[1]D. S. Yaney and C. W. Pearce, *International Electron Device Meeting Technical Digest* (IEEE, NY, 1981), p. 236.
[2]G. A. Rozgonyi, R. P. Deysher, and C. W. Pearce, J. Electrochem. Soc. **123**, 1910 (1976).
[3]T. Y. Tan, E. E. Gardner, and W. K. Tice, Appl. Phys. Lett. **30**, 175 (1977).
[4]A. J. R. de Kock, W. T. Stacy, and W. M. van de Wijgert, Appl. Phys. Lett. **39**, 611 (1979).
[5]A. J. R. de Kock and W. M. van de Wijgert, J. Cryst. Growth **49**, 718 (1980).
[6]C. W. Pearce and G. A. Rozgonyi, in *VLSI Science and Technology—1982*, edited by C. J. Dell'OCo and W. M. Bullis (The Electrochemical Society, Pennington, NJ, 1982), p. 53.
[7]G. A. Rozgonyi, R. J. Jaccodine, and C. W. Pearce, in *Defects in Semiconductors*, edited by S. Mahajan and J. W. Corbett (The Materials Research Society, Pittsburgh, PA, 1982), Vol. 2, p. 181.
[8]W. Dyson, L. Hellwig, J. Moody, and J. Rossi, in *Proceedings of the Symposium on Defects in Silicon*, edited by W. M. Bullis and L. C. Kimerling (The Electrochemical Society, Pennington, NJ, 1983), p. 246.
[9]H. Tsuya, Y. Kondo, and M. Kanamori, Jpn. J. Appl. Phys. **22**, L16 (1983).
[10]R. B. Fair, J. Appl. Phys. **54**, 388 (1983).
[11]G. A. Rozgonyi and C. W. Pearce, Appl. Phys. Lett. **31**, 343 (1977).
[12]Y. Yatsurugi, N. Akiyama, and Y. Endo, J. Electrochem. Soc. **120**, 975 (1973).
[13]J. C. Mikkelsen, Jr., in *Proceedings of the Symposium on Defects in Silicon*, edited by W. M. Bullis and L. C. Kimerling (The Electrochemical Society, Pennington, NJ, 1983), p. 95.
[14]C. W. Pearce, in *VSLI Technology*, edited by S. M. Sze (McGraw–Hill, NY, 1983), Chap. 2.
[15]W. Lin and D. W. Hill, in *Silicon Processing*, edited by D. C. Gupta (ASTM, Philadelphia, PA, 1983), p. 29.
[16]K. Graff, E. Grallath, S. Ades, G. Goldbach, and G. Talg, Solid State Electron. **16**, 887 (1973).
[17]A. Baghdadi, in *Proceedings of the Symposium on Defects in Silicon*, edited by W. M. Bullis and L. C. Kimerling (The Electrochemical Society, Pennington, NJ, 1983), p. 293; and other papers, same proceedings.
[18]E. A. Schweikert, Anal. Chem. **52**, 827A (1980).
[19]L. Jastrzebski, P. Zanucchi, D. Thebault, and J. Lagowski, J. Electrochem. Soc. **124**, 1638 (1982).
[20]R. J. Jaccodine and C. W. Pearce, in *Proceedings of the Symposium on Defects in Silicon*, edited by W. M. Bullis and L. C. Kimerling (The Electrochemical Society, Pennington, NJ, 1983), p. 115.
[21]K. E. Benson, W. Lin, and E. P. Martin, in *Semiconductor Silicon 1981*, edited by H. R. Huff and R. J. Kriegler (The Electrochemical Society, Pennington, NJ, 1981), p. 33.

Structure of the InP/SiO_2 interface

Z. Liliental[a] and O. L. Krivanek
Center for Solid State Science and the Department of Physics, Arizona State University, Tempe, Arizona 85287
J. F. Wager
Department of Electrical and Computer Engineering, Oregon State University, Corvallis, Oregon 97331
S. M. Goodnick
Department of Electrical Engineering, Colorado State University, Fort Collins, Colorado 80523

(Received 14 January 1985; accepted for publication 18 February 1985)

InP/SiO_2 interfaces have been studied by high resolution electron microscopy in cross section, by ellipsometry, and by x-ray photoelectron spectroscopy. The roughness of the interface is shown to vary from 10 to 100 Å peak to peak depending on the InP surface treatment prior to SiO_2 deposition, and some evidence is found for a small amount of native oxide and P segregation at the interface. Thermal oxide grown on InP at 350 °C is shown to consist of two separate layers, an inner one of 30–70 Å thickness and probably composition $InPO_4$, and an outer one of 60-Å thickness and probably composition In_2O_3.

Due to its potential for high-speed device applications, InP has recently come to prominence as a material for metal-insulator-semiconductor field-effect transistor (MISFET) devices.[1,2] Although mobilities exceeding two times the value of Si have been achieved in InP MISFET's,[2] there is a large and as yet unexplained variation of performance for devices prepared in different laboratories,[3] or even within the same laboratory.[4] InP MISFET's also exhibit a slow decrease of the drain current with time, which is thought to result from carrier tunneling to traps a short distance inside the insulator.[5] In this letter, we present the results of a high resolution electron microscopy (HREM) investigation of several $InP\text{-}SiO_2$ interfaces. We demonstrate that relative to the well controlled structure of $Si\text{-}SiO_2$ (Ref. 6) and even GaAs-anodic oxide interfaces,[7] the structure of the $InP\text{-}SiO_2$ interface exhibits an unusually large variation from one device to another, which may account for the large spread in the observed device properties.

Undoped (n type, $4\times10^{16}/cm^3$), (100) InP wafers were used in this study. The InP surface preparation consisted of degreasing boils in tetrachloroethylene, followed by rinses in methanol/acetone and methanol. Next, the InP surface was prepared in one of four ways:

A. *Room-temperature* KOH/*methanol*. The sample was treated for 1 min in a solution of KOH in methanol which was maintained at room temperature. The resulting oxide thickness was estimated as 15 Å by ellipsometry.

B. "*Hot*" KOH/*methanol*. The sample was treated for 1 min in a solution of KOH in methanol (2.5 g of KOH in 200 ml of methanol) which was heated to 70 °C. The resulting

[a] Present address: Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

 © 1985 American Institute of Physics

Downloaded 29 Jan 2010 to 128.193.163.179. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

oxide thickness was estimated as 9 Å.

C. *Iodic acid*. The sample was treated for 20 s in a 20% HIO_3:H_2O solution. Ellipsometric estimation of the resulting oxide thickness was precluded due to diffuse scattering of the laser beam from the roughened InP surface. X-ray photoelectron spectroscopy (XPS) analysis of samples prepared in a similar way indicates that the resulting native oxide is very thin ($\sim$10 Å).

D. *Hotplate oxide*. The sample was oxidized in air on a hot plate for 68 h at 350 $\pm$ 25 °C. The resulting thermal oxide thickness was estimated by ellipsometry as 107 Å.

These samples are henceforth identified as A, B, C, and D.

The samples were subsequently rinsed in methanol, isopropyl alcohol, and blown dry with nitrogen. All four InP samples and a Si witness sample were then coated in the same run with approximately 850 Å of plasma-enhanced chemically vapor deposited (PECVD) SiO_2.[8,9] The InP wafers were then separated into three parts. One was used for electrical measurements, one for XPS, and the third for HREM cross-sectional sample preparation. The results of the electrical and XPS measurements will be described in detail in a forthcoming paper; here we report principally on the HREM observations.

Problems arose during the cross-sectional sample preparation due to the brittleness of InP (compared to Si) and the tendency of InP to dissociate under ion bombardment, and become covered by metallic In particles. These problems were avoided by stopping the usual mechanical polishing of the cross sections at a thickness of around 100 μm, using a 3:1 Ar:O_2 gas mixture in the ion mill,[10] and holding the samples at liquid N_2 temperature during the milling.

Several interface cross sections were examined for each type of sample in a JEOL 200CX electron microscope at a point-to-point resolution of 2.5 Å. All images were recorded with the beam parallel to the InP [011] direction, i.e., with the (100) interface and two sets of (111) type planes edge on. Some evidence of radiation damage was found, particularly in the thermal oxide, by comparing images taken soon after a particular area was first illuminated with electrons, and images taken after several minutes irradiation. Efforts were, therefore, made to minimize irradiation prior to recording the first image of any new specimen area.

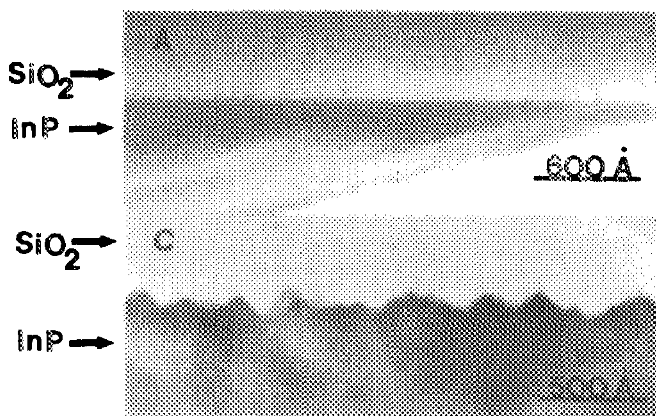

FIG. 1. Medium magnification images of InP-SiO_2 interfaces in samples A (room-temperature KOH/methanol treatment) and C (iodic acid treatment). Note the large roughness produced by iodic acid.

Results relating to samples on which no InP oxide layer was intentionally grown are shown in Figs. 1 and 2. Room temperature and hot KOH/methanol treatment of InP prior to the SiO_2 deposition produced fairly smooth interfaces, a typical example is shown in Fig. 1(a). The iodic acid etch, on the other hand, produced interfaces with roughness about 100-Å peak to peak. These rough interfaces showed a preference for facetting on the InP (111) planes [Fig. 1(b)].

Higher magnification images are presented in Fig. 2. Sample A interface (room-temperature KOH/methanol) is slightly rougher than the interface B (hot KOH/methanol) and is also decorated by small crystalline particles, which are absent in B. The size of the particles varies from about 10 to about 30 Å, and they show a spacing of 2.9 $\pm$ 0.1 Å. This is in reasonable agreement with the dominant spacing of 2.89 Å in black phosphorus,[11] as well as the major spacing of 2.71 Å in metallic indium. It is therefore not possible to distinguish conclusively which metal gave rise to these particles, and whether or not they are artifacts of the ion milling specimen preparation step. However, we note that the particles appear only at the interface, whereas In contamination particles which result when pure Ar gas is used for milling are always spread over the whole sample, and that the particles also appear to be dependent on the initial InP surface treatment, since they were not observed in samples B and C.

The native (InP) oxide thicknesses measured by ellipsometry prior to the SiO_2 deposition were 15 and 9 Å, and immeasurable due to diffuse light scattering (caused by the interface roughness) for samples A, B, and C, respectively. Native oxides whose refractive indices are substantially different from oxides deposited on top of them, as is the case for $InPO_4$, In_2O_3, and SiO_2, may appear in the HREM image as intermediate bands of different average contrast, and possibly also different fine textures. They should be clearly visible if the crystal oxide interface is atomically flat, and the oxide thickness is at least a few angstroms, as for example in previous studies of anodic oxides on GaAs.[7] In the present case, however, no intermediate band is observed at all in sample B,

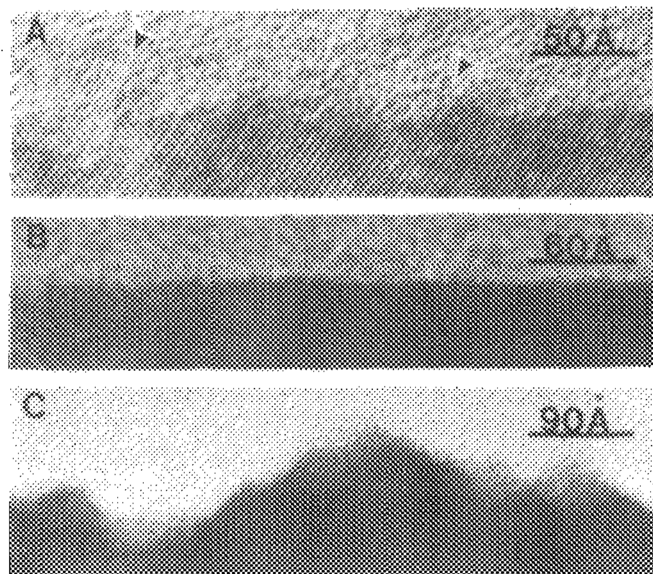

FIG. 2. High resolution images of InP-SiO_2 interfaces. Note the small crystalline particles (arrowed) at the interface in sample A, the smooth nature of B, and the large roughness in C.

Downloaded 29 Jan 2010 to 128.193.163.179. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

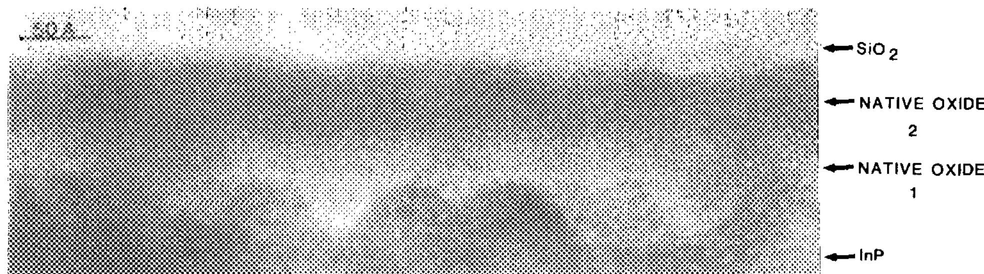

FIG. 3. InP-SiO_2 interface with a native InP oxide grown by oxidation in air at 350 °C ("hot-plate" oxide, sample D). The native oxide is separated into two layers of 30-Å and 70-Å thickness, respectivelly. The InP substrate shows pronounced pitting.

despite the fact that the interface is quite flat. In sample A there is some evidence for a dark band about 6 Å thick separating the InP crystal from the SiO_2 (Fig. 2, sample A). Therefore, it may be that ellipsometry is overestimating the oxide thickness by about a factor of 2, or that SiO_2 deposited on top of the native oxide reacts with it to a depth of a few angstroms, thus smoothing out the native oxide-SiO_2 interface, and making the observation of the intermediate oxide HREM more difficult. We note that in a previous study where the results of ellipsometry measurements and of an HREM determination for a thin thermal oxide on Si were compared, HREM gave the higher thickness figure[12] (25 Å vs 15 Å).

Figure 3 shows a high magnification image of the "hot-plate" oxide (sample D) interface. The oxidation at 350 °C has produced pits in the InP up to 40 Å deep and 20–100 Å across, but left some portions of the interface relatively flat. (This can be seen quite clearly in lower magnification images not reproduced here.) The thermal oxide consists of two separate layers, a darker upper one of about 60-Å thickness and a lighter layer next to InP, of thickness varying between 30 and 70 Å because of the pitting. Ellipsometry gave a total thickness of 107 Å for the oxide. XPS measurements of thermal oxides of various thicknesses[8] suggest that there should be a layer of $InPO_4$ next to the InP crystal about 30 Å thick, and the remaining thickness of any thermal oxide should be In_2O_3. The refractive index for high-energy electrons is approximately proportional to the average density of the material. In_2O_3 is about 50% denser than $InPO_4$, hence the HREM observation is in agreement with the XPS result. A precise composition analysis by analytical electron microscopy is unfortunately not possible on this scale as the native oxide suffers serious mass loss under electron irradiation. It might also be possible that P segregation directly at the InP-native oxide interface leads to a preferential attack by the ion beam during sample preparation, resulting in localized thinning which would also give lighter contrast. However, such effects would vary with the overall sample thickness (distance from specimen edge), and this variation was not observed. Finally, it is interesting to note that the textures of the image of the amorphous SiO_2 and of the amorphous InP oxide are substantially different. This is because the average local structure in SiO_2 is different (more open) from that in $InPO_4$ or In_2O_3. Hence, the identification of a thin native oxide by HREM should be possible even if its refractive index were quite similar to the oxide which covers it.

The detailed electrical properties of the four samples will be discussed elsewhere. Here we summarize them as follows: interface state densities determined from quasi-static *C-V* measurements were the highest for the "thermal oxide" sample D, where the interface was rough and two kinds of native oxides were present. This was followed by sample B (about two times better), and samples A and C (about three to four times better). Thus the best interface from the structural point of view (B) actually gave poorer electrical results than the very rough interfaces (C).

In conclusion, there is a large variation in the structure of the InP-SiO_2 interfaces, depending on the treatment of the InP surface prior to SiO_2 deposition. The interfaces can be very rough as well as very smooth, and contain a different thickness of a "native" InP oxide. The results show some correlation between the interface structural "quality" (degree of smoothness and absence of native oxide) and its electrical properties, but clearly much more work is needed if the InP-SiO_2 interface is to attain a degree of perfection similar to Si-SiO_2 interfaces.

This work was supported by NSF grants DMR811 7052 and CHE791 6098, and done in cooperation with Marion Clark from Hughes Research Laboratories, and Carl Wilmsen's group at Colorado State University.

[1]C. W. Wilmsen, J. F. Wager, and J. Stannard, Inst. Phys. Conf. Ser. **50**, 251 (1980).
[2]K. M. Geib, S. M. Goodnick, D. Y. Lin, R. G. Gann, C. W. Wilmsen, and J. F. Wager, J. Vac. Sci. Technol. B **2**, 516 (1984).
[3]C. W. Wilmsen, R. W. Kee, J. F. Wager, J. Stannard, and L. Messick, Thin Solid Films **64**, 49 (1979).
[4]S. M. Goodnick, T. Hwang, and C. W. Wilmsen, Appl. Phys. Lett. **44**, 453 (1984).
[5]C. W. Wilmsen, J. F. Wager, K. M. Geib, T. Hwang, and M. Fathipour, Thin Solid Films **103**, 47 (1983).
[6]Z. Liliental, O. L. Krivanek, S. M. Goodnick, and C. W. Wilmsen, Materials Research Society Meeting, Symposium, "Layered Structures, Epitaxy and Interfaces," Boston 1984 (in press).
[7]O. L. Krivanek and S. Fortner, Ultramicroscopy **14**, 121 (1984).
[8]J. F. Wager and C. W. Wilmsen, J. Appl. Phys. **53**, 5789 (1982).
[9]J. F. Wager, C. W. Wilmsen, and L. L. Kazmerski, Appl. Phys. Lett. **42**, 589 (1983).
[10]W. Katzschner, A. Steckenborn, R. Loffler, and N. Grote, Appl. Phys. Lett. **44**, 352 (1984).
[11]A. S. T. M. powder diffraction data files 1983.
[12]M. A. Green, A. W. Blakers, and O. L. Krivanek, J. Appl. Phys. **54**, 2885 (1983).

Downloaded 29 Jan 2010 to 128.193.163.179. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp