Two-dimensional electron-hole plasma at a germanium-electrolyte interface

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A new photoluminescence line has been observed when germanium is in contact with an electrolyte. This line is shown to be due to radiative recombination of two-dimensional layers of nonequilibrium electrons and holes which are localized near the germanium-electrolyte interface.

A new state of a nonequilibrium electron-hole system in a semiconductor was discovered and studied in silicon metal-oxide-semiconductor (MOS) structures in Refs. 1–4. This state consists of spatially separate two-dimensional layers of electrons and holes which are localized near a surface. A necessary condition for the existence of this state is the presence of a two-dimensional quantum well for the equilibrium charge carriers; this well is produced at the insulator-semiconductor interface by the application of an external electric field to the gate of the MOS structure. On the other hand, we know that inversion of accumulating conducting channels with a space-size quantization can also form at the surface of a semiconductor in contact with an electrolyte.[5,6]

In the present study we have produced, for the first time in such a structure, a two-dimensional state of a nonequilibrium electron-hole plasma in germanium.

In the experiments we use p-type germanium doped with gallium at a concentration of $(1–2) \times 10^{14}$ cm^{-3}. The surfaces of the parallel-plate samples coincide with one

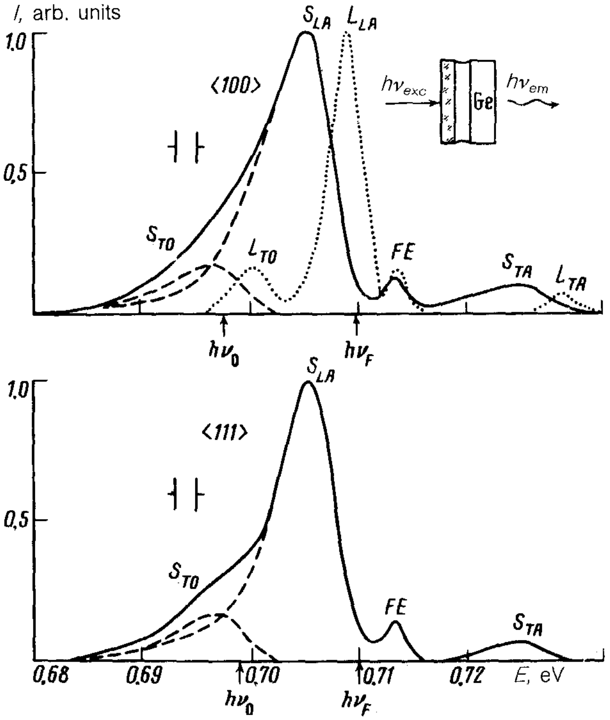

FIG. 1. Emission spectra at the interface between germanium and a 70% HNO_3 solution for various crystallographic orientations of the germanium surface. S_{TO}, S_{LA}, and S_{TA}—Phonon repetitions of the S line; dotted line—emission spectrum of germanium excited through its free surface; *FE*—free-exciton line; *L*—line of electron-hole droplets. $T = 4.2$ K; excitation level $G = 0.75$ W/cm^2. The inset shows the experimental geometry.

of the crystallographic planes. One side of the plate is used as a wall for a parallel-plate capillary electrochemical cell, into which an electrolyte is poured. The electrolyte is an acidic or basic solution. The germanium surface is etched for several minutes, and then the cell is placed in a helium Dewar and cooled to liquid-nitrogen temperature. Freezing the electrolyte stops the electrochemical reactions at the germanium surface and stabilizes the charge of the Helmholtz layer in the electrolyte. We then measure the photoluminescence at the semiconductor electrolyte interface. The luminescence is excited with a 1.5-W LGI-406B cw krypton laser. The sample is excited through the layer of electrolyte, and the luminescence is detected from the opposite side of the sample (Fig. 1).

Figure 1 shows some typical emission spectra of germanium in contact with a 70% HNO_3 solution for various crystallographic orientations of the surface. In addition to the familiar volume exciton line, the spectrum has an intense new $S1$ emission line, represented by *TO, LA,* and *TA* phonon repetitions. The position and shape of the new line depend on both the crystallographic orientation of the germaniun surface and the particular electrolyte used. Shown for comparison in Fig. 1 is the ordinary emis-

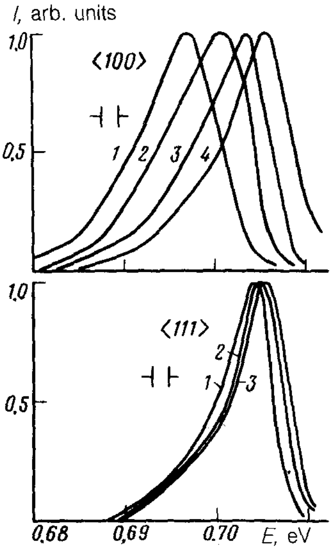

FIG. 2. Emission spectra of a structure consisting of germanium and a 70% HNO_3 solution at various excitation levels. ⟨100⟩ orientation: 1—0.04; 2—0.08; 3—0.33; 4—1.75 W/cm^2. ⟨111⟩ orientation: 1—0.14; 2—0.80; 3—1.75 W/cm^2. $T = 4.2$ K.

sion spectrum of germanium excited through the free surface. This spectrum consists of lines of an exciton and of electron-hole droplets. We see that the S emission line is shifted in the long-wave direction with respect to the line of the electron-hole droplets, so that the new state of the electron-hole system is preferered from the energy standpoint.

Figure 2 shows the position and shape of the S line versus the excitation level. Increasing the excitation intensity shifts the line in the short-wave direction. As the temperature is raised, the S line becomes weaker, diappearing at $T \approx 20$–30 K.

The properties of the new emission line of the germanium are analogous to those of the S line observed[1–4] in silicon MOS structures. That line is apparently due to the radiative recombination of alternating two-dimensional layers of nonequilibrium electrons and holes which are formed at a germanium surface in contact with an electrolyte. Electrochemical processes occurring at a contact between germanium and concentrated nitric acid are known to give rise to a negative potential of the surface with respect to the bulk of the semiconductor and to the formation of a strongly accumulating layer in p-type germanium. At a sufficiently low temperature, the potential well for holes is quantized. Size quantization is a necessary condition for the formation of nonequilibrium two-dimensional electron-hole layers near the surface of a semiconductor.[1–4] the holes produced by the light are captured to a hole quantum level in the potential well; this event gives rise to a field in the interior of the semiconductor which attracts nonequilibrium electrons toward the surface. These electrons in turn screen the field of the trapped holes. As a result, a quantum well for electrons forms. This well has a larger radius and a smaller depth than the hole well (Fig. 3). The distance between the two-dimensional layers of holes and electrons can be estimated in order of magnitude as $4\hbar^2\epsilon_0/(m_z^e e^2)$, where m_z^e is the mass of the electrons in the direction

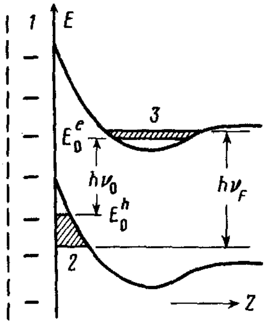

FIG. 3. Energy diagram of a contact of germanium with an electrolyte with a "frozen" Helmholtz layer during optical excitation. 1—Helmholtz layer; 2—two-dimensional hole layer; 3—two-dimensional electron layer.

perpendicular to the surface.[2] The effect is to cause a pronounced overlap of the hole and electron wave functions and a high probability for radiative recombination.

Analysis of the emission spectra reveals the basic characteristics of the hole and electron layers and of the quantum wells. The hole density in the two-dimensional layer can be found from an analysis of the shape of the S line, whose width is equal to the sum of the Fermi quasilevels of the holes and electrons. Using $n_S^e \ll n_S^h$ we find $E_F^h \approx h\nu_F - h\nu_0$ (Fig. 3). The approximate values of the characteristic energies $h\nu_0$ and $h\nu_F$ are shown in Fig. 1, with allowance for the energy blurring of the hole state density due to the particle-particle interaction. The density dependence of the Fermi energy for the hole two-dimensional layers at the surface of germanium was calculated in Ref. 7. From the results of that study and from Figs. 1 and 2 we find $n_{S\langle 100\rangle}^h \approx (2\text{–}2.5) \times 10^{12}$ cm^{-2} and $n_{S\langle 111\rangle}^h \approx (1.2\text{–}1.5) \times 10^{12}$ cm^{-2}.

The shift of the spectra in the short-wave direction with increasing excitation level means that the interaction between the electron-hole pairs in the system is repulsive. This phenomenon was observed previously in Refs. 2 and 4, where it was shown that its cause is a spatial separation of the electron and hole layers and that the repulsion energy can be estimated from $\Delta E_0^h \approx 2(\hbar^2/2m_z^e)^{1/3}(4\pi e^2 n_S^e/\epsilon_0)^{2/3}$, where n_S^e is the density of electrons in the second layer. Using this expression, we find estimates of the electron density in the second layer, $n_{S\langle 100\rangle}^e \approx 5 \times 10^{10}$ cm^{-2} and $n_{S\langle 111\rangle}^e \approx 2 \times 10^{10}$ cm^{-2}, at the maximum excitation level, which corresponds to $\Delta E_{0\langle 100\rangle}^h = 8$ meV and $\Delta E_{0\langle 111\rangle}^h = 2$ meV (Fig. 2). Finally, since the energy of $h\nu_0$ is known, we can determine the position of the hole ground level, E_0^h, in the surface well, because $h\nu_0 = E_g - \hbar\omega_{LA} - E_0^h - E_0^e$ and $E_0^e \ll E_0^h$. From the data in Fig. 2 we find $E_{0\langle 100\rangle}^h \approx 28$ meV and $E_{0\langle 111\rangle}^h \approx 20$ meV for the minimum excitation level.

An S line has also been detected at an interface between germanium and other electrolytes (solutions of bases, HF, H_2SO_4, etc.).

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