Spectroscopic Observation of a Vacancy Complex in GaP

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We report a new luminescence in GaP, which is attributed to a gallium vacancy complexed with an oxygen donor. We discuss evidence for this assignment and the roles of various radiative and nonradiative nearest neighbor complexes, which are created by replacement of the Ga vacancy with different impurities.

In this Letter we report the observation of a new luminescence in GaP, which we ascribe to a gallium vacancy (V_{Ga}) complexed with an oxygen donor ($\mathrm{O_P}$). Indirect evidence for the existence of such a complex was recently obtained by Dean[1] in his study of the complex $\mathrm{Li_{Ga}O_PLi_{Int}}$, where "Int" denotes interstitial. A detailed knowledge of the V_{Ga}-$\mathrm{O_P}$ complex is fundamental to the understanding of the recombination kinetics of GaP electroluminescence since (a) the impurities Zn and Cd can fill the gallium vacancy and produce the nearest-neighbor $\mathrm{Zn_{Ga}}^{-}$-$\mathrm{O_P}^{+}$ and $\mathrm{Cd_{Ga}}^{-}$-$\mathrm{O_P}^{+}$ radiative complexes responsible for the efficient red luminescence[2]; (b) impurities from Column IV can fill the gallium vacancy and produce nearest-neighbor complexes which are highly nonradiative, e.g., the $\mathrm{Si_{Ga}}$-$\mathrm{O_P}$ complex[3]; and (c) the vacancy complex is probably a center for nonradiative recombination.

The structured luminescence at 1.5°K, which we attribute to a V_{Ga}-$\mathrm{O_P}$ complex, occurs in the orange region of the spectrum, as shown in Fig. 1, for a nonintentionally doped GaP crystal grown by the water-vapor transport method[4] on a (111)-Ga face of a GaP substrate. It was also present in some samples grown by the HCl-transport method[5] in the presence of water vapor. The structure in this characteristic orange luminescence (henceforth referred to as COL) at 1.5°K is dominated by a sharp zero-phonon[6] line at 2.177 eV designated as the *A* line. Phonon-assisted transitions involving the LO and TO vibrations occur at 50.1 and 45.7 meV, respectively. Contribution from vibronic sidebands of the *A* line is also observed. The additional weak structure seen is possibly due to the contribution from other vibrational modes. At higher temperature the lines broaden, but no thermalization effects among the sharp structure is observed. The COL quenches rapidly above 30°K and an activation energy of 0.024 eV is obtained from the exponential part of the thermal quenching curve.

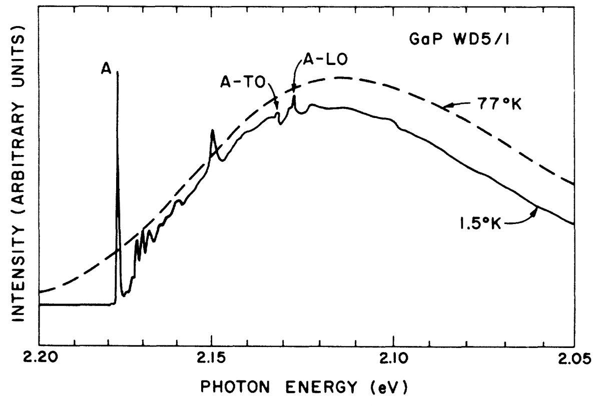

FIG. 1. Characteristic orange luminescence observed in nonintentionally doped water-vapor-grown crystals at 1.5 and 77°K. The emission at 1.5°K consists of a sharp zero-phonon line (*A* line) and additional lines due to localized vibrational and lattice modes.

Annealing such a crystal at 400°C for 15 h with small amounts of Li produces a red luminescence with a strong sharp line at 2.087 eV [as shown in Fig. 2(a)] which has recently been identified by Dean[1] as being due to a $\mathrm{Li_{Ga}}$-$\mathrm{O_P}$-$\mathrm{Li_{Int}}$ complex. The COL is completely quenched as predicted by Dean's model of Li replacing a V_{Ga} in a V_{Ga}-$\mathrm{O_P}$ complex. Annealing with Li also confirms the presence of oxygen in the undoped crystals (Ref. 4). Annealing a similar sample at 400°C for 15 h in vacuum also quenches the orange spectrum as shown in Fig. 2(a) by a dashed line. Presumably, trace impurities such as carbon or silicon move into the majority of empty Ga sites, giving rise to $\mathrm{C_{Ga}}^{+}$-$\mathrm{O_P}^{+}$ and $\mathrm{Si_{Ga}}^{+}$-$\mathrm{O_P}^{+}$ complexes, which are strongly nonradiative centers because they behave as doubly ionized donors in GaP.[3,7] The resultant spectra are difficult to resolve but may account for small increases in the ~1.63- and 1.55-eV region.[3] It is

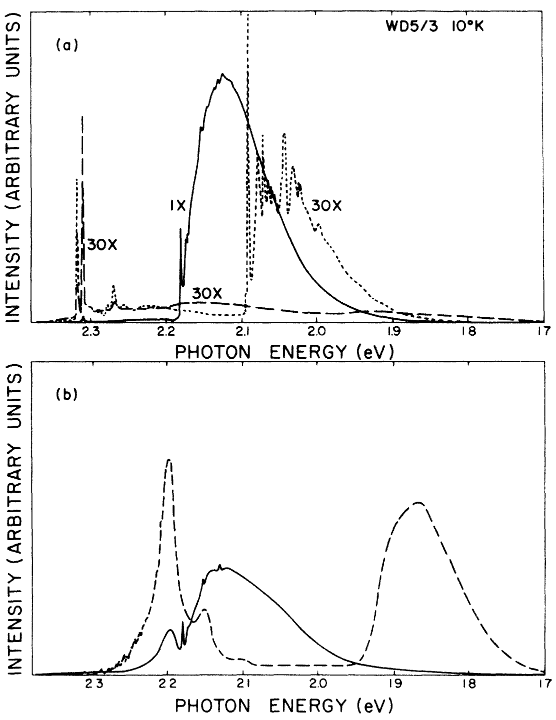

FIG. 2. Results of annealing (a) at 400°C for 15 h for an undoped water-vapor-grown GaP crystal in vacuum (dashed line) and in presence of Li (dotted line); (b) at 500°C for 15 h for a Zn-doped water-vapor-grown crystal (dashed line). Solid lines in both parts are for as-grown crystals.

also possible that other trace impurities like Cu may be filling Ga vacancies. Subsequent Li diffusion at 400°C for 15 h in the annealed sample, where COL was quenched, gave at least 30× less intense red luminescence due to the Li-O-Li$_{\mathrm{Int}}$ complex than that observed from Li diffusion into a grown (unannealed) sample. Further evidence was obtained by partial restoration of COL in an annealed crystal which was bombarded by 100-keV protons (dosage $\simeq 5\times10^{12}$ ions/cm^2).[8] These observations provide strong evidence for COL being due to a V_{Ga}-$\mathrm{O_P}$ complex.

Another important aspect of the COL is its behavior in Zn-doped GaP crystals. The spectra before and after annealing are shown in Fig. 2(b). After annealing, strong quenching of COL occurs with a simultaneous increase in the red Zn-O complex emission at 1.86 eV. This increase is substantially greater than that observed in typical solution-grown (Zn, O)-doped crystals.[9] The annealing process in the (Zn, O)-doped samples used in the present experiments can be interpreted as having a twofold effect. First, it increases the number of radiative centers (Zn-O complexes). Secondly, it decreases the number of V_{Ga}-$\mathrm{O_P}$ complexes, which act as nonradiative centers. Both of these types of effect are consistent with studies on solution grown (Zn, O)-doped GaP where one observes an increase in the ratio of the number of radiative to nonradiative centers on annealing.[9] Evidence for a decrease of the number of nonradiative centers is seen in Fig. 2(b) where the green emission at 2.20 eV due to S-Zn donor-acceptor pair transitions increases on annealing.

Having presented experimental evidence that COL is due to a V_{Ga}-$\mathrm{O_P}$ complex, it is reasonable to propose that COL is produced by a localized electronic transition from the excited state to the ground state of the V_{Ga}-$\mathrm{O_P}$ complex.[10, 11] The measured luminescent decay times for the COL are 110 μsec at 4°K and 57 μsec at 77°K, values which suggest that this internal transition is forbidden. From time-resolved spectroscopy we find that the decay time is independent of the spectral position.

In conslusion, we have presented evidence that observed characteristic orange luminescence which peaks at 2.125 eV is due to a V_{Ga}-$\mathrm{O_P}$ complex and that this complex plays an important role in determining the luminescent properties of GaP. The existence of vacancy complexes may be an essential prerequisite to the formation of radiative centers such as a Zn-O complex. In addition, it seem reasonable to expect that with proper control and filling of these V_{Ga}-$\mathrm{O_P}$ complexes, the low radiative efficiency of vapor-transport and liquid-encapsulated grown GaP could be improved.

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[6] The assignment of the *A* line as a zero-phonon line is tentative because of lack of observation of excitation spectra of COL. We feel that this is due to a low transition probability for the excitation.

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Multichannel Theory of Inelastic Electron Tunneling in Normal Metal-Insulator-Metal Junctions*

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A theory of inelastic electron tunneling due to phonons in normal metal-insulator-metal junctions is developed based on a multichannel tunneling model. The results are in good agreement with experiment and show that shifts in the bulk phonon energies observed by inelastic tunneling arise largely from kinematical factors. The observed harmonics are shown to arise due to two-phonon processes involving phonons at both sides of the barrier. A phonon polarization selection rule is shown to be operative in such tunneling processes. The model presented in this paper can readily be generalized to other types of inelastic excitations observed in tunnel junctions.

This Letter presents a theoretical calculation of the characteristic spectra observed in metal-insulator-metal junctions due to inelastic electron tunneling. Previous theoretical work on this problem has been discussed by several authors.[1] In an inelastic process, a tunneling electron with energy $eV \geqslant \hbar\omega$ [where ω is the frequency of any intermediate boson (excitation)] can excite a phonon at the metal-insulator interface. Because such a phonon excitation provides an additional tunneling channel, there is an increase in junction conductance $\sigma = dI/dV$ in the vicinity of $V = \hbar\omega/e$. Although such increases in conductance are usually less than 1% they can readily be observed by measurement of $d\sigma/dV$. In this paper we present a theory of such multichannel processes due to inelastic excitation of bulk metal phonons at the junction interfaces, and compare theoretical calculations with our measurements on both Pb-insulator-Pb and Al-insulator-Pb junctions.[2-4] The details of the experimental method have already been discussed elsewhere.[4] Our theory can readily be extended to take into account other inelastic excitations such as metal plasmons at the interfaces or oxide vibrations in the insulating barrier.

The reason for the choice of Pb as the material for our study here is twofold: Its electron-phonon coupling strength is high, and its spectra is well known from both neutron scattering[5] and superconducting tunneling[6] measurements. For simplicity, we restrict the present calculation to the region below 20 mV since the phonon spectrum of lead has a transverse peak near 4.4 meV and a longitudinal peak near 8.4 meV so that the whole spectrum and its first harmonics lie in this region. Moreover, we neglect the effect of aluminum whose phonon peaks occur above 20 meV and are weakly coupled to the electron system and also neglect any oxide vibrations which arise above 20 meV. Since our experiments were carried out at 1°K, we make a comparison with a theoretical calculation at absolute zero.

Our model is illustrated schematically in Fig. 1. We assume the insulator to be represented by

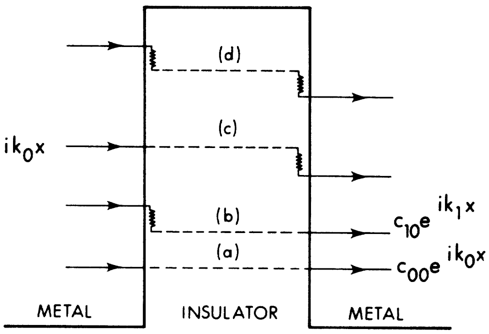

FIG. 1. Schematic diagram of model showing (a) the elastic channel, (b) and (c) inelastic phonon generation at each interface, and (d) two-phonon generation at both interfaces.