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TRANSISTOR FABRICATION BY THE MELT-QUENCH PROCESS

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Transistor Fabrication by the Melt-Quench Process

Approved

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Transistor Fabrication by the Melt-Quench Process

This bulletin discusses a novel method of making junctions in a germanium bar, which are suitable for use in transistors. In this "melt-quench" process of transistor fabrication, a suitably doped small bar of germanium is partially melted, then caused to freeze very rapidly. Two closely-spaced, plane-parallel p-n junctions can thus be formed in a matter of a few seconds. Since these junctions may be designed to have a variety of electrical properties, the melt-quench process promises to be applicable to the fabrication of a variety of devices. The simplicity and rapidity of this process appear attractive for exploitation in low-cost mass production of transistor devices. However, this possibility has not been fully evaluated.

Principle of Junction Formation

As shown in Fig. 1, a bar of germanium containing a concentration of N_d donors and N_a acceptors is melted from the right, so that the liquid-solid interface is at X_o. At this stage in the process the impurity distribution is not altered. The detail of choosing the impurities will be described later. Let N_d and N_a be respectively the donor and acceptor impurity concentrations and K_d and K_a their segregation coefficients. For the present, consider that $N_d > N_a$ (the crystal is n-type) and that the segregation coefficients are $K_d < K_a$.

The melt is caused to freeze at first slowly, then very rapidly. During the period of slow growth, the impurities are trapped according to the rules of impurity segregation. Consequently the initial impurity concentration is such that $K_a N_a > K_d N_d$ and the recrystallized material is p-type, thus forming a p-n junction. This junction will be referred to as the "melt junction".

If the crystal were allowed to continue to grow slowly as described by W. G. Pfann[1], the concentration of donors in the liquid would increase more rapidly than the concentration of acceptors. Eventually the donors would predominate and a second junction formed. The impurity concentration and their segregation coefficients determine the spacing between the junction and the emitter injection efficiency. In the case of slow regrowth these two transistor requirements place restrictions on the selection of impurities.

In the present process after a short period of slow regrowth, the crystal is caused to grow rapidly (quenched). This occurs at X_Q in Fig. 1 thus determining the spacing between junctions. Upon quenching, the impurities cease to segregate and the donors again dominate. The p-n junction produced upon quenching will be called the "quench junction". Since the thermal treatment (quenching) determines the spacing between junctions the impurities can be chosen independently to satisfy the requirements of good injection efficiency. This separation of parameters controlling the junction spacing and injection efficiency allows a freedom of design not attainable in a slow growth process alone. If the slowly grown region is small compared to

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(1) W. G. Pfann, "Segregation of Two Solutes, With Particular Reference to Semiconductors", J. of Metals 194 (August 1952), 861-865.

the quenched region, the impurity concentration in the quenched region is almost identical to the initial concentration in the crystal.

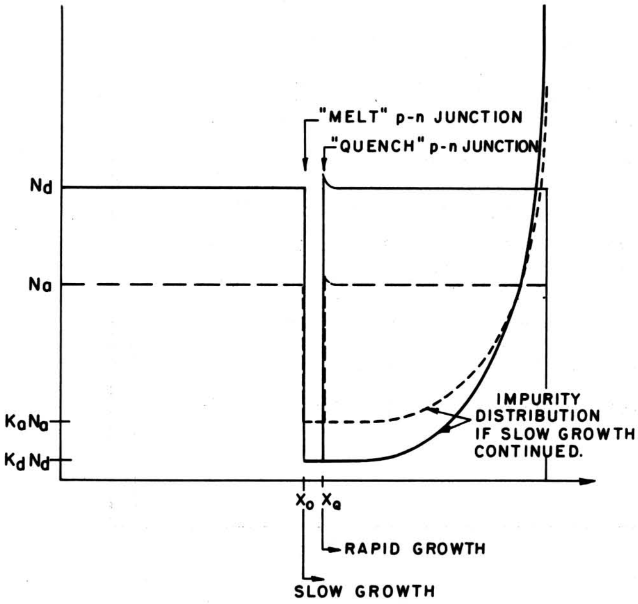

Fig. 1 - Impurity distribution in the melt-quench process.

Quenching, to form the second p-n junction, is done very rapidly and it might be expected that the quenched region would be polycrystalline. Under the proper conditions this does not turn out to be the case. X-ray examination shows the quenched region to be a single crystal.

Design Criteria

The following reasoning is applied to the design of an n-p-n unit. Analogous reasoning can be used for a p-n-p unit.

Since the unmelted region, i.e., the starting material, is n-type:

$$N_d > N_a \tag{1}$$

and the conductivity of this region is:

$$\sigma_n = (N_d - N_a)\, e\mu_n \tag{2}$$

where e and μ_n are respectively the electronic charge and mobility.

If g denotes the fraction of the liquid that has solidified, then

$$g = \frac{x - x_o}{x_e - x_o}$$

where x_e is the length of the bar.

In the slowly freezing region the impurity distributions are then given by:

$$n_a(x) = K_a N_a\, (1-g)^{K_a - 1}$$

$$n_d(x) = K_d N_d\, (1-g)^{K_d - 1}$$

But if the slowly grown region is small compared to the volume of liquid, i.e., g <<1:

$$\left.\begin{aligned} n_a(x) &\approx K_a N_a \\ n_d(x) &\approx K_d N_d \end{aligned}\right\} \tag{3}$$

Since the slowly grown region is required to be p-type it is required that:

$$n_a(x) > n_d(x)$$

and therefore from (3):

$$K_a N_a > K_d N_d \tag{4}$$

The conductivity in the p-type region is:

$$\sigma_p = (K_a N_a - K_d N_d)\, e\mu_p \tag{5}$$

where μ_p is the hole mobility.

To summarize (1) and (4), the important condition to be satisfied is:

$$\boxed{N_d > N_a > \frac{K_d N_d}{K_a}} \tag{6}$$

For closely spaced junctions and neglecting impurity pile-up due to segregation, the conductivity of both n-type regions is the same. Thus the units should be nearly symmetrical. For an efficient injection σ_n/σ_p should be made as large as possible.

That is,

$$\frac{\sigma_n}{\sigma_p} = \frac{(N_d - N_a)\,\mu_n}{(K_a N_a - K_d N_d)\,\mu_p} >> 1. \tag{7}$$

Substituting (4) into (7) it is found that:

$$\frac{K_d}{K_a} << 1. \tag{8}$$

Although (8) is satisfied by (6), the greater the inequality (8), the better the injection efficiency of the emitter will be.

The melt junction is always abrupt. The quench junction is abrupt also, but may be gradual if the growth rate is suitably controlled during the junction formation.

The Thermal Process

Thermal Characteristics

The thermal properties of germanium of importance here are given in Table I where they are also converted into units convenient for the case of a cylinder 30 mils in diameter.

Table I

Thermal Characteristics of Germanium

Heat of fusion(2)	8000 cal/At gr.	2.68 cal/cm
Specific Heat(3)	0.074 cal/gr °C	1.8×10^{-3} cal/cm °C
Thermal Conductivity(4)	0.1 cal/sec cm °C	$1/2.2\times10^{3}\ \frac{\text{cal cm}}{^{\circ}\text{C sec}}$
Emissivity(5)	0.1	

(2) S. E. Bradshaw, "Phenomena Observed in the Melting and Solidification of Germanium", J. Electrochemical Society 101 (January 1954), p. 293.

(3) HANDBOOK OF PHYSICS AND CHEMISTRY, Chemical Rubber Publishing Co., 33rd Edition, p. 1874.

(4) A. Grieco, H.C. Montgomery, "Thermal Conductivity of Germanium", Physical Review 86 (May 15, 1952), p. 570. Estimated also to be 0.1 cal/sec cm °C in liquid by applying the Wiedemann-Franz law.

(5) Estimated from comparison with values for other elements.

The above data show that at the melting point there is somewhat more heat stored in heat of fusion than as specific heat.

Temperature Distribution

Since the present thermal treatment is a dynamic process (as contrasted with an equilibrium process) and involves a varying boundary condition (motion of the liquid-solid interface) the exact heat flow problem is very difficult to solve. However, an approximate approach can yield useful information. The model considered here is one dimensional, has a perfect heat sink and a constant thermal conductivity.

In the melting process, heat is fed at one end of the germanium filament from a high temperature source while the other end is kept at a nearly constant low temperature, T_o. The time constant for the heat diffusion process in the solid is small compared to the duration of temperature rise at the heater. On the basis of a lumped RC representation the diffusion time constant comes out as 0.04 second; a distributed representation, which is more accurate, would give a shorter time constant. The time constant for the actual heating process, which in addition to supplying heat for the diffusion process also supplies heat of fusion, measures in the order of 0.3 second. Here it can consequently be assumed that heat flow is instantaneous. Therefore, as the temperature at the heated end rises up to the melting point, T_{MP}, the temperature is linearly distributed along the length of the crystal if the thermal conductivity is constant. As the heated end reaches the melting point, heat of fusion is supplied to the liquid solid interface in addition to the heat flow necessary to sustain the thermal gradient. In other words, more heat enters the heated end during the melting of the bar than goes out to the heat sink during this period. Consequently a larger temperature gradient exists in the liquid than in the solid. This is shown in Fig. 2. At equilibrium, the liquid-solid interface is stationary, no heat of fusion is supplied and the temperature gradient is uniform.

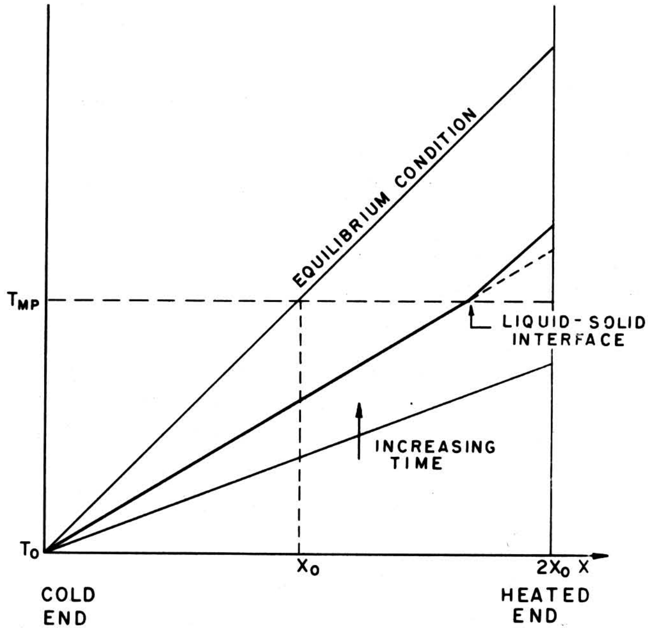

Fig. 2 - Temperature distribution in cylinder during melting process.

A. - Melting.

The rate of heat flow in the solid is:

$$\left(\frac{dQ}{dt}\right)_S = \sigma A \left(\frac{dT}{dx}\right)_S \qquad (9)$$

where σ = thermal conductivity, A = cross sectional area through which heat flows. In the liquid the rate of heat flow is:

$$\left(\frac{dQ}{dt}\right)_L = \left(\frac{dQ}{dt}\right)_S + HA\left(\frac{dx}{dt}\right) = \sigma A\left(\frac{dT}{dx}\right)_L \qquad (10)$$

where H = heat of fusion; $\frac{dx}{dt}$ = velocity of the liquid-solid interface. Since in practice the equilibrium condition (liquid-solid interface at $x_o = 0.1$ cm) is reached roughly 0.5 sec. after melting begins, the following evaluation can be made:

$$\left(\frac{dx}{dt}\right)_{\text{average}} = 0.2 \text{ cm/sec}$$

$$\left(\frac{dT}{dx}\right)_S = \frac{1000}{0.1} = 10^4 \ {}^{o}\text{C/cm} \qquad (11)$$

where the liquid solid interface is taken to be 1000 C° above the heat sink.

Substituting (11) into (9) and using the converted data of Table I:

$$\left(\frac{dQ}{dt}\right)_S = \frac{10^{-3}}{2.2} \times 10^4 = 4.55 \text{ cal/sec} = 19 \text{ watts} \qquad (12)$$

$$AH\frac{dx}{dt} = 2.68 \times 0.2 = 0.536 \text{ cal/sec}$$

Substituting into (10):

$$\left(\frac{dQ}{dt}\right)_{L_{ave}} = 4.55 + 0.54 = 5.09 \text{ cal/sec}$$

$$\left(\frac{dT}{dx}\right)_{L_{ave}} = \frac{1}{\sigma A}\left(\frac{dQ}{dt}\right)_{L_{ave}} = 1.12 \times 10^4 \ {}^{o}\text{C/cm}$$

Comparing this to (11) shows that the average increase in temperature gradient to produce fusion is only about 10 percent.

The above description neglects radiation and convection losses which would require that the temperature gradient be a function of temperature and largest at the hottest region. A rough estimate of the heat lost by radiation W_R can be made as follows:

$$W_R = \varepsilon KA\,(T^4 - T_o^4) \qquad (13)$$

where ε is the emissivity, K is the Stephan-Boltzmann constant and A the radiating area (about 3×10^{-2} cm² for a 0.1 cm length of liquid). If the temperature is assumed uniform in the liquid, the calculated radiation heat losses are given in Table II. This is negligible compared to the 19 watts lost by conduction according to (12).

The convection losses are very difficult to evaluate but there is experimental evidence indicating that they are not more than 1.1 watts.

Table II

Calculated Radiation Losses

T	W_R
1200° K	0.035 watts
1800° K	0.18 watts
2400° K	0.57 watts

Therefore, at the end of the melting process, the present model exhibits a uniform temperature gradient – the equilibrium condition of Fig. 2. Then:

$$\left(\frac{dQ}{dt}\right)_S = \left(\frac{dQ}{dt}\right)_L \qquad (14)$$

B. – Freezing

During freezing, latent heat of fusion is liberated. Assuming all the heat is lost by conduction through the solid, the process can be formulated as:

$$\left(\frac{dQ}{dt}\right)_S = \left(\frac{dQ}{dt}\right)_L + HA\,\frac{dx}{dt} \qquad (15)$$

where $\frac{dx}{dt}$ is the velocity of the liquid-solid interface or the growth rate. See Fig. 3. Because of the initial condition (14), the initial growth rate is zero. Physically this means that the initial heat flow comes from the specific heat stored in the liquid.

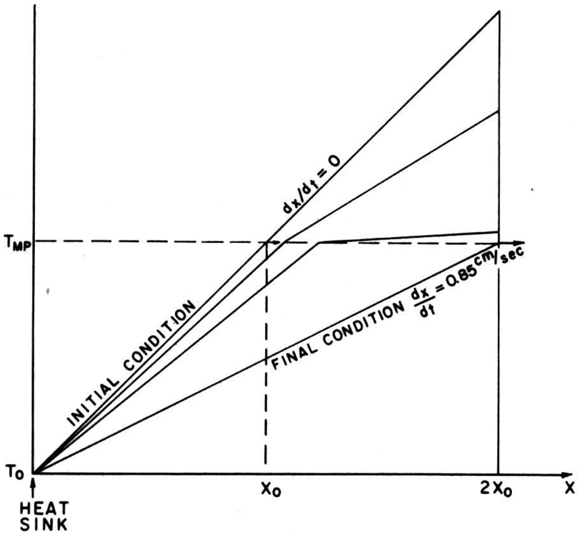

Fig. 3 - Temperature distribution in cylinder during freezing process (heat loss only by conduction to heat sink).

As mentioned previously, the time constant for the diffusion process is less than 0.04 sec. Hence the temperature in the liquid drops rapidly down to T_{MP}. During this time the growth rate is very low, the impurities are segregated and the p-type layer is formed.

Obviously all the liquid is at freezing temperature, T_{MP}, when the liquid-solid interface is at $x = 2x_o$, the end of the cylinder. Then $\left(\frac{dQ}{dt}\right)_L = 0$ and the growth rate is:

$$\left(\frac{dx}{dt}\right)_{x = 2x_o} = \frac{1}{HA}\left(\frac{dQ}{dt}\right)_S = \frac{1}{HA}\,\sigma A\,\frac{dT}{dx}$$

$$= \frac{1}{HA}\,\sigma A\,\frac{T_{MP}}{2x_o} \qquad (16)$$

$$= \frac{1}{2.68}\;\frac{10^{-3}}{2.2}\;\frac{10^{3}}{0.2} = 0.85\ \text{cm/sec}$$

which is a very rapid growth rate. Should the temperature of the liquid be T_{MP} before the liquid-solid interface reaches the end of the crystal the growth rate would be even higher. But it could not be higher than by a factor of 2 (i.e., 1.7 cm/sec) which corresponds to all the liquid being at temperature T_{MP} from X_o to the end of the crystal--except in the following case.

If the heat losses at the hot end of the cylinder are appreciably greater than the losses by conduction to the heat sink alone, then the temperature at $2X_o$ will drop so rapidly that the liquid will eventually comprise two regions as shown in Fig. 4. One region will be supercooled and separated from the solid by the other region composed of hot liquid. When the non-supercooled liquid reaches the freezing temperature (T_{MP}) the supercooled region suddenly sees the liquid-solid interface and freezes at an even greater rate than before.

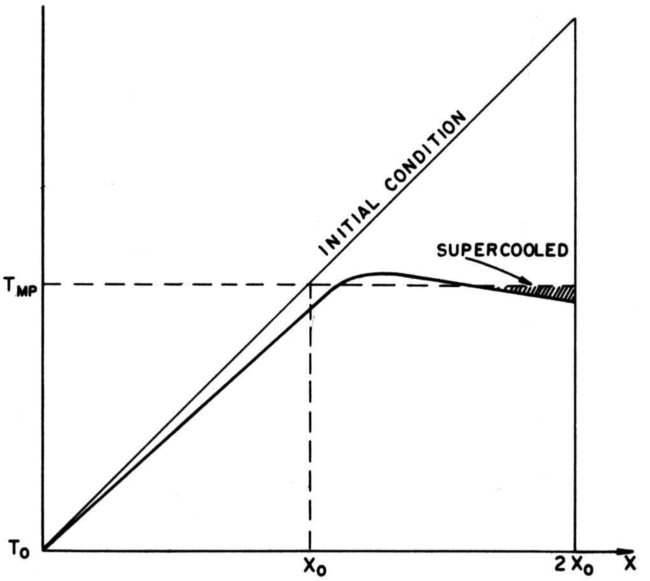

Fig. 4 - Temperature distribution in cylinder during freezing process (case of supercooled liquid).

Crystallographic Considerations

Since the growth is nucleated by a relatively large area single crystal it is reasonable to expect that the processed unit remain a single crystal in the region of slow growth. In the quenched region or region of rapid growth because of the very high growth rate discussed above it is not obvious that the crystal will remain monocrystalline. This growth rate is about 500 times greater than the rates used to pull single crystals of germanium by standard techniques. X-ray back reflection analysis of the interior of two samples showed these to be single crystals throughout, one with stresses in the recrystallized region, the other perfect. The physical appearance and electrical behavior of good samples not X-rayed lead to no suspicion that they are other than single crystals.

It is desirable to cut the cylinders along the [111] axis, for then the (111) equilibrium face of the freezing germanium will more probably form a flat quench junction normal to the cylinder's axis. The melt junction is almost always flat and normal to the cylinder's axis as determined by the thermal gradient. The [111] orientation is also desirable for obtaining a thin p-region or base layer, since crystal growth is slowest along the [111] direction.

Experimental Techniques

A germanium crystal doped with donors and acceptors as discussed under Design Criteria is cut up into 100-mil-thick slices which are examined for their resistivity and uniformity. For this experimental work resistivities up to 0.1 ohm/cm were used. The slices are cut up into 30-mil-diameter cylinders with an ultrasonic machine-tool. It has been found that etching the crystal prior to the melt-quench process is not necessary.

The cylinders are mounted in a heat sink and placed in a helium atmosphere in contact with a heating element which may be a carbon filament or a machined graphite strip. See Fig. 5. The position of the crystal is controlled by a micrometric screw until contact is indicated by an ohmmeter labelled Ω in Fig. 5.

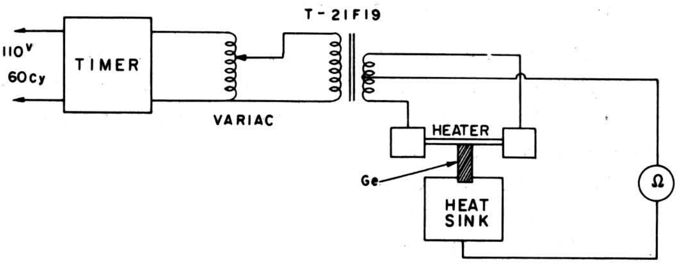

Fig. 5 - Experimental set-up for melt-quench process.

A timer is operated to pass a one-second pulse of current through the heating element. As the heater reaches a temperature of 2300 to 2900°C depending on the Variac setting, the crystal melts about halfway down its length. When the heating current is turned off, the crystal cools (mostly by conduction to the heat sink) at an initial rate of about 1000°C/sec at the liquid solid interface.

Actually the freezing process is slowed down by the fact that the heater remains hotter than the germanium while the latter freezes. Yet, the process is still rapid enough to give satisfactory results. A furnace has been built in which the heater is supported by the armature of a relay so that the heater can be removed from the liquid germanium at the end of the melting process. This arrangement has the advantage of decoupling the thermal capacity of the heater from the germanium, and of greatly reducing the possibility of strains in the growing crystal.

It is remarkable that in most cases the surface tension is able to restrain the liquid to the initial cylindrical shape.

Graphite, copper, and forced-cooled copper have been used for the heat sink with the crystal struck in a well in the case of graphite and soldered in the case of copper. The use of a heat sink is imperative in order to establish a strong longitudinal temperature gradient which causes the melting front to advance as a flat surface. Crystals supported by a thermal insulator show a lopsided melt junction.

It is possible to accelerate the cooling process by increasing the radiation losses if the crystal surface is blackened to increase its emissivity. Colloidal carbon condensed from smoke or deposited by the heater itself serves this purpose; but a coating of aquadag forms a nucleating surface and hence yields a polycrystalline region. Although radiation losses are usually negligible as shown in Table II, they are multiplied by a factor of 10 when the crystal is blackened.

Transistors by the Melt-Quench Process

The most suitable structure for the melt-quench process is a cylinder. Hence, the resulting transistor will have axial symmetry and will comprise a pair of plane parallel junctions separated by a distance w (Fig. 6). Considering the use of such a transistor at high frequency it is reasonable to design it for operation where its power gain varies at the rate of 6 db/octave so that the approximate power gain can be calculated from:[6]

$$\text{P.G.} = \frac{g_m}{4\omega^2 \, r_{bb'} \, C_{b'e} \, C_c} \qquad (17)$$

The base lead resistance $r_{bb'}$ can be minimized by making the connection completely surround the base layer. It is then:

$$r_{bb'} = \frac{\rho}{8\pi w}$$

The other terms to be evaluated are:

$$C_{b'e} = 1.33 \times 10^{-9} w^2 \, I_e \qquad \text{(mils, ma, f)}$$

$$C_c = \frac{0.071 \, d^2}{\sqrt{\rho V_c}} \qquad (\text{mils}, \mu\mu\text{f})$$

Hence, a 30-mil-diameter unit with $w = 0.5$ mils, $\rho = 1$ ohm cm, $V_c = 6$ volts, $I_e = 1$ max

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(6) L. J. Giacoletto - "Study of PNP Alloy Junction Transistor from DC through Medium Frequencies". RCA Review XV (Dec. 1954), p. 506.

gives:

$r_{bb'} = 31$ ohms

$C_{b'e} = 334$ $\mu\mu$f

$C_c = 26$ $\mu\mu$f

P.G. at 1M_c = 29.6 db

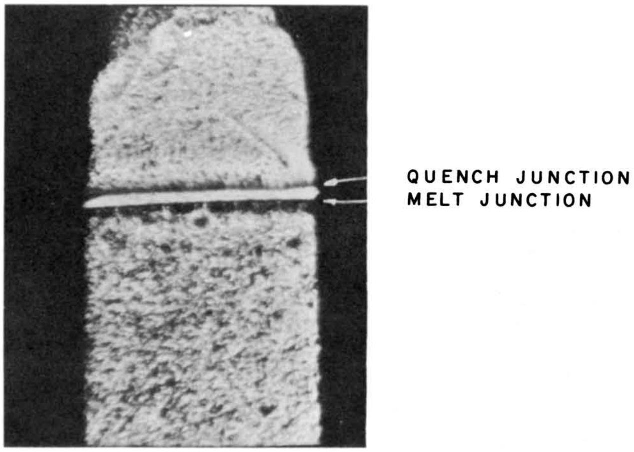

Fig. 6 - Etched cross section of germanium cylinder processed by the melt-quench technique. The spacing between the junctions is 1.2 mils.

The present bulletin is intended to describe the principles and techniques of the melt-quench process. Much of the evaluation has been done by direct physical observation (junction spacing, etc.) rather than by more indirect electrical measurements on completed transistors.

A wide variety of structures have been made with base widths from about 0.1 mil to over 1 mil. To make the principles and techniques of this new process known at this early time no attempt has been made to accummulate extensive transistor data on any one structure.

To give a rough estimate of the possibilities of this technique some individual measurements will be cited. An early unit of about 0.8 mil junction spacing gave the amplifier performance of Table III. This is considered promising in view of the fact that this unit had a collector-to-base current-gain factor of but 5. Its base lead resistance was 36 ohms. Other units have had current-gain factors up to 70. Measurements of junction capacitance show a dependence on voltage of $V^{-1/2}$ indicating that the transitions between the p and n type regions are abrupt.

Table III

Characteristics of Early Experimental Melt – Quench Transistor

	Audio Frequency	455 KC
Power Gain ($I_e = 1$ ma, $V_c = 3^V$)	31.5 db	33.4 db
Power Gain ($I_e = 2$ ma, $V_c = 6^V$)		37.1 db
Input impedance	200Ω	200Ω
Output impedance	30 kΩ	>52 kΩ
Neutralizing Capacitance		7-10 $\mu\mu$f

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Appendix

RADIATION BY GERMANIUM THROUGH ITS OWN SOLID

Since germanium is transparent to much of the infrared and since heat is carried by infrared radiation, it is interesting to evaluate this process. Since radiation is an instantaneous process compared to diffusion the question arises as to the relative importance of these two heat losses.

Wien's law for the spectral distribution of radiation from a blackbody gives the maximum energy at:

$$\lambda_{max} = \frac{2884}{T} \text{ (microns)}$$

Then, the radiation from the liquid-solid interface ($T \approx 1200^{\circ}K$) gives

$$\lambda_{max} = 2.4\ \mu.$$

This is well in the transparent region of room-temperature germanium. According to V. A. Johnson and H. Y. Fan (Phys. Rev. 79, Sept. 1, 1950, p. 899) the energy gap depends on temperature as:

$$E_g = 0.73 - 1.1 \times 10^{-4}\ \text{ev}/^{\circ}K \text{ i.e., } 0.60 \text{ ev at } 1200\ ^{\circ}K$$

which corresponds to a transmission threshold at $\lambda = 2.05\ \mu$. Hence the hot crystal is transparent to most of the radiation.

The number of thermally excited electrons at the solid near its melting point is calculated as:

$$\frac{(2\pi mkT)^{3/2}}{h^3} e^{-Eg/2kT} = 5.25 \times 10^{18}$$

This is such a small concentration that it should not contribute to the absorption. Therefore solid germanium is transparent to radiation from its liquid-solid interface.

The power radiated by the liquid solid interface is:

$$W_R = \varepsilon K\ (T^4 - T_o{}^4) = 1.14 \text{ watts/cm}^2$$

The power lost by thermal conduction through a slab of germanium of germanium of 0.1 cm thickness is:

$$W_c = \nabla A \frac{dT}{dx} = 3820 \text{ watts/cm}^2$$

Hence, in the present case the radiation loss to the heat sink supporting the cylinder is negligible.