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Electronic Raman scattering of the negative charge state of the 78-meV double acceptor in GaAs

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Intracenter $1S_{3/2}(\Gamma_8)-2S_{3/2}(\Gamma_8)$ electronic Raman scattering has been observed from the negative charge state of the 78-meV double acceptor that is commonly found in GaAs grown by the liquid-encapsulated Czochralski technique. The magnitude of this transition energy is identical to the separation between the photoluminescence bands that involve this double acceptor and occur at 1.441 and 1.283 eV. This observation indicates that *both* the 1.441- and 1.283-eV emission bands arise from the capture of an electron by the neutral charge state of the 78-meV double acceptor. The higher- or lower-energy emission bands occur when the hole bound to the negative charge state of this double acceptor occupies either the $1S_{3/2}(\Gamma_8)$ or $2S_{3/2}(\Gamma_8)$ hydrogenic states, respectively. Because a similar relationship should be observed between emission bands involving other double acceptors, the observation of such a relationship for an unidentified shallow acceptor provides strong evidence for its double-acceptor nature.

I. INTRODUCTION

GaAs that is grown by the liquid-encapsulated Czochralski (LEC) technique from Ga-rich melts commonly exhibits an acceptor with a binding energy of 78 meV. This acceptor has been studied extensively with photoluminescence (PL),[1-3] infrared absorption,[2,4,5] electronic Raman scattering (ERS),[6] and Hall effect.[1,7] In addition, it has been suggested that the chemical identity of this acceptor is either Ga (Refs. 1, 2, and 4) or B (Ref. 8) substituted on the As sublattice. However, recent evidence[9] suggests that B_{As} is not as likely a candidate. Nevertheless, in either case the acceptor level arises from the substitution of a group-III element on the group-V site and is therefore expected to be a double acceptor. This attribution has been proven by several experimental studies which clearly establish the double-acceptor nature of the 78-meV level.[1,2,5] In spite of these intense experimental investigations, uncertainty regarding the assignment of one of the luminescence bands (1.283 eV) which characterizes this double acceptor has persisted. We report here electronic Raman scattering measurements which eliminate this persistent uncertainty and confirm a model[10] which we have proposed to explain the spectral and time-decay characteristics of the photoluminescence data associated with the 78-meV double acceptor in GaAs. In addition, these results delineate features of the PL spectra that are characteristics of *all* shallow (effective-mass) double acceptors and, therefore, provide methods by which PL spectroscopy may aid in the determination of the double-acceptor nature of a defect whose properties are not understood.

Yu and co-workers[1] reported PL emission bands at 1.441 and 1.284 eV in GaAs grown from Ga-rich melts. The first of these emission bands was attributed to a superposition of emission energies arising from donor-acceptor pair and free-to-bound recombination processes involving the neutral charge state of the double acceptor. In the context of such a model, the binding energy of a hole bound to the neutral double acceptor would be near 78 meV. This value is consistent with those surmised from infrared absorption,[2,4,5] ERS,[6] and Hall effect.[1,7] Because Yu *et al.*[1] observed that the intensity of the 1.283-eV emission band was directly correlated with that of the 1.441-eV PL band, they suggested that the 1.283-eV emission band arises from the radiative capture of an electron by the negatively charged state of the double acceptor. In the context of this recombination model, the binding energy of the hole bound to the negative charge state of the double acceptor would be 236 meV. In contrast, subsequent infrared absorption studies by Elliott[2] suggested that the binding energy of the negatively charged state of the double acceptor was about 200 meV. Moore, Shanabrook, and Kennedy[5] performed far-infrared absorption studies of the 78-meV acceptor as a function of compensation ratio and clearly established, in agreement with Elliott, that the ionization energies of the neutral and negatively charged states of this double acceptor are 78 and 203 meV, respectively. Furthermore, their studies did not reveal any infrared absorption characteristic of an acceptor with a 236-meV ionization energy. Therefore, the relationship between the recombination processes that had been proposed by Yu *et al.*[1] for the 1.441- and 1.283-eV PL bands had to be reexamined. However, any reinterpretation must be consistent with the following observations: (a) The binding energies of the neutral and negatively charged states of this double acceptor are 78 and 203 meV, respectively,[2,5] (b) the intensity of the 1.283-eV emission band is always correlated with that of the 1.441-eV band,[1,3] and (c) that these two emission bands exhibit similar time-decay characteristics.[3] Recently, we have proposed a model that satisfies these criteria.[10] This model suggests that the capture of an electron by the neutral charge state of the double acceptor can result in the emission of a photon, where the remaining hole bound to the ionized (negatively charged) double acceptor occupies either the $1S_{3/2}(\Gamma_8)$ or $2S_{3/2}(\Gamma_8)$ state. (Hereafter these hydrogenic state notations will be abbreviated by $1S$ and $2S$, respectively.) Therefore, the separation between the 1.441- and 1.283-eV PL bands would be equal to the $1S$-$2S$ transition energy of the negatively charged state of the double acceptor. In this paper, we describe intracenter electronic Raman scattering measurements on the negative charge state of this double acceptor that confirm the applicability of this model.

II. EXPERIMENTAL

The GaAs crystals we examined were grown from Ga-rich melts and exhibited the 78-meV acceptor. These samples were characterized by Hall effect, PL, and far-infrared absorption. These measurements indicated that the 78-meV acceptor was uncompensated at low temperatures. Because the goal of this study was to observe the 1*S*-2*S* transitions of the singly ionized state of the 78-meV acceptor, a method had to be devised to partially compensate the 78-meV acceptor. This was accomplished by a 2-MeV electron irradiation which introduces deep hole traps in the sample. Our previous infrared absorption studies[5] indicated that a fluence of $\sim 1\times10^{16}$ cm^{-2} would result in the net introduction of one hole trap for every 78-meV double acceptor in the sample. This procedure results in the production of the maximum concentration of singly ionized double-acceptor states with a binding energy of 203 meV.

The Raman scattering and PL measurements were performed at temperatures between 1.5–10 K with a Spex double monochromator. The excitation source was a dye laser operated with Styril 9 dye and the emission was detected by photon counting with a cooled *S*-1 photomultiplier.

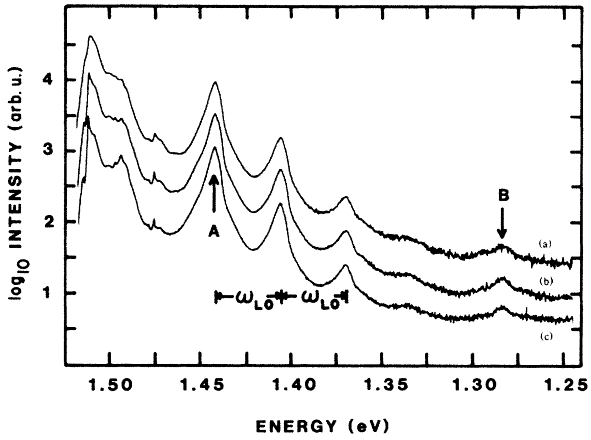

FIG. 1. 7-K photoluminescence spectra of a GaAs crystal excited by 1.55-eV radiation with a power density of (a) 40 W cm^{-2}, (b) 4 W cm^{-2}, and (c) 0.4 W cm^{-2}. Feature *A* arises from the recombination process depicted in Figs. 2(a) and 2(b), while feature *B* is shown to arise from the process shown in Figs. 2(a) and 2(c).

III. RESULTS AND DISCUSSION

The PL spectrum obtained at three different excitation laser powers from an as-grown GaAs crystal containing the 78-meV acceptor is shown in Fig. 1. The feature labeled *A* occurs at 1.442 ±0.0005 eV and arises from the capture of an electron by the neutral 78-meV acceptor by either of the processes denoted in Fig. 2(a). The remaining hole that is bound to the singly ionized double acceptor occupies the 1*S* state. In addition, one observes several phonon replicas of the emission labeled *A*. At lower energies, a feature labeled *B* is observed at 1.283 ±0.0005 eV. The intensities of this feature and of the phonon replicas are always correlated with that of feature *A*. As shown in Fig. 1 and previously discussed by Yu *et al.*[1] and Bishop, Shanabrook, and Moore,[3] this relationship is insensitive to the intensity of the excitation source employed for the PL measurements. Furthermore, the relative intensities of features *A* and *B* are constant irrespective of sample supplier.[3] We propose that feature *B* arises from a recombination process that is depicted in Fig. 2(a) but that the final state of this recombination process is shown in Fig. 2(c). If this proposition is true, then the separation between the *A* and *B* emission features should be equal to the 1*S*-2*S* transition energy of the hole bound to the singly ionized double-acceptor center.

We have performed infrared absorption measurements on a GaAs sample that had been electron irradiated with a fluence of 1×10^{16} cm^2. These measurements indicated that the neutral charge state of the 78-meV level was completely compensated and that the singly ionized level of this double acceptor was only slightly compensated. Shown in Fig. 3 is a Raman spectrum obtained from this sample when excited by 1.45-eV radiation. The two features denoted by the up arrows in the figure occur at constant energy *differences* of 159 and 195 meV from a variety of employed laser energies. Therefore, we conclude that these features, which are superimposed on a broad, smoothly varying luminescence

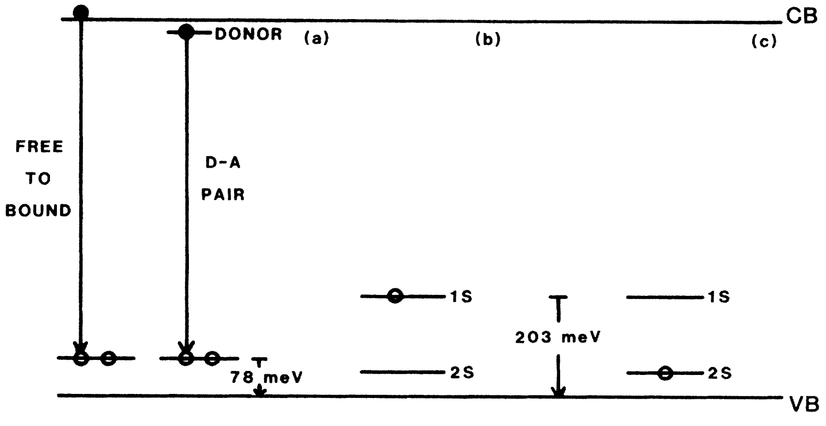

FIG. 2. (a) Two recombination processes that are important in the description of the luminescence that arises from the 78-meV double acceptor. These processes can result in final states that leave the hole bound to the singly ionized double acceptor in either the (b) 1*S* or (c) 2*S* state. This figure has been reproduced from Ref. 10.

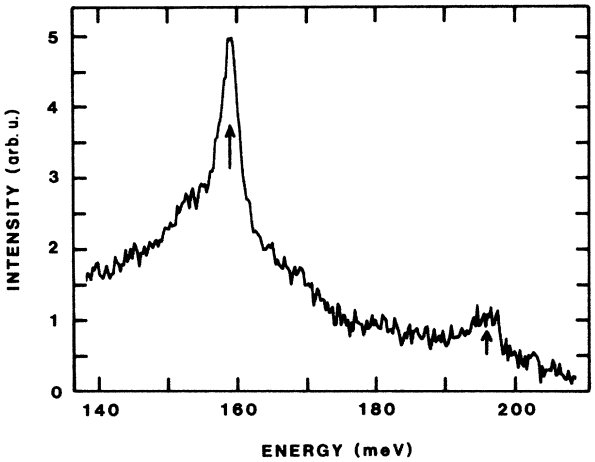

FIG. 3. Raman scattering peaks are denoted by the arrows in the figure. These features occur on top of a broad smoothly varying luminescence background. These measurements were performed in the $z(x',y')\bar{z}$ backscattering configuration where z is parallel to [100] and x',y' are along [110] and [1$\bar{1}$0].

background, arise from a Raman scattering process. These Raman peaks do not correspond to any multiphonon process that has been reported previously and are suggested to arise from a scattering process that is electronic in nature. Because the accceptor with the largest concentration of bound holes in this GaAs sample is the singly ionized state of the 78-meV double acceptor, we conclude that the Raman feature at 159 meV arises from a scattering process that results in the excitation of the hole bound in the 1*S* state of the singly ionized level of the double acceptor into its 2*S* state. The transition occurring at 195 meV is similar except that in addition an optical phonon is emitted. An estimate[10] of the 1*S*-2*S* transition energy determined from infrared measurements[5] and effective-mass theory[11] is in good agreement with these assignments. Similar 1*S*-2*S* intracenter transitions of shallow impurities have been observed in experiments that employ the selective excitation of luminescence (SEL).[12] In the present case, the SEL mechanism is not likely to be important because of the small population of doubly ionized double acceptors in this sample.

The energy difference between the *A* and *B* emission bands of Fig. 1 is 159 ± 1 meV. Because this separation is equal to the 1*S*-2*S* transition energy of the singly ionized state of the double acceptor measured by ERS, the recombination model shown in Fig. 2 for emissions labeled *A* and *B* has been verified. Specifically, we conclude that the emission band at 1.283 eV results from the capture of an electron by the 78-meV double acceptor, where the resulting singly ionized double acceptor is left in the 2*S* excited state. Furthermore, it follows that similar 1*S*-2*S* replicas or satellite transitions should be observed for other double acceptors. In cases where the identity of the shallow acceptor is unknown, the observation of 1*S*-2*S* replicas provides strong evidence for the double-acceptor nature of these defects.

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