Bound–double-exciton complexes in zinc-doped germanium

H. Nakata and E. Otsuka
Department of Physics, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan
(Received 24 October 1983)

Photoluminescence from zinc-doped germanium is examined at liquid-helium temperatures. Three pairs of impurity-associated lines, in the set of phonon replicas, have been assigned to be radiations from single and double excitons bound to zinc, a double acceptor with deep levels. The dissociation energies of the bound exciton and the bound–double-exciton complex are 5.7 and 3.2 meV, respectively. The bound–double-exciton complex is very stable because of a closed-hole-shell structure.

The bound-multiexciton complex (BMEC), more than one exciton attached to a single neutral impurity, has been observed in Si, Ge, and some other semiconductors.[1] Kirczenow proposed a shell model[2] to explain the Zeeman spectra of BMEC observed in Si.[3] According to this model, the BMEC has electron and hole shells just as an atomic nucleus has neutron and proton shells. In Si doped with substitutional donors, for example, the first electron shell can be filled with two electrons, the first hole shell with four holes, and so on. A closed-shell structure ensures stability.[1] The BMEC in Ge was also interpreted by the shell model.[4,5]

After successful investigations of the BMEC in Si and Ge with shallow impurities, people extended their study to the bound-exciton system in Si doped with deep impurities, namely, Si:Be, Si:Cu, etc.[6,7] In these materials, excitons bound to isoelectronic traps have been observed. But direct excitonic association with a neutral non-group-V donor or non-group-III acceptor has not been confirmed.

The idea of an exciton bound to a double acceptor was first raised by Hopfield in 1964.[8] It was not until 1978 when we heard of an experimental observation, and that was for accidentally present unidentified double acceptors in GaSb.[9] We recently observed "double acceptor bound excitons" in Zn-doped Ge as reported in our previous paper.[10] Zinc makes a double acceptor in Ge with ionization energies of 32.6 and 85.8 meV. However, the new experimental results presented in this paper drive us to conclude that some of the observed photoluminescence lines reported there are due to a BMEC consisting of two excitons bound to a neutral double acceptor.

The sample crystals used in this experiment were specially grown by the Toshiba Corporation with an extreme care of avoiding other impurities than Zn. Two samples, to be denoted Ge/Zn-1 and Ge/Zn-2, contain 1.2×10^{14} cm^{-3} and 2.1×10^{15} cm^{-3} of Zn, respectively. Specimens having a common size of $5\times6\times1$ mm^3 were placed in a conventional optical Dewar. Photoexcitation was made by 0.8-W argon ion laser (514.5 nm), whose beam was chopped at the frequency of 400 Hz. Dependence of photoluminescence on the intensity of excitation was examined by inserting neutral density filters in the optical path. The luminescence was led to a monochromator (SPEX 1704) and detected by a cooled (77 K) Ge PIN detector.

Figure 1 shows the spectra obtained at three levels of excitation. Six photoluminescence lines in addition to the LA-phonon associated free-exciton (FE^{LA}) line are observed. They are three doublet replicas associated with LA, TA, and zero phonon. Each doublet is denoted by α and γ with appropriate superscripts. In our previous paper we assigned both α and γ to photoluminescence from bound excitons (BE's): α from the ground state of BE's while γ from its excited state.[10] As we shall see below, dependence on excitation intensity of α is different from that of γ. This is

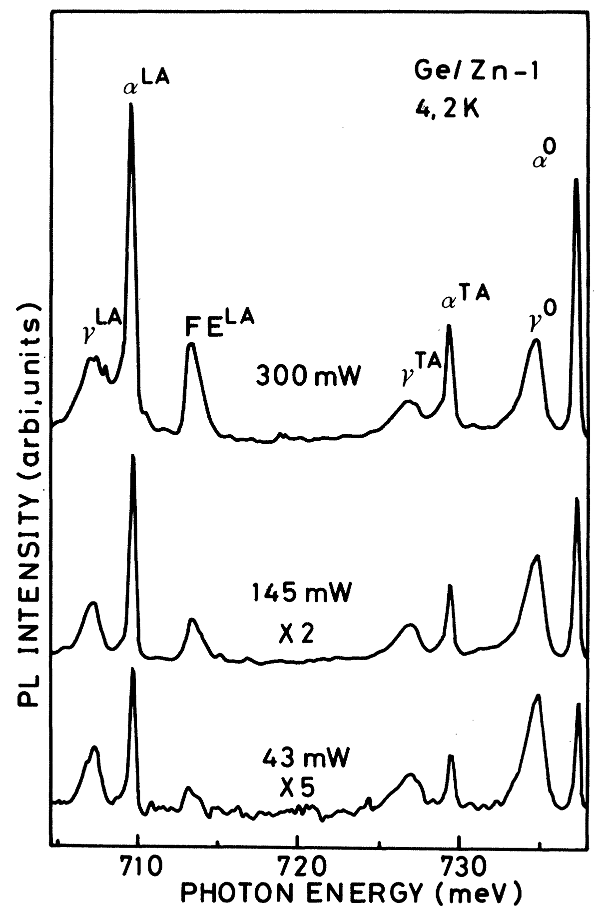

FIG. 1. Photoluminescence spectra at 4.2 K from a zinc-doped germanium sample, Ge/Zn-1, having a Zn concentration of 1.2×10^{14} cm^{-3}, at three different levels of excitation (relative magnifications indicated). Impurity-bound exciton lines always appear in doublet, α and γ, for each phonon replica which we denote by superscripts. FE^{LA} is the LA-phonon associated free-exciton line.

difficult to explain if both α and γ are photoluminescence from BE's. The line α depends more strongly on excitation intensity than the line γ. It thus seems more probable that γ is associated with a recombination in BE's while α with that in the BMEC.

The peak intensities of α^0 and γ^0 lines are given for Ge/Zn-1 in Fig. 2 as a function of excitation intensity. The photoluminescence intensity I_{PL} depends on excitation intensity I_{EX} as $I_{PL}=I_{EX}^n$. The exponent n for α^0 is 1.60 and that for γ^0 is 0.93. Similar dependence is observed for other phonon replicas. When the excitation intensity exceeds 300 mW, I_{PL} starts saturating both for α^0 and for γ^0. A similar measurement was made also on Ge/Zn-2. The exponents for α^0 and γ^0 were found ~ 1.2 and ~ 0.7, respectively. No saturation in I_{PL} was observed.

In general, the exponent n for BE's is somewhat less than unity. It also depends on the impurity concentration. Thus the value 0.93 as well as ~ 0.7 is reasonable for the BE's assignment. On the other hand, the exponent n for the BMEC is considerably larger than that for BE's as observed in Si:B and Si:P by Sauer.[11] The value of $n=1.60$ as well as ~ 1.2 obtained here strongly suggests that α comes out of the BMEC.

As the temperature was raised above 4.2 K, luminescence from the FE increased drastically by dissociation from bound states, as shown in Fig. 3. The ratio in intensity of the line γ to that of the line α increased as the temperature became higher. This can also be explained favorably by our model, since the proportion of the BMEC becomes higher at lower temperatures.[12]

For the more heavily doped sample Ge/Zn-2, luminescence from the FE is not seen because of the complete capture by impurities. This is also shown in Fig. 3. The intensity of the line α from Ge/Zn-2 is almost the same as that from Ge/Zn-1, whereas the intensity of the line γ from Ge/Zn-2 is stronger than that from Ge/Zn-1. These experimental results are similar to Sauer's on the BMEC in Si:B and Si:P.[11]

The linewidth of γ is always broader than that of α for every phonon replica, indicating that γ consists of more than one line. In fact, a splitting of ~ 0.8 meV was observed at 2 K in an extremely low excitation (10 mW) measurement. Since our independent magneto-optical absorption experiment by an optically pumped far-infrared laser shows a splitting of ~ 0.2 meV in the states of BE's,[13] we are inclined to admit a splitting also on the part of the neu-

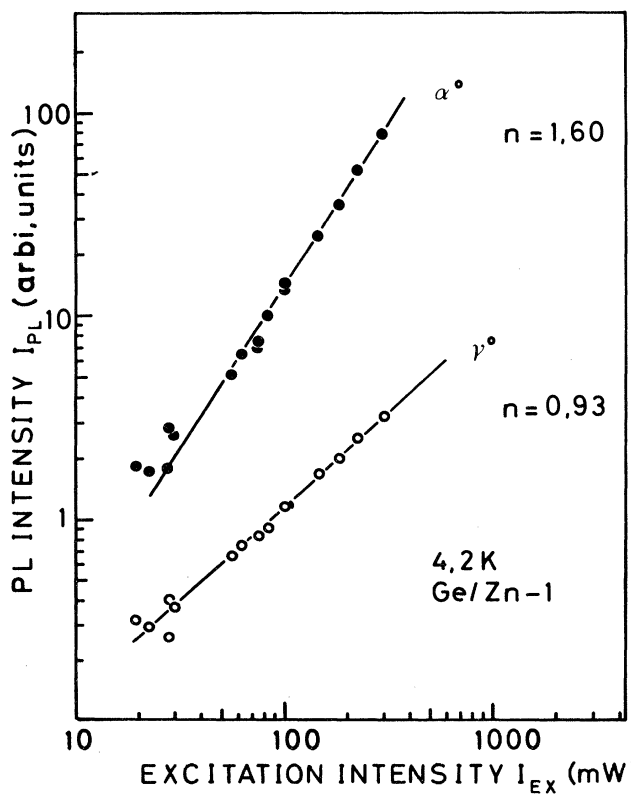

FIG. 2. Luminescence intensities of the zero-phonon replica lines α^0 and γ^0 vs excitation intensity, observed at 4.2 K from the same sample Ge/Zn-1 as cited in Fig. 1. The obtained slopes $n=1.60$ and $n=0.93$ strongly indicate that α^0 arises from bound–double-exciton complexes and γ^0 from bound–single-exciton centers.

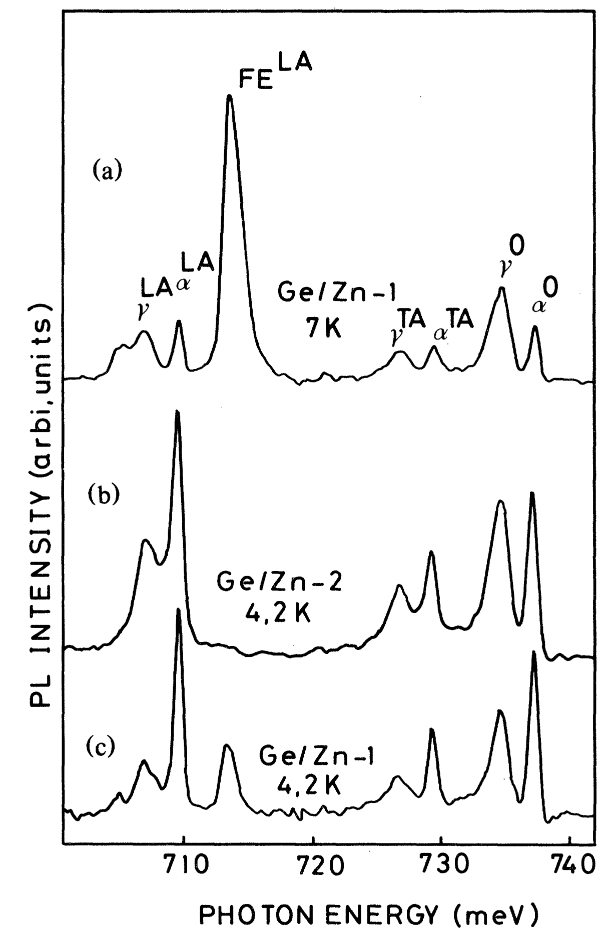

FIG. 3. Photoluminescence from (a) Ge/Zn-1 ($N_A-N_D=1.2\times10^{14}$ cm^{-3}) at 7 K, (b) Ge/Zn-2 ($N_A-N_D=2.1\times10^{15}$ cm^{-3}) at 4.2 K, and (c) Ge/Zn-1 at 4.2 K. The free-exciton line is stronger at 7 K than at 4.2 K, indicating thermal dissociation of excitons from impurities. The bound–double-exciton line (α) is more intensive than the bound-exciton line (γ) at 4.2 K for Ge/Zn-1. The free-exciton line has not been observed in Ge/Zn-2, and intensity of the bound-exciton line is relatively strong.

tral double-acceptor ground state in order to account for the 0.8-meV splitting of γ at low temperature, though there exists a separate infrared work that denies such a splitting.[14]

For the bound–double-exciton complex, one can expect two states corresponding to the total angular momenta $J=0$ and $J=1$. It is highly probable that these states are degenerate or almost degenerate, since only one sharp line α has been observed in all cases.

The relative intensity of α to γ depends on the kind of replica. It is seen, e.g., in Fig. 1 that the intensity of α^0 is almost the same as that of γ^0 in Ge/Zn-1 under 43 mW excitation, whereas intensity of α^{LA} is twice as strong as that of γ^{LA}. This might be explained as follows: Electrons and holes in BE's are tightly bound to the impurity center. But those in the BMEC are less tightly bound, so that the phonon-independent transition would be less frequent than in the case of BE's. A similar result was reported by Thewalt for Si:P.[12]

Photoluminescence from the BMEC ($m=2$) in Ge/Zn is very strong. For example, α^{LA} is four times as strong as γ^{LA} in Ge/Zn-1 under 300 mW excitation (Fig. 1). Although the BMEC in Si:B is stable, too, and their photoluminescence is strong, the intensity ratio of the BMEC ($m=2$) to BMEC ($m=1$) (BE's) is at most 0.8.[11] For a single acceptor BMEC in Ge, the corresponding ratio is only ~ 0.1.[15] We thus find that the photoluminescence from the BMEC ($m=2$) in Ge/Zn is exceptionally strong. Of further interest is that photoluminescences from the BMEC ($m=3,4,\ldots$) have been unobserved. As the complete shell around a neutral rare-gas element is inactive in chemical reactions, so would be the closed-hole shell around Zn, and a third exciton would have little chance to make the BMEC ($m=3$).

Allowing for our assignments of α and γ, we find, from the obtained positions of the spectral lines, that the dissociation energy of BE's in Ge/Zn is 5.7 meV. This value is larger than that expected from a simple Haynes's rule which states that the dissociation energy of BE's is nearly one-tenth of the ionization energy of the relevant impurity.[16] Of course, Haynes's rule should not outright be extensible to a double impurity. The dissociation energy of an exciton from the BMEC ($m=2$), on the other hand, is 3.2 meV. Incidentally, this is very nearly one-tenth of the first ionization energy.

Any possibility that we are watching luminescence from isoelectronic trap bound excitons has been excluded by a time-resolved far-infrared measurement for BE's,[13] absence of the local-mode phonon structure in spectra, small binding energies, dependence on excitation intensity, etc. It thus seems that neither α nor γ is due to such isoelectronic trap BE's as observed in Si:Cu, Si:Be, etc.

In conclusion, double-acceptor-bound excitons and bound–double-exciton complexes are observed in Zn-doped Ge. Their binding energies of an exciton are 5.7 and 3.2 meV, respectively.

We are grateful to Professor T. Nishino, Y. Fujiwara, and T. Sada for their technical assistance and for the loan of photoluminescence instruments. We would like to thank Dr. H. Nakayama, Professor T. Ohyama, and T. Yodo for discussions. This work has been supported by the Grant-in-Aid for the Scientific Research from the Ministry of Education, Science, and Culture.

[1]See, for example, M. L. W. Thewalt, in *Proceedings of the Fourteenth International Conference on Physics of Semiconductors, Edinburgh—1978*, edited by B. L. H. Wilson, IOP Conf. Proc. No. 43 (IOP, Bristol and London, 1979), p. 605, and references therein.

[2]G. Kirczenow, Can. J. Phys. 55, 1787 (1977).

[3]R. Sauer and J. Weber, Phys. Rev. Lett. 36, 48 (1976).

[4]A. E. Mayer and E. C. Lightowlers, J. Phys. C 12, L945 (1979).

[5]Yia-Chung Chang and T. C. McGill, Phys. Rev. B 25, 3945 (1982).

[6]S. P. Watkins, U. O. Ziemelis, M. L. W. Thewalt, and R. R. Parsons, Solid State Commun. 43, 687 (1982).

[7]M. L. W. Thewalt, C. P. Watkins, U. O. Ziemelis, E. C. Lightowlers, and M. O. Henry, Solid State Commun. 44, 573 (1982).

[8]J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964*, edited by M. Hulin (Academic, New York, 1964), p. 725.

[9]R. A. Noack and W. Rühle, Phys. Rev. B 18, 6944 (1978).

[10]H. Nakata, T. Yodo, and E. Otsuka, Solid State Commun. 45, 55 (1983).

[11]R. Sauer, Phys. Rev. Lett. 31, 376 (1973).

[12]M. L. W. Thewalt, Can. J. Phys. 55, 1463 (1977).

[13]H. Nakata and E. Otsuka (unpublished).

[14]E. Kartheuser and S. Rodriguez, Phys. Rev. B 8, 1556 (1973).

[15]E. C. Lightowlers and Zofia E. Ciechanowska, J. Phys. C 14, L719 (1981).

[16]J. R. Haynes, Phys. Rev. Lett. 4, 361 (1960).