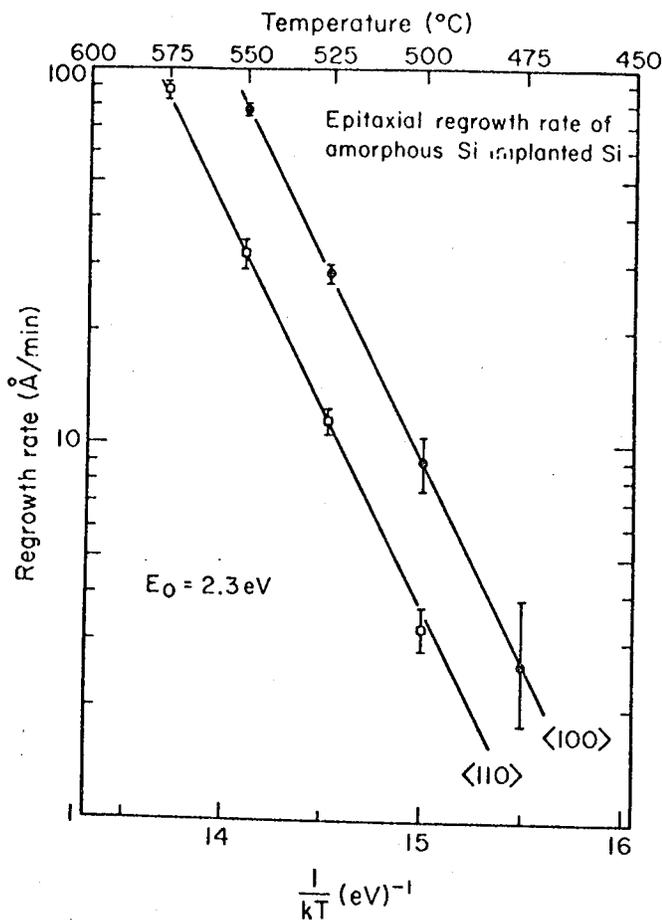


Fig. 4 Epitaxial regrowth rates for various crystal directions in Si. The results obtained for Ge are similar with a regrowth rate of Å/min at 325°C for the (100) direction. The rates for the (111) directions are about ten times smaller than for the (100) directions. Reprinted with courtesy of Ref. 15.

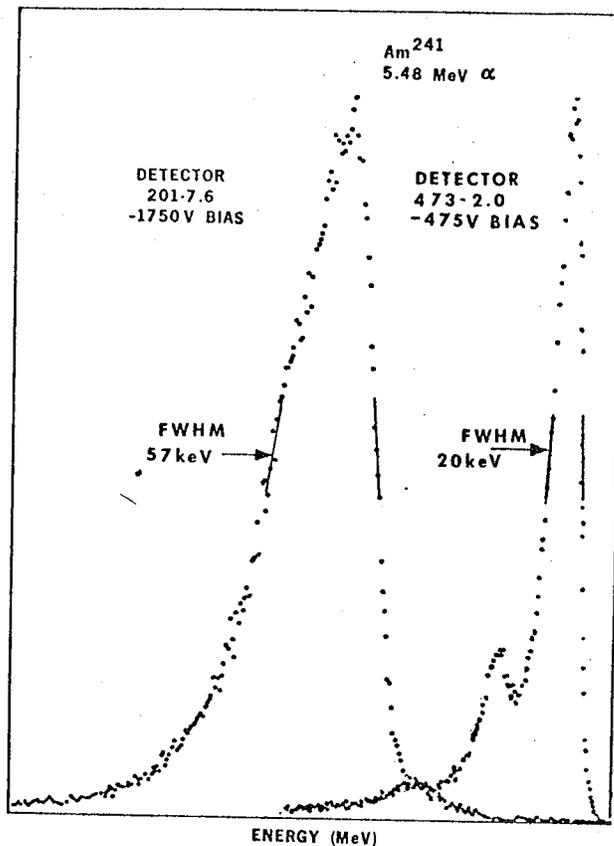


Fig. 6 5.48 MeV alpha particles are passed through n<sup>+</sup> contact. Detector 473-2.0 has been given an additional "pre-annealing" stage of 1 1/2 hours at 420K. The shift in peak position is due to the difference in dead layer thickness. 20 keV represents a window of 0.3-0.4 μm. Reprinted with courtesy of Ref. 12.

Fig. 5

Detector	$(N_A - N_D)$ (atoms/cm <sup>3</sup> )	$V_d$ (Volts)	$V_a$ (Volts)	$E_c$ (Volts/cm)	Comments
457-5.5	$3 \times 10^{10}$	430	6	200	None
457-5.0	$3 \times 10^{10}$	320	20	370	None
466-3.2	$4.5 \times 10^{10}$	250	7	270	None
194-5.0	$8 \times 10^9$	200	350	1000	1% HF
201-7.6	$-1.7 \times 10^{10}$	1100	2500	1300	1% HF
473-2.0	$4 \times 10^{10}$	400	475	2000	1% HF
482-10.0	$2 \times 10^{10}$	1200	600	1900	"Pre-anneal" after implantation

$(N_A - N_D)$ : Net shallow impurity concentration

$V_d$ : Depletion voltage

$V_a$ : Maximum operating voltage

$E_c$ : Electric field on n<sup>+</sup> contact at  $V_a$

Reprinted with courtesy of Ref. 12.

It is now possible for the first time to stack many high-purity germanium detectors to obtain a virtually windowless telescope. A seven- and a three- detector telescope are under construction at Lawrence Berkeley Laboratory (LBL).

A new technique for the production of coaxial germanium detectors with nearly constant electrical field was introduced by Hall.<sup>16</sup> He demonstrated that by controlled out- or in-diffusion of limited amounts of lithium it is possible to obtain radial concentration gradients which lead to uniform field at a defined bias.

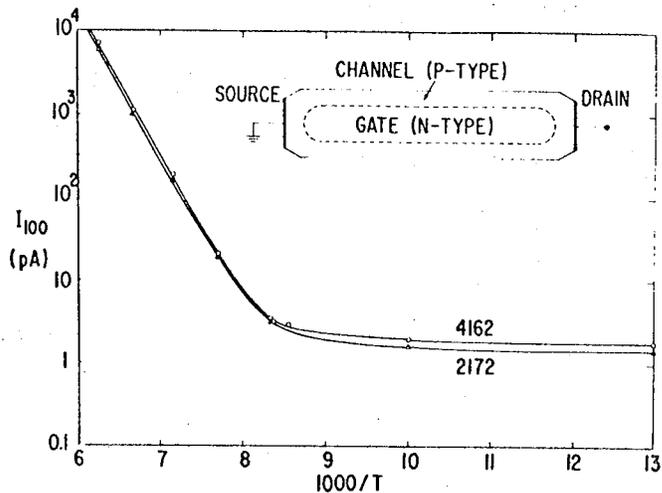
### High-purity Germanium

Despite the fact that high-purity germanium has been commercially available for quite some time, we have the feeling that it is still in the development stage. This point can be illustrated by some of the recent results obtained from experiments with zone refining, "monodes," hydrogen in germanium and infrared photoelectric spectroscopy with stressed crystals.

Once it was clear that the difficulties in obtaining high-purity germanium were not caused by random or systematic contamination from the crystal pulling equipment but were due to the poor segregation of the impurities boron and aluminum,<sup>17</sup> it was possible to concentrate the effort towards this problem. Hubbard, et.al.,<sup>18</sup> have demonstrated that oxygen and silicon form with the acceptors boron and aluminum complexes which are electrically inactive and segregate very poorly (segregation coefficient  $k$  close to 1). This kind of gettering action can be beneficial because it reduces the acceptor concentration. On the other hand, it prevents efficient segregation, the basis of purification of semiconductors and other substances. Hubbard, et.al., showed that both silicon and oxygen can be controlled by appropriate choice of container and coating materials and ambient atmosphere. They have succeeded to reduce Al and B to levels below  $10^{10} \text{ cm}^{-3}$  independent of the concentrations in the intrinsic grade polycrystalline Ge ingots which are commercially available.

The "monode" as invented by Hall<sup>19</sup> has made an old dream of device people real (Fig. 7). The monode is a piece of semiconductor crystal which shows one type of electrical conduction in the interior and the opposite type on the whole surface. In other words, it is a buried junction. Application of a high-voltage electrical pulse can partially deplete the buried junction. Conductivity measurements are used to determine the depletion depth. With this device, it is possible to study the origin of the reverse biased junction leakage current without any influence of surfaces. Preliminary studies showed that gamma radiation from the environment can influence measurements. Experiments with monodes are in progress and we hope that the dominant recombination center(s) can be characterized.

The understanding of the role of hydrogen dissolved in germanium has rapidly advanced in recent times. As in the case of ion implantation, this progress was hindered by earlier investigations. These lead to the conclusion that hydrogen is dissolved atomically in Ge and is electrically neutral. The discovery of the so called "fast defects" by Hall<sup>20</sup> and the recent experiments by Haller<sup>21</sup> which give proof that these centers contain hydrogen have changed the point of view. Let me spend a little more time on this subject because it illustrates nicely how a combination of techniques can be used

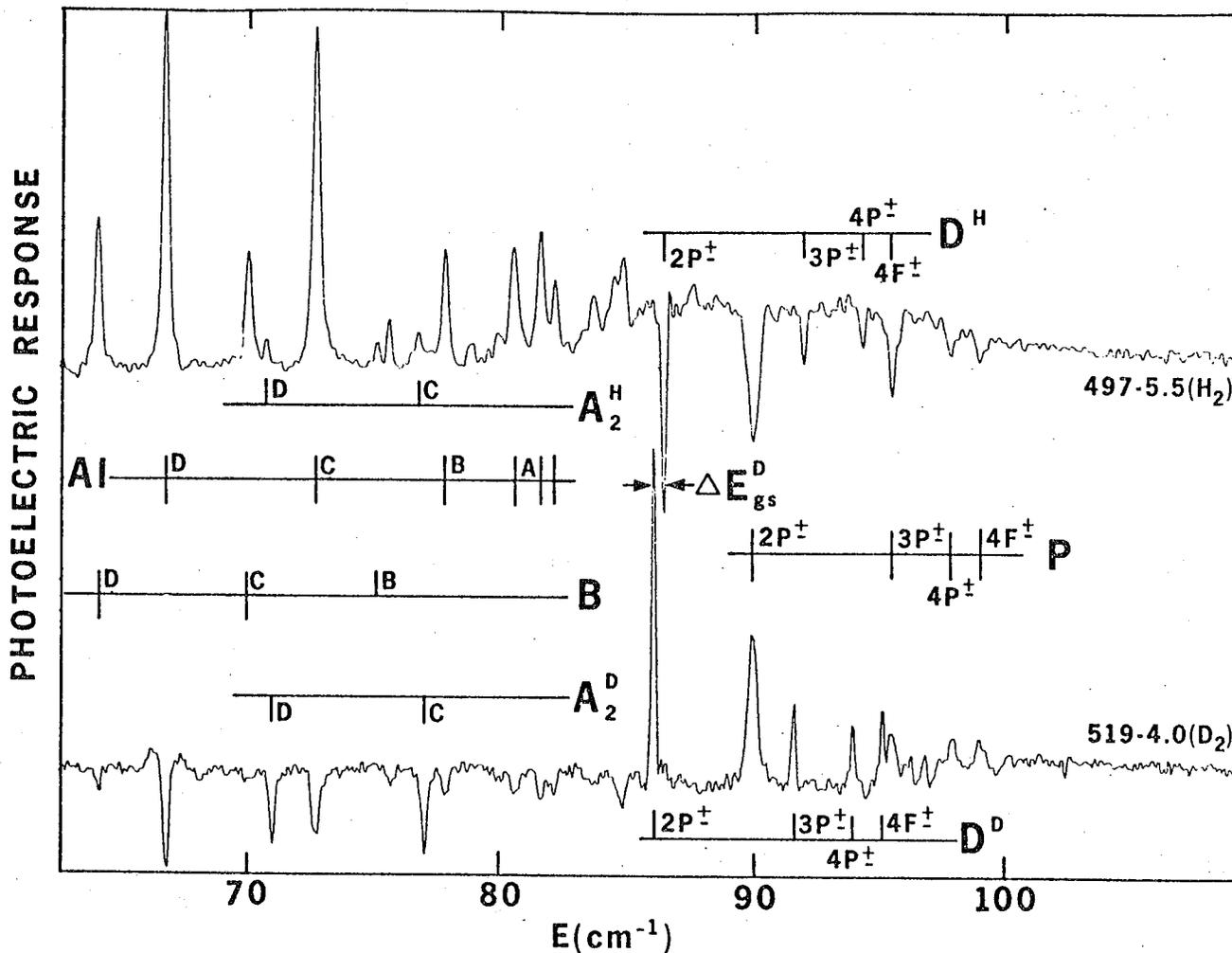


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Fig. 7 Bulk leakage current measured at 100V. The inset shows the monode structure and the method of measurement. Reprinted courtesy of Ref. 19.

to solve such a problem. Hall showed with his studies of rapidly quenched Ge-samples that at temperatures around  $400^\circ\text{C}$  a defect or impurity center later named  $A_2$ <sup>22</sup> exists at concentrations around  $4 \times 10^{11} \text{ cm}^{-3}$  in germanium.  $A_2$  is a shallow acceptor and it is unstable at room temperature. How can a defect be unstable at room temperature but exist at temperatures around  $400^\circ\text{C}$ ? The solution to this paradox is the continuous generation and recombination of  $A_2$  at  $400^\circ\text{C}$ . The generation rate increases faster with temperature than the recombination rate, causing the quasi-equilibrium concentration of  $A_2$  to rise with temperature. When  $A_2$  anneals a donor D is created.<sup>22</sup> The concentration of D reaches values very close to the ones of  $A_2$ . Around  $160^\circ\text{C}$ , D anneals and the crystal returns to its original stage. Hall suggested a model based on interaction between a neutral impurity M and some thermal defects. Using two rate equations, he was able to fit his results. Silicon was believed to play an important role in the generation and recombination of  $A_2$  and D. Haller<sup>23</sup> has succeeded in proving with an isotope effect that  $A_2$  and D are related to hydrogen in germanium (Fig. 8). From the behavior of infrared photoelectric<sup>24</sup> spectra of D, it is evident that the structure of D has not the same symmetry as the elemental Group V donors and all the germanium atoms have (Fig. 9). The symmetry axis of D is parallel to the [111] directions. Experiments which should show if there are further impurities involved in the formation of  $A_2$  and D are in progress.

The exploration of  $A_2$  and D satisfies by no means only academic curiosity. Experience of detector-makers shows that the formation of the "fast" defects can take place during the preparation of the  $n^+$ - contact with lithium diffusion. The presence of  $A_2$  and D can alter the net-impurity concentration to the point where a



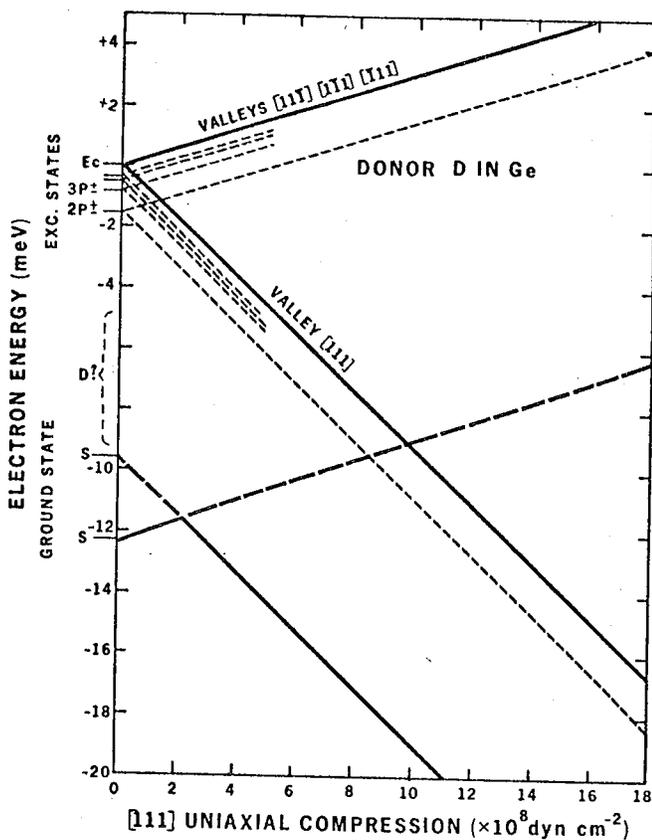
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Fig. 8 Photoelectric spectra of germanium samples of a crystal grown in hydrogen (497-5.5) ( $H_2$ ) and in deuterium (519-4.0) ( $D_2$ ). The lines of the elemental acceptors A1 and B and the donor P appear at exactly the same energies in the two spectra. The lines of the donor D and the acceptor  $A_2$  exhibit an isotope shift which is direct proof of hydrogen/deuterium being present in these centers. The opposite sign of the lines in the two spectra is due to the fact that the two germanium samples are of opposite types. Reprinted courtesy of Ref. 21.

value Ge-slice becomes useless. To minimize the appearance of these defects it is recommended that all temperature changes are made slowly so that sufficient annealing can take place.

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Fig. 9 Dependence of the energies of the ground-state components of the hydrogen related donor D on uniaxial compression along the [111] direction. The excited states and the [111] valleys are the same as in Fig. 2. Contrary to elemental substitutional donors the lines of the D-spectrum do not move under uniaxial compression but, their intensity drops rapidly around  $2.1 \times 10^8$  dyn  $\text{cm}^{-2}$ . A new set of lines appears at 2.7 meV lower energies. This behavior is explained by a crossing of two singlet states (S). A doublet (D) or two more singlet (S) components of the ground state must exist close to the conduction band minima but, they cannot be populated and are therefore not observed at the temperature used. Reprinted with courtesy of Ref. 21.

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