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The Influence of a Hydride Preflow on the Crystalline Quality of InP Grown on Exactly Oriented (100)Si

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Several microns thick epitaxial InP films have been successfully deposited on exactly oriented (100) Si substrates by metal-organic vapour-phase epitaxy. We have studied the influence of a hydride preflow before buffer growth on the crystalline quality of the InP by measuring the surface roughness, by X-ray diffractometry, TEM and SEM investigations, and by detection of anti-phase-domains. Generally, an AsH_3 preflow instead of PH_3 improved the crystalline perfection considerably. Furthermore, if AsH_3 is introduced only during cool-down between 700 and 900° C after the thermal cleaning step anti-phase-domain free InP is grown.

Key words: InP-on-Si heteroepitaxy, MOVPE, hydride preflow

I. INTRODUCTION

Recently, the quality and reliability of optoelectronic devices based on the InP/Si material system has been improved considerably. This technological approach to combine the advantageous properties of both InP and Si promises opto-electronic integrated circuits for Gbit/s applications in the computer and telecommunication field integrated with VLSI Si circuits. Stable multi quantum-well lasers for cw operation with an emission wavelength matched to optical fibers have now reached lifetimes of some 2000 hours with a constant light output power without considerable variations of the driving current.[1,2] The good function of many lattice-mismatched heteroepitaxial devices has been convincingly shown.[3–7] Their continued success competing with other integration techniques will largely depend on further improvements of the crystalline quality of the active device layers. For the growth of III/V epitaxial layers on exactly oriented (100)Si it is common practice to use a metal-organic vapour-phase epitaxy (MOVPE) or molecular beam epitaxy process consisting of a short thermal cleaning step at elevated temperature, the nucleation of an InP buffer layer at low temperature, and the subsequent growth of device layers of InP and related materials at normal growth temperatures. We studied the epitaxial crystal growth on exactly (100) oriented Si substrates which are the industry standard. We employed MOVPE since this growth method is most promising for a future mass-production. There is evidence that the presence of hydrides in the time interval between the thermal substrate cleaning step and the buffer growth is of great impact on the layer quality.[8–11] We investigate the influence of a PH_3 or AsH_3 ambient and the onset temperature for this hydride flow when cooling the thermally cleaned substrates down to the buffer nucleation temperature. Though AsH_3 is not commonly used in the actual growth of arsenic free III/V compound semiconductors it was found to be beneficial for their growth since it promotes two-dimensional growth,[10] is a viable tool to clean the substrate surface,[9] and may under certain conditions help to avoid monolayer surface steps which are primarily responsible for anti-phase-domains (APD).[11] This point of view is not commonly accepted,[12] though. The evaluation of the samples is based on transmission and scanning electron microscope investigations, on X-ray diffractometric results and on measurements of the InP surface roughness as well as on a wet chemical surface analysis to reveal anti-phase-domains.

II. CRYSTAL GROWTH

The cleaning of the Si substrate was started with a 20 min boiling in $H_2SO_4:H_2O_2:H_2O = 5:1:1$, followed by five rinse cycles in DI water of 18MΩcm. The substrate was spin dried and then dipped in 5% HF in a buffered solution for 30 s. Finally another five rinses in DI water followed, after which the substrate was again dried by spinning and transferred to the epitaxy apparatus. This cleaning procedure is compatible with Si-MOS-technology,[13] because it can be performed at virtually any step in MOS-production, a necessary prerequisite for the heterointegration of III/V- into Si-technology.

The crystal growth was performed in an MOVPE machine designed by AIXTRON and using an IR heater. It was operated under low pressure (20 to 100 mbar) under a hydrogen flow of 8 l/min.

The Si substrate was then thermally cleaned and deoxidized at 950° C for 15 min solely under H_2. A hydride gas flow (PH_3 or AsH_3, both at 100 ml/min) was added either still at 950° C or at a certain temperature during the cool-down phase. Details on this will be given in subsequent chapters of this paper.

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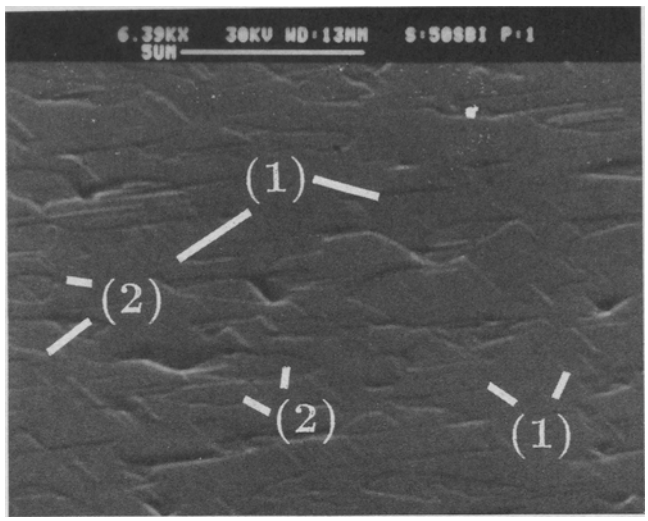
A typical growth run commenced with an InP nuclation step at 400° C for 20 min at 100 mbar yielding an 80 nm buffer. Based on this initial layer the growth of the InP layer continued for 120 min at 640° C and 20 mbar depositing a total of 2.5 μm InP. We also checked growth at 100 mbar but attained only inferior results. This is in agreement with observations made by Fujita *et al.*[14] for GaAs-on-Si. V/III-ratios of about 2200 and 550 were used for the buffer and the main layer, respectively. The growth was terminated by cooling to room temperature under phosphine flow. This study compares InP/Si layers of 2.5 μm thickness. Except for variations in connection with the hydride flow, the same and otherwise optimized growth procedure was employed for all layers under investigation.

III. SURFACE ANALYSIS

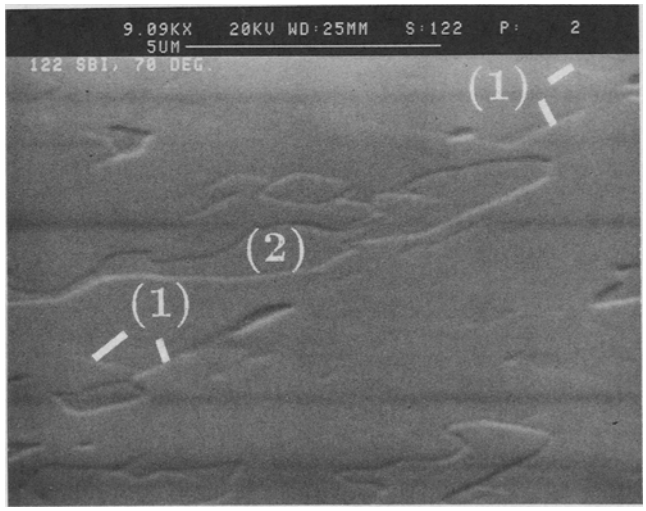
Figure 1a shows the typical surface morphology of an InP-on-Si film taken with a scanning electron microscope (SEM). A PH_3 flow was injected 10 min after the start of the thermal cleaning step and maintained throughout the entire cool-down phase. With respect to all the other growth parameters the process is already optimized. Figure 1b shows the results of a virtually identical growth run except that AsH_3 instead of PH_3 was used during the phase in question. Basically, two types of surface features are present which can readily and without any further surface investigation be interpreted as follows. Short straight lines (1) parallel to each other and intersecting at an oblique angle on the photograph are traces of twin lamellae.[15] We determine their average line density to be reduced by a factor of 10 when AsH_3 was used (Fig. 1a compared to Fig. 1b). The other prominent surface features are the bent segments (2) originating from anti-phase-domains.[16] Using AsH_3 pushed their number down to one third of the PH_3 value. We conclude that defects such as twins and APDs which degrade the electrical and optical properties of InP can be considerably reduced by replacing PH_3 by AsH_3 during the cool-down phase prior to buffer growth.

In order to give a quantitative measure of the surface quality we performed measurements of the surface roughness R_a with a DEKTAK surface profiler. This is a valuable undestructive method to determine the film's surface properties.[17] The sample in Fig. 1a has an R_a of 11 nm, the best value we ever measured for a PH_3 grown film. Standard values for AsH_3 grown layers (Fig. 1b) range from 4 to 6 nm. Substrate R_a of InP as well as of Si vary from 3 to 6 nm. Roughness analysis revealed smoother and more regular layers indicating a better crystalline structure when AsH_3 is used.

One reason for the improvements achieved by the use of AsH_3 lies in the fact that AsH_3 is stable only up to 700° C, whereas for PH_3 this temperature is about 800° C.[18] So AsH_3 decomposes more readily setting free a greater number of group V components to enhance growth by forming doublelayer steps and more stable Si-As bonds.[19,20] PH_3 is under identical conditions less inclined to decompose, therefore PH_3 is only the second choice after AsH_3.



(a)



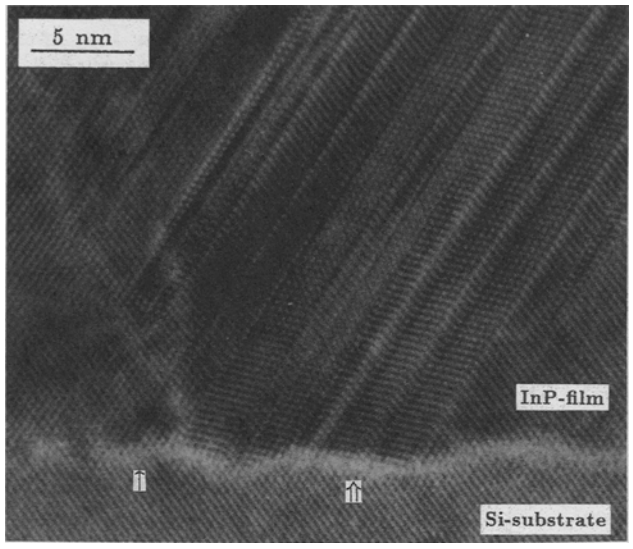
(b)

Fig. 1 — a) SEM topograph with traces of twins (1) and anti-phase-domains (2) of a PH_3 grown film and b) of a AsH_3 grown film.

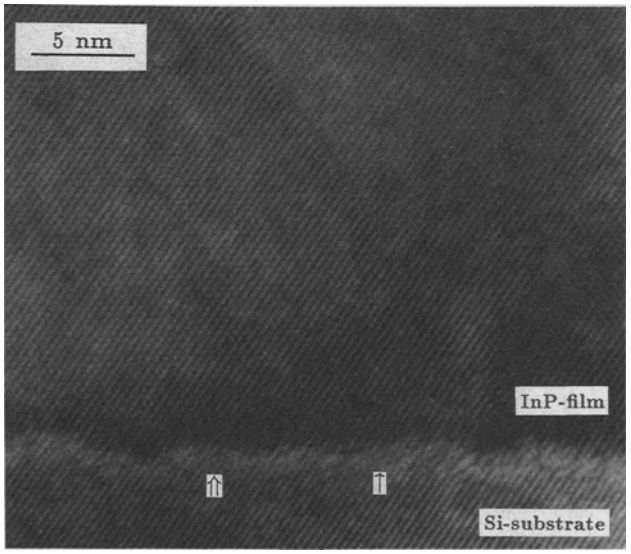
IV. TEM, X-RAY, AND ETCHING INVESTIGATIONS

A detailed microstructural analysis was done by Transmission Electron Microscopy (TEM). We used a Philips CM30T at 300 kV. TEM samples were prepared by ion thinning and by Chemical Assisted Ion Beam Etching using iodine to prevent In droplets.

Differences of the crystalline quality of the epitaxial layer are born out by high-resolution electron micrographs. Examples for both hydrides are reproduced in Fig. 2a and b. They show the InP/Si interface, from where (particularly in the case of Fig. 2a with PH_3 preflow) a number of twin lamellae



(a)



(b)

Fig. 2 — a) HREM picture of the InP/Si interface of a PH_3 grown film and b) of a AsH_3 grown film. ↑ and ↑↑ denote examples of type I and II dislocations, respectively.

Table I. Relation between X-ray FWHM and Surface Roughness R_a for InP-on-Si Layers

FWHM in arcsec	R_a in nm
430	7.6 ± 1.8
450	7.7 ± 0.9
490	6.7 ± 1.2
680	8.3 ± 0.6
800	8.7 ± 1.4
1055	8.7 ± 1.6
1370	11.0 ± 0.3
1600	11.4 ± 0.9
1650	12.7 ± 0.9

originate. All twin lamellae have a strong preferential direction and regularity. Similar distinct crystalline features were also reported for GaAs-on-Si.[21]

Generally, we find regions of high crystalline quality and those with inferior structural conditions. For the PH_3 grown sample we see a substantial number of twins and crystalline disturbances propagating through the layer towards the surface thus marring the entire film (Fig. 2a). Again, the AsH_3 grown sample reached a much higher degree of perfection with less twins and imperfections visible (Fig. 2b).

Alerhand *et al.*[22] discussed for the case of GaAs on (100)Si that double-layer steps on the (100)Si surface act as nucleation sites in the initial stages of growth whereas flat terraces lead to the formation of mixed layers of the group III and the group V component inhibiting the development of a zinc-blende lattice.

Furthermore, type I or 90° dislocations as well as type II or 60° dislocations can be found. With type I dislocations (marked by ↑ in Fig. 2a) two extra half crystal planes terminate at the dislocation core, whereas with type II dislocations (marked by ↑↑) this is only one.[23] Not all dislocations are separately marked in Fig. 2. We count an average period of type I or type II dislocations of 5.5 nm along the heterointerfaces displayed in Fig. 2a and b with no specific preference for either dislocation type. This value agrees fairly well with the Vernier period of interfacial dislocations, which is $P = a_1 \cdot a_2/(a_1 - a_2)$ with a being the respective nearest neighbor distance in the closest-packed lattice direction.[24] For the case of InP on Si we calculate $P = 5.4$ nm. Therefore, we conclude that the epitaxial InP film is almost free of stress originating from lattice mismatch.

We conducted an X-ray investigation to clarify the nature of the surface irregularities. The X-ray diffraction properties were investigated with a double-crystal diffractometer (DCD) in parallel $(n,-n)$-arrangement using CuK_α-radiation and (400)-reflection. The first crystal (collimator) was a perfect silicon crystal with an exact (100)-surface orientation (symmetrical Bragg case).

Two separate Bragg peaks were found at Bragg angles of 34.6° and 31.7° for the silicon substrate and the InP layer, respectively, corresponding to their different lattice constants. The silicon peak shows a full width at half maximum (FWHM) of 8.8 arcsec, which is more than twice the value of a perfect crystal (4.02 arcsec).[25] It can be concluded from measurements with a different geometry of the X-ray beam that this is not caused by bending of the substrate but by direct influence of the InP layer. Obviously, a thin Si substrate layer near the interface is strained by the structures of the InP layer.

The InP reflection is broadened with a measured FWHM of 1650 arcsec (0.46°) for the PH_3 processed film and 430 to 470 arcsec for various AsH_3 grown samples, the latter exhibiting a more pronounced curve sharpness, an indication of an improved crys-

Table II. Effect of Thermal Cleaning and Passivation with AsH_3 for Si Substrates

InP/Si Sample	Thermal Cleaning (950° C, 15 min)	Cooling after Thermal Cleaning (950° C-400° C)	Roughness of InP/Si	Morphology of InP/Si
292	with AsH_3	with AsH_3 (from 950° C)	5.0 nm	−
191	no AsH_3	with AsH_3 (from 950° C)	3.4 nm	+
244	no AsH_3	with AsH_3 (from 900° C)	4.0 nm	++
234	no AsH_3	with AsH_3 (from 700° C)	4.0 nm	++
235	no AsH_3	no AsH_3	5.5 nm	−−
198	no thermal cleaning	no thermal cleaning	9.0 nm	−−

++: very good and no APD; +: good, but with some APD; −: with many APD; −−: bad and many defects.

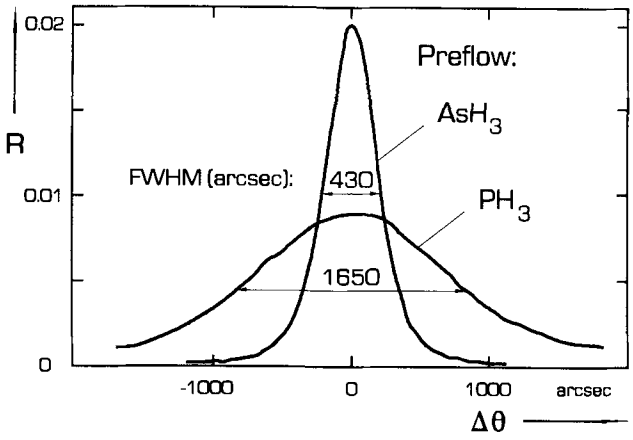


Fig. 3 — X-ray peak of InP-on-Si, grown with PH_3 or AsH_3 preflow, respectively. The ordinate is the X-ray reflectivity of the sample (measured intensity normalized by the intensity behind the first crystal).

tal quality. Figure 3 summarizes the X-ray findings. The FWHM range of AsH_3 grown samples compares quite well with results obtained by other authors[26] without resorting to commonly used techniques of incorporating strained layer superlattices, subjecting the InP-on-Si to additional annealing cycles, or growing on slightly misoriented Si-substrates. Actually, we favour the epitaxial crystal growth on (100) oriented Si substrates, since the III/V-device performance will not deteriorate on these substrates as was recently shown for misoriented diode lasers.[27] Furthermore, post-growth anneals might negatively affect co-integrated Si-components due to additions to the thermal budget.

For all the InP-on-Si films investigated the FWHM, measured to an accuracy of better than 5%, is correlated with R_a in an essentially linear form. Relevant figures are given in Table I. We mention, though, that in the FWHM-range around and below 500 arcsec we measured two layers, which were even smoother ($R_a = 4 \pm 0.9$ nm). Taking into account the dispersivity of the DCD arrangement as used with Si-(400)-collimator and InP-(400)-sample reflection, the expected value of FWHM of a perfect InP crystal would be approximately 11 arcsec.[25,28] For a *perfect* InP substrate we measured a FWHM of 11.2 arcsec. From the fact that the FWHM remains practically unchanged also at other orders (200, 600) of the InP reflection we conclude that the reasons for the reflection-curve broadening are not so much internal stress rather than a tilt of crystalline regions against each other.

APDs can be detected when the epitaxial film is subjected to a chemical treatment. We obtained the best results with a solution of composition $HBr:CH_3COOH = 1:3$.[29] If we etch the layer for 40 s at room temperature we could always find APD features for PH_3 grown films, regardless of process variations. With AsH_3 APD-free samples can be grown, subject to process optimization as we will show in the next chapter.

V. EFFECTS OF THE ARSINE-EXPOSURE TEMPERATURE

While a preflow generally improves the crystalline quality of the InP/Si films they are still troubled by the presence of detrimental anti-phase-domains which down-grade the electrical and optical performance and must therefore be avoided. There are several reports on the effects of the AsH_3 onset temperature when growing GaAs on Si.[8–12] We varied the presence of AsH_3 during the thermal cleaning and cool-down phase. Table II lists the relevant process parameters and their influence on the layers. Figs. 4a to c further illustrate our findings. While omitting the thermal cleaning step all together leads to the worst layers in our series of investigations (Fig. 4a), thermal cleaning and cooling alone without AsH_3 is no major step forward and the quality remains inferior due to large quantities of twins and APDs. A slight improvement can be achieved by a continuous AsH_3 flow, yet the layers are marred by defects (Fig. 4b). The density of twins was greatly reduced though APDs are still present in substantial numbers. Major improvements are obtained when AsH_3 is flowing only during the cooling phase and not while the substrate is still at 950° C. We have grown visually perfect and APD-free InP films on (100)Si when the AsH_3 flow commenced between 700 and 900° C (Fig. 4c). A further reduction of the onset temperature was found to be incompatible with APD-free material growth.

Aspects of this behaviour have already been discussed in literature although mainly for GaAs/Si.[8–12,14,18–20] There is a tendency to stress either the high or the low end of the temperature scale, but this alone cannot explain our observations. For various reasons some authors consider a high onset tem-

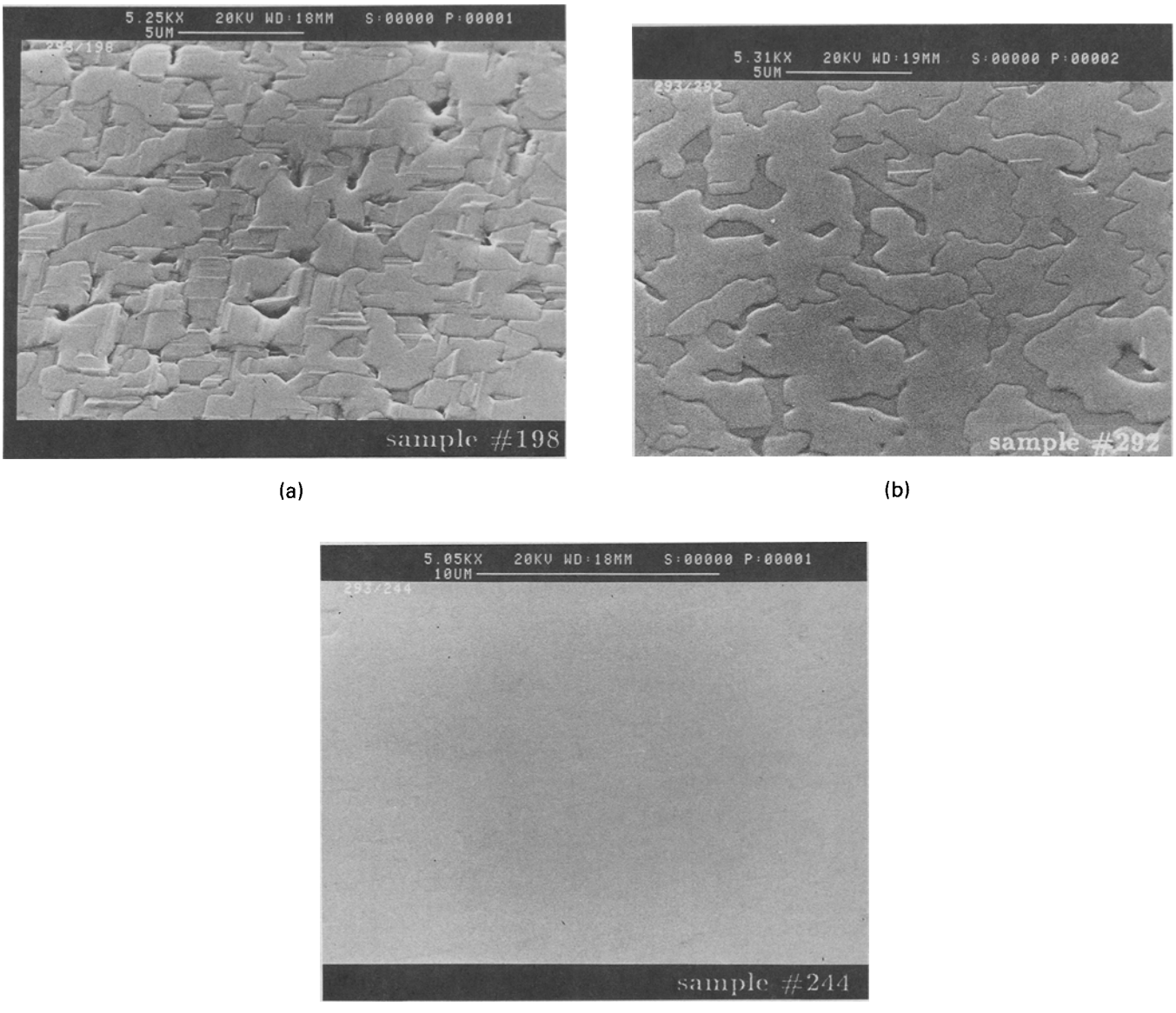


Fig. 4 — a) SEM topograph of a InP-on-Si layer without AsH_3 preflow (sample #198), b) with AsH_3 preflow throughout the 950° C thermal cleaning step (sample #292), and c) with AsH_3 preflow below 900° C (sample #244).

perature favorable for lattice-mismatched heteroepitaxial growth. We also believe a higher temperature to be advantageous for the formation of Si-As bonds at the surface to passivate the substrate for a two-dimensional growth. On the other hand there is evidence that at a low hydride onset temperature the crystallinity of the grown material improves[19] and a smoother interface is generated leading to a more orderly growth.[30]

The doping of Si with As is also a strong function of temperature and becomes fairly sizable at 950° C. Due to the incorporation of the dopant and the resulting lattice disturbance near the Si surface its roughness increases. Hence, if the Si sample is subjected to predeposition-like doping before buffer growth, this will lead to an inferior crystalline quality. We support this interpretation by experimental evidence, since identical layers grown on intentionally doped Si-substrates have R_a-values around 10 nm. Furthermore, injecting the hydride too early at too high a temperature might lead to arsenic or phosphorous silica glass contamination due to its reaction with any surface oxide still left.

VI. CONCLUSIONS

We have investigated the influence of a hydride preflow on the quality of InP layers grown heteroepitaxially on exactly oriented (100)Si-substrates. Various measurement techniques were employed. For an otherwise optimized growth process we found that an AsH_3 ambient yielded largely improved crystalline quality as compared to PH_3 because the former leads to a better Si-surface preparation due to easier cracking at high temperatures. As for the

optimum AsH_3 exposure during the cooling phase prior to buffer growth we found the temperature range from 700 to 900° C, a compromise between crystallinity considerations and an advantageous substrate preparation. Neither AsH_3 presence during the entire period nor its complete absence was supportive for good growth quality. For a satisfactory understanding of this behaviour not one factor alone can be singled out but all tendencies must be taken into account. A publication on the optical and electrical characteristics of these InP/Si-layers is currently in preparation.

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