CONCERNING THE PRODUCTION OF SINGLE CRYSTALS OF GERMANIUM-SILICON ALLOYS

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CONCERNING THE PRODUCTION OF SINGLE CRYSTALS OF GERMANIUM-SILICON ALLOYS

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The development of new fields of modern technology such as automation, radio-electronics and telemechanics depends a great deal on the production of semiconductor materials and on their properties.

Among semiconductor materials of special importance are alloys of the well-known semiconductors germanium and silicon.

Continuous variation in the width of the forbidden zone [1, 2], carrier mobility, resistance to thermal effects, etc., make it possible, by constructing certain instruments, to choose material with the necessary properties combining the advantages of silicon with those of germanium.

In connection with the above there is the very important problem of obtaining and studying monocrystals of germanium-silicon solid solutions.

The well-known method of growing crystals consists of pulling them out of a melt by means of a seed. This method had been successfully employed with germanium and silicon. However for growing monocrystals from a solid solution it is necessary to make essential modifications in view of the difficulty of obtaining homogeneous crystals [3].

The literature is lacking in information on methods for obtaining monocrystals from germanium-silicon solid solutions. Davis and De Mars [4] obtained large-crystal ingots of alloys of widely varied composition by slow cooling of the melt at a rate of 2°C per hour.

B. P. Mitrenin and N. Ye, Troshin [5] pointed out that they succeeded in obtaining homogeneous large-crystal ingots of alloy by zone melting.

Two methods are described below which we investigated in order to obtain monocrystals from a germanium-silicon melt. One of them is similar to the Davis method. The other one uses the principle of continuous feeding of the melt [6].

In order to carry out the experiments the authors of the present work were supplied with especially constructed equipment
Vacuum apparatus for growing monocrystals of Ge-Si alloy using continuous feeding of the melt. (in operation)

The method of slow cooling of the melt. The prepared ingot of melt of necessary composition was melted in an evacuated quartz tube located in a Silit pot furnace of the ShP-I type. Crystal growth was aided by a temperature gradient of the order of 20°C in the tube, from the lowest temperature at its upper region to the highest temperature at its lower region. The temperature was controlled by means of two thermocouples whose junctions were located at the ends of the tube. The melt was preheated to 200-250°C above the melting point of the mixture and was held at that temperature for a period of four hours, after which the cooling process began at a rate of 1.5°C per hour.

By this method monocrystals of germanium-silicon melt of various compositions were obtained, with 0.5-5 at. percent silicon content. Photographs of the macrostructure of the monocrystalline samples obtained are shown below (Fig. 3a, b and c). X-ray analysis of sample 1 showed crystal growth of the (100) orientation (Fig 4).
Fig. 2.
Vacuum apparatus for growing monocrystals of Ge-Si alloy with continuous feeding of the melt. (open view)

Table 1 gives the results of investigation of three monocrystals.

Table 1

<table>
<thead>
<tr>
<th>Monocrystals</th>
<th>Sampel</th>
<th>at. % Si</th>
<th>Elect. Resist. ohm cm</th>
<th>Type of conductivity</th>
<th>Peak reverse voltage V</th>
<th>Mobility cm²/V sec</th>
<th>Silicon content in the melt</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>3.5</td>
<td>7.3</td>
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<tr>
<td>3</td>
<td>1.5</td>
<td>5.4</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td>0.5</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>1</td>
<td>4.5</td>
<td>9.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>8.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>3</td>
<td>0.7</td>
<td>4.7</td>
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</tr>
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<td>4</td>
<td>0.5</td>
<td>3.1</td>
<td></td>
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<td>5</td>
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<td>0.8</td>
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<td>14</td>
<td>2.8</td>
<td></td>
<td></td>
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<td>1</td>
<td>0.4</td>
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</table>

* Starting material was low quality.
Fig. 3.
Monocrystals of germanium-silicon alloy grown by the slow cooling method; a - outer view of monocrystal 1; b - outer view of monocrystal 4; the sharply defined geometrical form of a hexahedron is visible on the grown crystal; c - outer view of monocrystal 5.

Fig. 4.
Lauegram of sample 1

Fig. 5.
Monocrystals grown by continuous feeding of the melt in the direction of axial growth (111)
Fig. 6
Lauergram taken from the seed on the surface of pulling of monocrystal 81.

Fig. 7.
Lauergram taken at the end of monocrystal 81.
As is apparent from the table above, monocrystals obtained by slow cooling are non-homogeneous in composition; a gradient can be observed in the distribution of silicon and in the electrical resistivity from the upper part to the lower.

A sharp decrease is also observable in the variation of minority carrier mobility, which regularly corresponds to a change in the distribution of silicon along the length of the monocrystals.

![Graph](image)

**Fig. 8.**

Curves of the variation of specific resistivity in ohm cm along the length of the monocrystals obtained by continuous feeding of the melt.

A method for pulling crystals of a solid solution by feeding the melt. Monocrystals of a solid solution of germanium and silicon were obtained by this method in the vacuum apparatus shown in Fig. 1. The main body of the apparatus is enclosed in a water-cooled cylinder upon which is placed the upper part of the apparatus that contains the revolving and vertical movement mechanisms. In Fig. 2 the inner construction of the apparatus is visible. A graphite heater, into which the quartz crucible is placed, is connected to the copper clamps of a current-carrying electrode.

The upper part is shown separately, with two rods. One of them carries the feeding ingot and the other carries the monocrystalline seed.

In the lower part of the operating body is mounted the mechanism for rotating and moving the crucible up and down. A vacuum of the order of 10^{-5} mm of mercury is maintained in the working chamber. The temperature is regulated manually. In order to avoid vibrational strains in the lattice, ferro-resonating stabilizers are included in the electrical circuitry of the apparatus.

Polycrystalline ingots which contained an even distribution of silicon along their length were used to feed the melt. The ingots were prepared by casting the melt in quartz tubes in an argon atmosphere.

The composition of the feed ingot corresponded to that of the pulled monocrystal. Feeding of the melt began soon after pulling began, when the length of the pulled monocrystal reached 3-5 mm.

The pulling temperature was maintained such that the diameter of the crystal grown was equal to that of the feed ingot. By having identical diameters in the grown and the feed ingots the
rate of their oppositely directed movement was kept constant, equal to 1.7 mm/min. The rate of seed rotation was five revolutions/min and the crucible rate was 10 revolutions/min.

By the method described, 10 monocrytalline ingots of germanium-silicon alloy were obtained with an even silicon distribution. The characteristics of the samples obtained are shown in Table 2.

Table 2.

<table>
<thead>
<tr>
<th>Sampler Nr</th>
<th>at. % Si</th>
<th>Type of conductivity</th>
<th>Resistivity ohm cm</th>
<th>Lifetime in microsec</th>
<th>Peak reverse voltage, V</th>
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<tr>
<td>50</td>
<td>0.70</td>
<td>p</td>
<td>5</td>
<td>4</td>
<td>30-45</td>
</tr>
<tr>
<td>53</td>
<td>2.00</td>
<td>p</td>
<td>3.4-3.7</td>
<td>-</td>
<td>40-50</td>
</tr>
<tr>
<td>72</td>
<td>0.75</td>
<td>p</td>
<td>1.15</td>
<td>-</td>
<td>15-18</td>
</tr>
<tr>
<td>81</td>
<td>1.00</td>
<td>p</td>
<td>5.4-38</td>
<td>40-65</td>
<td>70-90</td>
</tr>
<tr>
<td>91</td>
<td>0.75</td>
<td>p</td>
<td>50-62</td>
<td>8-76</td>
<td>—</td>
</tr>
<tr>
<td>93</td>
<td>1.00</td>
<td>p</td>
<td>22-23</td>
<td>20</td>
<td>—</td>
</tr>
</tbody>
</table>

In Fig. 5 monocrytalline are shown which have been grown with an axial growth orientation of [111]. In Fig. 6 and 7 Lauergams are shown that were taken from the seed and the crystal. The electrical resistivity along the length varied on the average between the limits of 6-8 percent and along the cross-section it remained practically constant.

In alloys containing silicon up to 2 at. percent the specific resistivity increases sharply in comparison to that of the starting material. The lifetime of the minority carriers is 2-3 times lower than in the original germanium and 4-5 times higher than in the original silicon.

Conclusions

1. The conditions for obtaining monocrytalline germanium-silicon ingots by stationary slow cooling were studied. Monocrystals obtained by this method, using a cooling speed of 1.5° per hour, have a sharply defined gradient in distribution of silicon and electrical resistivity.

2. A method was worked out for obtaining homogeneous germanium-silicon alloy monocrystals by using continuous feeding of the melt during crystal growth. Monocrystals were obtained by this method with an even distribution of silicon and with the same electrical resistivity in the cross-section as in the length.

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