Liquid-Phase Epitaxy of NdAl₃(BO₃)₄ and Yb-Doped YAl₃(BO₃)₄

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Abstract—Epitaxial layers of NdAl₃(BO₃)₄ (NAB) and YAl₃(BO₃)₄(Yb) (YAB(Yb)) containing up to 10 at % Yb have been grown by liquid-phase epitaxy on YAB substrates. Their growth kinetics have been studied at relative supersaturations of the high-temperature solution from 2 × 10⁻² to 16 × 10⁻². The ytterbium concentration in YAB(Yb) has been shown to vary little during the epitaxial process. Near the edges of the substrate, the surface morphology of the layers is complicated by vicinals, which have a spiral form in the case of YAB(Yb). On {1011} YAB substrates, homogeneous single-crystal NAB films have been grown.

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INTRODUCTION

There is considerable interest in rare-earth aluminum borate crystals with the general formula RA₃(BO₃)₄ (R = yttrium or lanthanide), motivated by their attractive functional (nonlinear-optical, lasing, nonlinear-active, and other) properties in combination with their high thermal, chemical, and mechanical stability and unique thermal conductivity, 14–15 W/(m K) [1]. An important practical aspect is the possibility of extensive isomorphous substitutions on the rare-earth site, which makes it possible to radically modify the properties of these materials. They can be used in engineering high-efficiency miniature lasers and other electrooptic and acoustoelectronic devices and, more importantly, new high-tech nonlinear-active devices.

In particular, (Nd,Y)Al₃(BO₃)₄ crystals were used to create a cw green laser [2]. There is considerable interest in NdAl₃(BO₃)₄(Cr), which shows an insignificant concentration quenching of luminescence and offers the largest gain coefficient among the existing miniature solid-state lasers [3]. A key feature of NdAl₃(BO₃)₄ (NAB) crystals is the extremely high activator (neodymium) concentration, which makes them potential candidates for the fabrication of disk-shaped gain elements with an effective pump absorption depth in the range 100–200 μm.

YAl₃(BO₃)₄ (YAB) crystals doped with Cr³⁺ and Yb³⁺ are being studied intensely as potential materials for advanced compact optoelectronic devices [4, 5]. YAB(Yb) nonlinear-active crystals about 3 × 3 × 3 mm in dimensions can be pumped by light-emitting diodes, e.g., InGaAs [5]. Single-crystal YAB(Yb) films are potentially attractive as components of planar waveguides. Therefore, small crystals and thin layers of YAB(Yb) and NAB offer considerable potential for use in next-generation devices for scientific, medical, industrial, and other applications. Since no studies in this area have been conducted since the report by Lutz et al. [6], we made an attempt to bridge this gap. In this paper, we report the growth of YAB(Yb) and NAB epilayers from high-temperature borate–molybdate solutions and analyze the effect of growth conditions on the composition, structure, and morphology of the epilayers.

CRYSTAL-CHEMICAL ANALYSIS

The selection of substrates is a critical issue in the growth of epitaxial films and is determined primarily by crystallographic and physicochemical factors. We considered a number of well-known single crystals, taking into account their composition, crystal structure (in particular, interatomic distances), melting point, thermal expansion coefficient, and refractive index, as substrates for subsequent epitaxial growth of rare-earth alumina borate layers. In the fabrication of planar waveguides, it is of key importance that their refractive index slightly exceed that of the substrate. Detailed analysis of all the above factors leads us to conclude that only undoped YAB crystals are capable of fully meeting all of these requirements.

The principal quantitative characteristic for controlling the perfection and composition of growing layers is the growth rate. In liquid-phase epitaxy (LPE), it can be determined on a real time scale of a particular experiment. It is well known that diffusion-controlled mass transport to the crystal surface leads to diffusion-con-
trolled growth, while slower surface processes lead to kinetic control. It is not, however, uncommon that volume and surface processes are comparable in rate, and crystal growth follows mixed kinetics. It is this situation which should be expected based on earlier data on the seeded growth kinetics of bulk single crystals of Y–Al and Y–Fe borates [7]. It has been found that, as the temperature is lowered, boron, present in both the solvent and nutrient, and oxygen can form anions of various compositions and configurations, as well as polyanions made up of BO₃ and BO₄ groups. This, in turn, increases the viscosity of the high-temperature solution. The growth rate is limited by the transition of the BO₃ triangles, which prevail in multicomponent high-temperature borate melts, from a boron–oxygen network, distorted to different degrees, to an isolated state and also, though to a lesser extent, by the change in the coordination number of boron (from 4 to 3). This rearrangement requires significant energy. According to earlier work [8], the activation energy for crystal growth is 320 kJ/mol, which is comparable to the boron–oxygen bond energy. Thus, the growth kinetics in viscous glass-forming systems depend on the restructuring (depolymerization) of the multicomponent high-temperature solution, which limits the growth rate.

Table 1. Charge compositions for YAB(Yb) and NAB LPE

<table>
<thead>
<tr>
<th>Charge</th>
<th>Borate composition</th>
<th>Solvent composition, wt %</th>
<th>wt % borate</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Yb₀.⁰⁵Y₀.⁹⁵Al₃(BO₃)₄</td>
<td>88.₁K₂Mo₃O₁₀ + 8.₆B₂O₃ + 3.₃(Yb,Y)₂O₃</td>
<td>17</td>
</tr>
<tr>
<td>II</td>
<td>Yb₀.₄Y₀.₆Al₃(BO₃)₄</td>
<td>91.₀K₂Mo₃O₁₀ + 8.₀B₂O₃ + 1.₀Y₂O₃</td>
<td>17</td>
</tr>
<tr>
<td>III</td>
<td>NdAl₃(BO₃)₄</td>
<td>69.₄K₂Mo₃O₁₀ + 12.₅B₂O₃ + 1₈.₁Nd₂O₃</td>
<td>1₈</td>
</tr>
</tbody>
</table>