OPTICAL EVALUATION OF RADIATIVE RECOMBINATION IN III–V COMPOUND SEMICONDUCTORS

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This paper reviews experimental techniques and recent results concerning the evaluation of III–BV compound semiconductor materials by means of analysis of radiative recombination processes. Photoluminescence is a particularly sensitive and informative technique to reveal low concentrations of impurity admixtures and fine details of their electronic structure. The technologically important materials GaAs and GaP have most thoroughly been investigated. The application of external perturbations lifts degeneracies and indicates the structure of exciton-binding centers. Time-resolved spectroscopy down to the picosecond-regime has been utilized to directly measure phonon lifetimes, energy relaxation, and other phenomena. Photoluminescence scanning with high spatial resolution yields information about dopant incorporation and the effects of line defects and interfaces on recombination. Excitation spectroscopy, an important variant of luminescence spectroscopy, is reviewed.

INTRODUCTION

The analysis of radiative recombination processes in semiconductors by means of optical spectroscopy represents a powerful tool for the analysis of these materials [1–3]. Radiative recombination of excess electron/hole-pairs is severely affected by extrinsic perturbations of the ideal crystal, such as impurity admixtures, point and line defects, surfaces and interfaces, stresses and strains, and deviations from stoichiometry. These perturbations may display a direct signature in spectrum of the recombination radiation, if new energy levels within the forbidden gap are created and participate in the recombination. Indirect influences are exerted, most frequently to the magnitude and rate of the radiative emission. The competition between various branches of recombinative paths and, yet more importantly, the little understood nonradiative shunt paths, make a quantitative impurity analysis, however, almost impossible except for a few simple cases [4].

The III–V compound semiconductors, especially GaAs and GaP, have been widely studied. Available high-purity crystals, controlled doping, and the ease of exciting and detecting radiative recombination have contributed to the detailed understanding of these materials. Less information is usually available for II–VI compounds [5], which are difficult to purify and dope; and even for the elemental semiconductors, whose emission falls in regions more difficult to detect [4, 6, 7].

Luminescence is by far the most widely used technique to analyse radiative recombination. Photoluminescence, in particular, is a simple and rapid method, requires neither large samples nor additional handling, such as needed for contacts. Extremely low concentrations, down to $10^{11}$ foreign atoms/cm$^3$ can be detected.
It is, however, very important to use as low an excitation power as possible to avoid complications and to obtain sharp and meaningful optical spectral output!

This paper reviews some recent aspects of optical analysis of recombination in III–V compounds. I shall emphasize experimental techniques where additional features are added to luminescence measurements: applications of external fields are discussed in Sec. 2., time resolution is covered next; Sec. 4 concerns spatially resolved luminescence; finally, Sec. 5 gives a brief survey on excitation spectroscopy of luminescence. A general discussion is presented in the concluding Sec. 6.

2. LUMINESCENCE FROM SAMPLES UNDER EXTERNAL FIELDS

The introduction of a foreign atom as a dopant into a III–V host crystal will typically result in three distinctive new features in the emitted radiative response [8]: (i) a sharp line, fairly close in energy to the free-exciton emission, this line is caused by the radiative decay of an exciton bound to the (neutral) impurity usually called \((D^0, X)\) or \((A^0, X)\), (ii) a broader, deeper-lying emission caused by the radiative transition of an electron or a hole bound to the impurity to a free state in the valence or conduction band usually called \((e, A^0)\) or \((h, D^0)\), and (iii) a very broad and still deeper band, caused by transitions of bound electrons to bound holes, called “pair bands” or — when resolved into discrete emissions — “pair lines”, \((D^0, A^0)\). Besides these typical resulting effects from adding a dopant, there may be further complications since the impurity could cause formation of complexes with native point defects, such as vacancies [8, 9].

Straightforward identification is often restricted to simple donors and acceptors, where the chemistry of incorporation is easy and controllable. A reliable analysis nowadays calls for a more detailed study, especially under the influence of a degeneracy-lifting external field. We shall now briefly discuss a few examples.

a) Magnetic fields

Figure 1 shows a nomogram [10] representation of a radiative recombination in GaAs for an exciton \(X\) bound to the neutral acceptor Sn under the influence of an external magnetic field \(H = 10\ T\) [11]. The initial \((A^0, X)\) and final \((A^0)\) states are shown in the uppermost and lowermost parts of the diagram. The field causes both a linear Zeeman splitting and a quadratic diamagnetic splitting of the originally sharp excitonic line. The \(g\)-values and the symmetry of the \(g\)-tensor can thus be derived from the spectra for different polarizations (upper part) and compared to group-theoretical predictions, as shown in the lower part. The predicted oscillator strengths are encircled in Fig. 1.

The details of such magneto-luminescent studies reveal a great deal of information. The multiplicity of the splitting indicates the symmetry of the binding center, above all, it answers the question whether or not an impurity occupies a lattice site or...