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Abstract. The family of ternary compounds of composition $In_xGa_{1-x}As$ are of considerable interest for thermophotovoltaic energy converters. The recombination lifetimes of the various compositions are critical to the successful application of these materials as efficient converters. Here we will describe experimental results on the composition, $In_{0.53}Ga_{0.47}$, that is lattice-matched to InP. We will also describe lifetime results on the compositions $In_{0.68}Ga_{0.32}As$, with a bandgap of 0.60 eV to compositions $In_{0.78}Ga_{0.22}As$ with a bandgap of 0.50 eV. Double heterostructure confinement devices have been made over a range of both n- and p-type doping. These results are preliminary, but the goal is to obtain the radiative and Auger recombination coefficients for the alloys in this composition range.

INTRODUCTION

InGaAs is a ternary III-V semiconductor that is of current interest for thermophotovoltaic (TPV) devices. Of particular interest are the compositions that produce bandgaps of 0.5 eV to 0.6 eV, because these can be used with lower-temperature thermal radiators. The minority-carrier and recombination (high-injection) lifetimes are intimately related to photovoltaic efficiency. As the minority-carrier diffusion length is directly proportional to the square root of the lifetime, the short-circuit current J_{sc} varies accordingly. In addition, the reverse-saturation current J_o increases as the inverse square root of the lifetime. Obtaining acceptable lifetimes and even maximizing the lifetime is a crucial component of material development.

For the both lattice-matched and small-bandgap ternaries, limited lifetime data have been available (1). Henry and coworkers (2) measured the minority-carrier lifetime in n- and p-type lattice-matched $Ga_{0.47}In_{0.53}As$ grown on InP substrates. They measured the lifetime over a doping range from 5×10^{17} cm^{-3} to 1×10^{19} cm^{-3} in both n- and p-type $Ga_{0.47}In_{0.53}As$. They found that the lifetime decreased with doping density over these doping levels. The lifetime first deceased with the inverse of the doping level, which is indicative of radiative recombination. Finally, they found relatively higher lifetimes in n-type than in p-type $Ga_{0.47}In_{0.53}As$. Higher doping levels produced a lifetime that decreases as the inverse square, which is indicative of Auger recombination. In the low doping range, Gallant and Zemel (3) measured a photoconductive lifetime of 18.5 μs in an undoped InP/$Ga_{0.47}In_{0.53}As$/InP double heterostructure (DH). Recent work by the NREL group has measured the lifetime of the lattice-matched composition $In_{0.53}Ga_{0.47}$ over a doping range from 2×10^{14} cm^{-3} to 2×10^{19} cm^{-3} (4). As a result of these measurements, the radiative (B-coefficient) and Auger (C-coefficient) parameters were obtained

for this composition from an analysis of the data. Some more recent results with lattice-matched compositions will be described here.

Very little information exists in the literature on the properties of the compositions of $In_xGa_{1-x}As$ with $x > 0.47$ and $E_g < 0.73$ eV. The author and coworkers (5) described some early results on these compositions that were both undoped and doped. We measured the lifetime of an undoped film of composition $In_{0.78}Ga_{0.22}As$ with a bandgap of 0.5 eV. The lifetime decreased to 52 ns as compared with lifetimes of several microseconds in a similar lattice-matched film. The decrease was attributed to recombination at the threading dislocations arising from mismatch. Owing to large improvements in the growth and materials technology, the results to be described here are markedly improved.

EXPERIMENTAL RESULTS

MOVPE Film Growth

Our samples were grown by metalorganic vapor phase epitaxy (MOPVE), as described in another paper presented at this conference (6). The $In_xGa_{1-x}As$ DH was grown on step-graded layers from a InP substrate. The graded structure consists of 10 steps that are each 0.3 μm thick. The composition of these layers is $InAs_xP_{1-x}$ (as x varies from 0 to the final composition $InAs_yP_{1-y}$). Here the lattice constant of $InAs_yP_{1-y}$ matches that of the active layer $In_xGa_{1-x}As$. After the step-graded layer is complete, a 1.0-μm window layer of the final composition $InAs_yP_{1-y}$ is grown. Next, an active layer of $In_xGa_{1-x}As$ is grown that varies between 0.25 and 2.0 μm in thickness. Finally, a lattice-matched top window layer of $InAs_yP_{1-y}$ is grown that is 300 Å thick. These passivating window layers are critical improvements over earlier lattice-mismatched devices (5).

Lifetime Measurement Techniques

Recombination lifetime measurements were made by two complementary techniques. A radio-frequency photoconductive decay (RFPCD) technique was used (7) to measure the samples in the lower doping range. The RFPCD technique can resolve lifetimes greater than about 20 ns. A second RFPCD system provides variable sample temperature from about 80 to 300 K. Using temperature as a variable provides additional information for identifying the recombination mechanism, as well as providing data for low-temperature device applications. The pulsed-light sources were used here included light-emitting diodes (LED), an attenuated pulsed YAG laser, and a tunable optical parametric oscillator (OPO) driven by a tripled YAG laser. The latter could be tuned to a wavelength of about 400 nm to 2.2 μm. The long wavelength range was used to find the InGaAs bandgap by the onset of photoconductivity.

Samples in the higher doping ranges were measured by photon-counting technique that involved up-conversion of photoluminescence. As the intrinsic photoluminescence for InGaAs is in the infrared (about 1.7 to 2.4 μm), the sum-frequency up-conversion technique allows the use of photon counting (8). The samples were pumped by 90 femtosecond (fs) pulses at 82 MHz repetition rate. The pump laser was a Spectra-Physics mode-locked titanium- sapphire (Ti:S) laser tuned to 762 nm wavelength output. The collected luminescence was mixed with the Ti:S laser pulse for sum-frequency generation (SFG) in a 1-mm lithium iodate ($LiIO_3$) crystal. The SFG signal was dispersed by a SPEX 270 meter monochromator and detected by a Hamamatsu R464 photomultiplier tube. The system time resolution is approximately 110 fs.

The bandgaps of the alloy films were determined by either Fourier Transform infrared photoluminescence or Raman scattering. The bandgaps were also confirmed by using the tunable OPO in the infrared range and measuring an excitation spectrum for photoconductivity.

Recombination Mechanisms

The low-injection lifetime in dislocation-free films of InGaAs can be written as:

$$\frac{1}{\tau_B} = B\,N + CN^2 + \frac{1}{\tau_{SRH}}, \qquad 1)$$

where B is the radiative B-coefficient, C is the Auger coefficient, and N is the majority-carrier density. The bulk Shockley-Read-Hall recombination lifetime due to point defects is given by τ_{SRH}. When two surfaces are included with recombination velocity S_1 and S_2, the total lifetime becomes:

$$\frac{1}{\tau_B} = B\,N + CN^2 + \frac{1}{\tau_{SRH}} + \frac{S_1 + S_2}{d}, \qquad 2)$$

Lifetime of In(0.53)Ga(0.47) as a Function of Doping Level

Figure 1 shows the minority-carrier lifetime of a series of $In_{0.53}Ga_{0.47}$ double heterostructures of both n- and p-type over five orders of magnitude of doping concen-

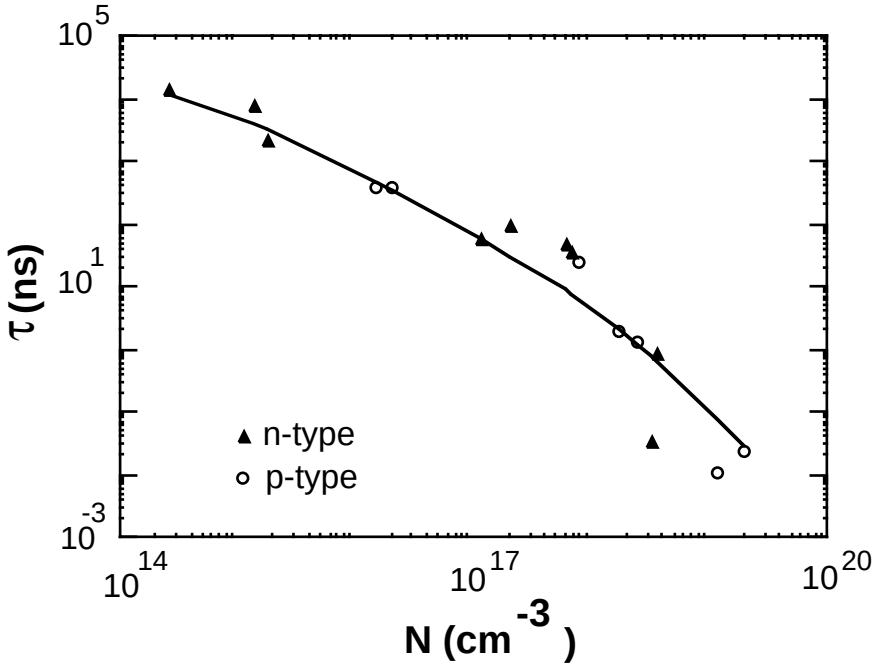

FIGURE 1. The minority-carrier lifetime of lattice-matched $In_{0.53}Ga_{0.47}$ versus free-carrier concentration. The solid line is a fit of Eq. 1. to these data.

tration. The data could be fit with Eq. 2 where the B- and C-coefficients were found to be:

$$B = 1.43 \times 10^{-10}\ cm^{-3}s^{-1}$$

$$C_{n,p} = 8.1 \times 10^{-29}\ cm^{-6}\ s^{-1},$$

These values compare very favorably with earlier values found by Sermage and coworkers (9). The lifetime at the lowest carrier concentrations is defect dominated as predicted by the Shockley-Read-Hall theory (10,11). In this sample set, the largest lifetimes in undoped films were about 20 μs. These data on lattice-matched samples form a basis for comparison of the new work on lattice-mismatched alloys. For undoped DH structures, one hopes to get lifetimes in the microsecond range, indicating that dislocation-induced recombination has been reduced. For the heavily doped alloys, the B- and C-coefficients for lattice-matched material serve as starting points and estimates for finding these constants in mismatched material.

Lattice-mismatched Films

Undoped n-type In(0.68) Ga(0.32)As DH Structure

A series of lattice-mismatched DHs of composition In_xGa_{1-x} with x varying between 0.68 and 0.77 were grown on InP substrates. A grading layer was grown between the InP

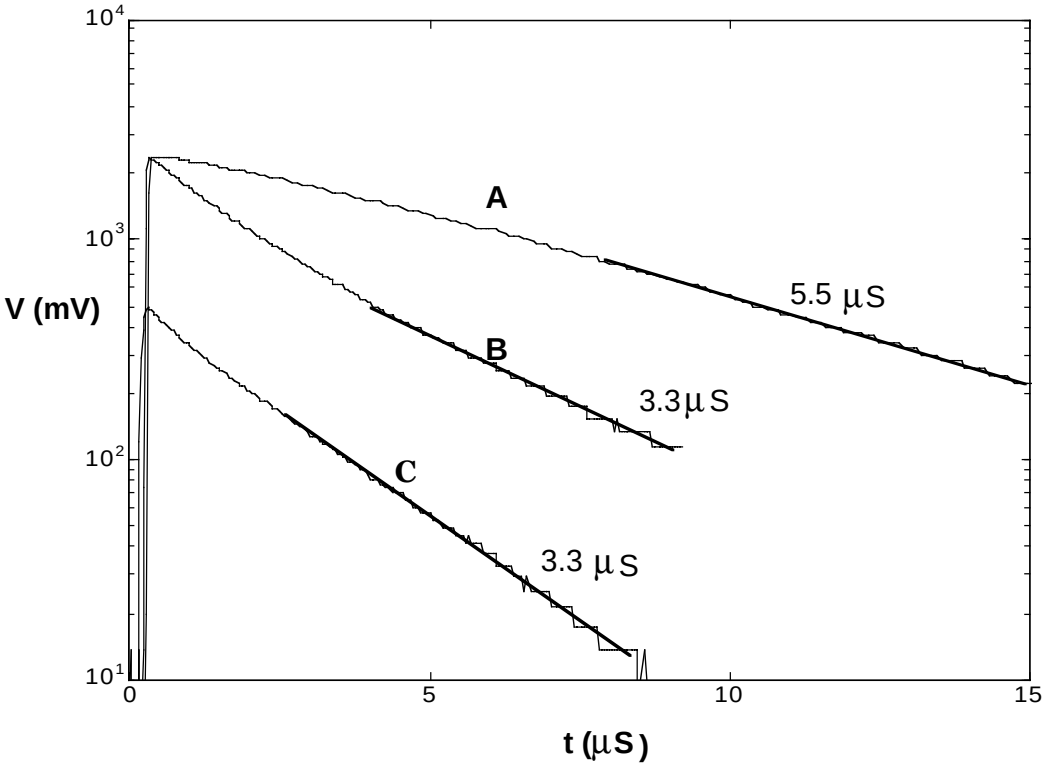

FIGURE 2. RFPCD data on two undoped, n-type DH structures with bandgaps A: 0.58 eV and B,C: 0.55 eV. The laser excitation wavelengths are: A: 532 nm, B: 532 nm, C: 2.3 μm. The donor concentrations are: A: 1.43 x 10^{15} cm^{-3}; B, C:2.6 x 10^{15} cm^{-3}.

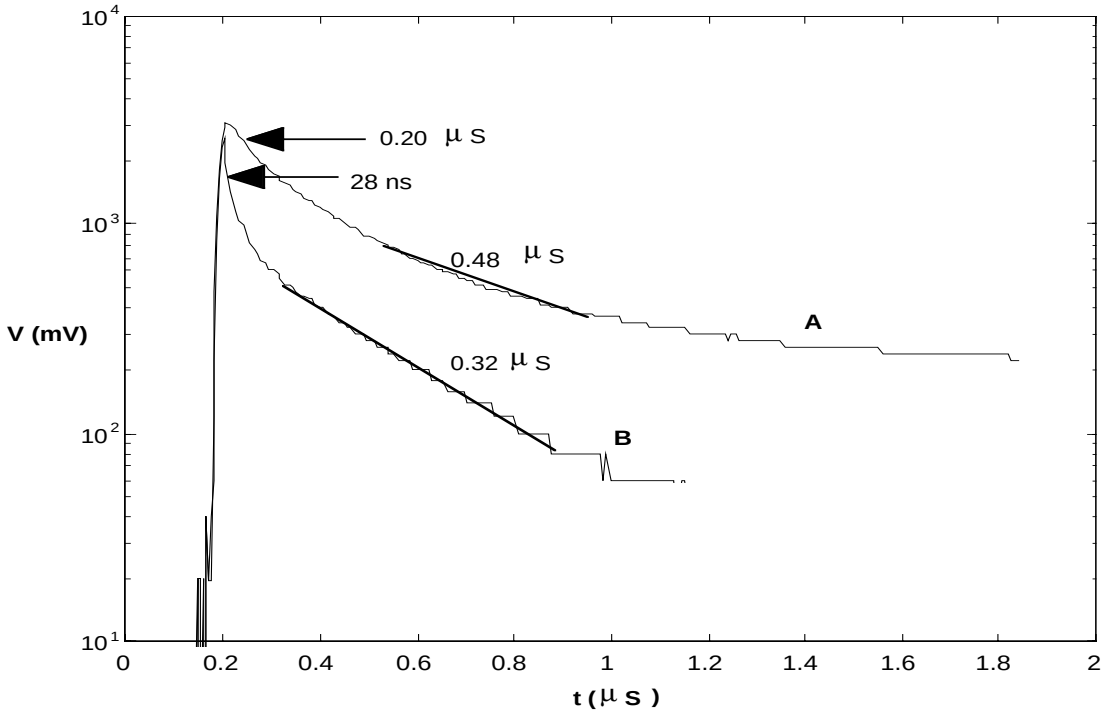

FIGURE. 3. RFPCD data of a p-type InGaAs DH with Eg = 0.52 eV and N_A = 1.7 x 10^{16} cm^{-3}. The data of Curve A was measured with a excitation wavelength of 1064 nm. The data of Curve B used a wavelength of 532 nm.

substrate and DH structure. The indium composition was increased from 0.53 until the active layer composition x was reached. The InGaAs film thicknesses are about 2 μm for each sample. Fig. 2 shows RFPCD data on two undoped DH structures with bandgaps of 0.58 eV (Curve A) and 0.55 eV (Curves B and C), respectively. The excitation source for Curves A and B is the doubled-YAG wavelength of 532 nm. For sample A, the capacitance-voltage (C-V) measurement show the conductivity to be n-type with n = 1.43 x 10^{15} cm^{-3}. The low-injection lifetime of this sample is 5.5 μs, as seen in the figure. Sample B is n-type with an electron concentration of 2.6 x 10^{15} cm^{-3} as measured by C-V. The lifetimes here, as shown by curves B and C, are 3.3 μs. Curve C was obtained by exciting the sample with the optical parametric amplifier tuned to about 2.3 μm wavelength. This wavelength corresponds to a photon energy of 0.54 eV, which is slightly less than the bandgap determined by photoluminescence. The response died for slightly longer wavelengths. As the samples show lifetimes of several microseconds, the results indicate high-quality epitaxial films with low dislocation densities. These lifetimes are slightly smaller than found in the best lattice-matched films of prior work (12). These data also indicate that dislocations must be of fairly low density, contrasted with the results of earlier work (5).

P-type In(0.78) Ga(0.22) As DH Structure

This sample was grown with the above target composition and was Zn-doped for p-type conductivity. C-V measurements showed p-type conductivity with a hole concen-

tration of 1.7 x 10^{16} cm^{-3} at the front window layer. However, the carrier type appears to reverse deeper into the structure. The RFPCD lifetime is shown in Fig. 3 using two excitation wavelengths. Curve A is drawn from data with the laser wavelength set to 1064 nm, and Curve B from data with the wavelength set to 532 nm. The light pulse is absorbed very near the front surface for the 532 excitation. The steep initial slope with a 28-ns decay time is indicative of a high surface recombination velocity between the

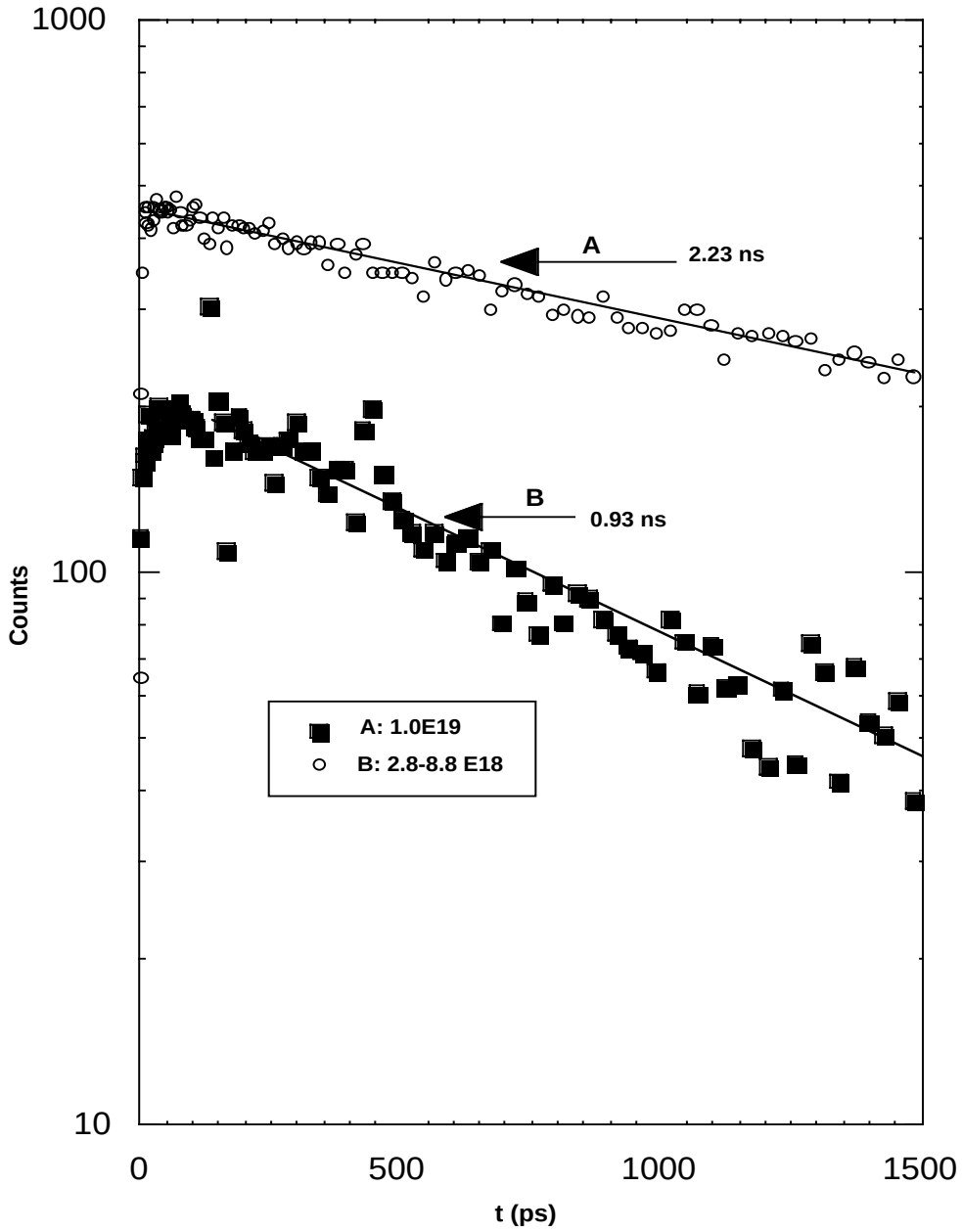

FIGURE 4. The minority-carrier lifetime measured by the upconversion technique described in the text. The DH samples are n-type with the doping levels shown. The bandgaps of these samples are about 0.63 eV.

active InGaAs region and the InAsP window layer (13). In both cases, the excess carrier decay has positive curvature. Such behavior can be indicative of either bimolecular (high-injection) radiative recombination or a shallow SRH-defect dominated recombination process (14). Using the B-coefficient obtained from the analysis of lattice-matched InGaAs, the calculated radiative lifetime is about 0.39 μs. The portion of the decay between 0.4 μs and 1.0 μs is in the range of the predicted radiative lifetime. The dominant recombination mechanism can be clarified with further studies such as the temperature dependence of the lifetime (15). The general conclusion however, is that the lifetimes are much improved compared to the earlier devices reported by the author and coworkers (5).

Heavily doped n-type In(0.68) Ga(0.32) As

The RFPCD technique is only useful for lifetime measurements when the lifetime exceeds about 10 ns. For shorter lifetimes, we have developed that photon up-conversion technique that has been described above. With up-conversion, we can resolve lifetime values to less than 1 ps. Figure 4. shows up-conversion data on two samples that are heavily doped with sulfur to produce n-type conductivity. Sample A has a doping-density profile that varies from 2.8 x 10^{18} cm^{-3} to 8.7 x 10^{18} cm^{-3}. The lifetime measured here is 2.2 ns measured at the peak of the photoluminescence spectrum. Optical measurements indicate that the bandgap of this sample is 0.63 eV. Sample B has a lifetime of 925 ps and the electron concentration is 1.0 x 10^{19} cm^{-3} as measured by CV. Using the B-coefficient from the lattice-matched material, the calculated radiative lifetime of sample A is about 1.6 ns compared with the 2.23 ns measured here. We see from Fig. 1 that the lifetimes in this doping range is in the 10-to-100-ps range and are controlled by Auger recombination. The C-coefficient predicts an Auger lifetime of 367 ps for sample A.

For sample B, we calculate a radiative lifetime of 700 ps and an Auger lifetime of 11 ps, compared with a measured lifetime of 930 ps. The measured lifetime for the mismatched films are much larger than one would extrapolate from the lattice-matched case. These preliminary data may indicate that the lifetimes are consistent with predicted radiative lifetimes. The Auger coefficients appear to be *much smaller* then predicted from the lattice-matched C-coefficient. The reduction of the Auger effect is a very puzzling feature of these data.

These are preliminary experiments and further work will be required to establish reliable recombination parameters. The Auger coefficient is a very important parameter for devices that are operating in a high-injection mode. A suspected weak Auger coefficient awaits confirmation by characterizing more samples as a function of carrier concentration.

CONCLUSIONS

Measurements on lattice-matched InGaAs were made over a wide doping range to produce values of the radiative and Auger recombination coefficients. These measurements provide a basis or starting point for comparing the radiative and Auger coefficients for mismatched ternaries. Measurements on lattice-mismatched films with bandgaps ranging from 0.5 to 0.6 eV has also shown much improved electronic properties. Lifetimes of about 2 to 5 μs were measured in undoped DH film structures. Measurements were made on n-type samples doped in the range of 5 x 10^{18} cm^{-3} to 1 x 10^{19} cm^{-3} by the new up-conversion technique. These preliminary lifetimes were much larger than found in lattice-matched material of comparable doping.

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