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GALLIUM ARSENIDE NITRIDE: A NEW MATERIAL FOR OPTICAL INTERCONNECTS ON SILICON CIRCUITS

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13. ABSTRACT *(Maximum 200 words)*

A proposed direct bandgap ternary material, lattice matchable to silicon, was explored in this exploratory effort. About a dozen molecular beam epitaxy growth runs were performed on gallium arsenide and gallium phosphide, and growths analyzed via Auger spectroscopy, x-ray diffraction, and transmission electron microscopy. Up to 20% nitrogen was incorporated. Single crystal quality material with about 2% nitrogen was detected. Segregation into gallium nitride and gallium arsenide was always seen.

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Gallium Arsenide Nitride: A New Material for Optical Interconnects on Silicon Circuits

I. Introduction

Future Air Force signal processing systems require large increases in computational bandwidth to meet system needs. Throughput of advanced computational systems is limited by interconnect speeds, both on-chip and off-chip. Optical interconnect removes bandwidth limitations due to RC time constants of metal lines, and is required for future systems needs. However at present optical interconnect is not available on chip, due to the poor optical properties of Si, and is implemented off chip by expensive hybrid technologies which combine III V compound chips on carriers with Si chips.

A technique for monolithic integration of direct-bandgap, III V material with Si chips would enable monolithic optical interconnect and Si electronics to be produced at low cost-eliminating costly hybrid integration.

The objective of work under this cooperative agreement is to explore the growth of GaAsN, lattice matched to silicon, as a direct bandgap material which may in the future be suitable for an optical laser monolithic on Si. The two tasks in the program are to investigate the feasibility of growing GaAsN compounds lattice matched to Si, and if successful, to demonstrate an optically-pumped Fabry-Perot laser in the material.

Prior to this work there were only sketchy reports of any experimental work on GaAsN as a direct bandgap material on Si. The most active group was associated with Kondow at Hitachi in Japan and some U.S. work directed by Texas Instruments and involving U. Utah and U.C. San Diego was going on, but with sketchy reports. There were a number of theoretical computations of band structures - most of them predicting that materials with substantial N concentration (18% required to match Si lattice) would be semi metallic, having a negative bandgap, and the experimental work had produced only low N concentration (<2%) and showed the bandgap decreasing in agreement with theoretical predictions.

During the last year we have learned much from our own work and from the other groups whose experimental work antedated ours. Our progress is summarized in the following sections. As a frame of reference, the original work statement is given as contained in the original proposal.

II. Statement of Work

1.0 Objective

The objective of this work is to explore the growth of GaAsN, lattice matched to silicon, as a direct bandgap material which may in the future be suitable for an optical laser monolithic on Si.

2.0 Scope

The project involves two tasks. The first task is to investigate the feasibility of growing either by MOCVD, or by MBE, GaAsN compounds lattice matched to a silicon substrate. The grown material will be characterized by optical and SEM microscopy, by photoluminescence measurements, by TEM cross section microscopy, by Raman spectroscopy and perhaps by electrical measurements. The second task depends upon the successful synthesis in the first task of suitable, good optical quality GaAsN material on Si. The objective of this task is to optically pump this material after it has been formed into a Fabry-Perot laser cavity to demonstrate lasing. The entire effort will be done in cooperation and collaboration with personnel from the Rome Photonics Laboratories under the direction of Dr. Richard Michalak. The Rome Laboratory personnel will play a major role in the second task in patterning the laser cavity and doing the optical pumping and measurements on this laser.

3.0 Background

Existing materials growth and laser fabrication expertise in the university groups of Professor Ballantyne and Professor Salzman, together with the device capability at the Rome Photonics laboratory form the basis for this work. The two materials groups each have extensive experience in synthesizing new materials, and the groups together have extensive experience in processing novel lasers, including lasers with dry etched planar cavities.

4.0 Task/Technical Requirements

The required deliverables for this program shall include monthly status reports and a final technical report. These reports shall contain the results of the technical work on the tasks described in this section.

4.1 Material Synthesis

4.11 Conduct preliminary growth runs of GaAsN on Si or GaP/Si substrates using Cornell MBE System (Cornell Personnel).
4.12 Explore the synthesis of GaAsN by MOCVD in the Technion reactor (Technion Personnel).
4.13 Characterize grown materials by optical and SEM microscopy, TEM, Photoluminescence techniques (Cornell and Technion personnel - some done at Rome Laboratory by Cornell personnel).

4.2 Device Work

4.21 If good optical quality GaAsN is grown, develop etching technique for Fabry-Perot laser cavity (Rome lab personnel).
4.22 Optically pump Fabry-Perot laser cavity in GaAsN to produce laser emission and characterize this emission (Rome Lab and Cornell personnel at Rome Lab).

III. Accomplishments

1. Growth Runs

Our growths were done in conjunction with L. Eastman's group by Molecular Beam Epitaxy under the direction of W. Schaff. The growth runs are summarized in Table I. The growth temperatures shown in Table I are thermocouple temperatures in the holder, they are typically around 200C higher than pyrometer temperature of the wafer. So most growths were done in the range of 580 -

630 C except for SO138, which was hotter. For runs 151 & 152 it was subsequently determined the Ga cell was empty, so the result should have been surface nitridation only. the optical voltage is proportional to the amount of atomic nitrogen flux, and shows a discontinuity between runs 188 and 357. The reason is the optical fiber was cleaned. For runs 357 - 362 streaky RHEED was lost quickly when the plasma was fired. Spotty RHEED is indicative of 3D growth rather than planar growth. This change was determined to be due to a change in the temperature of the nitrogen entering the source - it being cooler than before, resulting in more ionized N_2 in the chamber. In more recent runs this problem has been fixed by growing at high (>1μm/hr) GaAs rates when the plasma is struck. Then streaky RHEED can be maintained longer.

We have subsequently learned from Prof. Tu's group at San Diego that they always see spotty RHEED when growing GaAsN. Our results are consistent (if a little better during nucleation) with their result.

Auger analysis of the grown films was done by R. Michalak. Some early results are summarized in Table II. The main conclusions are that the grown films contained substantial nitrogen, around 20%, showed abrupt interfaces under depth profiling (cf Fig. 1), and in some regions of the film which had an island-like texture showed evidence of phase segregation (cf Figs 2 & 3). Figure 2 shows the island structure and Fig. 3 is the Auger result on an individual island showing phase separation: region 2 is primarily GaAs, region 1 GaAsN, and region 3 GaN. Auger measurements on later growths confirmed similar total nitrogen content in the films. An example is shown in Fig. 4, for growth #306. Two layers were grown, each about 200 nm thick. The first was low nitrogen content, the second (top) high nitrogen. Fig. 4 clearly shows this and the interface between the two.

3. X-Ray Diffraction

X-Ray diffraction is the most direct indication of crystal structure, and by inference, material perfection and composition. R. Michalak, J. Lee and Y. Salzman did x-ray measurements on the material grown. Fig. 5 shows a relatively narrow, clearly resolved GaAsN epi peak in the rocking curve on sample SO122. Data was taken by J. Lee. The narrow peak shows a good quality film containing 1-2% N. Data from Salzman and Michalak confirm the peak, but it is much broader in their measurement. In some locations on the sample the peak was not observed - indicating the spatial inhomogeneity (perhaps due to temperature variation across the wafer) of the GaAsN component. Fig. 6 shows data from Michalak taken over a wider range of angles. Here GaN peaks are clearly seen, but the ternary is missing. This is characteristic of most films, and shows that the GaN is segregating.

This observation was also corroborated by the Tu group, who found that they always saw segregation in MOMBE GaAsN films grown much above 500C. At 500C they were able to get GaAsN films with up to 15% N. These films showed somewhat broader x-ray lines than those in Fig. 5, and direct bandgap in the 1 eV range as revealed by optical absorption measurements.

4. Photoluminescence

Photoluminescence measurements were done on runs showing x-ray peaks from GaAsN films. Luminescence was observed from the substrate, but not from the epi layers. Most of this work was done by D. Fekete. This result was disappointing, but also corroborated by the Tu group, who saw no photoluminescence from any GaAsN film, even though their x-ray and optical absorption showed clear indication of ternary crystalline films and direct bandgap. However, their result may not be surprising given the low growth temperature they used.

5. Raman Spectroscopy

Micro-Raman spectra were taken by Y. Salzman. An example is shown in Fig. 7 which also contains the spectrum of a reference GaN sample. The spectrum clearly shows the GaP substrate and well defined film peaks which are different from GaN. The results have not been interpreted, but warrant further study and may be related to ordering.

6. TEM Studies

Transmission electron microscopy observations were done by J. Lee on samples on both GaP and GaAs substrates. The epi layers were clearly seen and seemed to be homogeneous and free of dislocations. Evidence of segregation was seen in the diffraction patterns, but was not observed in the plan views. Well defined electron diffraction patterns were obtained which clearly show ordering. R. Michalak has confirmed through simulations that the observed diffraction pattern is consistent with an ordered supercell containing a 4x4x4 arrangement of conventional FCC cells (or 256 primitive cells) with N occupying corner and face center locations on the supercell. This is the first observation of such behavior in GaAsN and is the subject of a paper being prepared by R. Michalak. The lack of evidence of segregation and dislocations in the plan views may not be surprising given the spatial inhomogenity of the samples evidenced by x-ray, auger and SEM results, and the small volume in the TEM samples. These results are shown in Fig. 8.

7. Other Measurements

SIMS and RBS measurements on a few films were also done. The results on N concentration were consistent with Auger measurements. RBS was found not to be too accurate for this purpose, but did show evidence of the epitaxial film.

8. Calculations

Some interesting work analyzing recent calculations was done by K. Johnson & N. Ashcroft. It supports the hypothesis of a direct bandgap, and is included as Appendix 1.

IV. Conclusions

We have studied the growth of GaAsN on GaAs and GaP substrates. A tabular summary is given in Table III. The compound proves more difficult to grow homogeneously at high N concentrations than we anticipated. Our work has elucidated some inhomogenity and segregation issues and has encompassed a much wider range of characterization techniques than others have employed.

Due to machine problems, we made less progress on MOCVD growth at the Technion than anticipated. Hopefully, this shortcoming will be overcome in a follow-on or continuation of the work.

We determined conditions for maintaining good RHEED for quantum well GaAsN growth, which has eluded the Tu group. The major technical accomplishment is the observation of an ordered phase of GaAsN, which should be a publishable result. We could not pursue several goals of the initial work statement, such as laser demonstration, because our films were of poor optical quality and did not show photoluminescence. Most of our results have been corroborated by other workers, and we have some good understanding of growth limitations.

We are encouraged that the project should continue, and are not at a dead end. The Tu group showed single crystal GaAsN with high enough N to nearly lattice-match Si. Their films show direct bandgap (no luminescence), thus putting to rest theoretical speculations about semi-metallic material. The remaining major challenge is to duplicate their result, but with good optical quality.

This may be possible by further exploration of MBE growth parameters; by including the possibility of ordered and island structures, and not giving up when spotty RHEED is observed; by going further from equilibrium using selective area epi and MOCVD; by giving more attention to GaP or Si substrates rather than GaAs so as to take advantage of lattice matching and lattice constant pulling; by cutting back on the nitrogen content to be closer to the lattice-matched regime; and by pursuing the Raman and TEM work to elucidate ordering.

Table I: Summary of GaAsN MBE Runs

ample ID	Date	Substrate	Growth	Ga	As	Si	Plasma	Nitrogen Presure	Optical Voltage
S0122	5/2/96	GaAs	730	1070	312	1300	500	1.e-6	.189
S0138	5/11/96	GaP	940	1070	310	1245	500	1.3e-6	.168
S0151	5/28/96	GaP	800	1070	310	1246	500	1.5e-6	.23
S0152	5/28/96	GaAs	790	1070	310	1246	500	1.5e-6	.23
S0187	8/8/96	GaP	800	953	400	400	355	2.7e-6	.16
S0188	8/8/96	GaAs	800	953	430	400	355	2.7e-6	.16
S0307	12/10/96	GaAs	830	997	330	400	500	3.53e-6	.42
S0306	12/10/96	GaAs	830	997	330	1310	500	5e-6	
S0311	12/12/96	1/4 3in	740	997	330	400	400	3.8e-6	
S0312	12/12/96	1/4 3in	780	997	330	400	400	1.5e-6	
S0357	1/15/97	GaAs	750	860.	330.	400	400	7.e-6	.51
S0358	1/15/97	GaAs	750	860.	330.	400	400	7.e-6	.51
S0359	1/15/97	GaAs	750	860.	330.	400	400	7.e-6	.51
S0360	1/16/97	GaAs	750	860.	330.	400	300	6.e-6	.51
S0361	1/16/97	GaAs	750	860.	330.	400	400	7.e-6	.56
S0362	1/16/97	GaAs	750	860.	330.	400	.43	1.9e-6	.56

Table II

AUGER RESULTS ON GaAsN MBE GROWTHS, TO 26 JUNE 96

To date, two MBE runs have been performed, one consisting of about 4000A of GaAsN on GaAs in three varying [N], the second on GaP. Several Auger runs were performed on the two pieces, on defects seen in the GaP run, on a virgin GaAs wafer, and on a commercial laser structure for comparison. An outside XPS run was done on the GaAsN on GaAs sample, for Auger [N] calibration. All [ ] are AES atomic concentration (AC) massaged estimates, valid if [C] and [O] contamination is low (after initial cleaning sputter), except values in **bold** which are "normalized" AC estimates re-calculated by ignoring significant surface [C] and [O]

Run & Comment	**Date**	**[Ga As N] after C, O stripping**	**[Ga As N P Al] at end of sputter**	**epi thickness @200A/min rate**	**epi thickness via α-step**
GaAs / AlGaAs AES on Spire laser reference material To calibrate Auger But [Al] should be 60%??? To be re-run later against Al standard foil...	26June	48 52% -	21 51 - - 28%	3000A (2500A actual)	3750A
GaAsN / GaP About 2000A down [P] quickly increases as [N] ->0, very abrupt interface <100A thick	26 June	65 6 28%	53 4 - 41% -	500A	2000A??
GaAsN / GaAs Slow steady [N] decrease to zero over 0.5μ sputter depth, no abrupt interfaces, very grainy surface	26 June	70 7 23%	59 38% - - -	3500A	2442A
GaAsN / GaAs Gradual decrease of [N] with depth to about 3500A where [N] is zero	25 June	54 10 25%	61 34 - - -	5800A	3500A
GaAsN / GaP Abrupt [N] / [P] interface about 4666A down	25 June	64 5 28%	52 4 - 42% -	700A	4666A
GaAsN / GaP Area "D", [N] profile leveled off at 10%??? Did not sputter far enough?	20 June	71 - 16%			
GaAsN / GaP Area "E", profile leveled off?? Did not sputter down far enough?	20 June	- - 17%			
GaAsN / GaAs Shiny GaAs side - good GaAs	20 June	46 49 -			
GaAsN / GaAs Grey N side. MBE side, again shows slow decrease of [N] with depth	20 June	59 11 26%			<4000A
GaAsN / GaP Metal mask now used in profiling; Area "B", abrupt [P] increase.	19 June	64 5 28%	52 6 - 40% -		TBD

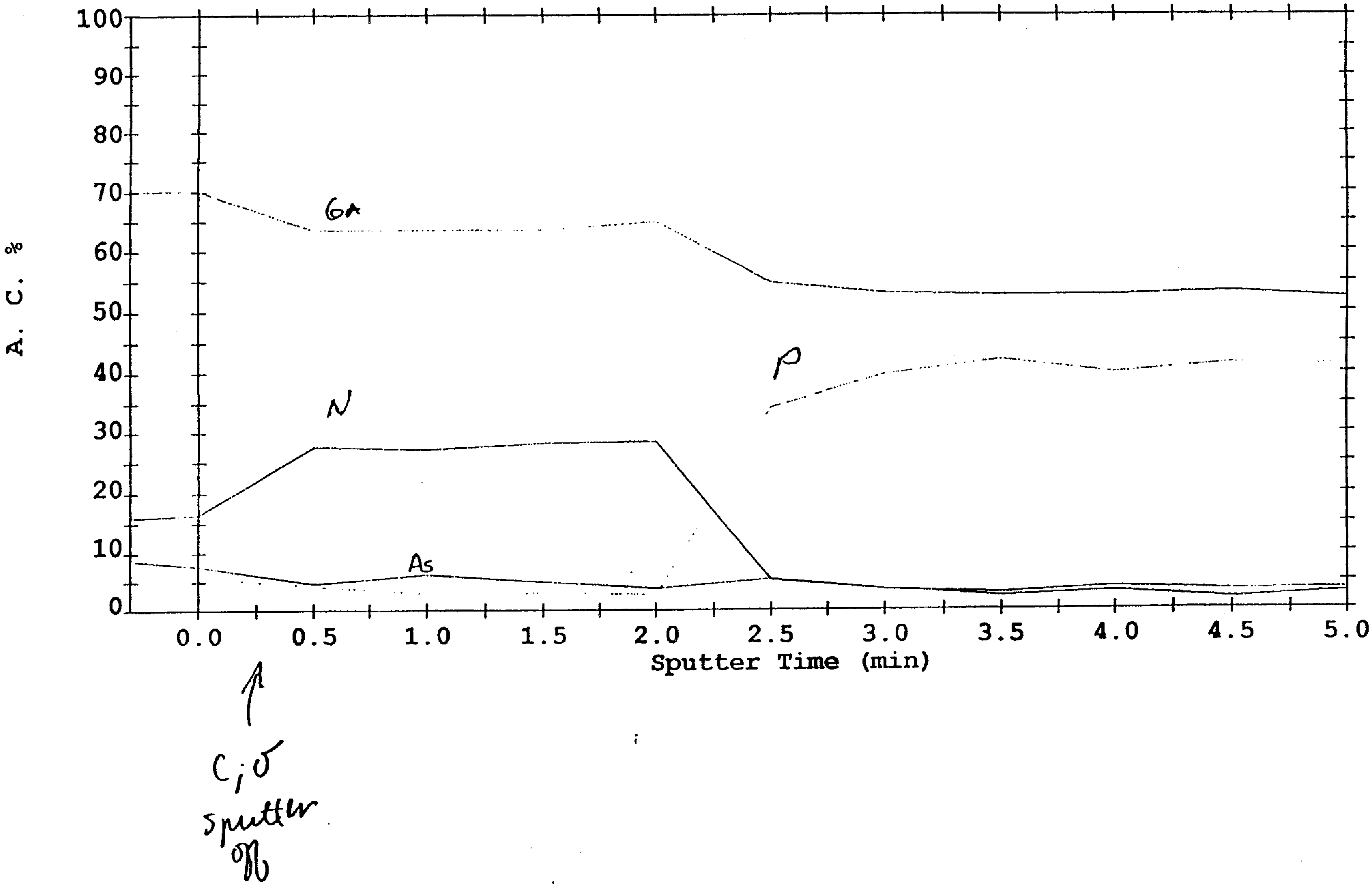
Run & Comment	**Date**	**[Ga As N] after C, O stripping**	**[Ga As N P Al] at end of sputter**	**epi thickness @200A/min rate**	**epi thickness via α-step**
GaAsN / GaAs Usual gradual [N] decrease... did not sputter long enough	18 June	56 23 10%			
GaAsN / GaP Immediately sputtered through [N] epilayer.	18 June	66 7 23%	50 5 - 43% -		TBD
GaAsN / GaP Defect region AES sputter runs, Area C	14 June				
Region 1............		50 30 5%	50 12 11 - -		TBD
2............		75 5 5%	59 6 20 - -		
3............		60 5 23%	55 6 14 17 -		
High initial [C], [O] in area 2 [P] began to increase at end of sputter run (2 mins). Ar pressure believed low -> low sputtering.					
GaAsN / GaP Area D, [N] high, gradual decrease to zero and [P] increase between 1.5 - 3 min.	14 June				
GaAsN / GaP Defect density measurements Area Density (cm^{-2}) A 10^6 B $2\ 10^6$ C $3.6\ 10^6$	11 June				
GaAsN / GaP Area A through epilayer in 1 min. Area B no [P] after 1.5 mins	23 May				
GaAsN / GaAs Evans East result: 66 11 23% Sean reports 1% [N] via XRD.	21 May				
GaAsN / GaAs Sean reports no XRD epi peak.	21 May				
GaAs Calibration run on GaAs piece. High carbon.	21 May	**45 55%**			
GaAsN / GaP Good [N] survey result on horizontal piece. But, AES on vertical piece (cleave edge) showed NO [N]???	15 May	70 7 23%			
GaAsN / GaAs First AES run. Good [N] peak	7 May	56 23 22%			

Fig 1: Auger Depth Profile of gaAsN Film on GaP

AES Profile PC Alt. 26 Jun 96 Region: 4(P1) Area: 1 Sput Time: 5.00 min

File: RM60626_5 GaP sputters

Scale: 0.042 kc/s Offset: 0.000 kc/s Ep: 9.97 kV Ip: 9.077e-09A



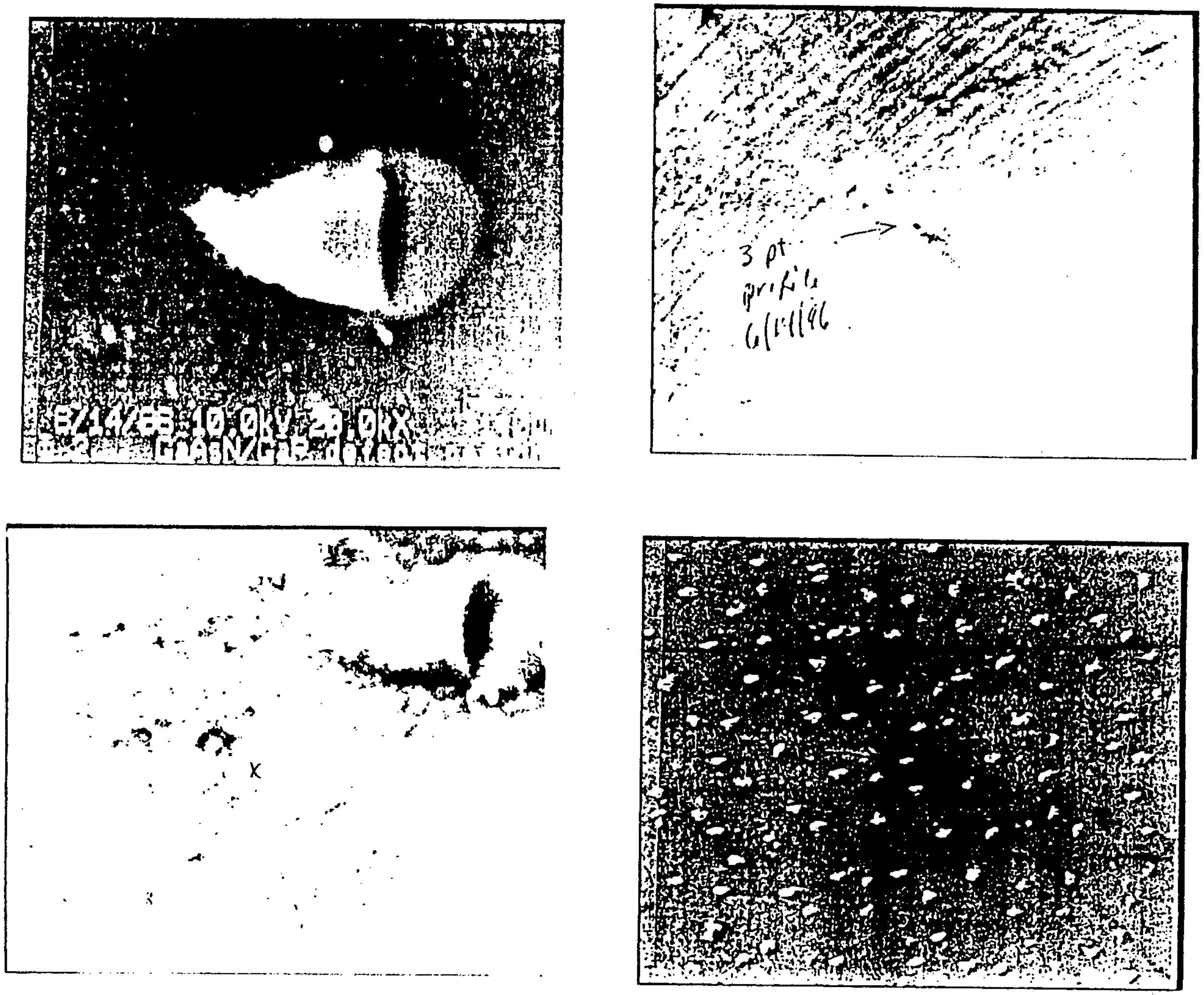
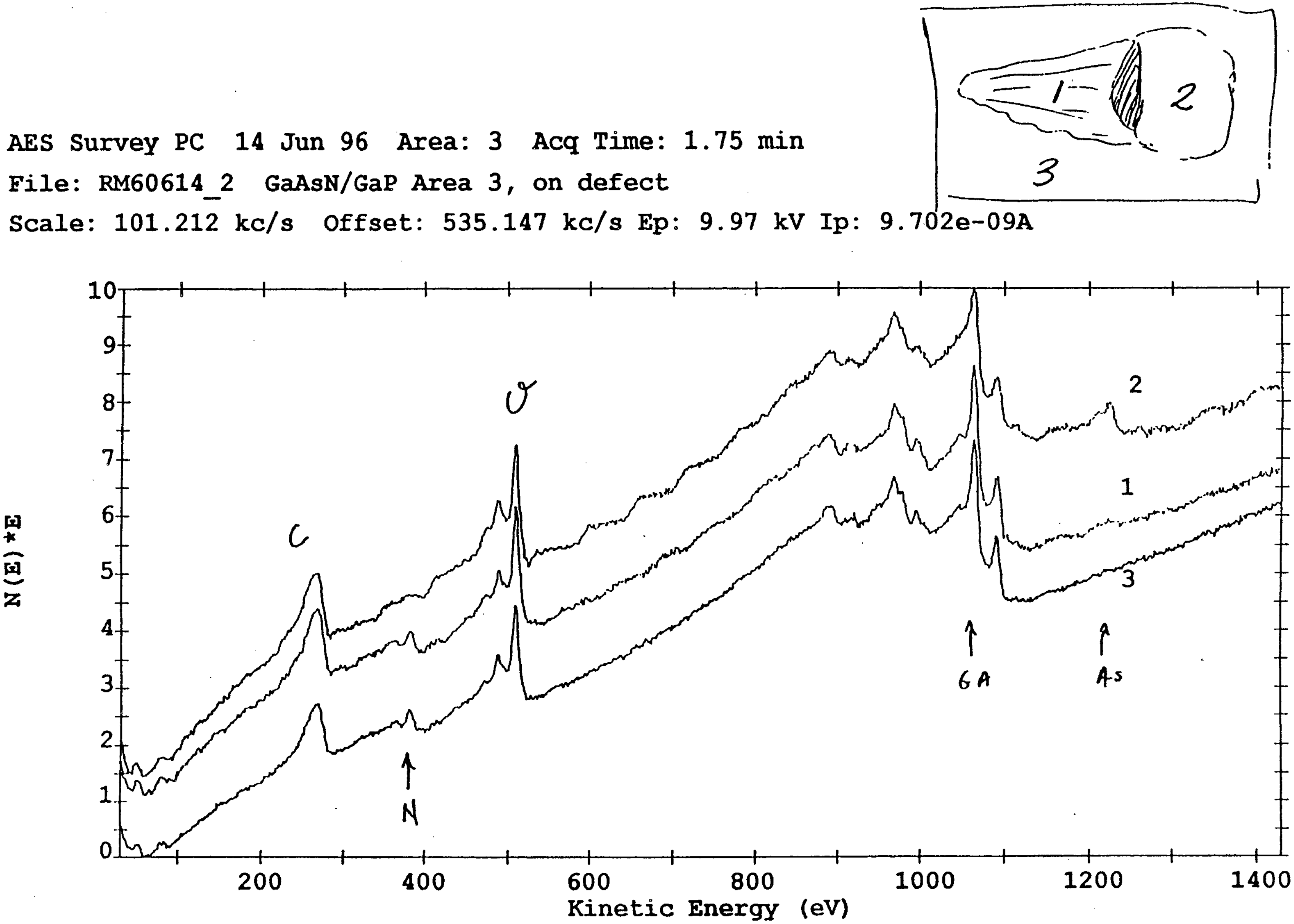


Fig 2: surface texture of gaasN grown on GaP. Lower Right shows regular island structure. Upper left shows "ice cream cone" shape of individual islands



AES Survey PC 14 Jun 96 Area: 3 Acq Time: 1.75 min

File: RM60614_2 GaAsN/GaP Area 3, on defect

Scale: 101.212 kc/s Offset: 535.147 kc/s Ep: 9.97 kV Ip: 9.702e-09A

Fig. 3: Auger analysis of GaAsN/GaP islands of Fig. 2.

AES Profile PC Alt.   12 Dec 96   Region: 3(As1) Area: 1   Sput Time: 15.50 min
File: rm61212_3   mbe 5, 6 sputter aes
Scale: 0.042 kc/s   Offset: 0.000 kc/s Ep: 9.97 kV Ip: 9.032e-09A

MBE #6

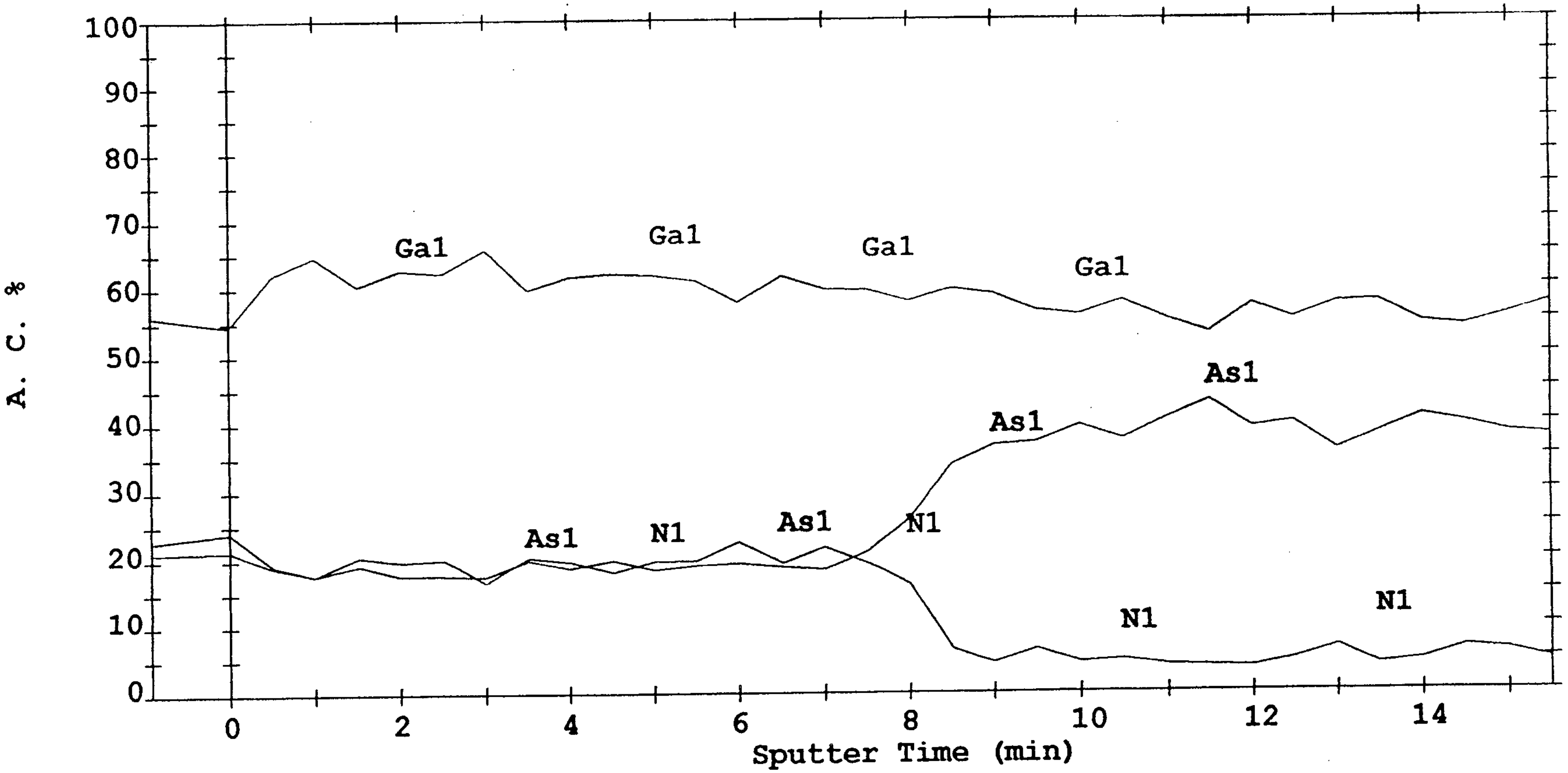


Fig. 4: Auger profile of MBE #306

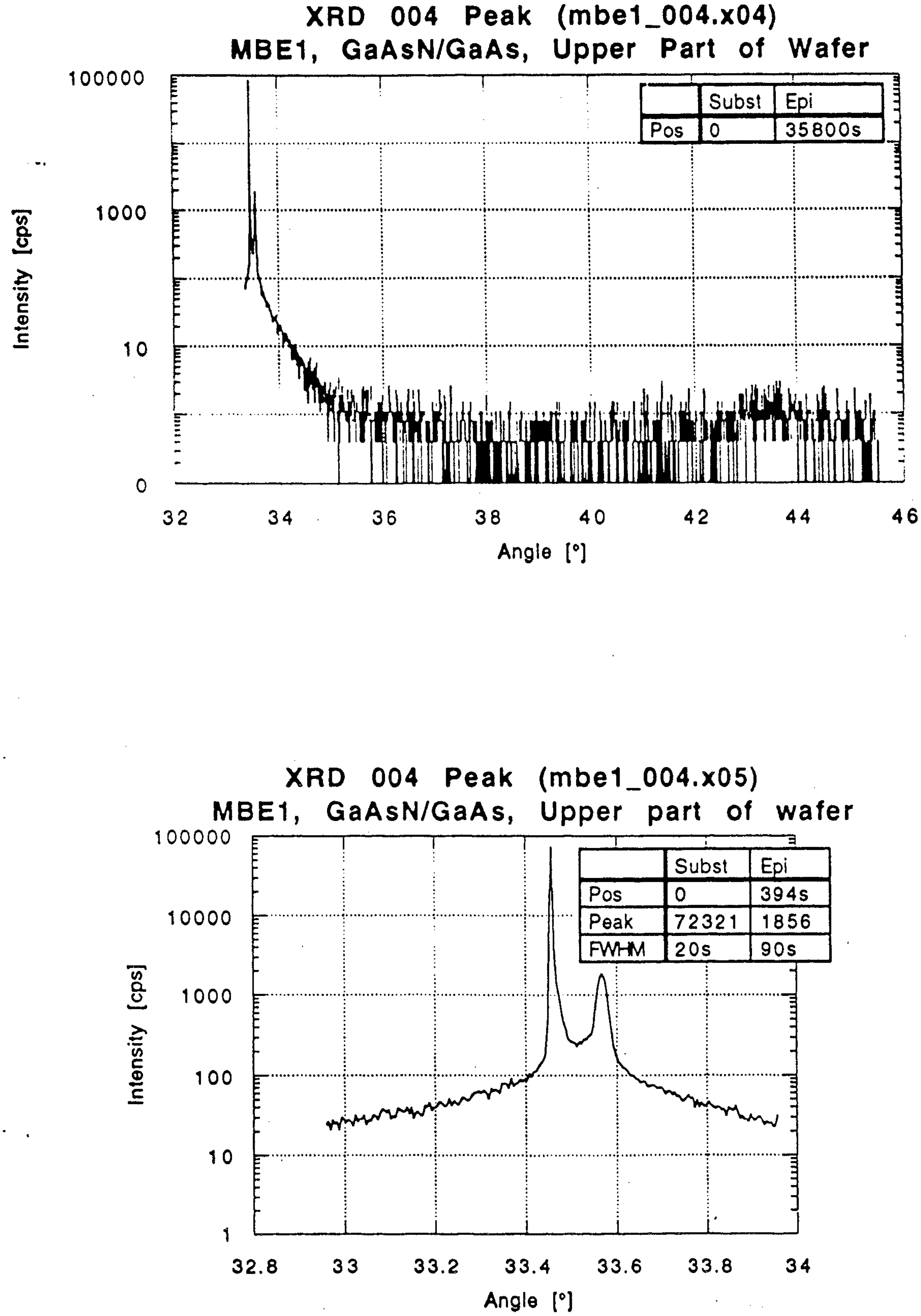


Fig. 5: X-ray analysis of GaAsN film

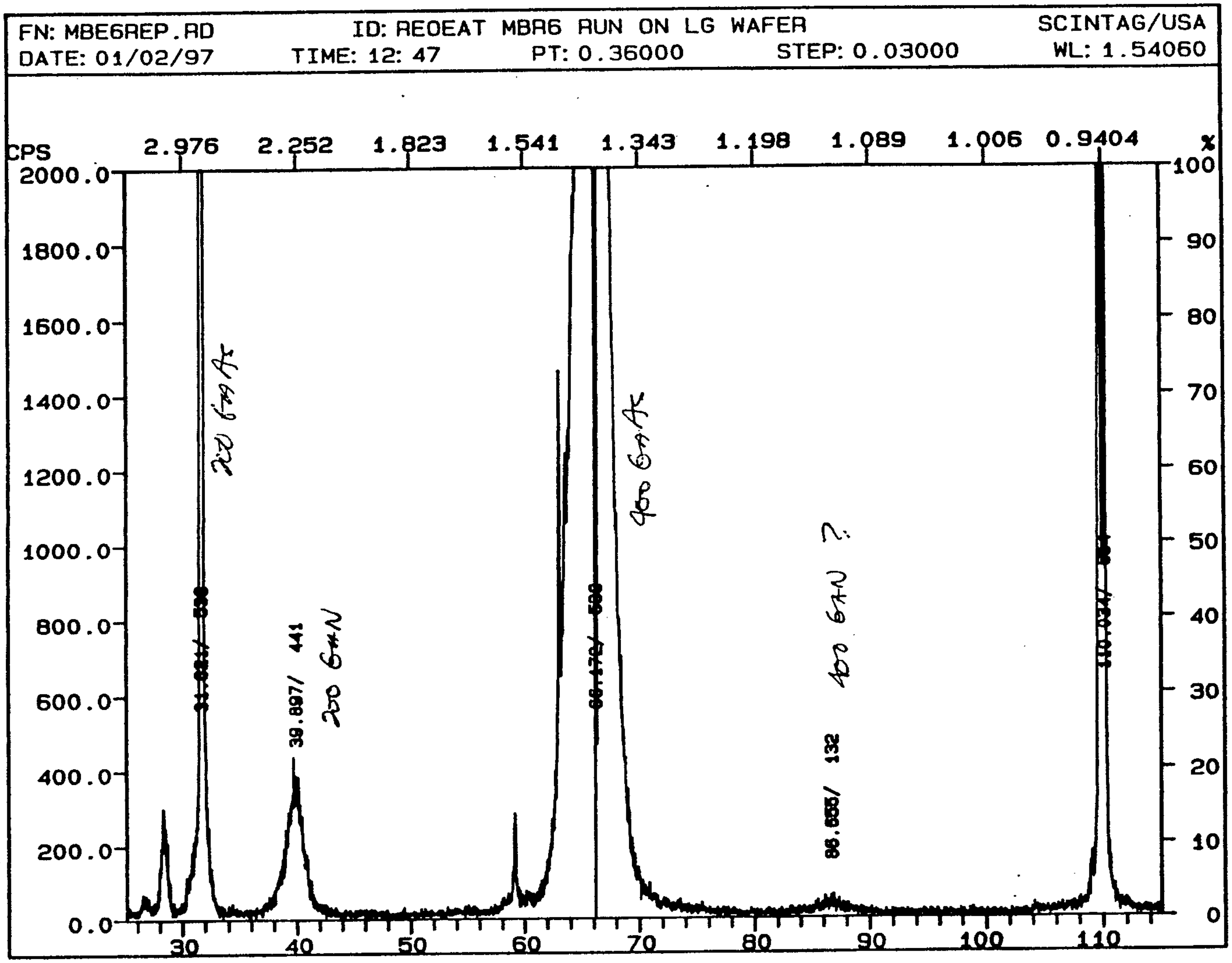


Fig. 6: X-Ray rocking curve of run 306

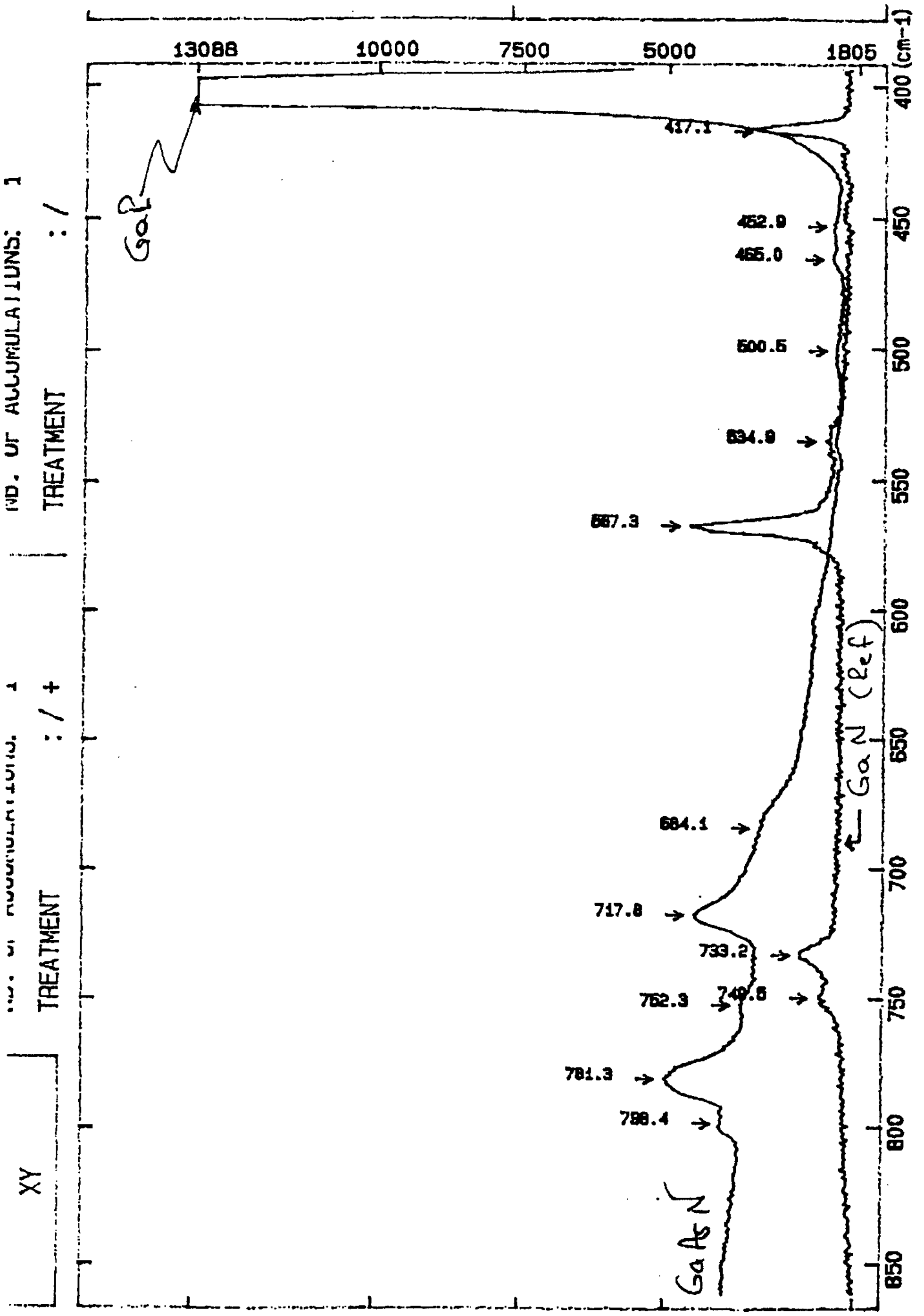


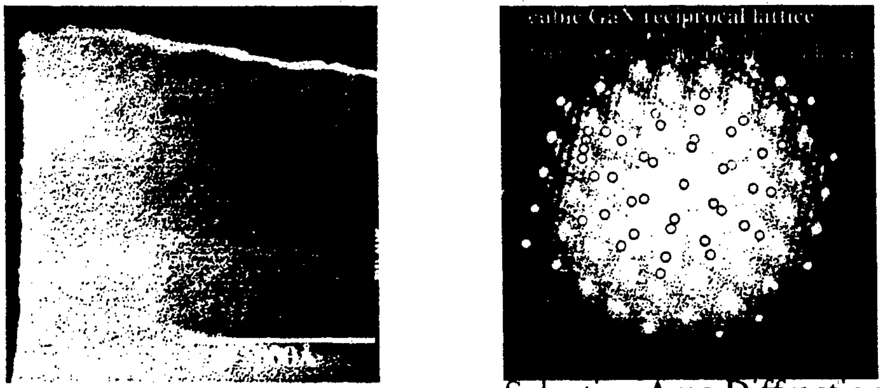
Fig. 7: Micro Raman spectra of gaAsN on GaP.

SEMICONDUCTOR RESEARCH CORPORATION

SRC Center of Excellence in Microscience & Technology at Cornell University

Cross-sectional TEM Analysis of GaAsN Films

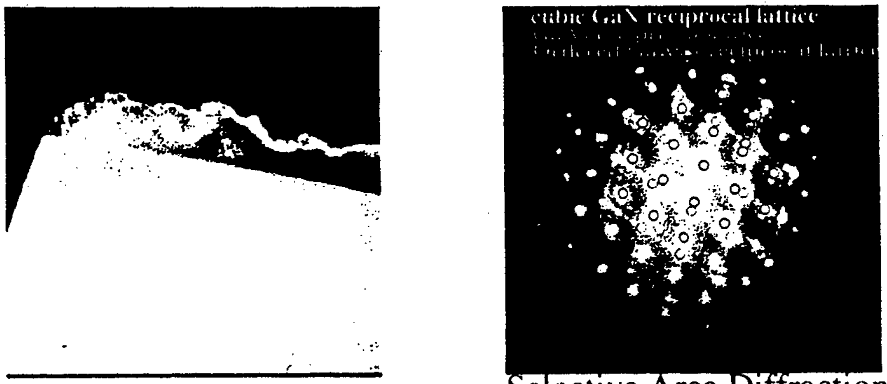
GaAsN/GaAs



(002) Dark Field

Selective Area Diffraction from epilayer

GaAsN/GaP



(002) Dark Field

Selective Area Diffraction from epilayer

- Phase-segregated ordered GaAsN and GaN domains.

Fig. 8: TEM Observations on GaAsN Films

Table III (from Michalak)

$GaAs_{1-x}N_x$ MBE RUN SUMMARY February 1997

MBE	GROWTH	XRD	AUGER	PL
1 - 10944- 22 GaAs #122	(3) 2000A layers, increasing N, T=540°, buffer grown, plasma on, Rheed showed GaAsN	asymmetric GaAs peak, and clear, epi-peak, $d\theta=0.11 \to x=0.013$, GaN present	25 atomic % N after C, O strip, about 3000A thick via sputtering	No epi-PL seen
2 - GaP(S) #138 (100) 2°	More N than MBE - 1	GaN peak	28% N, about 3000A thick via sputtering	No epi-PL seen
3 - GaP(S) (100) 2° #187	2000A grown, good Rheed ODD SURFACE RECONSTRUCTN	no GaN, symmetric GaAs peak	30% N, 600A thick?	No epi-PL seen
4 - 10944-7 GaAs #188?	500A GaAs / 50A GaAsN QW / 2000A GaAs / 50A AlGaAs - GaAs superlattice x10 (for TEM)	asymmetric GaAs peak, interference fringes visible	No QW N seen…	No epi-PL seen
5 - 650306 GaAs	µ/4 layer, N control problem, no buffer, ? spontaneous GaAsN from Rheed Note- most 100 GaAs wafers used may have been 2° wafers…	asymmetric GaAs, GaN seen, GaAs "hump" on small ω side, one HRD scan had clear peak at 41.1°->x=.87 400 GaAsN or x=.14 233 GaAsN or x=.25 124 GaAsN??? One Scintag scan had several peaks corresponding to x=.36 and x=.56???	9% N	Not done
311 312	GaAsN FORMED FROM N₂ ? MANUAL MEE m GaAs - UNUSUAL RHEED			
6 - 650307 GaAs	2000A GaAsN (increased N) / GaAsN / GaAs, GaAsN again formed immediately. - SPOTTY RHEED	symmetric GaAs, no epi-peaks	20% N	Not done
357, 8, 9 GaAs	failures, T increased too quickly damaging surface . MEE RUNS	DO X RAY ON THESE		
10 - 65360 GaAs	MEE run, N plasma struck while growing buffer->Rheed dies, 200 layers, plasma died near end	symmetric GaAs	9% N	Not done
11- 65361 GaAs	MEE, Higher power (300W) & more N, buffer grown, then plasma turned on …	symmetric GaAs, no GaN	45% N!	Not done
12 - 65362 GaAs	MEE, plasma on first, but GaAsN formed… failure HI T		Not done	Not done

Appendix 1

Preliminary Notes on Recent Theoretical Calculations of the $GaAs_{1-x}N_x$ Band Gap

Kurt A. Johnson

May 10, 1996

This GaAsN alloy problem seems quite complicated. The real difficulty in interpreting all of the theoretical work is determining how well a random alloy can be modeled using an ordered structure. A small unit cell can perhaps give misleading results due to artifacts of the calculation method. For instance, band folding occurs when a unit cell larger than the primitive unit cell is used in a calculation. If we take an element from the Group IV's which exists in the diamond structure among others, one primitive unit cell is the FCC structure with a two atom basis (i.e. diamond.) One can also choose a simple cubic cell with an eight atom basis. Physical nothing has changed, but we have enlarged the real space unit cell to include eight atoms rather than two. The reciprocal space structure of course is also altered by this choice, and, as we remember from Ashcroft & Mermin, the volume of the reciprocal space unit cell for the larger real space cell is smaller than that of the primitive real space cell. It's reciprocal. In calculating a band structure we limit ourselves to the first Brillouin zone (BZ) or simply a primitive reciprocal space cell and find the electronic states at any point in **k** space. All possible single electron states are included within the first BZ and looking outside of this zone we find everything repeated periodically. Then it's obvious we must have the same information contained within a smaller volume of **k** space (compared to the choice of a primitive real space structure which would give the largest reciprocal space cell.) Therefore electronic states which originally existed outside of the small BZ are translated (or folded) into the new zone.

We should also remember something about the tragedy of density functional theory (DFT) and its current implementations. DFT requires the knowledge of a special functional of the single electron density for which we need to know the ground state energy of a many-electron system (actually a general many-body solution of the problem.) Needless to say we don't have such a solution, but we have some approximations for the functional. It should be noted that there is also a particular formalism used in achieving the DFT solution known as the Kohn-Sham (KS) formalism. It is well known that this KS formalism along with the approximate form for the functional (known as the local density approximation (LDA)) will not give correct single electron excited states such as the conduction bands in a semiconductor or insulator; we can not get true band gaps. In fact band gaps are always (based on empirical evidence) underestimated.

With the basics of folding and the KS-LDA problem introduced we can now see how a calculation can go bad. Imagine taking an indirect gap material such as Ge which has an experimental band gap of about 0.7eV. Were we to perform a band structure calculation for Ge, we might choose a non-primitive unit cell (for as yet unknown reasons) and set the computer going. If it turns out that we have chosen our cell in such a way as to fold the indirect gap state of Ge into the center of the BZ (the point Γ), then the final results will show a direct gap material; the valence band maximum (VBM) of Ge is at the zone center, and now the previous indirect gap, the conduction band minimum (CBM), also appears at the zone center. If we then calculate optical transition matrix elements from the VBM to the CBM, we will find a zero transition strength. There should be no new information here, and there isn't since Ge never had lower direct gap. Now let's consider the possibility that the LDA gap for Ge is zero or slightly less than zero, so we have a semi-metal; the bands touch or cross at Γ. It just happens that this is the case for LDA calculations of Ge. Using the same unfortunate choice of unit cell the folded bands produce what looks like a metal. This may be harmless as in the case of the "new" direct gap appearing, or it can be worse. Every ab-initio calculation requires the choice of a cut-off energy in the expansion of the crystal wave functions in plane waves, and the selection of **k** points in the first BZ which are used to calculate the electron density. The electron density is just a sum of the modulus of the wave function over all occupied states which is an integral over the entire BZ in the case of a periodic system. This integral is normally approximated by a sum over a few **k** points (2 - 12 usually) in the BZ. Imagine choosing one or more **k** points at a location in the BZ at which the LDA conduction band is lower in energy than the valence band. When the electron density is calculated, the computer naively fills the lowest energy bands, one of which is actually a conduction band. We obviously obtain an incorrect electron density and likely the wrong electronic structure. A case like this has occured in the calculation of a Ge-Sn structure. With only 2 Sn atoms in 18 Ge atoms in a cell, the result was a metal. This seems quite unlikely in a real alloy of $Ge_{1-x}Sn_x$ with say x=0.1. Calculating the properties of a real metal requires two things: *a priori* knowledge that you have a metal and some finesse with the computer algorithm.

This is enough to analyze the various theoretical results for GaAsN. First, the paper by Rubio and Cohen (Phys. Rev. B **51**, 4343 (1995)) shows a semiconductor for all ranges calculated 25%, 50%, and 75% N. They include a GW correction which corrects for the LDA band gap underestimate although they show no metallic results even with the LDA only calculations. However they include no internal atomic relaxation in the unit cell, so none of the bond lengths are representative of an actual material. The authors only wished to give a qualitative explanation of the experimental red-shift, so these results aren't meant to be exact.

A second paper by Neugebauer and Van de Walle (Phys. Rev. B **51**, 10568 (1995)) show quite different results. They indicate or at least imply metallic behavior over the entire range of N from 25 - 75%. Their calculation includes atomic relaxation, and they state that even with a GW correction the materials would remain metallic; no numerical values are provided within the article. Similar results are obtained with the Corning planewave code which show a metal for a GaAsN (111) superlattice with a 50/50 ratio. For some (100) superlattices we find quite different results. A 75% N superlattice shows a -0.58eV *indirect* gap. With a GW correction of 0.7 - 1.1eV (somewhere between the correction for GaAs and GaN) we obtain an indirect gap semiconductor. At the other end, a (100) superlattice with 25% N, the band structure (Fig. 1) shows a direct gap of 0.06eV. Again, a small GW correction produces a reasonable semiconductor. Perhaps the significant piece of information is that the direct gap at Γ has zero optical strength. The 75% N superlattice also has a zero strength transition at Γ, but it of course has an indirect gap lower in energy. Why could this be the case? Since we have used small unit cells, we are finding electronic states folded into the zone center. In general a folded state will not have a finite transition strength unless the crystal symmetry is broken in some interesting way. The question remains as to why the folded state should be lower in energy than the original direct gap. Both GaN and GaAs are direct gap materials, and there should not be any conduction band states lower in energy than those at Γ. As it happens, GaAs under strain becomes an indirect gap material near 5% compression (see Fig. 2.) It is most likely that this indirect gap state is folded into the center of the BZ producing what looks like a direct gap. In the LDA calculations it is quite possible, as mentioned above, to get a metal with this type of folding. Neugebauer and Van de Walle actually looked at (111) superlattices and (100) superlattices. It is likely that their (100) results would contain this artifact of the small unit cell and indirect gap folding. The (111) calculations may also have similar problems. They do not give any details of the crystal structure or unit cell for the (111) results, so it is difficult to say for certain.

To attribute this metallic behavior to a true closing of the gap we expect some volume dependent (or perhaps bond length dependent) effect to be significant (as with the transition from direct to indirect character in GaAs.) Fig. 3 shows the volume dependence of the band gap of GaN. The direct gap at Γ decreases linearly from a 2.0eV LDA gap to 0eV at a 10% increase in lattice constant. Does the zero gap indicate a metal? Probably not. GaN has a nearly 1.1eV many-body correction to the LDA result which would make it a semiconductor throughout this range and beyond. In GaAs the direct gap at Γ increases from a 0.42eV LDA gap to 3.04eV at 10% compression; roughly the same lattice constant as GaN stretched by 10%. If we average these gaps at Γ, we have something greater than zero at the intermediate ranges (assuming continued linearity) because the GaAs gap is increasing faster than the GaN gap decreases. This simple average is certainly wrong since we are not including any charge transfer from the As to N atoms which could give a larger weight to the GaN gap decrease. However, with the inclusion of many-body corrections to these LDA gaps it is unlikely that an alloy within the range of $x = 0.25...0.75$ should become a metal.

In studying the Wei and Zunger (Phys. Rev. Lett. **76**, 664 (1996)) work, it appears they have used the best theoretical method for calculating alloy properties from ordered structures. They find a strong dependence of the alloy bowing parameter on the alloy composition. Fig. 4 shows the resulting band gap using their results for $b(x)$, the bowing parameter. We find for their three results a nearly constant correction to the band gap (1.7, 1.4, and 1.7eV) for each alloy composition. This seems strange as it does not look like an expected parabolic bowing of the gap, and the gap is only close to being metallic at $x = 0.125$. They have only used one possible structure for the $x = 0.125$ point and this may imply a statistical problem in the results here.

It is certainly true that for small concentrations of N impurities in GaAs there will be a red-shift cause by impurity states forming in the gap of GaAs. The N potential is deep compared to As and P where the red-shift is also seen in GaP. In the N rich alloy, the As atoms will effectively serve to increase the lattice constant of the alloy and produce an expected red-shift caused by the decrease in the GaN gap from an increase in the average lattice constant (Fig. 3.) The intermediate regime is difficult because in some region the GaAs material becomes indirect. In fact, examination of GaP vs. lattice constant (Fig. 5) shows a striking similarity to the GaAs calculation. If we place the GaAs gaps over the GaP results, adjusting for a small offset in energy and lattice constant (about 4%), they match well. The GaP and GaAs materials show the same systematic variation in their primary gaps. GaAs has an electronic structure equivalent to GaP at some densities, and we may then get some insight into what happens in this intermediate concentration range if we have some experimental results for $GaP_{1-x}N_x$ for significant N concentrations. Current calculations on the (100) GaAsN structures suggest an indirect or quasi-direct gap material in this range. A quasi-direct gap is one in which the lowest optical transition has a zero transition strength, but transitions nearby in energy have a finite strength coupling. This type of transition requires a low momentum phonon to assist the electron. A best guess for the entire range of alloy compositions is shown in Fig. 6. This shows GaAsN to be a semiconductor at all N concentrations. The single point at $x = 0.125$ has been thrown out because only one ordered structure was used to calculate it. The point at $x = 0.25$ appears good since it also compares well with a GaAsN heterostructure with an LDA gap of 0.06eV which would have a corrected gap near 0.7eV; this is close to the Wei & Zunger result. The point at $x = 0.5$ is more complicated. Many calculations predict metallic behavior here and a zero gap fits in well with some nearby points $x = 0.75, 0.833$ which, after a many-body correction, would fall within the indicated ranges. However, these values are indicative of particular ordered structures and again do not best represent a random alloy but are shown for completeness. The best guess attempts to stay faithful to the Wei & Zunger results.

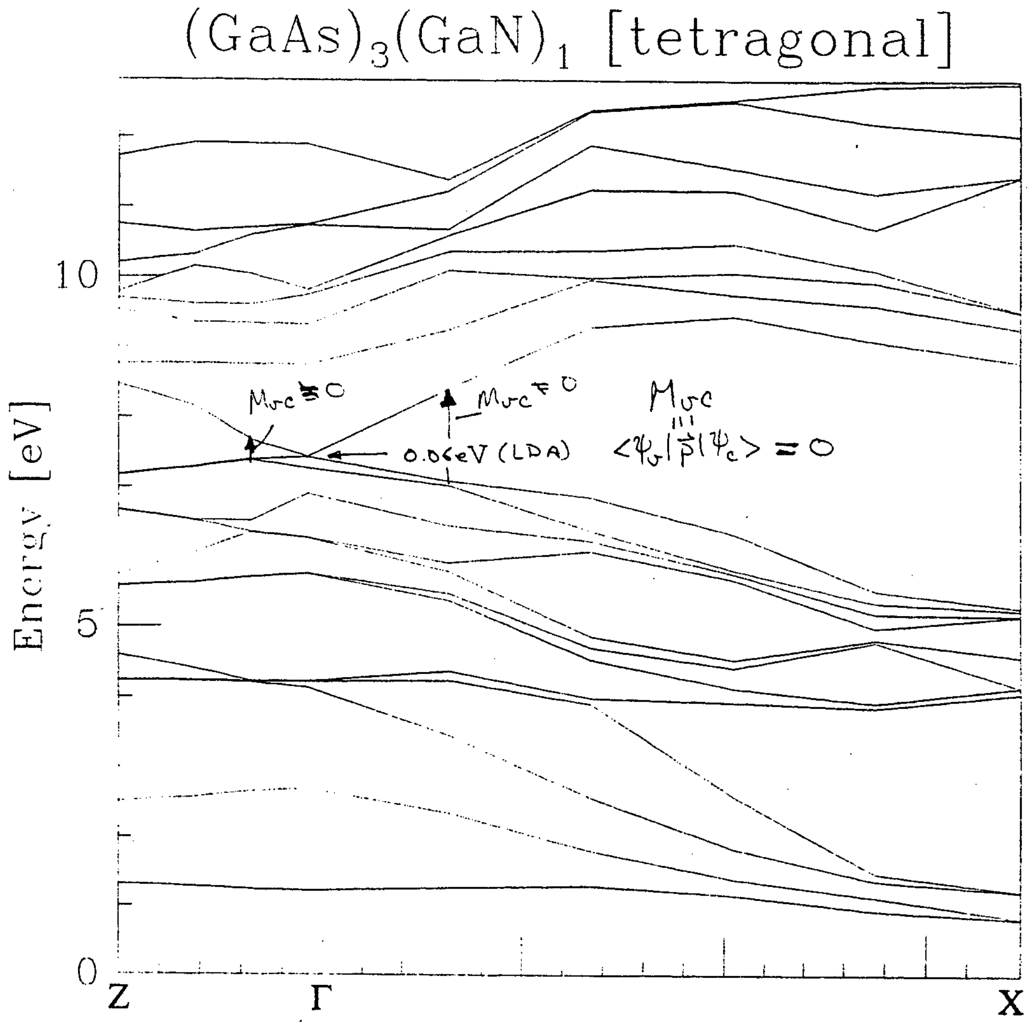

(GaAs)$_3$(GaN)$_1$ [tetragonal]
Energy [eV]
10
5
0
Z
Γ
X
$M_{vc} \neq 0$
$M_{vc} \neq 0$
0.06eV (LDA)
$M_{vc} \equiv \langle \psi_v | \vec{p} | \psi_c \rangle = 0$

Figure 1.

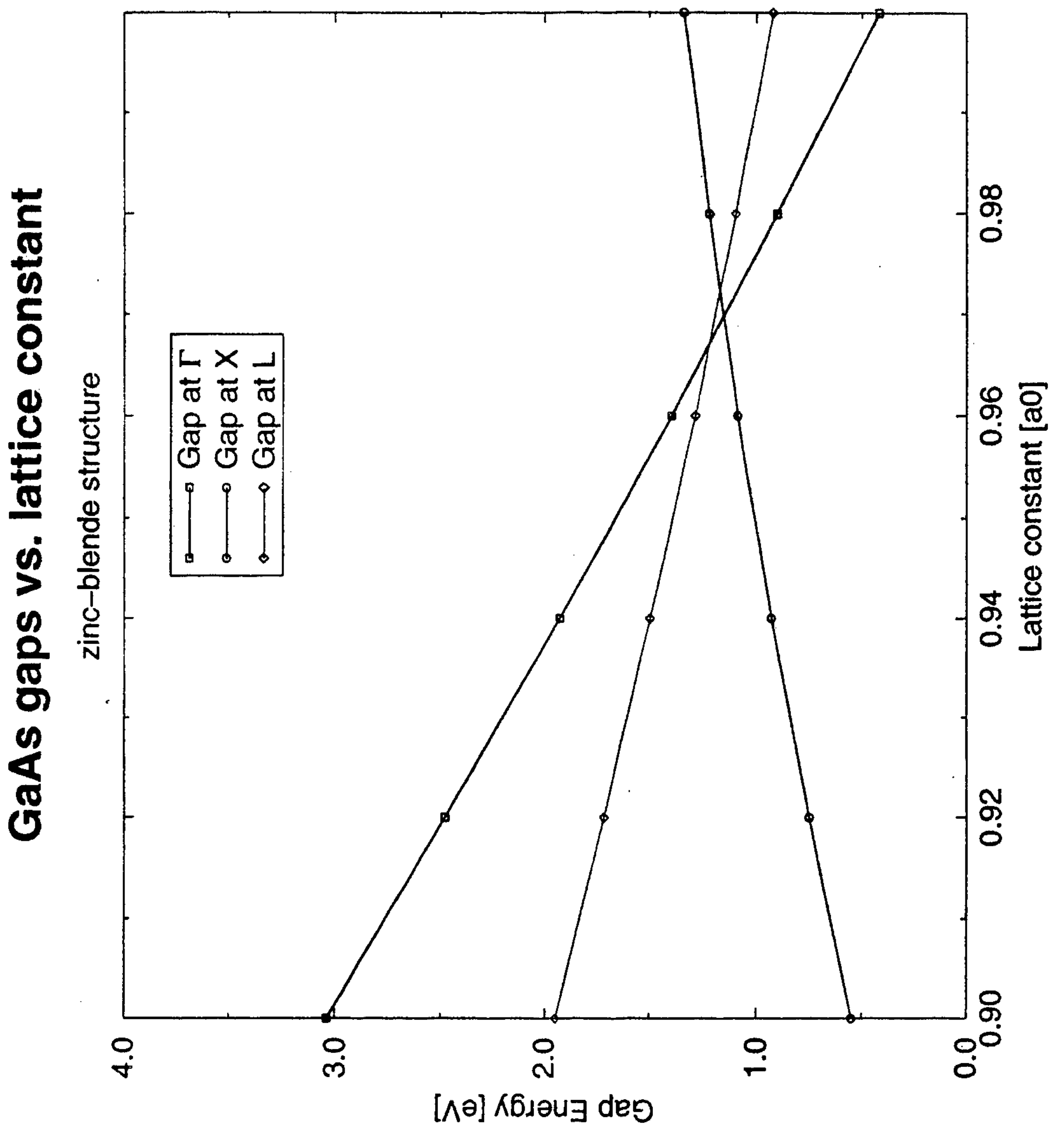

GaAs gaps vs. lattice constant
zinc–blende structure
Gap at Γ
Gap at X
Gap at L
Gap Energy [eV]
0.0
1.0
2.0
3.0
4.0
Lattice constant [a0]
0.90
0.92
0.94
0.96
0.98

Figure 2.

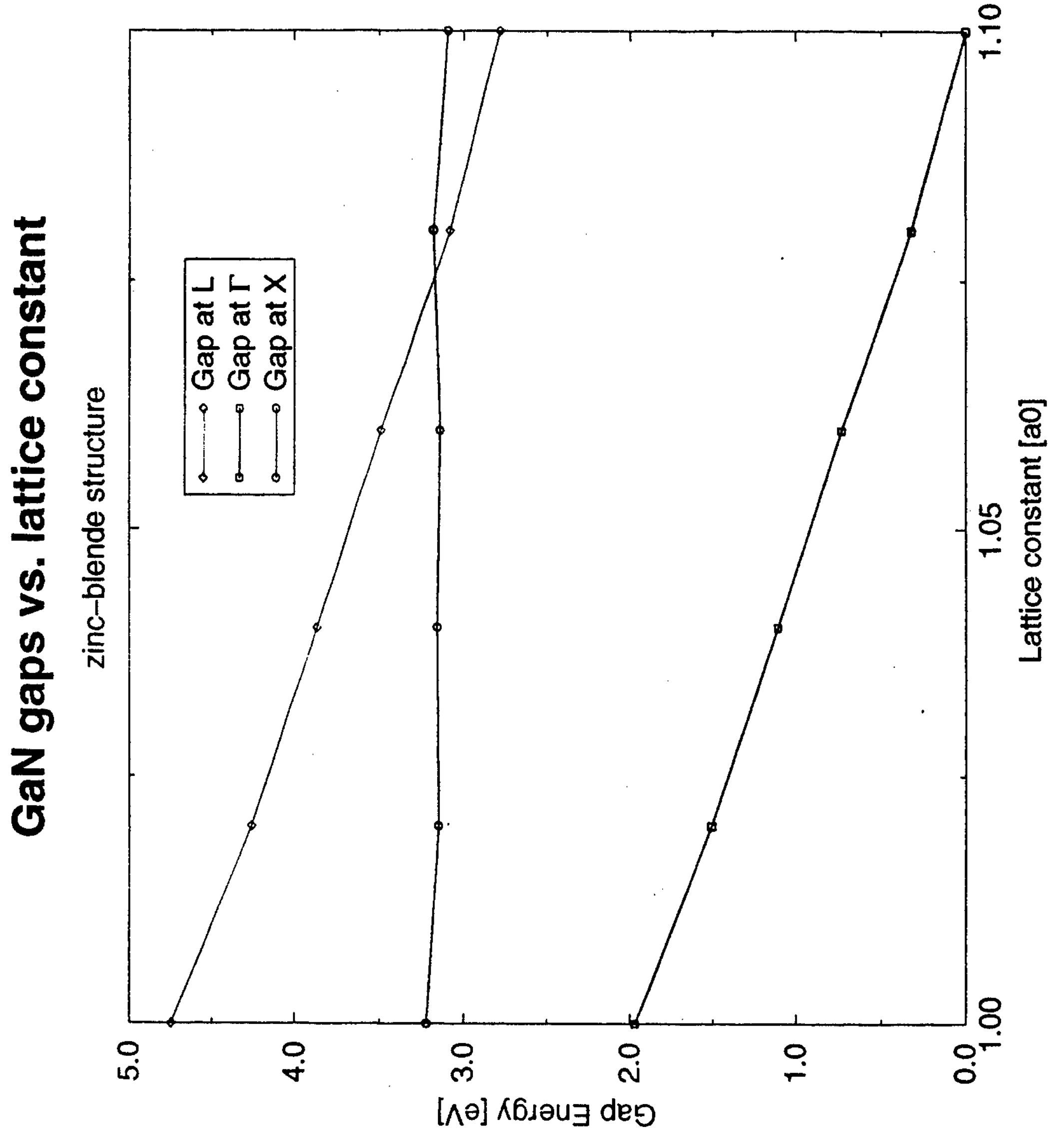
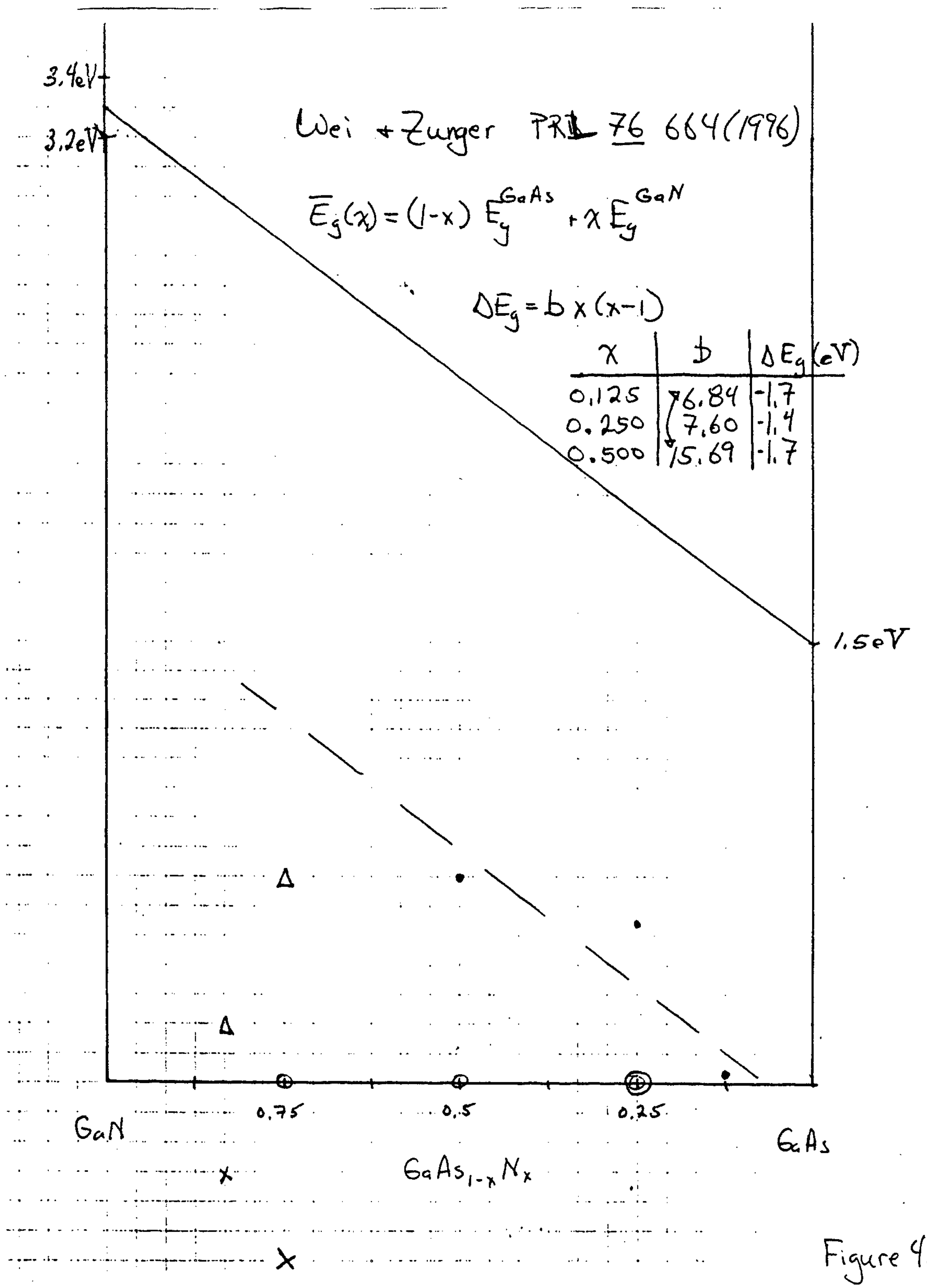

GaN gaps vs. lattice constant
zinc–blende structure
Gap at L
Gap at Γ
Gap at X
Gap Energy [eV]
5.0
4.0
3.0
2.0
1.0
0.0
Lattice constant [a0]
1.00
1.05
1.10

Figure 3.



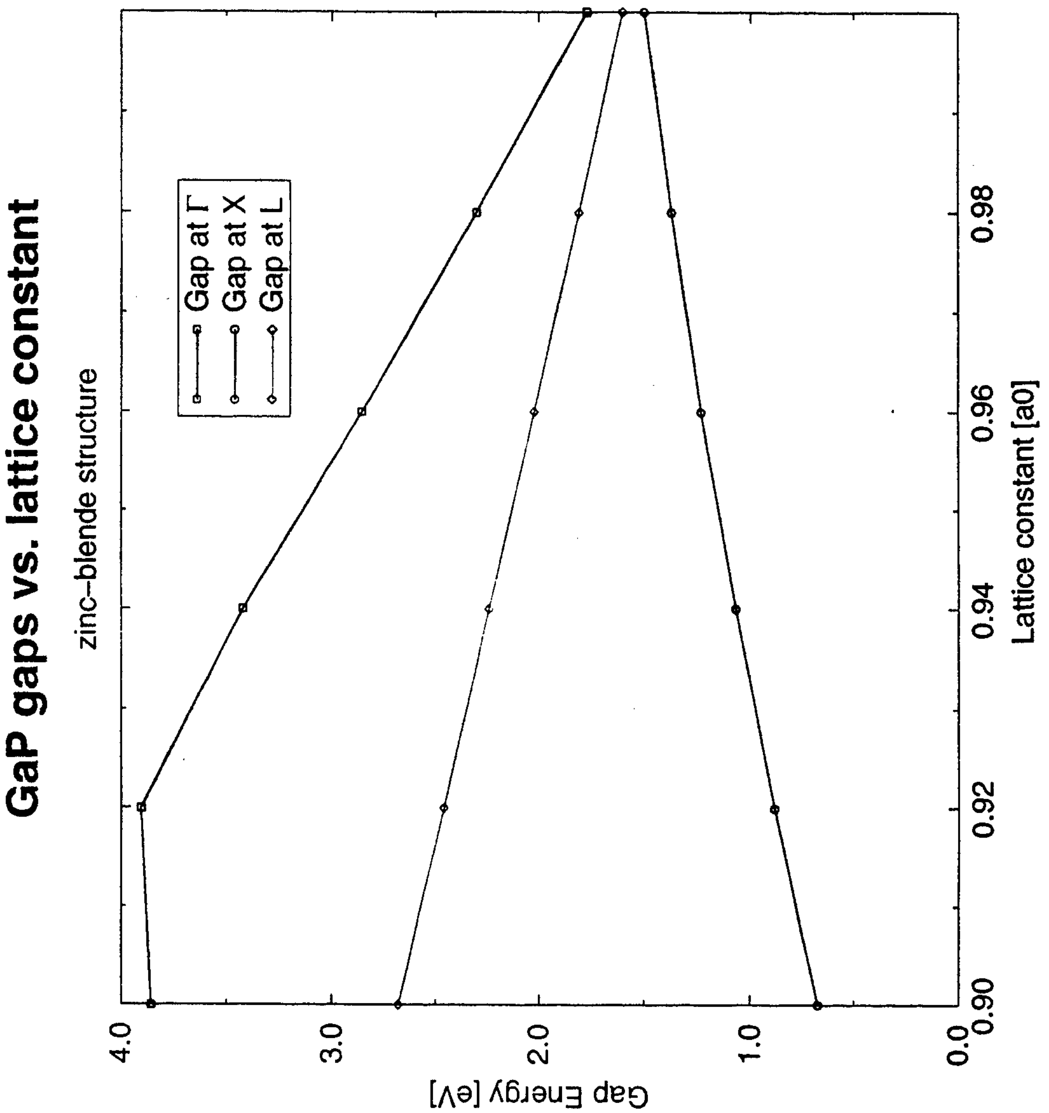
Wei + Zunger PRL 76 664(1996)

$$\overline{E}_g(x) = (1-x)\,E_g^{GaAs} + x\,E_g^{GaN}$$

$$\Delta E_g = b\,x\,(x-1)$$

x	b	ΔE_g (eV)
0.125	6.84	-1.7
0.250	7.60	-1.4
0.500	15.69	-1.7

Figure 4.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Lattice constant [a0]
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Figure 5.

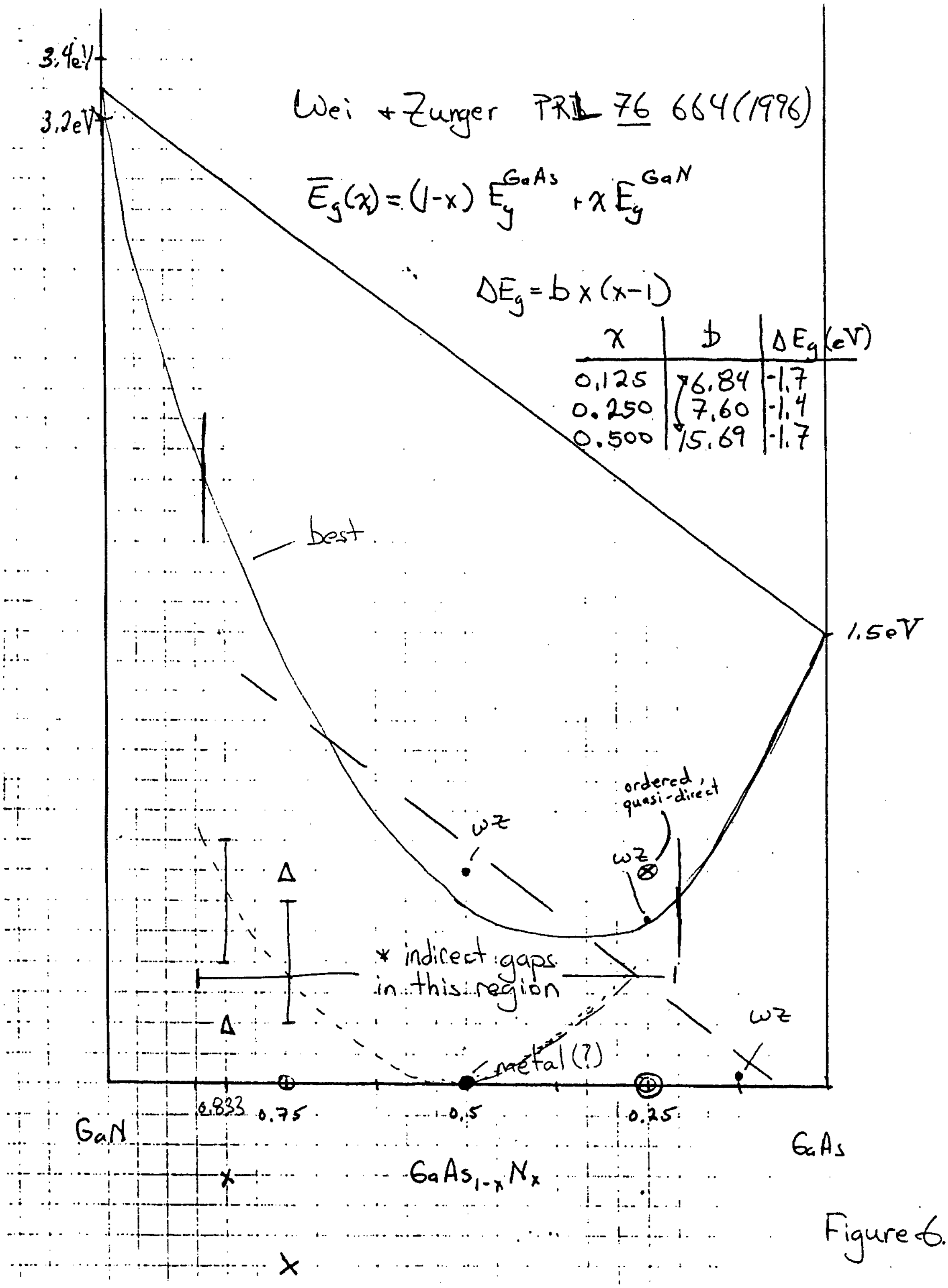

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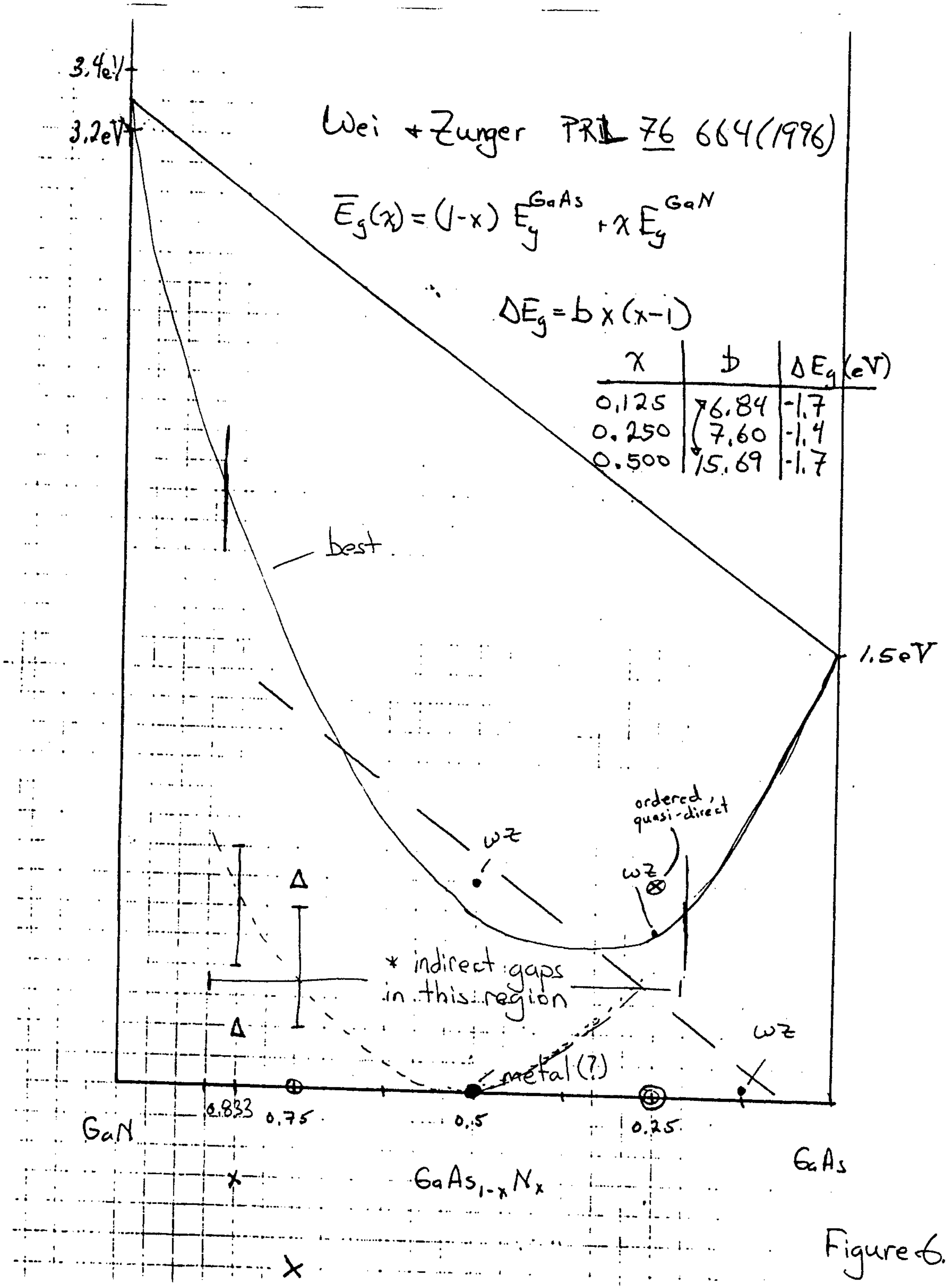
Figure 6.



Wei + Zunger PRL 76 664(1996)

$$\overline{E}_g(x) = (1-x)\,E_g^{GaAs} + x\,E_g^{GaN}$$

∴ $$\Delta E_g = b\,x(x-1)$$

x	b	ΔE_g (eV)
0,125	6.84	-1.7
0.250	7,60	-1,4
0.500	15.69	-1.7

Figure 6.

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e. Maintains leading edge technological expertise in the areas of surveillance, communications, command and control, intelligence, reliability science, electro-magnetic technology, photonics, signal processing, and computational science.

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