

Properties of the electron-hole condensate in Ge double-injection diodes. II *

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The recombination spectra at 4.2°K from three different electrically excited, double-injection structures are compared and contrasted with the spectra obtained by laser excitation of pure Ge and Li-doped Ge. The spectrum from the mesa-type p-i-n is found to be similar to that observed by laser excitation of Li-doped Ge. The spectra obtained by electrical injection of the other p-i-n structures, which were fabricated to minimize the quantity of Li contained in the device, were found to exhibit the same spectral features as those obtained from pure Ge. These facts lead us to conclude that features of recombination spectrum of the electron-hole condensate do not depend on the method of excitation but do depend on the impurity content of the Ge.

I. INTRODUCTION

The electron-hole condensate produced by optical and electron-beam excitation of Ge and Si at liquid-He temperatures has been extensively studied.^{1,2} In the preceding paper³ (henceforth referred to as I), we presented the results of the first extensive study of electron-hole condensate formation via double injection on mesa-type p-i-n structures. This study demonstrated the feasibility of producing electron-hole condensate by electrically injecting electrons and holes. However, a number of the features of the recombination spectra suggested that the electron-hole condensate was being formed in a region containing Li.

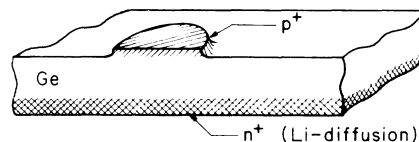
Impurity effects have been investigated for Ga-, In-, Sb-, P-, and As-doped Ge.⁴⁻⁹ The principal changes in the recombination spectra induced by the impurities are the presence of additional lines due to exciton complexes bound to the impurities,⁹ a reduction in the free-exciton intensity relative to the intensity of the radiation from the condensate,⁸ a change of the linewidth of the condensate from that observed in pure material,⁷ and an excitation-dependent linewidth of the condensate line.⁷

In this paper we will investigate whether the difference in recombination spectrum obtained from electrically and optically excited Ge is due to the presence of impurities or due to the method of excitation. To accomplish this, we have fabricated different injection device structures and investigated the spectral features of recombination spectra of these devices and laser-excited pure and Li-doped Ge. Section II of this paper contains a brief description of three different types of p-i-n structures which have been investigated. In Sec. III, we present the experimental results of spectra obtained by electrical injection in mesa, surface, and limited-area p-i-n structures. These spectra then are compared with spectra obtained by laser excitation of pure Ge, Li-doped Ge, and the surface p-i-n structure. A summary and discussion of these results is presented in Sec. IV.

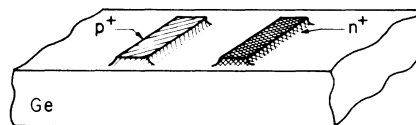
II. EXPERIMENTAL TECHNIQUE AND DEVICE STRUCTURES

Three different double injection device structures were fabricated. These three structures are shown in Figs. 1(a)–1(c). All the structures were fabricated using the procedure described in detail in I. The mesa p-i-n structure [Fig. 1(a)]

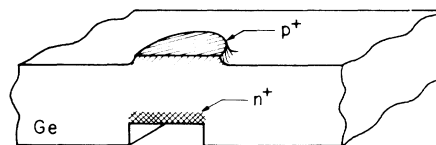
(a) Mesa p-i-n



(b) Surface p-i-n



(c) Limited-area p-i-n



(d) GaAs Laser Excitation

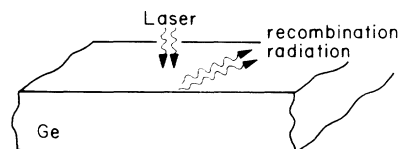


FIG. 1. (a) Schematic representation of a mesa-type p-i-n double-injection device. (b) Schematic representation of surface-type p-i-n double-injection device. (c) Schematic representation of a limited-area p-i-n double-injection device. (d) Schematic representation of laser excitation of a sample of Ge.

consisted of a small-area p^+ contact opposite to a large-area n^+ contact made by diffusing in Li. The thicknesses of the devices were between 1 and 3 mm. Both the surface p-i-n [Fig. 1(b)] and the limited-area p-i-n [Fig. 1(c)] were fabricated in such a way as to minimize the Li in the active region of the device. The surface p-i-n structure consisted of two mesa-type n^+ and p^+ contacts formed from Li and Al, respectively. The device was fabricated on a rectangular slice of high-purity Ge that was 2 mm thick with an area of linear dimensions of 13 by 16 mm. This 44 mm spacing between the contacts made it possible to laser excite the region between the contacts, and hence, to compare directly electrical and optical excitation. The mesalike contact structure was formed by protecting the n^+ and p^+ contacts with black wax prior to a final etch with 3 parts HNO_3 to 1 part HF which removed about 100 μm of the Ge surface.

The limited-area p-i-n structure [Fig. 1(c)] was produced by defining a n^+ Li contact which had a limited area of approximately the same size as the area of the p^+ Al mesa contact. To allow a large flat area for thermal connection between the structure and the copper heat sink, the Li contact was recessed. The area of the Li diffusion was approximately 9 mm^2 which is approximately the same size as the p^+ contact. The contacts were separated by 4.4 mm. The reduction in the area of the Li diffusion and the increased separation between the contacts from that used in the original mesa structure shown in Fig. 1(a) should decrease the concentration of Li in the active volume of the device.

For optical excitation [Fig. 1(d)], a GaAs laser diode was mounted on a Cu heat sink inside of the Dewar. The GaAs laser was mounted a few mm above the sample surface. The laser produced a pulse with a width of 2 μsec , a maximum duty cycle of 2% and a maximum current of 6 A were used. The recombination radiation emitted from the Ge was passed through an interference filter to block out stray laser light and then imaged onto the entrance slit of a spectrometer. All spectra were taken at a bath temperature of 4.2 $^\circ\text{K}$. The experimental techniques are the same as described in I.

III. EXPERIMENTAL RESULTS

A detailed report of the properties of the mesa p-i-n structures was given in I. However, for completeness a recombination spectrum from a p-i-n mesa structure is shown in Fig. 2(a). The spectrum shows the well-known LA- and TO-phonon-assisted recombination lines from the condensate. The linewidth of the LA-phonon-assisted line is 2.5 meV which corresponds to a density using the simple model of Pokrovskii of about 1.2

$\times 10^{17} \text{ cm}^{-3}$. As noted in I this density is somewhat less than the density previously observed in optical-excitation experiments on pure Ge. Also, as noted in I, no threshold is observed for the observation of the condensate lines. As the current through the double-injection device is decreased, the signal simply decreased below the noise level.

In Fig. 2(b), the recombination radiation spectrum from a piece of laser excited pure Ge is shown. This spectrum is similar to published optically excited recombination spectra at^{1,2} 4.2 $^\circ\text{K}$ in that in this energy range it contains peaks due LA- and TO-phonon-assisted recombination of excitons and electron-hole pairs in the condensate. The width of the line associated with the condensate is 3.3 meV which gives a density of $2.1 \times 10^{17} \text{ cm}^{-3}$. The condensate line exhibited a well-defined threshold. That is, a threshold value of laser excitation was required to see the condensate line. Below the threshold value in laser excitation, only the free-exciton lines could be observed.

Comparison of Fig. 2(a) and Fig. 2(b) shows a number of differences between the recombination spectra. First, the spectrum from the mesa double-injection device does not contain any evidence of a free-exciton line while the line due to the free-exciton recombination is clearly visible in the spectrum obtained by laser excitation of pure material. Further, the condensate line shapes are noticeably different. The line shape obtained from the double-injection mesa structure is slightly narrower, has its low-energy edge shifted to slightly higher energy, and has its high-energy edge shifted to slightly lower energy when compared with the condensate line from the pure material. This narrowing of the line is reflected in a lower density of $1.2 \times 10^{17} \text{ cm}^{-3}$ as compared to $2.1 \times 10^{17} \text{ cm}^{-3}$ obtained from the laser excited spectrum.

The above noted dissimilarities in the recombination spectra from double-injection mesa-type structure and those obtained by laser excitation of pure Ge could be due to at least three differences between the two experimental approaches. First, the fabrication of the p-i-n device requires temperature cycling. Second, the mesa-type p-i-n structure may contain significant amounts of Li in the active region of the device. Third, electrical excitation requires fields and currents in the active region of the device which may not be present in optical excitation.

To test if temperature cycling is responsible for the dissimilarities between the spectra, high-purity Ge was subjected to the same heat-treatment cycle that was used in device fabrication. The spectrum from this heat-treated sample when it was excited by laser excitation was identical to

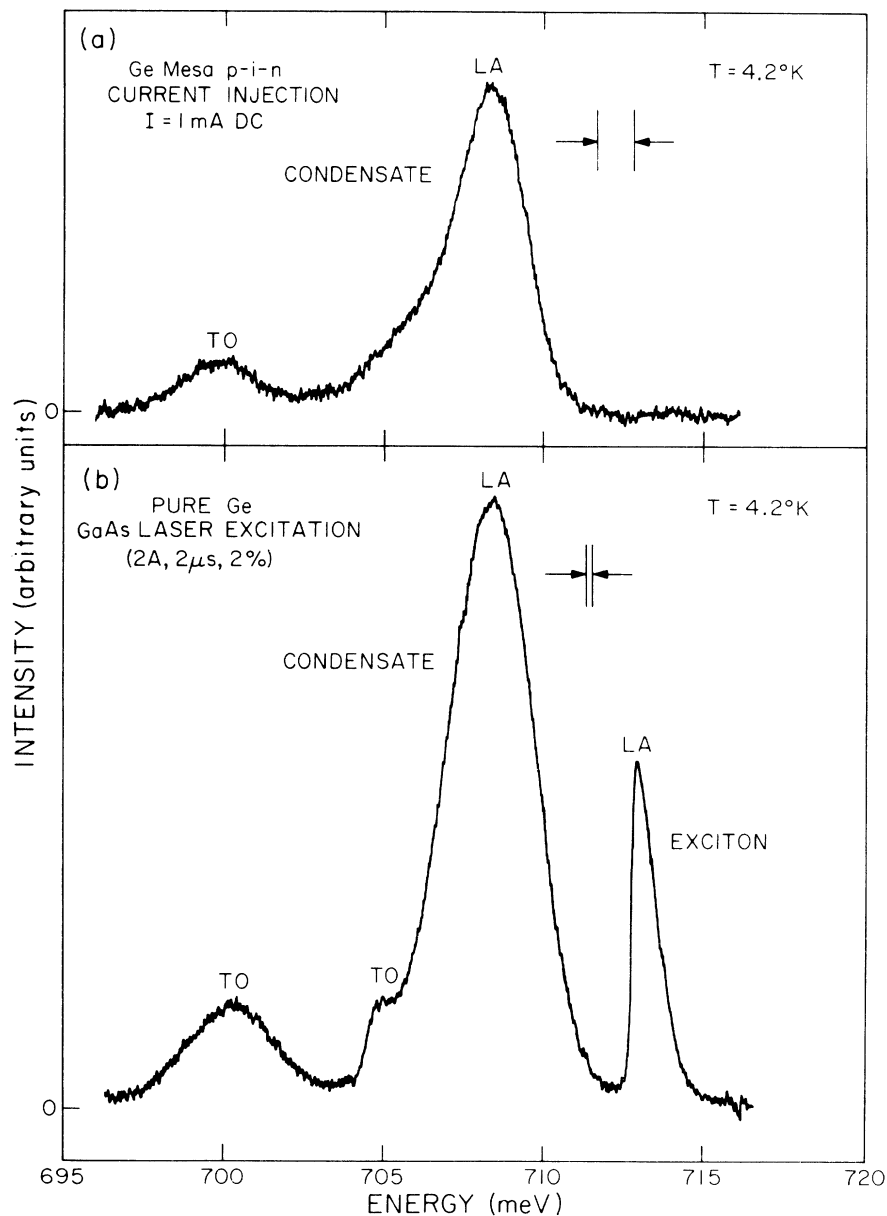


FIG. 2. (a) Recombination spectrum from a Ge mesa-type double-injection device. The spectrum was produced using electrical excitation. (b) Recombination spectrum of a sample of high-purity Ge produced by a GaAs laser excitation.

that obtained from the pure Ge which had not been heat treated. Hence, the temperature cycles used in device fabrication are not responsible for the dissimilarities between the spectra in Fig. 2.

The influence of Li as the cause of the difference between electrical excitation of a mesa p-i-n and laser excitation of pure Ge was investigated by studying the recombination radiation spectrum of a piece of Li diffused Ge which is illuminated with a laser. The Li diffusion was carried out at 325 °C for 20 min. Samples were lapped and etched to produce a surface concentration of between 2 and $6 \times 10^{16} \text{ cm}^{-3}$ as determined by differential resistivity measurements. The recombi-

nation spectrum is shown in Fig. 3. The linewidth of the condensate line is 2.7 meV which gives a corresponding density of $1.4 \times 10^{17} \text{ cm}^{-3}$. The spectrum shows no evidence of a line from the recombination of free excitons. The spectral features are very similar to those observed in electrical excitation of the mesa p-i-n structures. These results are highly suggestive that the origin of the dissimilarities between the spectrum obtained from the mesa-type structure and the spectrum obtained from the laser excitation of pure Ge is due to Li introduced during the processing.

Finally, it was necessary to determine if the method of excitation, electrical or optical, was

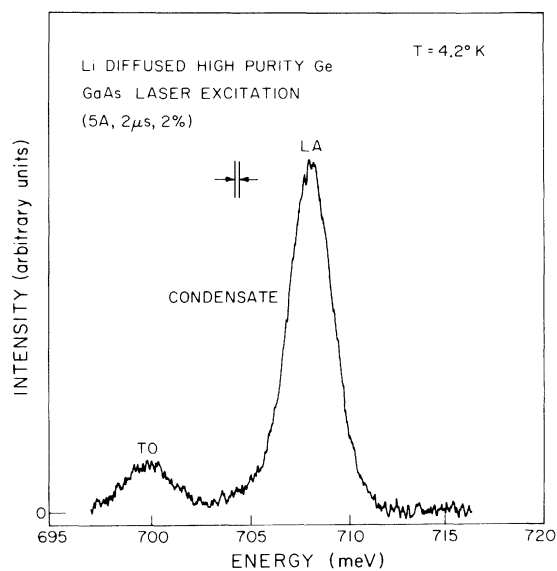


FIG. 3. Recombination spectrum of a sample of high-purity Ge into which Li had been diffused for 20 min at 325°C. The face on which the Li diffusion had taken place was illuminated by a GaAs laser.

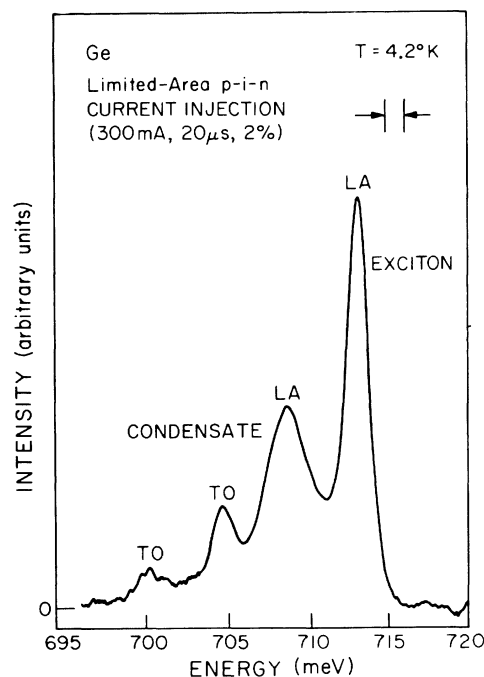


FIG. 5. Recombination spectrum from a limited-area p-i-n double-injection device. The device was excited using electrical injection.

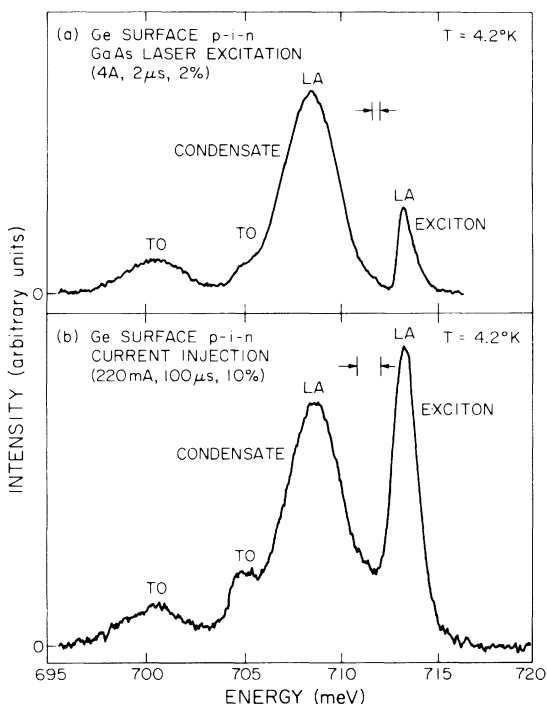


FIG. 4. (a) Recombination spectrum from a surface p-i-n double-injection structure. The sample was excited by illuminating the area between the p^* and n^* contacts with a GaAs laser. (b) Recombination spectrum from a surface p-i-n, Ge double-injection device structure. The device was excited by passing a current between the contacts.

responsible for the dissimilarities between the recombination spectrum. Figures 4 and 5 show spectra from electrical injection devices designed to minimize the Li concentration in the active region of the devices. Figure 4 (b) gives the spectrum from a surface p-i-n structure [see Fig. 1 (b)]. The spectrum exhibits peaks due to the LA- and TO-phonon-assisted recombination of free excitons and electron-hole pairs in the condensate. The width of line associated with the condensate is 3.3 meV which yields a density of $2.1 \times 10^{17} \text{ cm}^{-3}$, in good agreement with that obtained by using laser excitation of pure Ge.¹⁰ In contrast to results obtained by electrical excitation of a mesa-type structure, this spectrum contains a well-defined free-exciton peak. The intensity of the optical signal from this device was much less than that obtained from the mesa structure or from the optical excitation of pure Ge. The rather small signal-to-noise ratio precluded a systematic search for current threshold in observation of the condensate recombination line. To compare directly electrical and optical excitation, we have excited the region between the contacts of this same p-i-n surface structure with a GaAs laser. The recombination radiation spectrum obtained in this fashion is shown in Fig. 4(a). The linewidth of the condensate line is 3.3 meV, again giving a density of about $2.1 \times 10^{17} \text{ cm}^{-3}$. The spectral features of the spectrum in Fig. 4(a) are very similar to

those of Fig. 4(b). This fact again indicates the similarity between the results obtained by optical excitation and double injection.

Finally, in Fig. 5 the recombination spectrum from a limited-area p-i-n structure [Fig. 1(c)] using electrical injection is shown. The spectrum exhibits lines due to the LA- and TO-phonon-assisted recombination from free excitons and electron-hole pairs in the condensate. The linewidth of the condensate line is about 3.3 meV which yields a density of about $2.1 \times 10^{17} \text{ cm}^{-3}$, in good agreement with that found in laser excitation of pure Ge.¹⁰ The spectrum is qualitatively similar to that observed in the laser excitation from pure material and electrical injection in the surface p-i-n structure.

Although the features of the recombination spectra are similar, we have noted some differences in the intensity of the recombination radiation between optically excited and double-injection structures. In the surface and limited-area p-i-n structures, the signal-to-noise ratio is lower than in the laser-excited samples. This reduced intensity in double-injection structures may be due to impact-ionization effects. Calculations suggest that impact ionization could occur under the conditions in the double-injection devices. At present it does not appear that this phenomenon influences the recombination features.¹¹ At present it does appear that this phenomenon could re-

duce the exciton recombination intensity, but it does not appear that impact ionization will change the linewidth and line position of the recombination from the condensate.

IV. SUMMARY AND CONCLUSIONS

In this paper we have examined possible causes of the dissimilarities between the recombination spectra from electrically excited mesa-type p-i-n diodes and laser excited high-purity Ge. We produced spectra via electrical excitation from structures fabricated to minimize the amount of Li in the device and compared these spectra with those obtained by laser excitation of Li-doped and high-purity Ge. The spectral features in the recombination spectra from current injection in low-Li-content devices were found to be the same as those from laser excitation of high-purity Ge. On the other hand, electrical excitation of mesa-type Ge p-i-n structures and laser excitation of Li-doped Ge produced similar spectra. We conclude that the features of the recombination spectrum of the electron-hole condensate do not depend on the method of excitation but do depend on the impurity of the Ge.

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