$\times 10^{16}$ electron/cm^3, and the relaxation time in the thermal equilibrium $\tau_0 = 1.9 \times 10^{-12}$ sec. Sample 1 was 1.2 mm and sample 2 was 1.55 mm long in the direction of the transmission of the radiation. The other dimensions were 0.45×6 and 0.5×5 mm^2, respectively. The resistance of the samples was about 10 Ω measured along the longest axis. The electrical contacts had been Ohmic and were made similar to the procedure which is described by Guion and Ferry.[7] These contacts at the ends of the samples were connected to a voltage pulse generator, the pulses being 30 and 300 nsec long, the latter pulse had a step at the trailing edge, as shown in Fig. 1. The radiation of a chopped CO_2 laser transmitted the sample and was detected by a CdHgTe detector with a response time < 1 nsec.[8] The laser pulses were 1 msec long, the repetition rate of the laser and voltage pulses was 16 Hz, and the laser radiation was polarized parallel to the electric field of the voltage pulses and parallel to the (110) direction of the crystal.

Two modulated transmission signals are shown in the figure. The signal of sample 1 was observed at a field of 3.8 kV/cm, the modulation was 2.7% of the total transmission signal. The modulation of 2.2% of sample 2 was measured at 3.3 kV/cm. From the current-voltage characteristic measured at the samples, we got 1.48 and 1.3 for the ratio of the zero-field mobility to the mobility at the electric field the modulations were measured. The decrease of mobility with increasing electric fields, which corresponds to a decrease in infrared transmission, might be caused by an increase of the effective mass due to intervalley scattering and due to a decrease of the relaxation time. Since the experiments were performed at 300 K, we may neglect the change of the effective mass.[5]

At samples with non-Ohmic contacts, we observed besides the described optical modulation due to the change of τ a further modulation caused by injected carriers, i.e., due to the change of carrier density. The first type of modulation follows instantaneously the applied voltage pulse, whereas the second type shows a very slow decay of the optical signal compared with the applied voltage pulse. The measured decay of the optical signal corresponds to a carrier lifetime of about 10 μsec. This type of modulation was extensively investigated by Gibson[1] and by McQuistan and Schultz.[9]

The relatively small modulation of only a few percent in spite of the large mobility change seems to be caused by the fact that the absorption of our samples at 10.7 μm is not only determined by free carriers. We measured the absorption coefficient of the samples at wavelengths in the range of 9 to 14 μm with an infrared spectrometer. Between 9 and 11.5 μm, a rather constant absorption coefficient of 2 cm^{-1} was found. At wavelengths between 11.5 and 14 μm, we observed a quadratic dependence of k on wavelength λ, which is characteristic of the absorption of free carriers. From this $k \propto \lambda^2$ dependence between 11.5 and 14 μm, we deduced a value of 0.46 cm^{-1} for k at the laser wavelength, which is much smaller than the measured 2 cm^{-1}. We do not know the cause of the bigger absorption coefficient, but the observed transmission modulation of the laser radiation can be explained by the deduced value of 0.46 cm^{-1}.

We could show that hot carriers modulate the transmission of CO_2-laser radiation. The modulation at short times is theoretically only limited by the relaxation time of the carriers. More favorable samples, i.e., samples made of semiconductor material with an absorption determined by free carriers only and a strong dependence of the relaxation time on electric field, should result in a corresponding high modulation.

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Formation of Injecting and Blocking Contacts on High-Resistivity Germanium*

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The behavior of Al and Sb/Ge/Sb layers evaporated on high-purity Ge and heat treated at 280 °C is studied by reverse-recovery, double-injection, and nuclear-particle-response techniques. The results indicate that the contacts have the injection and blocking characteristics of p- and n-type material, respectively. Backscattering measurements with 1.8-MeV $^4He^+$ ions show that solid-solid reactions occur.

Very-high-purity Ge has recently been produced for radiation detectors.[1–4] To fully exploit the possibilities offered by this material, it is desirable to form thin blocking and injection contacts at processing temperatures low enough to prevent a deterioration of the starting material. Previously, low-temperature reactions have been used to form Ohmic or blocking contacts to Si and GaAs.[5,6] We have found that n- and p-type

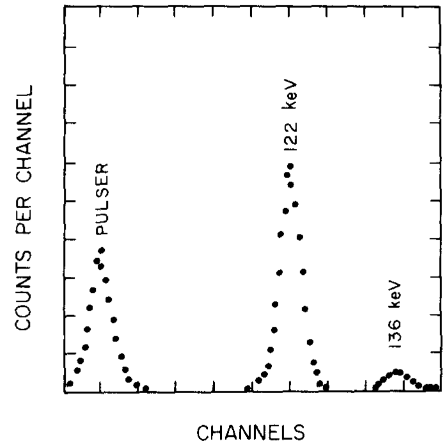

FIG. 1. Spectrum of ^{57}Co taken at 77 °K with a 25-mm^2 × 0.8-mm ν-type ($N_D - N_A = 5 \times 10^{11}/\text{cm}^3$) Ge detector. The resolution (FWHM) of the electronic chain is 3.1 keV. The reverse-bias voltage is 60 V.

layers can be formed in Ge at temperatures below 300 °C by using solid-solid reactions between Ge and evaporated metal films. This work demonstrates for the first time that injecting contacts for minority carriers can be formed with these low-temperature reactions.

Germanium samples with net dopant concentrations between 2×10^{10} and $5 \times 10^{11}/\text{cm}^3$ were obtained from R. N. Hall (General Electric Research Center, Schenectady, N.Y.) and W. L. Hansen (Lawrence Radiation Laboratory, University of California, Berkeley, Calif.). Surfaces were lapped, polished with Mirrorlux,[7] etched with a solution of $3\text{HF} : 5\text{HNO}_3 : 3\text{CH}_3\text{COOH}$ (parts per volume), rinsed in deionized water, and immersed in HF. Before evaporation, samples were washed in deionized water and dried. To make n contacts, three layers were deposited sequentially (200–400 Å of Sb, 200–400 Å of Ge, and 500–1500 Å of Sb) without breaking vacuum. For p contacts, a 500–1000-Å-thick Al film was deposited. Just after evaporation, the samples were heat treated for 1 h in a tube furnace with N_2 atmosphere at a temperature of 280 °C and slowly cooled (Ge-Al eutectic, 424 °C; Ge-Sb eutectic, 590 °C). Delays between evaporation and heat treatment generally resulted in poor contacts.

Nuclear-particle-detector techniques were chosen to establish the blocking nature of the contacts. Thin (< 1-mm) samples were used so that reverse-bias voltages greater than that required to fully deplete the sample could be applied easily. There was no appreciable change in reverse current for voltages from 1 to 20 times the full-depletion voltage, indicating that both contacts are blocking. Figure 1 shows the pulse-height distribution obtained with ^{57}Co and a 0.8-mm-thick structure (25-mm^2 area, $N_D - N_A = 5 \times 10^{11}/\text{cm}^3$) at 77 °K with at least a factor of 3 over voltage. The three peaks are the response to a pulse generator and to 122- and 136-keV x rays. The resolution (FWHM) of 3.1 keV for all three peaks is that of the electronic chain. These values of resolution indicate that the contacts are blocking with low noise levels. The resolution at 77 °K to α particles from ^{238}Pu incident on the Al contact and on the Sb contact is sufficient to clearly resolve the peaks at 5.46 and 5.5 MeV, demonstrating that the contacts are thin (< 1 μm).

Measurements of reverse recovery time on 20-Ω cm p-type Ge from room temperature down to 77 °K established that the n contacts inject electrons. In that same temperature range, the I-V characteristics were those of a rectifying p-n junction; p contacts on 20-Ω cm n-type Ge showed similar characteristics. To confirm the injecting property of these contacts, a p-ν-n device was constructed with ν-type Ge of about $5 \times 10^{11}\text{-cm}^{-3}$ doping concentration. Figure 2 shows the forward I-V characteristic of such a structure at 182 °K. The current at 1 V exceeds by two orders of magnitude the current calculated from the Ohmic conductivity of the ν-type material. This indicates strong modulation of the base region by both holes and electrons injected by the contacts. The current transient response (see insert, Fig. 2) to a differential voltage step agrees with that expected from double injection. The ambipolar diffusion length calculated from the time constant ($\tau = 700$ μsec) of the current transient is comparable to the length of the device. Under this condition, double injection is

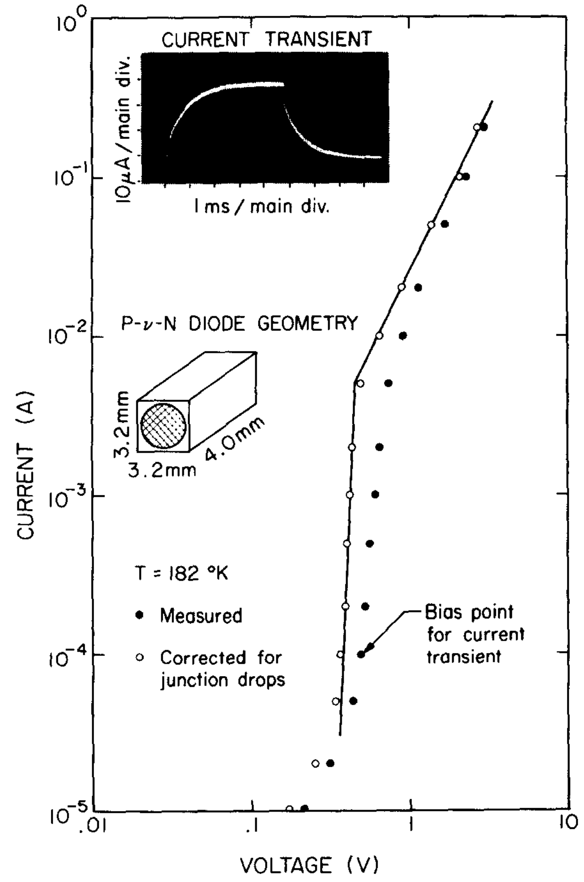

FIG. 2. I-V characteristics of a p-ν-n diode operating with forward bias. The closed circles, the measured values; the open circles, the values corrected for the junction drop (Ref. 8). The insert shows the small-signal current transient response to a differential voltage step.

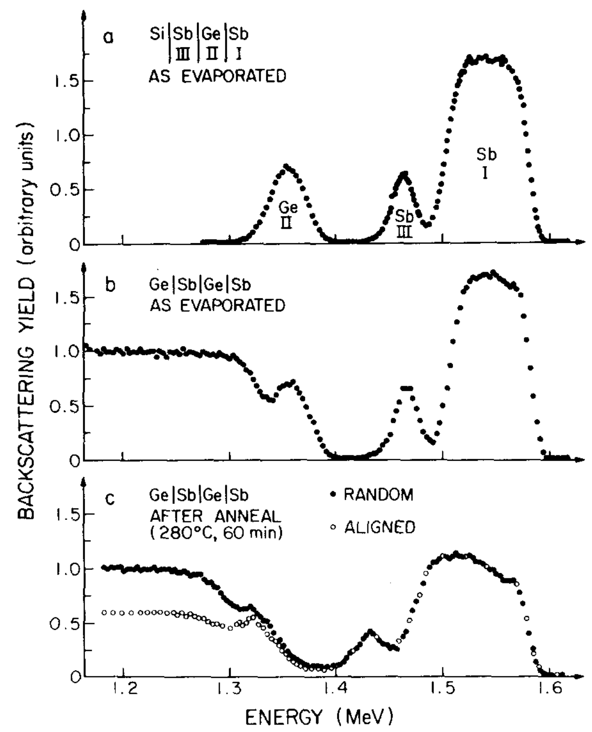

FIG. 3. Energy spectra of 1.8-MeV $^4\mathrm{He}^+$ ions backscattered from a composite layer of Sb/Ge/Sb, evaporated on Si (a), on Ge before (b), and after (c) heat treatment. The closed and open circles in (c) represent the random and the aligned ($\langle 111 \rangle$) spectra.

dominated by carrier diffusion and the current is expected to exhibit a steep characteristic nearly independent of the applied voltage, as is indeed observed. At still higher current levels, the observed V^2 behavior is attributed to junction saturation.[8]

Backscattering experiments[5,6] have established directly that the contacts described are formed through a solid-solid reaction with the thin evaporated layers. Figure 3 shows energy spectra for 1.8-MeV $^4\mathrm{He}^+$ ions backscattered from Si and Ge substrates covered simultaneously with a composite layer of Sb/Ge/Sb on Si [Fig. 3(a)], and on Ge before and after heat treatment at 280 °C [Figs. 3(b) and 3(c), respectively]. In Fig. 3(a), the highest-energy peak (SbI) represents the outermost Sb layer. The lower-energy Sb peak (SbIII) is separated from the (SbI) peak by energy loss in the sandwiched Ge (GeII). A spectrum for the sample with Ge as substrate is shown in Fig. 2(b); the substrate Ge produces an additional signal which extends into the signal of the evaporated Ge. After heat treatment the signals from the composite layer broaden and diminish in amplitude. The edge of the signal from the Ge substrate also is less distinct. This indicates intermixing of the various components. The spectrum obtained with the incident beam aligned in the $\langle 111 \rangle$ axis of the substrate suggests some crystallization in the evaporated Ge layer.[9]

Evaporated layers of Sb without Ge, which were subjected to the same heat treatment, did not exhibit injection. Backscattering spectra taken before and after heat treatment showed no change in the composition of the layers. In this case the presence of the evaporated Ge layer seems to be necessary for solid-solid reaction. A corresponding backscattering analysis[10] was performed on the Al contacts and shows that heat treatment activates the reaction Ge (substrate)$\rightleftharpoons$Ge (dissolved in metallization).

In summary, these results establish that thin contacts can be obtained at low processing temperatures by solid-solid reactions. The blocking and injection properties of these contacts have the characteristics of *n*- and *p*-doped layers. In connection with very-high-purity Ge, contacts produced at low processing temperatures allow the fabrication of thin-window detectors and the evaluation of the material.[11]

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