fresh surface may be more than repaid if it is attacked avidly enough by the atmosphere; there is then an effective negative surface tension $-\gamma$. We might have perhaps $\gamma b^2 \sim 1$ *ev* (b=lattice constant). The ratio γ/μ (μ=shear modulus) would then be about 1A. The surface tension forces on a small hump on the surface [Fig. 1(a)] obviously have the right character (a central pull

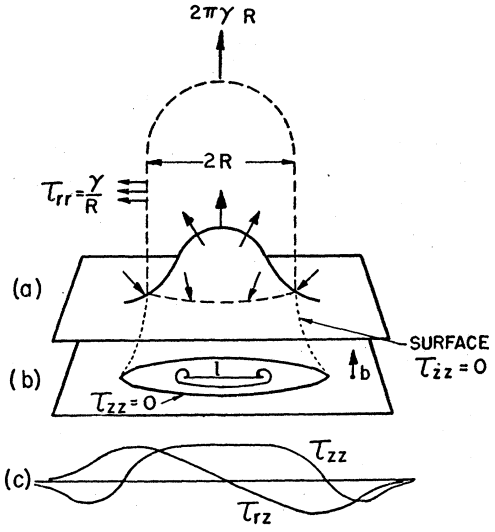

FIG. 1. Model for whisker growth.

surrounded by a restraining pressure) to "wire-draw" it into a whisker according to intuitive ideas of plastic flow. For the observed whisker size ($R \sim 10^{-4}$ cm) the stress of order γ/R in and just below the hump might exceed the actual yield stress, though not the theoretical yield stress ($\sim\mu/20$). However, on this small scale one must consider in detail how flow is catalyzed by dislocation.

The model of Fig. 1 lends itself to rough calculations. A Frank-Read source of length l and vertical Burgers vector b lies in a horizontal plane (b) at a depth of order l below the hump. The stress τ_{zz} [Fig. 1 (c)] makes the source emit a dislocation loop by "climb." The loop expands in the plane (b) until it reaches a radius where $\tau_{zz}=0$. Here the stress τ_{rz} assisted by image forces makes the loop glide vertically, so adding one atomic layer to the base of the hump. When by repetition of this a reasonable whisker has grown, τ_{zz} will be $2\gamma/R$ in the whisker and about γ/R at the source. To operate the source, τ_{zz} must be at least $\mu b/l$. With $\gamma/\mu \sim 1\text{A} \sim b$, this will be so if $R \sim l$. The stress at the source ultimately falls off both for $R \gg l$ and $R \ll l$ if the source depth stays constant. The whisker radius is thus tied to the length of a Frank-Read source, which is usually supposed to be about one micron. The surface $\tau_{zz}=0$ forms a "stress funnel" which guides each loop more or less unerringly to break surface at the base of the whisker, and so keeps its diameter constant. If the motion of the source is not to be stopped by the back-pressure of the vacancies it emits, there must be suitable sinks for them. It can be shown that surface tension changes the volume of a body of any shape with compressibility χ by $\frac{2}{3}\gamma\chi$ times its surface area. For a macroscopic specimen the corresponding mean pressure, $\frac{2}{3}\gamma\chi$ (surface/volume) would fall far short of the value required to make Frank-Read sources in the interior act as the necessary sinks. However, it should not be hard to find them at the surface. Frank[5] has shown that even with positive surface tension it may be energetically an advantage for a dislocation reaching the surface to develop a hollow core. Or again, if we had a depression instead of a hump in Fig. 1 the source would work in reverse, absorbing vacancies and deepening the depression.

We may use a calculation of Mott's[6] to find the rate of growth. He showed that, if a cube has normal stresses P on one pair of opposite faces and $-P$ on another pair, a volume $V \sim NbD(Pb^3/kT)$ of material is transferred from one pair of faces to the other in unit time if there are N points on dislocations which can absorb or emit vacancies and the coefficient of self-diffusion is D. Our case is analogous. P is γ/R times a factor κ depending on the detailed stress-distribution, including a possible stress concentration if successive loops help one another. N is about l/b, the number of lattice sites per loop, times the fraction β (perhaps$\ll$1) of them which can emit or absorb vacancies times n, the number of loops in transit between source and surface at one time. The rate of change of the whisker length h will thus be

$$\dot{h} = V/\pi R^2 \sim \kappa\beta n D(b/l^2)(\gamma b^2/kT).$$

With the value of D for tin at room temperature,[7] we can get a growth rate of a millimeter or a centimeter per year with $\kappa\beta n \sim 100$ or 1000. The small number of accidental coincidences of sources and suitable surface irregularities may be enough to account for the number of whiskers per unit area. If not, we might suppose that the sources build their own humps by operating initially without stress as the result of a subsaturation of vacancies due to a change of temperature.

Many variations of this model are possible. The transfer of loops to the surface might occur by the formation and joining up of secondary loops in a vertical plane as in "prismatic punching,"[8] where the stress distribution is similar. The whiskers might then be prismatic. Professor Seitz (to whom the writer is indebted for helpful discussions) has suggested a mechanism involving a spiral prismatic dislocation,[9] which is the internal counterpart of spiral growth on the surface and which leaves a screw dislocation along the axis of the whisker.

* Work done under U. S. Office of Naval Research contract.
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Oxygen-Induced Surface Conductivity on Germanium

EDWARD N. CLARKE
Sylvania Electric Products, Bayside, New York
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MOTT has suggested[1] that oxygen may introduce acceptor energy levels on a germanium surface. The present note reports mainly on gas adsorption and resulting surface electrical conductance at a temperature of 197°K.

A very thin high-resistivity (40 ohm-cm at room temperature) n-type single crystal rectangular bridge of germanium was assembled for electrical measurements in a high vacuum system. The voltage probes are germanium and an integral part of the single crystal and are separated by 0.5 cm. The crystal width is 0.2 cm and the thickness about 0.004 cm, made purposely thin to amplify any surface changes. The surface was prepared by etching with an etchant of HF, HNO_3, and H_2O, and then rinsing with H_2O.

The residual gas pressure was reduced to about 5×10^{-8} mm Hg after pumping for 20 hours, and after heating the experimental tube containing the Ge to about 450°C for one half-hour. This treatment decreased the germanium conductance by a factor of two, representing a decrease in conductance of 4×10^{-6} mho. If one assumes a surface carrier mobility of 1000 cm²/volt sec this represents a decrease of 4×10^{10} carriers per cm² of surface. A different carrier concentration will correspond to a different mobility. The germanium was heated to near its melting point for a short period of time (seconds) and then quenched rapidly by radiation

to the surroundings at room temperature. This heating and quenching in a high vacuum may have produced a surface cleaner than the original etched surface, but also has changed the bulk characteristics. As described below, the germanium appears now to be more sensitive to surrounding gases than was the original crystal with etched surface.

After the above heating and quenching, gases at several different pressures were admitted slowly through the vacuum system. Figure 1 shows a typical plot of germanium conductance at 197°K varying as the residual gas pressure varies from 10^{-7} mm Hg to 10^{-3} mm Hg (by shutting off the diffusion pump). Dry argon admitted to the germanium at 0.3 mm Hg for one minute has little effect upon the conductance but dry oxygen at 0.3 mm Hg for one minute increases the conductance by a factor of ten. The largest surface conductance at 197°K obtained during similar observations is 8×10^{-4} mho, representing about 10^{13} carriers per

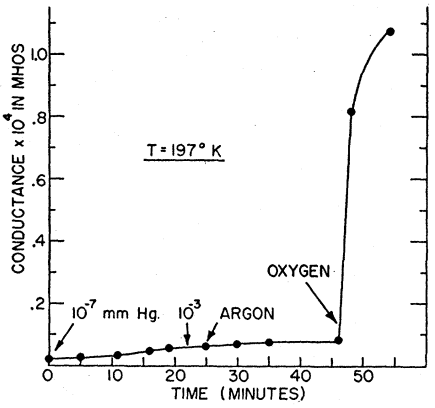

FIG. 1. Dependence of Ge conductance upon surrounding atmosphere. The diffusion pump was shut off at time $t=0$; argon was admitted at $t=25$ min and removed after one min; oxygen was admitted at $t=47$ min and removed after one min.

cm² of surface (if a mobility of 1000 cm²/volt sec is assumed). Oxygen is also adsorbed at room temperature. Initially, it appeared possible to remove most of the absorbed gas (as measured by electrical conductance) by simply heating the experimental tube containing the Ge in a high vacuum at about 450°C for one half-hour. However, Fig. 2 shows that as the number of cycles increased (each cycle corresponding to a maximum conductance with gas adsorption and then a minimum conductance after heating in a high vacuum), the minimum conductance became larger. By the twelfth cycle, heating the tube at 450°C had a much smaller effect in reducing the surface conductance. This might be

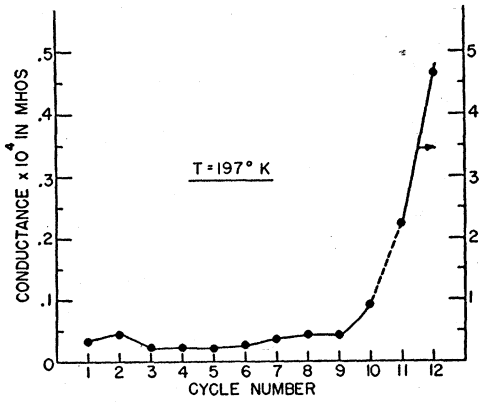

FIG. 2. Conductance of Ge after heating in high vacuum. Each cycle corresponds to a maximum and minimum conductance. Cycles 11 and 12 correspond to right-hand ordinate.

described in terms of a thin layer (oxide) being built up on the surface. It is not unreasonable to assume that oxygen may introduce surface acceptor energy levels resulting in hole conductivity.

Further work will include measurements to determine surface carrier type and surface mobility of carriers.

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Thermally Induced Acceptors in Single Crystal Germanium

R. A. LOGAN
Bell Telephone Laboratories, Murray Hill, New Jersey
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WHEN germanium is heated above 600°C and then cooled, it has been shown[1] that the acceptor density increases markedly. This effect is reversible in that prolonged reheating at 475°C "anneals" out these acceptors. More recently, simlar acceptors have been produced in experiments[2] where the cooling time has varied from a very rapid quench to a time of the order of several minutes.

It has been shown[3] that copper as an impurity in germanium has the same activation energy, diffusivity, solid solubility, and "annealing" property as these acceptors. Since no precautions were taken to avoid copper contamination, and since very small concentrations of copper will produce these acceptors, this evidence led to the conclusion[3] that in all of the above experiments copper produced the observed acceptor centers. A method has been developed by which it is possible to heat germanium to high temperature for extended periods of time and avoid copper-like contamination. This makes it possible to examine more closely the phenomena associated with quenching germanium from high temperature.

In these experiments, small samples were cut from single crystal n-type germanium which contained about 6×10^{12} donors per cc. The specimens were cleaned[4] by acid etching followed by a rinse in twice-distilled water. They were then soaked in a strong aqueous KCN solution. The cyanide forms soluble complexes with copper, as well as other metallic ions, which are then removed by rinsing the specimens in twice-distilled water.

To study the effect of rapid quenching from high temperatures, a sample was placed on a carbon boat furnace in a quartz tube and heated in a hydrogen atmosphere by rf induction. A castor oil bath was located about one inch below the boat. The sample could be dropped from the boat into the oil bath in about 0.1 second. If one of the samples was heated at an elevated temperature for one minute and allowed to cool slowly to room temperature by simply turning off the rf heater, no detectable change in resistivity occurred. Resistivity was measured at −78°C, where the measurement was sensitive to impurity concentrations as low as a few times 10^{12} per cc or about one per 10 billion germanium atoms. In this experiment, the sample cooled to 500°C in about 15 seconds and reached room temperature in a few minutes (hereafter this will be referred to as the regular cooling cycle). However, if the sample was quenched in the oil bath, a change in resistivity resulted and acceptor centers were found uniformly throughout the sample. The effects of heating at different temperatures before quenching are shown in Fig. 1.

If the quenched samples were recleaned, as described above, and reheated to a high temperature followed by the regular cooling cycle, they returned to nearly their original resistivity.

It has been proposed[5] that lattice defects such as vacancies and interstitial germanium atoms may act as acceptors in germanium. If the acceptor centers produced by quenching are thermally produced lattice defects,[6] then to a close approximation the density of acceptor centers n_Q present when the sample is in thermal equilibrium at temperature T_Q is given by

$$n_Q = n_L e^{-E/kT_Q},$$