

Review

Metastable cubic zinc-blende III/V semiconductors: Growth and structural characteristics

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Abstract

III/V semiconductors with cubic zinc-blende crystal structure, for example GaAs, GaP or InP, become metastable if atoms with significantly smaller or larger covalent radius than the matrix atoms are alloyed. Examples are the incorporation of Boron, Nitrogen and Bismuth in the above-mentioned materials. The resulting multinary compound semiconductors, like for example (Ga,In)(N,As), Ga(N,As,P) and Ga(As,Bi), are extremely interesting for several novel applications. The growth conditions, however, have to be adopted to the metastability of the material systems. In addition, structure formation can occur which is different from stable materials. This paper summarizes our current knowledge on growth characteristics of several metastable materials. Mainly examples for Metal Organic Vapor Phase Epitaxy (MOVPE) are given. The MOVPE growth characteristics are compared to selected examples using Molecular Beam Epitaxy growth to highlight that the observed growth characteristics are intrinsic for the studied metastable material systems. Furthermore, structural peculiarities of dilute borides, nitrides and bismides occurring during growth as well as in growth interruptions are summarized and correlated to the growth conditions. © 2015 Elsevier Ltd. All rights reserved.

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1. Introduction

III/V semiconductors can become metastable when they are alloyed with atoms having a significantly larger or smaller covalent radius than that of the matrix atoms. Table 1 summarizes the covalent radii of the group V atoms along with their electronegativity and the lattice constant of the respective Ga-compound. The covalent radius increases from N to Bi, whereas the electronegativity decreases from N to Bi. Ar-

senides and phosphides are most similar and hence Ga(As,P) is a stable material system in the temperature range above room temperature [1–3]. In contrast to that, the properties – like covalent radius and electronegativity – of N and Bi, respectively, are highly different from Ga(As,P) and hence alloys of Ga(As,P) with N or Bi are metastable, meaning that they can only be grown under certain conditions, as will be illustrated in the following. $\text{Ga}_x\text{Bi}_{1-x}$ ($x \neq 0$ or 1) has even never been observed experimentally and is predicted to be immiscible in the solid phase over the entire composition range theoretically [4]. The empirical observations on immiscibility of alloys have been summarized in the Hume-Rothery rules, which have been introduced for metals and alloys of metals first [5–7]. For substitutional solutions, as also the mixed III/V

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Table 1
Characteristic properties of group-V elements.

Element	Covalent radius (pm)	Lattice constant Ga-compound (nm)	Electro-negativity
N	75	0.452	3.04
P	106	0.54505	2.19
As	119	0.565325	2.18
Sb	138	0.609593	2.05
Bi	146	0.637 (theory)	2.02

semiconductors considered in this work are, the following rules for solubility are derived: first of all, the crystal structure of the solute and the solvent should be the same if complete solubility over the entire range of compositions is expected. This is, for example, already not the case for the dilute nitride alloys considered here: the equilibrium crystal structure of GaN and InN is hexagonal, whereas the equilibrium crystal structure of (Ga,In)(P,As) is the cubic zinc-blende one. Secondly, the atomic size difference between the solute and the parent should be less than 15%. This condition is not met when N, Sb or Bi are alloyed into Ga(As,P), hence resulting in unstable alloys. Thirdly, the electronegativity difference between solute and solvent should be small. For the III/V materials studied here, this is certainly not the case for solutions with N. The fourth Hume-Rothery rule treats the influence of different valency of atoms which are mixed and says that the solubility of a metal with higher valency in a solvent of lower valency is larger than vice versa. This is not an issue for the mixed III/V semiconductors studied here, as only atoms from the 3rd group of the periodic table are mixed on the group III sublattice and only atoms of the 5th group of the periodic table are mixed on the group V sublattice. The mixed alloys are denoted in the following for example with $(\text{III}_1, \text{III}_2)(\text{V}_1, \text{V}_2)$ (e.g. (Ga,In)(N,As) or Ga(N,As,P)), meaning that the respective sublattices can be occupied with different amounts of III_1 and III_2 , for example, but that the sum of $\text{III}_1 + \text{III}_2$ has to add to 100% of the group III sublattice. It should be noted here that although these rules are simple and of course applicable for a first guess on the stability of mixed alloys, there are many factors not considered: for example, there is an influence of strain with respect to a substrate [8], which is important in heteroepitaxial approaches as also considered here. There might also be an influence of morphology on the stability of the alloys treated here, as addressed theoretically in Reference 9. A schematic of a thermodynamic phase diagram of a metastable material system is given in Fig. 1 [10].

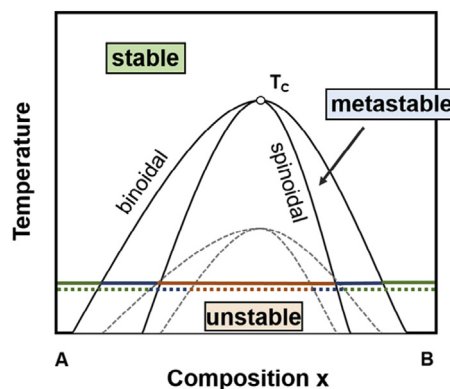


Fig. 1. Schematic phase diagram of metastable materials [10]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

In this version of the phase diagram, the stability regions (of compositions) of an alloy are plotted versus the (growth) temperature. Looking at the solid lines first, one can see that the stable region of composition, where the crystal can be grown at the respective temperature, is separated from the unstable region by a region of metastability. In the unstable region the alloy with that composition cannot be grown; the curvature of Gibb's free energy is negative in this region. In the metastable region, one is able to freeze the metastable compositions by tuning the growth conditions, as the curvature to Gibb's free energy is still positive in this composition range and for phase separation an activation energy barrier has to be exceeded. The curves separating the stable from the metastable regions and the metastable from the unstable regions are called binoidal and spinoidal, respectively. The temperature, above which the alloy is completely miscible, is called critical temperature T_c . This temperature is highly different for the individual III/V alloys. For Ga(As,P) it is at 277 K [1–3], for dilute nitrides it is in the range of 10.000 K [10], meaning that these alloys are highly metastable and can only be grown under non-equilibrium conditions. If T_c shifts to lower temperatures (dashed curves), what could be achieved for example by changing the macroscopic strain state of the alloy [8], the regions of stability are extended at the cost of the region of instability. This is sketched with colored bars for the two phase diagrams shown in the figure. Stable compositions (for a given temperature) are marked in green and are separated from the orange unstable regions by the metastable region, marked in blue. Going toward a “less metastable” material, stable and metastable composition regions are expanded. The

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