

SHORT COMMUNICATION

M. Udhayasankar · J. Kumar · P. Ramasamy

New electrolytes for n-type InP and electrochemical *C-V* profiling of a semiconductor optical amplifier device structure

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Abstract New electrolyte systems for profiling n-type indium phosphide (InP) have been reported and are compared with the conventional HCl electrolyte. Among the new electrolytes, the electrolyte comprising HNO₃-HF-H₂O has better characteristics and is best suited for profiling InP material. Both epitaxial layers and substrate materials have been subjected to electrochemical carrier concentration profiling using the new electrolyte and the estimated concentration values are compared with that of Hall effect measurements. Barrier heights of the new electrolytes have been calculated. For the first time, the dopant profiling of a complete device structure grown by the chemical beam epitaxy technique for the realization of laser and semiconductor optical amplifier structures has been presented.

Key words Indium phosphide · Electrochemical capacitance-voltage profiling · Chemical beam epitaxy · Electrolytes · Semiconductor optical amplifiers

Introduction

Indium phosphide (InP) is a widely used material in conjunction with other III-V ternary and quaternary alloy semiconductors in optoelectronic devices for optical fibre communications. It is very difficult to form high quality, reproducible solid-state Schottky contacts on InP owing to low barrier heights, native oxides and metal-semiconductor chemical reactions ([1] and references therein). Much effort has been devoted to enhancing the barrier height of InP Schottky junctions by special treatments [2–7]. Alternatively, an electrolytic

liquid barrier [8] has been employed to overcome the difficulties for majority carrier concentration profiling in the as-grown material. Using such an electrolyte with controlled dissolution, continuous profiling to virtually any depth is possible without the usual problem of dopant-dependent depth limitations due to reverse breakdown voltage in the conventional capacitance-voltage (*C-V*) measurements. However, electrolytes with satisfactory barrier and dissolution properties are rather demanding. Moreover, accuracy of this profiling is strongly dependent on the electrolyte chosen and its properties. A new electrolyte for electrochemical *C-V* (ECV) profiling of n-type InP has been reported [1], but it employs additional steps for alloying the ohmic contact and also for special sample mounting. The choice of electrolytes for profiling InP by a simple method is very limited (as per the literature). In this article, new electrolyte systems are reported for ECV profiling of n-type InP. The characteristics of these electrolytes are discussed and are compared with the conventional 0.5 M hydrochloric acid electrolyte.

Epitaxial growth of lattice matched and strained heterostructures by chemical beam epitaxy (CBE) has become important and is receiving a great deal of attention in terms of the understanding of growth phenomena and also in terms of the development of high-performance, novel electronic and opto-electronic devices. Planar monolithic opto-electronic integrated circuits (OEICs) and photonic integrated circuits (PICs) are becoming increasingly important in the development of low-cost components for optical telecommunication and optical processing systems. A key to the realization of this integration is the ability to localize and integrate various devices, namely lasers, detectors, wave guides, amplifiers etc. High-speed performance of these devices are mainly dependent on the precise control of doping, thickness and composition. Usually such devices consist of layers of different materials with different doping concentration levels. An attempt has been made to profile such multi-layers of a complete device structure. Included as a second part of this work is the study of

M. Udhayasankar (✉) · J. Kumar · P. Ramasamy
Crystal Growth Centre, Anna University,
Chennai-600 025, India
e-mail: mudhayasankar@hotmail.com
Tel.: +91-44-2352774; Fax: +91-44-2352774/2352870

interface control and the dopant profiling of a CBE grown semiconductor optical amplifier (SOA) device structure by ECV measurements.

Experimental

Chemical beam epitaxial growth

The CBE growth was performed in a VG80H MBE system with pressure-controlled hydride and metallorganic gas lines at the Centro Studi e Laboratori Telecomunicazioni (CSELT), Turin, Italy. The growth apparatus has been described in detail elsewhere [9–11]. The hydrides (AsH_3 , PH_3) are injected into a high-pressure cracker cell held at a constant temperature of 1173 K and Group V species (As, P) were thermally cracked. The metallorganic precursors trimethylindium (TMIn) and triethylgallium (TEGa) were used as Group III sources. Solid silicon and beryllium were used as n-type and p-type dopant, respectively. The growth temperature was monitored by thermocouple and double checked with an optical pyrometer periodically calibrated against an indium antimonide (InSb) melting point of 800 K. The usual growth pressure is typically in the 10^{-5} mbar range. The samples were indium bonded on molybdenum blocks. A thermal cleaning procedure under phosphine overpressure at 803 K for 5 min was adopted to completely desorb the surface oxides on the substrate. InP layers have been grown on (001) InP substrates with growth rate $1 \mu\text{m/h}$ at a temperature of 783 K. Indium gallium arsenide (InGaAs) and multiple quantum wells (MQW) were grown at 798 K.

Electro chemical C - V profiling

The operating principle, capabilities, limitations and potentials of the ECV measurement technique have been presented in detail [1, 12–16]. Current-voltage (I - V) and capacitance-voltage (C - V) measurements and ECV profiling were carried out using a Bio-Rad (PN4200) semiconductor profiler. For photo I - V measurements, a 24 V, FCS-type quartz halogen bulb with necessary filters was used as an illumination source. The intensity of illumination was controlled by the computer using a triac power system. The lamp intensity was on an arbitrary power scale (0 = off to 100 = maximum intensity; 40 = minimum), related to the phase angle of the lamp supply. There were three electrodes employed other than the semiconductor (working) electrode: a platinum electrode for C - V measurements, a carbon (counter) electrode for etching and a saturated calomel electrode (SCE) for reference. The description and further details of the apparatus have already been reported [1, 14]. The electrolyte is stationary, but is refreshed by an electrolyte pump system for each profile measurement point in order to remove any film or generated gas during etching. All the potentials were measured with respect to the SCE (reference electrode) and the measurements were carried out at room temperature. The volume of the electrolyte used was approximately 7 ml and this was sufficient to almost fill the chamber of the electrochemical cell. The diagram of the measuring electrochemical cell can be found elsewhere [17].

The basic properties of a good electrolyte for ECV profiling are: (1) it should make a good rectifying contact (i.e. very low leakage current); (2) it should have negligible free chemical etch rate; (3) it should not possess a variable dissolution number (i.e. only one anodic dissolution reaction should take place); and (4) it does not form a wetted area outside the contact area. We have examined different electrolytic solutions, namely 1HNO_3 (70%)- $20\text{H}_2\text{O}$, 1HNO_3 (70%)- $20\text{H}_2\text{O}$: 1HF (48%)- $25\text{H}_2\text{O}$, $1\text{H}_3\text{PO}_4$ (88%)- $0.1\text{H}_2\text{O}_2$ (30%)- $320\text{H}_2\text{O}$ + 0.5 M HCl , other than the conventional 0.5 M hydrochloric acid for n-type InP. All these electrolytes are suited both for dissolution and for good barrier formation. The samples are chem-

ically etched in dilute HF solution for 30 s before the actual experiments in order to remove any surface oxides and also to enhance the wetting. However, such a special, separate cleaning or other preparation steps of the specimen are not mandatory. The dissolution process, the quality of surfaces, etch craters and ECV depth profiles were characterized by: (1) an analysis of I - V measurements in the dark and also at different intensity of illumination, $1/C^2$ - V and conductance-voltage (G - V) characteristics; (2) examination of etched surface topography using interference contrast microscopy; and (3) Tencor stylus profiler inspection of the etch craters. From our analysis, the second electrolyte solution behaves as a very good anodic etchant, well suited for ECV profiling.

Results and discussions

Characteristics of the electrolytes

The two major factors that predominantly affect the accuracy of the carrier concentration profiling are the series resistance and the precise determination of the contact area of the electrolyte. Table 1 shows the electrolyte resistance values for the electrolytes under study. The chemical etch rates under dark conditions are much lower than the anodic dissolution rates. It is clear from Table 1 that electrolyte 2 has both a very low free chemical etch rate and a low electrolyte resistance value. The effect of series resistance (R_s) can be inferred by the dissipation factor (D factor), which is the inverse of the quality factor (Q) of the model circuit of the electrolyte/semiconductor interface. For a negligible effect of an additional series resistance, the value of the D factor has to be a minimum. From Table 2 it can be seen that all the electrolytes studied have low D factor values. Particularly electrolyte 2 has a very low value, which indicates that the contribution to the series resistance by the electrolyte is negligible. Further, electrolyte 2 has a reasonable barrier height value, similar to a conventional HCl electrolyte. Even though electrolyte 3 has a comparable barrier height value, it has a higher free etch rate. Moreover, observation of the etched surface using this electrolyte shows a black surface with the deposition of tiny black particles, indicating that the electrochemical reaction is not smooth. Electrolyte 4 has a very negligible etch rate, but with a very low barrier height value. Hence, these two electrolytes (3 and 4) were discarded. Based on the free chemical etch rate, D factor value and good barrier height properties, electrolyte 2,

Table 1 Resistance values and free etch rate of different electrolytes

No.	Electrolyte	Resistance of the electrolyte solution (Ω)	Free chemical etch rate for 4 h (μm)
1	0.5 M HCl	16	0.012
2	1HNO_3 : $20\text{H}_2\text{O}$: 1HF : $25\text{H}_2\text{O}$	20	0.004
3	$1\text{H}_3\text{PO}_4$: $0.1\text{H}_2\text{O}_2$: $320\text{H}_2\text{O}$ + 0.5 M HCl	32	0.133
4	1HNO_3 : $20\text{H}_2\text{O}$	15	–

Table 2 The electrochemical C - V profiling of n-type InP material

Sample	Electrolyte	Expected concentration (cm ⁻³)	Measured concentration (cm ⁻³)	Expected thickness (μm)	Measured thickness (μm)	D^a	Flat band potential (V)	Barrier height ϕ_B (V) ^b
In P:S	0.5 M HCl	3.8×10^{18} – 4.6×10^{18}	4.1×10^{18} – 4.3×10^{18}	1.000	1.003	0.07	-0.60	0.671
In P:S	1HNO ₃ :20H ₂ O:: 1HF:25H ₂ O	3.8×10^{18} – 4.6×10^{18}	4.2×10^{18} – 4.3×10^{18}	0.617	0.615	0.06	-0.43	0.621
In P:S	1H ₃ PO ₄ :0.1H ₂ O ₂ :: 320H ₂ O+0.5 M HCl	3.8×10^{18} – 4.6×10^{18}	4.6×10^{18}	0.564	0.570	0.14	-0.34	0.606
In P:S	1HNO ₃ :20 H ₂ O	3.8×10^{18} – 4.6×10^{18}	4.6×10^{18}	1.000	1.032	0.07	-0.31	0.416
I-1313 In P:Si/ In P:S	1HNO ₃ :20 H ₂ O:: 1HF:25H ₂ O	1.0×10^{18}	1.1×10^{18}	1.100	1.045	0.02	-0.44	0.621
QW-1086 In P:Si/ In P:S	1HNO ₃ :20 H ₂ O:: 1HF:25H ₂ O	1.2×10^{18}	1.1×10^{18}	0.800	0.768	0.04	-0.56	0.626
MCD In P:Sn/ In P:S	1HNO ₃ :20H ₂ O:: 1HF:25H ₂ O	1.8×10^{18}	1.6×10^{18}	0.500	0.460	0.03	-0.38	0.621
TBS24 In P:Si/ In P:S	1HNO ₃ : 20H ₂ O:: 1HF:25H ₂ O	3.0×10^{18}	3.2×10^{18}	0.600	0.610	0.09	-0.38	0.621

^a D is the dissipation factor and is the inverse of the quality factor (Q) of the model circuit of the electrolyte/semiconductor interface

^b ϕ_B is the barrier height of the electrolyte/semiconductor junction

namely 1HNO₃ (70%)-20H₂O:1HF (48%)-25 H₂O was selected for profiling.

For ECV measurements, the contact area definition is most critical since the accuracy of both the carrier concentration results and the etch depth values are dependent on the correct area estimation. Hence, accurate physical confinement of the electrolyte by the sealing ring without seepage was maintained throughout the measurements by regular checks. The contact area defined by the plastic sealing ring was calibrated against a “blue slice” sample and was ensured by repeated calibrations. Another essential characteristic of electrolyte 2 is that it does not form any rounding of the crater edge (i.e. enhanced etching at crystal edges is minimal). This was evidenced by an optical micrograph of the etched crater and stylus surface profilograph after the ECV measurements and is shown in Fig. 1a and b, respectively. The electrolyte is contained well within the sealing ring and produces sharp crater walls and a flat crater bottom. Further, the dissolution number of the electrolyte (i.e. the number of holes required to dissolve one InP molecule) was found to be constant (equal to 6) from the crater depth measurements performed optically and with a stylus step profilometer. Since the dissolution number for InP is 6 [1], the presence of only one significant dissolution reaction is involved in the electrochemical dissolution process.

I - V and C - V measurements

Figure 2 shows the I - V curves obtained from a CBE grown silicon-doped InP epilayer with a carrier

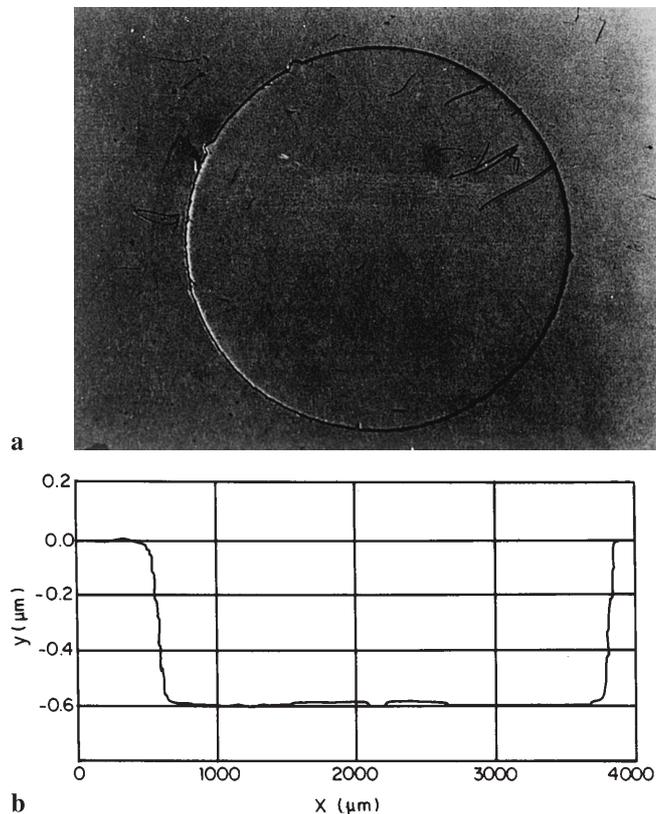


Fig. 1 a The optical micrograph (mag. 1.5×) of the crater after ECV profiling. b Tencor stylus profile of the crater after ECV profiling using the proposed electrolyte

concentration of $1.8 \times 10^{18} \text{ cm}^{-3}$ and a $1\text{HNO}_3\text{-}20\text{H}_2\text{O:}1\text{HF-}25\text{H}_2\text{O}$ (1:1) electrolyte barrier measured both in the dark and under different illumination intensities. The dark I - V characteristic shows a very low reverse leakage current density for this heavily doped sample. The electrolyte/semiconductor Schottky I - V characteristics are inverted with respect to the conventional I - V characteristics and consequently the top right-hand quadrant displays reverse bias conditions. A positive anode potential corresponds to reverse bias across the depletion region. From the photo I - V curves, well-behaved saturation currents are observed and the photocurrent level is directly proportional to the illumination intensity. The holes created by the illumination give rise to a photocurrent through the depleted region. This current is directly proportional to the minority carrier density created by the photons and is therefore controlled only by the level of the illumination intensity. The dark current is nearly zero and hence the rate-determining factor for dissolution is the availability of photogenerated holes at the InP surface.

If the electrolyte is concentrated, the electrolyte/semiconductor junction behaves as a Schottky junction so that the potential drop across the Helmholtz layer is constant and the remaining applied potential is dropped across the depletion layer. Figure 3 is the capacitance and $1/C^2$ versus voltage plots for the same electrolyte/InP barrier. It can be seen that $1/C^2$ is linearly proportional to the voltage over a wide range of potentials. Therefore, the capacitance-voltage behavior of this new electrolyte/semiconductor junction is in accordance with the Schottky law. From the plot of $1/C^2$ versus V , the barrier height of the electrolyte is determined using the relationship [18]:

$$\phi_B = -V_i + V_0 + kT/q; \quad V_0 = (kT/q)\ln(N_c/N_D)$$

where N_c is the effective density of states in the conduction band (for InP, $N_c = 5.66 \times 10^{17} \text{ cm}^{-3}$). N_D is the donor concentration, k is the Boltzmann's constant, q is the electron charge, T is the temperature and V_i is

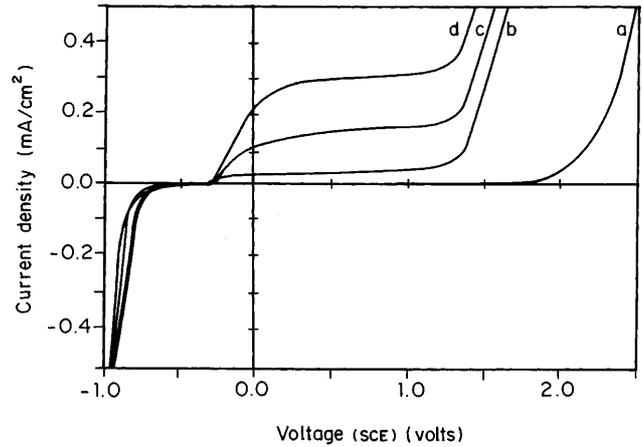


Fig. 2 I - V characteristics of electrolyte/semiconductor contact for the CBE grown silicon doped (n^+) InP epilayer. Curve a was measured in the dark, and curves b - d under increasing illumination intensities. The potentials are measured with respect to the SCE

the intercept voltage of $1/C^2$. The barrier heights of different electrolyte/semiconductor junctions are given in Table 2. The obtained barrier height values are nearly or equal to that for typical metal/semiconductor contacts. Further, although many electrolyte solutions form high quality rectifying barriers with the semiconductors, owing presumably to ionic motion in the liquid, a large amount of drift that causes hysteresis in the C - V curves is invariably observed [19]. The proposed electrolyte does not suffer from any such kind of restriction, as was shown from the essential absence of hysteresis in the C - V characteristics (Fig. 3). Further, the I - V , C - V and G - V (not shown) characterizations demonstrate that there is no significant parasitic contribution to the interface capacitance due to the electrolyte, surface oxide layer and surface states. This is a very important advantage. From the I - V and C - V characteristics, it is clear that the new electrolyte/InP barrier can be considered as a Schottky barrier that can lead to reliable, accurate estimations of

Fig. 3 Plots of capacitance (C) and $1/C^2$ versus bias voltage for the same electrolyte/ n^+ InP contact. The potentials are measured with respect to the SCE

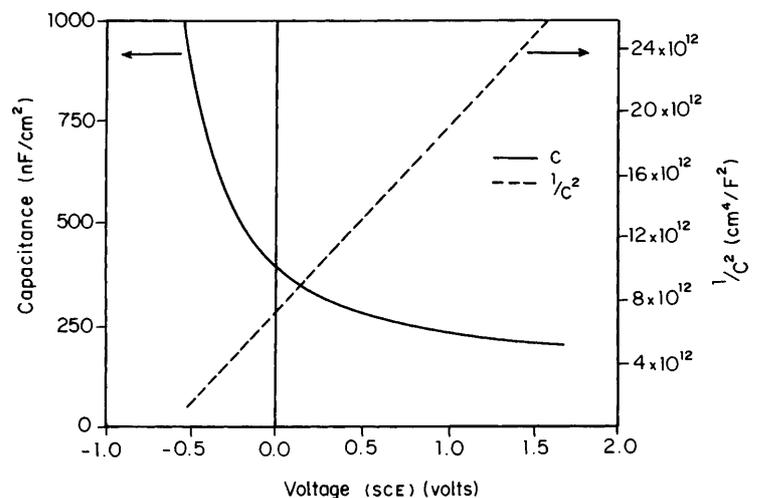
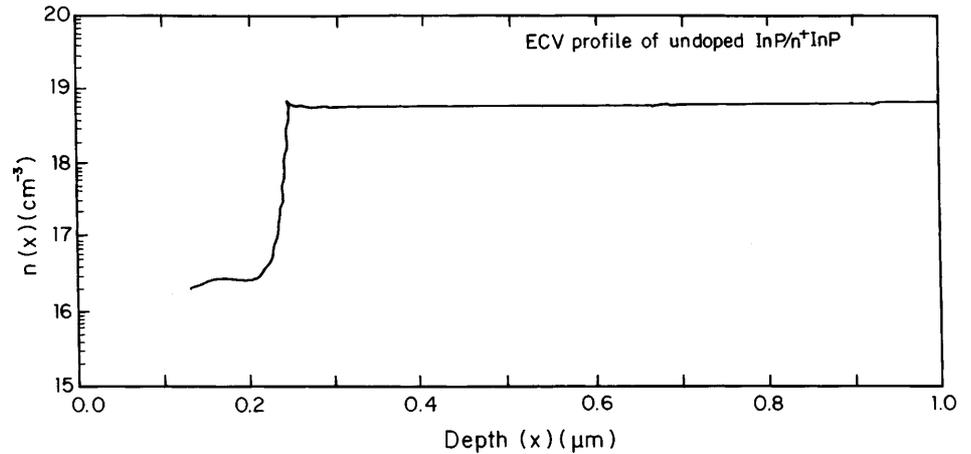


Fig. 4 ECV profile of an undoped InP epitaxial layer of thickness 0.22 μm grown on a n^+ sulfur-doped InP substrate



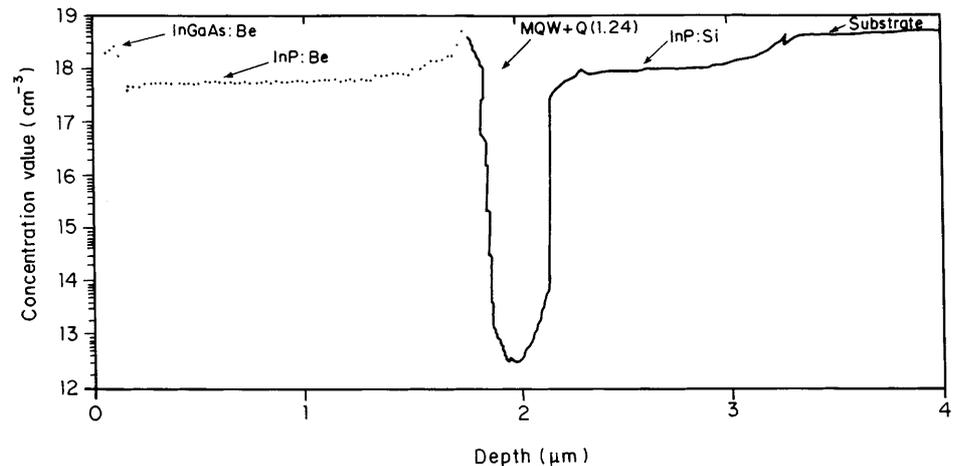
carrier concentration values. Hence, the new electrolyte makes a good rectifying contact with InP while exhibiting the other properties for an ideal electrolyte discussed earlier and is well suited for ECV profiling of InP.

ECV profiling

Several measurements were performed by applying the proper V_{etch} and V_{meas} and the condition for reliable profiling is optimized for both the substrate and the epilayers using this new electrolyte system. The ECV profile on the n^+ InP substrate gives a flat profile (not shown) and the results of profiling on the CBE grown undoped InP epilayer on a n^+ InP substrate (“low-high” structure) is shown in Fig. 4. The measured carrier concentration and etched thickness values are in good agreement with that of Hall effect measurement (expected values) and stylus profiler measurement. Preliminary studies have also shown that this electrolyte works fairly well for the profiling of p-type InP material and its suitability for other materials such as InGaAs and indium gallium arsenide phosphide (InGaAsP) is under study.

In order to understand the problems associated with profiling of multi-layers containing both p-type and n-type materials, ECV profiling has been performed with the conventional HCl electrolyte on a complete test device structure of a SOA. The HCl electrolyte is the most studied conventional electrolyte and it may be used for profiling all InP based compounds [20]. The device structure consists of ternary (InGaAs) and quaternary (InGaAsP) III-V alloy compounds with both p-type and n-type materials. The influence of junction series resistance (p-n junctions, hetero junctions) on the profile determination is not fully understood and hence the conventional HCl electrolyte is employed in order to avoid any other complications. The SOA structure consists of 0.15 μm thick InGaAs:Be (p^+ contact layer), 1.8 μm thick InP:Be (p^+ cladding layer), 0.15 μm thick 3 periods quantum wells (QWs) (undoped)/0.17 μm thick InGaAsP ($\lambda = 1.24$) (undoped), 1 μm thick InP:Si (n^+ cladding layer) on InP:S (n^+ sub). The complete ECV profiling of the device structure is shown in Fig. 5. The profiling is paused as soon as the junction is approached and respective material parameters are fed for the continuous successful profiling. The junction is realized by observing abnormality in the D factor, flat band po-

Fig. 5 An electrochemical carrier concentration profiling for a test device structure grown by CBE, where the *solid* and *dotted lines* of the profile indicate n-type and p-type dopant, respectively



tential values and also in the depletion width. The small “bump” in the ECV profiling represents the junctions and it shows the interface control of the grown epilayers. The measured thickness of the epilayers and its concentration values are in good agreement with the expected thickness and concentration values and the complete profiling as a whole is satisfactory. However, the multi-quantum well (MQWs) structures are not well resolved. Further studies are in progress for detailed profiling of MQWs.

Conclusions

New electrolytes were realized for ECV profiling of n-type InP. The barrier heights of the electrolytes/semiconductor contacts have been evaluated. Among the electrolytes, the $\text{HNO}_3\text{-HF-H}_2\text{O}$ electrolyte system is well suited for profiling. The characteristics of this new electrolyte are: (1) it exhibits a low resistance value and has very negligible additional series resistance effect; (2) there is only one dissolution reaction involved in the electrochemical dissolution with the new electrolyte since its dissolution number (equal to 6) is constant; (3) it does not form a rounding crater edge, in addition to the other properties of a good electrolyte. The $I\text{-}V$ and $C\text{-}V$ characteristics of this electrolyte/semiconductor junction are good and show good barrier and dissolution properties. The ECV estimated concentration and the etch depth values are in very good agreement with the values measured using the Hall effect and stylus profiler, respectively. The ECV measurements of epilayers combined with the stylus profiler measurements show abruptness of the growth interface and confirm the interface control. Finally, the results of profiling of a complete device structure grown by the CBE technique for the realization of laser and SOA structures for optoelectronic and photonic applications was also presented.

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