



Influence of Surface Roughness on Interdiffusion Processes in InGaP/Ge Heteroepitaxial Thin Films

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In the present work, we report on the study of InGaP/Ge heterojunctions grown by metal organic vapor phase epitaxy at different growth temperatures, with the aim of analyzing properties of the layer and interface between InGaP epilayer and germanium substrate. Secondary Neutral Mass Spectroscopy, Rutherford Backscattering Spectrometry, High Resolution X-Ray Diffraction, Transmission Electron Microscopy and Atomic Force Microscopy have been used to characterize the layers. The main goal of this work is to get information about diffusion processes of Ga, In, P in the substrate and of Ge in the epitaxial film. Since the interface roughness during sputtering and the effect of diffusion depends on the growth temperature, depth profiles measured experimentally were combined with surface roughness data in order to get more reliable information about diffusion profiles and the real depth distribution of elements in the interface.

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Indium gallium phosphide (InGaP) is the fundamental material for many electronic and optical devices¹ such as heterojunction bipolar transistors, metal oxide semiconductor field effect transistors (MOS-FETs), light emitting diodes (LEDs), lasers and multi-junction solar cells.²⁻⁶ The properties of InGaP and germanium (Ge) make them interesting materials for diffusion studies. Hence, the knowledge of diffusion mechanisms is significant in order to understand the different processes involved in the interface. Germanium junctions in high efficiency solar cells are usually realized by diffusion between the substrates and epitaxial GaAs or InGaP layers.⁷ For example, deposition of a GaAs layer on n-type germanium substrate⁸ can result in p-n junction due to higher concentration of gallium (Ga) in the top-most part of the Ge substrate. On the other hand, InGaP deposition on p-type germanium substrate produces n-p junction due to the different diffusion process between phosphorous (P), indium (In) and Ga elements, resulting in a top layer doped highly with P.

In spite of its large application capability, this compound suffers problems connected with the lattice mismatch between the epitaxial/binary/ternary compounds and germanium substrate. Spontaneous formation of ordered phase and different surface morphology can be due to the different growth conditions.⁹ The poor surface quality is a critical factor for junction abruptness. Moreover, the ordering process occurs through the formation of a mosaic of ordered domains dispersed in disordered matrix that cause materials inhomogeneity, which negatively affects the device performance.

In the present paper, we performed the study of InGaP/Ge thin films grown by low pressure metal organic vapor phase epitaxy (MOVPE) and were characterized from the interdiffusion point of view, in particular, the role of the surface morphology and roughness in the real depth profile determination. This work gives a detailed insight into the diffusion profiles of the film/substrate interface induced by the growth temperature.

Experimental

The InGaP films were grown on Ge (001) substrates by MOVPE technique in a horizontal reactor without substrate rotation at different growth temperatures of 600, 650 and 675 °C with a pressure of 60 mbar. The precursors used were trimethylgallium (TMG) and trimethylindium (TMI) for the elements of group III and phosphine (PH₃) in a 10% mixture of hydrogen for the group V element. In a typical growth experiment, the Ge substrate was thermally etched at 650 °C for 5 minutes in order to remove the native oxide prior to

introduction of the precursors into the reactor chamber. In order to obtain the same composition for all the samples, the ratio of In/Ga was varied from 1.1 to 1.4, while the ratio of V/III groups elements ranged from 95 to 87. The InGaP was not intentionally doped.

Secondary Neutral Mass Spectroscopy (SNMS, type INA-X, SPECS GmbH) in the direct bombardment mode using Ar⁺ ions with a fairly low energy for sputtering ($E_{Ar^+} = 350$ eV) was employed. The erosion area was confined to a circle of 2 mm in diameter by means of a tantalum (Ta) mask. The lateral homogeneity of the ion bombardment was checked by a profilometric analysis of sputtered craters. Rutherford Backscattering Spectrometry in combination with Channeling (RBS/C) analysis was performed in a scattering chamber with a two-axis goniometer connected to a 5 MV Van de Graaff accelerator. The 1 MeV ⁴He⁺ analyzing ion beam was collimated with two sets of four-sector slits with the dimensions of 0.5 × 0.5 mm², while the beam divergence was kept below 0.06°. The beam current was measured by a transmission Faraday cup.¹⁰ In the scattering chamber, the vacuum measurement was about 10⁻⁴ Pa. In order to reduce the hydrocarbon deposition, liquid N₂ cooled traps were used along the beam path and around the wall of the chamber. Backscattered He⁺ ions were detected using an ORTEC surface barrier detector mounted in Cornell geometry at scattering angle of $\theta = 165^\circ$. The energy resolution of the detection system was 16 keV. Atomic Force Microscopy (AFM) in contact mode (Digital Instruments Nanoscope IIIa) was employed to study the surface morphology. The average surface roughness values were estimated from the analysis of AFM images. AFM measurements were performed over 15 × 15 μm² areas on four different randomly selected places of the sample surface and the AFM image analysis was carried out by Gwyddion software. Transmission Electron Microscopy (TEM) operated in two-beam diffraction contrast and high resolution (HR-TEM) modes, using a JEOL 2200FS TEM/STEM field emission gun at 200 kV was employed.

Results and Discussion

In order to estimate the composition of the layer, the mismatch ($\Delta d/d$) was determined from X-ray diffraction profiles recorded for the three samples grown at different temperatures (600, 650 and 675 °C). We used the first order formula $\Delta d/d = -\Delta \theta / \tan \theta$ to obtain the average indium content of 0.43 (In_{0.43}Ga_{0.57}P). In addition, the X-ray measurements showed that the layers were crystalline with defects inside the lattice and reciprocal lattice map of the same sample in 115 geometry indicated the presence of strain release.

AFM images of the samples grown at three different temperatures were presented in Fig. 1. Average surface roughness values were

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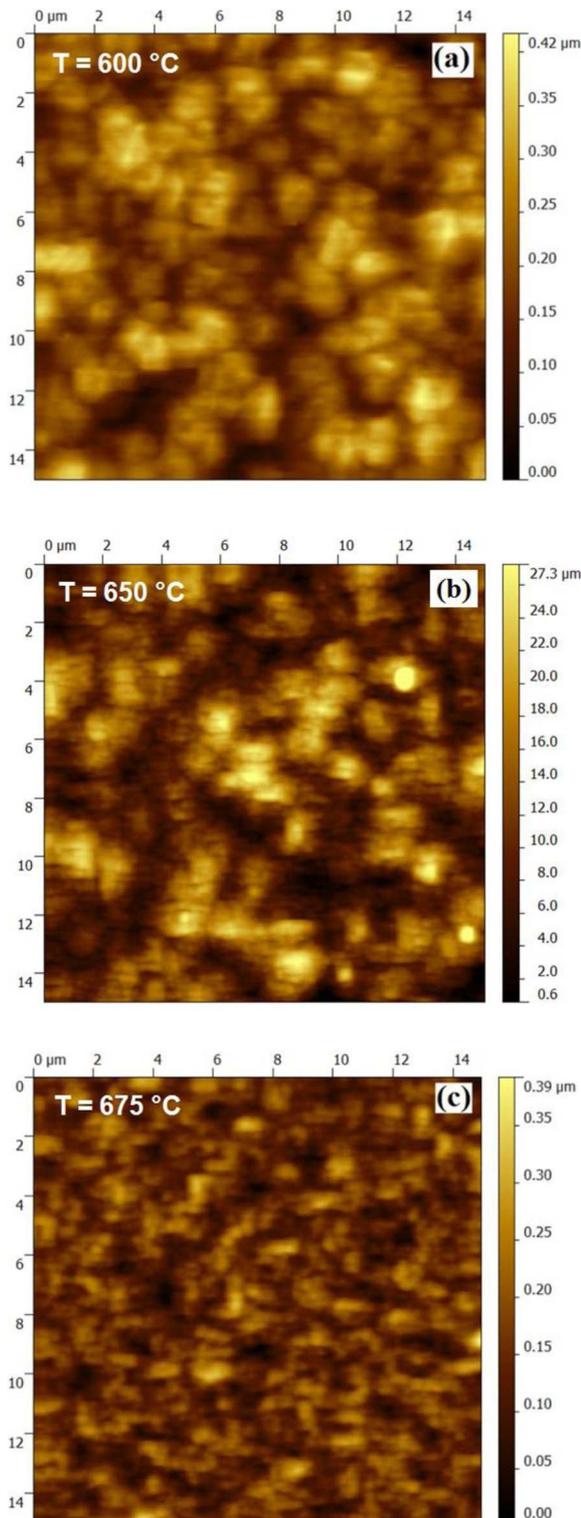


Figure 1. AFM images of InGaP layers grown on germanium substrates at a) 600 °C, b) 650 °C and c) 675 °C.

determined from large image areas ($15 \times 15 \mu\text{m}^2$) and it was assured that the scan area was always large enough to yield a representative roughness value for the whole sample. AFM measurements show that the average surface roughness of the samples decreases from about 42 to 20 nm with the increase in the growth temperature from 600 to 675 °C (Table I).

Table I. Roughness and Interface width vs Growth Temperatures.

Sample	Growth temperature (°C)	Average surface roughness (nm)*	Interface width (nm)**
1	600	~42	195
2	650	~32	60
3	675	~20	45

* Determined from AFM.

** Determined from SNMS.

The diffusion of constituents of the InGaP layer into Ge substrate was checked by RBS measurements. Fig. 2 shows the RBS/C spectra for two samples where the InGaP layer was chemically removed using HCl solution from the substrate prior to measurements in order to have only the contribution of the elements In, Ga, P diffused into the Ge substrates during growth time. Among elements, the background free detection was only possible for In, while the Ga signal was detected very close to Ge (see Fig. 2). The detection limit was the highest for P due to its low atomic number and backscattering cross section. The presence of about 1–3 at% In can be observed in the subsurface region of the samples. The higher amount of In diffused into the substrate of Sample 1 can be explained by an intensive grain boundary diffusion in the twin crystal structure which characterizes the 600 °C growth mechanism, see the AFM patterns in Fig. 1a and 1c. It is difficult to estimate the presence of Ga and P due to overlapping with Ge and the high detection limit compared to In. The channelling spectrum for the sample grown at 650 °C showed a minimum yield of about 5% indicating a good crystalline quality for the Ge substrate.

Depth distribution of constituents determines the physical properties of thin films and has an important role in doping of Ge substrate, particularly in study of the infrared cell doping behavior. According to chemical reactions of CVD technology, the substrates are usually kept at high temperatures during sample preparation. As this time is long enough to let any atomic motion or diffusion between the substrate and film to take place, it is very important to determine the in-depth chemical composition, mainly at the interface. Since the main elements composition of a film determine the basic properties, the diffusion from the overlayer through the substrate during preparation time can modify these basic properties, as it is practically a doping process. In our previous works,^{9,11} we have already shown that a sputter-based depth profile analysis is a unique tool for revealing interface

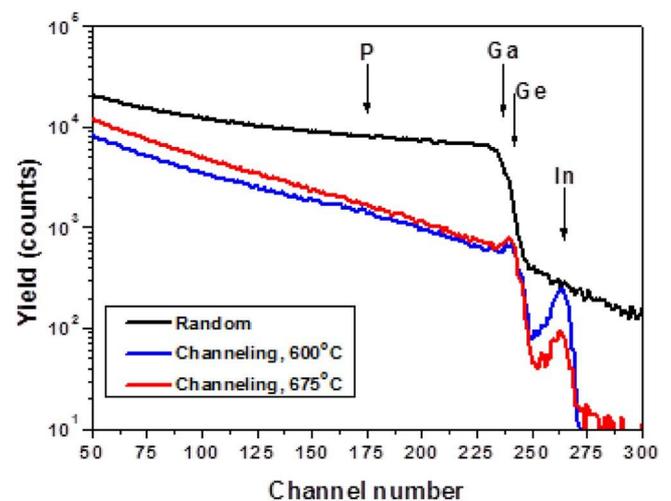


Figure 2. RBS channeling spectra of two substrates after removal of the InGaP layers grown at different temperatures of 600 and 675 °C. For comparison a random spectrum is also shown. Surface peak positions for In, Ga, Ge, and P are represented by the arrows.

142 structures. However, the depth resolution determining the quality of
 143 such measurements depends strongly on the roughness of the sputtered
 144 surface which is the bottom of the crater. Moreover, this roughness
 145 can change during sputtering. Since the depth profile analysis of a
 146 sample starts at the surface, the high surface roughness plays a crucial
 147 role in determination of depth resolution. In case of high surface
 148 roughness (e.g. 250 nm peak-to-valley value of Sample 1), it is unex-
 149 pected that the surface becomes smooth at the end of sputtering. Even
 150 if the roughness decreases by sputtering, the thickness of the layer is
 151 not high enough to obtain finally a smooth surface. In this way, the
 152 interface roughness is expected to be high when the surface roughness
 153 is high. Here the interface roughness is the real surface roughness at
 154 the bottom of the crater during sputtering through the interface re-
 155 gion between the film and substrate. At high interface roughness, the
 156 interface width is mainly determined by the roughness independent
 157 of sputtering processes and it is high as well. In contrary to this, the
 158 interface width is small when the interface surface is smooth, i.e. the
 159 sample surface is smooth. In general, the definition of interface width
 160 is arbitrary and phenomenological. Experimentally, it is usually given
 161 by the difference between the depth coordinates belong to 10% and
 162 90% intensities of the analysed element. This is similar to the defini-
 163 tion of depth resolution at a sharp interface.¹² In Fig. 3a we have
 164 shown the method for determining the interface width.

165 In our experiments, from the surface analyses it turned out that our
 166 samples had high surface roughness depending on the growth temper-
 167 ature (Table I). As the growth temperature increases, the roughness
 168 decreases. The depth distribution of elements was revealed by SNMS
 169 technique. Fig. 3 shows the trend of elements in InGaP layers grown
 170 at 600, 650 and 675 °C with the layer thickness of about 400 nm. As
 171 it can be seen, the interface width decreases with the decrease of the
 172 surface roughness. According to Table I, the surface roughness of the
 173 sample grown at 675 °C much higher than that is of the sample grown
 174 at 600 °C.

175 From the point of surface roughness, the depth profile analysis
 176 of A/B interface can be critical. Due to sputtering mechanism, the
 177 elements of A and B can be mixed by the sputtering itself even they
 178 were not mixed before. In this manner, the atomic mixing means that
 179 both the elements are sputtered at the same time. This type of atomic
 180 mixing can be evoked by ion bombardment, crater shape and surface
 181 (interface) roughness. The main goal of this work is to get informa-
 182 tion about diffusion processes of Ga, In, P in the substrate and of
 183 germanium in the film. However, it is not simple to make a distinction
 184 between the processes of diffusion mechanism and surface roughness
 185 with only depth profile analysis. A sharp change in concentration at
 186 a rough surface/interface can result in the same effect as a diffuse
 187 change in concentration at a smooth surface/interface.¹³ Both phe-
 188 nomena result in the same depth distribution of elements which can
 189 be characterized by the error function. In order to get information
 190 about the surface roughness contribution to the depth distribution of
 191 elements, we supplemented our SNMS measurements with calcula-
 192 tions of element depth distribution induced by the surface roughness.
 193 If the depth distribution measured experimentally differs from this
 194 calculated one, the deviation is caused by diffusion. Moreover, in
 195 a sputter depth profile analysis this deviation solely gives the real
 196 information about diffusion process.

197 The surface roughness determined experimentally was approached
 198 by a Gaussian distribution similar to that reported previously.¹² Using
 199 this measured value and assuming a Gauss type depth distribution
 200 of the surface roughness, the depth concentration of elements can
 201 be calculated. If the calculated value fit with the experimental one, the
 202 depth distribution was only determined by the surface roughness, if
 203 not, it was governed by other physical process, e.g. by diffusion. Con-
 204 sequently, the difference between the calculated and experimentally
 205 measured concentration profiles refers to diffusion. Fig. 4 shows the
 206 In and Ge depth distributions at two growth temperatures (650 °C and
 207 675 °C) measured by SNMS. As it can be seen, the measured values
 208 of Ge intensity in the interface region are higher than the calculated
 209 ones. This implies that the diffusion of Ge into the film took place
 210 more intensively at higher growth temperatures.

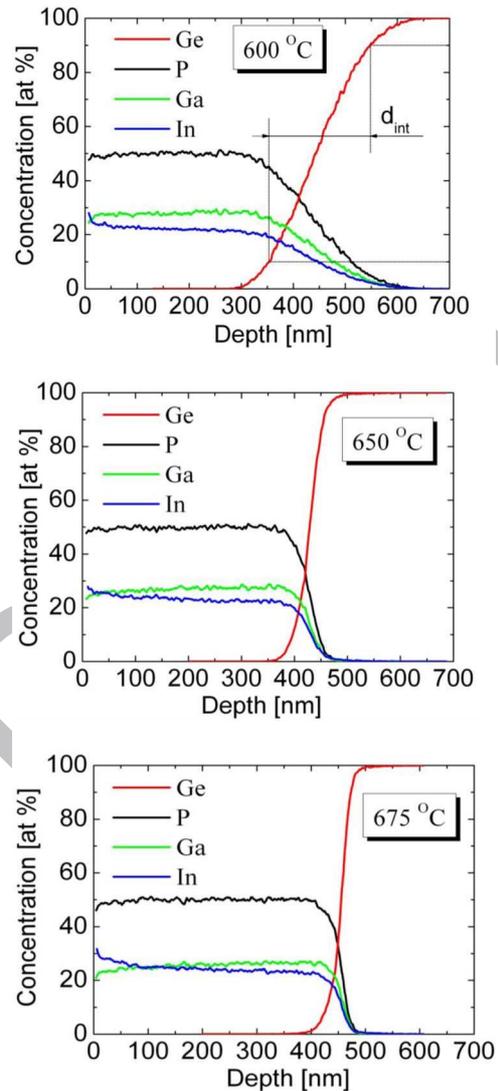


Figure 3. SNMS profiles for the InGaP/Ge sample grown at 600, 650 and 675 °C. The method of interface thickness (d_{int}) determination for Ge of Sample 1 is shown in the upper figure.

211 The volume diffusion and grain boundary diffusion compete with
 212 each other in the diffusion mechanism accompanied by MOVPE
 213 growth process. The linear fittings of the tails of $\ln C$ vs. d^2 and
 214 $\ln C$ vs. $d^{6/5}$ functions, where C is the concentration and d is the depth
 215 as given in Fig. 4 which yield a possibility to estimate the diffusion
 216 coefficients.^{14,15} While $\ln C$ vs. d^2 function gives information about
 217 the effective diffusivity, the linear part of $\ln C$ vs. $d^{6/5}$ curve deter-
 218 mines the grain boundary diffusion coefficient. The effective diffusion
 219 coefficient of Ge in InGaP layer was estimated to be $3.7 \cdot 10^{-23}$ m²/s
 220 in case of Sample 2, and $1.5 \cdot 10^{-22}$ m²/s in case of Sample 3. We
 221 also found that the linear part of $\ln C$ vs. $d^{6/5}$ function was longer
 222 seen in Sample 3 than in Sample 2, i.e. the effect of grain boundary
 223 diffusion was higher in Sample 3 than in Sample 2. The results of
 224 Sample 1 could not be used to determine the diffusion coefficient
 225 because the thickness of the interface layer was so high that the infor-
 226 mation concerning to the diffusion was totally smeared out. A deeper
 227 understanding of the diffusion process took place during preparation
 228 requires more experiments. Our results showed that a diffusion con-
 229 trolled doping effect can exist only when the substrate is kept at high
 230 temperature during preparation.

231 Diffusion of film constituents into the opposite direction, i.e. into
 232 the substrate, also exists with lower intensity because the substrate is a

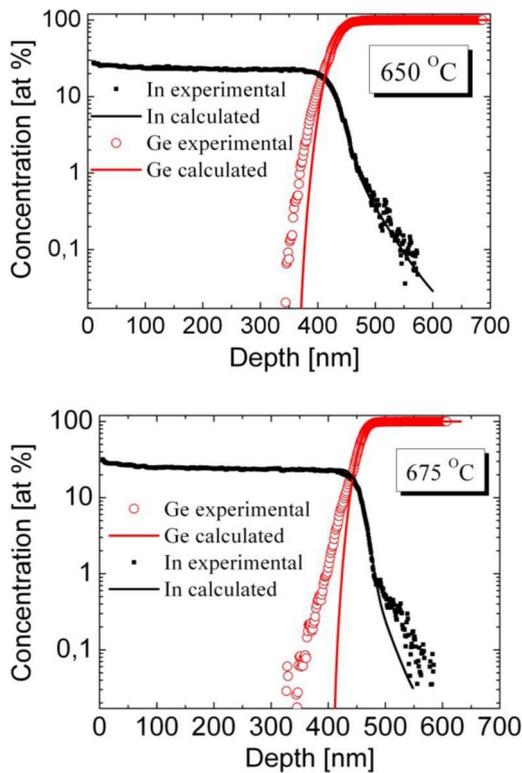


Figure 4. Indium and germanium depth distributions in Samples 2 and 3. The symbols denote the values measured experimentally, the lines are the calculated depth distribution. It can be seen that the diffusion process is more effective at temperature of 675 °C than it is at 650 °C.

single crystal. The indium signal in Fig. 4 and the RBS spectra in Fig. 2 represent the result of this process. Although the interface width of the sample grown at 650 °C was higher than that of the Sample 3 grown at 675 °C, the diffusion was more intensive at higher temperature. This result supports our conclusion that the interface width is mainly determined by the surface roughness and not by the diffusion.

The largest interface width of 195 nm was found in sample 1. The explanation for that lies in the crystal structure. The InGaP layer grown at 600 °C has an ordered phase.⁹ Fig. 5a shows the TEM image of sample grown at 600 °C taken in cross section, i.e. by viewing the sample along $[011]$ direction. It was taken in $[220]$ bright field mode

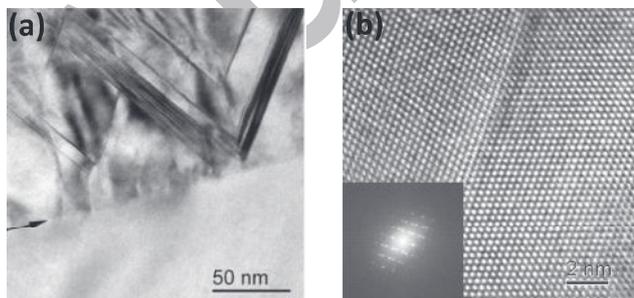


Figure 5. a) TEM image of the sample grown at 600 °C taken in cross section; b) HRTEM image of a twin in the top part of the layer. Inset: Diffraction pattern extracted by fast Fourier transform of the image, showing the twin 1/3 extra spots along the $[011]$ direction perpendicular to the twin plane.

of operation of TEM. The interface was indicated by the black arrow. The defects shown in the image were stacking faults and twins lying on (111) planes inclined 54.7° to the (100) plane. The HR-TEM image of a twin is shown in Fig. 5b. Such defects in the InGaP film originated at the Ge surface, but sometimes quite far (30–50 nm). During sputtering the surface of this region is rough, the interface widens due to the twin structure, and the surface roughness is non-Gaussian type preventing the calculation of depth distribution.

Conclusions

InGaP layers grown by MOVPE were characterized to understand the diffusion mechanism between the film and substrate. Surface analysis by AFM showed a temperature dependency of surface roughness. The roughness decreased with the increase of growth temperature. SNMS technique reported the depth distribution of elements and revealed that the interface width decreased with decreasing the surface roughness. Supplementary measurements with calculations based on surface roughness showed that Ge diffused in the film more intensively at higher temperature. Diffusion of film constituents into the opposite direction, i.e. into the substrate, can also exist. We demonstrated that although the interface width of the sample grown at 650 °C was higher than that of the sample grown at 675 °C, the diffusion was more intensive at the higher temperature, i.e. the interface width is determined by the surface roughness and not by the growth temperature.

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