Optical quenching of bound excitons in CdTe and $Cd_{1-x}Zn_xTe$ alloys: A technique to measure copper concentration

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A noncontact, nondestructive optical technique with potential to measure the acceptor impurity concentrations in bulk CdTe and $Cd_{1-x}Zn_xTe$ alloys is described here. The technique, called optical quenching, uses an infrared light source in conjunction with the above-band-gap excitation beam used in standard photoluminescence spectroscopy. The quenching, or decrease, of acceptor-bound exciton emission is related to the incident infrared beam flux. The rate at which the infrared photons ionize neutral acceptors can be used to determine relative concentrations of the substitutional centers. We have applied this technique to the copper acceptor-bound exciton in CdTe and $Cd_{1-x}Zn_xTe$ bulk samples. The 1.064 μm output from a Nd:YAG laser provided near-resonant absorption with the copper acceptor level. Relative copper concentrations in the range from 4×10^{14} to 1×10^{16} cm^{-3} were obtained. These values agree reasonably well with sample comparisons based on atomic absorption data.

I. INTRODUCTION

Bulk CdTe and $Cd_{1-x}Zn_xTe$ are commonly used as substrate materials for epitaxial growth of HgCdTe layers for infrared device structures, and have been increasingly promoted as viable materials for x-ray and gamma ray detectors.[1,2] Contamination with acceptor impurities, such as copper, silver, sodium, and lithium elements, has been identified as a leading cause of performance problems in fabricated device structures from the CdTe and CdZnTe materials. As-purchased Cd, Zn, and Te elements typically include contamination of these particular impurities at levels of about 10^{16} cm^{-3}. Even with copper levels of between 10^{15} and 10^{16} cm^{-3} in the substrate material, growth of HgCdTe epilayers by molecular beam epitaxy (MBE) can provide pathways for Cu diffusion. Cu levels of greater than 10^{17} cm^{-3} have been observed in Hg-based epilayers grown on substrates of lower copper concentrations, due to selective Cu extraction.[3] This high contamination level subsequently limits the performance of the infrared detector material. In order to improve device performance, the background levels of the acceptor impurity atoms in the substrate materials must be lowered.

Purification processes on the starting elements are commonly used to reduce the overall background level of copper (and other common contaminates) prior to bulk crystal growth. The relative merits of the various purification processes to produce high purity single crystalline bulk samples can be evaluated by performing analysis of samples after growth. Analytical techniques, such as graphite furnace atomic absorption, involve complete destruction of the crystalline material and are limited in detection sensitivity to copper atomic concentrations from low 10^{15} cm^{-3} or higher. A nondestructive technique to provide accurate determination of copper concentration in the actual samples used in device fabrication is highly desired. In addition, improvement in impurity detection to levels below 10^{15} cm^{-3} is

needed to further distinguish the merits of various elemental purification and growth techniques.

There have been previous attempts to relate photoluminescence (PL) emission intensities to impurity concentrations in II-VI semiconductors. Because the intensity of a particular recombination line may be influenced by crystalline quality, surface preparation, and PL excitation conditions, the measured signal intensity alone is not a reliable parameter to compare from sample to sample. Alternative approaches for II-VI materials include measuring the intensity ratios of bound-exciton lines to the free-exciton first LO-phonon satellite as a function of laser power, and extrapolating to zero excitation rate, as has been reported for CdTe.[4] This approach is then dependent on resolution of the contributions from closely lying bound-exciton emission lines, such as may only be possible by using a double- or triple-grating spectrometer. A second approach for evaluating acceptor concentrations in ZnSe:N also involves monitoring PL emission as a function of incident laser power.[5] The intensity of donor-acceptor (DAP) emission under saturation conditions was found to correlate well with excess acceptor concentration ($N_A - N_D$) in a series of intentionally doped materials. This second method requires monitoring a recombination process involving a second (donor) impurity center.

We report here a noncontact, nondestructive optical technique which is a variation on the standard PL technique, but requires a simple single-grating spectrometer setup. Simultaneously with the above-band-gap excitation source used to excite the PL signal, an infrared beam is directed onto the sample. With the appropriate choice of infrared photon energy, one can resonantly change the population distribution of the neutral to charged state of a particular impurity species, thus providing controlled quenching of radiative recombination lines related to the neutral impurity, such as the neutral acceptor-bound exciton (A^0, X). The rate of decrease in emission intensity of PL emission about the neutral sub-

TABLE I. Copper concentrations in Cd and Te raw materials, and in selected CdTe slices from the as-grown ingots as measured by graphite furnace atomic absorption. CdTe sample No. 6004 was chosen as the calibrated standard for determining relative substitutional copper concentrations by the optical quenching technique (N/A=data not available).

Sample No.	Cd Cu $\times 10^{15}$ cm^{-3}	Te Cu $\times 10^{15}$ cm^{-3}	Ingot tip Cu $\times 10^{15}$ cm^{-3}	Ingot heel Cu $\times 10^{15}$ cm^{-3}	Ingot avg Cu $\times 10^{15}$ cm^{-3}	PL Cu $\times 10^{15}$ cm^{-3}
6000	7.44	7.03	1.54	3.94	2.74	1.2 ± 0.1
6004	7.39	21.27	4.38	5.55	4.97	5.0
6005	2.91	34.04	N/A	N/A	N/A	8.0 ± 2.0
6005[a]	2.91	34.04	N/A	N/A	N/A	4.0 ± 1.0
6127	(below detection limit of atomic absorption technique, $<10^{15}$ cm^{-3})					0.4 ± 0.2

[a]Subject to post-growth anneal.

stitutional copper center (Cu_{Cd} or Cu_{Zn}) is related to the concentration of substitutional copper in II-VI alloys. Recombination involving other impurity centers, such as DAP recombination, is not required for evaluation by our technique. Because the PL technique can be used to laterally probe impurity distributions across the surface of a semiconducting wafer by rastering of the focused probe (above band gap) beam, the technique described here allows determination of electrically active impurity concentrations in the material used for device fabrication.

Infrared quenching of PL emission has been reported for ZnS,[6] CdS and ZnS,[7] and ZnSe.[8] The low energy infrared photons excite valence band electrons to acceptor levels within the band gap. These acceptor levels, when neutral, form the lower states for radiative recombination. Once these lower states are filled with photoexcited electrons, radiative recombinations are reduced in intensity, or quenched. For example, in CdTe, acceptor-bound exciton recombination (A^0,X) will be observed for neutral centers only. Once the acceptor center has trapped an electron, thus changing its charge state to A^-, bound exciton radiative recombination about the ionized acceptor center is not allowed.[9] The primary goal of the previous quenching studies[6-8] was to determine the particular infrared photon energy which would produce the maximum decrease in PL intensity of some deep level. This photon energy could then be related to the ionization energy of the deep level. Determination of impurity concentrations was not attempted in these early studies.

II. EXPERIMENTAL DETAILS

In this work, optical quenching of Cu_{Cd} (A^0,X) PL emission at liquid helium temperature was performed on a series of bulk CdTe and $Cd_{1-x}Zn_xTe$ ($x \sim 0.07$) samples grown by the Bridgman technique at II-VI Inc. (Saxonburg, PA). Ingots were grown under identical conditions except for different grades of starting materials. Cu concentrations in the CdTe starting materials, as well as some companion samples were obtained by the Direct Zeeman Corrected Graphite Furnace Atomic Absorption (DZCGFAA) technique (performed by VHG Labs, Inc.). This technique gives total atomic copper concentrations to an accuracy of $\pm 1 \times 10^{15}$ cm^{-3}, with a detection limit of about $1-2 \times 10^{15}$ cm^{-3}. The data for the bulk CdTe samples is summarized in Table I. Note that values for sample 6127 were below the detection limit of the atomic

absorption technique. This suggests that the copper concentration is below 10^{15} cm^{-3}. In addition, Hg-based MBE growth experiments carried out on substrates from this same boule did not show gettering of copper into the epilayer,[10] providing additional evidence of a low level of Cu in this boule.

The experimental apparatus used in the present PL studies has been described elsewhere.[11] Above-band-gap excitation was provided by the output from a cw argon ion laser (514.5 nm). The infrared 1.064 μm output from a Nd:YAG laser (CVI Laser model C-95 YAG MAX) was focused to a beam spot of about 0.7 cm in diameter on the sample surface.

III. RESULTS AND DISCUSSION

A schematic of the band structure near $\mathbf{k}=0$ for CdTe is shown in Fig. 1. The lowest conduction band (Γ_6) has a minimum at $\mathbf{k}=0$. Γ_8 is the topmost valence band, and Γ_7 is the spin-orbit split-off band. Cu_{Cd} is the neutral substitutional copper acceptor level in CdTe at 0.146 eV above the top of the valence band.[12] At liquid helium temperatures, the energy gap ($\Gamma_6-\Gamma_8$) of CdTe is 1.606 eV, and the spin-orbit split-off energy is about 0.95 eV.[13] The energy difference between the Cu_{Cd} level and the Γ_7 band is therefore about 1.096 eV.
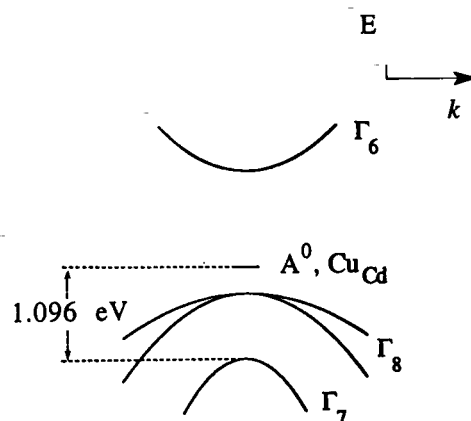

FIG. 1. Schematic of CdTe band structure. The spin-orbit split-off band (Γ_7) is 0.95 eV below the Γ_8 band at liquid helium temperatures. The Cu_{Cd} acceptor level is shown at 0.146 eV above Γ_8, thus giving an energy difference ($Cu_{Cd}-\Gamma_7$) of 1.096 eV.
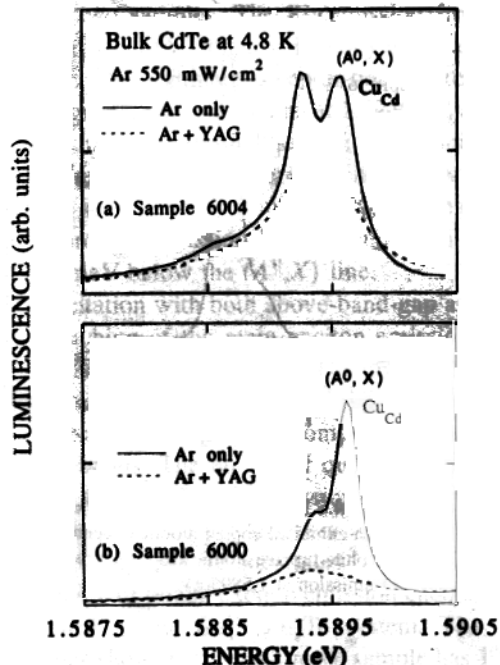
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FIG. 2. Representative PL spectra (solid lines) from CdTe samples 6004 and 6000 excited with 550 mW/cm² of above-band-gap (514.5 nm) light. Optical quenching spectra (dashed lines) excited with argon (550 mW/cm²) and Nd:YAG (1.064 μm, 850 mW/cm²) shows resonant saturation of Cu-bound exciton emission at 1.5895 eV.

FIG. 3. Normalized PL amplitude of Cu_{Cd} (A^0,X) emissions vs relative incident infrared photon flux for CdTe samples showing different optical quenching rates. The relative Nd:YAG output required to quench to 80% is indicated by dashed lines.

For the ternary alloy, $Cd_{1-x}Zn_xTe$, the energy band structure is similar to that shown in Fig. 1. The energy difference ($\Gamma_8 - \Gamma_7$) and copper acceptor level ionization energy may increase slightly for low zinc concentrations. In the binary compound ZnTe, the energy difference ($Cu_{Cd} - \Gamma_7$) at low temperatures is 1.119 eV.[13] Thus, the energy difference between the Γ_7 band and the Cu_{Cd} level for both the CdTe and mixed alloy samples is believed to be about 1.1 eV. This value is close to the infrared photon energy of 1.165 eV (1.064 μm) from the Nd:YAG laser producing near-resonant ionization of substitutional copper centers. The number of electrons available to ionize the Cu_{Cd} acceptors will be proportional to the photon flux (or power) in the infrared beam. A tunable infrared source of sufficient power would provide photons of the exact energy for improved resonance with a particular acceptor level. Fortunately, the Nd:YAG laser output is well matched to the copper acceptor in these II-VI materials.

Other common acceptor impurities in CdTe create more shallow neutral acceptor levels. For example, Na_{Cd} and Li_{Cd} point defects create acceptor levels which are 58.7 and 58.0 meV, respectively, above the valence band. Infrared light from the Nd:YAG laser can ionize these acceptor levels as well, however, the effect will not be as enhanced as the ionization of the copper levels.

Optical quenching of Cu_{Cd} (A^0,X) PL emission with the infrared output from the ND:YAG laser was performed on five bulk CdTe and two $Cd_{1-x}Zn_xTe$ samples at liquid helium temperature. Figure 2 shows PL and optical quenching spectra of (A^0,X) emission lines for CdTe samples 6004 [Fig. 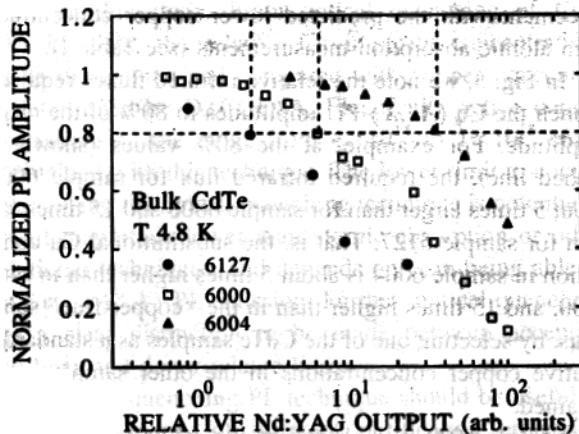2(a)] and 6000 [Fig. 2(b)]. The solid lines represent the conventional PL emission signal in the region of (A^0,X) emission in CdTe as excited with 550 mW/cm² from an argon ion laser (514.5 nm). The dashed lines show the reduction in bound exciton emission which occurs when the sample is simultaneously excited with the above-band-gap beam and 850 mW/cm² of infrared radiation. The emission energies of (A^0,X) for several different impurities have been well identified in bulk CdTe.[12] The emission line at about 1.5895 eV is due to bound exciton recombination about a neutral Cu_{Cd} center, and the 1.5892 eV emission is related to Na_{Cd} and/or Li_{Cd}. In sample 6000, the 1.5892 eV emission line appears as a shoulder. Note that the copper emission is almost completely quenched in Fig. 2(b) (dashed line), while the emission related to the more shallow acceptors can still be observed at the highest infrared flux used.

The other bulk CdTe samples in our study show similar spectra to that in Fig. 2. As cautioned in previous reports,[6,7] the (A^0,X) emission amplitude varies from sample to sample and cannot by itself be used as a reliable indication of impurity concentration. The bulk CdTe samples, however, show consistently different quenching rates with increasing power from the Nd:YAG laser, which we take to indicate different concentrations of substitutional acceptors. As expected, the infrared radiation has a much greater effect on Cu_{Cd} (A^0,X) emission line than on emissions related to the more shallow Na_{Cd} or Li_{Cd} point defects.

The normalized amplitude of the (A^0,X) emission, which is the ratio of the PL intensity under simultaneous above-band-gap and Nd:YAG excitation to the PL intensity under above-band-gap excitation only, was used to monitor the quenching rate of the PL emission. The intensity of the Cu-related bound exciton peak was separated from other closely lying emission lines through the use of standard fitting procedures assuming Gaussian line shapes for bound exciton radiative recombination. Figure 3 shows a plot of the normalized Cu_{Cd} (A^0,X) PL amplitudes as a function of relative infrared excitation power for samples 6127 (circles), 6000 (squares), and 6004 (triangles). Note that the PL emissions from samples 6000 and 6127 quench at a faster rate, in

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agreement with the predicted lower copper concentrations from atomic absorption measurements (see Table I).

In Fig. 3, we note the relative infrared fluxes required to quench the Cu (A^0, X) PL amplitudes to 80% of the original amplitude. For example, at the 80% values (shown with dashed line), the required infrared flux for sample 6004 is about 5 times larger than for sample 6000 and 15 times larger than for sample 6127. That is, the substitutional Cu concentration in sample 6004 is about 5 times higher than in sample 6000, and 15 times higher than in the "copper-free" sample. Thus, by selecting one of the CdTe samples as a standard, the relative copper concentrations in the other samples can be obtained.

Sample 6004 was chosen as the calibrated copper standard for this study assuming a Cu concentration of about 5×10^{15} cm^{-3} (see value for ingot average in Table I). This sample was chosen, rather than sample 6000, because the ingot average concentration was further above the detection limit of the atomic absorption technique, and therefore is believed to be more reliable. Of course, the atomic absorption values take into account the total copper concentration including that amount which may be tied up in Te precipitates. The PL quenching technique monitors only the relative amount of electrically active substitutional copper sites. Thus, our optical quenching PL values represent an upper limit to the relative amount of substitutional copper in our series of samples. To determine relative copper concentrations in the other CdTe samples, we averaged the values obtained by measuring the 90%, 80%, and 50% quenching levels of the other samples to arrive at a reasonable approximation of relative copper concentration. Relative substitutional copper concentrations based on our PL quenching results are also included in Table I. The uncertainty reflects the spread in values obtained at the 90%, 80%, and 50% quenching levels.

The optical quenching PL method allows measurement of copper concentrations below the detection limit of the atomic absorption method. Sample 6127, which is considered to be copper free based on other techniques, has a predicted substitutional copper concentration of about 4×10^{14} cm^{-3}. The (A^0, X) PL emission from the copper-free sample is shown in Fig. 4, as excited by 100 mW/cm^2 of above-band-gap radiation (514.5 nm). The copper (A^0, X) emission is seen clearly at 1.5895 eV. Surprisingly, the bound exciton PL emission from the copper-free sample is similar to that of sample 6000 [Fig. 2(b)]. Thus, one can see how misleading conventional PL spectra analysis can be in determining impurity concentrations. The optical quenching technique, however, provides unambiguous comparisons between samples with low levels of impurities.

As a test for our technique, we obtained atomic Cu concentration from DZCGFAA (VHG Labs, Inc.) for the as-grown sample 6005. This sample exhibited the highest relative amount of substitutional Cu from our optical quenching PL experiments. The total atomic copper concentration for 6005 is 1.4×10^{16} cm^{-3}, or roughly 2.8 times greater than sample 6004. Our PL results predict an increase in electrically active copper of up to 2 times more than in sample 6004. We find then that the optical quenching technique
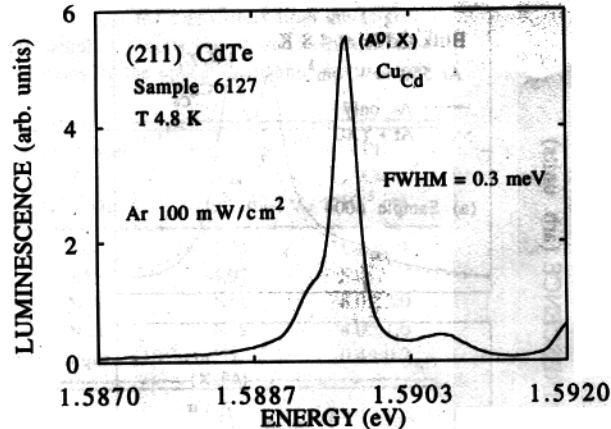

FIG. 4. Low temperature (4.8 K) PL emission in bound exciton region for CdTe sample 6127, which exhibited copper atomic concentration below the detection level of the graphite furnace atomic absorption technique. Note the dominant Cu$_{Cd}$ (A^0, X) emission at 1.5895 eV.

should be accurate to within at least a factor of 2 in predicting copper concentrations.

We have also applied the optical quenching technique to measure relative acceptor concentrations in Cd$_{1-x}$Zn$_x$Te $(x \sim 0.07)$. Two samples from the same boule slice, one as grown and one subject to a post-growth anneal, were included in our study. The zinc concentrations were determined based on the emission energy of the free exciton recombination.[14] The low temperature PL in the region of acceptor-bound exciton emission is shown in Fig. 5 (solid
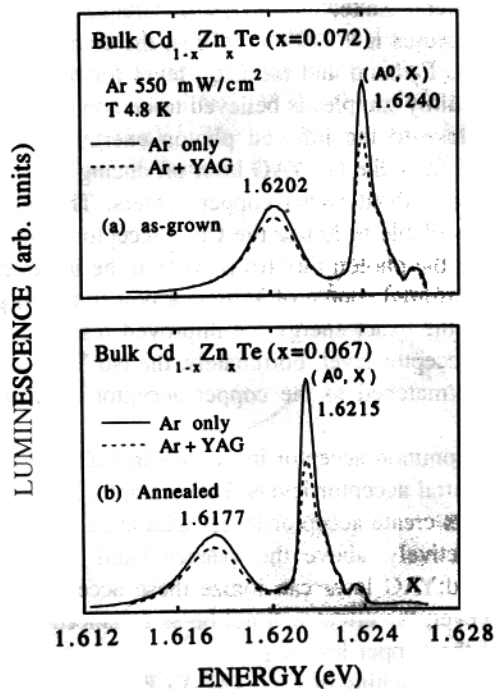

FIG. 5. Conventional PL (solid lines) and optical quenching (dashed lines) spectra for Cd$_{1-x}$Zn$_x$Te excited with 550 mW/cm^2 of above-band-gap (514.5 nm) light. Optical quenching spectra (dashed lines) excited also with Nd:YAG laser shows resonant saturation of acceptor-bound excitons.

lines) for the two samples. The PL emission from the as-grown sample occurs at slightly higher energy due to the larger x value. The dominant acceptor-bound exciton emission in the as-grown material occurs at 1.6240 eV, and occurs at 1.6215 eV in the annealed sample. The emission line shapes from the two samples were similar. A low amplitude donor band is seen at about 2 meV above the main (A^0,X) emission. A broader emission band of unknown origin appears at 3–4 meV below the (A^0,X) line.

Under excitation with both above-band-gap and infrared beams, a quenching of the main exciton emission from the $Cd_{1-x}Zn_xTe$ samples was observed. The lower energy bound exciton peak also decreases in intensity. The donor band reduces in intensity only slightly in comparison with the other two emission bands. The enhanced quenching of the main peak leads us to identify this emission as being related to substitutional copper. Copper has been reported as a leading contaminant in $Cd_{1-x}Zn_xTe$ substrates.[3] Unfortunately, precise identification of bound exciton emission energies has not been performed in the $Cd_{1-x}Zn_xTe$ system. The relative quenching rates show that the as-grown sample has 1.5 times more substitutional copper than the annealed sample. The little to no quenching that is observed for the donor and free exciton (X) emission in the $Cd_{1-x}Zn_xTe$ samples is consistent with our observations in the bulk CdTe samples. In fact, the optical quenching technique using the Nd:YAG laser allows acceptor-related emission lines to be distinguished from donor lines in these II-VI materials. Thus, the emission bands at 1.6202 eV in the as-grown material, and at 1.6177 eV in the annealed sample are also related to a neutral acceptor site.

Finally, it is important to note that the rate of quenching, or change of charge state of the copper centers, in these II-VI materials will also depend on the lifetime of the trapped electron at the impurity site. This electron lifetime depends only slightly on the doping level in the samples studied here. However, if the optical quenching technique is used to determine copper impurity concentrations in heavily doped samples or samples which have a large concentration of some other impurity or defect, an appropriate calibration sample may be needed to attain the desired accuracy.

IV. CONCLUSIONS

The potential of the noncontact, nondestructive optical quenching of Cu_{Cd} (A^0,X) PL has been evaluated for measuring electrically active copper concentrations in bulk CdTe and $Cd_{1-x}Zn_xTe$ $(x\sim0.07)$ samples. The optical quenching reduction in neutral substitutional copper PL was obtained using the infrared output at 1.064 μm (1.165 eV) from a Nd:YAG laser. This infrared photon energy is in close resonance with the $(Cu_{Cd}-\Gamma_7)$ energy difference at liquid helium temperatures for both the CdTe and ternary alloy samples

included in this study. From optical quenching of Cu_{Cd} (A^0,X) PL data, the relative Cu impurity concentrations could be determined and compared with copper concentrations determined by DZCGFAA. Electrically active copper concentrations in the range from 4×10^{14} to 1×10^{16} cm^{-3} were obtained with this technique. The lower limit to copper detection using the optical quenching technique is potentially orders of magnitude lower than atomic absorption or other conventional techniques, and depends only on being able to detect Cu_{Cd} (A^0,X) PL emission. Further, optical quenching allows a clear distinction to be made between acceptor-related lines and donor-related lines.

The optical quenching PL technique should be useful in evaluating the merits of different purification processes. Resonant quenching of the PL emission associated with a particular impurity species can be obtained with the appropriate choice of infrared photon energy. Although the technique only probes substitutional, or electrically active acceptor centers, the values obtained from optical quenching agree well with comparisons based on atomic absorption data for copper.

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