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Tunnel Diodes by Vapor Growth of Ge on Ge and on GaAs

Because junction-fabrication techniques such as diffusion, growing and rate-growing generally are not capable of producing steep impurity gradients, they have not been employed in the fabrication of tunnel-type junctions. As far as is known, deposition of Ge from a liquid-metal solution is the only procedure which has been successful up to now. The most common example of this technique is the well-known "alloy" process. Even with the alloy process, care must be taken that impurity diffusion is not extensive, or the impurity gradients will not be sufficiently steep for tunneling to occur.

Since *p-n* junctions can be made by vapor growth at low temperatures[1] (~300°C), interdiffusion in the junction region can be sufficiently minimized to make possible abrupt, highly doped junctions of the tunnel type. This note describes two modifications of the vapor-growth techniques which have been used to form such junctions not only between epitaxially deposited germanium and a germanium substrate, but also between epitaxially deposited germanium and a gallium arsenide substrate. Tunnel diodes were prepared from these junctions; preliminary results are discussed and compared with similar studies on alloy junctions.

Procedure

The process steps utilizing a Ge-I_2 reaction[1-3] have been modified in the following significant ways in order to achieve suitably doped junctions.

- *"Closed Tube" Process*[1]

The monocrystalline germanium source was phosphorus-doped to a much higher level ($>3\times10^{19}/\mathrm{cm}^3$) than previously employed. A relatively smaller concentration of iodine was used to allow the deposit zone to be operated at ~300°C with the source at ~550°C. The Ge substrates or seeds were monocrystalline wafers with Ga concentrations of $\sim5\times10^{19}/\mathrm{cm}^3$, $8\times10^{19}/\mathrm{cm}^3$, or $8\times10^{20}/\mathrm{cm}^3$. The tube was then evacuated and sealed. After positioning the tube in the furnace shown in Fig. 1, the temperature profile was adjusted so that both the source and seed material at ~500°C etched away, and the Ge being removed was deposited in the "dump zone" at ~300°C. After about 1 to 2 hours, the temperature profile was changed so that the seed region dropped quickly to 300°C. Deposition on the substrates was then carried out for 4 to 30 hours at the temperature of ~300°C. Under these conditions, the thicknesses of the deposits varied from about 10 to 100μ. Ge deposits vapor-grown under these conditions have a resistivity of about 0.001-0.002 ohm-cm.

- *"Open-Tube" Process*

This process, applicable to any appropriate seed material, is depicted schematically in Fig. 2. Some experimental junctions were made from either arsenic- or phosphorus-doped source Ge and gallium-doped seed Ge. The deposition proceeded as shown in Fig. 2 for 4 to 8 hours, during

Figure 1 **"Closed-tube" apparatus for deposition of tunnel junctions.**

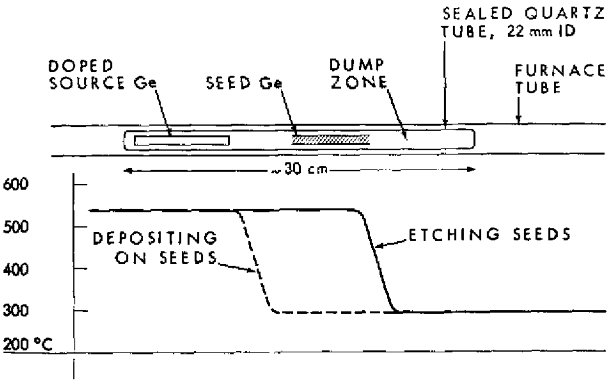
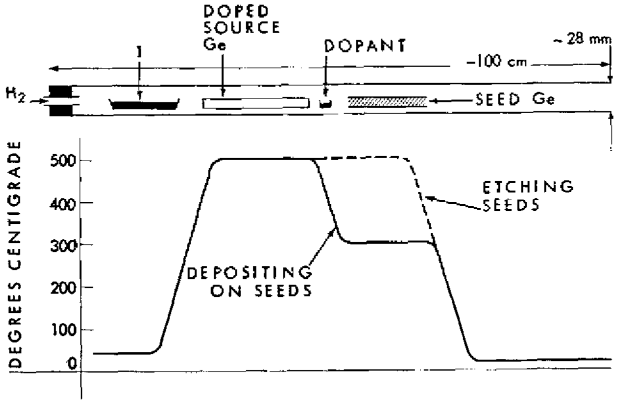


Figure 2 **"Open-tube" apparatus for deposition of tunnel junctions.**



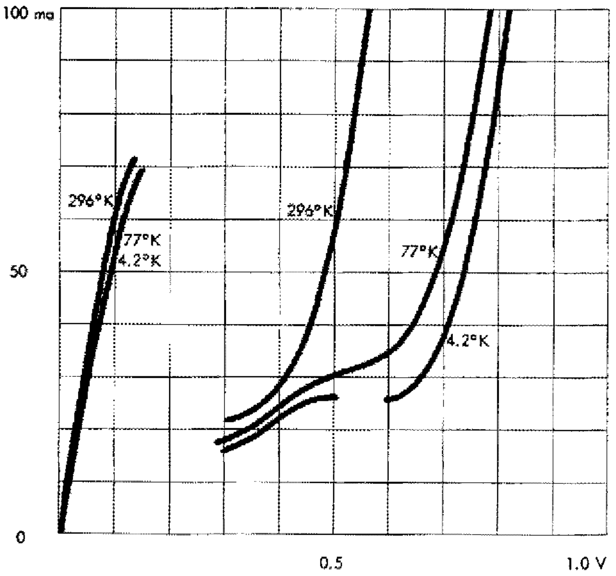


Figure 3 **Characteristics of a Ge-Ge vapor-grown tunnel diode at three temperatures.**
The P-doped Ge was deposited on a Ga-doped Ge substrate. This unit was held for one second at about 600°C during alloying of the ohmic contacts.

which time a degenerate *n*-type layer ranging in thickness from 10 to 75μ was grown on the seed. The source Ge with P dopant produced tunnel junctions. Although doping concentrations of As slightly beyond degeneracy have been achieved, these so far have not been as high as the P concentrations, which were $\sim 10^{19}/\text{cm}^3$.

GaAs has a lattice parameter and an electronic structure very close to that of Ge. It has been possible to epitaxially deposit P-doped, degenerate *n*-type layers on heavily Zn-doped ($> 5 \times 10^{18}$ Zn atoms/cm^3) GaAs seeds in the manner described for Ge seeds. The junctions so prepared also showed tunnel characteristics. The general Ge-GaAs heterojunction is described more fully elsewhere in this Journal.[4]

Tunnel diode fabrication

Experimental diodes were fabricated by conventional procedures of soldering or low-temperature alloying (~ 450°C) ohmic contacts to each member of a p^+-n^+ junction, which had been previously cut into disks approximately 0.025″ in diameter. The resultant diodes were mounted on standard circular transistor headers and then electrolytically etched.

Results

Ge-Ge Junctions

After ohmic contacts were applied to a number of diodes by low-temperature short-time alloying, it was observed that those diodes which had received an alloying time-temperature cycle greater than the minimum had higher values of I_p/I_v, the peak-to-valley ratio.[5] The unit shown in Fig. 3 is typical of the better units which were held at approximately 600°C for about one second during the alloying of the ohmic contacts. This unit was made by the closed-tube process.

This behavior seems to contradict the generally observed behavior in alloy tunnel junctions; namely, that greater time-temperature cycles reduce the peak-to-valley ratios I_p/I_v. To investigate this unexpected result, four groups of about five disks each were heat-treated in air at 665°C for the following periods of time: 0 seconds, 20 seconds, one minute, 10 minutes. Tunnel diodes from each group were fabricated under similar conditions; the time-temperature cycle for the alloying of ohmic contacts was kept as low as possible. In Table 1, the average peak-current density as well as peak-to-valley ratio is given for each group.

The data shown in Table 1 are representative of a given closed-tube deposition. The maximum in current density ($I_p/Area$) is significant. This behavior of current density, plus several other observations, leads one to believe that the phosphorus concentration at the interface is lower than it is in the bulk of the deposited layer. Some heat-treatment causes an increase in phosphorus concentration at the interface by diffusion from the bulk of the layer. It is possible that transitions of phosphorus can occur from the precipitated or interstitial states to the substitutional state in the disturbed region near the interface. This too would increase the current density. Further heat-treatment then would appear to cause further diffusion, which widens the depletion layers sufficiently to curtail tunneling, and consequently current density decreases. A rough approximation shows that a phosphorus concentration one-half its value in the bulk layer could be expected 700 A distant from the phosphorus-containing region after 10 minutes at 665°C. The probable reason that tunneling occurs at all after this heat-treatment is that the phosphorus concentration is only slightly above the degeneracy level in the bulk of the layer itself. The effects noted above are less pronounced in deposited diodes with still smaller peak-to-valley ratios than those given in Table 1. As mentioned in the Procedure section, substrates of three different Ga doping levels were used; namely, 5×10^{19}, 8×10^{19}, and 8×10^{20}. Best peak-to-valley ratios were obtained with the 8×10^{19} doping level in the substrates.

Table 1 **Heat treatment effect on vapor-grown Ge-Ge tunnel diodes (representative values).**

Group	$\frac{I_p}{I_v}$	$\frac{I_p}{Area}\left[\frac{A}{cm^2}\right]$	$\frac{C}{Area}\left[\frac{\mu f}{cm^2}\right]$
No heat treatment	3/2	900	- - -
20 sec at 665°C	3	1500	4.5
1 min at 665°C	3	1000	- - -
10 min at 665°C	5/2	200	2

The peak-to-valley current ratio is not the only figure of merit for tunnel diodes. Another important criterion is the ratio of junction capacitance to the peak current. The values observed for vapor-grown diodes are quite comparable to those for alloy junction diodes.

The large magnitude of the valley current is not unexpected in view of the very imperfect nature of the junction region[6] on the diodes reported here. Radiation damage studies on alloy junctions have shown that the valley current increases linearly with dosage.[7] Furthermore, low peak-to-valley ratios are characteristic of alloyed junctions on phosphorus-doped Ge substrates. The magnitude of valley current suggests a tunneling mechanism via deep-lying intermediate states in the gap due to either interstitial phosphorus or lattice imperfections.[7]

Referring now to Fig. 3, the peak (~0.45 v) seen in the characteristic at 77°K and 4.2°K has been seen numerous times on these diodes. Similar characteristics have been observed[8] in junctions alloyed on phosphorus-doped material. This phenomenon thus seems characteristic of phosphorus rather than the particular details of the mode of junction fabrication using phosphorus.

• *Ge-GaAs Junctions*

As mentioned earlier, in an "open-tube" run a layer of Ge degenerately doped with phosphorus was deposited epitaxially upon a seed of GaAs degenerately doped with zinc. Using as low a time-temperature cycle as possible, the characteristic of such a junction was quite similar to that of n^+-p^+ Ge junctions produced in the same deposition run. It was observed, however, that higher temperature soldering often produced diodes with characteristics which were comparable to those of alloyed GaAs tunnel diodes. A typical characteristic of a Ge-GaAs tunnel heterojunction (see page 246) is depicted in Fig. 4. It is tentatively believed that the junction actually exists at the Ge-GaAs interface for the following reasons:

(a) The voltage swing has never been as high as that found in GaAs tunnel diodes.

(b) The characteristic is certainly different from that of an ordinary phosphorus-doped Ge tunnel diode, (cf. Fig. 3) and the characteristic showed little change upon cooling to 4.2°K. Therefore, it is not likely that the junction is in the Ge.

(c) In similar deposition runs where in the doping level in the Ge was not quite degenerate, tunnel junctions did not result. Therefore, it is not likely that the junction is in the GaAs.

(d) Pressure dependence of tunneling in these junctions differs from that of Ge-Ge or GaAs-GaAs junctions.[9]

Conclusion

In the experimental work reported here it has been shown that degenerately doped n-type Ge can be vapor-grown epitaxially on degenerately doped p-type Ge or GaAs substrates, yielding tunnel junctions in either case. The vapor growth was performed at a low temperature in order to minimize interdiffusion of impurities at the junction. However, it was found that some heat treatment (subsequent to the vapor-growth step) increased peak current densities. Ge-Ge junctions were further heat treated and peak current densities then decreased.

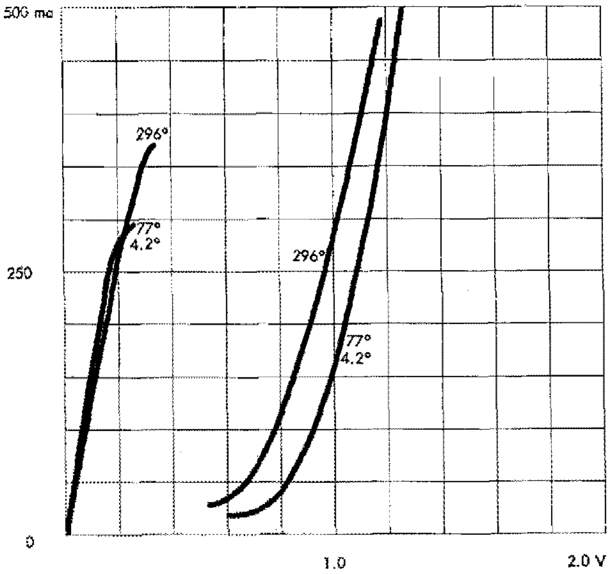


Figure 4 **Characteristics of a Ge-GaAs vapor-grown tunnel heterojunction at three temperatures.**
The P-doped Ge was deposited on a Zn-doped GaAs seed.

Both P and As have been used to dope the vapor-grown Ge. Up to the present time, higher concentrations have been achieved with phosphorus. Since it has been observed in alloyed tunnel junctions that As doping will give better peak-to-valley ratios, and since all the As incorporated in vapor-grown Ge is electrically active,[10] further work is being done on As doping.

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