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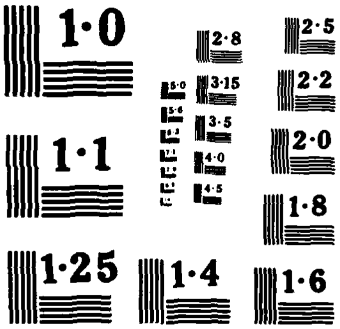

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AD-A158 516

IN SITU SELECTED AREA DOPING OF GaAs BY MOLECULAR BEAM EPITAXY

FINAL REPORT FOR THE PERIOD
June 1, 1983 through May 31, 1985

CONTRACT NO. DAAG29-83-C-0019

Prepared for

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

D.L. Miller
Principal Investigator

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AD-A158516

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS:

2a. SECURITY CLASSIFICATION AUTHORITY:

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE:

3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S): MRDC41135.4FR

5. MONITORING ORGANIZATION REPORT NUMBER(S):

6a. NAME OF PERFORMING ORGANIZATION:
Rockwell International
Microelectronics Research and
Development Center

6b. OFFICE SYMBOL (If applicable):

7a. NAME OF MONITORING ORGANIZATION:

6c. ADDRESS (City, State and ZIP Code):
1049 Camino Dos Rios
Thousand Oaks, CA 91360

7b. ADDRESS (City, State and ZIP Code):

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U.S. Army Research Office

8b. OFFICE SYMBOL (If applicable):

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: Contract No. DAAG29-83-C-0019

8c. ADDRESS (City, State and ZIP Code):
P.O. Box 12211
Research Triangle Park
NC 27709

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE (Include Security Classification): IN SITU SELECTED AREA DOPING OF GaAs BY MOLECULAR BEAM EPITAXY (U)

12. PERSONAL AUTHOR(S): Miller, D.L. and Kowalczyk, S.P.

13a. TYPE OF REPORT: Final Technical Report

13b. TIME COVERED: FROM 06/01/83 TO 05/31/85

14. DATE OF REPORT (Yr., Mo., Day): JULY 1985

15. PAGE COUNT: 69

16. SUPPLEMENTARY NOTATION
The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Army Research Office or the U.S. Government.

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Molecular Beam Epitaxy, Selected Area Doping, GaAs, Organotin Compounds, UV Photolysis, Arsenic, Dopant Incorporation, Growth/Regrowth, Photochemical Etching

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This final report contains a description of the technical progress for the final six month period of this program and a summary of the most important previous results of this program. In this final period a new in situ selected area doping process was investigated which appears to the most promising of the three evaluated in this program. During an investigation of UV photolytic deposition of tin from organotin compounds, it was found that during the initial stages of deposition with halogenated tin compounds, etching of the semiconductor surface occurs affecting the surface stoichiometry. This result has important implications for application of UV photolytic deposition of metals on semiconductors as well as photochemical etch processing. Initial experiments involving in situ photochemical etching of GaAs MBE substrates was carried out. Originator supplied keywords included

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL:

22b. TELEPHONE NUMBER (Include Area Code):

22c. OFFICE SYMBOL:

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

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1.0 INTRODUCTION

The goal of this project has been to investigate selected area processes for MBE GaAs. Two classes of selected area processes were investigated. One class dealt with in situ selected area doping. Three selected are doping processes were evaluated during the course of this program. The other class of selected area processes studied involved regrowth of MBE GaAs over a previous grown MBE GaAs epilayer which had been removed from the MBE chamber for ex situ processing. In this study, we concentrated on developing surface cleaning and/or passivation procedures to produce useful growth/regrowth interfaces (i.e., electrically "invisible"). Three procedures were tested. Below we briefly summarize the major results, concentrating on the progress of the last sixth-month period.

2.0 IN SITU SELECTED AREA DOPING

The first selected area doping process investigated was based on using a desorbable As mask. As reported in our first progress report (MRDC41135.1PR) this method produced rather variable results. The second approach involved UV photolysis of tin containing compounds. However, studies of the desorption step[1] show that molecules were pyrolytically decomposed rather than desorbed making this method unsuitable as a selected area process. During the Auger electron spectroscopy studies of the adsorption/desorption steps it was discovered that the dopant containing molecules had a much lower sticking coefficient to As passivated GaAs surfaces than to clean GaAs surfaces. This lead to the new approach which combined the idea of a desorbable As mask with pyrolytic decomposition of dopant molecules.[2] This selected area doping procedure consisted of the following steps: (1) MBE growth of GaAs on a clean GaAs (001) substrate, (2) adsorption of an As passivation cap which would be patterned for selected area doping, (3) adsorption of an organotin compound, in the unpassivated regions, and (5) regrowth of GaAs with selected area Sn incorporation into the regrowth layer. Experiments primarily on steps (3) and (4) showed that this process is the most promising procedure studied.

During the course of UV photolytic depositions of Sn primarily from organotin compounds, x-ray photoelectron spectroscopic studies demonstrated that when the compounds were halogenated, etching of the GaAs surface occurred during the initial stages of metal deposition resulting in extremely nonstoichiometric surfaces. This result has important implications for UV photolytic deposition of metals on semiconductors as well as development of photochemical etching procedures for semiconductors.

3.0 GROWTH/REGROWTH INTERFACES

Arsenic passivation was investigated and shown to produce useful growth/ regrowth interfaces under a number of conditions. These results have been reported in detail in Refs. 3 and 4. Experiments using ozone to produce growth/ regrowth interfaces was reported in a previous progress report (MRDC41135.3SA). Those experiments showed that the ozone treatment produced an improved but not ideal growth/regrowth interface. Preliminary experiments were started involving in situ UV photochemical etching of GaAs substrates for MBE with HCl. The initial experiments with this in situ dry etching technique showed that the GaAs surfaces are photochemically etched but there are problems due to In contamination from the In used to mount the substrates on the Mo substrate holder. Also, more importantly, C contamination does not appear to be removed by this procedure. Thus, it appears that the ultimate process to produce an ideal growth/regrowth interface will involve a number of steps such as ozone treatment and photochemical etching. Additional work needs to be done to develop an optimal procedure.

4.0 PUBLICATION LIST

Manuscripts Published

1. "MBE GaAs Regrowth with Clean Interfaces by Arsenic Passivation," D.L. Miller, R.T. Chen, K. Elliot and S.P. Kowalczyk, J. Vac. Sci. Technol B 3, 560 (1985).
2. "Molecular Beam Epitaxy GaAs Regrowth with Clean Interfaces by Arsenic Passivation," D.L. Miller, R.T. Chen, K. Elliot and S.P. Kowalczyk, J. Appl. Phys. 57, 1922 (1985).
3. "Photochemical Deposition of Sn for Use in Molecular Beam Epitaxy of GaAs," S.P. Kowalczyk and D.L. Miller, J. Vac. Sci. Technol. B (to be published in Sept./Oct. 1985).

Manuscripts Submitted for Publication

1. "Photochemical Etching During Ultraviolet Photolytic Deposition of Metal Films on Semiconductor Surfaces," S.P. Kowalczyk and D.L. Miller.
2. "Arsenic Passivtion of GaAs and Pyrolytic Decomposition of Organotin Compounds for *In Situ* Selected Area Doping of GaAs Molecular Beam Epitaxy," S.P. Kowalczyk and D.L. Miller.

Conference Presentations

1. "MBE GaAs Regrowth with Clean Interfaces by Arsenic Passivation," D.L. Miller, R.T. Chen, K. Elliot and S.P. Kowalczyk, 3rd Int. MBE Conf., San Francisco, Aug 1-3, 1984.
2. "Photochemical Deposition of Sn for *In Situ* Selected Area Doping of MBE GaAs (001) Epilayers," S.P. Kowalczyk and D.L. Miller, Topical Conference on Microphysics of Surfaces, Beams and Adsorbates, Santa Fe, Feb. 4-6, 1985.
3. "Arsenic Passivation of GaAs and Pyrolytic Decomposition of Organotin Compounds for *In Situ* Selected Area Doping of GaAs Molecualr Beam Epitaxy," S.P. Kowalczyk and D.L. Miller, Sixth Molecular Beam Epitaxy Workshop, Minneapolis, Aug. 14-16, 1985 (submitted).

5.0 PARTICIPATING PERSONNEL

Dr. D.L. Miller

Dr. S.P. Kowalczyk

Dr. R.T. Chen

Dr. K. R. Elliot

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APPENDIX I

PHOTOCHEMICAL DEPOSITION OF Sn FOR IN SITU SELECTED AREA DOPING OF MBE GaAs (001) EPILAYER

(J. Vacuum Science and Technology, in press)

PHOTOCHEMICAL DEPOSITION OF Sn FOR IN SITU SELECTED AREA DOPING OF MBE GaAs (001) EPILAYER

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ABSTRACT

The suitability of several Sn-containing molecules (tetramethyltin, tetrabutyltin, dibutyltin dibromide and stannic chloride) as gas phase sources of Sn for use in molecular beam epitaxy of GaAs was evaluated. In situ Auger electron spectroscopy showed that the Sn molecules absorbed at approximately the monolayer level at room temperature on GaAs (001) epilayer surfaces and pyrolytically decomposed before desorption. Capacitance-voltage and secondary ion mass spectrometry profiles demonstrated that the pyrolytic Sn deposits incorporated as a n-type dopant into newly regrown GaAs epilayers. Sn films were UV photolytically deposited on GaAs from each of these Sn-containing molecules and characterized by x-ray photoelectron spectroscopy.

I. INTRODUCTION

Ultraviolet (UV) initiated microchemistry has recently emerged as a potential new tool in microfabrication for solid state electronic applications.[1-4] The employment of such a technique offers attractive new possibilities for microelectronic processing. Much of the recent research has centered on delineated deposition of metal films by laser UV photolysis of gaseous metal-containing compounds.[5-15] The effort in this area has been successful in highlighting the capability of photodeposition and begun to illuminate some of the fundamental processes involved. One intriguing possibility for semiconductor device processing that this capability opens up is that of selected area (i.e., lateral area) doping of semiconductors. In particular, we are interested here in developing in situ selected area doping within molecular beam epitaxy (MBE) technology.

The purpose of the work reported here is the investigation of the possibility of selected area Sn doping in GaAs MBE. There are several attractive features in such a combination. The selected area doping scheme proposed here involves UV photolysis. As applied to GaAs, it consists of five steps (Fig. 1).

1. Growth of a GaAs MBE epilayer (buffer layer) on an atomically clean and crystallographically ordered GaAs (001) substrate.
2. Adsorption of approximately one monolayer of the dopant atom (Sn) containing molecules on the epilayer surface.

3. UV irradiation of selected areas of the epilayer to produce photolytic decomposition of the dopant molecule, resulting in the dopant atom on the selected areas of the epilayers of the surface and the adsorbed molecules remaining on the unirradiated portions of the epilayer.
4. Thermal desorption of the nondecomposed physisorbed molecules, while the more strongly bound atoms remain on the surface.
5. Regrowth of GaAs and incorporation of dopant atoms in the selected areas of the new GaAs epilayer.

However, before such a fabrication process can be implemented, many fundamental aspects associated with the basic mechanism of each of the above steps must be clarified. In this paper, we present the results of our initial studies of steps 2 through 5. The adsorption (step 2) and desorption (step 4) of Sn-containing molecules on GaAs (001) surfaces was studied by means of in situ Auger electron spectroscopy (AES). UV photolytic deposition (step 3) of Sn films on GaAs (001) was studied separately by ex situ experiments using x-ray photoelectron spectroscopy (XPS) for characterization of the photodeposited Sn films. Sn incorporation (step 5) was studied by means of secondary ion mass spectrometry (SIMS) and electrolytic capacitance-voltage (C-V) profiling techniques.

II. EXPERIMENTAL ASPECTS

The MBE growths utilized a multichambered, cyropumped, LN shrouded, homebuilt MBE apparatus. The MBE system consists of three chambers: a load-lock chamber, an antechamber primarily for degassing of substrates, and a growth chamber equipped with a cylindrical mirror analyzer for AES, a reflection electron diffraction (RED) system, and a quadrapole mass spectrometer. The sample can be moved between all three chambers while maintaining ultra-high vacuum ($< 10^{-9}$ Torr). The MBE open crucible cell sources, which are mounted vertically, are filled with elemental As and Ga for production of As_4 and Ga beams. With growth rates of 1 m/h, standard MBE growth temperatures and As_4/Ga flux ratios, unintentional doping levels in the 5×10^{14} to 5×10^{15} atoms/cm^3 range were normally achieved. For these experiments, a manifold for handling and purification by means of freeze-thaw cycles of the Sn-containing molecules was built and attached to the antechamber of the MBE system through a UHV leak valve.

The substrates were pieces of GaAs (001) (n^+ and semi-insulating) wafers which had been polished and given a standard solvent degrease and chemical etch. After mounting on a Mo substrate holder with In, the substrates were spun-etched with $H_2O:H_2O_2:NH_4OH$ (10:1:1) and blown dry with N_2. The substrates were immediately loaded into the MBE system, pumped and transferred to the antechamber, where they were degassed and then transferred to the growth chamber, where they were thermally cleaned in an As_4 flux. Epilayer growth then commenced on an As-stabilized surface.

Sn is a n-type dopant for MBE GaAs,[16-19] which is particularly good for the proposed selected area doping scheme because it incorporates in MBE GaAs by a surface accumulation mechanism.[17] Thus, one can deposit a small amount of Sn on a GaAs surface and upon regrowth of GaAs, the Sn incorporates into the newly grown epilayer. The compounds investigated as Sn sources in these experiments were tetramethyltin $(CH_3)_4Sn$ (TMT), tetrabutyltin $(C_4H_9)_4Sn$ (TBT), dibutyltin dibromide $(C_4H_9)_2SnBr_2$ (DBTB) and stannic chloride ($SnCl_4$). All of these compounds are high vapor pressure liquids at room temperature.[20] TMT and $SnCl_4$ exposures were performed at their room temperature equilibrium vapor pressures, while the TBT and DBTB exposures were performed at their 100°C equilibrium vapor pressures.

The adsorption/desorption experiments were performed by placing a freshly grown epilayer at room temperature in the preparation chamber (base pressure $\sim 1 \times 10^{-9}$ Torr) and exposing the epilayers to the Sn compound vapor pressure for between 15-30 min. The surfaces were then examined by AES in the growth chamber. The temperature was ramped in ~ 50-100°C steps up to approximately the growth temperature of ~ 580°C and the desorption/pyrolysis characteristics were followed by in situ AES measurements. At the conclusion of the desorption measurements, a new undoped epilayer of GaAs was grown and Sn incorporation was studied by electrolytic C-V[21] and SIMS profiling.[22]

UV photolysis experiments were performed in separate experiments. GaAs (001) wafers were etched with a 4:1:1 $H_2SO_4:H_2O_2:H_2O$ solution, quenched in deionized H_2O and dried in a N_2 flow. Such a procedure produces a layer containing ~ 15Å Ga_2O_3/As_2O_3, approximately 15Å on the surface.[23] The wafer was placed in a quartz ampoule containing several drops of the liquid Sn compound and the ampoule was then sealed. This procedure was performed in a N_2 ambient in a glovebag. The sample was exposed to UV irradiation from either a high pressure Xe arc lamp (500 W) or an array of five low pressure Hg lamps (5 W each). The main Hg lines are at 2537 and 1849Å. For convenience of analysis, broad areas were exposed, since the main area of interest in these experiments is in Sn deposition properties, and pattern delineation has been amply demonstrated for a number of metals in other laboratories. After UV photolysis of the Sn-containing compounds, the sample was transferred to an XPS system via air and the surface was analyzed. The XPS system which was used is a Hewlett-Packard HP5950A electron spectrometer with a monochromatized AlKα ($h\nu$ = 1486.6 eV) x-ray source.

III. RESULTS AND DISCUSSION

A. Tetramethyltin

Exposure of fresh GaAs (001) epilayers to TMT resulted in approximately a monolayer of TMT being adsorbed. The TMT adsorption had no effect on the As/Ga ratio observed with AES, suggesting physisorption. All adsorption experiments with TMT showed significant oxygen contamination despite performing up to six freeze/thaw purification cycles prior to adsorption. Figure 2 shows AES spectra in the carbon and Sn region for TMT adsorption/desorption, and Fig. 3 summarizes some of the data for the AES lines of Sn, C, Ga and As as a function of temperature. The main conclusion is that TMT starts to pyrolytically decompose around 200°C and is completely decomposed by 600°C. This results in a

Sn film with a small amount of residual carbon contamination. The unintentional oxygen contamination was not observed above ~ 450-500°C. Since the TMT pyrolyzes before it can desorb, it can be ruled out as a source for selected area doping. When GaAs is regrown over a surface in which TMT has been pyrolytically decomposed, Sn is incorporated across the entire surface as a n-type dopant, as shown by the C-V analysis in Fig. 4. The C-V profile shows the expected exponential profile. SIMS analysis (Fig. 4) shows a similar Sn profile and also shows a large sharp carbon and much smaller oxygen buildup at the regrowth interface.

UV photolysis of TMT in sealed ampoules using either Xe or Hg radiation produced a metallic-looking film on the GaAs surface. XPS analysis showed the GaAs to be covered by Sn, but with significant carbon and oxygen contamination, which is not surprising due to non-UHV ambient in the ampoules. Upon heating the sample in the 200-450°C range, carbon was removed while the oxygen remained, suggesting that the carbon was mainly adsorbed on the surface as a monolayer of TMT and/ or carbon contamination from the air transfer to the XPS system, while the oxygen was in the Sn film, perhaps due to the Sn photolytically reacting with the residual oxygen in the quartz ampoule. Experiments involving sputter profiling would be helpful for further clarification of these two points.

B. Tetrabutyltin

TBT also adsorbed at the monolayer level on GaAs (001). It adsorbed without any oxygen contamination. AES spectra are shown in Fig. 2. TBT was completely pyrolyzed by 270°C with no residual carbon contamination. UV photolysis in a sealed ampoule with Hg radiation resulted in a Sn film which had much less oxygen contamination than in the case of TMT.

C. Dibutyltin Dibromide

A brief screening experiment with DBTB was performed. DBTB adsorbed, but similar to the above organometallic compounds, it pyrolytically decomposed, thus ruling it out as a selected area dopant source. Also, under UV irradiation with a Hg lamp, it produced a Sn film.

D. Stannic Chloride

Stannic chloride was the only inorganic compound evaluated in this investigation. $SnCl_4$ adsorbed at approximately the monolayer level as determined by AES. Its desorption characteristics are shown in Fig. 3. It partially desorbs, but eventually decomposes with no Cl observed at the surface. C-V profiles after regrowth showed that Sn did incorporate into the GaAs material as a dopant, as expected.

One $SnCl_4$ adsorption was done on a GaAs surface which had been thermally cleaned at a temperature which was not high enough to desorb the Ga oxide. Adsorption on this Ga oxide surface (Fig. 2) resulted in Sn, but little Cl on the surface, especially when compared with adsorption on the clean surface. One explanation could be that the $SnCl_4$ reacted with the Ga oxide to produce Sn oxide with liberation of Cl_2.

UV photolysis was done in a sealed ampoule using Hg lamp irradiation. This produced a thick film which contained Sn, Cl, a little oxygen and no carbon (Fig. 5). In another experiment, a thin film of ~ 30Å was deposited, such that the substrate core levels could be seen by XPS (Fig. 5) It is known that the surface treatment given the sample yields about equal amounts of As and Ga within the XPS sampling depth.[23] However, for the sample which had undergone UV photolytic deposition of Sn, the Ga/As ratio was ~ 30/1. This suggests that at the interface, UV photolytic etching may have occurred. The UV photolysis may have decomposed $SnCl_4$ into excited Sn atoms and radical Cl_2 species with the chlorine species etching the surface, producing volatile As chlorides and nonvolatile Ga chlorides.

IV. CONCLUSIONS

The main results of this study are: 1) MBE GaAs can be doped with Sn from a vapor phase source, 2) Sn films can be UV photolytically deposited from all four of the Sn compounds investigated in this work, 3) each of the Sn molecules adsorbed on GaAs (001) surfaces at room temperture, 4) each compound pyrolytically decomposed before desorbing, and 5) there appear to be complicated interface interactions occurring on adsorption, desorption and pyrolysis of these Sn-containing molecules on GaAs surfaces, which must be understood before practical application can be undertaken. Because the pyrolytic decomposition resulted in Sn films over the entire epilayer surface, none of the Sn compounds thus far investigated were found to be suitable for use in the proposed selected area doping scheme.

The key to further development of this proposed selected area doping process would be to find a Sn molecule which desorbs before it pyrolytically decomposes, i.e., one with stronger Sn-ligand bonding, but which is still very weakly physisorbed to GaAs (001). Other approaches to selective area doping may be possible. We have recently performed preliminary adsorption/desorption experiments on an As overlayer on GaAs, where it appears that the Sn molecule (DBTB) is more weakly adsorbed to the amorphous As surface than to the GaAs (001) surface. This suggests a selected area doping process that consists of making an As cap,[24] patterning the cap (e.g., by laser or electron beam desorption), adsorption of the desired Sn molecule, and thermal treatment (~ 580°C) which in the As capped areas results in clean GaAs via desorption of As and Sn molecules, and in the uncapped area results in metallic Sn via pyrolytic decomposition of the Sn molecule. GaAs regrowth would produce Sn doping in the selected areas. This approach is actually a hybrid of the method investigated in this paper and a previously proposed method[25] which involved As capping. This new approach would surmount the problem encountered here due to pyrolysis; it would, in fact, use pyrolytic decomposition to advantage and avoid the limitation due to the metallic Sn desorption mechanisms from As[26] in the earlier As cap technique. We are investigating this new approach in more detail.

ACKNOWLEDGEMENTS

This work was supported by the Army Research Office, Research Triangle Park, NC. The help of Dr. K. Hess in handling of organometallic compounds and of L.A. Wood for substrate preparation are greatly appreciated.

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FIGURE CAPTIONS

Fig. 1 The five steps of the proposed in situ selected area doping scheme for MBE GaAs.

Fig. 2 AES spectra for the adsorption/desorption experiments of several Sn molecules on GaAs (001): (a) tetramethyltin, 1. freshly MBE grown GaAs epilayer, 2. room temperature adsorption of TMT, 3. heated to 270°C, 4. heated to 570°C, and 5. MBE regrowth; (b) stannic chloride, 1. adsorption of $SnCl_4$ on an oxide surface, and 2. adsorption on a clean epilayer; (c) tetrabutyltin, 1. room temperature adsorption of TBT, 2. heated to 270°C, 3. heated to 600°C, and 4. MBE regrowth.

Fig. 3 Relative AES intensity ratios for TMT and $SnCl_4$ on GaAs (001) as a function of thermal treatment.

Fig. 4 (a) C-V profile and (b) SIMS carbon, oxygen and Sn profile through an epilayer which had Sn incorporated from pyrolytic decomposition of TMT on GaAs, followed by MBE regrowth after the decomposition.

Fig. 5 XPS spectra for films from UV photolytic deposition from $SnCl_4$: (a) thick film and (b) thin film.

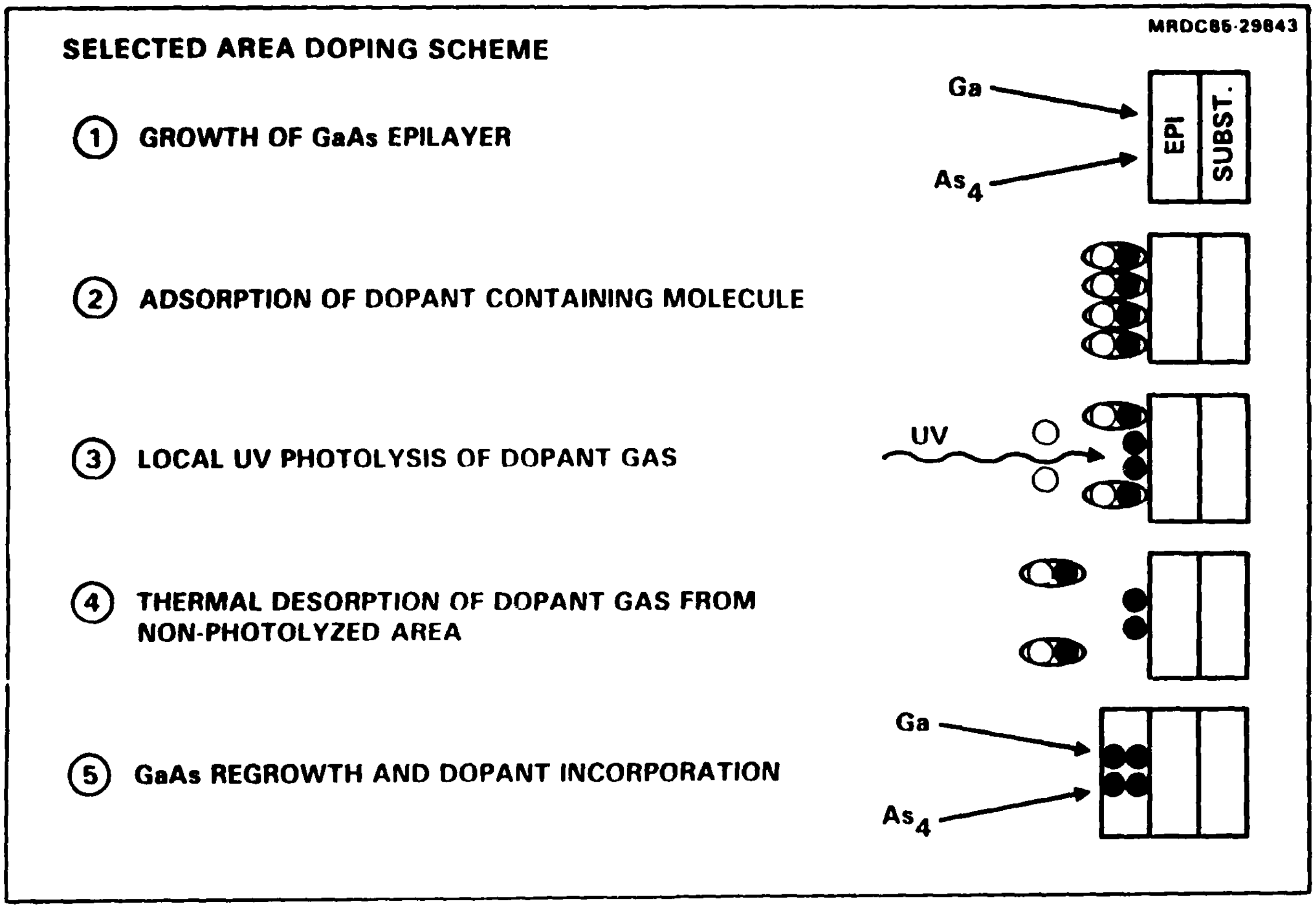
MRDC85-29843
SELECTED AREA DOPING SCHEME
① GROWTH OF GaAs EPILAYER
② ADSORPTION OF DOPANT CONTAINING MOLECULE
③ LOCAL UV PHOTOLYSIS OF DOPANT GAS
④ THERMAL DESORPTION OF DOPANT GAS FROM NON-PHOTOLYZED AREA
⑤ GaAs REGROWTH AND DOPANT INCORPORATION
Ga
As4
EPI
SUBST.
UV
Ga
As4

Figure 1.

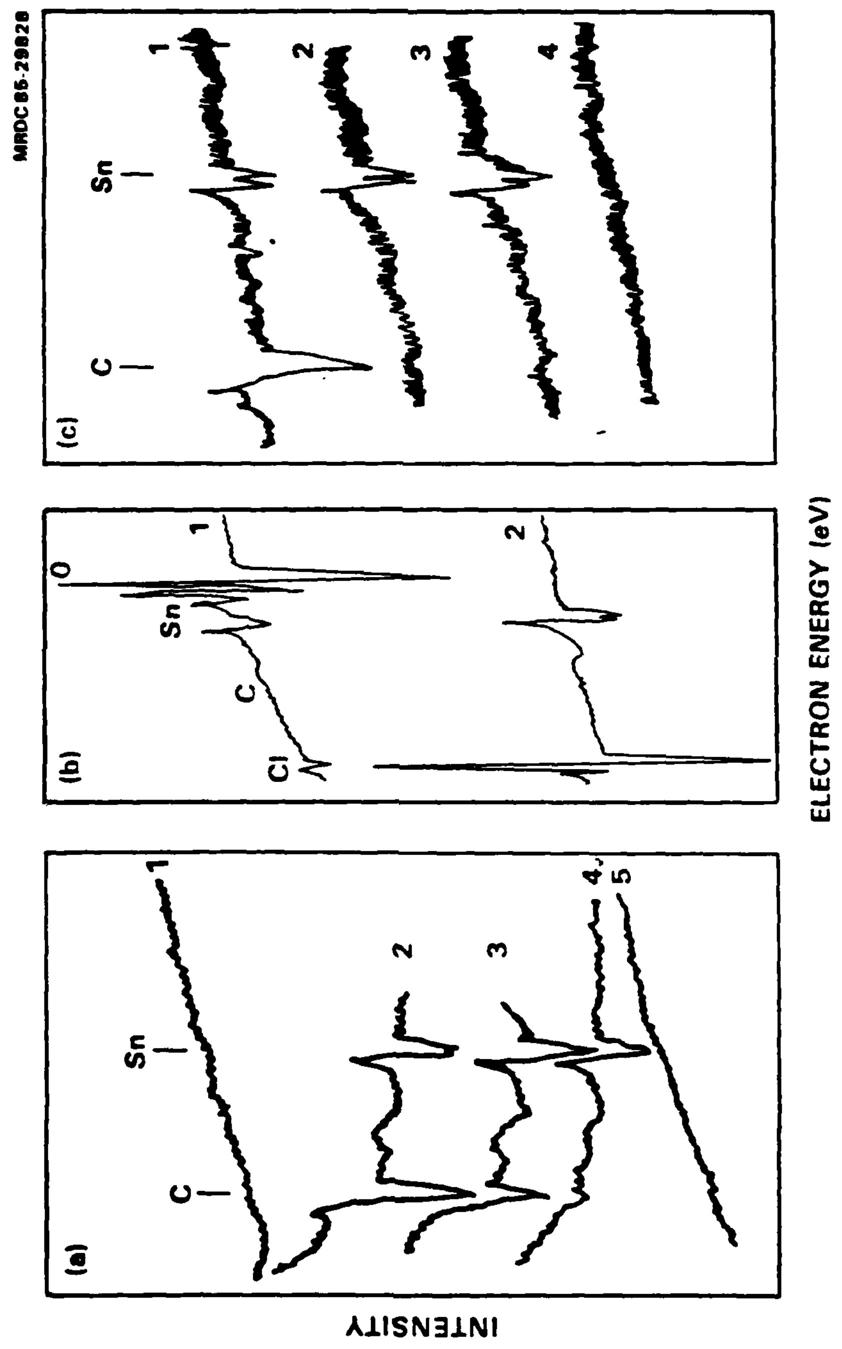
MRDC86-29828
(a)
C
Sn
1
2
3
4
5
(b)
Cl
C
Sn
O
1
2
(c)
C
Sn
1
2
3
4
INTENSITY
ELECTRON ENERGY (eV)

Figure 2.

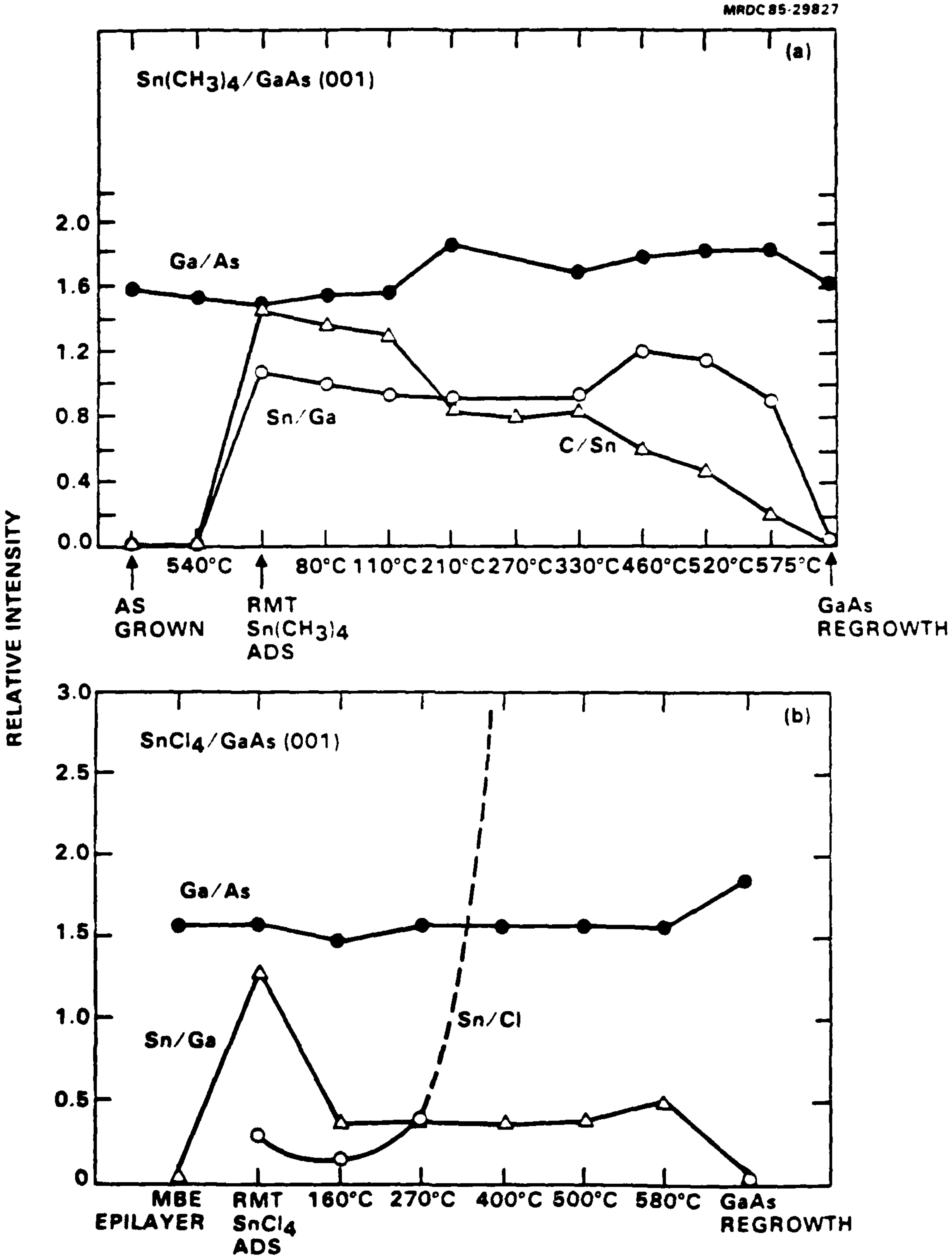
MRDC 85-29827
(a)
Sn(CH3)4/GaAs (001)
2.0
1.6
1.2
0.8
0.4
0.0
Ga/As
Sn/Ga
C/Sn
540°C
80°C
110°C
210°C
270°C
330°C
460°C
520°C
575°C
AS GROWN
RMT Sn(CH3)4 ADS
GaAs REGROWTH
RELATIVE INTENSITY
(b)
SnCl4/GaAs (001)
3.0
2.5
2.0
1.5
1.0
0.5
0
Ga/As
Sn/Ga
Sn/Cl
MBE EPILAYER
RMT SnCl4 ADS
160°C
270°C
400°C
500°C
580°C
GaAs REGROWTH

Figure 3.

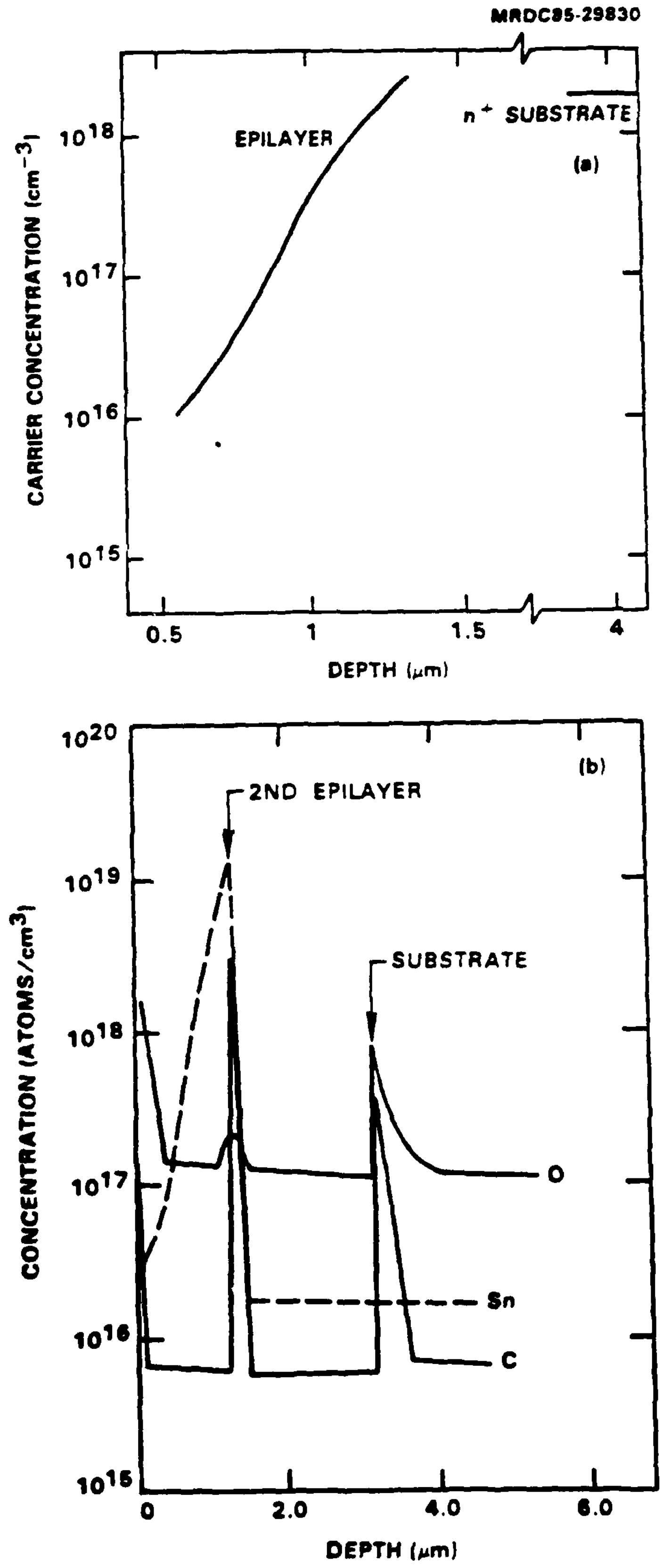
MRDC85-29830
CARRIER CONCENTRATION (cm^{-3})
10^{18}
10^{17}
10^{16}
10^{15}
EPILAYER
n^{+} SUBSTRATE
(a)
0.5
1
1.5
4
DEPTH (μm)
CONCENTRATION (ATOMS/cm^{3})
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
(b)
2ND EPILAYER
SUBSTRATE
O
Sn
C
0
2.0
4.0
6.0
DEPTH (μm)

Figure 4.

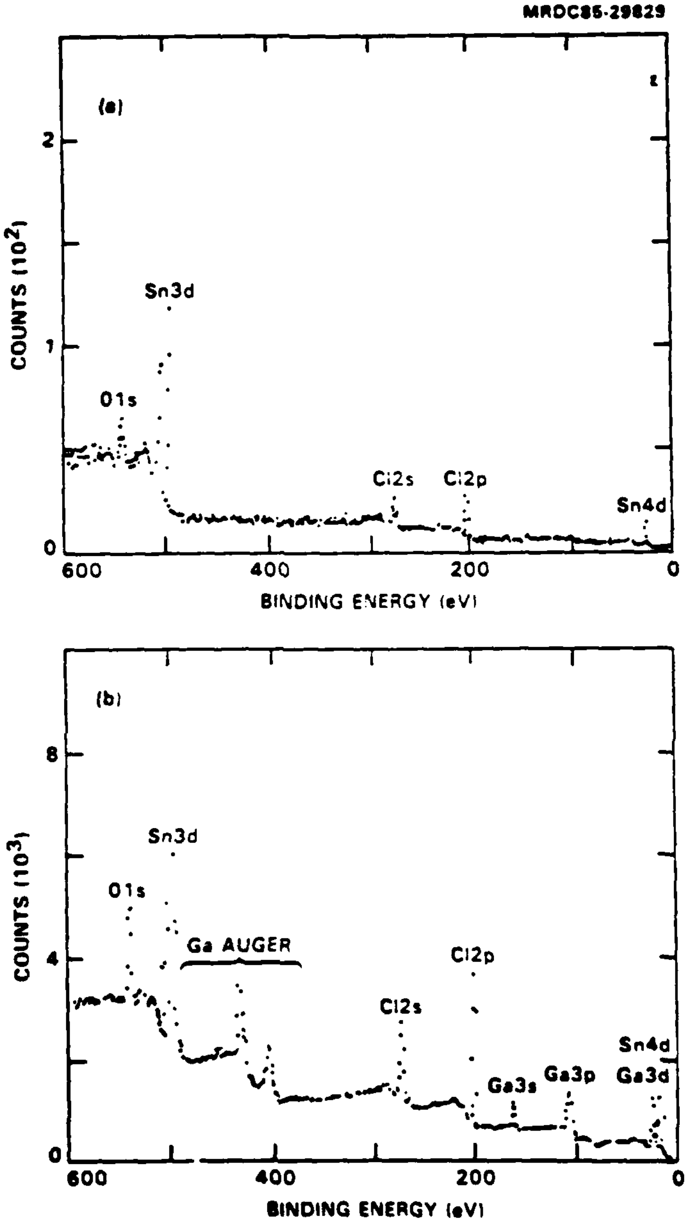
MRDC85-29829
(a)
COUNTS (10^2)
0
1
2
Sn3d
O1s
Cl2s
Cl2p
Sn4d
600
400
200
0
BINDING ENERGY (eV)
(b)
COUNTS (10^3)
0
4
8
Sn3d
O1s
Ga AUGER
Cl2s
Cl2p
Ga3s
Ga3p
Sn4d
Ga3d
600
400
200
0
BINDING ENERGY (eV)

Figure 5.

APPENDIX II

ARESENIC PASSIVATION OF GaAs AND PYROLYTIC DECOMPOSITION OF ORGANOTIN COMPOUNDS FOR IN SITU SELECTED AREA DOPING OF GaAs MOLECULAR BEAM EPITAXY

(Abstract submitted for
The Sixth Molecular Beam Epitaxy Workshop,
Minneapolis, August 14-16, 1985)

ARSENIC PASSIVATION OF GaAs AND PYROLYTIC DECOMPOSITION OF ORGANOTIN COMPOUNDS FOR IN SITU SELECTED AREA DOPING OF GaAs MOLECULAR BEAM EPITAXY

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Development of in situ selected area doping techniques would add a powerful new dimension to GaAs MBE technology. The selected area doping procedure which we report here consists of the following steps: (1) MBE growth of GaAs on a clean GaAs (001) substrate, (2) adsorption of an As passivation cap which would be patterned for selected area doping, (3) adsorption of an organotin compound, (4) thermal desorption of the organotin compound along with the As cap in the passivated areas and with pyrolytic decomposition of the organotin compound in the unpassivated regions, and (5) regrowth of GaAs with selected area Sn incorporation into the regrowth layer. In this process, the As layer acts much like the photoresist in a conventional liftoff process.

In this study of the proposed selected area doping process, we evaluated steps (3) - (5). The patterning of the As (Step (2)) could be done in a number of ways, e.g., evaporation through a mask, laser desorption, etc. Steps (3) and (4) were investigated by means of in situ Auger electron spectroscopy (AES) and Step (5) by electrolytic C-V profiling of the carrier concentration. The organotin compounds used in this study were tetrabutyltin (TBT) and dibutyltin dibromide (DBTDB). Previous studies have shown that TBT and DBTDB adsorb on GaAs(001) surfaces in the 1-2 monolayer range. Upon thermal treatment these compounds pyrolytically decompose resulting in a Sn layer on the GaAs surface.[1] In the present study adsorption of TBT and DBTDB on the As passivation layer resulted in considerably less adsorption than on the GaAs surface. The adsorbed organotin compound ranged from below AES detection limits to 1/2 the amount adsorbed on the GaAs surface. Upon regrowth of GaAs after As desorption, C-V profiles showed significantly less carrier concentration than for the unpassivated surfaces, but the carrier concentration was not as low as expected from the AES measurements.

ACKNOWLEDGEMENTS

This work was supported by the Army Research Office, Research Triangle, North Carolina.

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APPENDIX III

PHOTOCHEMICAL ETCHING DURING ULTRAVIOLET PHOTOLYTIC DEPOSITION OF METAL FILMS ON SEMICONDUCTOR SURFACES

(Preprint)

PHOTOCHEMICAL ETCHING DURING ULTRAVIOLET PHOTOLYTIC DEPOSITION OF METAL FILMS ON SEMICONDUCTOR SURFACES

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ABSTRACT

UV photochemical deposition of Sn films on GaAs (001) surfaces from a variety of tin containing compounds (tetramethyltin, tetrabutyltin, dibutyltin dibromide, stannic chloride, hexamethylditin, dibutyltin sulfide, and iodotrimetyltin) was studied. X-ray photoelectron spectroscopy showed that during the initial stages of deposition from the halogenated compounds, the GaAs surface was photochemically etched, most likely by a halogen radical species. The photochemical etching resulted in an arsenic deficient surface which was particularly dramatic for the case of $SnCl_4$. These results have important implications for the choice of sources for photochemical deposition when the metal-semiconductor interface is important and for photochemical etching if stoichiometric surfaces are required.

The availability of excimer lasers with high intensities in the UV region has resulted in the development of the field of UV initiated microchemistry at surfaces. There are many important applications in the area of microfabrication for solid state electronics. One of the most vigorous areas of investigation of the uses of laser microelectronic processing is the deposition of delineated metal films by UV photolysis of gas-phase metal compounds, particularly organometallics.[1-10] A number of fundamental issues such as film purity and beam induced interactions with the surface must be addressed before such techniques can be used as a reliable device processing tool. In this paper we report the observation by X-ray photoelectron spectroscopy (XPS) of photochemical etching of GaAs surfaces during the initial stages of UV photolytic deposition of tin from some of the gas-phase tin compounds being screened as possible tin sources.

The experimental method used to photolytically deposit Sn films on GaAs surfaces is shown schematically in Fig. 1. Approximately 0.1 ml of a tin containing compound (all the compounds used in this study were liquids at room temperature and atmospheric pressure) was placed in a quartz ampoule and sealed. This procedure was done in a glove bag filled with N_2. The tin containing compounds investigated were tetramethyltin, tetrabutyltin, hexamethylditin, dibutyltin dibromide, stannic chloride, dibutyltin sulfide and iodotrimethyltin.[11] The samples were irradiated with UV light from an array of five low pressure Hg (A) lamps (main line at 2536.5)[12] for 30 m under the room temperature equilibrium vapor pressure of the tin compound and the N_2 in the sealed ampoule. The GaAs (001) surfaces were prepared by chemically etching the surface with a 4:1:1 H_2SO_4:H_2O_2:H_2O solution for approximately 1 m, quenching in flowing deionized water and blowing dry with N_2. The XPS experiments were performed with a Hewlett Packard HP5950A electron spectrometer system equipped with a AlK ($h\nu$ = 1486.6 eV) monochromatized x-ray source.

Tin films could be UV photolytically deposited from all of the tin containing compounds investigated here. However here we are primarily interested in studying the interactions at the interface during the formation of the initial interface. This is accomplished by depositing only a thin Sn film $<$ 30Å so that the metal-GaAs interface could be studied.[13,14] Figure 2 shows the XPS spectra of the surface of GaAs (001) after the chemical etching. This surface has a thin layer ($\sim$ 15Å) of mixed oxide As_2O_3 and Ga_2O_3.[15] It is onto this surface that tin is deposited. Elemental Sn has been shown previously to be nonreactive with GaAs.[13] Figure 3 shows the XPS spectrum after a thin Sn deposition from UV photodeposition of hexamethylditin. The spectrum shows that the underlying GaAs surface remains basically unreacted. Similar results were obtained for tetrabutyltin and dibutyltin sulfide. However, the halogenated tin compounds appeared to act differently (Figs. 4 and 5). $SnCl_4$ showed the most dramatic effect as can be seen in Fig. 4. The surface is greatly depleted in As. It appears likely that the UV photodecomposition of $SnCl_4$ results in a reactive chlorine radical species which etches the GaAs by forming chlorides, with the As chloride volatile and the Ga chloride nonvolatile at room temperature. These results are compatible with recent photochemical etching experiments with HCl[16] and plasma etching experiments with chlorinated hydrocarbons[17].

The implications of this work are twofold. First, in the interest of fabricating abrupt metal-semiconductor interfaces by means of UV photolytic deposition, the composition of the metal containing compound is important so as to preclude the formation of highly reactive species. Secondly, these experiments point out the complexity that may be involved in using UV induced photochemical etching of semiconductor surfaces.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Army Research Office, Research Triangle Park, N.C.

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FIGURE CAPTIONS

Fig. 1 Schematic of UV photolytic deposition of Sn on GaAs surfaces from vapor phase of tin containing compounds.

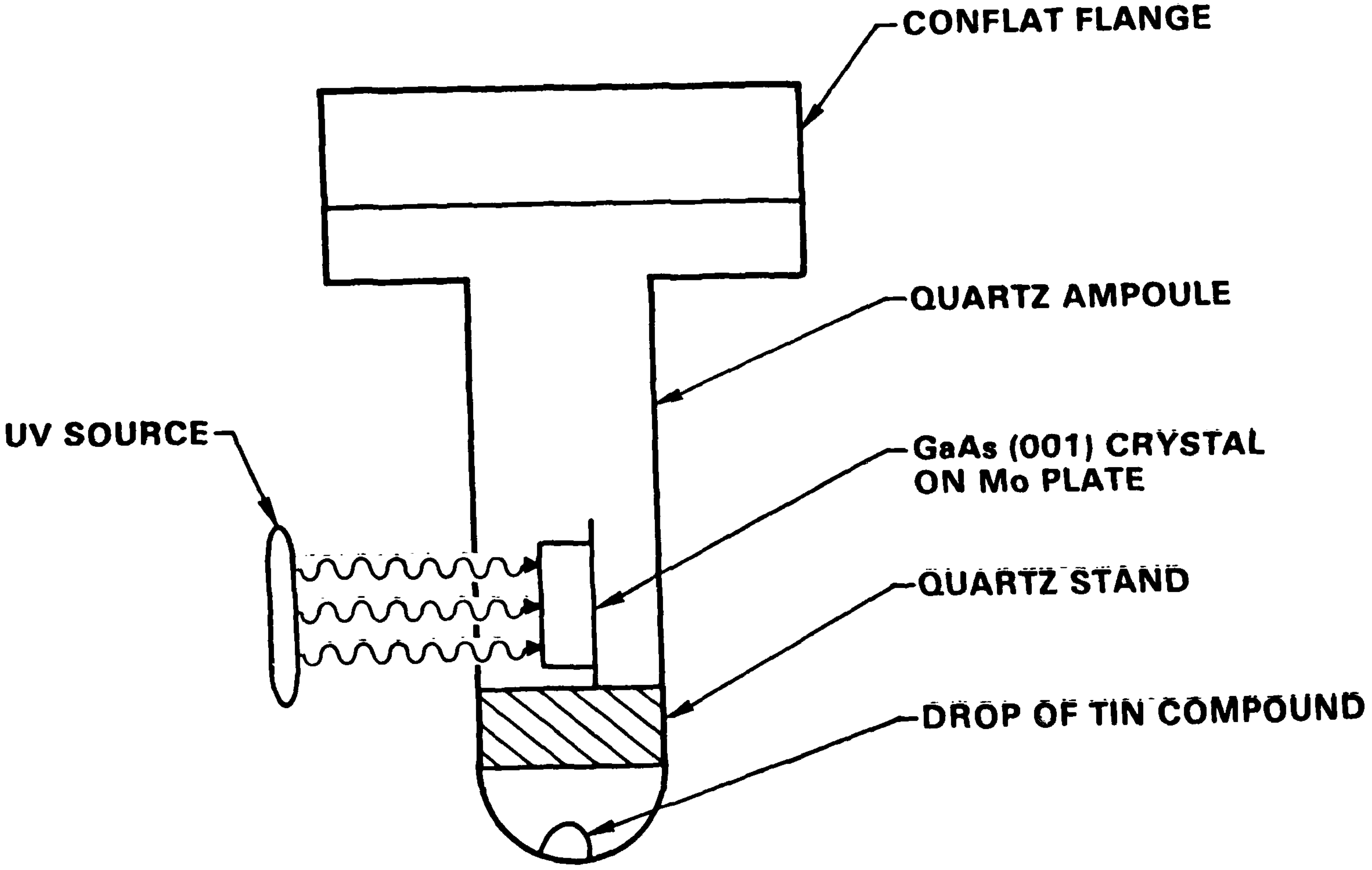
Fig.2 XPS spectrum of the Ga3d and As3d region from a GaAs surface after the standard wet chemical etch.

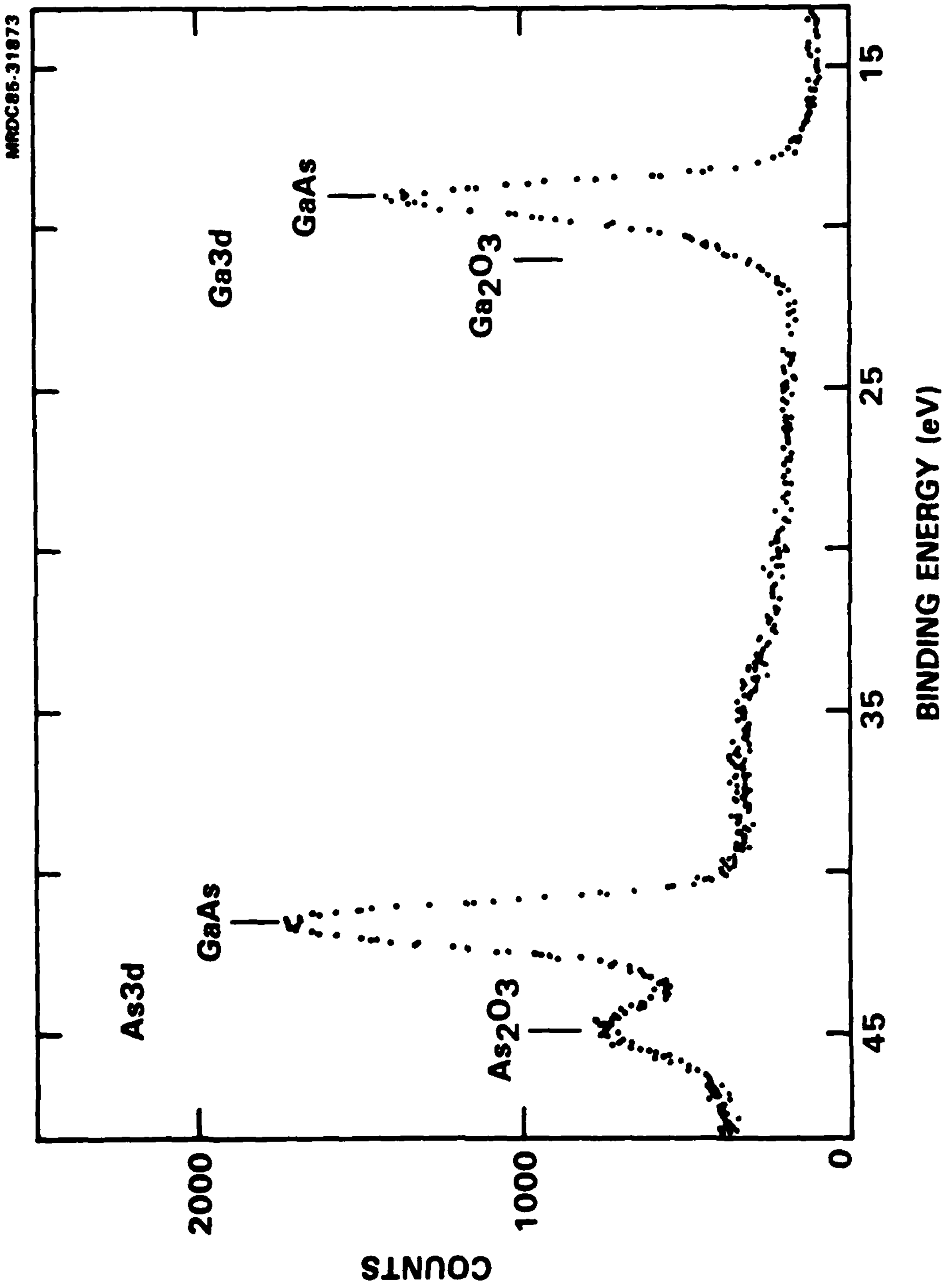
Fig. 3 XPS spectrum of the Ga3d, Sn4d and As3d region after UV photodepositon of a thin Sn film from hexamethylditin on a chemically etched GaAs (001) surface.

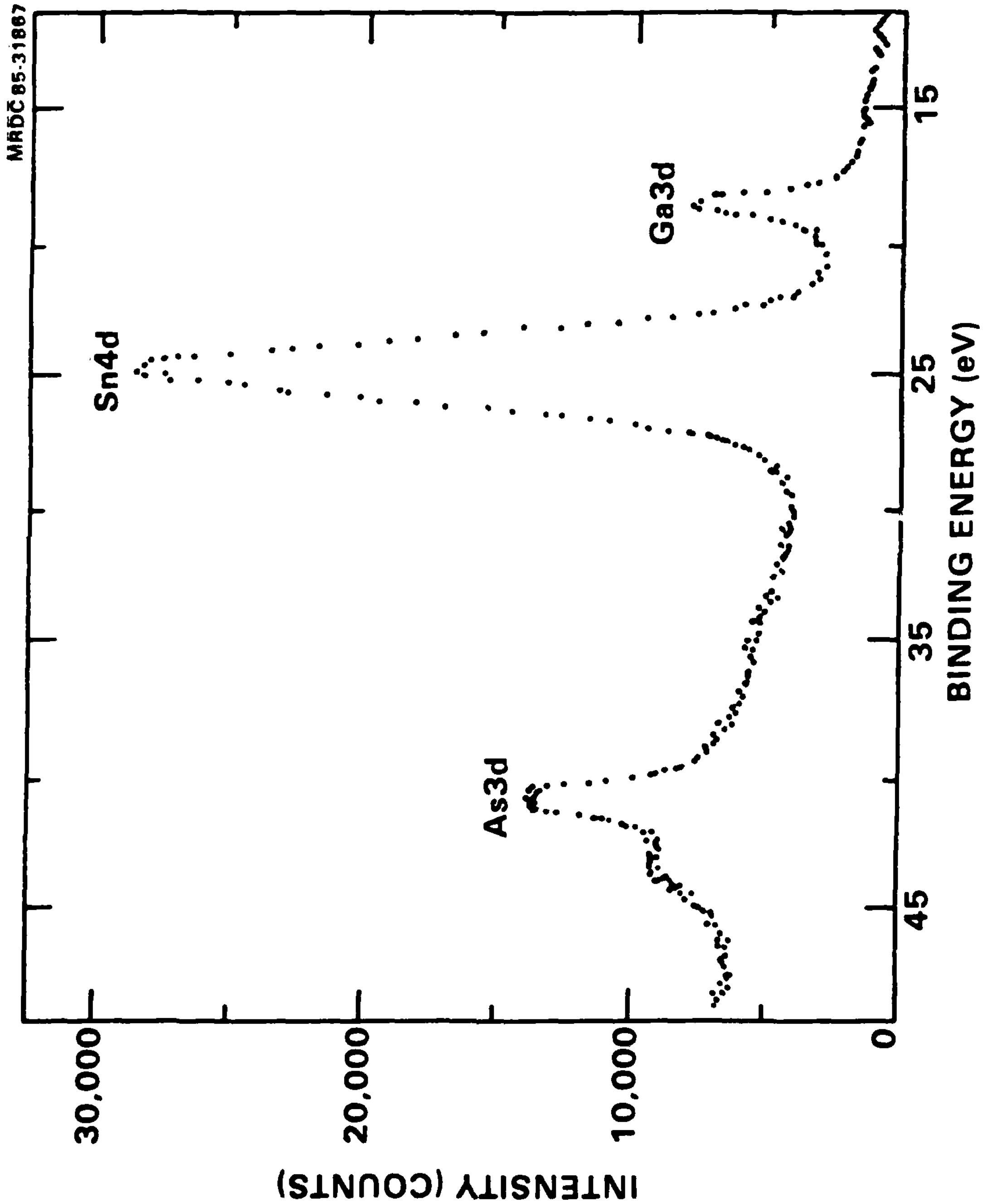
Fig. 4 XPS spectrum of the Ga3d, Sn4d and As3d region after UV photodeposition of a thin Sn film from $SnCl_4$ on a chemically etched GaAs (001) surface.

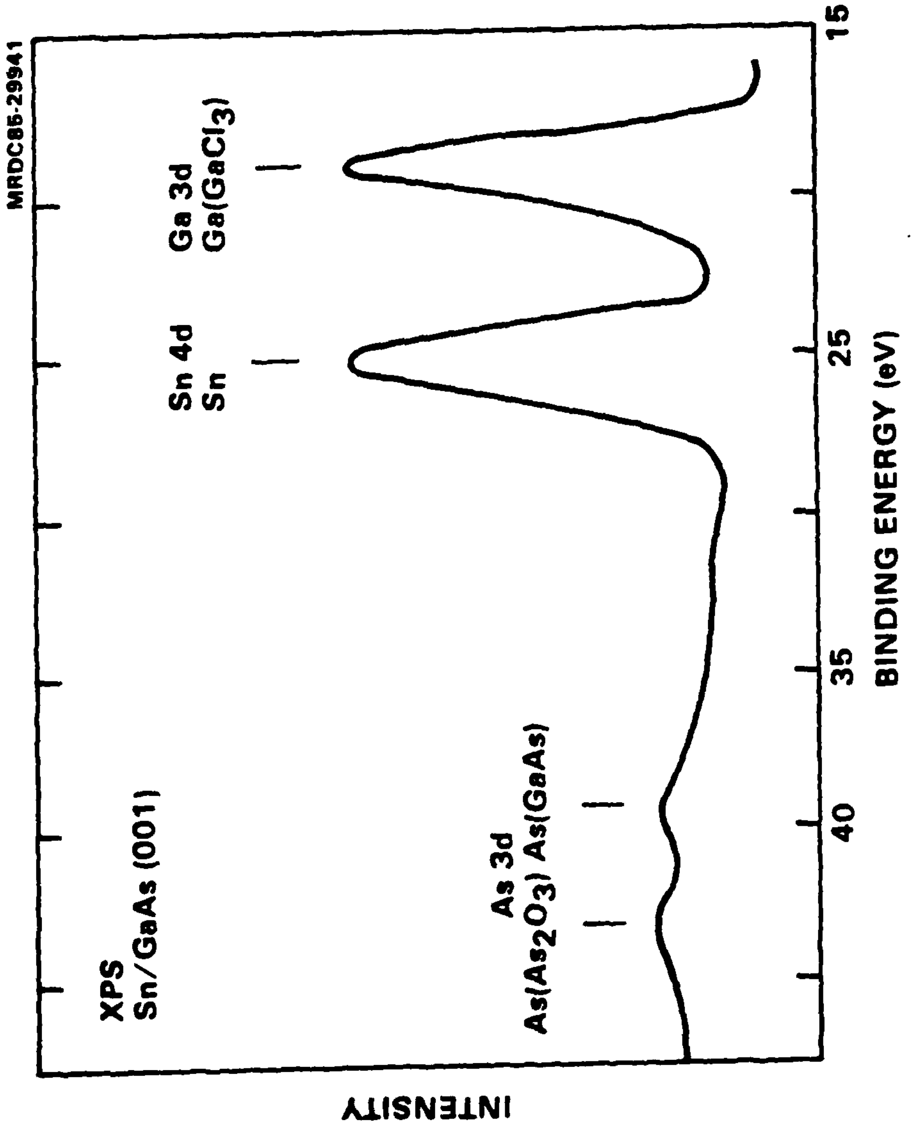
Fig. 5 XPS spectrum of the Ga3d, Sn4d, As3d and I4d region after UV photodeposition of a thin tin film from iodotrimetyltin on a chemically etched GaAs (001) surface.

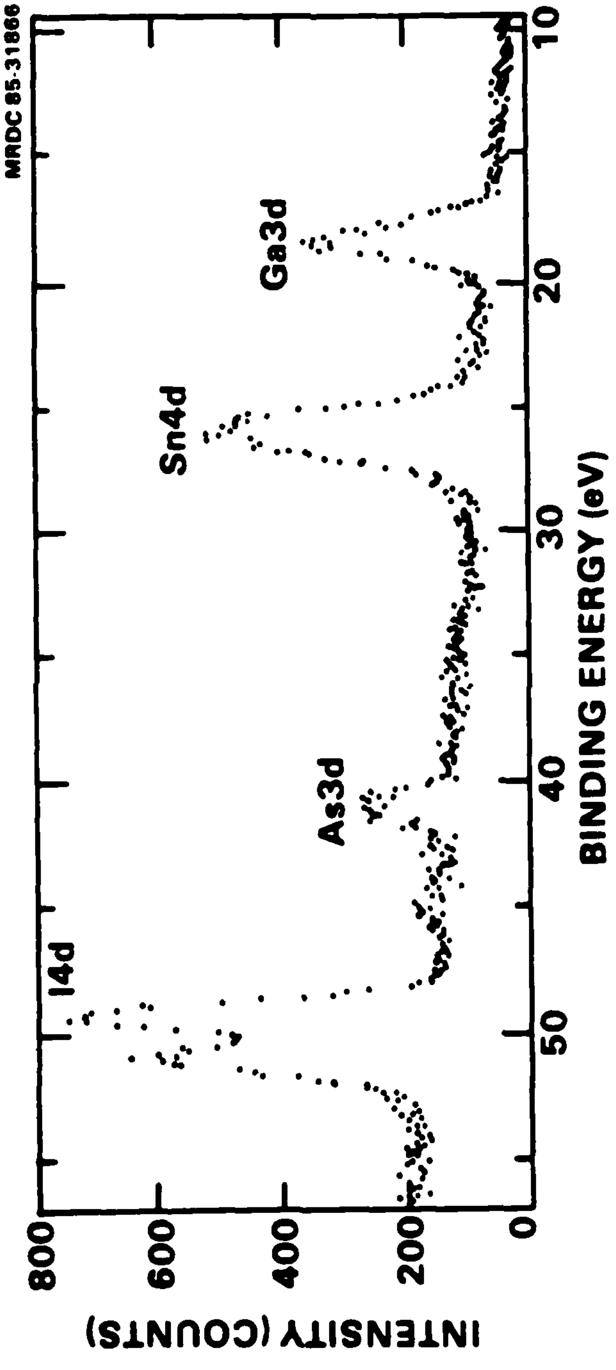
MRDC85-31854




MRDC85-31873
Ga3d
GaAs
Ga_2O_3
As3d
GaAs
As_2O_3
COUNTS
2000
1000
0
BINDING ENERGY (eV)
15
25
35
45


MRDC 85-31867
Sn4d
Ga3d
As3d
15
25
35
45
BINDING ENERGY (eV)
30,000
20,000
10,000
0
INTENSITY (COUNTS)


MRDC85-29941
XPS
Sn/GaAs (001)
Sn 4d
Sn
Ga 3d
Ga(GaCl$_3$)
As 3d
As(As$_2$O$_3$) As(GaAs)
15
25
35
40
BINDING ENERGY (eV)
INTENSITY


MRDC 85-31866
I4d
As3d
Sn4d
Ga3d
INTENSITY (COUNTS)
800
600
400
200
0
BINDING ENERGY (eV)
50
40
30
20
10

APPENDIX IV

ARSENIC PASSIVATION OF GaAs AND PYROLYTIC DECOMPOSITION OF ORGANOTIN COMPOUNDS FOR IN SITU SELECTED AREA DOPING OF GaAs MOLECULAR BEAM EPITAXY

(Preprint)

MRDC41135.4FR

ARSENIC PASSIVATION OF GaAs AND PYROLYTIC DECOMPOSITION OF ORGANOTIN COMPOUNDS FOR IN SITU SELECTED AREA DOPING OF GaAs MOLECULAR BEAM EPITAXY

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ABSTRACT

Development of *in situ* selected area doping techniques would add a powerful new dimension to GaAs MBE technology. We report here a study of a *in situ* selected area doping procedure based on the following steps: (1) MBE growth of GaAs on a clean GaAs (001) substrate, (2) adsorption of an As passivation cap which would be patterned for selected area doping, (3) adsorption of an organotin compound, (4) thermal desorption of the organotin compound along with the As cap in the passivated areas and with pyrolytic decomposition of the organotin compound in the unpassivated regions, and (5) regrowth of GaAs with selected area Sn incorporation into the regrowth layer. In this study we evaluated steps (3)-(5). Steps (3) and (4) were investigated by means of *in situ* Auger electron spectroscopy and step (5) by electrolytic C-V profiling of the carrier concentration. The organotin compounds used in this study were tetrabutyltin and dibutyltin dibromide.

INTRODUCTION

Molecular Beam Epitaxy (MBE) technology has become an important fabrication technique for fast GaAs device structures such as high electron mobility transitors and heterojunction bipolar transitors. The strength of the MBE technique is due to the high controllability of layer thickness, composition and purity. An important advance in MBE technology would be the addition of lateral dimension capability such as selected area doping, particularly if such a process was done in situ to maintain the advantage of the ultra-high vacuum environment of MBE. Such a capability would greatly enhance MBE and permit development of new device structures. There have been a number of previous approaches to selected area processing for MBE of GaAs.[1-6] In this paper, we report an investigation of an in situ selected area doping process which is a hybrid of two previous approaches.[5,6]

The selected area doping process proposed here for doping MBE GaAs with Sn is shown schematically in Fig. 1 and consists of the following steps: (1) standard MBE growth of a GaAs buffer epilayer on a clean GaAs (001) substrate, (2) adsorption of an As passivation cap (~1000Å) which for selected area doping would be patterned, (3) adsorption of an organotin compound, (4) desorption of the organotin compound with the As cap in the passivated areas and simultaneous pyrolytic decomposition of the organotin compound in the unpassivated areas of the GaAs resulting in a clean GaAs surface in the passivated regions and a layer of Sn in the unpassivated regions, and (5) regrowth of GaAs with Sn incorporation as n-type dopant into the regrowth layer in the region which had been unpassivated. In this process, the As layer acts much like the photoresist in a conventional lift-off process.

Before implementation of such a process the basic interactions in the key steps of the process must be understood. In this study we have concentrated primarily on steps (3) and (4) with some work on step (5). The technique of As capping has been studied previously as a way for passivation of GaAs, AlAs, and InAs surfaces[7-10] and as a way for GaAs regrowth in MBE.[11-13] The As cap has been studied as a "lift-off" mask for elemental tin in a selected area doping process[5] but was only partially successful due to the fact that the elemental Sn does not fully "lift-off" with the As.[11] In a previous study of adsorption of organotin compounds it was suggested that organotin compounds might have a much smaller sticking coefficient on As passivated GaAs surfaces than on clean GaAs surfaces.[6] This in conjunction with the observation of pyrolytic cracking of organotin compounds[6] suggested the selected area doping process proposed above. Thus it was important to study the adsorption of organotin compounds on As and their desorption and/or pyrolytic cracking on As which are key to steps (3) and (4). In this study we use in situ Auger electron spectroscopy (AES) to investigate steps (3) and (4) and C-V profiling was used to study Sn incorporation in step (5).

EXPERIMENTAL ASPECTS

The MBE system used in this study was a three chambered, cyropumped, liquid nitrogen shrouded homebuilt apparatus. The three chambers consist of a load-lock chamber for fast introduction of the GaAs substrate wafers into vacuum, an antechamber employed for initial degassing of substrates and for exposure of substrates to the organotin compounds via a variable controlled leak valve, and the main growth chamber equipped with vertically mounted open crucible MBE sources, the AES system, reflection electron diffraction system and a quadrapole mass spectrometer. Using standard MBE growth temperatures (~560-580°C) and As_4/Ga flux ratios with growth rates of ~ 1 μm/h, GaAs epilayers with unintentional doping levels ranging from ~5 × 10^{14} to 5 × 10^{15} atoms/cm^3 could be achieved.

The substrates were n^+ GaAs (001) wafers which after standard solvent degrease and chemical etch were mounted on a Mo substrate holder with In. The mounted wafers were given a spin etch with 10:1:1 $H_2O:H_2O_2:NH_4OH$, rinsed with a flowing deionized water rinse, and blown dry with N_2. After loading into the MBE system, the substrates were thermally degassed in the preparation chamber and then thermally cleaned in a As_4 flux in the growth chamber. Epitaxial growths were initiated on As stabilized surfaces.

Arsenic passivation layers[7] were prepared by bringing the edge of the substrate holder (with the substrate heater off) into contact with the liquid nitrogen-cooled shroud of the MBE system while the substrate remained within the central portion of the As_4 beam. It is necessary for the substrate to be slightly below room temperature for deposition of sufficiently thick As capping layers from As_4. Patterning of the As layer by masking the substrate by means of the system's shutter was only partially successful, probably due to As_4 vapor making several bounces from room-temperature surfaces to the shadowed GaAs surface.

Sn is one of the common *n*-type dopants for MBE GaAs. Because of its incorporation by means of a surface accumulation mechanism[14-17] it is well suited for the proposed process. If a small amount (~1 monolayer) can be deposited on a GaAs surface, upon regrowth of GaAs, Sn incorporates as a dopant into the regrowth layer. We have previously investigated the adsorption/desorption characteristics of a number of organotin compounds in conjunction with their use as sources for photochemical deposition of Sn on GaAs.[6,18] In the present study we have used two tin compounds, tetrabutyltin $(C_4H_9)_4Sn$ (TBT) and dibutyltin dibromide $(C_4H_9)_2SnBr_2$ (DBTDB).[19] Their adsorption/desorption characteristics on As layers and on GaAs (001) surfaces were studied. All the adsorptions were performed on room temperature substrates with ~30 m exposures to the 100°C equilibrium vapor pressure of TBT and DBTDB. The adsorptions were studied by AES. After thermal treatments the surfaces were restudied by AES. After final thermal treatments (~560°C), GaAs was regrown on these surfaces. The carrier concentration of the regrowth layers were profiled by an electrolytic C-V technique.[20]

RESULTS AND DISCUSSION

Adsorption and desorption of TBT and DBTDB on GaAs (001) have previously been reported.[6] Both TBT and DBTDB adsorb on GaAs (001) at approximately the monolayer level, however, both pyrolytically crack before desorption, resulting in a Sn layer. Figure 2 shows a comparison of TBT adsorption on an As passivated layer with that on an atomically clean GaAs layer. The adsorptions were carried out under identical conditions. It can be seen in Fig. 2 that little or no TBT could be observed to stick on the As layer though some C contamination was observed. The C contamination was variable and depended on the state of the vacuum system. Figure 3 shows similar results for DBTDB. Figure 4 shows the result of an experiment in which As was deposited only on a portion of the wafer by shadowing it with a shutter. An unpassivated and As-passivated section of the same wafer were therefore exposed with results similar to Figs. 2 and 3. Little or no organotin compound is adsorbed on the As passivated surfaces, in contrast to what is observed on GaAs. After the As cap is desorbed, an essentially Sn-free surface is produced, while for unpassivated surfaces, a Sn layer is produced. These results were reproducible. One would thus expect to have significant differences in the Sn-derived carrier concentration profiles between As passivated and nonpassivated samples. Figure 5 shows the best results that were obtained. Differences approaching an order of magnitude were observed. However, run-to-run reproducibility was not good. Also, the doping differential achieved between the passivated and unpassivated surfaces has not been as large as expected from the AES results.

The reasons for these problems are not yet understood but there are several possible contributions. One is that great care must be taken so that a high Sn background is not built up in the growth chamber. In the course of these experiments and those of Ref. 6, we have observed that this problem is particularly severe with the halogenated Sn compounds. After use of a halogenated compound, the preparation chamber and gas inlet manifold required thorough bakeout before a different gas could be used. Our experience also suggests that the halogenated compounds should be avoided when using In to mount substrates. After exposure of samples to halogenated compounds we have often observed In on the sample surface probably due to the halogen reacting with the In to form a volatile and mobile In halide species. We find that this In species is desorbed from the surface at growth temperatures. Finally we note that we have not investigated whether there is an optimum thickness for the As passivation layer.

CONCLUSIONS

Exposure of GaAs (001) surfaces passivated by a layer of As to either TBT or DBTDB resulted in little if any adsorption of the molecules as detected by means of AES. Desorption of the As passivation cap resulted in a GaAs surface essentially free of Sn. GaAs surfaces given the same exposure of TBT or DBTDB were shown to have about a monolayer of these molecules adsorbed. Thermal treatment resulted in pyrolytic cracking of the organotin compound producing a GaAs surface coated with a layer of Sn. C-V profiling exhibited a difference in the carrier concentration between these two types of surface, thus demonstrating a selected area doping process.

ACKNOWLEDGEMENTS

This work was supported by the Army Research Office, Research Triangle Park, North Carolina.

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20. Polaron Instruments semiconductor profile plotter. See for example, T. Ambridge and M.M. Faktor, J. Appl. Electrochem. 5, 319, (1975).

FIGURE CAPTIONS

Figure 1. Steps in the proposed selected area doping process for MBE GaAs.

Figure 2. AES spectra in the CKLL, OKLL and Sn$M_4N_{45}N_{45}$, $M_5N_{45}N_{45}$ region. a) GaAs epilayer, a') As cap, b) TBT adsorption, c) 530°C thermal treatment, d) regrowth of GaAs.

Figure 3. AES spectra in the region of C, O, Sn, Ga and As lines. a) GaAs epilayer, a') As cap, b) DBTDB adsorption, c) 530°C thermal treatments.

Figure 4. AES spectra in the C, O, Sn, Ga and As lines. a) GaAs epilayer, b) As deposition, c) DBTDB adsorption. Left panel is for part of wafer which was masked during As cap deposition.

Figure 5a. C-V profile through GaAs regrowth layer after adsorption and pyrolysis of DBTDB. a) on GaAs epilayer, and b) on As cap layer.

Figure 5b. C-V profile through GaAs regrowth layer after adsorption and pyrolysis of TBT. a) on GaAs, and b) As cap layer.

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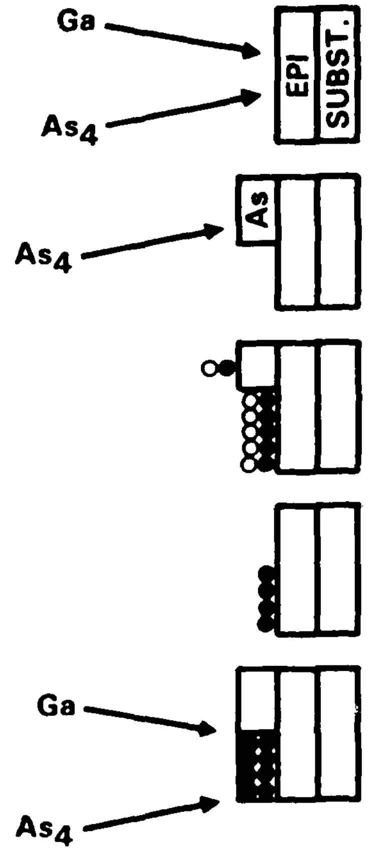
SELECTED AREA DOPING SCHEME



① GaAs EPILAYER GROWTH

② As PASSIVATION CAP DEPOSITION

③ ADSORPTION OF ORGANOTIN COMPOUND

④ DESORPTION OF As CAP/PYROLYSIS OF ORGANOTIN COMPOUND

⑤ GaAs REGROWTH AND Sn INCORPORATION

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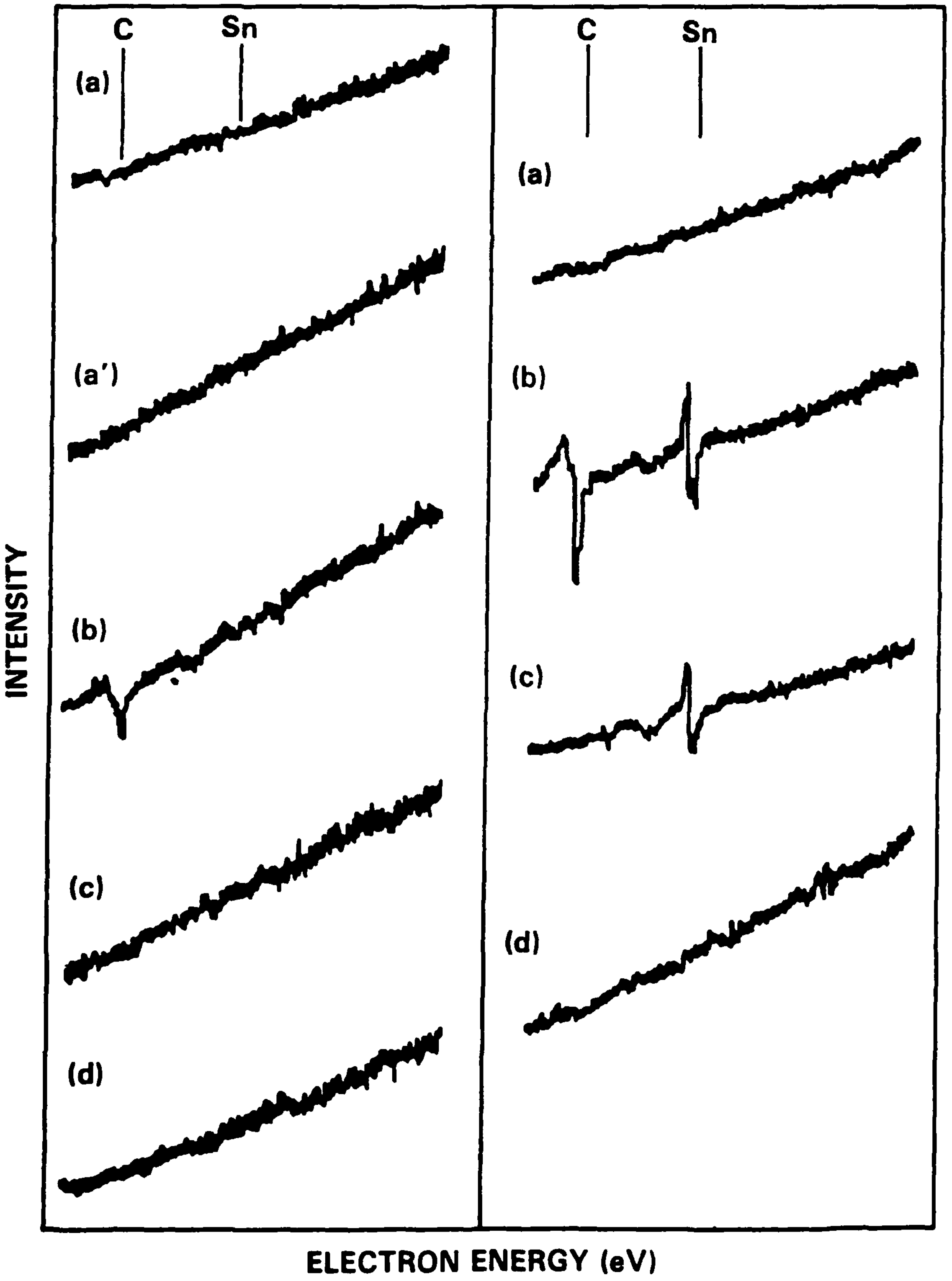

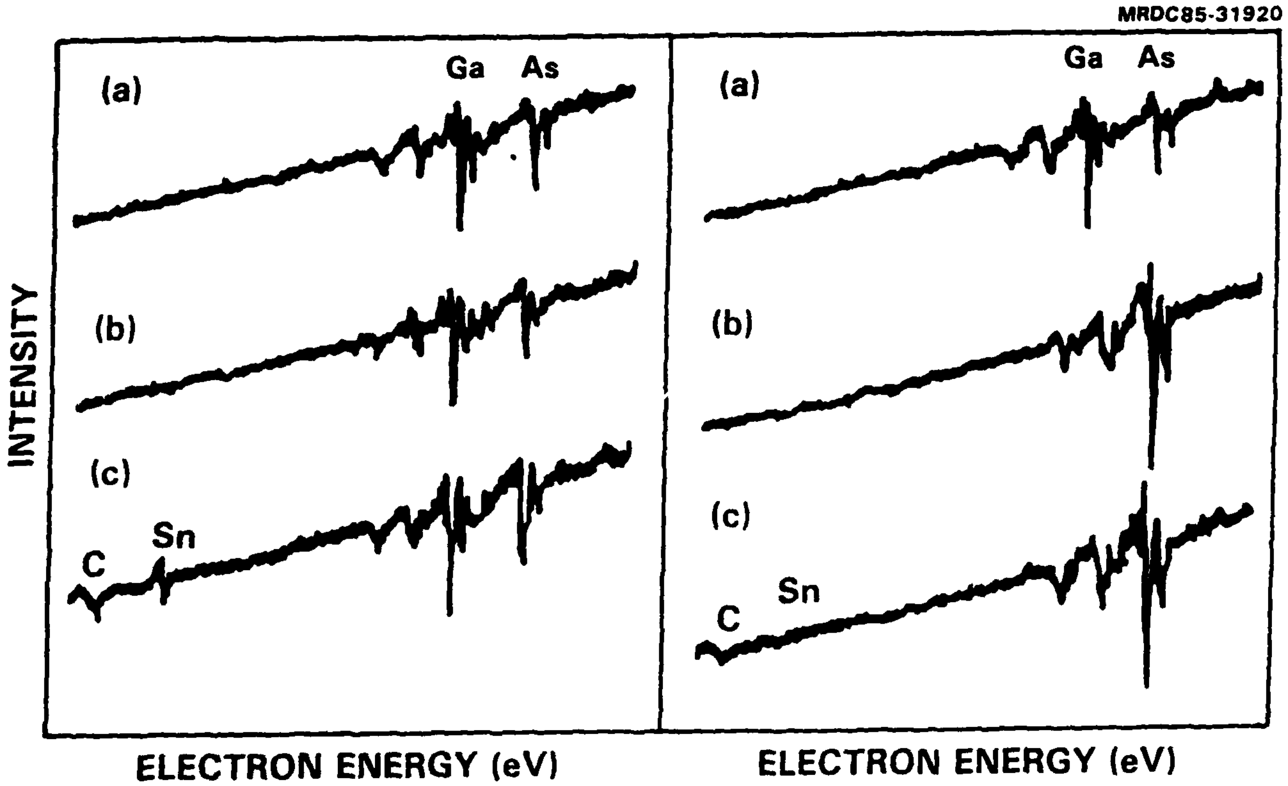
MRDC85-31920
INTENSITY
(a)
(b)
(c)
Ga
As
C
Sn
ELECTRON ENERGY (eV)
(a)
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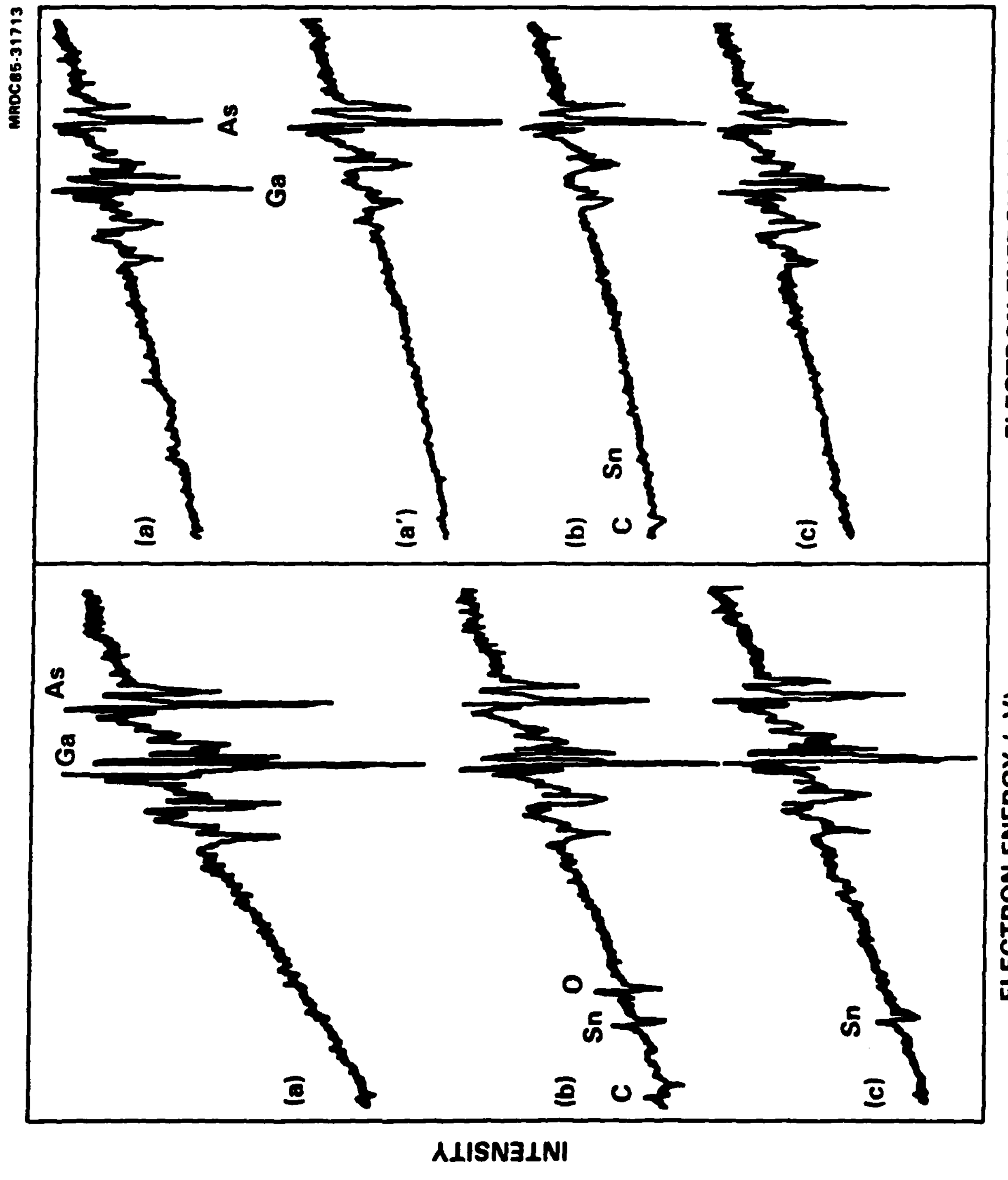
(c)
Ga
As
C
Sn
ELECTRON ENERGY (eV)



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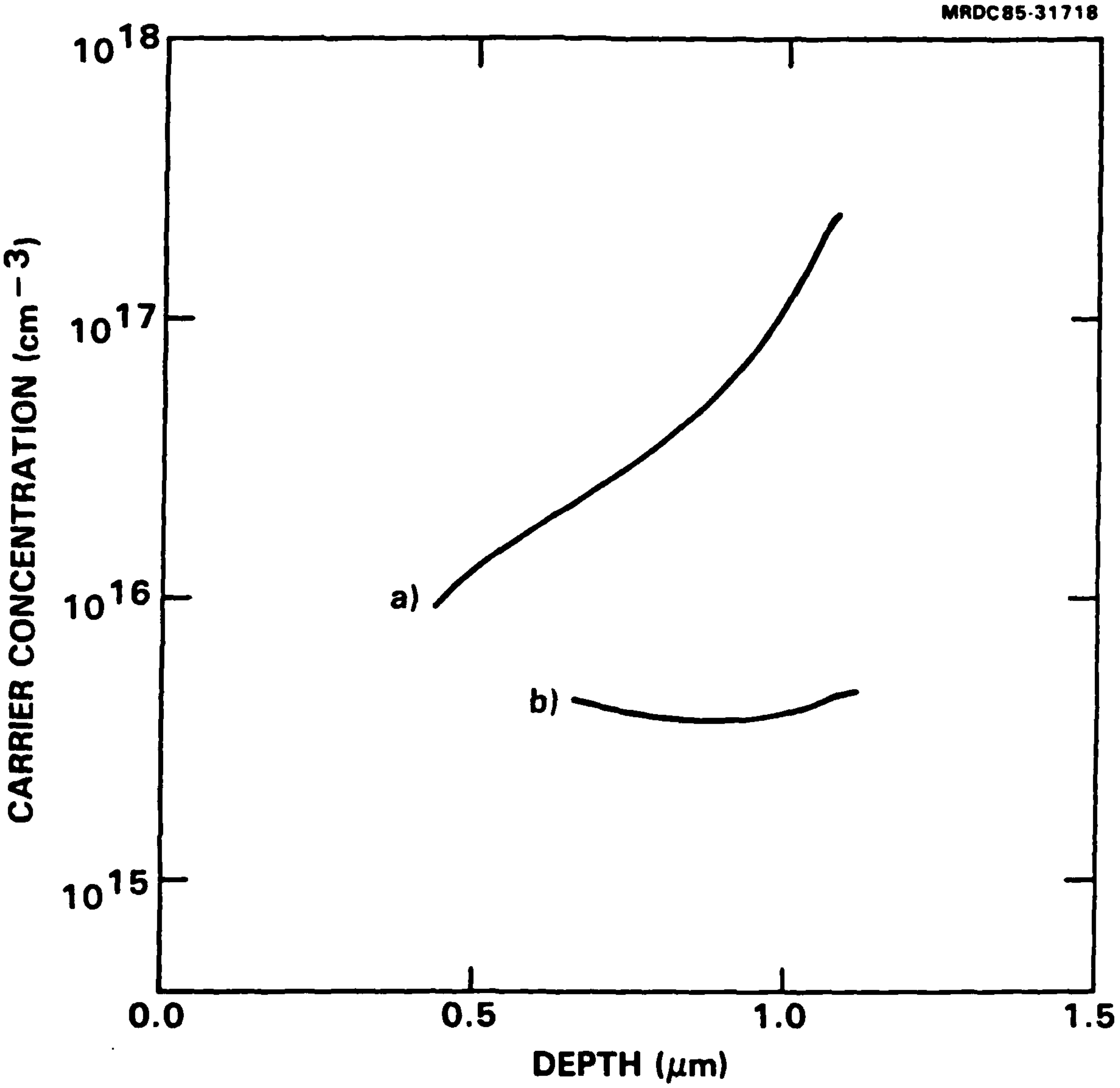
MRDC85-31718
10^{18}
10^{17}
10^{16}
10^{15}
CARRIER CONCENTRATION (cm^{-3})
a)
b)
0.0
0.5
1.0
1.5
DEPTH (µm)

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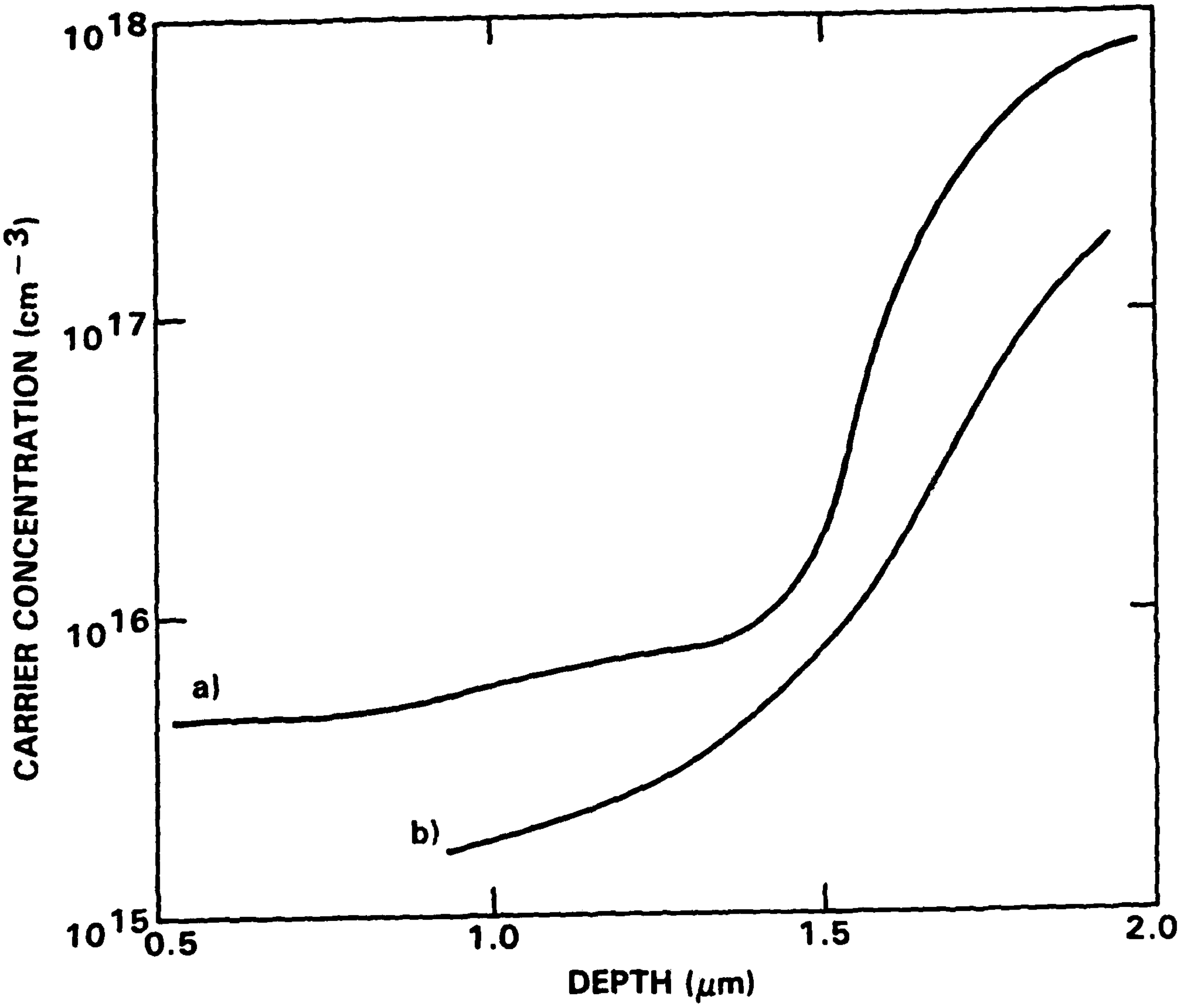

APPENDIX V

MBE GaAs REGROWTH WITH CLEAN INTERFACES BY ARSENIC PASSIVATION

(Reprint)

Summary Abstract: MBE GaAs regrowth with clean interfaces by arsenic passivation[a]

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(Received 15 September 1984; accepted 15 October 1984)

Techniques for interrupting the molecular beam epitaxy growth process in order to contact or modify layers already grown, while retaining a high-quality interface between the original and post-interruption growth, would be beneficial for many device applications. Previous investigations have shown that standard molecular beam epitaxy (MBE) substrate preparation procedures, consisting of chemical etches to clean the substrate followed by vacuum desorption of oxides, lead to free carrier loss at the substrate-epilayer interface.[1-3] Exposure of the clean surfaces of MBE-grown layers to the atmosphere results in adsorption of a layer of contaminants. The interface formed by regrowth of GaAs over this surface also shows a loss of free electrons in *n*-type material. Clean surfaces of MBE-grown GaAs may be passivated against such atmospheric contamination by the *in-situ* condensation of As.[4] Recently, Kawai *et al.*[5] have reported that substantial improvements of electronic properties of interfaces formed by regrowth of MBE GaAs over surfaces exposed to air and deionized water may also be obtained by first passivating the surfaces using thin arsenic layers condensed *in situ*.

We discuss here an extension of the experiments of Kawai *et al.* to include *p*-type material and the chemical identification of some interfacial contaminants.

We have used the combination of electrolytic carrier profiling, DLTS and SIMS, to measure the degree of surface passivation of GaAs provided by arsenic layers condensed in the MBE apparatus. We find that condensed arsenic layers can provide excellent passivation of GaAs to laboratory air and deionized water. The data are summarized in Table I. For passivated GaAs layers which had been exposed to vacuum or laboratory air, no interfacial carrier loss, DLTS signal, or SIMS impurity peak was observed. This implies that the arsenic passivation layers themselves contribute no measurable impurities to the interface, and provide excellent passivation to atmosphere oxidation or contamination. Exposure of arsenic-passivated layers to deionized water resulted in an apparent free electron loss of $\sim 2.5 \times 10^{10}/\text{cm}^2$ or acceptor increase of $1 \times 10^{10}/\text{cm}^2$ and the appearance of small and variable amounts of 11 (B), 12 (C), 24 (Mg), and 56 (Fe) at the regrowth interface. Arsenic-passivated layers, however, resulted in clearly superior interfaces in compari-

TABLE I. C-V, DLTS, and SIMS data for passivated and nonpassivated interfaces.

SAMPLE	SUBSTRATE TYPE	TREATMENT	CARRIER LOSS GAIN	DLTS	SIMS MASS PEAKS**					
					11(B)	12(C)	16(O)	24(Mg)	28(Si)	56(Fe)
1	n^+, Si	As PASSIVATION VACUUM EXPOSURE	$< 5 \times 10^9/\text{cm}^2$ *	$< 4 \times 10^9/\text{cm}^2$ *	N.D.	N.D	N.D	N.D.	N.D	N.D
2	n^+, Se	As PASSIVATION AIR EXPOSURE	$< 5 \times 10^9/\text{cm}^2$ *	$< 4 \times 10^9/\text{cm}^2$ *	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3	n^+, Se	As PASSIVATION H_2O EXPOSURE	$2.5 \times 10^{10}/\text{cm}^2$	$< 4 \times 10^9/\text{cm}^2$ *	$2 \times 10^{10}/\text{cm}^2$	N.D.	N.D.	$4 \times 10^{10}/\text{cm}^2$	N.D.	$4 \times 10^{11}/\text{cm}^2$
4	n^+, Si	NO PASSIVATION ETCHED	$3.0 \times 10^{11}/\text{cm}^2$	$6 \times 10^9/\text{cm}^2$	$1 \times 10^{11}/\text{cm}^2$	$2 \times 10^{11}/\text{cm}^2$	$4 \times 10^{10}/\text{cm}^2$	N.D.	$4 \times 10^{11}/\text{cm}^2$	$4 \times 10^{11}/\text{cm}^2$
5	p^+, Zn	As PASSIVATION H_2O EXPOSURE	$(1 \times 10^{10}/\text{cm}^2)$	-	N.D.	$5 \times 10^{10}/\text{cm}^2$	N.D.	$4 \times 10^9/\text{cm}^2$	N.D	N.D
6	p^+, Zn	NO PASSIVATION ETCHED	$(5 \times 10^{10}/\text{cm}^2)$	$1 \times 10^{11}/\text{cm}^2$	N.D	$2 \times 10^{11}/\text{cm}^2$	$7 \times 10^{11}/\text{cm}^2$	$4 \times 10^{10}/\text{cm}^2$	$2 \times 10^{11}/\text{cm}^2$	$4 \times 10^{11}/\text{cm}^2$

* - DETECTION LIMIT
N.D. - NO PEAK DETECTED AT GROWTH-REGROWTH INTERFACE
** - SIMS CONCENTRATION CALIBRATIONS ARE APPROXIMATE
NUMBERS SHOULD BE USED FOR COMPARISON WITHIN THE TABLE ONLY

son with nonpassivated layers. For our typical wafer preparation scheme, which has an etch in $NH_4OH:H_2O_2:H_2O$ (1:1:10) and deionized water rinse as its final step, nonpassivated wafers had an electron loss at the interface of about $3\times10^{11}/cm^2$, an acceptor increase of $\sim5\times10^{10}/cm^2$ with $6\times10^9/cm^2$ deep donor levels, $1\times10^{11}/cm^2$ deep acceptor levels, and large 11 (B), 12 (C), 16 (O), 28 (Si), and 56(Fe) peaks observed as well. Even the water-exposed passivated layer had an interface with a much smaller perturbation in the carrier profiles and fewer detected impurities at the interface.

These experiments suggest that interfaces of GaAs grown by MBE with use of arsenic passivation, would be acceptable in many electron devices. This sequence in which layers are passivated with arsenic *in situ*, removed from the chamber for patterning or implantation, then returned to the MBE chamber for desorption of passivating layer and continued epitaxial growth, may result in devices with buried interfaces of superior quality.

Acknowledgments: The authors wish to thank Mr. P. G. Newman and Mr. L. A. Wood for assistance in MBE growth, Dr. Neng-Huang Sheng for assistance in DLTS measurements, and Dr. J. S. Harris and Dr. F. Eisen for encouragement and support. This work was partially supported by the U. S. Army Research Office.

[a] A more complete description of this work has been submitted for publication to the Journal of Applied Physics.

[1] C. E. C. Wood and B. A. Joyce, J. Appl. Phys. 49, 4953 (1970).

[2] A. Y. Cho and F. K. Reinhart, J. Appl. Phys. 45, 1812 (1974).

[3] N. J. Kawai, C. E. C. Wood, and L. F. Eastman, J. Appl. Phys. 53, 620 (1982).

[4] S. P. Kowalczyk, D. L. Miller, J. R. Waldrop, P. G. Newman, and R. W. Grant, J. Vac. Sci. Technol. 19, 255 (1981).

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APPENDIX VI

MOLECULAR BEAM EPITAXY GaAs REGROWTH WITH CLEAN INTERFACES BY ARSENIC PASSIVATION

(Reprint)

Molecular-beam-epitaxy GaAs regrowth with clean interfaces by arsenic passivation

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(Received 12 September 1984; accepted for publication 5 December 1984)

Clean interfaces between GaAs layers grown by molecular-beam epitaxy (MBE) have been achieved by deposition of arsenic on the surface of the first layer grown, before removing it from the vacuum. Secondary ion mass spectroscopy, deep level transient spectroscopy, and capacitance-voltage carrier profiling show that this arsenic passivation procedure results in no measurable impurity incorporation, no deep levels, and no perturbation of carrier profiles in either *n*-type or *p*-type GaAs growth/regrowth interfaces after exposure to air. This is in contrast to growth over nonpassivated etched surfaces which showed large perturbations in free carrier profiles, deep level densities, and impurity incorporation at the interface. This demonstrates that nearly ideal growth/regrowth interfaces are achievable in MBE if impurity incorporation and nonstoichiometry are controlled.

INTRODUCTION

Modern epitaxial semiconductor growth techniques such as molecular beam epitaxy (MBE) have the ability to create structures which controllably interleave multiple layers with a wide range of dopings or compositions. This allows the designer of III-V devices, for example, to create new material configurations for the purpose of improved device performance. Devices created in such a way include the modulation-doped transistor, heterojunction bipolar transistor, quantum well laser, and many others. These multilayer structures often pose difficulties, however, in device processing, which requires contacting buried layers or otherwise modifying layer properties after growth. Techniques for interrupting the epitaxial growth process in order to contact or modify layers already grown, while retaining a high-quality interface between the original and postinterruption growth, would be beneficial.

Previous investigations have shown that standard MBE substrate preparation procedures, consisting of chemical etches to clean the substrate followed by vacuum desorption of oxides, lead to free carrier loss at the substrate-epilayer interface.[1-3] Exposure of the clean surfaces of MBE-grown layers to the atmosphere results in adsorption of a layer of contaminants. The interface formed by regrowth of GaAs over this surface also shows a loss of free electrons in *n*-type material. Clean surfaces of MBE-grown compounds may be passivated against such atmospheric contamination by the *in situ* condensation of the higher vapor pressure element of the compound. The passivating layer may be removed by gentle heating. This has been reported for PbTe,[4] GaAs,[5-8] and AlAs.[5,9] These studies have focussed on surface cleanliness and atomic order, and have not reported the electronic properties of interfaces formed by regrowth over passivated surfaces. Recently Kawai *et al.*[10] have reported that substantial improvements in interfaces formed by regrowth of MBE GaAs over surfaces exposed to air and deionized water may be obtained by first passivating the surfaces using thin arsenic layers condensed *in situ*. They found arsenic passivation provided a large reduction in the carrier loss normally seen in carrier concentration depth profiles of regrowth interfaces in lightly doped ($2\times10^{16}/\mathrm{cm}^3$) *n*-type material.

We discuss here an extension of the experiments of Ref. 10 to include *p*-type material and the chemical identification of some interfacial contaminants. We have used electrolytic carrier concentration profiling to compare the interfaces of passivated and nonpassivated samples, both *n*-type and *p*-type. Deep level transient spectroscopy (DLTS) has been used to determine electron trap densities at the regrowth interfaces, and secondary ion mass spectroscopy (SIMS) has been used to identify interfacial contaminants.

We find here that condensed arsenic layers can provide excellent passivation of GaAs to laboratory air and deionized water. Interfaces which had been grown on passivated GaAs showed only a very small ($<2.5\times10^{10}/\mathrm{cm}^2$) donor compensation and no donorlike deep levels above our sensitivity limit of $4\times10^9/\mathrm{cm}^2$. SIMS analysis of these interfaces showed a large reduction in surface contamination otherwise obtained from our usual MBE substrate preparation practices.

EXPERIMENTAL PROCEDURE AND RESULTS

The first step in preparing the interfaces to be investigated was to grow 1.5 μm of GaAs, doped with Si or Be to about $1\times10^{16}/\mathrm{cm}^3$, on an n^+ (Si- or Se-doped) or p^+ (Zn-doped) GaAs substrate. This was done in a commercial MBE apparatus.[11] Substrates were prepared with a solvent degrease followed by an etch in hot H_2SO_4:H_2O_2:H_2O (7:1:1) for 30 s. This etch was quenched with deionized water followed by hot 2-propanol, and was dried with N_2 gas. The sample was then mounted to the substrate holder block with In. Just prior to insertion into the MBE load lock, the mounted substrate was etched for 20 s on a slow-speed spinner[12] in flowing NH_4OH:H_2O_2:H_2O (1:1:10) followed by a deionized water rinse while spinning. The sample was spun dry in laboratory air, and heated briefly to about 100 °C.

GaAs growth was done at a substrate temperature of 600 °C, at a rate of 1 μm/h, with an As_4/Ga beam-equiva-

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lent-pressure ratio of about 16:1. This resulted in an As-stabilized surface reconstruction observed with reflection electron diffraction.

The underlying epitaxial growth was terminated by shutting the Ga beam shutter and allowing the substrate to cool to near room temperature in the As_4 beam. The substrate was then rotated to face the internal LN_2-cooled shrouding of the growth chamber while the source ovens were shuttered and reduced in temperature to minimize radiative heating of the substrate holder. About 90 min of radiative cooling in the LN_2 shrouded growth chamber was sufficient to reduce the substrate temperature below room temperature and to ensure condensation of As_4 onto the GaAs surface. The arsenic passivating layer was condensed by exposing the substrate to the As_4 flux typically used in GaAs growth for 10 to 20 min.

The resulting arsenic layer averaged about 0.3 μm in thickness, but was not uniformly deposited. Condensation occurred initially to produce a thin, uniform specularly reflecting coating about 500 Å thick. This was found in previous experiments to provide passivation against ambient atmosphere during transfer of samples between vacuum chambers for surface investigations.[5,8,9] Continued As condensation resulted in a matte appearance, caused by small closely spaced thicker islands of As. Figure 1 is a photograph of such an As coating.

Four *n*-type samples and two *p*-type samples were prepared. Three *n*-type samples and one *p*-type sample represent different contaminant exposures of the arsenic-passivated GaAs layer; one sample of each *n* and *p* type was not passivated. The three *n*-type passivated samples received the following exposure: (1) 10 min at 10^{-10} Torr in the MBE growth chamber, (2) 5 min in laboratory air, and (3) 30 s in flowing deionized water followed by a spin dry in air. The *p*-type passivated sample 5 was also treated with deionized water, in a manner identical to the *n*-type sample 3.

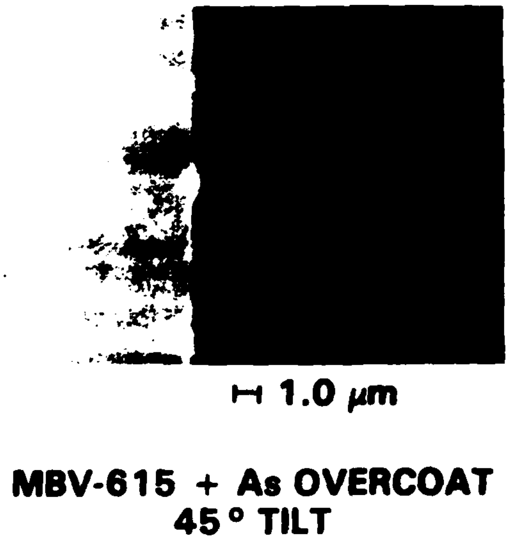


FIG. 1. Arsenic coating from the condensation of As_4 in the BEM growth chamber. The substrate temperature during condensation was below 20 °C. Sample was tilted at 45° for photograph; the featureless area at left is a (110) cleavage plane perpendicular to the (100) arsenic-coated surface.

The nonpassivated samples (designated sample 4, *n* type; and sample 6, *p* type) were removed from the chamber and given an etch which represents the final step of our standard GaAs substrate preparation procedure. This consists of an etch in flowing $NH_4OH:H_2O_2:H_2O$ (1:1:10) on a slow-speed spinner followed by a water rinse and air dry by rapidly spinning the sample.

Prior to regrowth of GaAs, the passivated samples were heated to about 350 °C in the MBE growth chamber to desorb the arsenic layer. At this point, the substrate was rotated to face the As_4 beam used for GaAs growth, and was heated to 600 °C. GaAs growth was then begun by opening the Ga and dopant shutters. The unpassivated samples were heated in As_4 to about 620 °C to desorb oxides, then growth of 1 μm of GaAs was begun at 600 °C. Growth conditions for the overgrowths were identical to the conditions used for the underlying layers before passivation. The surface appearance was specular for all samples and the density of surface defects was comparable to noninterrupted layers of the same total thickness.

All four *n*-type samples were grown using the same Ga oven and charge within a period of 30 days. The three passivated samples were grown and passivated using the same arsenic oven and charge, while the unpassivated sample was grown with a separate arsenic oven containing arsenic from the same supplier and batch as was used for the passivated samples. There was no measured difference in GaAs mobilities or carrier compensation between material grown from the two arsenic ovens. The *p*-type samples were grown several months later, using other Ga and arsenic charges. Conditions of growth, and material quality, were similar to the earlier *n*-type runs.

The interfaces at the point of growth interruption were characterized by electrolytic carrier profiling,[13] deep level transient spectroscopy (DLTS), and secondary ion mass spectroscopy (SIMS).[17] Figure 2 shows the carrier density profiles of the four *n*-type samples. They are offset vertically for clarity. A slight drift in the Si oven temperature or As_4 flux may have caused the offset in carrier concentration visible at the interface in the profiles of samples 1 (vacuum exposure) and 2 (air exposure); dips in the electron density at the

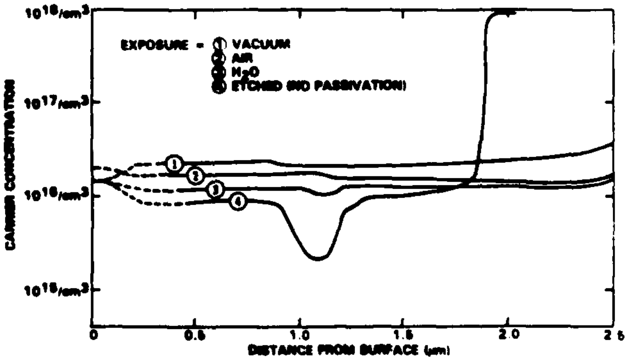


FIG. 2. Carrier concentration profiles, obtained by electroytic *C-V* profiling, of *n*-type samples containing passivated (1, 2, 3) and nonpassivated (4) interfaces. Profiles are offset vertically for clarity, as indicated by the dashed lines. The substrate occurs closer to the interface in sample 4 because the chemical etch prior to regrowth removed about 0.6 μm of material.

interface are visible for samples 4 (etched substrate with no passivation) and 3 (passivated substrate, H_2O exposure). For the unpassivated sample 4, the dip corresponds to a carrier loss at the interface of about $3\times10^{11}/cm^2$, in good agreement with the results of Kawai *et al.*[3] For the passivated and H_2O exposed sample 3, the carrier loss is about $2.5\times10^{10}/cm^2$, more than an order of magnitude less. The other two *n*-type samples (1, passivated with vacuum exposure and 2, passivated with air exposure) show no carrier loss at the interface, with an estimated detection limit of $5\times10^9/cm^2$. Arsenic passivation therefore provides interfaces in *n*-type samples with considerably lower carrier loss than standard MBE substrate preparation techniques.

Carrier concentration profiles for the *p*-type samples are shown in Fig. 3. In place of the dip in electron concentration observed in the *n*-type samples, a peak and dip combination is observed for the hole concentration in the *p*-type samples. The hole excess indicated by the peaks in these profiles is about $5\times10^{10}/cm^2$ for the unpassivated sample 6 (etched surface) and $1\times10^{10}/cm^2$ for the passivated sample 5 (exposed to deionized water). The hole excess in sample 5 may be due to a drift in Be dopant oven temperature. This agrees with the results for *n*-type samples, and shows that arsenic passivation results in a reduction of the charged states associated with the interface.

DLTS data was taken on both *n*-type and *p*-type samples. For the unpassivated *n*-type sample 4, a signal was detected corresponding to a deep level density of approximately $6\times10^9/cm^2$. This was also near the limit of detection sensitivity, and no activation energy was obtained. In all of the *n*-type passivated samples 1–3, no DLTS signal was detected. For the *p*-type unpassivated sample, six hole traps ($H_1 \rightarrow H_6$) were detected for which densities increased in the vicinity of the interface as shown in Fig. 4. Activation energies ranged from 0.19 eV to 0.72 eV above the valence band; densities ranged from $1.7\times10^{10}/cm^2$ to about $3.2\times10^{10}/cm^2$. Data for the hole traps is summarized in Table I. The H_4 ($E_c + 0.39$ eV) and H_6 ($E_c + 0.72$ eV) peaks probably correspond to native defect levels *A* and *B*, respectively, as reported by Lang and Logan.[14] The H_5 ($E_c + 0.44$ eV) peak is probably due to Cu even though no Cu accumulation at the interface was measured by SIMS (see Table II). Further, the H_3 ($E_c + 0.34$ eV) peak may be due to Fe,[15,16] however, the existence of the other reported Fe-related peak at $E_c + 0.55$ eV,[14] which is probably obscured by the broad H_6 peak, cannot be ruled out. The possible identification for H_1 ($E_c + 0.19$ eV) and H_2 ($E_c + 0.21$ eV) peaks is unknown. No DLTS data was obtained for the *p*-type passivated sample.

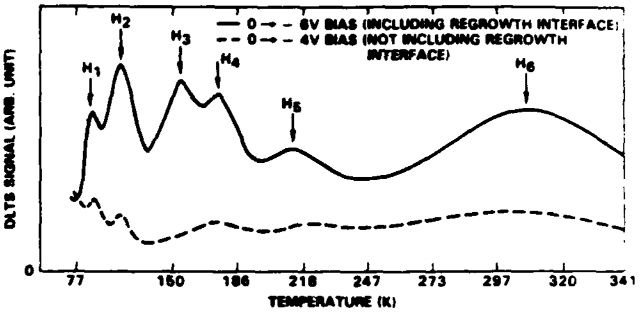


FIG. 4. DLTS spectra of the *p*-type unpassivated sample showing six hole traps ($H_1 \rightarrow H_6$) in the vicinity of the regrowth interface. Rate window of 36.4 s^{-1} was used in the measurements.

Secondary ion mass spectroscopy (SIMS) was used to profile the concentrations of atomic masses of 11(B), 12(C), 16(O), 24(Mg), 28(Si), 52(Cr), 55(Mn), 56(Fe), 58(Ni), and 65(Cu) for both the *n*-type and *p*-type samples. The element names in parentheses are the nominal assignments to these masses; interferences from molecular ions in some cases may confuse this identification. Sheet impurity concentrations were obtained by integrating the SIMS signal peaks at the interface using calibrations supplied by the analysts.[17] This data is best used to compare the amount of a given element incorporated in different samples, rather than to compare amounts of different elements for the same sample, because of uncertainties in elemental sensitivities. No enhancement in the concentration of the elements profiled was detected at the interface for passivated *n*-type samples 1 (vacuum expo-

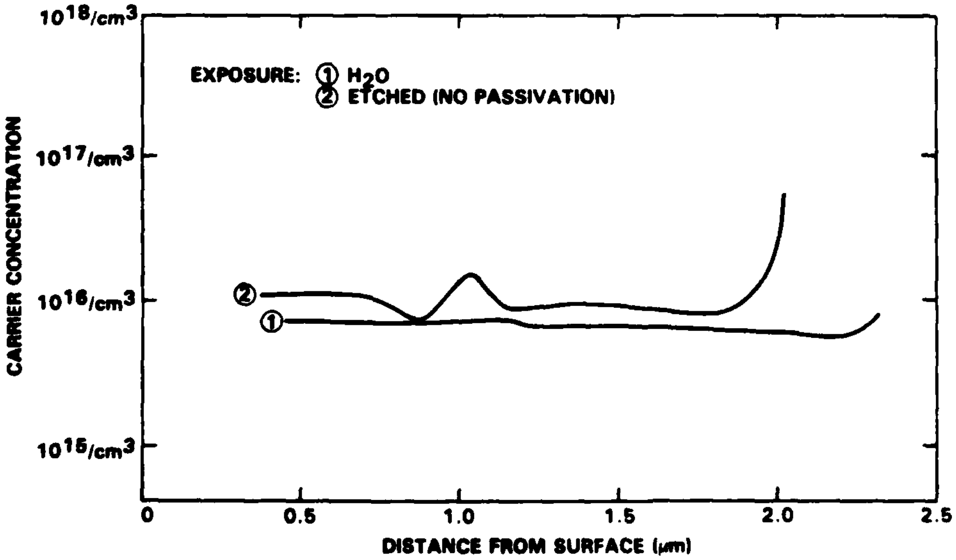


FIG. 3. Carrier concentration profiles, obtained by electrolytic *C-V* profiling, of *p*-type samples containing passivated (1) and nonpassivated (2) interfaces. Profiles are offset vertically for clarity.

TABLE I. Hole traps associated with an etched unpassivated growth/regrowth interface.

	H1	H2	H3	H4	H5	H6	Total
Density (cm^{-2})	2.0×10^{10}	3.2×10^{10}	3.2×10^{10}	2.6×10^{10}	1.7×10^{10}	2.1×10^{10}	1.5×10^{11}
Activation energy (eV, from valence-band edge)	0.19	0.21	0.34	0.39	0.44	0.72	

TABLE II. Summary of *C-V*, DLTS, and SIMS data for passivated and nonpassivated interfaces.

Sample	Substrate type	Treatment	Carrier loss (gain)	DLTS	SIMS mass peaks[c]					
					11(B)	12(C)	16(0)	24(Mg)	28(Si)	58(Fe)
1	n^+, Si	As passivation vacuum exposure	$<5\times10^{9}$ cm^{2}[a]	$<4\times10^{9}$ cm^{2}[a]	b	b	b	b	b	b
2	n^+, Se	As passivation air exposure	$<5\times10^{9}$ cm^{2}[a]	$<4\times10^{9}$ cm^{2}[a]	b	b	b	b	b	b
3	n^+, Se	As passivation H_2O exposure	2.5×10^{10} cm^{2}	$<4\times10^{9}$ cm^{2}[a]	2×10^{10} cm^{2}	b	b	4×10^{10} cm^{2}	b	4×10^{11} cm^{2}
4	n^+, Si	No passivation etched	3.0×10^{11} cm^{2}	6×10^{9} cm^{2}	1×10^{11} cm^{2}	2×10^{11} cm^{2}	4×10^{10} cm^{2}	b	4×10^{11} cm^{2}	4×10^{11} cm^{2}
5	p^+, Zn	As passivation H_2O exposure	(1×10^{10} cm^{2})	...	b	5×10^{10} cm^{2}	b	4×10^{9} cm^{2}	b	b
6	p^+, Zn	No passivation etched	(5×10^{10} cm^{2})	1.5×10^{11} cm^{2}	b	2×10^{11} cm^{2}	7×10^{11} cm^{2}	4×10^{10} cm^{2}	2×10^{11} cm^{2}	4×10^{11} cm^{2}

[a] Detection limit.

[b] No peak detected at growth-regrowth interface.

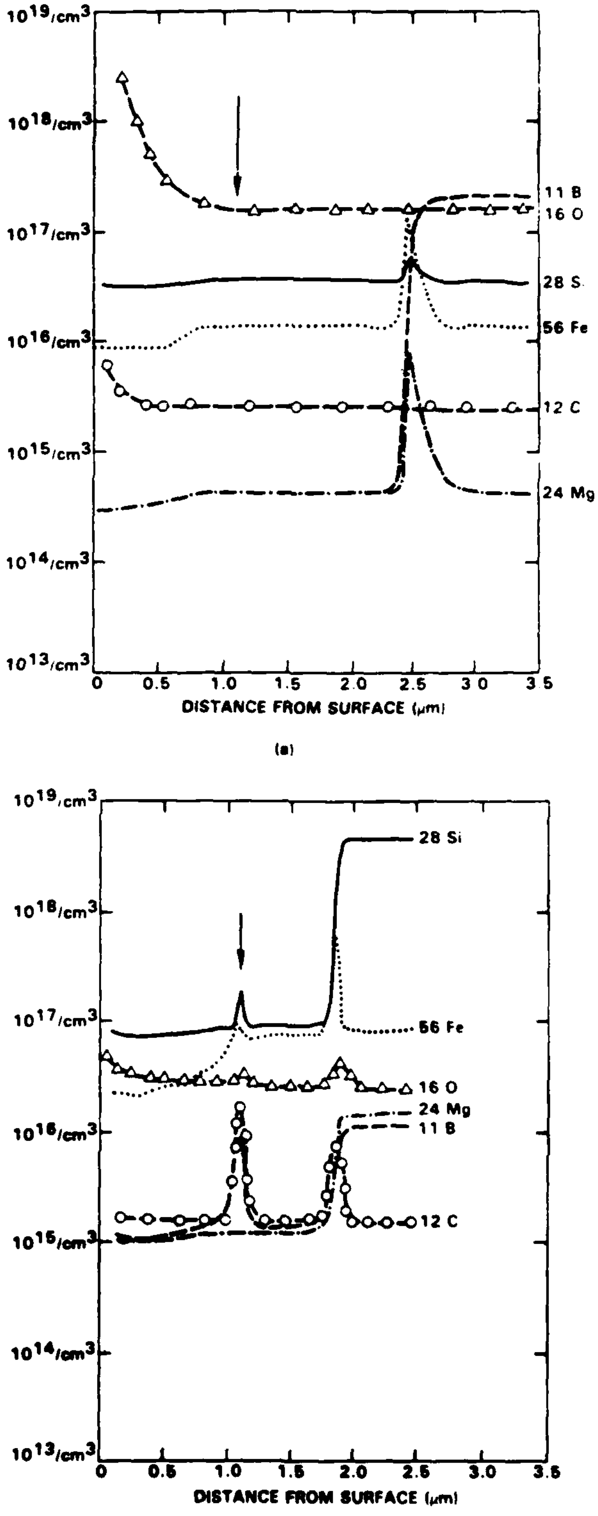
[c] SIMS concentration calibrations are approximate, numbers should be used for comparison within the table only.

sure) or 2 (air exposure). Peaks in concentration at masses 11, 24, and 56 (B, Mg, and Fe) were found at the interface region for passivated *n*-type sample 3 (water exposure), whereas for the passivated *p*-type sample 5 (water exposure) only 12 (C) and a very small amount of 24 (Mg) was detected. Peaks at masses 11, 12, 16, 28, and 56 (B, C, O, Si, and Fe) were found in the *n*-type unpassivated and etched sample 4, while the corresponding *p*-type unpassivated, etched sample 6 showed 12, 16, 24, 28, and 56 (C, O, Mg, Si, and Fe). Figure 5(a) shows the SIMS profiles for passivated sample 2; Fig. 5(b) shows the profiles of the same elements for nonpassivated sample 4. Note the interfacial peaks in sample 4. Peaks are also visible at the substrate-epilayer interface; all samples exhibited peaks of mass 56 (Fe) at this interface and most samples also showed varying amounts of 12 (C), 16 (O), 24 (Mg), and 28 (Si) at this interface. A summary of the carrier profile, DLTS and SIMS results of the growth-regrowth interface for all samples is contained in Table II.

DISCUSSION

The combination of carrier profiling, DLTS, and SIMS provides a measure of the degree of surface passivation of GaAs provided by arsenic layers condensed in the MBE apparatus. For passivated GaAs layers which had been exposed to vacuum or laboratory air, no interfacial carrier loss, DLTS signal or SIMS impurity peak was observed. This implies that the arsenic passivation layers themselves contribute no measurable impurities to the interface, and provide excellent passivation to atmosphere oxidation or contamination. Exposure of arsenic-passivated layers to deionized water resulted in an apparent free electron loss of about $2.5\times 10^{10}/\mathrm{cm}^2$ or acceptor increase of $1\times 10^{10}/\mathrm{cm}^2$ and the appearance of small and variable amounts of 11 (B), 12 (C), 24 (Mg), and 56 (Fe) peaks at the regrowth interface. These impurities may have originated in the water itself. Alternatively, their inclusion might be attributed to increase sensitization of the arsenic-passivated wafer surface to impurities from other sources. The questions of the origin of interfacial impurities is not resolved by this experiment. Arsenic-passivated layers, however, resulted in clearly superior interfaces in comparison with nonpassivated layers. For our typical wafer preparation scheme, which has an etch in NH_4OH:H_2O_2:H_2O (1:1:10) and deionized water rinse as its final step, apparent electron loss at the interface was about $3\times 10^{11}/\mathrm{cm}^2$, acceptor increase was about $5\times 10^{10}/\mathrm{cm}^2$ with $6\times 10^{9}/\mathrm{cm}^2$ deep donor levels, $1.5\times 10^{11}/\mathrm{cm}^2$ of deep acceptor levels, and large 11(B), 12(C), 16(O), 28(Si), and 56(Fe) peaks observed as well. Even the water-exposed passivated layer had an interface with a much smaller perturbation in the carrier profiles and fewer detected impurities at the interface.

Caution must be applied in interpreting the data for the free carrier profiles measured by *C-V* techniques. Since the hole trap density measured in the nonpassivated *p*-type samples is comparable to the free carrier density, the measured carrier profile in the *p*-type sample 6 depends on the spatial distribution, emission rates, and energy levels of the traps, as well as the frequency employed for the *C-V* measurement.[18] This is felt to be the origin of the complex peak and dip structure in the carrier profile for this sample. It is therefore not possible to determine the density of shallow acceptors at this interface, other than to say that they are probably fewer in number than the hole traps ($\sim 1.5\times 10^{11}/\mathrm{cm}^2$). If they



(a)

(b)

FIG. 5. SIMS profiles of masses 11(B), 12(C), 24(Mg), 28(Si), and 56(Fe) for samples 2 (passivated with air exposure), Fig. 5(a), and 4 (nonpassivated, etched), Fig. 5(b). Arrows designate regrowth interfaces. Concentration calibrations are approximate.

were of greater density than the hole traps, a simpler structure, consisting of an increase in measured hole density, would appear at the growth/regrowth interface in the C-V profiles. For the n-type samples 3 and 4, the hole trap occupation does not change appreciably as the Schottky barrier depletion region at the electrolyte-GaAs interface passes through the interface during carrier profiling, and the carrier profile therefore probably represents N_D-N_A, where N_A corresponds to the hole trap density.

These experiments suggest that interfaces of GaAs grown by MBE with use of arsenic passivation would be acceptable in many electron devices. This sequence in which layers are passivated with arsenic *in situ*, removed from the chamber for patterning or implantation, then returned to the MBE chamber for desorption of the passivating layer and continued epitaxial growth, may result in devices with buried interfaces of superior quality.

ACKNOWLEDGMENTS

The authors wish to thank Mr. P. G. Newman and Mr. L. A. Wood for assistance in MBE growth, Dr. Neng-Haung Sheng for assistance in DLTS measurements and Dr. J. S. Harris and Dr. F. Eisen for encouragement and support. This work was partially supported by the U.S. Army Research Office.

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