



MODIFICATION OF II-VI AND III-V MATERIALS USING ION BEAMS

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13. ABSTRACT (Maximum 200 words)

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The III-V work done on this program benefitted Hughes directly, and other industry through other ARO contracts and our joint publications. Also AT&T (Bell Labs/Pearson) and Hughes collaborate on programs like MMIC, in which III-V technology is used substantially.

Possible technological applications of research performed: the results of the work on hydrogen-exchanged LiNbO_3 and LiTaO_3 may ultimately have application to fabricating improved wave guides for appropriate wavelengths and the results of the work on SIMS profiling of HgCdTe may be used to fabricate improved infrared detectors in the future.

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Personnel, degrees, inventions

Scientific personnel supported by this contract: Drs. R.G. Wilson and O. Wu, and C. Haeussler of Hughes Research Laboratories. No degrees were awarded to anyone directly under this contract. However, graduate research leading to degrees at two universities is described below. No invention disclosures were filed during the period of this contract.

Collaborative research with or support of universities and research institutions, and technology transfer to them:

This contract supported research and graduate student progress to a substantial degree at two universities during 1992 and 1993, namely, UCLA (five students under Professor Kang Wang) and Carnegie Mellon University (under Professor A.G. Milnes). The work at CMU also involved collaboration with Drs. C.R. Abernathy and S. J. Pearton at Bell Laboratories. The students, post docs, and research associates at these universities learned about and utilized the two technologies of ion implantation and secondary ion mass spectrometry through this contract.

Technology transfer to industry:

A major part of this program involved characterization of II-VI materials and device structures, primarily HgCdTe. The results of this research benefitted MBE growth of HgCdTe for infrared detector technology. The primary industry beneficiary of these results has been Santa Barbara Research Center (SBRC), but because of a collaborative agreement that began at the end of 1992 with Rockwell, their Science Center may also have benefitted. Both SBRC and Rockwell manufacture IR detector systems for the US government.

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Research Summary

A major area of research performed under this contract was that of growth and characterization of II-VI materials grown using molecular beam epitaxy (MBE) for application to infrared detector systems, in particular, HgCdTe layers grown on CdTe or ZnCdTe substrates of $\langle 111 \rangle$, $\langle 211 \rangle$, or $\langle 100 \rangle$ orientation and doped with In and/or As as single, double (pn), or triple

(pnp) layers. Single and double layers of HgCdTe doped with In and/or As were successfully grown and characterized using the secondary ion mass spectrometry analysis technique developed under this program. Figure 1 shows the As and In profiles in a three-layer device, and Fig. 2 shows a multi-layer structure grown to demonstrate the ability to control In doping. A study to determine the relative merits of doping using Sb instead of As was initiated, but As is the dopant of choice as of now. See publication 33 in the list at the end.

Another major area of research under this program comprised studies of H in III-V semiconductor materials, especially their thermal stability or outdiffusion properties. Much collaboration with Dr. J.M. Zavada occurred in this area and relevant papers in the publication list given at the end are 8, 16, 19, 20, 21, 23, 25, 29, and 31, 23 being a book chapter. Representative results of this work are shown as Figs. 3, 4, 5, and 6.

A focused area of research performed under this contract was a study of the effects of H in GaSb, InAs, and AlGaAsSb. Samples of these materials were hydrogenated or deuterated using plasma diffusion by S. J. Pearton at Bell Laboratories or in Moscow at the Institute of Rare Metals, from which the samples of GaSb came. This work was done in collaboration with Dr. A. Y. Polyakov, who is working at Carnegie-Mellon University, on leave from the Institute of Rare Metals in Moscow, and with Professor A.G. Milnes of Carnegie Mellon University in Pittsburgh. We provided calibrated SIMS measurements of the H profiles, as well as analysis of the structure of the materials. These III-V materials were grown using several techniques in Moscow and at Carnegie-Mellon University and were undoped, p-doped, and n-doped with different dopants to different densities. We measured the doping densities and depth profiles of the dopants and plasma diffused H using our

SIMS technology developed for these materials. Papers related to this area are 7, 9, 11, 12, 14, 15, 18 and 19. Figure 7 is a set of figures taken from reference 8, for GaSb and InSb, materials that are becoming important for infrared detectors.

Another area of research performed under this contract was a study of the implantation of LiNbO_3 and LiTaO_3 for waveguide applications. One aspect is depth profiling of H in hydrogen- or proton-exchanged waveguides in LiNbO_3 and LiTaO_3 . We implanted ^2H and other elements in LiNbO_3 on the previous contract and implanted LiTaO_3 obtained from Univ. of Colorado and from Stanford Univ. in the same way, in a collaborative effort with Dr. S.W. Novak at Evans East, Inc, in New Jersey. LiTaO_3 implanted with ^2H and other elements was annealed at 200, 300, and 400°C. Another area of research was hydrogen passivation of multiple quantum wells (MQW) in AlGaAs/GaAs structures. This work involved collaboration with ARD contractors in France (F. Voillot and B. Theys), as well as scientists at the National Institute of Standards and Technology in Maryland. Papers in the publication list related to this area are 3, 4, 10, 16, and 21.

Another area of research involved the characterization of porous Si materials for potential applications in areas of visible light emission, again collaboratively with the ARD contractor at UCLA, Prof. K. Wang. Also in collaboration with Prof. Wang and several of his students, we studied the doping concentrations and depth profiles of Si and SiGe HBT and QW structures device applications.

A study of III-V nitrides (GaN, AlN, InGaN, and AlGaN) was initiated near the end of this program. GaN, AlN and their ternary compounds are of interest for blue/green light emitters and lasers, for high temperature electronics, for optical communications systems, and as passivation layers

on other semiconductor systems, especially because of their wide bandgaps (3.4-6.2 eV). Material grown on GaAs using MBE was provided by Dr. C. Abernathy of AT&T Bell Laboratories. Material grown on sapphire using low energy ion assisted MBE was provided by Dr. Nate Newman of Lawrence Berkeley Laboratories. The materials from Bell Labs were implanted with ^2H and F, and plasma diffused, and annealed at temperatures from 300 to 700°C for studies of passivation effects, and the resulting depth distributions were measured using SIMS. Neither of these two elements moved in the nitrides for temperatures as high as 700°C. We have observed many emission lines from transitions between Stark split levels of the $^4\text{I}_{13/2}$ first excited state and the $^4\text{I}_{15/2}$ ground state with wavelengths near 1.54 μm , emission that is characteristic of Er in any host. Some of the results of this work are reported in publications 25, 28, 31, and 32. Figures that illustrate some of this work are 6, 8, and 9.

The potential p-type dopants, Be, C, Mg, and Zn, and the potential n-type dopants, Si, S, and Se were also implanted into samples of the nitrides, which were subsequently annealed at temperatures up to 800°C. The resulting depth distributions were measured using SIMS; no redistribution was observed for any dopant except S, which redistributed slightly during 800°C annealing. See publication 27.

Er, Pr, Nd, Yb, and other rare earth elements were implanted, alone and together with O, into AlN and GaN for photoluminescence studies. We have successfully observed optically stimulated 1.54- μm photoluminescence for Er atom in the GaN lattice at 6, 77, and room temperature. The emission at room temperature is nearly as intense as it is at 6 or 77K, attributed to the wide bandgap of GaN. We also observed the same emission from AlN at 6K, but have not yet made similar measurements at room temperature. We plan to

wait until we obtain better AlN grown on sapphire substrates that have been provided to C.R. Abernathy at Univ. of Florida. Publications related to this work are 26 and 32, with more in preparation.

Samples of Er-doped AlGaAs and GaAs were obtained from Prof. Robert Kolbas of NCSU. Samples were analysed using SIMS for O and Er. The O concentration was about $5 \times 10^{17} \text{ cm}^{-3}$ and the Er density varied between 1 and $5 \times 10^{17} \text{ cm}^{-3}$. We performed random/channelled RBS on one sample to determine whether we can determine whether the Er is substitutional or interstitial. The answer is yes, and the Er is substitutional when observed from the (100) direction. We will now look in the (110) direction to complete the determination.

Also near the end of the program, a study was begun in collaboration with Professor James Kolodzey at the University of Delaware on SiGeC compound materials. In particular, we began to measure impurities in these materials, both intentionally introduced and unintentional. We also implanted Er into samples of different compositions, for photoluminescence studies.

We have implanted a variety of other lanthanide rare earth elements in Si, GaS, GaP, GaN, AlN, etc., and have begun to study optically stimulated PL emission from them. We will soon investigate stimulated emission from these sample of visible and uv light, created by upconversion from light nearer $0.9 \mu\text{m}$.

Conferences and Technical Interactions

Wilson attended the ERO Army/ARO-sponsored Workshop on Hydrogen Stability in Semiconductors held in Horben bei Freiburg, Germany, 4-6 Nov 1991, where he presented a paper that described the work performed in collaboration with Pearton of Bell Labs and with Polyakov and the group at Carnegie-Mellon Univ. on hydrogen stability in GaSb, plus preliminary work in InSb. Wilson and Zavada (ARO program manager) met extensively during the time of the Horben conference in Germany to review progress and plan future research under this contract. They also met with Prof. K. Wang of UCLA and Mme. F. Viollet from France, who also attended the workshop, to discuss and plan collaborative work in the areas of porous Si, hydrogen-passivated B-delta doped MBE Si, and hydrogen-passivated GaAs/AlGaAs multiple quantum wells (MQW) and superlattices in MBE Si. They also discussed further collaborative research in the areas of LiNbO_3 waveguides (with S. Novak of Evans East in the USA and A. Loni or R. De La Rue of the UK) and ion implantation and annealing of III-V materials and MQW and superlattice structures, especially implanted with H, (just Wilson), and As- and In-doped (p and n) layers in MBE-grown HgCdTe for infrared detector applications (Wu and Wilson of HRL).

The Rare Earth Doped Optoelectronic Materials Workshop was sponsored by ARO and held at Pepperdine University/Hughes Research Laboratories Auditorium on 16 and 17 June 1994, hosted by R.L. Schwartz and R.G. Wilson of HRL.

Wilson and Zavada met personally three times during 1992, three times during 1993, and three during the first part of 1994 to discuss data, joint publications, and continuing research (and to host the REDOM workshop. In

addition to the extended meetings described above between Wilson and Zavada of ARO, they talked many times on the telephone and much technical information was sent between them via FAX and US mail; Wilson and Zavada corresponded both directions in the course of preparing the papers numbered 3, 5, 6, 8, 10, 16, 21, 23, 25, 27, and 28 above.

Our plan during this contract for II-VI materials was to characterize MBE-grown layers of HgCdTe using SIMS. The layers were doped with As (p) and/or In (n). We grew double and triple layers (np, pn, npn, pnp) primarily for infrared detector device applications. We successfully grew layers doped with In or with As. We have learned to control the doping density of In to within about a factor of two, and to do it reproducibly (predictably). We have learned how to dope layers with As, but have not yet learned to control and reproduce the doping density of As to within better than about one order of magnitude. The doping density of In is uniform through the In-doped layer; the uniformity for As is not quite so good. There is also an issue of doping spikes that can occur at the beginning of HgCdTe layer growth. We have learned how to prevent such spikes of In at these interfaces, but not of As. In summary, we can now control and reproduce In doping density in MBE-grown HgCdTe, and have learned how to dope similar layers with As, but not yet with the desired accuracy and reproducibility

Publications

A list of manuscripts submitted or published under ARD sponsorship, plus papers presented at conferences during this contract period follows.

1. R.G. Wilson, "Implantation range statistics in III-V materials," J. Electrochem Soc. 138, 718-722 (1991)
2. R.G. Wilson and S.W. Novak, "Systematics of secondary ion mass spectrometry relative sensitivity factors versus ionization potential and electron affinity for semiconductors and insulators," J. Appl. Phys. 69, 466-74 (1991).
3. A. Loni, R.M. De La Rue, R.G. Wilson, S.W. Novak, and J.M. Zavada, "Direct comparison of refractive index profiles and modified SIMS hydrogen concentration profiles in annealed and proton-exchanged LiNbO_3 waveguides," Electronics Lett. 27, 1245-1256 (1991)
4. S.W. Novak, P. Matthews, W. Young, and R.G. Wilson, "SIMS depth profile measurements of H, Li, Nd, and Er in LiNbO_3 and LiTaO_3 ," Secondary Ion Mass Spectrometry SIMS VIII, A. Benninghoven, K.T.F. Janssen, J. Tumpner, and H.W. Werner, Eds. [Wiley, NY, 1992] pp. 471-474
5. J.M. Zavada, R.G. Wilson, H.A. Jenkinson, S.W. Novak, S.J. Pearton, "Hydrogen incorporation and carrier reduction in hydrogenated n-GaAs:Si and p-GaAs:Zn crystals," Materials Research Society Fall Meeting, Boston, MA, Dec 1991
6. J.M. Zavada, R.G. Wilson, S.W. Novak, "As-implanted and annealing behavior of H and Be implants in InP and comparison with GaAs," Materials Research Society Fall Meeting, Boston, MA, Dec 1991

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12. A.Y. Polyakov, M. Stam, A.G. Milnes, R.G. Wilson, Z.Q. Fang, P. Rai-Choudhury, and R.J. Hillard, "High resistivity GaSb grown by molecular beam epitaxy," J. Appl. Phys. 72, 1316-19 (1992)
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"Hydrogen depth distributions and refractive index profiles in annealed proton-exchanged LiNbO₃," Presented at IBMM 92, Sept 1992, Heidelberg, FRG
17. R.G. Wilson, "Experimental implantation ranges compared with profile calculations for metals, insulators, polymers, and semiconductors,"
Presented at IBMM 92, Sept 1992, Heidelberg, FRG
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27. R.G. Wilson, S.J. Pearton, C.R. Abernathy, and J.M. Zavada, "Thermal stability of impurities implanted in GaN and AlN," submitted to Appl Phys Lett for 1994 public. Ranges and redistribution???
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32. R.G. Wilson, R.N. Schwartz, C.R. Abernathy, S.J. Pearton, N. Newman, M. Rubin, T. Fu, and J.M. Zavada, "1.54- μm photoluminescence from Er-implanted AlN and GaN," Nato Advanced Workshop on Wide Bandgap Electronic Materials, Minsk Belarus, 4-6 May 1994
33. D. K. Wu, G.E. Chapman, C.A. Cockrum, S.M. Johnson, and J.A. Wilson, "MBE-grown double-layer heterojunction HgCdTe focal plane arrays for long wavelength infrared detection," to be published in J. Crystal Growth

Papers that in some way benefitted from or that utilized technology supported by ARD, but that were not primarily supported by the ARD contract:

- A. R.G. Wilson, "Depth Profiling in SIMS," Invited paper at the East Coast Workshop on SIMS, 20-22 May 1992, Somerset, PA
- B. R.G. Wilson, "Quantitative measurements in dynamic SIMS," Invited paper at the Seventh International Conference on Quantitative Surface Analysis, 8-11 Sept 1992, Univ. of Surrey, Guildford, Surrey, UK

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- D. R.G. Wilson, F.A. Stevie, G. Lux, C.L. Kirschbaum, S. Frank, and J. Pallix, "Depth profiles, projected ranges, and secondary ion mass spectrometry relative sensitivity factors and for more than 50 ele from hydrogen to uranium implanted into metals," Surface and Coat Technology 51, 358-363 (1992)
- E. R.G. Wilson, F.A. Stevie, G.E. Lux, C.L. Kirschbaum, and S.W. Novak, "Secondary ion mass spectrometry relative sensitivity factors and systematics for more than 50 elements from H to U implanted into Insulators," Amer. Vac. Soc. National Symposium, Orlando, FL, Nov 1993 Paper 640

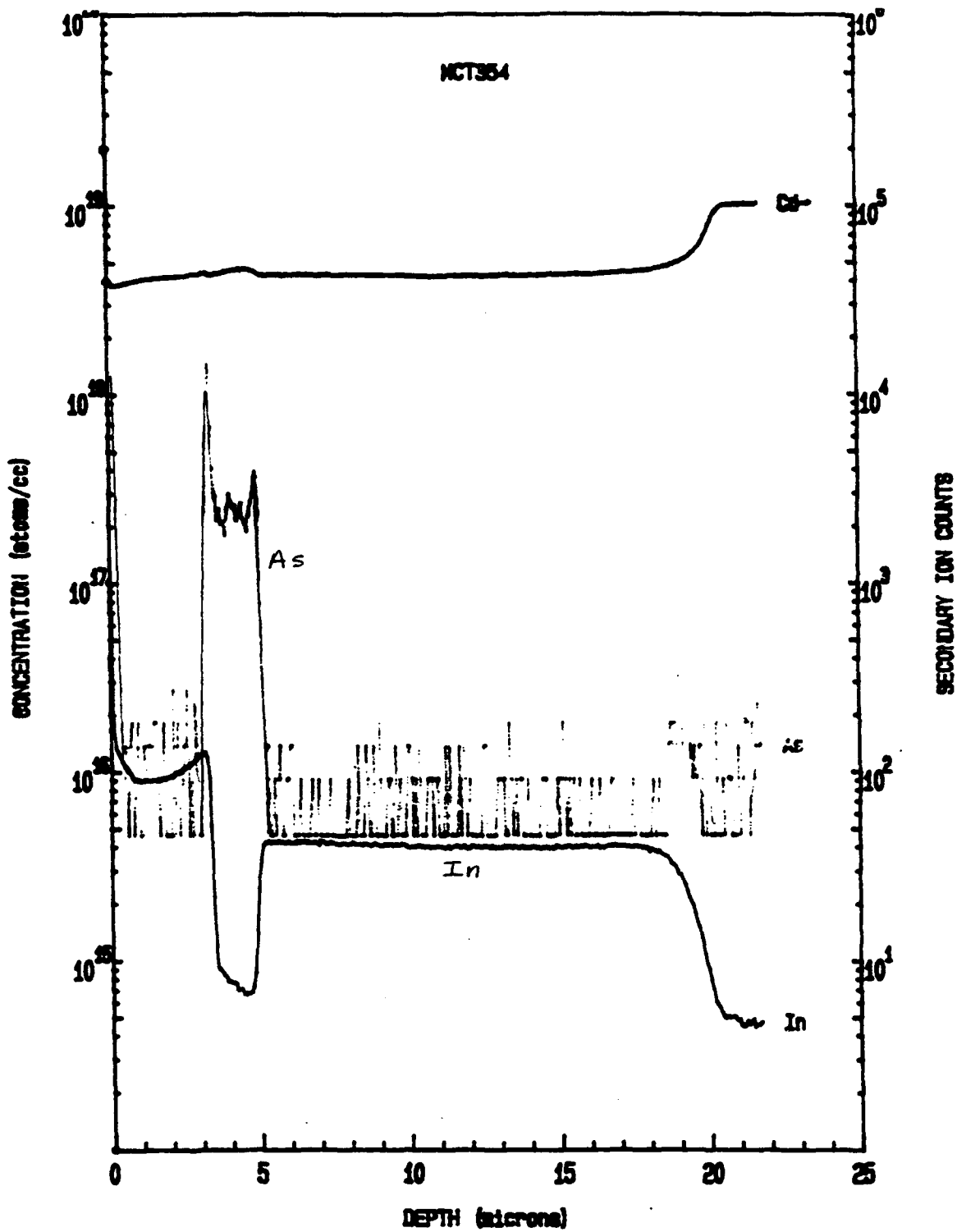


Fig. 1. As and In depth profiles in a three-layer HgCdTe device grown using MBE and measured using SIMS.

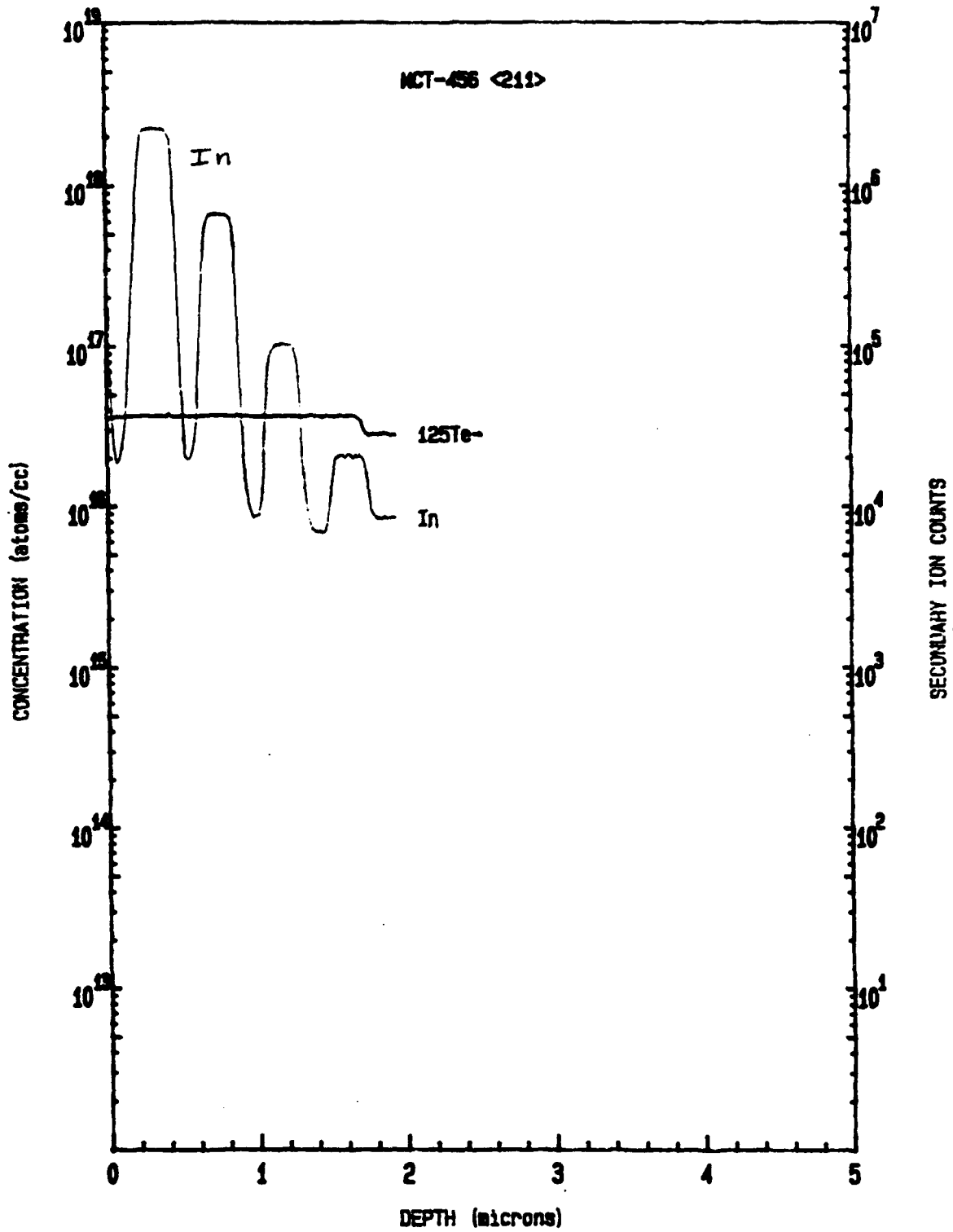


Fig. 2. Controlled In doping in a multi-layer structure in HgCdTe grown using MBE and measured using SIMS

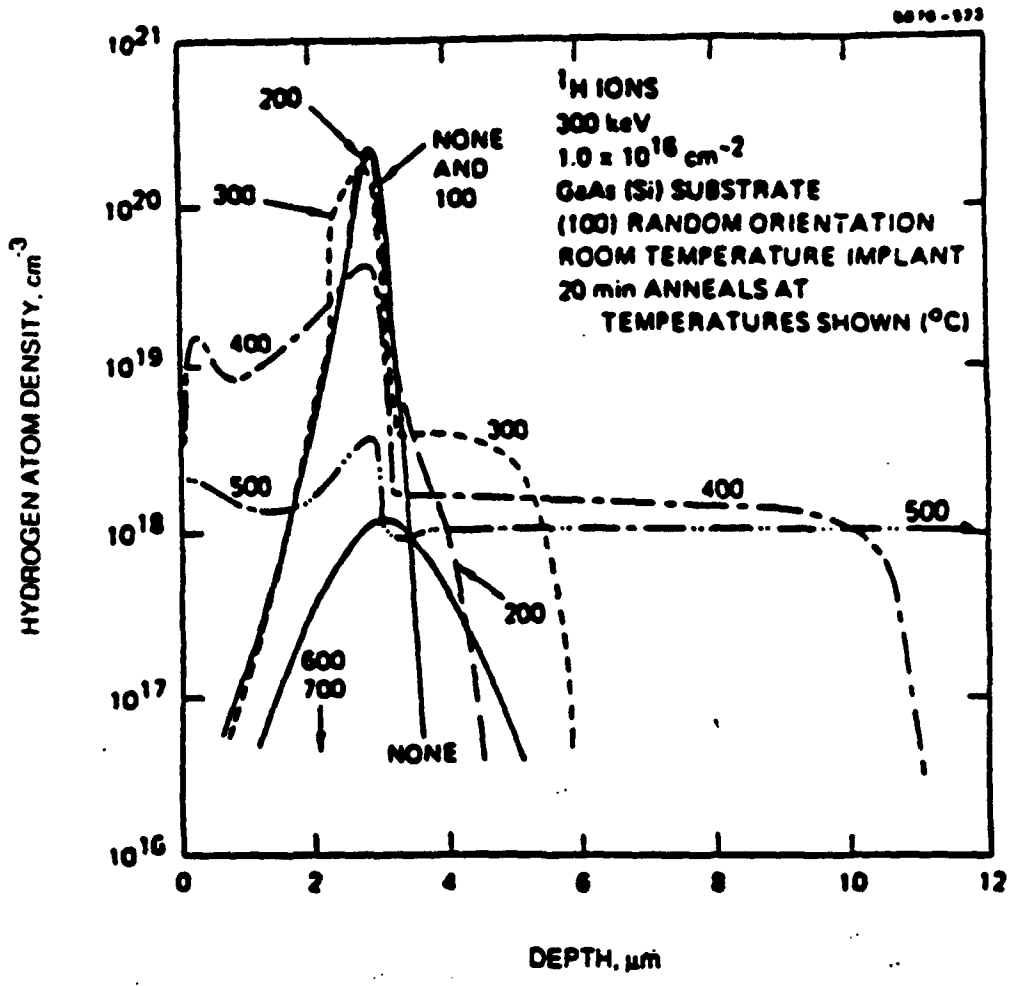


Fig. 3. Depth distributions for ¹H implanted into n-GaAs(Si) in the (100) random orientation and annealed at indicated temperatures.

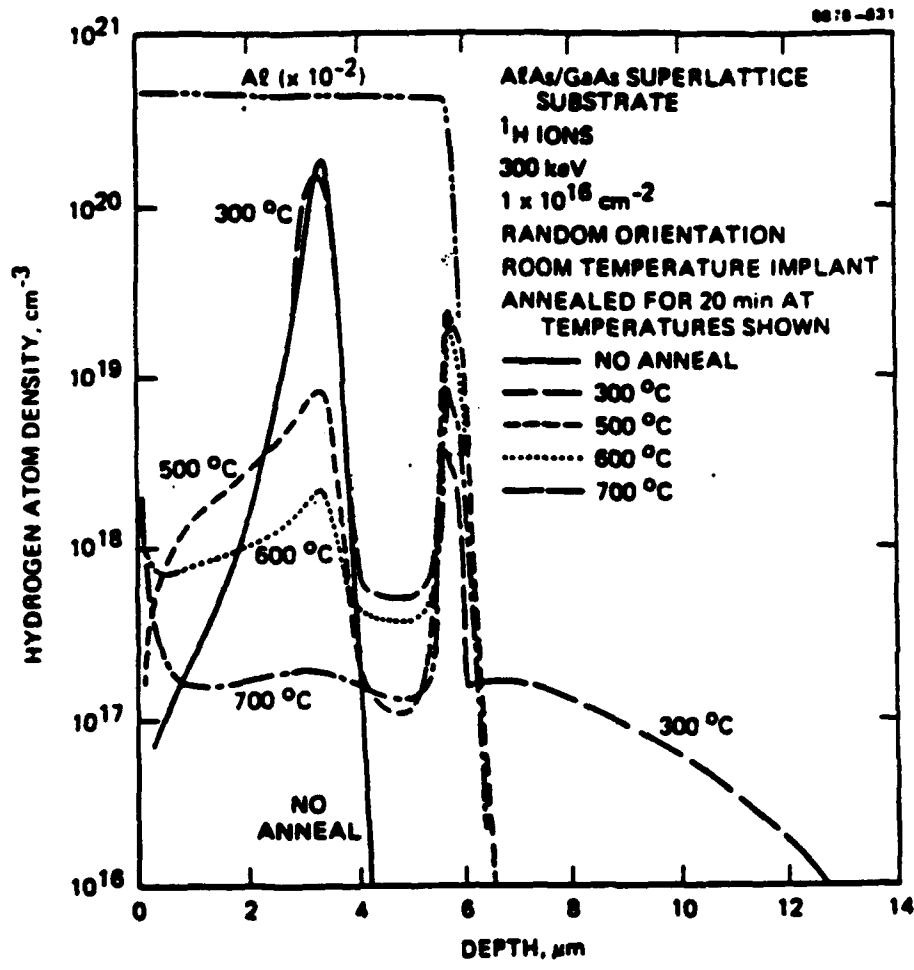


Fig. 4. Depth distributions for ^1H implanted into GaAs/AlAs superlattice and annealed at indicated temperatures.

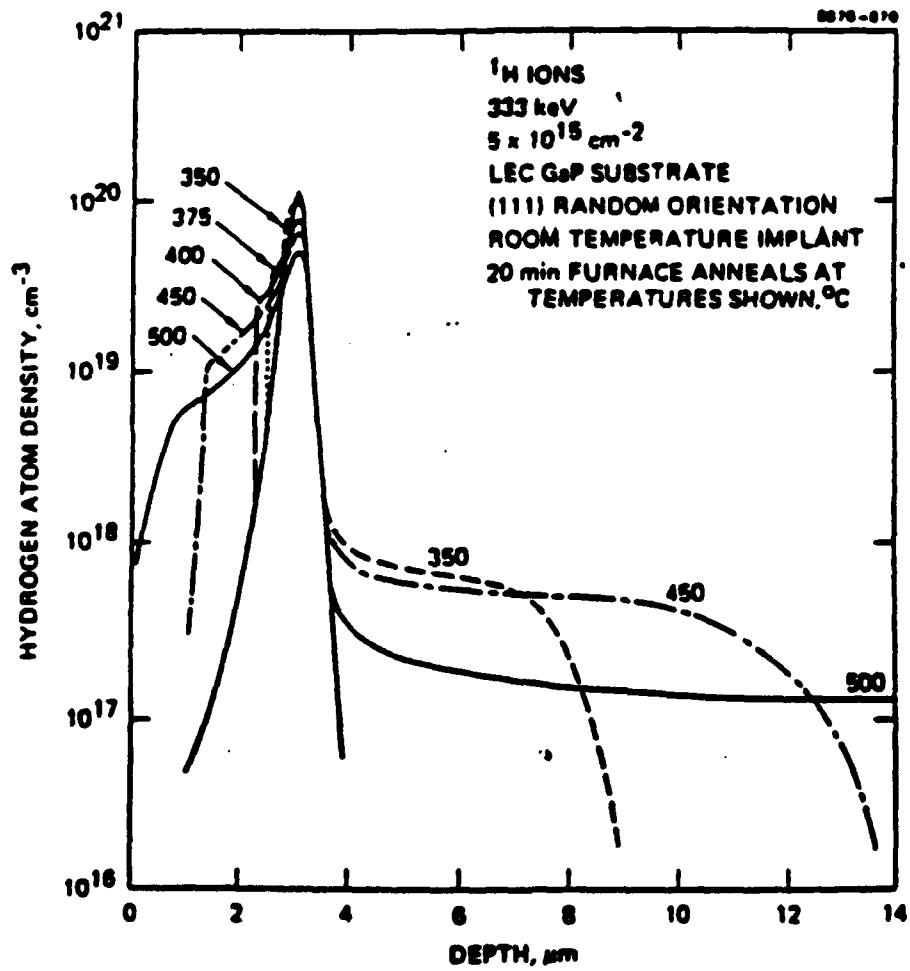


Fig. 5. Depth distributions for ^1H implanted into n-GaP in the (111) random orientation and annealed at indicated temperatures.

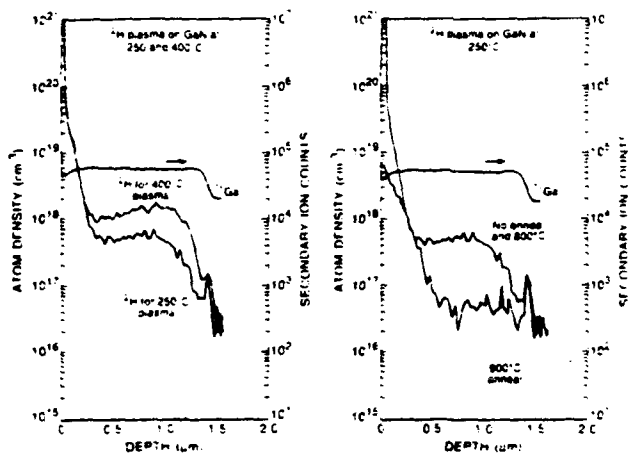


FIG. 1. SIMS profiles of ^2H in GaN after exposure to a deuterium plasma for 30 min at either 250 or 400 °C (left-hand side) and after subsequent annealing at 800 or 900 °C (right-hand side).

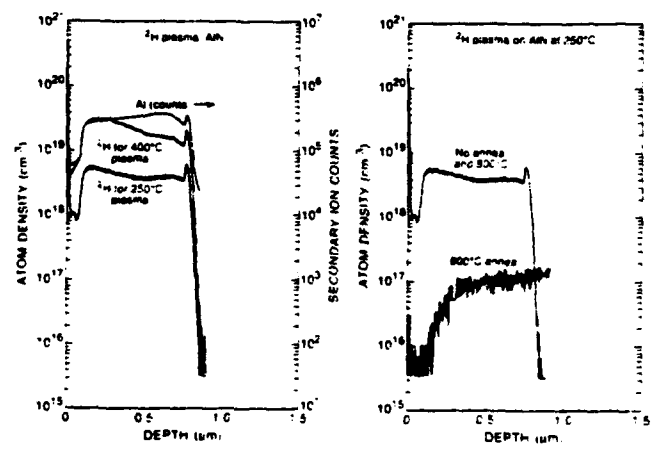


FIG. 2. SIMS profiles of ^2H in AlN after exposure to a deuterium plasma for 30 min at either 250 or 400 °C (left-hand side) and after subsequent annealing at 800 or 900 °C (right-hand side).

Fig. 6. Two figures taken from reference 25 that illustrate work done for hydrogen in AlN, GaN, and InN.

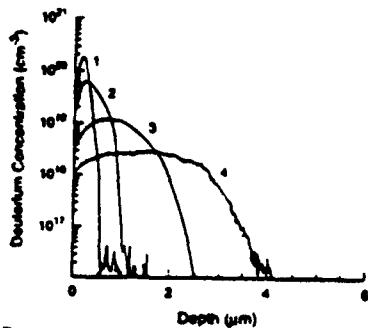


Fig. 1. ²H profiles (SIMS) in p⁺-GaSb(Zn); 1-100, 2-150, 3-200, 4-250°C; exposure time 0.5h

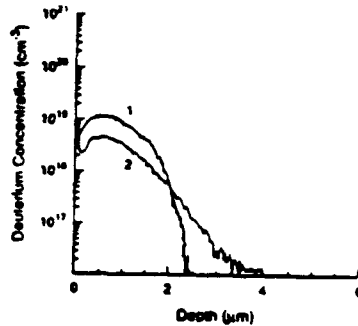


Fig. 2. ²H profiles (SIMS) in p⁺-GaSb (Zn) (1) and in n⁺-GaSb(Te) (2); treated at 200°C

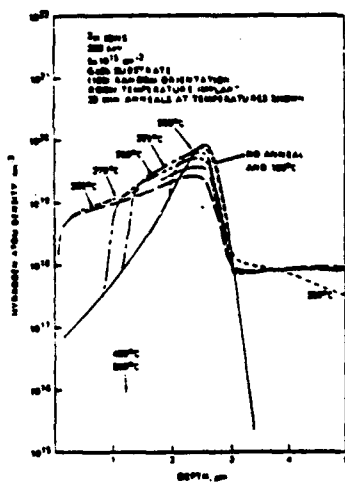


Fig. 5. SIMS depth profiles for ²H implanted into GaSb and annealed

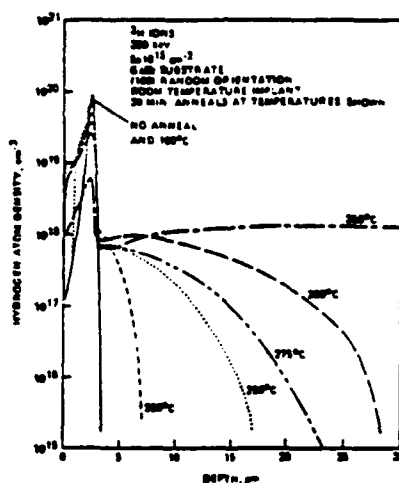


Fig. 6. SIMS depth profiles for ²H implanted into InSb and annealed

Fig. 7. A set of figures taken from reference 8, concerned with GaSb and InSb, materials that are becoming important for infrared detectors.

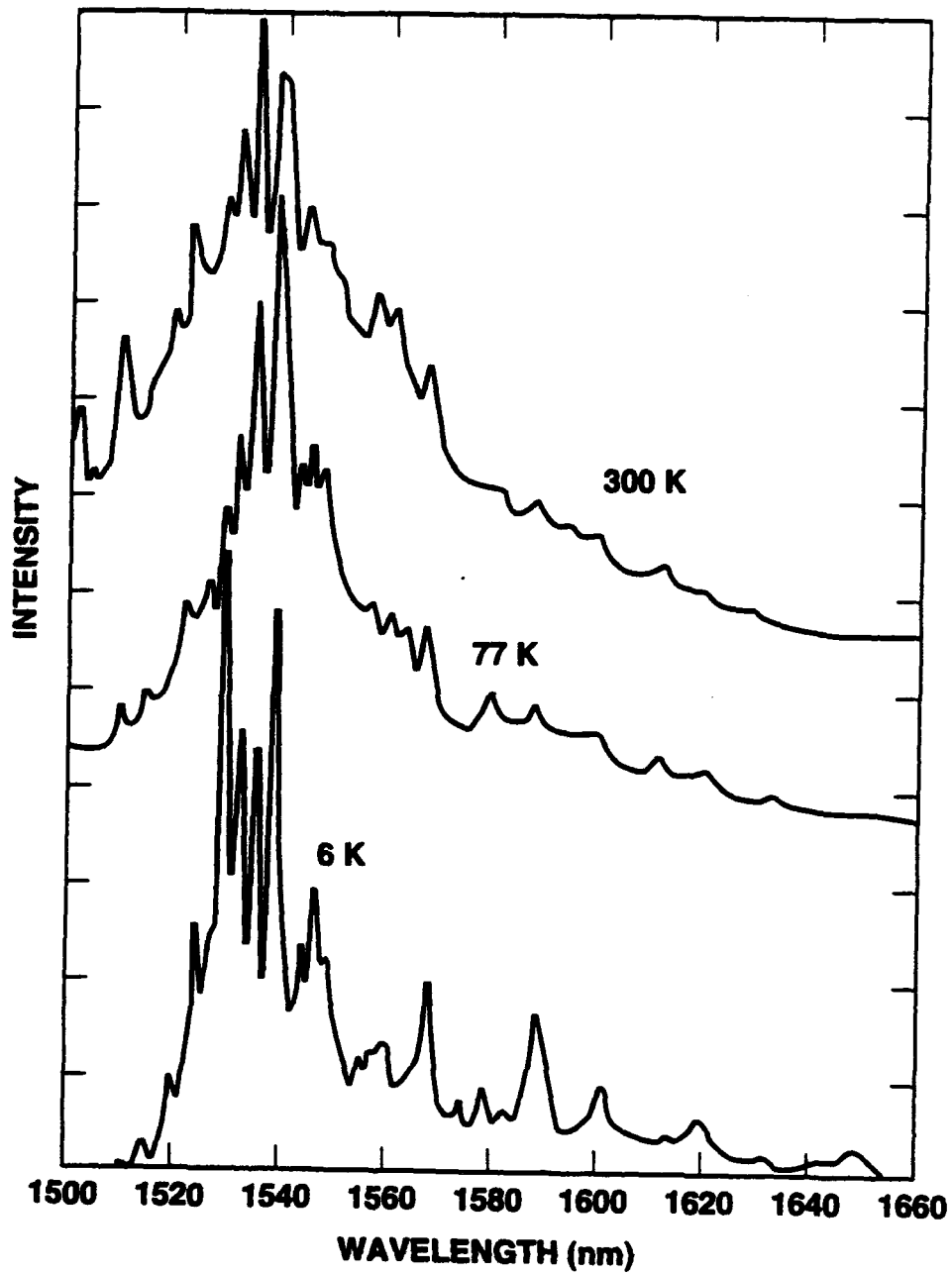


Fig. 8. Photoluminescence spectra from Er-implanted, MBE-grown GaN/sapphire annealed at 7000C, and measured at 6, 77, and 300 K

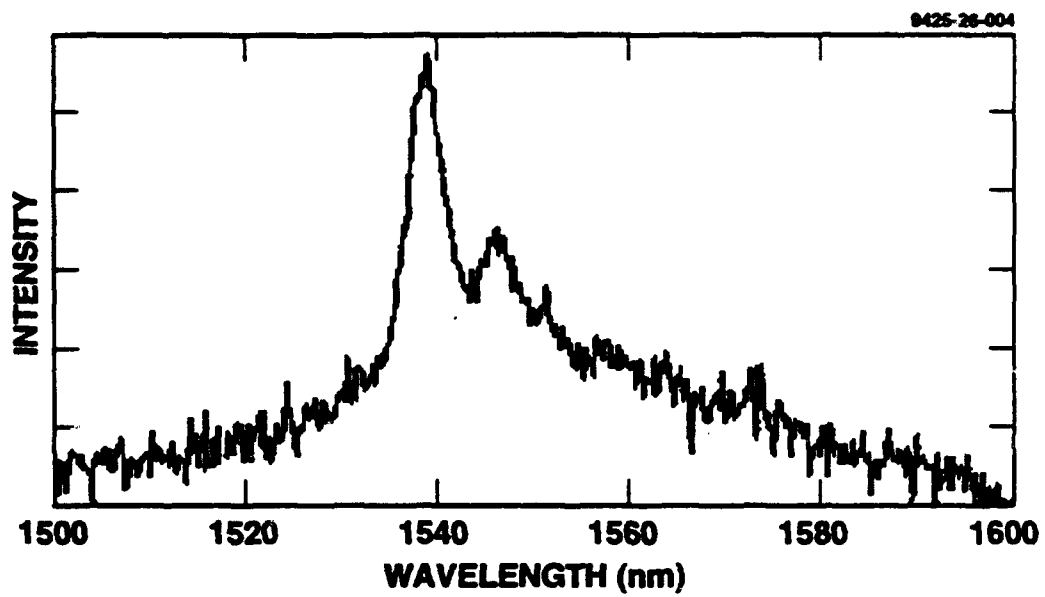


Fig. 9. Photoluminescence spectrum from Er-implanted MOMBE-grown AlN/GaAs annealed at 6500C and measured at 6 K