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Maria Faur
Lewis Research Center
Cleveland, Ohio

Mircea Faur
Cleveland State University
Cleveland, Ohio

Dennis J. Flood and Phillip P. Jenkins
Lewis Research Center
Cleveland, Ohio

Manju Goradia
Cleveland State University
Cleveland, Ohio

David M. Wilt
Lewis Research Center
Cleveland, Ohio

National Aeronautics and
Space Administration

ELECTROCHEMICAL CHARACTERIZATION OF InP AND GaAs BASED STRUCTURES FOR SPACE SOLAR CELL APPLICATIONS

Maria Faur[1][*], Mircea Faur[2], Dennis J.Flood[1] , Phillip P.Jenkins[1], Manju Goradia[2] and David M.Wilt[1]

[1]NASA Lewis Research Center, MS 302-1, Cleveland, OH 44135, USA
[2]Cleveland State University, SH 305, Cleveland, OH 44115, USA

ABSTRACT

In this paper the emphasis is on accurate majority carrier concentration EC-V profiling of structures based on InP and GaAs, using a newly developed electrolyte based on HF, CH_3COOH, o-H_3PO_4, $C_9H_{14}CIN$ and NH_3F_2. Some preliminary data on the use of this electrolyte for determining the energy distribution of surface and deep states of these structures, applicable to fabrication process optimization and radiation induced defects studies of solar cells, are also provided.

INTRODUCTION

For high efficiency III-V compound semiconductor space solar cells, InP and GaAs based materials are fabricated in a large variety of multilayer structures, grown on InP, GaAs, or inexpensive substrates such as Si or Ge. To design any of these structures, it is necessary to engineer changes of semiconductor properties in the surface active layers as a function of depth. If the electrolyte and the working conditions are well chosen, electrochemical (EC) techniques represent a simple and yet accurate method to characterize InP and GaAs related structures. Various surface and bulk properties such as the diffusion length and lifetime of minority carriers and the surface recombination velocity can be determined at any depth from electrochemical I-V, C-V and G-V characteristics. These characteristics can also be used for net EC-V majority carrier concentration depth profiling as well as for determining the density and energy distribution of surface states and traps as a function of depth.

EC-V profiling [1] is the most often used and convenient method for accurate majority carrier concentration depth profiling of semiconductors. As seen in Table 1, not one of the previously reported electrolytes recommended for EC-V profiling of InP and GaAs based structures works with all materials listed in the table. The most common problems encountered when using these electrolytes are: (i) a poor electrolyte/semiconductor Mott-Schottky barrier (as with AT), (ii) preferential dissolution at the defect areas (as with HCl), (iii) high chemical etch rates (as with HCl,

Tiron); (iv) formation of insoluble products on the surface (as with Pear etch, EDTA), (v) large parasitic capacitance components (as with HCl, Tiron and AT); (vi) a rough bottom of the etch crater (as with all, except FAP for InP and EDTA for GaAs), (vii) rounding at the crater rim (as with HCl), and (viii) electrolyte seeping under the edge of the sealing rim (as with AT). Additionally, these electrolytes do not work well with either Si or Ge and are therefore not useful for EC-V profiling of thin layer structures grown on thin lower-cost substrates.

Table 1. Recommended electrolytes for EC-V profiling of selected III-V compound semiconductors

Electrolyte/ Material	HCl	Tiron	Pear etch	EDTA	AT	FAP
InP	x		x			x
GaAs		x		x	x	
InGaAs	x			x	x	
InGaP	x					
GaAsP		x				
AlGaAs		x		x	x	
InGaAsP	x				x	

HCl = 0.5 M HCl in water [2];
Tiron = 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt, $C_6H_2(OH)_2(SO_3Na)_2 . H_2O$ [3];
pear etch = 37% HCl-70% HNO_3-methanol (36:24:1000) [4];
EDTA = 0.1 M Na_2EDTA basified with ethylenediamine to pH 9.1 [5];
ammonium tartrate (AT) = $(NH_4)_2C_4O_6$, basified with aqueous NH_3 to pH 11.5 or higher [5];
FAP = 48% HF-99% CH_3COOH-30% H_2O_2-H_2O (10:2:1:200) [6].

EXPERIMENTAL

We have conducted an extensive experimental study using electrolytic solutions based on HCl, o-H_3PO_4, HI, HNO_3, HF, CH_3COOH, $C_9H_{14}CIN$, H_2O_2, NH_3F_2, KOH and NaOH in an effort to find an appropriate electrolyte that will work well with all multilayer InP

and GaAs based structures, while avoiding the above-mentioned problems. This study used a large number of n- and p-type InP, GaAs, Si and Ge substrates and a relatively smaller number of multilayer structures fabricated by thermal diffusion or epitaxy made of n- and p-type InP, GaAs, InGaAs and InGaAsP layers.

The electrochemical I-V, C-V, and G-V characteristics were acquired using a commercial Polaron PN 4200 profiler. The etched surfaces and craters were examined using Nomarski and SEM microscopy, a Dektak profiler, and for selected samples EDAX and XPS data. The energy distribution of surface states and traps, derived from low-frequency G-V characteristics, was compared with that obtained from low temperature PLI data.

RESULTS AND DISCUSSION

A new electrolyte was developed for EC-V profiling of InP and GaAs based structures [7]. The composition of the new electrolyte is:

A-B-C (1 : 4 : 1), where:

Solution A: 48% HF : 99% CH_3COOH : 85%
o-H_3PO_4 : H_2O (5 : 1 : 2 : 100) ;

Solution B: 0.1 M N-n-Butylpyridinium Chloride $(C_9H_{14}ClN)$, and

Solution C: 1 M NH_3F_2.

Solution A works very well with InP layers. Although it works with GaAs layers, the accuracy of EC-V profiles in this case is rather poor due to a high chemical etch rate of GaAs of up to 0.5 μm/hour. Solution B works well with GaAs layers but it cannot be used for InP layers due to insoluble oxide formation on the etched surface. The combination solution A-solution B (1:4) can be used for EC-V profiling of InP, GaAs and InGaAs layers; however, it causes incomplete dissolution of anodic oxides in the case of InGaAsP layers. We have found a combination of solutions A:B:C (1:4:1), which we call the UNIEL electrolyte, to be a very good choice for profiling of InP and GaAs based multi-layer structures because it avoids all of the above problems.

The UNIEL electrolyte has been tested with very good results for EC-V profiling of structures made of n- and p-type InP, GaAs, InGaAs and InGaAsP layers. Generally, using the UNIEL electrolyte, accurate EC-V profiles are obtained when the anodic dissolution current density is from 0.5 to 1.5 mA/cm^2. The anodic dissolution rate under these conditions is from 0.8 to 1.5 μm/hour, that is much higher than the chemical etch rate, which for all tested materials is less than 0.015 μm/hour. Except for the lightly doped InGaAsP, the craters have smooth bottoms with straight walls, and the calculated crater depths agree within 5% with Dektak measured values.

An example is given here of an n$^+$n-InP structure grown by MOCVD on an n$^+$ $^+$-InP substrate. From the EC dark I-V (not shown) and C-V, 1/C^2-V and G-V characteristics (Fig.1), which in this case were taken at

the surface of n$^+$-InP at 3 kHz, one can see that the UNIEL electrolyte makes a very good Mott-Schottky contact with n$^+$-InP over a large bias voltage range. Also, the parasitic contributions to the liquid junction capacitance due to the electrolyte, surface oxide layer and surface states are negligible.
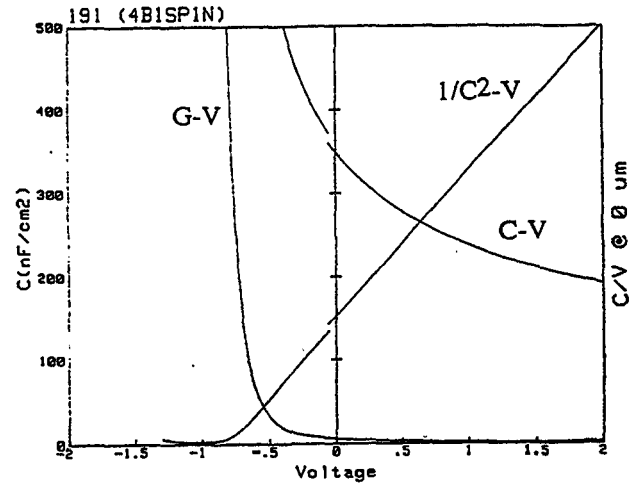

Fig.1. EC-V, 1/C^2-V and G-V characteristics at the surface of an n$^+$nn$^+$ $^+$- InP structure.

Geometric considerations, required for an accurate EC-V depth profile are also met using the new electrolyte. As seen in Fig. 2, the etch crater, after profiling the above structure to about 5 μm, has a smooth bottom, straight walls, and no rounding at the crater rim. This means that the calculated depth profile shown in Fig. 3 is accurate, since, as mentioned above, the parasitic interface capacitance components are negligible.
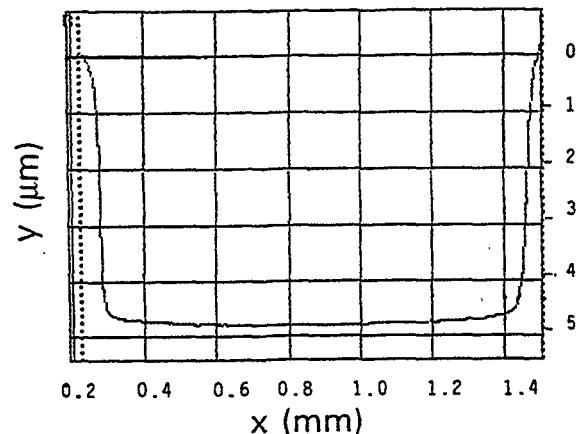

Fig.2. Dektak profile of the etch crater after profiling the structure in Fig.1 to 5 μm.

By examining (i) the dark and illuminated I-V, C-V and G-V characteristics, and (ii) the etched surface

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oxidation stage and stoichiometry using XPS, we concluded that there is no significant contribution to the semiconductor/UNIEL electrolyte interface capacitance from the surface states, surface oxide layer or the electrolyte, even for higher defect density structures fabricated by thermal diffusion. Hence, since the geometric conditions of the etch crater are also met, EC-V depth profiles of structures such as shown in Fig.4 should be accurate. This is most important for applications where small variations in carrier concentration depth profiles are to be evidenced. As an example, in Fig.5 are shown EC-V carrier concentration profiles of a thermally diffused p^+n (Cd,S) InP structure prior to and after irradiation with 10^{13} cm^{-2} 3 MeV protons. As is seen in this case, the carrier removal rate in the n-InP base is large while the hole removal rate in the Cd-doped emitter is much smaller.
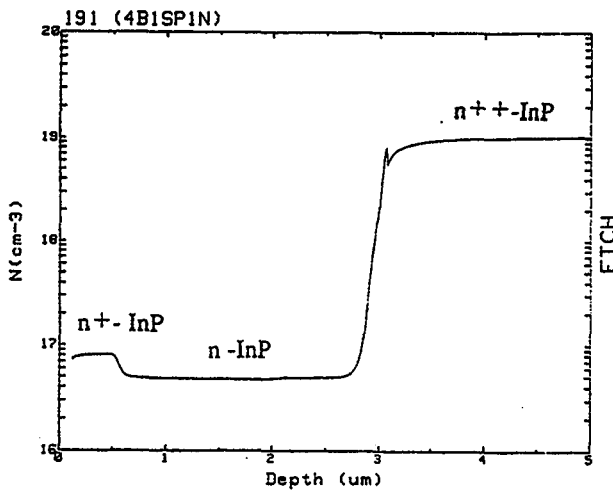

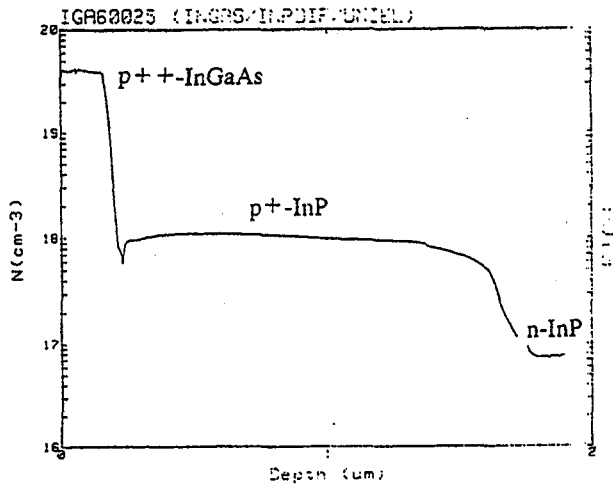Fig.5. EC-V profiles of an p^+n (Cd,S) InP diffused structure, prior to and after proton irradiation.

Fig.3. EC-V profile of structure in Fig.1.

Fig.4. EC-V profile of a p^+n (Cd,S) InP structure, diffused at 600 °C through an undoped InGaAs cap layer.
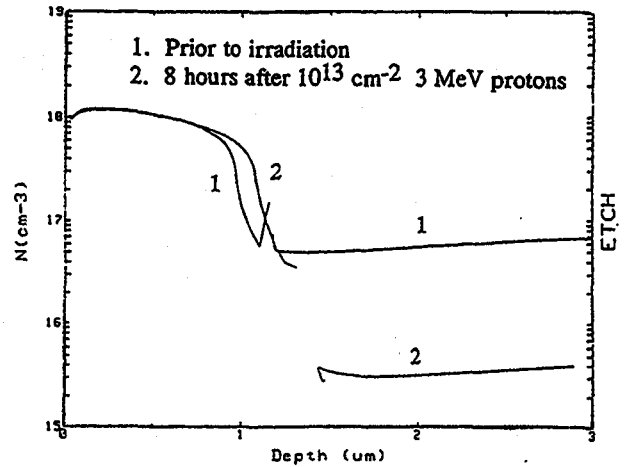
Preliminary studies have shown that UNIEL-based electrolytes can also be used for accurate EC-V profiling of structures made of epitaxially grown GaP, AlGaP (high Al content, e.g. >20%), InGaSbP, as well as Ge and Si substrates. This is very important since none of the previously reported electrolytes seems to work well, especially with high Al-content AlGaP and InGaSbP layers. In addition, UNIEL might be useful for EC-V profiling of thin film III-V semiconductor solar cell structures grown on cheaper substrates (e.g. Si or Ge).

Our preliminary work has shown that for structures made of InP, GaAs, InGaAs and InGaAsP layers, fabricated by thermal diffusion or epitaxy, using the UNIEL electrolyte and an anodic dissolution current density of 0.5 to 1.5 mA/cm^2, resulted in very smooth surfaces and negligible preferential dissolution of any of the components. The resulting surfaces, after dissolution to different depths, of samples with initially smooth surfaces are very smooth; for epitaxially grown structures which have had features grown on the surfaces, the same density and shape of these features (inside of a given layer) can be seen after anodic dissolution to different depths. Relative EDAX and XPS data of etched surfaces have shown that no preferential dissolution of any of the components takes place. Hence, since no parasitic levels are expected (such as V_{In} - related parasitic levels due to preferential dissolution of In from the InP or InGaAs surfaces which occurs when using 0.5 M HCl), the UNIEL electrolyte can also be used for EC photocapacitance or photoconductance study of main defect levels. As an example, the position and intensity of defect levels, derived from low frequency (0.3 kHz) EC G-V measurements in diffused p^+n (Cd,S) InP structures, after irradiation with 3 MeV protons are shown in Fig.6. The two plots were acquired after first removing about 60 nm of nonstoichiometric layer from the surface of the sample at two illumination levels as shown.
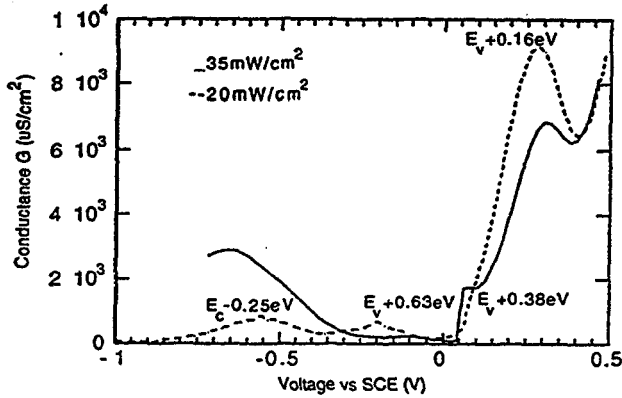
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Fig.6. Low frequency G-V characteristics 60 days after irradiation with 10^{13} cm^{-2} 3 MeV protons of a p$^+$n (Cd,S) InP structure. Diffusion temperature: 660 °C; Junction depth: 4.1 µm; Surface acceptor concentration: 3.6 x 10^{18} cm^{-2}.

The position of three acceptor levels and one donor level at E_v + 0.16 eV, E_v + 0.37 eV, E_v + 0.63 eV and E_c-0.35 eV were calculated at the illumination level of about 20 mW/cm^2. A shallow acceptor level at E_v + 40 meV which we observed prior to removing the 60 nm of surface layer has disappeared.

Fig.7 shows, for comparison, a low temperature (5K) PLI spectrum of the sample in Fig.6, acquired prior to the removal of 60 nm of nonstoichiometric surface layer. As seen a good match is obtained between the two techniques. The 0.94 eV PLI peak is most likely a neutral donor to acceptor transition (D°-A°) from E_c-0.25 eV to E_v + 0.16 eV. Since the bandgap at 5 K is 1.419 eV, the 1.378 eV PLI peak could be due to an e°-A° transition from the conduction band to the shallow acceptor level at E_v + 0.04 eV we observed from the photoconductance measurements prior to removing the nonstoichiometric layer from the surface of the sample.
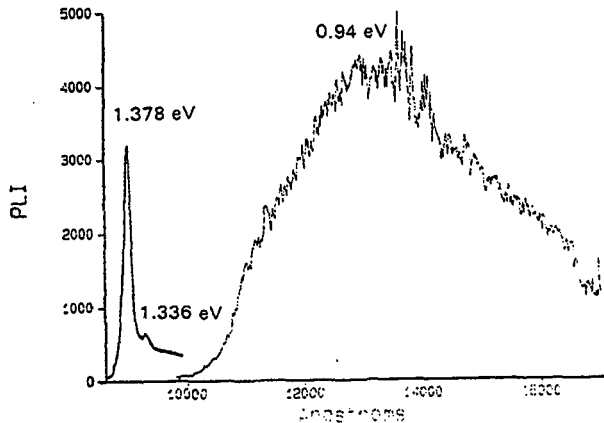

Fig.7. Low temperature (5 K) PLI spectra of sample in Fig.6.

The PLI shoulder at 1.336 eV is probably due to exciton transitions associated with the deep acceptor levels at E_v + 0.38 eV or E_v + 0.63 eV.

No attempts were made so far to positively identify the nature of the defects corresponding to the defect levels suggested by the two techniques.

CONCLUSIONS

A new electrolyte which we have called UNIEL, based on HF, CH_3COOH, o-H_3PO_4, $C_9H_{14}ClN$ and NH_3F_2, has been developed for EC-V profiling of III-V compound semiconductor structures. It was tested with very good results on n- and p-type InP and GaAs substrates and homo- and hetero-structures made of InP, GaAs, InGaAs and InGaAsP layers. Preliminary studies have also shown that UNIEL-based electrolytes work fairly well for profiling GaP, AlGaP (high Al content) and InGaSbP epitaxial layers as well as with Si and Ge substrates.

Owing to its etching characteristics, the UNIEL electrolyte appears to be a good candidate for determining the energy distribution of surface and deep states of these structures, applicable to fabrication process optimization and radiation induced defect studies of solar cells.

Even if the EC determination, contrary to PLI, or other solid-state techniques (e.g. DLTS) is destructive it might be preferred for complex structures, since the main defect levels can in this case be recorded virtually at any depth below the surface either inside of a given layer or at the interfaces between layers.

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Maria Faur, Mircea Faur, Dennis J. Flood, Phillip P. Jenkins, Manju Goradia, and David M. Wilt

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