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"Radiative Recombination in Semiconductors"

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15 September 1968 - 14 September 1971

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Heavily doped n-type single crystals of GaN were grown epitaxially by the vapor phase reaction of GaCl and NH_3 on Sapphire substrates. GaN is a direct gap semiconductor with a bandgap of 3.25eV. It fluoresces efficiently in the visible as well as the UV. Single crystals of AlP were prepared by the disproportionation of gaseous AlI in the presence of PH_3 either as freely nucleated whiskers or epitaxially on GaAs or Si substrates. Attempts to determine the mechanisms of the efficient Cu green luminescence in ZnS and the mechanism responsible for room temperature lasing in CdS were unsuccessful. In order to design semiconductor alloy systems to achieve high efficiency luminescence in the visible, we have observed the effects of alloying small amounts of InP and AlP with GaP on the luminescence of GaP.

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FINAL REPORT

"Radiative Recombination in Semiconductors"

Abstract

Heavily doped n-type single crystals of GaN were grown epitaxially by the vapor phase reaction of GaCl and NH_3 on sapphire substrates. GaN is a direct gap semiconductor with a bandgap of 3.25 eV. It fluoresces efficiently in the visible as well as the UV. However, attempts to prepare p-type material for p-n junctions were unsuccessful due to the large densities of native donor defects.

Single crystals of AlP were prepared by the disproportionation of gaseous AlI in the presence of PH_3 either as freely nucleated whiskers or epitaxially on GaAs or Si substrates. The crystals are not as unstable as expected in a humid ambient. Controlled doping, photoluminescence and p-n junction measurements remain to be completed.

Attempts to determine the mechanisms of the efficient Cu green luminescence in ZnS and the mechanism responsible for room temperature lasing in CdS were unsuccessful. Instead, the effect of the native S donor vacancy in CdS on luminescence of bound excitons and donor-acceptors has been determined.

In order to design semiconductor alloy systems to achieve high efficiency luminescence in the visible, we have observed the effects of alloying small amounts of InP and AlP with GaP on the luminescence of GaP. The GaP spectral

lines observed in photoluminescence at 4.2°K on solution grown crystals of $In_xGa_{1-x}P$ due to excitons bound to S and N, and donor-acceptor pair lines associated with C-S pairs, shift, broaden and become weaker as x increases from 0 to 3%. At 25°K the S bound exciton splits with increasing In doping.

Attempts to observe sharp-line donor-acceptor pair photoluminescence in Si doped with B and P were unsuccessful. Samples diffused with Li and Au exhibited photoluminescence which depended on the presence of both. It is our hypothesis that Li and Au pair to form an isoelectronic trap. We are also seeking the exact mechanism responsible for a series of evenly-spaced sharp lines which occur on the low energy side of bound-exciton emission lines.

I. Crystal Growth and Electrical and Optical Properties of GaN Single Crystals"

Abstract

We have been able to grow GaN epitaxially from the vapor phase by halide transport. The as-grown crystals were always heavily doped n-type.. Optical measurements show GaN to have a 3.25 eV gap at room temperature

Crystal Growth

We have tried several methods to grow GaN single crystals. The most successful one has been an open-tube vapor phase growth technique, in which Ga, transported to the deposition zone as a gaseous halide, reacts with NH_3 to form GaN epitaxially on a sapphire substrate. We have obtained large, transparent single crystals of GaN by this method. Several substrates have been tried and we have found that sapphire is the most successful one. However, GaN grown on itself has been shown to be better than GaN grown on sapphire. Growth rates ranged from 1-40μ/hr, depending on temperature, substrate and substrate orientation and substrate position relative to the NH_3 source. We have found that the best films grown were those closer to the NH_3 source.

Structure and Properties

Debye-Scherrer and back-reflection Laue x-ray diffraction patterns confirmed our identification of GaN with a = 3.182 Å, and c= 5.1717 Å. We have found that $\frac{\Delta a}{a} = 11\%$ and $\frac{\Delta c}{c} = 4\%$ for a 30.0μ thick layer while the strain was reduced to $\frac{\Delta a}{a} = 0.8\%$ and $\frac{\Delta c}{c} = 2\%$ for a 100μ thick layer, i.e. the strain decreases with growing thicker layers of GaN. This strain is believed due to the lattice mismatch between sapphire and GaN.

Electrical and Optical Properties

The as-grown crystals were always heavily-doped n-type with room temperature mobilities between 15 and 20 $cm^2/V.sec.$ and carrier concentrations between 2×10^{20} and 5×10^{20} cm^{-3}. The carrier density was independent of the growth temperature (750-1050°C) and orientation but did show a decrease of about a factor of 5 with increasing layer thickness (2-100μ). Chemical analyses indicated no impurity in the $10^{20} cm^{-3}$ range. Therefore, we have concluded that the high donor concentration is due to native defects such as nitrogen vacancies or Ga interstitials or a complicated complex. It has been noted that this defect decreases as the crystal strain is decreased as the layers are grown thicker.

From optical measurements we concluded that GaN has a direct bandgap close to 3.5 eV at room temperature and has an optical electron effective mass of 0.27 m_o. We have measured both reflectivity and absorption from 0.27 to 30 μ and photoluminescence spectra. We note that photoluminescence efficiencies were much lower near the substrate interface than from the front face of thick layers.

We were not able to convert the conductivity type from n-type to p-type for getting a p-n junction.

II. Growth and Characterization of AlP for LED Applications

Introduction AlP crystals are to be prepared in pure and doped form for evaluation as a possible material for LED applications in the blue region of the spectrum. The crystals are to be grown epitaxially by open tube halide transport and doped both during growth and by diffusion with expected shallow donors, shallow acceptors and radiative recombination centers. The samples will be evaluated by Hall and resistivity measurements, Schottky barrier properties, optical absorption and photoluminescence. P-n junctions will then be fabricated and their electrical and luminescent properties measured, emphasizing optimal distribution and quantum efficiency with a view toward optimizing visible light emissions.

Progress AlP crystals are currently being grown in an all-alumina open-tube type reaction tube. Gaseous aluminum iodide is introduced upstream in the reaction zone by passing HI gas over molten Al metal and transported down the reaction tube to the deposition zone where PH_3 gas is introduced. The resultant mixture and reaction deposits AlP in the form of whiskers on the walls of the tube and epitaxial films on strategically placed substrates.

So far, the best results have been obtained with a temperature profile of approximately 1150°C and 1050°C in the reaction and deposition zones respectively; and with input flow rates of approximately 1000cm^3/min. of 1% $HI:H_2$ mixture and 25 cm^3/min. of an 8% $PH_3:H_2$ mixture.

Whiskers thus obtained were of size ~1mm X 2 cm, triangular in cross section and bluish-green to dark brown in transmitted light. Epitaxial films of ~50μ thickness on high resistivity <111>Si substitutes revealed a good degree of crystalline perfection under the microscope and looked greyish-brown in reflected light.

The AlP crystals react with the moisture in the air to form Al_2O_3 and gaseous PH_3 over a period of half day to 2 days for the epitaxial films and the whiskers respectively. The Al_2O_3 is in the form of a white powder which, in the case of the epitaxial films, flakes off the substrate. The crystals have been kept from decomposition by placing them in a box filled with dry N_2.

X-ray photographs of powdered AlP in a Debye-Scherrer type camera confirmed that the AlP crystals have the zinc-blende structure and a lattice constant of 5.45 Å. Measurements on the AlP epitaxial films with a four-point resistive probe indicated the films to be n-type with high impurity content ($\sim 10^{19}$ to 10^{20} cm^{-3} free carriers). Preliminary optical absorption measurements on the AlP whiskers indicated the band edge to be in the green region of the spectrum with an impurity tail pushing into the yellow region of the spectrum and that AlP has an indirect bandgap.

Experiments in the near future will be focussed on the choice of suitable substrates and optimization of growth parameters.

III. Luminescence from ZnS and CdS

The highly efficient green emission in Cu-activated ZnS phosphorous has been studied for years but no mechanism has been generally accepted. The most likely mechanism is donor-acceptor recombination and a definitive experiment would be observation of the characteristic sharp line spectrum. We attempted to observe this spectrum by saturating the transition using ultraviolet light. We focussed light from a molecular nitrogen pulsed laser on samples of doped ZnS immersed in liquid helium. The luminescence was observed using both a spectrograph (2 Å /mm dispersion) and a spectrometer-photomultiplier - boxcar integrator system. Sharp lines were not observed and the experiment was abandoned.

Room temperature photoexcited CdS lasers have been investigated in an attempt to deduce the mechanisms and type of mode confinement responsible for the laser action. Small rectangular prisms were cleaved from thin platelets of pure material and excited with the focussed ultraviolet radiation from a pulsed nitrogen laser. Laser action was achieved, but the threshold power did not vary with the excited length of the cavity in an expected manner. Variable temperature spectra and threshold experiments were begun by us, but a recent paper by others reported that the results of such experiments failed to define the laser mechanism. We have abandoned this approach.

It has long been suspected that native defects play a large part in the photoluminescent properties of CdS. Spectra depended more on crystal growth and preparation than on doping, but results were difficult to interpret because the concentration of native defects could not be measured nor could it be calculated, given the preparation conditions. The defect chemistry of CdS has recently been put on a more quantitative basis. Hershman and Kroger(1) performed Hall effect and resistivity measurements on CdS crystals in equilibrium with known partial pressures of Cd vapor at high temperature. The carrier concentration varied as $P_{Cd}^{1/3}$ at temperatures above 700°C, and this was interpreted in terms of a doubly ionized native donor. The equilibrium constant was evaluated so that for a given temperature and Cd pressure the concentration of this native donor could be predicted. Kumar and Kroger(2, 3) then confirmed that the donor was a sulfur vacancy, $V_S^{\bullet\bullet}$, and determined the relevant diffusion coefficient.

We attempted to relate photoluminescent spectra to the concentration of sulfur vacancies in CdS. A first experiment has been completed. Four samples, cut from the same boule, were annealed at high temperature and cadmium pressure, and rapidly quenched. Photoluminescence was excited using a Hg arc, with the sample immersed in liquid He at 1.6°K. Spectra were recorded on photographic plates using a spectrograph with 2 Å/mm dispersion.

Low temperature photoluminescence was very bright even after this drastic treatment. One sample was angle-lapped and its luminescence was uniform with depth, showing that the quenching was indeed quick enough. Two of the annealed samples were then re-annealed at low temperature and one of them was annealed a third time at high temperature. Photoluminescence was drastically different between high ($[V_s] \cong 2.7 \times 10^{17} cm^{-3}$) and low ($[V_s] \cong 1.2 \times 10^{16} cm^{-3}$) temperature anneals but was reversible (i.e., single-annealed and triple-annealed samples were similar). Many, though not all, of the observed lines have been identified from the literature and a series of experiments has been begun in which the vacancy concentration is systematically varied.

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IV. Luminescence from $Ga_{1-x}In_xP$ and $Ga_{1-x}Al_xP$ Alloys

We have been studying the photoluminescence of $Ga_{1-x}In_xP$ as a function of x in order to understand the changes in luminescence properties caused by the isoelectronic substitution of indium in the GaP lattice. Some preliminary work has been completed on the related alloy $Ga_{1-x}Al_xP$.

The alloy crystals are grown in a gallium plus indium melt at temperatures up to 1200°C, using quartz ampoules as containers. The crystals grow as platelets with (111) major faces. Because of the 8% difference in lattice constant between GaP and InP, it would be expected that the resulting stresses would show up as lattice imperfections which should increase to a maximum in the middle range of alloy concentration. Consistent with this, we have observed an increase in etch pits on the gallium surface of the alloy platelets as the indium concentration is increased, starting from the GaP rich side. At about 20% indium, platelets no longer grow and only amorphous chunks of alloy can be produced from solution growth.

In photoluminescence, the relative luminescence integrated over wavelength drops by a factor of ten which 1% indium is added to GaP, and the sharp edge emission lines of GaP broaden and finally merge into one broad band at about 7% indium.

By contrast the LPE alloy crystals reported in the literature[1,6] do not exhibit any luminescent efficiency changes, except at the cross-over between indirect gap and direct gap behavior for the alloy. This is presumably the result of the fact that a thin epitaxial layer will have a very small alloy concentration gradient, and can more easily relax the strains built up as a consequency of the growth conditions--as compared to the relatively larger solution grown platelets.

The fact that edge emission lines are not resolvable with more than a few per cent indium in $Ga_{1-x}In_xP$ alloys grown from solution limits our ability to detect shifts in photoluminescent lines due to indium composition; however, the ease of solution growth enables us to survey a range of dopants in $Ga_{1-x}In_xP$ with the goal of finding reference photoluminescence emission lines to use to measure the various effects of alloy concentration on luminescence properties.

Our spectral data were recorded on spectrographic plates using a Bausch and Lomb 2 meter spectrograph equipped with a 600 lines/mm and 1200/mm grating. The alloys were immersed in liquid helium or placed in a flow of helium vapor and excited with a 200 watt mercury lamp.

In our as-grown alloy platelets, edge emission[2] due to bound excitons on nitrogen and sulphur, plus donor-acceptor pair lines due to sulphur-carbon and zinc-sulphur pairs have been observed in alloys with up to 3% indium. In this range the edge emission have varied with indium in an approximately linear fashion consistent with the reported variation of the indirect gap with indium doping.[3]

The donor-acceptor pair lines, which could be resolved only at low In dopings for the as-grown platelets at 4.2°K, have been observed for slightly higher In levels in experiments at 25°K where the nitrogen exciton becomes ionized and cannot produce light, resulting in an enhancement of the pair spectral lines. Epitaxially grown alloys also show better resolved lines for a given doping level. This is probably a result of the higher alloy homogeneity and lower strain expected for epitaxial growth.

The sulfur bound exciton, which is still observable at 25°K, is split into two levels which diverge for higher In dopings. This effect is attributed to a uniaxial strain generated by In in the GaP lattice. A uniaxial strain could be produced by a gradient in the In doping level, or by a pairing effect between In and S with a strain generated along the axis of the pair.

Crystals of $Ga_{1-x}Al_xP$ have been grown from solution in nitreous carbon boats. The luminescence spectra of these crystals shows only the broad for pair band of the donor-acceptor spectrum. Growth of crystals with lower Al content and more of the characteristic GaP spectra is in progress.

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V. Radiative Recombination in Silicon

Since Si is a well understood semiconductor, with the energy levels and capture cross sections of many impurities known,[1,2] radiative recombination processes should be more easily interpretable in it than in those semiconductors not as well characterized. Because it was our belief that a study of the photoluminescence of Si could yield knowledge applicable to the radiative processes in the less understood semiconductors, this work was undertaken.

Our original experiment, which was to observe sharp-line donor-acceptor pair recombination spectra in photoluminescence,[3,4] was unsuccessful and the project was discontinued. Work was begun to introduce isoelectronic traps chemically by trying to form nearest-neighbor pairs of Li-Au and Li-In. Initial experiments have revealed a new luminescence band which seems to depend on the presence of both Li and Au. Preliminary samples doped with Li and In show no evidence of an isoelectronic trap. We have observed sharp lines occuring at low temperatures ($\lesssim 10^{o}K$) and on the low energy side of emission lines due to bound excitons at neutral donors and acceptors.[5]

Experimental

The near-band gap Si luminescence at low temperatures is usually due to decay of free or bound excitons. These mechanisms are very inefficient, therefore great care must be taken in assembling the apparatus for taking high resolution spectra.[5] We describe in this section our experimental methods.

Photoluminescence is excited by a 200W mercury arc filtered to remove infrared energy by a $CuSO_4$ solution and Corning 1-69 filters. The recombination radiation is chopped, filtered to remove short wavelengths (<0.95μ) and focussed onto the entrance slit of an f/8 Perkin-Elmer E-1 scanning spectrometer which has a dispersion of 14 Å/mm. The detected signal is amplified by phase-sensitive techniques using a lock-in amplifier. In our early work an InAs photodiode cooled to 77°K was used as a detector. Recently we have discovered that a cooled (~200°K) RCA 7102 (S-1 photoresponse) photomultiplier improved our detectivity by a factor of approximately 50 for near bandgap luminescence (1.0-1.2 eV). This enables us to take spectra routinely at a resolution of 0.3 meV, an improvement of a factor of six over spectra previously reported.[5] For lower photon energies (0.5-1.0 eV) the InAs detector must still be used.

To minimize non-radiative surface recombination,[5] the Si must be scrupulously cleaned and etched immediately prior to taking data. The procedure consists of soaking in hot trichloroethylene, then hot methyl alcohol, rinsing with deionized water, soaking in hot HNO_3, then hot H_2SO_4 and finally hot NHO_3 again. The samples are briefly etched in a solution of NHO_3 and HF (5:3 by volume, in their usual concentrated strengths)[6], quenched with deionized water, rinsed with HF and then deionized water, steamed[5] for 5 min., dried and immersed in liquid helium.

Results

Broad bands attributed to recombination at distant donor-acceptor pairs have been previously observed for a number of donors and acceptors.[3,4] We grew by the float zone method a crystal of B- and P-doped Si with concentrations ranging from $N_B \sim N_P \sim 2 \times 10^{16} cm^{-3}$ to $N_B \sim 1 \times 10^{14} cm^{-3}$ and $N_P \sim 2 \times 10^{15} cm^{-3}$. No sharp lines were observed and in retrospect our choice of B and P was wrong since the states associated with these impurities are strongly coupled with phonons[5] which broaden the sharp lines. This project was discontinued and a search begun for isoelectronic traps which might be controllable, efficient radiative recombination centers.

Both N[7] and nearest-neighbor pairs of Zn and O[8] have been shown to be efficient recombination centers in GaP, due to the absence of a competing non-radiative auger process.[9] By analogy with the Zn-O center, we chose to investigate the Li-In and Li-Au nearest neighbor pairs as possible isoelectronic traps. An initial feasability experiment, in which Au was diffused into Si wafers at high temperatures and Li at low, has shown a new emission band with a sharp peak at 0.765 eV and an associated lower energy broad band. This spectrum is observed only when both Li and Au are present, and resembles that of the Bi isoelectronic trap in GaP.[10] Work is in progress to characterize further the nature of the center. Crystals of Si doped with In were grown by the float zone method, and subsequently diffused with Li. No new luminescence was observed.

An experiment to define the photoluminescence associated with Li has revealed a series of sharp, evenly-spaced lines which appear to be associated with bound-exciton emission at neutral Li and which begin about 2 meV below the bound-exciton line. The lower energy lines only appear at temperatures below 10°K, while the bound exciton emission remains for temperatures at least up to 30°K. We have observed similar lines associated with B and P, and believe we are seeing luminescence which has been attributed to the formation of electron-hole condensate drops.[11] We are continuing this research since the exact recombination mechanism remains to be established.

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