Correlation between gas phase and solid composition in $B_x\,Ga_{1-x}\,As$/GaAs epilayers grown by MOVPE

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Abstract

The MOVPE growth of the BgaAs alloy with the influence of the boron gas phase composition Xv is reported followed by a thermodynamical approach. The incorporation behavior of boron into GaAs is complex as the rate of incorporation is highly non linear with Xv. Due to the lack of available thermodynamical data for Bas, we proposed by extrapolation to determine the order of magnitude for the enthalpy of formation and Gibbs free energy values of the alloy. Our approach is based on the comparison of the trend between several series in different systems (BP, BN, AlAs, GaAs). The calculation yields the boron partial pressure P_B being much lower than P_{Ga}. The alloy content is controlled by the Ga equilibrium partial pressure. A surface segregation of boron is due to several factors such as a high vapor supersaturation needed during growth or a complex phase diagram.

I. Introduction

It recently appeared that the growth of the $B_xGa_{1-x}As$ alloy may be useful for obtaining the BGaInAs quaternary alloy or could be used as a tensile strained epilayer in the frame of strain compensation for InGaAsN−based heterostructures for emission at 1.3−1.5 mm. Despite this opportunity, little is known about the incorporation of boron into the group III sublattice which seems complex. Both the thermodynamical stability of the binary BAs compound and that of the alloy are questionable. A large gap of miscibility is also excepted as atomic boron is smaller than Ga. A reduction in the GaAs lattice parameter is expected but the presence of several cristalline phases for BAs (zinc−blende, rhomboedral) makes the problem difficult. It is thus important to identify the nature of parameters that control the film properties.

This report is a study of $B_xGa_{1-x}As$/GaAs epilayers obtained by metalorganic vapor phase epitaxy followed by a thermodynamical discussion.

II. Experiments

Lattice mismatched $B_xGa_{1-x}As$/GaAs epilayers were grown by metalorganic vapor phase epitaxy onto GaAs(001) substrates. The incorporation behavior has been studied in detail as a function of growth temperature, diborane flux, gallium precursor and carrier gas in a previous study [1]. We used triethylgallium (TEG), and diborane as group III precursors. Arsine was used for the arsenic source. The initial molar flow rate ratio Xv = $2[B_2H_6]/(2[B_2H_6] + [Ga])$ was used to quantify the boron concentration in the gas phase, where $[B_2H_6]$ and [Ga] are the diborane and the TEGa molar flow rates respectively.) misoriented towards [110]. The surface morphology was observed by AFM and detailed of XPS experiments were reported elsewhere [2]. Bulk compositions of epilayers, determined by x−ray diffraction using Ka line on (004) plane, were ranging from 0.01 to 0.07. It was observed that the crystalline quality of epilayers deteriorates as x increases.

III. Results and discussion

A previous study has shown the wide energy range (0−500 eV) XPS spectra of $B_xGa_{1-x}As$ samples compared to that of a GaAs wafer which can serve as reference. One could note main peaks at 18 eV , 42 eV and 107 eV for the GaAs wafer characteristic of the Ga 3d, As 3d core level. While no B 1 s core level peak was seen for the films at low B content i.e. B<0.05, a strong peak was observed at » 260 eV for higher B composition. The most likely origin of this photoelectron emission is the Auger recombination of As which is known to be strong in XPS spectra of elemental As. It is an indirect signature of the boron incorporation because this recombination was not observed in the spectrum of GaAs wafers. As we tried to incorporate more boron, the V/III ratio was kept constant at » 50, a peak emerges at 188 eV corresponding to the B1s core−level very close to the binding energy of boron in BN (189−190 eV). Together with the As−Auger peak, The B1s core level intensity increases rapidly by increasing the gas phase ratio Xv from 0.1 to 0.5 but did not follow the solid composition as indicated in Table I. While keeping the V/III ratio constant, it appears that the surface atomic ratio [B]/([B] +[Ga]) increases abruptly with increasing Xv > 0.5 to reach much larger values than the bulk composition.

III.2 Evolution of the AFM surface morphology

The AFM images taken from the BGaAs surface with increasing Xv showed that the surface morphology evolves while the surface roughness is increasing. Most of the films with a good crystalline quality with x < 0.05 where mirror−like as seen in which is the AFM image For those obtained under growth conditions for Xv > 0.4−0.5, the surface becomes covered with randomly distributed islandlike features. This image did indicate that growth was not uniform over the surface but controlled by 3 dimensional−like nucleation.

III.3 Discussion and thermodynamical analysis

Chemical composition estimated from the preceding XPS analysis showed that the relative ratio of B to Ga does not follow a linear relationship with the gas phase composition. By increasing the boron partial pressure in the reactor during growth, the progressive change in the film composition, as measured by x−ray diffraction, is only observed for Xv < 0.4 [2]. The reason for this increment is a surface−enrichment in boron indicating that the surface stoichiometry is disrupted. We will now look at a more detailed analysis of growth conditions to see whether such an inhomogeneous evolution of the growth process could be interpreted thermodynamically.

In order to simplify, the reactions of the alloy formation are taken from a combination of reaction (1) and (2) for GaAs and BAs respectively:

$Ga_{(g)}$ + ¼ $As_{4(g)}$ −−−> $GaAs^{(s)}$ (1)

$B_{(g)}$ + ¼ $As_{4(g)}$ −−−> $BAs_{(s)}$ (2)

The $B_xGa_{(1-x)}As$ random alloy, is formed following reaction (3):

(1−x) GaAs + x BAs −−−> $B_xGa_{(1-x)}As$ (3)

There are no thermodynamical data to our knowledge about the BAs formation and thus for reaction (2). As it is needed to study the $B_xGa_{(1-x)}As$ growth, we first plot in Fig.3 the 800 K standard enthalpy of formation DH°, entropy of formation S° and Gibbs free energy DG° of binaries as a function of atomic number Z for Nitrides (BN, AlN, GaN), Phosphides (BP, AlP, GaP, InP) and arsenides series that are known. For each family, a decrease could be seen for DH° and DG° from In to Al. To be noted is a rapid increase for their boron−based binaries (BP and BN). Values of DH°, DS° and DG° for BAs were extrapolated assuming a similar trend from AlAs to BAs. It is graphically determined a low DH°(BAs) = 0 kJ/mol, (DH°(GaAs) = −50 kJ/mol and DG°(GAs) = −146 kJ/mol were calculated) and DG°(BAs) = − 65 kJ/mol. BAs compound seemingly less stable than GaAs. Starting from thermodynamical data calculated for the formation of binary compounds we could calculate values for Gibbs free energy of reaction (1) and (2) at different temperatures by writing :

”H_1(GaAs) = ”H°(GaAs)− ¼ ”H°(As_4) − ”H°(Ga)(g)

We could estimate the reaction constants K_1 and K_2 at 4×10^{18} and 9×10^{32} at 800K respectively, the value of K_1 being in agreement with reported data. As $K_2 >> K_1$, and owing that $K_1/K_2 = P_B/P_{Ga}$ this means that $P_B << P_{Ga}$ and gallium is much more volatil than boron at thermal equilibrium. It results that the gallium partial pressure does control the B incorporation. In normal growth conditions we also have $P_B^{\circ} >> P_B$ yielding a high probability for boron to segregate. The role of the V/III ratio has been experimentally identified as the more is V/III, the but is under the scope of the present study.

Conclusion

The evolution of the solid content with the gas phase composition has been followed by comparing the chemical structures analysed by XPS, X−ray diffraction and by observing the surface morphology of BGaAs samples. Those results support the narrow range of growth conditions for this material. High boron content epilayers were not obtained for $x > 0.07$. The thermodynamical approach enables a better understanding of the correlation of the chemical structures and the gas phase composition. We propose a set of data for BAs growth based on the general trend with group III and group V atomic number of binary compounds. Boron−containing species exhibit a sudden variation in their thermodynamical properties in comparison to Al and Ga−based species.

References

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