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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 devices[1] such as heterojunction bipolar transistors, metal oxide semiconductor field effect transistors (MOSFETs), 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 substrate[8] can result in p-n junction due to higher concentration of gallium (Ga) in the topmost 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 (PH_3) 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 mm^2, 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 N_2 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 $\theta = 165°$. 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 μm^2 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 (□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 □d/d = −□θ/tanθ 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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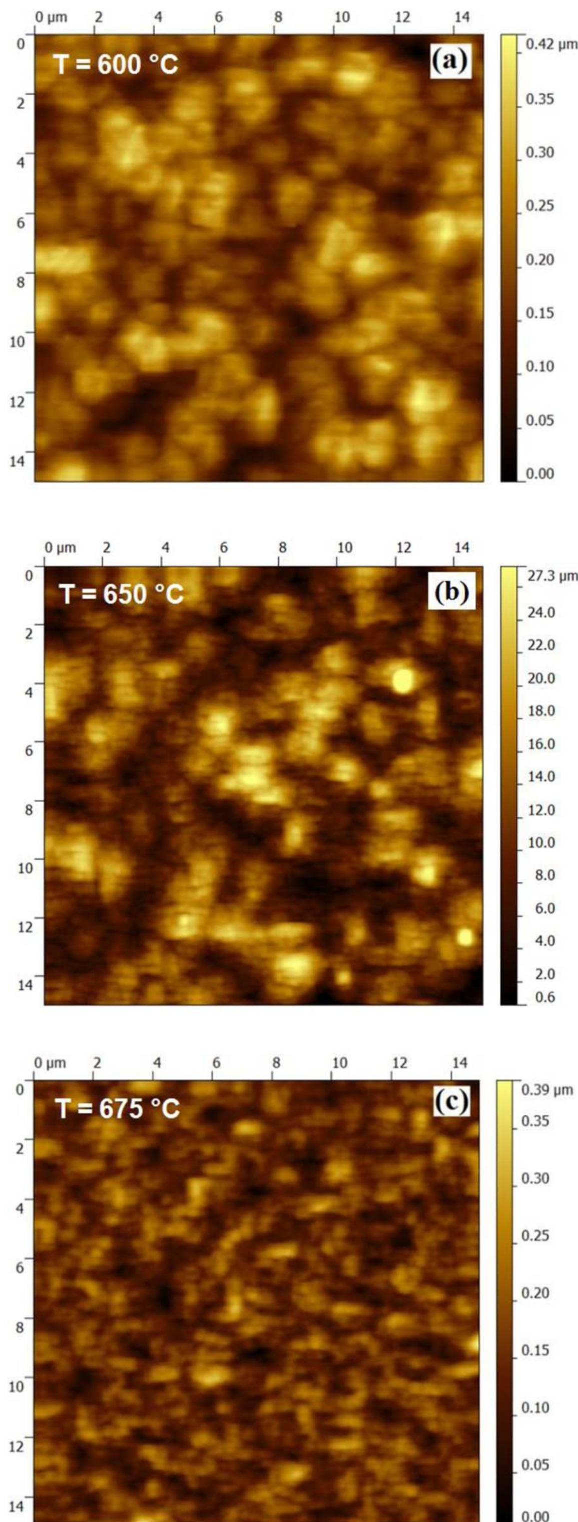

Figure 1. AFM images of InGaP layers grown on germanium substrates at a) 600° C, b) 650° C and c) 675° C.

determined from large image areas (15 × 15 µm^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

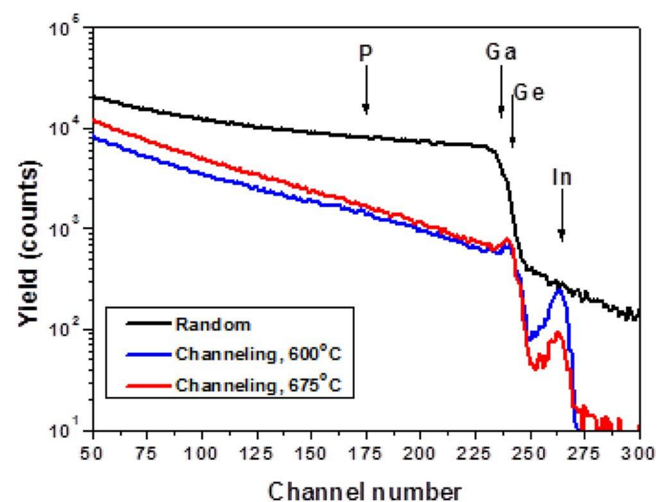

Figure 2. RBS channeling spectra of two substrates after removal of the InGaP layers grown at different temperatures of 600 and 675° C. For comparison a random spectrum is also shown. Surface peak positions for In, Ga, Ge, and P are represented by the arrows.

structures. However, the depth resolution determining the quality of such measurements depends strongly on the roughness of the sputtered surface which is the bottom of the crater. Moreover, this roughness can change during sputtering. Since the depth profile analysis of a sample starts at the surface, the high surface roughness plays a crucial role in determination of depth resolution. In case of high surface roughness (e.g. 250 nm peak-to-valley value of Sample 1), it is unexpected that the surface becomes smooth at the end of sputtering. Even if the roughness decreases by sputtering, the thickness of the layer is not high enough to obtain finally a smooth surface. In this way, the interface roughness is expected to be high when the surface roughness is high. Here the interface roughness is the real surface roughness at the bottom of the crater during sputtering through the interface region between the film and substrate. At high interface roughness, the interface width is mainly determined by the roughness independent of sputtering processes and it is high as well. In contrary to this, the interface width is small when the interface surface is smooth, i.e. the sample surface is smooth. In general, the definition of interface width is arbitrary and phenomenological. Experimentally, it is usually given by the difference between the depth coordinates belong to 10% and 90% intensities of the analysed element. This is similar to the definition of depth resolution at a sharp interface.[12] In Fig. 3a we have shown the method for determining the interface width.

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

From the point of surface roughness, the depth profile analysis of A/B interface can be critical. Due to sputtering mechanism, the elements of A and B can be mixed by the sputtering itself even they were not mixed before. In this manner, the atomic mixing means that both the elements are sputtered at the same time. This type of atomic mixing can be evoked by ion bombardment, crater shape and surface (interface) roughness. The main goal of this work is to get information about diffusion processes of Ga, In, P in the substrate and of germanium in the film. However, it is not simple to make a distinction between the processes of diffusion mechanism and surface roughness with only depth profile analysis. A sharp change in concentration at a rough surface/interface can result in the same effect as a diffuse change in concentration at a smooth surface/interface.[13] Both phenomena result in the same depth distribution of elements which can be characterized by the error function. In order to get information about the surface roughness contribution to the depth distribution of elements, we supplemented our SNMS measurements with calculations of element depth distribution induced by the surface roughness. If the depth distribution measured experimentally differs from this calculated one, the deviation is caused by diffusion. Moreover, in a sputter depth profile analysis this deviation solely gives the real information about diffusion process.

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

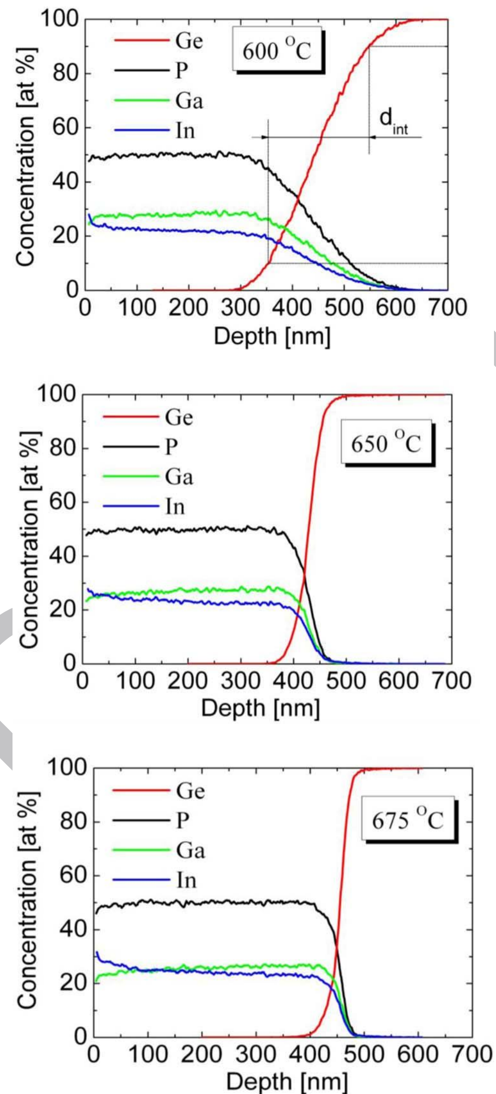

Figure 3. SNMS profiles for the InGaP/Ge sample grown at 600, 650 and 675°C. The method of interface thickness (d_{int}) determination for Ge of Sample 1 is shown in the upper figure.

The volume diffusion and grain boundary diffusion compete with each other in the diffusion mechanism accompanied by MOVPE growth process. The linear fittings of the tails of ln C vs. d^2 and ln C vs. $d^{6/5}$ functions, where C is the concentration and d is the depth as given in Fig. 4 which yield a possibility to estimate the diffusion coefficients.[14,15] While ln C vs. d^2 function gives information about the effective diffusivity, the linear part of ln C vs. $d^{6/5}$ curve determines the grain boundary diffusion coefficient. The effective diffusion coefficient of Ge in InGaP layer was estimated to be $3.7 \cdot 10^{-23}$ m^2/s in case of Sample 2, and $1{,}5 \cdot 10^{-22}$ m^2/s in case of Sample 3. We also found that the linear part of ln C vs. $d^{6/5}$ function was longer seen in Sample 3 than in Sample 2, i.e. the effect of grain boundary diffusion was higher in Sample 3 than in Sample 2. The results of Sample 1 could not be used to determine the diffusion coefficient because the thickness of the interface layer was so high that the information concerning to the diffusion was totally smeared out. A deeper understanding of the diffusion process took place during preparation requires more experiments. Our results showed that a diffusion controlled doping effect can exist only when the substrate is kept at high temperature during preparation.

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

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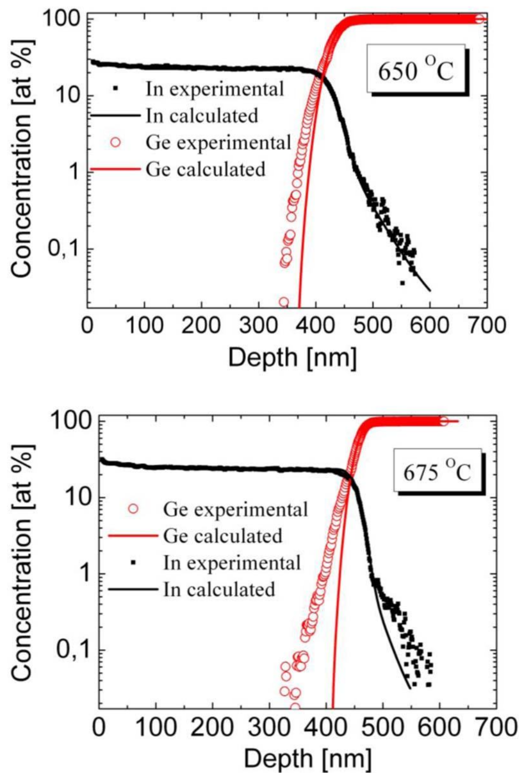

Figure 4. Indium and germanium depth distributions in Samples 2 and 3. The symbols denote the values measured experimentally, the lines are the calculated depth distribution. It can be seen that the diffusion process is more effective at temperature of 675° C than it is at 650° C.

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 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.

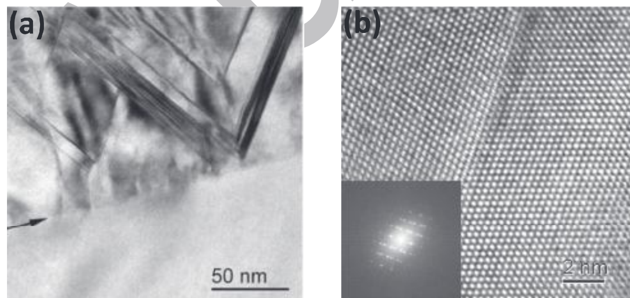

Figure 5. a) TEM image of the sample grown at 600° C taken in cross section; b) HRTEM image of a twin in the top part of the layer. Inset: Diffraction pattern extracted by fast Fourier transform of the image, showing the twin 1/3 extra spots along the ⟨111⟩ direction perpendicular to the twin plane.

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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