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Preparation and test of special surfaces for epi-ready InP wafers

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Abstract

The results of the development of two different technologies for the preparation of special surfaces for ready-to-use ('epi-ready') InP wafers are presented. The epi-ready state was studied by means of X-ray photoelectron spectroscopy. The quality of the substrates stored for 4–12 months was tested by growing an epilayer by metal–organic vapor phase epitaxy and by characterizing it with high-resolution X-ray diffraction and photoluminescence techniques. Evidence that one of our technologies could be adopted industrially is given. © 1997 Elsevier Science S.A.

Keywords: Epi-ready technology; Epitaxial growth; Metal–organic vapor phase epitaxy

1. Introduction

The control of the surface conditions of III–V substrates is known to be of crucial importance for the quality and reproducibility of epitaxial growth. A substrate can be considered as 'epi-ready' if high-quality layers can be grown on its surface with no previous chemical pretreatment. An epi-ready technology should assure protection from contamination and oxidation before growth with no aging effects (up to 6 months or more), and lead to high-quality and more reproducible layers. Different InP suppliers have selected their own epi-ready technology. For instance, one supplier [1] relies on "high-quality polishing, and new cleaning and packaging methods": a cleaning and packaging (in nitrogen gas) process was largely improved in order to preserve the surface cleanliness and keep the native oxide layer thickness to a minimum. Another one relies on a "dry oxidation process" [2]: protective thin oxide layers were grown by thermal or ultraviolet oxidation. In the present work, we describe the results of the development of two different technologies for the preparation of epi-ready surfaces, evolved from studies performed on 2″ InP wafers produced by Centro Ricerche Venezia (CERIVE)–ENIRISORSE SpA.

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2. Experimental

The epi-ready surfaces were prepared starting from (100)-oriented undoped InP CERIVE substrates with carrier concentration $n = 9 \times 10^{15}$ cm^{-3}, resistivity $\rho = 1.6 \times 10^{-1}$ Ω cm, mobility $\mu = 4390$ cm^2 V^{-1} s^{-1} and EPD $\sim 5 \times 10^4$ cm^{-2}. One of the technologies, TA, is based on a specific treatment during final polishing, under a rigorously controlled atmosphere, leading to the formation of a protective film, followed by packaging under nitrogen in hermetic and clean containers. Extremely low humidity and oxygen levels are present at the end of this process. A second one, TB, is based on a particular chemical etching which creates a very stable passivated surface that does not need packaging in a protective inert atmosphere.

For a comparison, two additional types of substrates (a standard one, S, and an epi-ready commercial substrate, E, Fe-doped InP, EPD $\sim 10^4$ cm^{-2}, stored under nitrogen) were considered. The pre-treatment in the case of the substrate S is just the typical one used for non-epi-ready wafers by the growers: the wafer is degreased and cleaned with two solvents (trichloroethylene and acetone) at elevated temperature, rinsed with isopropyl alcohol at room temperature, etched with the $5H_2SO_4{:}1H_2O_2{:}1H_2O$ solution, flushed in de-ionized water, rinsed in isopropyl alcohol at room temperature and dried with high-purity nitrogen. In this

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way, the state of the surface in S immediately after pre-treatment and the quality of the film grown on it become the reference for our present work.

The X-ray photoelectron spectroscopy (XPS) technique (VG-scientific Escalab 210 spectrometer; Al Kα non-monochromatic 300 W X-ray source and a CHA analyzer working at constant pass energy of 50 and 20 eV for wide and narrow scan spectra, respectively) has been widely used to characterize the wafers, in order to identify the chemical composition of the surface oxides and their thickness. Film oxide thickness was measured by two different methods: angle resolved XPS at constant wavelength steps and in situ Ar^+ ion beam sputtering at constant etching time followed by normal angle analysis step by step. A detailed description of sample manipulation before tests, measurements and data analysis is given elsewhere [3].

A second evaluation of the epi-ready surfaces was done by an InP epitaxial growth by low-pressure metal–organic vapor phase epitaxy (LP-MOVPE) (Aixtron Aix 200) on wafers TA (after 12 months), TB (after 4 months), E and S. The growth (4 μm thick) was carried out in a single run onto the four (1/4 wafer each) samples. Source materials were trimethylindium and 100% phosphine, the carrier gas was Pd-purified H_2, the growth temperature 640°C and the growth rate 2.5 μm h^{-1}. The films were characterized by high-resolution X-ray diffraction (HRXRD) and photoluminescence (PL) techniques. The rocking curves were recorded with a Philips MRD 1835 five-crystal-diffractometer with a Bartels monochromator set on the (440) Bragg reflection. For the (117) reflection, they were recorded at different points on each sample. PL analysis was performed with a custom-made apparatus [4] using He–Ne laser, a grating spectrometer, an LN_2 cooled germanium detector and a helium flux cryostat. The excitation power density on the sample was 4 W cm^{-2}. Lateral variations of intensity were about 30% on all the samples.

3. Results and discussion

3.1. XPS

A survey scan was executed on each sample to identify the most significant elements and then compare them with those revealed on the survey scan of reference sample S. The most significant species were acquired in detail to determine their composition and their depth distribution. The thickness values, found with both the methods mentioned above, were in strict agreement with each other. The information regarding identification of the elements, their depth distribution and atomic percentages is shown in Fig. 1.

Samples TB (stored for 20 days) and E (stored for 6 months) exhibit the thickest oxide layers (at least 38 Å). They show a form of oxide stratification, In_2O_3 being the compound at the InP (bulk) surface, while a $InPO_4$ and $In(OH)_3$ mixture represents the external layer. The main difference between these samples is in the In_2O_3 thickness, higher in TB than in E. The situation found on the surface of wafer TA (stored for 6 months) is similar to that found on the reference wafer S (immediately after pre-treatment); in both cases, no In_2O_3 was detected and only a 25 Å layer of $InPO_4$ has been found on sample TA. No contamination was present either in S or in TA. Aging effects were monitored by XPS on the surfaces of samples TB and TA after some hours, weeks and 6 months. The main result is that the species (and thicknesses) present on the surfaces evolve only slightly at the beginning of the aging period (TA), or do not evolve at all (TB). For the TB case, some contamination (a heavy element) was detected.

3.2. Epitaxial growth

After growth, all the samples appear mirror-like. Hall-effect measurements at 77 K on the epitaxial layer of sample E ($n = 1.1 \times 10^{15}$ cm^{-3}, mobility $\mu = 50\,100$ $cm^2\ V^{-1}\ s^{-1}$) were used as a first test of the quality of the epitaxial deposition. These values of n and μ are among the best obtained with our MOVPE, and they are nominally due to 'spike' contamination of O and Si at the substrate/epilayer interface.

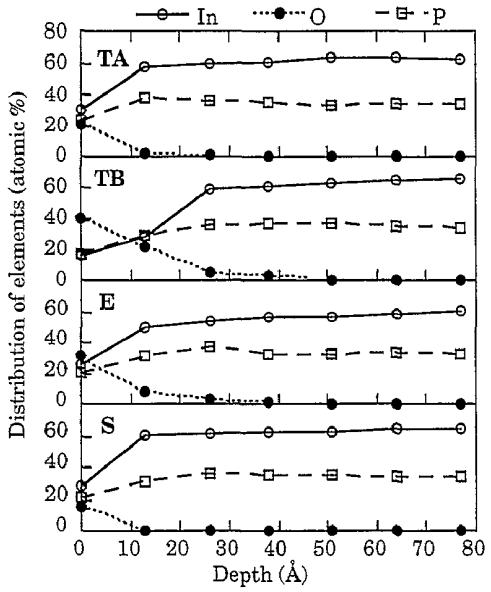

Fig. 1. XPS In, P and O atomic percentage depth profiles in epi-ready and standard InP wafers.

Table 1
Average values of FWHM for the (117) Bragg peak and PL intensities at different temperatures

Sample	HRXRD: FWHM (arcsec)	PL at 295 K (a.u.)	PL at 4 K (a.u.)
DFC (crystal)	9.7 ± 0.5	—	—
S (film)	10.4 ± 0.5	2.5	490
E (film)	10.9 ± 0.5	0.003	0.7
TB (film)	11.1 ± 0.5	0.24	—
TA (film)	11.8 ± 0.5	3.1	640

DFC, dislocation-free crystal.

3.3. HRXRD

Table 1 reports the average FWHM (full width at half maximum) values for the (117) Bragg peak measured at different points on each sample, together with their dispersions. The theoretical ratio of the intensities diffracted from the film and from the substrate is 1.5, as determined from a dynamical simulation. The FWHM values for all samples (substrate plus film) are about the same, suggesting that their crystalline quality is comparable. Compared with a nominally dislocation-free crystal (a 'Showa Denko' InP reference crystal; DFC in Table 1), the FWHM values of the four samples are higher by about 1–2 arcsec, mainly due to the higher dislocation density of the four substrates.

3.4. PL

The crystalline quality of the films was compared by evaluating the luminescence intensities of the band-to-band transition at 295 K and of the excitonic region at 4 K (Figs. 2 and 3, respectively, and Table 1).

The PL intensities show that the films grown on wafers TA and S have much better optical quality. The intensity given by sample TA is slightly higher than in S and much higher than in TB and E. This fact could be an indication that the surfaces in wafers TA and S after the oxide desorption, due to the heat treatment in the reactor and before growth, also have a more perfect surface condition. The spectra at 4 K of samples TA and S in Fig. 3 are similar and again much more intense than the spectrum of E. In the spectra of samples TA and S, there is evidence of an intense (D°, A°) peak at 1.374 eV and a (A°, X) doublet at 1.415 eV, suggesting that all the samples are quite compensated. The spectrum of sample E shows also peaks at 1.362, 1.393 and 1.403 eV which are associated with point defects [5].

4. Conclusions

The characterization of wafers and epitaxial layers give substantially the same results for the reference wafer S and for the wafer TA, thus proving that both substrates are equivalent for the requirements of the epitaxial growth, while technology TB still requires further research work. These results indicate that our epi-ready TA technology could be adopted industrially.

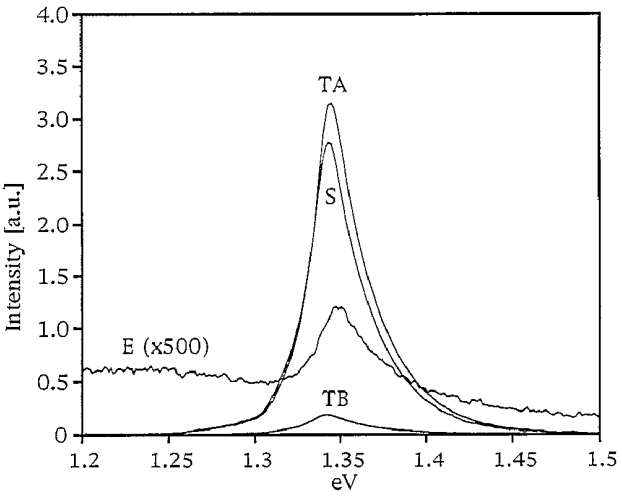

Fig. 2. PL spectra at 295 K of InP films growth on epi-ready and standard InP wafers.

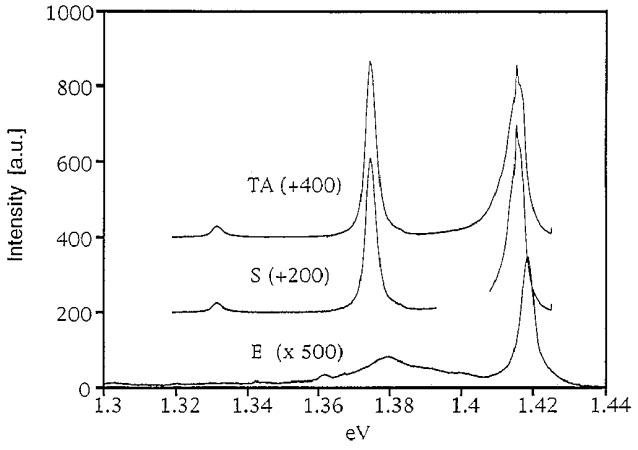

Fig. 3. PL spectra at 4 K of InP films growth on epi-ready and standard InP wafers.

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References

[1] S. Katsura, T. Fukui, Y. Takahashi, M. Takakusaki, M. Nakamura, O. Oda, Y. Sugiyama and M. Tacano, *Proc. 4th Int. Conf. InP and Related Materials, Newport, USA, 1992*, p. 270.

[2] A. Overs, G. Jacob, M. Besland, V. Drouot, M. Gendry, G. Hollinger, M. Ganeau, D. Lecrosnier and J. Bechimol, *Proc. 5th Conf. InP and Related Materials, Paris, France, 1993*, p. 267.

[3] B. Molinas, M. Guadalupi, L. Meregalli, L. Mirenghi, A. Passaseo, G. Rossetto and M. Natali, *4th Symp. Optoelectronics SIOEL '96, Bucharest, Romania, 11–13 Sept., 1996*, to be submitted.

[4] D. Ajo, G. Torzo, G. Rossetto, P. Zanella, F. De Zuane, M. Favaro, A. Camporese and M. Mazzer, *Vuoto; Sci. Tecnol., 13* (2) (1994) 128.

[5] O. Aina, M. Mattingly, S. Steinhauser, R. Mariella and A. Melas, *J. Cryst. Growth, 92* (1988) 215.