RADIATIVE RECOMBINATION IN GERMANIUM CRYSTALS BOMBARDED BY FAST ELECTRONS

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Data are presented on the infrared spectrum accompanying the recombination of electrons and holes in germanium single crystals. It is shown that with increasing concentration of Frenkel defects caused by fast-electron bombardment the relative intensity of the emission band with a peak at 2.35 μ also increases.

INVESTIGATION of the emission spectrum accompanying electron-hole recombination in semiconductor single crystals with diamond structure - germanium and silicon - has provided new information concerning their band structure,[1] energy levels of impurities and dislocations[2,3] and phonon spectrum (lattice vibrations).[4] It may be expected that when carrier recombination occurs through capture by defects produced by fast-particle, especially electron, bombardment,[5] it will be accompanied by infrared emission, whose spectrum will provide a means of determining defect energy levels. We know of no published data on recombination emission from germanium containing defects produced in this manner. In the present work, which was performed for the purpose of obtaining such data, the crystal samples were Weierstrass spheres[6] with 4 mm radius; these were used in order to increase the emission yield, which is usually severely limited by total internal reflection. All samples were made of germanium with n-type conductivity $\rho = 10$ ohm-cm and carrier lifetime $\tau_0 = 220$ μsec.

The results to be presented were obtained from three samples which differed as follows: In sample No. 1 emission was excited by hole injection from an alloyed indium junction, and in samples Nos. 2 and 3 from a pressure contact with indium. Sample No. 3 was irradiated with fast (0.7 Mev) electrons directed against its flat back surface, against the center of which the contact was then pressed. The active acceptor level concentration of defects produced by the bombardment was calculated to be about 5×10^{13} cm^{-3} near the surface, with decrease to zero at a depth of about 0.3 mm. It can be assumed in first approximation that the concentration of bombardment-produced recombination centers equals the concentration of active acceptor levels.

In experiments performed at T = 78°K the back surface of the sample was in direct contact with liquid nitrogen. Spectra were recorded by means of a quartz-prism spectrograph and dry-ice-cooled PbS photoconductive cell, from which signals were fed to a narrow-band amplifier, synchronous detector and EPP-09 recorder.

The spectra of all samples contain a band (Fig. 1) with 1.85 μ (0.67 ev) maximum at room temperature and 1.67 μ (0.74 ev) at 78°K, which was attributed[1] to the intrinsic emission of germanium crystals produced by inter-band transitions of electrons with the cooperation of lattice vibrations. The shift of the long-wave edge of this band is in good agreement with the width change of the forbidden germanium band. From our data the temperature coefficient β is 3.2×10^{-4} ev/deg, which is close to the result obtained by Haynes and Burstein.[1,7]

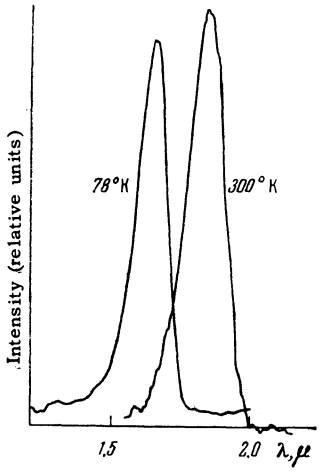

FIG. 1. Intrinsic germanium bands at 300° and 78° K.

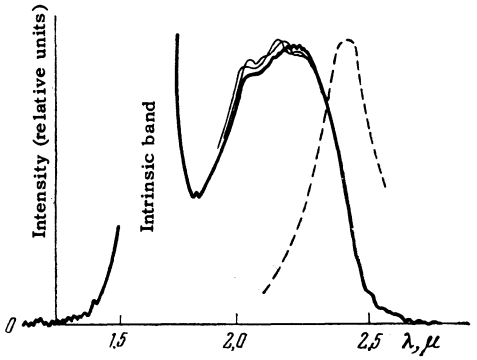

FIG. 2. Extrinsic and intrinsic spectra of germanium sample with alloyed indium junction at 78° K. The maximum of the intrinsic band lies far outside of the figure. Three successively recorded curves are given, and are compared with the spectrum observed by Newman (dashed line).[3]

All samples also yielded a weaker band from 2 to 2.5 μ, which is shown for sample No. 1 by the continuous curves in Fig. 2. Newman[3] and Benoit[8] have observed a band in this region, which Newman attributed to radiative recombination at dislocations because deformed germanium crystals were used in his experiments. The shape and position of the band that we observed at 78°K differ essentially from the spectra given by Newman, which are represented by the dashed curve in Fig. 2. We obtained curve a with spectrograph slits ($\Delta\lambda = 0.175\ \mu$) whose narrowness was limited by photoresistor noise. This broad band is observed in the region where germanium is transparent and there is reason to believe that it consists of a few narrower bands corresponding to impurity or dislocation levels; however, its structure could not be resolved.

The extrinsic spectrum of sample No. 2 at T = 78°K is shown in Fig. 3. The peak is located near 2.35 μ (0.53 ev), and the asymmetry of the curve suggests the existence of additional unresolved peaks.

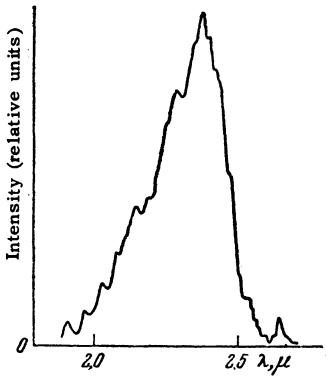

FIG. 3. Extrinsic emission spectrum of n-type germanium sample with neither alloyed indium nor electron bombardment; T = 78° K.

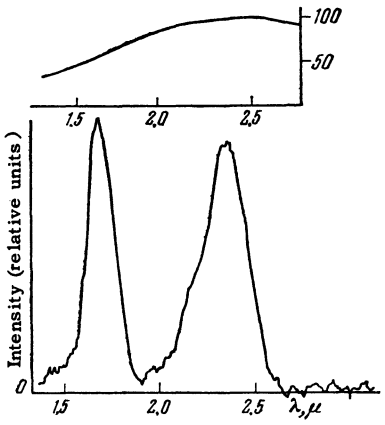

FIG. 4. Spectrum of n-type germanium at T = 78°K after irradiation by 0.7-Mev electrons at room temperature. The sensitivity curve of the PbS photoconductive cell is shown above.

Fig. 4 shows the spectrum of sample No. 3, which was not subjected to alloying with the indium and was irradiated by 0.7-Mev electrons, which strongly attenuated the intrinsic band. For an injection current of 100 μa the signal-noise ratio at the amplifier output for the intrinsic peak was 50 for sample No. 2 and unity for sample No. 3. The intensity of the extrinsic emission was of the same order for both samples.

If electron bombardment had not produced additional levels at which radiative recombination takes place, but only reduced the carrier lifetime (a well-known effect), the intensity of extrinsic radiation, proportional in first approximation to the carrier excess and therefore (for constant injection) to the lifetime ($\Delta p = G\tau$), should be reduced just as strongly. This is not observed, and it is therefore reasonable to assume that radiative recombination takes place at bombardment-produced levels, which evidently belong to Frenkel defects. The energy of these emitted photons is close to the extrinsic spectrum of unbombarded germanium (sample No. 2).

The nature of the centers that cause the extrinsic band of an unbombarded sample has not been established, but it may be assumed that the original material possesses a large number of structural defects or dislocations. The observed emission band may be associated with a level located 0.53 ev from one band of energy levels and therefore 0.22 ev from the other band. A conclusive answer will require experiments with germanium crystals containing a very small initial number of defects and dislocations.

According to existing ideas concerning the nature of recombination radiation, in the case of a large departure from equilibrium concentrations of electrons and holes (strong excitation) their direct recombination, which results in intrinsic radiation, is a bimolecular process; with a carrier lifetime which is independent of excitation the intrinsic band intensity should be proportional to the square of the carrier concentration. In our experiments on samples with an alloyed contact the emission intensity B near the intrinsic peak and the injection current J were related as $B \sim J^m$, where the exponent m is close to 1.7.

The experimental dependence of emission intensity on injection current can be used to give only very approximate results, as it is well known that the recombination rate in germanium usually changes with the injected carrier density. However, according to the statistics of Schockley and Read[9] the lifetime may be constant at large injection levels. Our experiments, with an injection current density above 10 amp/cm^2, may have reached a region where the lifetime is only slightly dependent on the injection level.

It must be pointed out that the intensity of the principal emission peak is a direct measure of carrier lifetime and that intensity measurements can therefore be used to obtain data on the rates of surface and volume recombination.

For the extrinsic band the recombination process obeys first-order kinetics and we may expect a linear dependence between the intensity B and excess concentration, with unchanged lifetime. In our experiments, for the extrinsic band with small injection currents the linear dependence of B on J gradually became sublinear. This can be accounted for by a shorter lifetime as well as by the fact that with increased injection recombination occurs in a larger region, while the concentration of recombination centers decreases with distance from the p-n junction.

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