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Investigation of Anodic and Chemical Oxides Grown on p-type InP with Applications to Surface Passivation for n^+-p Solar Cell Fabrication

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Introduction

Most of the previously reported InP anodic oxides were grown on n-type InP with applications to fabrication of MISFET structures [refs. 1-3] and have been described as a mixture of In_20_3 and P_20_5 stoichiometric compounds [refs. 4-5] or nonstoichiometric phases which have properties similar to crystalline compounds $In(OH)_3$, $InPO_4$, and $In(P0_3)_3$ [refs. 1,3]. Details of the compositional change of the anodic oxides grown under different anodization conditions have been previously reported [ref. 6]. Here we investigate the use of P-rich oxides grown either by anodic or chemical oxidation for surface passivation of p-type InP and as a protective cap during junction formation by closed-ampoule sulfur diffusion. The investigation is based on but not limited to correlations between PL intensity and XPS chemical composition data.

Experimental

The (100) InP substrates used in this study were p-type Cd-doped to a concentration of $1.7E16cm^{-3}$, and Zn-doped to 2.6E16 and $1.2E18cm^{-3}$. The as-received 2-inch diameter Crystacomm, Inc. and Nippon Mining, Inc. wafers were cut into suitable size substrates. Prior to anodic or chemical oxidation, the substrates underwent a standard degreasing procedure by sequential light boiling in trichloroethylene, acetone and methanol, followed by the removal of about $10\mu m$ from the surface in Br_2-methanol (0.5% Br_2) solution and, finally, native oxide removal in 10% HF solution, just prior to oxidation.

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Anodic oxides, 15 to 90 nm thick, have been grown in $o - H_3P0_4 : H_20 : ACN$ solutions under no illumination (dark), low intensity (about 40 mW/cm^2), and strong illumination conditions (about 100 mW/cm^2), at room temperature and constant current density (J_c) of 0.1 to 1 mA/cm^2. The oxide thickness was measured via a Dektak profilometer prior to and after oxide dehydration in vacuum or pure hydrogen at temperatures from 150 to 300°C for 10 minutes to 1 hour. Other previously reported electolytes for InP and GaAs oxidation [refs. 2,5,7] were also examined but they proved to be unsatisfactory in terms of oxide uniformity, stability, or contamination level.

Chemical oxides have been grown in 15% $HN0_3$ solution under strong illumination and a bath temperature of about 60°C.

n^+-p junctions have been formed in Cd- and Zn-doped InP substrates by an evacuated closed ampoule diffusion of sulfur through anodic or chemical oxide cap layers. Thermal diffusion was done for 3 hours at several temperatures in the range of 615°C to 675°C.

The composition of the oxide layers was determined prior to and after sulfur diffusion. This was done by XPS analysis of the two parts of the same substrate, one of which was sulfur diffused. XPS spectra were taken and analyzed using VG MKII ESCALAB with VGS 5000 Plus enchanced data processing software. Depth profiles were done using a VG AG60 differentially pumped ion gun with an argon ion beam of 5 mA emission current at 2.5 keV.

PL intensity and its time-dependent behavior data correlated the level of surface passivation to different processing steps (i.e. surface preparation, annealing) and to the oxide composition profiles obtained from the XPS data. The PL intensity data have been measured at room temperature with the 514 nm line of an Ar^+ laser of 1 W/cm^2 power density.

Anodic and Chemical Oxides

Investigation of the oxides grown in various electrolytes at different viscosity, pH, constant current density, and illumination level values have indicated that the depth profiles of the anodic oxides are strongly dependent upon the growth conditions [ref. 6]. The anodic oxide on p-type InP appears complex, and depending on the growth parameters, the presence of $In(OH)_3$, In_20_3, $InPO_4$, $In(P0_3)_3$, $In(P0_3)_4$ and other nonstoichiometric InP_xO_y compounds have been identified.

In general, there is an In-rich oxide at the surface and a P-rich oxide at the interface and their composition varies as a function of anodization conditions. As an example, the effect of variation in current density on the oxide depth profile is shown in Figures 1 and 2. The two oxides were grown under similar conditions in an electrolyte of 0.5% $o - H_3P0_4$ mixed with acetonitrile (4:6 vol. ratio), under dark,

but the current densities were 0.25 and 0.6 mA/cm^2, respectively. Both oxides were grown while the sample voltage was increasing with time, i.e., in that region where the growth rate is the predominant process as compared to the disolution rate. Although not shown here, the oxide grown at 0.25 mA/cm^2 is made up of a surface layer of $In(OH)_3$ and $InPO_4$, an inner layer of $In_x(PO_3)_y$, and an interfacial layer of $In(PO_3)_4$. The oxide grown at 0.6 mA/cm^2 has a surface layer of $InPO_4$, an inner-layer of In_2O_3 and an interfacial layer of a mixture of nonstoichiometric InP_xO_y polyphosphates rich in $In(PO_3)_3$.

P-rich interfacial oxide components are of interest for surface passivation of InP as we are going to see in the next section. Anodization parameters appear to control the thickness and composition of this P-rich interfacial layer, as mentioned. The parameter which seems to control the composition of this layer to the largest extent is the illumination level. Under dark conditions at 0.6 mA/cm^2 current density, a thin $In(PO_3)_3$-rich layer is formed at the interface as mentioned above. Under low illumination, for oxide grown under otherwise identical conditions, the interfacial P-rich oxide layer is made up of $In_x(PO_3)_y$ and $In(PO_3)_4$ compounds as shown in Figures 3a and b.

Under strong illumination the front oxide layer was a mixture of $In(OH)_3$, $InPO_4$ and In_2O_3. The $In3d_{5/2}$ and O1s lines indicated a higher concentration of In_2O_3 in the inner layer as compared to the low illumination case. P-rich interfacial layer, however, was made up of a thinner $In_x(PO_3)_y$ and a thicker $In(PO_3)_4$ layers, as compared to the oxide described above. The $In3d_{5/2}$, $P_{0X}2p$, $P_{bulk}2p$, and O1s depth profiles presented in Figure 4a have been recorded for an anodic oxide grown under strong illumination, after two consecutive oxidation-removal of the front In-rich oxide layer, and finally regrowing the oxide under the above mentioned conditions. As seen in Figure 4b, which represents the P2p spectra, the oxide of about 18nm thick still showed a layered structure with a surface layer consisting of $In(PO_3)_3$, and an interfacial layer of $In(PO_3)_4$. No indication of $In(OH)_3$, In_2O_3, or $InPO_4$ formation could be found from the $In3d_{5/2}$, P2p, and O1s photoelectron binding energies. However, the Auger kinetic energy for In indicated the existence of a very low intensity line of 405.55 eV, which suggests that a low concentration of $In(OH)_3$ still exists at the surface.

The chemical oxide was grown in 15% HNO_3 solution under strong illumination, and a bath temperature of about 60°C. As previously reported for the case of n-type InP oxidation [ref. 1], the chemical oxide is homogeneous in depth and it is an $In(PO_3)_3$-rich polyphosphate. However, in the case of p-type InP which we report on here, the thickness of the oxide layer appear to be limited to less than 40Å , as opposed to n-type substrates, in which case the oxide thickness can be larger than 100 nm.

Surface Passivation

Based on previously reported information on insulators formed on InP (e.g. as gate insulator for MISFET's) [refs. 2,8], the ideal insulator to be used as a cap in view of application to surface passivation and solar cell fabrication, should have the following bulk and interfacial properties:

a) It should have good physical and chemical stability. This means that the cap should adhere well to the substrate, be insensitive to environmental effects such as moisture, and gas absorption, be relatively scratch resistant, and be compatible with semi-conductor processing steps, e.g., masking, etching, diffusion, annealing, AR coating, and metallization.

b) It should act as a preferential diffusion barrier. In this case, it implies that the cap layer should allow in-diffusion but prevent the In and P out-diffusion.

c) It should reduce or eliminate initial surface defects and interface roughness. This means that the oxide growth should occur by the consumption of the underlying InP substrate.

d) It should exhibit a low density of interface states. This means that a minimum of unsaturated bonds should remain at the semiconductor-oxide interface.

e) It should have good dielectric properties, such as a wide energy bandgap, high resistivity, and a low density of defects.

A well established characteristic of the InP surface is that near midgap the density of surface states depends strongly on the surface preparation procedure prior to insulator deposition. Hence, a combination of an appropriate surface chemical treatment and a P-rich oxide layer, should result in low density of states throughout the bandgap.

Different chemical surface treatments have been tried in this study, and a correlation is being made between the PL intensity (PLI) and the XPS chemical composition. Figure 5 shows the time-dependent PLI of ptype substrates after different chemical treatments as compared to the "bare" substrate. A large PLI enhancement is observed for surfaces treated in HF and HNO_3 solutions as compared to the "bare" surface, and the surfaces treated in $o-H_3PO_4$ and H_2SO_4 solutions. The changes in surface chemistry as a function of dlfferent chemical treatments as revealed by XPS data [ref. 9] have shown that phosphorus enriched surfaces are responsible for the PLI enhancement. The passivating properties of P-rich surfaces is consistent with the prevailing concept that P-enriched surfaces eliminate P vacancies that produce a large density of states near the conduction band edge.

Figure 6 shows steady state PLI before and after annealing in hydrogen of p-type substrates exposed to different chemical treatments, as compared to those with anodic oxides grown under different illumination conditions. The enhancement of

PLI observed in the case of oxidized substrates could indicate that the interface has a low density of surface states due, probably, to the structural compatibility between the oxide layer and InP substrate. We believe that the PLI enhancement as a result of annealing in hydrogen is due to passivation of the intergrain-defects and grain boundary defects in the bulk nonstoichiometric oxide layers and at the oxide-InP interface.

In order to identify the best candidate for the use as a passivating cap layer, we are presently investigating the physical, chemical and optoelectronic properties of the P-rich layers grown under different anodization conditions. As an example, Figure 7 shows the time-dependent PLI for Cd-doped substrates with anodic oxides grown in two different solutions under similar anodization conditions. The XPS compositional data, not shown here, reveal that the anodic oxide in the case of G10 sample, has a thin In-rich outer-layer and the thicker P-rich interfacial layer is mainly made up of $In(PO_3)_3$. In the case of CP series, the oxides have a thicker In-rich surface layer and a thin mixture of $In(PO_3)_3$ and $In(PO_3)_4$ interfacial layer. It is believed that the large enhancement of the PLI in the case of "G10" sample is due to the formation of $In(PO_3)_3$ at the interface, which has a lower bulk defect density and a lower density of interface defects. On the other hand, In-rich surface layers have been previously identified to be the cause of the high density of interface states [refs. 2,10]. From the large enhancement of PLI as a result of removing the In-rich surface oxide layer, as seen in Figure 8, it is apparent that this is the case. It has been assumed [ref. 11] that the donor states which have been found to appear near the InP conduction band minimum as a result of oxidation are associated with indium surface oxides rather than with P vacancies or other native defects.

Junction Formation

As mentioned before, n^+-p junctions have been formed in Cd- and Zn-doped p-type substrates by closed-ampoule diffusion of sulfur through P-rich anodic or chemical cap layers. Thick anodic oxides grown in dark conditions appear to be stable at diffusion temperatures of up to 620°C, except for the In-rich surface oxide layers. An example is shown in Figure 9, which represents the $In3d_{5/2}$, P2p, S2p, and O1s depth profiles after S diffusion at a temperature of 620°C for 3 hours, through the anodic oxide of Fig. 2. It appears that the compounds of the In-O system, i.e. $In(OH)_3$ and In_2O_3, are entirely replaced by compounds of the In-S system, i.e., In_2S_3, InS, or In_6S_7. The front oxide layer appears to be rich in $InPO_4$, and InP_xO_y nonstoichiometric compounds are found at the interface. After a 3 hour diffusion at 650°C, through an oxide similar to that of Fig. 3, the front In-rich oxide decomposed completely, as seen in Figure 10. A thin nP_xO_y oxide layer, less than 60Å thick can still be found at the surface.

Further, closed ampoule diffusion of sulfur was performed through thin (less than 200Å thick) anodic and chemical P-rich oxide cap layers. The P-rich oxides appear

stable even after 3 hours diffusion at 660°C. The surface topography of the S diffused Zn- and Cd-doped substrates through P-rich chemical oxide (about 40Å thick) can be seen in Figure 11. As seen, In_xS_y droplets [ref. 12] accumulate at the oxide-n InP interface at the etch pit areas. In the case of diffusion into Cd-doped substrates the droplets density is about one order of magnitude less than that for Zn-doped ones, indicative of a lower rate of new dislocations introduced by S diffusion in Cd-doped materials [ref. 13].

The histogram in Figure 12 shows the initial and steady state PLI values after S-diffusion into Cd-doped (NPDC) and Zn-doped (NPDZ and FPDZ) substrates for 3 hours at 660°C. The three sets of data in each case were taken after the post-diffusion surface preparation [ref. 11], followed by 5 minutes chemical treatment in 10% HF solution, and finally after annealing in pure H_2 (about 2 atm.), at 275°C for 30 minutes. The differences between the values of PLI in the case of the two structures (NPDZ and NPDC) diffused through a thin P-rich chemical oxide, as compared to the structure diffused through a clean surface (FPDZ), we assumed to be mainly due to recombination centers introduced in the i) front oxide layer and ii) In_xS_y droplets accumulation at the defect areas, rather than V_P or V_{In} vacancies-type defects introduced in the front n^+ layer. This assumption, however, seems to be in disagreement with the differences observed in the PLI values in the case of NPDZ and NPDC structures, since the droplet density in the case of Cd-doped substrates is smaller than that of Zn-doped ones. However, the differences observed in the surface donor density, S diffusion profiles and diffusion depths, in the case of Zn and Cd substrates [ref. 13], should also be taken into account.

Solar Cell Fabrication

Small area (0.48 cm^2) n^+-p InP solar cells have been fabricated on structures diffused through either anodic or chemical oxides, and performance data have been compared with those of solar cells fabricated on structures diffused through clean surfaces. However, no solar cells have been fabricated to date on structures diffused through P-rich oxide cap layers grown under strong illumination (see Fig. 4), which have proven to be stable even at diffusion temperature of 660°C, and which are expected to perform better. Furthermore, the design and fabrication of contacts and AR coating have not been optimized in this work. These aspects are vital to optimal cell performance and good design is essential if unambiguous analytical information is to be obtained from the performance parameters. Therefore, for now, only qualitative information is given from an analysis of these solar cell parameters.

The best overall solar cell parameters were obtained in the case of cells fabricated on structures diffused for 3 hours at 640 to 660°C, through 150 to 250Å thick anodic oxides grown in dark or low illumination. In these cases, the In-rich surface components have been removed prior to diffusion. For these cells AM0, 25°C efficiencies of over 12.5% have been obtained as compared to solar cells fabricated on structures

diffused through as-grown oxides which showed efficiencies of 9 to 11%. The limiting parameter here was Voc, i.e., a maximum value of 760 mV, as compared to values of up to 812 mV for the former cells.

Solar cells fabricated on structures diffused for 3 hours at 660°C through chemical oxide cap layers (about 40Å thick) gave a best AM0 efficiency of 12.6%.

Efficiencies of solar cells fabricated under similar conditions on structures diffused through clean surfaces, gave a best efficiency of 12.1%. In general, cells fabricated on structures diffused through thin oxide layers, gave a slightly higher V_{oc}, higher I_{sc}, and a slightly smaller FF, associated with higher series resistance, as compared to those fabricated on substrates diffused through clean surfaces.

Suggestions for Further Research and Conclusions

Thin P-rich anodic and chemical oxide cap layers have proven to be stable during the close-ampoule diffusion of sulfur at temperatures of up to 660°C. An experiment was done to see if these cap layers can be used for the formation of n^+-p or p^+-n InP structures in an open tube system. In-rich oxide (about 900Å thick) and P-rich oxide (about 150Å thick), have been grown on the same substrate. The surface topography of this surfaces as compared to a clean area, after 1 hour heat treatment in air at 660°C, is shown in Figure 13. As seen, the P-rich oxide is relatively smooth, while large bubbles appeared on the surface with In-rich oxide (inside circle), and on the initially clean area. The bubble formation have previously been reported in the case of thermal oxides on InP grown in dry O_2 at temperatures above 600°C [ref. 14]. The bubbles indicate that the In-rich oxide has softened and has then been pushed away from the InP surface by pressure from beneath the oxide. In the case of the clean surface, the P vapor, which is believed to provide this pressure, breaks the smaller bubbles which form below the thin growing thermal oxide.

This experiment indicates that P-rich oxides could be used as caps during n^+-p or p^+-n InP junction formation in an open tube system. Due to the fact that $In(PO_3)_3$ acts as a good diffusion barrier [ref. 12], we anticipate that the use of P-rich cap layers could be especially beneficial for an open-tube p^+-n InP junction formation. In this case, the passivating P-rich cap not only protects the surface during diffusion, but can also control the depth of acceptor diffusion so as to permit the formation of shallow p^+-n junctions, required for the fabrication of high efficiency solar cells.

Due to the fact that the diffusion temperatures, and time required to form p^+-n InP structures is significantly lower than those in the case of n^+-p junction formation, we anticipate that In accumulation at the defect areas, which we believe introduces a large number of recombination centers, does not occur. Hence, the P-rich cap layer, in this case, could be used as the first layer AR coating in a double or triple layered structure. For the use as a first layer AR coating, $In(PO_3)_3$ has good dielectric properties; that is, a wide bandgap of 6.8 eV [ref. 2], and a resistivity of $10^{13}\Omega$-cm

[ref. 3]. Furthermore, we speculate that a suitable match can be realized with a second layer AR coating material such as MgF_2, both in terms of optimum optical coupling, and a low interface states density.

In conclusion, it appears that P-rich anodic or chemical oxides grown on p-type InP are good candidates for surface passivation, and as protective caps during thermal diffusion. However, more experimental studies are required to understand the complex oxidation process of InP, and to clarify the structural and chemical composition of these oxides as a result of different oxidation conditions and post-oxidation treatments. Further experimental insights on the chemistry of complex systems such as In-P-O-S-Cd(Zn) under various diffusion conditions are needed before designing higher-performance solar cells by this method of junction formation.

References

[1.] G. Hollinger, E. Bergignat, J. Joseph and Y. Robach, J. Vac. Sci. Technol. **A3**, 2082, 1985.

[2.] G. Hollinger, J. Joseph, Y. Robach, E. Bergignat, B. Commere, P. Viktorovitch and M. Froment, J. Vac. Sci. Technol. **B5**, 1108, 1987.

[3.] J. Joseph, Y. Robach, G. Hollinger, P. Ferret and M. Pitaval, *1st. Int. Conf. on InP and Related Materials for Advanced Electronic and Optical Devices*, 1989.

[4.] C. W. Wilmsen, J. Vac. Sci. Technol. **19**, 279, 1981.

[5.] A. Yamamoto, M. Yamaguchi, and C. Uemura, J. Electrochem. Soc.: Solid-State Science and Technology **129**, 2795, 1982.

[6.] Maria Faur, Mircea Faur, Manju Goradia, Chandra Goradia, Douglas Jayne, Navid Fatemi, David J. Brinker, *11th Symposium on Applied Surface Analysis*, 1989. To be published in "Surface and Interface Analysis".

[7.] C. W. Wilmsen and R. W. Kee, J. Vac. Sci. Technol. **14**, 953 1977.

[8.] "Physics and Chemistry of III-V Compound Semiconductor Interfaces", ed. by C. W. Wilmsen, Plenum Press, New York, 1985.

[9.] Maria Faur, Mircea Faur, Manju Goradia, Chandra Goradia, Phillip Jenkins, Douglas Jayne, Sheila Bailey, Irving Weinberg, Extended Abstract submitted for the 2lst IEEE, PVSC, Orlando, Florida, 1990.

[10.] J. F. Wager, Appl. Phys. Lett., **42**, 589, 1983.

[11.] K. A. Bertness, T. Kendelewicz, R. S. List, M. D. Williams, L. Lindan and W. E. Spicer, J. Vac. Sci. Technol. **A4**, 1424, 1986.

[12.] Maria Faur, Mircea Faur, Manju Goradia, Chandra Goradia, D. Jayne, F. Honecy and I. Weinberg, *1st Int. Conf. on InP and Related Materials for Advanced Electronic and Optical Devices*, in press, 1989.

[13.] Mircea Faur, Maria Faur, Chandra Goradia, Manju Goradia, Ralph D. Thomas, David J. Brinker, Navid Fatemi and Frank Honecy, this conference.

[14.] J. J. McLaren, A. Nelson, K. Geib, R. Gann, and C. W. Wilmsen, J. Vac. Sci. Technol. **A1**, 1486 1983.

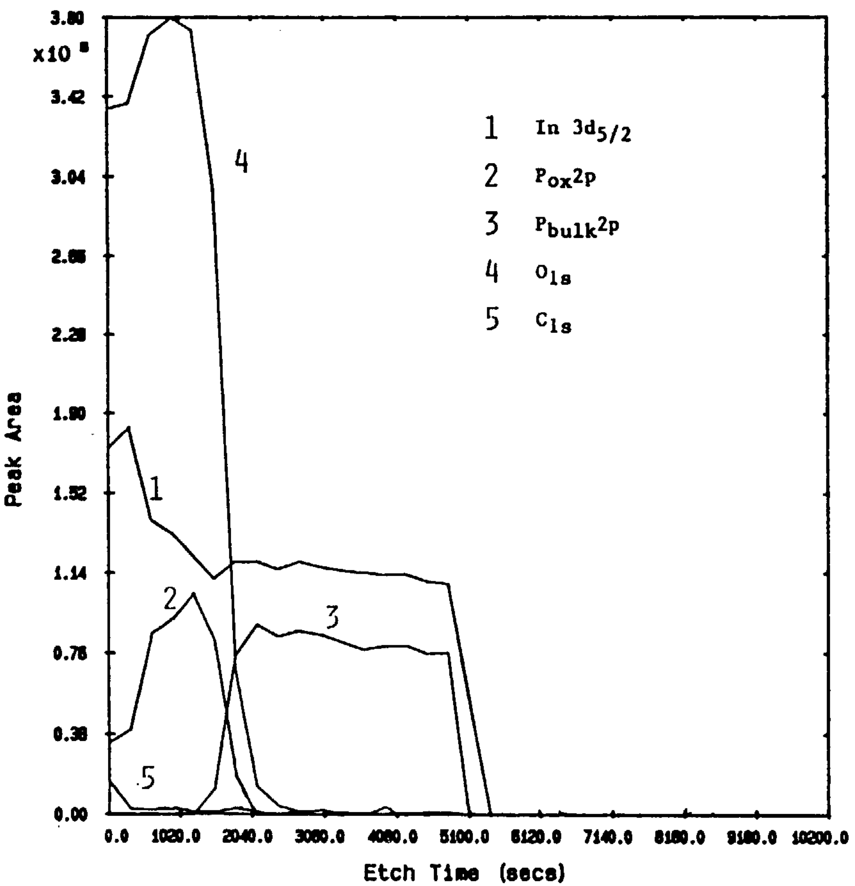


Figure 1. XPS depth profiles of an anodic oxide (about 50nm thick) grown in an O-H_3PO_4:H_2O:ACN (1:200:300) electrolyte under dark conditions at a constant current density (J_c) of 0.25 mA/cm^2 on Cd-doped InP substrate.

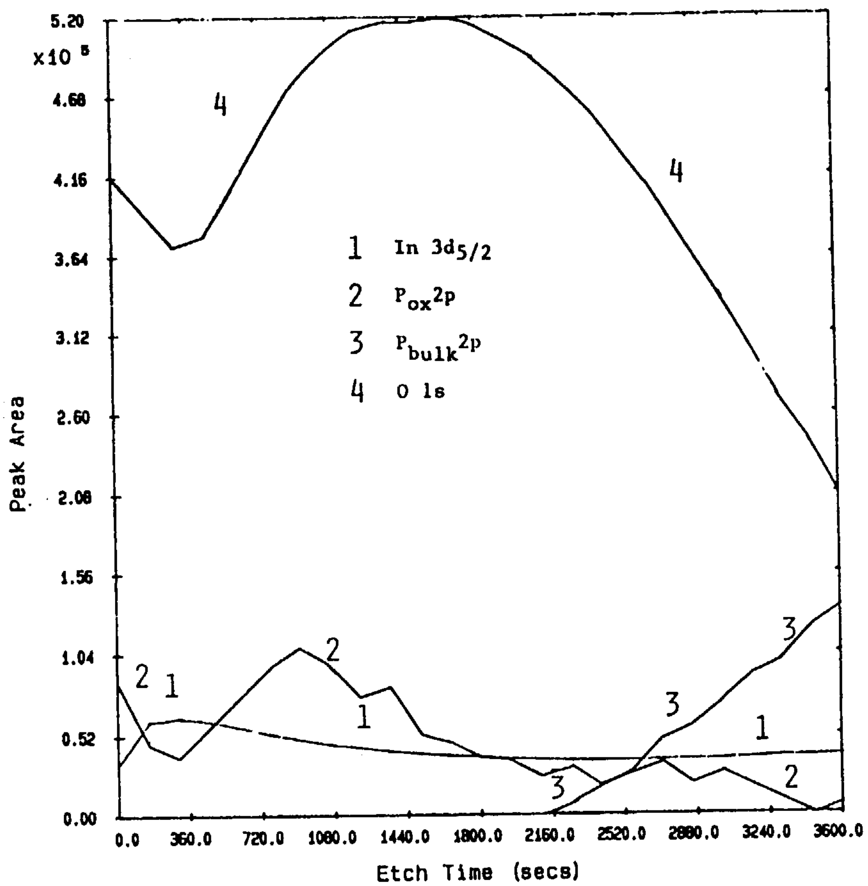
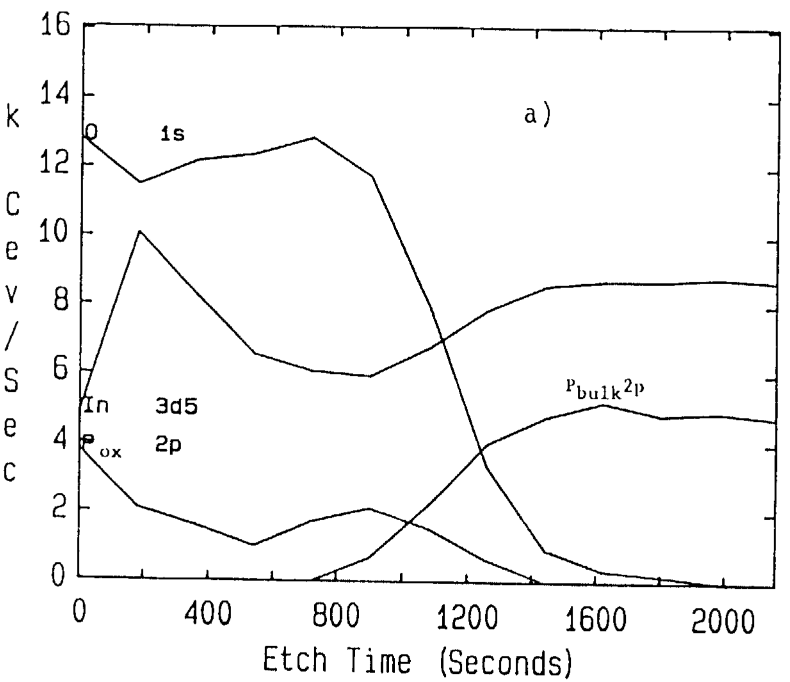


Figure 2. XPS depth profiles (about 90nm thick) grown in similar conditions as indicated in Fig. 1, but at J_c = 0.6 mA/cm^2



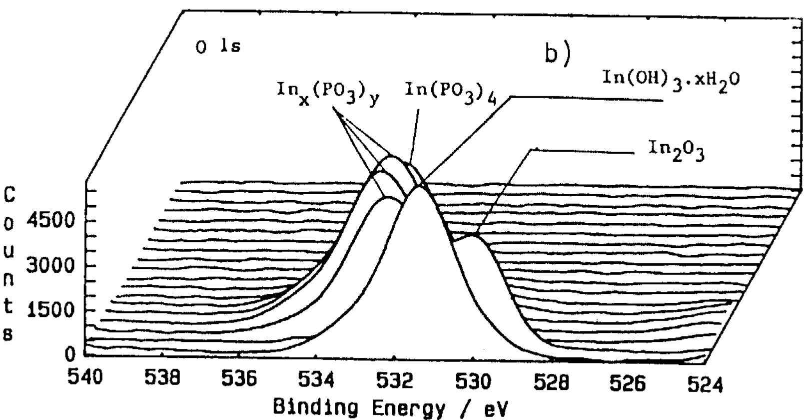
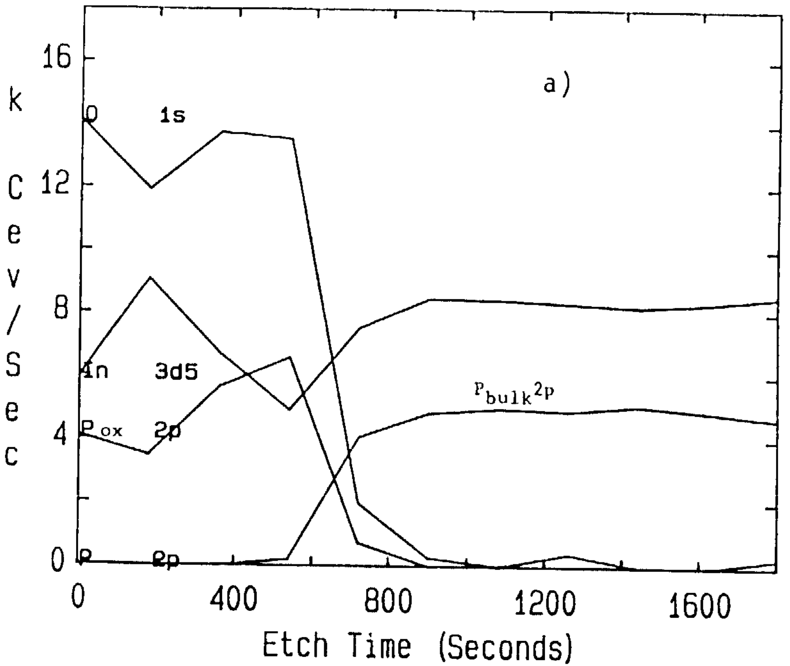


Figure 3. XPS profiles of an anodic oxide (about 30nm thick) grown in $O-H_3PO_4:H_2O:ACN$ (0.1:10:100) under low illumination (about 40 mW/cm^2) at J_c = 0.6 mA/cm^2. a) depth profiles; b) O_{1s} spectra for 23 depths with 180 secs. cyclic sputtering (about 30 Å material removed) and analysis.



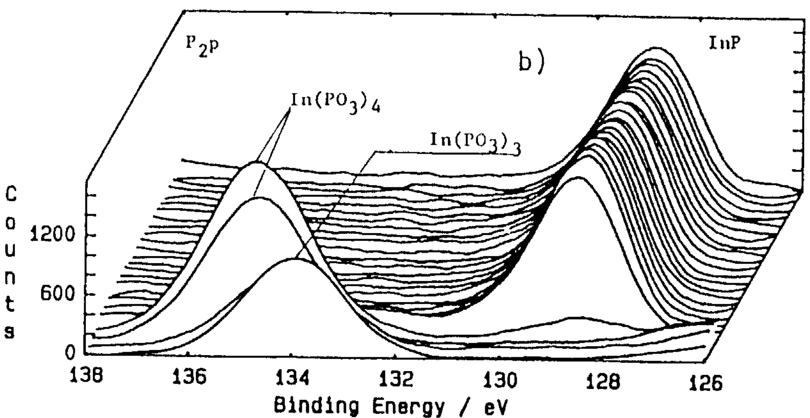


Figure 4. XPS profiles of a P-rich anodic oxide (about 18nm thick) grown in conditions in Fig. 3, but under strong illumination (about 100 mW/cm^2). a) depth profiles; b) P_{2p} spectra after 30 cycles of 180 secs. sputtering and analysis.

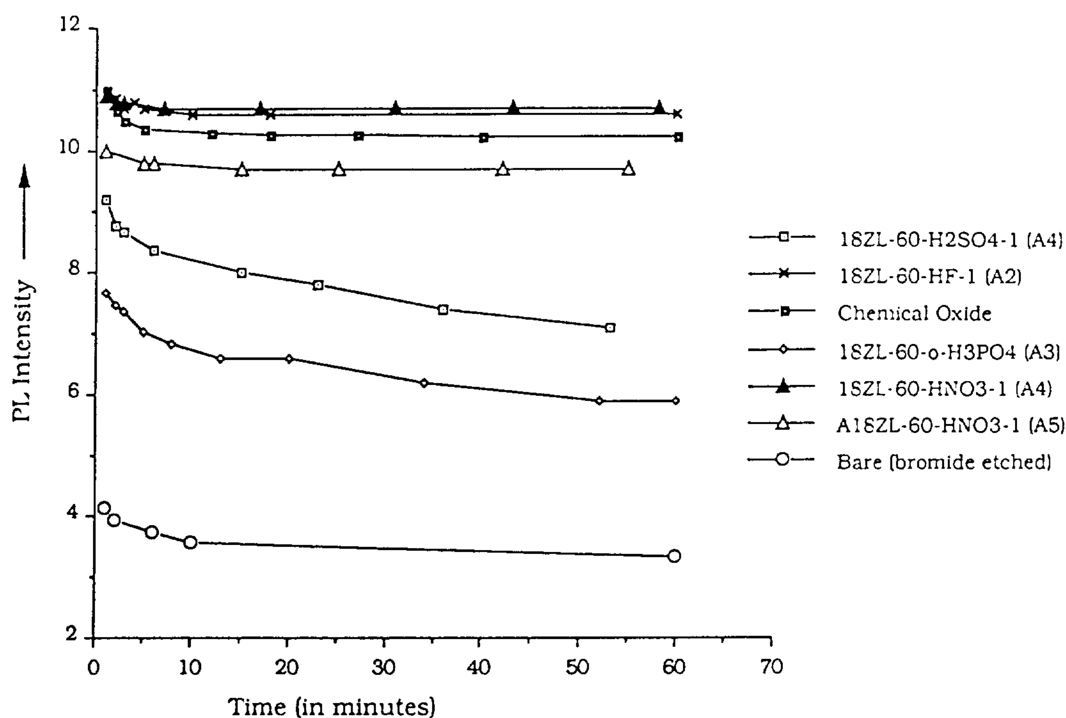


Figure 5. Time dependent PL intensity of p-type InP (Zn-doped to 1.2E18 cm^{-3}) exposed to different etching solutions (15% vol. ratio) at 60°C under strong illumination as compared to the "bare" surface. The chemical treatment was done on degreased surfaces, and after removal of about 10μm layer ("bare" surface) in Br_2-methanol (0.5% Br_2) solution. A5 refers to A4 after annealing in H_2(P ≈ 1,000 torr) at 275°C for 30 min.

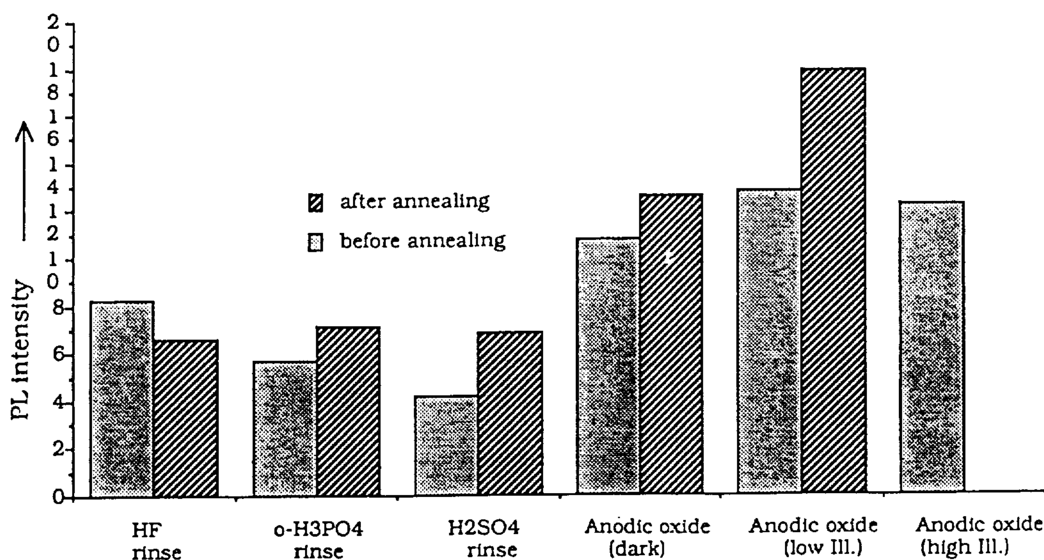


Figure 6. Steady-State PL intensity data after chemical treatment as compared with anodic oxides grown in O-H_3PO_4:H_2O:ACN (1:10:100) solution at constant current density of 1 mA/cm^2 in dark and illumination conditions. Same substrates, chemical treatment and H_2 annealing conditions as described in Fig. 5 have been used.

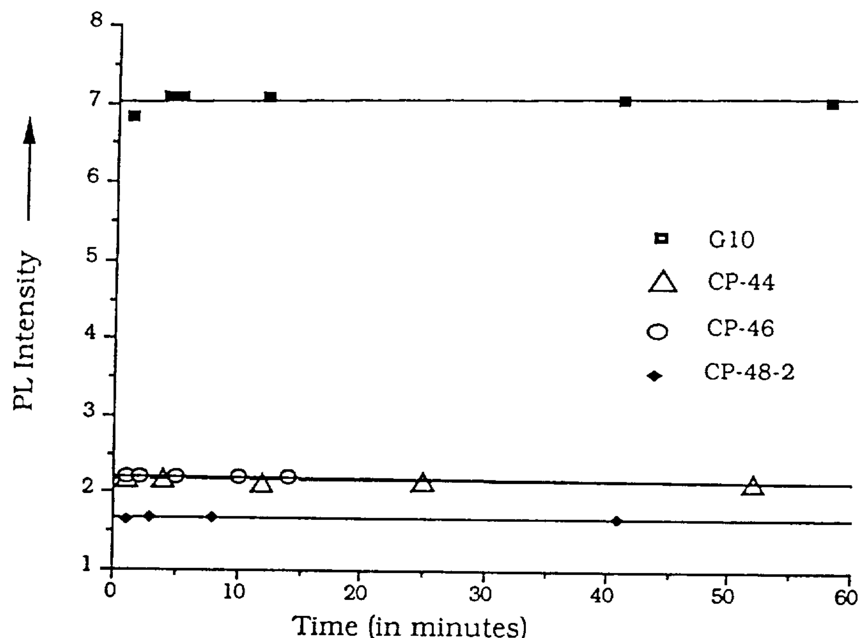


Figure 7. Time dependent PLI of Cd-doped substrates with as-grown anodic oxides. "CP"-series have oxides grown under conditions described in Fig. 2. G10 is grown in 3% citric acid in etylene glycol (1:3) under strong illumination.

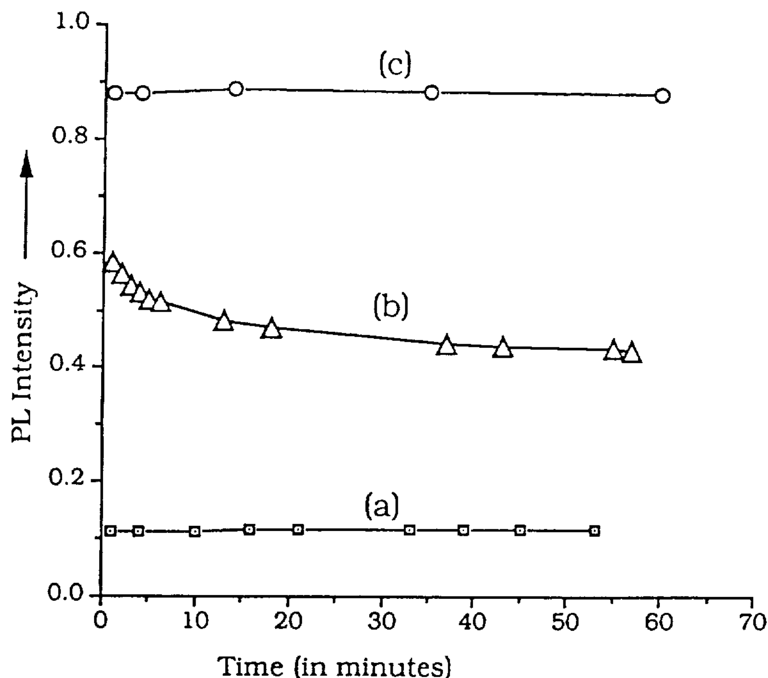


Figure 8. Time-dependent PLI for an anodic oxide grown on Zn-doped (2.6E16cm^{2}) InP substrates in same conditions as in Fig. 4. a) as grown; b) after annealing the as-grown oxide in H_2 at 275°C for 30 min.; c) after removing the In-rich surface oxide layer (prior to annealing).

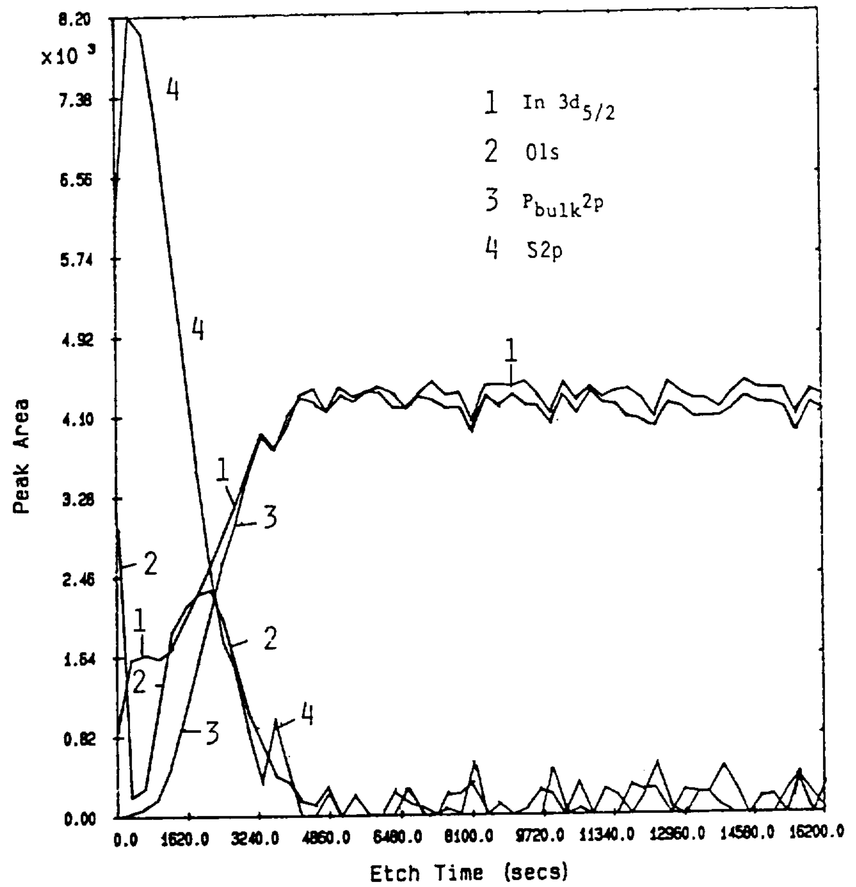


Figure 9. XPS depth profiles of a n⁺-p InP structure, S-diffused for 3 hours at 620°C through an anodic oxide as shown in Fig. 2.

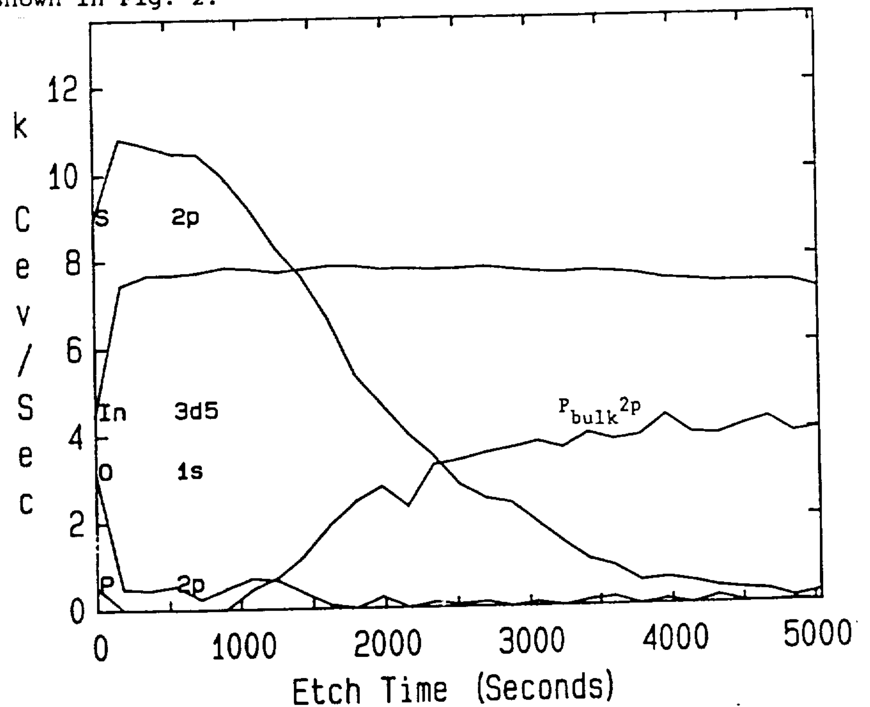


Figure 10. XPS depth profiles of a n⁺-p InP structure, S-diffused for 3 hours at 650 °C through an anodic oxide similar to that presented in Fig. 3.

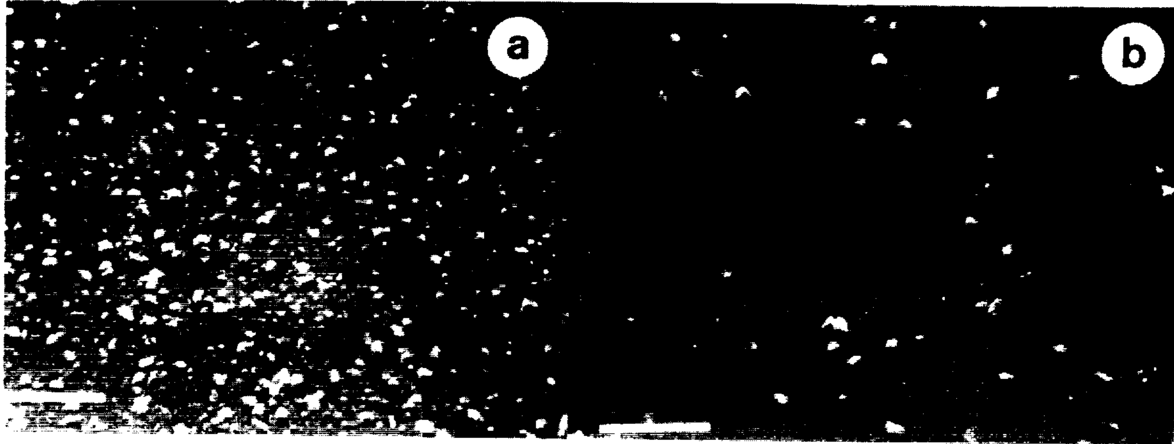


Figure 11. Surface topography after 3 hours S diffusion through a P-rich chemical oxide (about 4nm thick) into a) Zn-doped, and b) Cd-doped substrates.

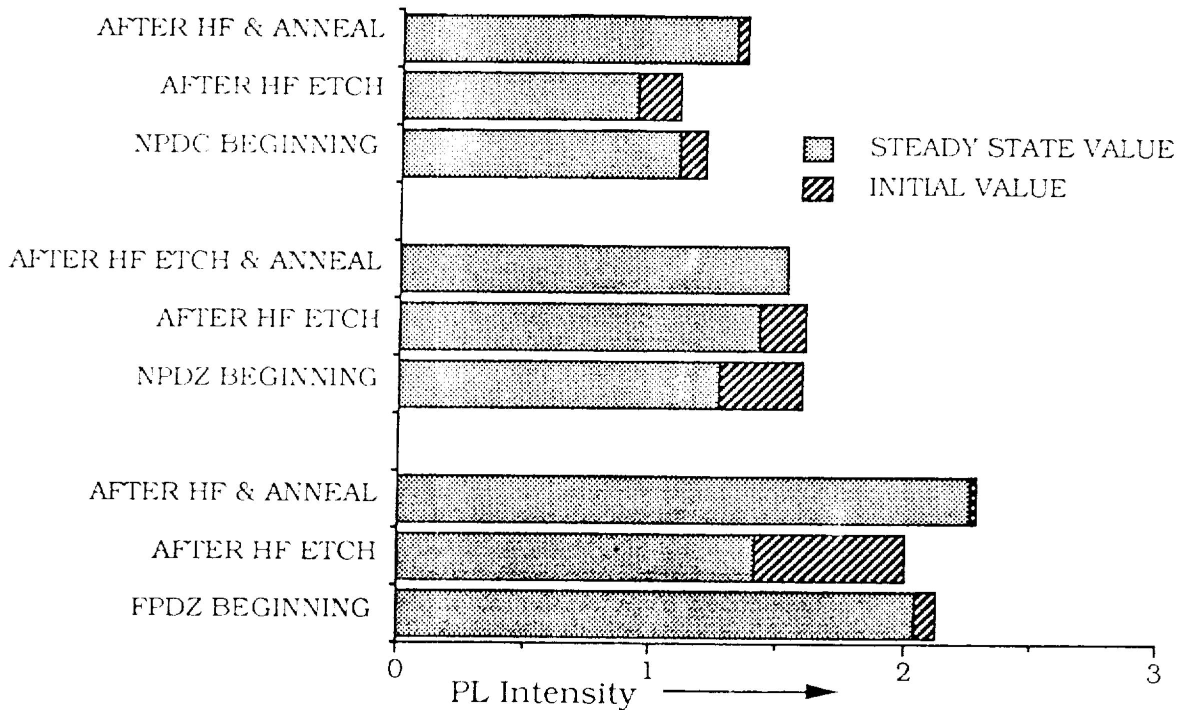


Figure 12. PLI data after S-diffusion into Cd-doped (NPDC) and Zn-doped (NPDZ and FPDZ) substrates for 3 hours at 660°C. FPDZ refers to a pre-diffusion chemical treatment as "A_2" in Fig. 5. NPDZ and NPDC refers to diffusion through a thin P-rich chemical oxide grown as "A_4" in Fig. 5.

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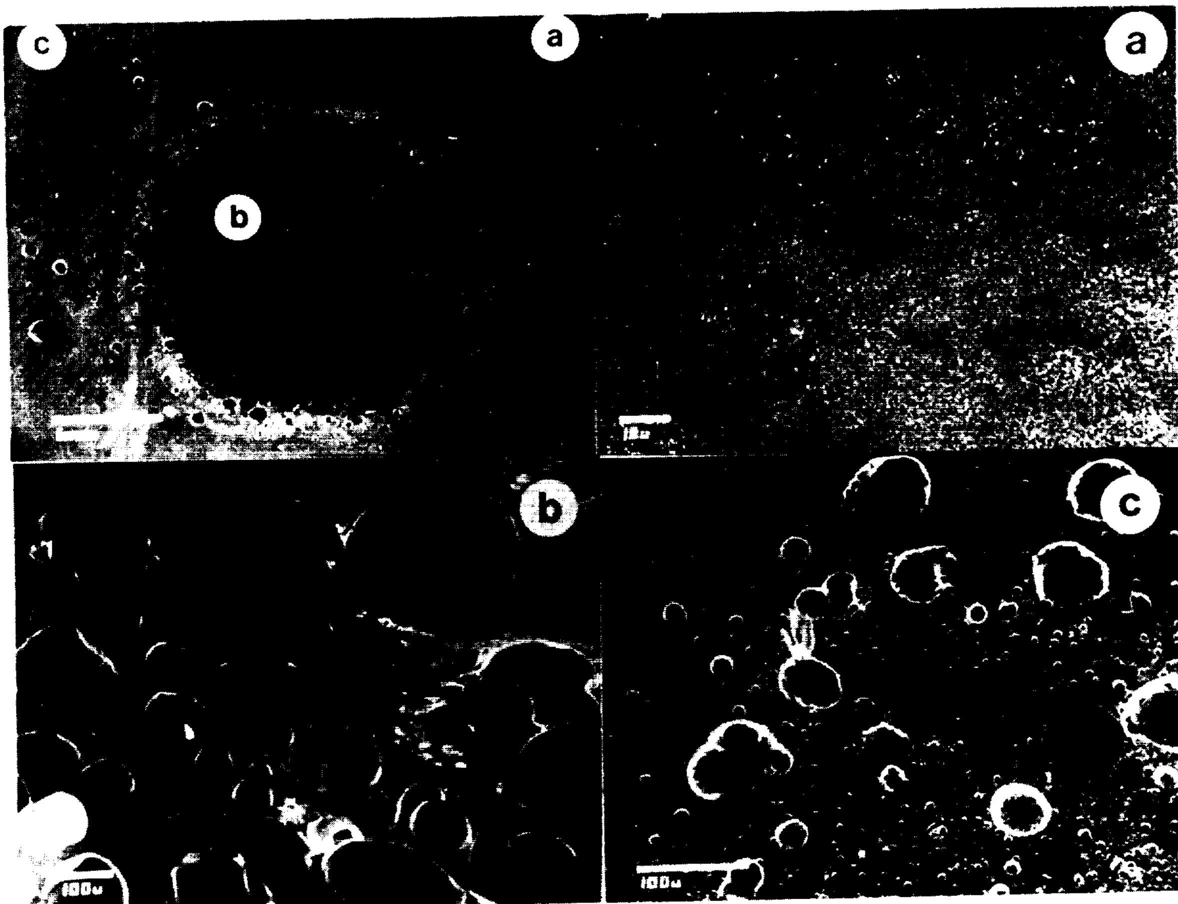

Figure 13. Surface topography of a) P-rich, b) In-rich and c) clean surface after 1 hour heat treatment in air at 660°C.

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