RECENT ADVANCES IN COMMON SEMICONDUCTOR MATERIALS

E. E. Haller

April 1977

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.
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 and Bertolini and Coche which give a lively description of work done up to about ten years ago.

Around that time, Hall at General Electric predicted that 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)

Meyer’s group at the California Institute of Technology has worked for several years on SPE. 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 aluminium-germanium system has already been successfully applied in high-purity germanium detector fabrication. 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 or germanides. 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., PbS: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 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 of Herzer and Kalbitzer and Pompon, et al., 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.

This work was supported by the General Science and Basic Research Division of the Department of Energy under Contract No. W-7405-ENG-48.

E. E. Haller
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

LBL-7280
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., 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, 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, L.N. et al., found that at room temperature interactions between ion created defects take place which can lead to unannealable complexes. Sigmon 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. (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.
Epitaxial regrowth rates for various crystal directions in Si. The results obtained for Ge are similar with a regrowth rate of 5 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.

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

<table>
<thead>
<tr>
<th>Detector</th>
<th>(N_A-N_D)</th>
<th>V_d (Volts)</th>
<th>V_a (Volts)</th>
<th>E_c (Volts/cm)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>457-5.5</td>
<td>3 x 10^{10}</td>
<td>430</td>
<td>5</td>
<td>200</td>
<td>None</td>
</tr>
<tr>
<td>457-5.0</td>
<td>3 x 10^{10}</td>
<td>320</td>
<td>20</td>
<td>370</td>
<td>None</td>
</tr>
<tr>
<td>466-3.2</td>
<td>4.5 x 10^{10}</td>
<td>250</td>
<td>7</td>
<td>270</td>
<td>None</td>
</tr>
<tr>
<td>194-5.0</td>
<td>8 x 10^{9}</td>
<td>200</td>
<td>350</td>
<td>1000</td>
<td>1% HF</td>
</tr>
<tr>
<td>201-7.6</td>
<td>-1.7 x 10^{10}</td>
<td>1100</td>
<td>2500</td>
<td>1300</td>
<td>1% HF</td>
</tr>
<tr>
<td>473-2.0</td>
<td>4 x 10^{10}</td>
<td>400</td>
<td>475</td>
<td>2000</td>
<td>1% HF</td>
</tr>
<tr>
<td>482-10.0</td>
<td>2 x 10^{10}</td>
<td>1200</td>
<td>600</td>
<td>1500</td>
<td>&quot;Pre-anneal&quot; after implantation</td>
</tr>
</tbody>
</table>

(N_A-N_D): Net shallow impurity concentration
V_d: Depletion voltage
V_a: Maximum operating voltage
E_c: Electric field on n⁺ 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. 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, it was possible to concentrate the effort towards this problem. Hubbard, et al., 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 A1 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 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 signal shows the electrically active part of the buried junction. Conductivity measurements are used to determine the depletion depth. With this device, it becomes 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 and the recent experiments by Haller demonstrate, for example, that these centers contain hydrogen which have (Fig. 7). 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 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
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 Al 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.

References
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 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.

Fig. 9
