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Direct Evidence for Random-Alloy Splitting of Cu Levels in $GaAs_{1-x}P_x$

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A splitting of the Cu-related 1.36-eV luminescence in GaAs into a set of lines in the $GaAs_{1-x}P_x$ alloy system is interpreted in a model with only the nearest-neighbor group-V shell influencing the defect levels. Experiental peak intensities are in good agreement with simple calculations and the binding energies of the defects are found to follow calculated chemical trends for defect pairs. Results for the ternary alloys are extrapolated to and compared with the case of Cu in GaP.

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In spite of considerable theoretical and experimental efforts,[1,2] the understanding of deep impurities in semiconductors is still far from satisfactory. One approach to investigate such defects systematically has been to use a well-defined host semiconductor, like Si, and study the electronic properties of different impurity centers. Unfortunately, even closely related elements in the periodic table often behave too differently to allow interpretation of trends in their electronic properties. A different approach is to use the same impurity but gradually change the host material. We use this method in order to study the influence of variations in the composition of the host crystal on the properties of a specific deep-impurity center and report, as far as we know, for the first time on resolved random-alloy splitting of a defect due to different local surroundings of the defect core.

One important property of a deep-impurity level which is difficult to investigate experimentally is the extent of the wave function in space. In the one extreme, 4*f*-shell wave functions of rare-earth impurities are strongly localized. In the other extreme, wave functions of shallow hydrogenlike impurities sample a very large crystal volume, averaging out local fluctuations in, for example, the composition of an alloy. In this paper we are able to estimate the extent of the luminescent Cu-related state in GaAs (the 1.36-eV emission line)[3] from a detailed study of photoluminescence lines arising when an increasing number of As atoms are replaced by P atoms in the $GaAs_{1-x}P_x$ alloy.

Cu in GaAs is thought to occupy a Ga site which results in a defect level responsible for the well known 1.36-eV luminescence band.[3] The center seems to be distorted although the exact symmetry of the defect is still under debate.[4,5] A substitutional Cu_{Ga} center in GaAs is surrounded by four more or less symmetrically oriented nearest-neighbor As atoms, twelve next-nearest-neighbor Ga atoms, etc. In an alloyed ternary material like $GaAs_{1-x}P_x$, each Ga-site defect can be characterized by a great number of neighbor configurations. The number of different surroundings is, however, reduced, if only the first or the first few shells of surrounding atoms are sampled by the defect wave function. In such a case a set of discrete levels, characteristic for each differently alloyed surrounding, may be expected.

If we assume random mixing of the two alloying atoms, in our case As and P, the statistical occurrence of the two types of atoms among N sites is simply given by the binomial distribution,

$$P(m,N-m)=\begin{pmatrix} N \\ m \end{pmatrix} x^m(1-x)^{N-m}. \tag{1}$$

This is the probability that, in an alloy with composition x, m of N sites will be occupied by that atom species which appears with probability x, e.g., P in $GaAs_{1-x}P_x$. The expression in Eq. (1) becomes exceptionally simple if the defect is only influenced by the first four nearest neighbors ($N=4$), since then only five configurations can occur, i.e., with $m=0,1,\ldots,4$ P atoms adjoining the Cu atom.

The samples used in this study are $GaAs_{1-x}P_x$ alloys grown by metal-organic vapor-phase epitaxy.[6] The composition, x, of each sample studied was determined with microprobe analysis. Into this material, with background shallow doping levels of 1×10^{15}–1×10^{16} cm^{-3}, Cu was introduced by diffusion from an evaporated film of ≈ 1000 Å Cu on the sample surface. Diffusion was carried out in an evacuated quartz ampoule at temperatures in the range 500–700 °C for 30–100 min. Prior to optical studies the samples were mechanically and chemically polished to remove the remaining Cu on the surfaces. Photoluminescence measurements were carried out at 2 K with 10–100 mW of 5145-Å excitation light from an Ar^+-ion laser, with a detection system including a 0.75-cm double-grating monochromator and an S1 photomultiplier.

Photoluminescence spectra of Cu-doped GaAs, $GaAs_{0.95}P_{0.05}$, $GaAs_{0.89}P_{0.11}$, and $GaAs_{0.80}P_{0.20}$ are shown in Fig. 1. The $x=0$ spectrum shows band-edge emission lines around 1.5 eV consisting of excitonic as well as free-to-bound and donor-acceptor luminescence lines. The Cu-related luminescence band appears with a no-phonon line at 1.36 eV and LO-phonon replicas on the low-energy side. With increasing P content the band-edge emission shifts to higher energies following the Γ band gap.[6] Similarly, the Cu-related peak occurring at 1.36 eV in GaAs shifts with increasing x to higher energies. However, the energy position relative to the band-edge luminescence peaks increases with x which means that the $E_A \approx 0.15$-eV Cu level in GaAs becomes deeper in the alloy. The marked feature of the ternary-alloy system is clearly found to be the appearance of new luminescence lines on the high-energy side of the 1.36-eV Cu line. Two peaks can be clearly resolved, one shifted by ≈ 35 meV and the other by ≈ 70 meV towards higher energy. The ≈ 35-meV satellite is found to appear first as x is increased from zero. For $x \geqslant 0.2$, individual luminescence lines can no longer be resolved. It is, anyway, obvious that more peaks appear on the high-energy side when x is increased.

If we tentatively assign values of $m=0,1,\ldots$ to the series of peaks starting with $m=0$ for the 1.36-eV peak in GaAs, we can compare calculated occurrences of $CuAs_{4-m}P_m$ molecules according to Eq. (1) with the measured spectra. The results are shown in Fig. 2 where each of the spectra for $x>0$ has been shifted in energy to make the shallow acceptor peaks coincide. The agreement between the measured and calculated peak intensities is quite satisfactory and may indicate that the different defect levels have similar radiative probabilities. We thus conclude that the observed structure of Cu-related emission bands in $GaAs_{1-x}P_x$ can be ex-

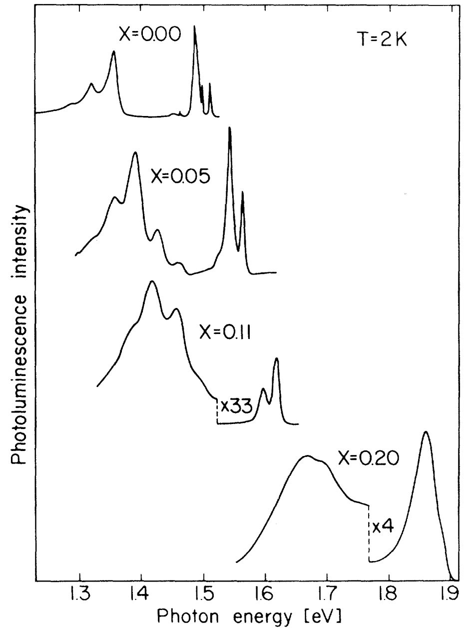

FIG. 1. A set of low-temperature photoluminescence spectra of Cu-doped $GaAs_{1-x}P_x$ obtained for four different values of x.

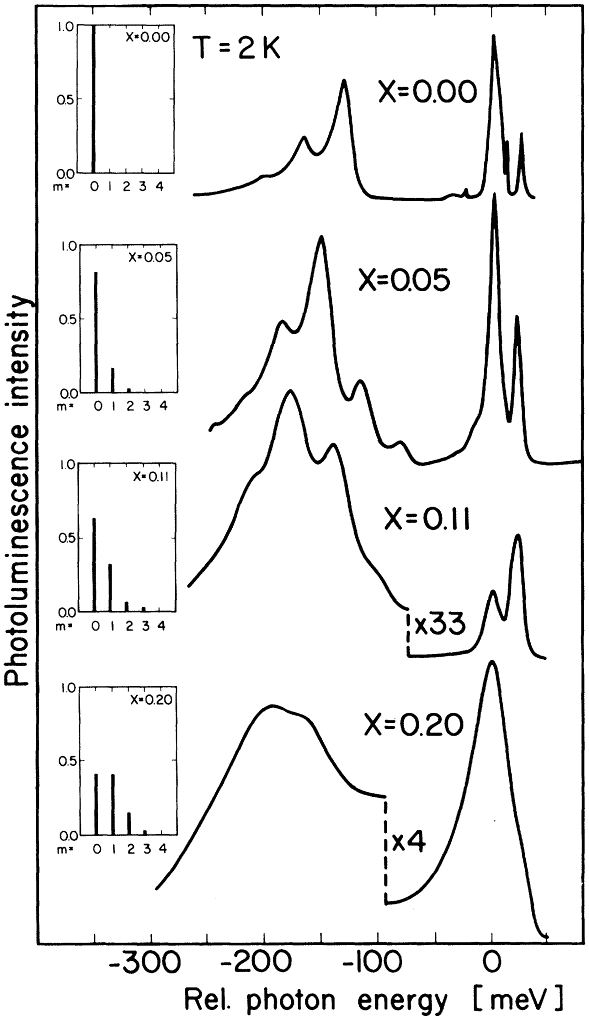

FIG. 2. Comparison of the calculated statistical occurrence (the inset) of different $CuAs_{4-m}P_m$ molecules, Eq. (1) with $N=4$, and the measured photoluminescence spectra for various alloy compositions x in $GaAs_{1-x}P_x$. The spectra have been shifted in energy to make the shallow acceptor peaks coincide. The identification of the dominant band-edge emission for $x=0.20$ as being free to bound is made from a comparison with undoped reference samples where free to bound and excitonic peaks are clearly resolved.

plained by a simple model where each composition of the four-atom nearest-neighbor shell is assumed to give rise to one type of energy level. Since the energy levels observed appear to be governed in zeroth approximation by the composition of the nearest-neighbor shell, we conclude that the impurity wave function is effectively limited to the volume inside the next-nearest group-V shell. The relatively strong broadening of the Cu luminescence peaks in the alloy may indicate that the hole wave function does have a nonnegligible amplitude even at more distant neighbors. The remaining differences between calculated and observed peak intensities are, at least partly, due to overlap between the different phonon-broadened contributions.

Within the framework of this model the observed energy position of the Cu levels for each composition is plotted in Fig. 3. Obviously, for GaAs only the $E_A^0(x=0) \approx 0.15$ eV level can occur. The binding energy of this level relative to the valence-band edge is found to vary approximately linearly with x, as

$$E_A^0(x) \approx E_A^0(x=0) + 0.43x. \tag{2}$$

Each of the states occurring for $x > 0$ and corresponding to $m = 1$, 2, 3, and 4, $E_A^m(x)$, is displaced to lower energies by $m\,\Delta E$ (where $\Delta E \approx 35$–40 meV), with a slope approximately equal to that for the $m = 0$ level. For a comparison with GaP data we can estimate the expected position of the $m = 4$ level for $x = 1$, which should occur at

$$E_A^4(x=1) \approx E_A^0(x=0) - 4\,\Delta E + 0.43 \approx 0.44 \text{ eV}$$

from the valence-band edge. The close agreement with the accepted binding energy of the radiative Cu level in GaP, $E_A \approx 0.5$ eV,[7] is an additional support of our defect identification. It has so far not been possible to determine the identity of this Cu-related level in GaP, although it has been suggested that it might be due to substitutional Cu on a Ga site. This assumption is thus supported by the present investigation where the luminescence due to substitutional $\mathrm{Cu_{Ga}}$ in GaAs has been traced through the $\mathrm{GaAs_{1-x}P_x}$ alloy to GaP.

The data and interpretation presented above can be compared with theoretical estimates of chemical trends in the binding energies of substitutional defect pairs.[8] Theory suggests that $\mathrm{Cu_{Ga}}$ produces a dangling-bond-like T_2 acceptor level above the valence-band edge.[9] Chemical trends in T_2 energies of substitutional defect pairs calculated in Ref. 8 can be used to estimate the expected change in binding energy when a simple $\mathrm{Cu_{Ga}}$ defect is transferred into a $(\mathrm{Cu_{Ga}}, \mathrm{P_{As}})$ defect pair in GaAs.

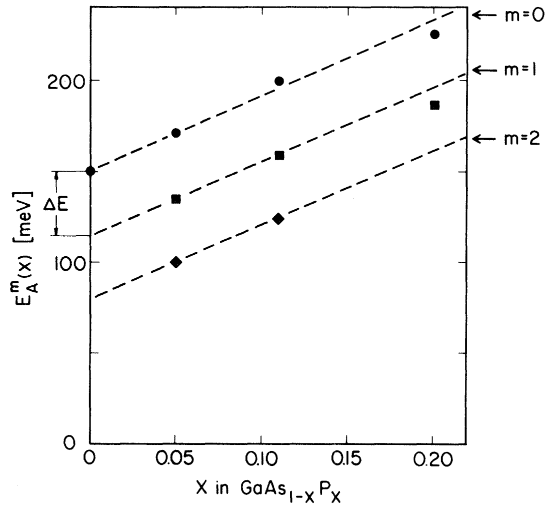

FIG. 3. Estimated energetic positions relative to the top of the valence band, $E_A^m(x)$, of the different Cu defects vs the alloy composition x in $\mathrm{GaAs_{1-x}P_x}$. $E_A^m(x)$ is the binding energy for $\mathrm{Cu_{Ga}}$ surrounded by m P atoms and $4-m$ As atoms.

Because of the difference in p potentials of As and P, the acceptor level of the defect pair $(\mathrm{Cu_{Ga}}, \mathrm{P_{As}})$, $E_A^1(x=0)$, is expected (Fig. 2 of Ref. 8) to be positioned closer to the valence-band edge than that of isolated $\mathrm{Cu_{Ga}}$, $E_A^0(x=0)$. The qualitative agreement with the binding energies of different defect configurations in $\mathrm{GaAs_{1-x}P_x}$ extrapolated to GaAs as deduced in Fig. 3 lends further support to our interpretation of the data.

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