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Growth of beta barium borate (β-BaB_2O_4) thin films by injection metal organic chemical vapour deposition

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Abstract

Thin films containing beta barium borate (β-BaB_2O_4 so called β-BBO) were grown on silicon (100) substrates by injection metal organic chemical vapour deposition for different deposition temperatures. The films were characterized by optical microscopy, micro-Raman spectroscopy and X-ray photoelectron Spectroscopy (XPS). The micro-Raman spectra show an intense peak at 637 cm^{-1} that is the fingerprint of β-BBO. Our XPS analysis permits the measurement of the Ba, B and O core levels, which are reported here for the first time for β-BBO thin films. The formation of a new spectral component appearing with lower growth temperatures has been observed as well.

Keywords: Thin film growth; β-BBO; Borates; CVD; Injection-MOCVD

1. Introduction

Thin films of nonlinear optical (NLO) material provide excellent prospects for integrated optical applications requiring UV waveguides. Among the family of NLO borate compounds, the low temperature phase of barium metaborate (beta barium borate β-BaB_2O_4, so called β-BBO) is particularly attractive because it has a variety of favourable properties such as a wide optical transmission range (190–3500 nm), rather large nonlinear optical coefficients, a high damage threshold and a large birefringence. To date, β-BBO thin films have been grown by pulsed laser deposition [1–3], magnetron sputtering [2], chemical solution deposition [4,5], polymeric precursor method [6], metal organic chemical vapour deposition [7] and liquid phase epitaxy [3]. The main objective of the present work was the growth and characterization of β-BBO thin films by using an injection metal organic chemical vapour deposition (injection MOCVD) technique. This method, commonly used for the deposition of various oxide thin films, in particular $YBa_2Cu_3O_7$ (YBCO) [8–10], is based on the computer-controlled injection of micro amounts of a solution containing precursors dissolved in an appropriate solvent into an evaporator system. Since the solution is sequentially flash evaporated, relatively unstable precursors such as barium β-diketonate can be used. The injection technique also offers the possibility to vary the amount of injected precursor and thus control the film growth rate by varying the precursor concentrations in the solution as well as by changing the frequency and duration of the injection pulses.

Studebaker et al. [7,11] also report the growth of β-BBO by injection-MOCVD. However, their method is based on continuous precursor injection and an inverted vertical reactor geometry, whereas in our work pulsed precursor injection was implemented with a vertical downstream apparatus. Additionally Studebaker et al. [7] used a different solvent for the precursor solution (tetraglyme) and different carrier and reactive gases (nitrogen, oxygen and nitrous oxide).

The aim of our work is the determination of the optimum experimental conditions for the deposition of β-BBO films with this new setup. In this article we report the first growth of β-BBO thin films by pulsed injection MOCVD and their characterization by optical microscopy, Raman spectroscopy and XPS.

2. Experimental details

The design of the injection MOCVD setup is reported in Fig. 1. A solution containing the organometallic precursors and the solvents was sequentially injected into the evaporator by a

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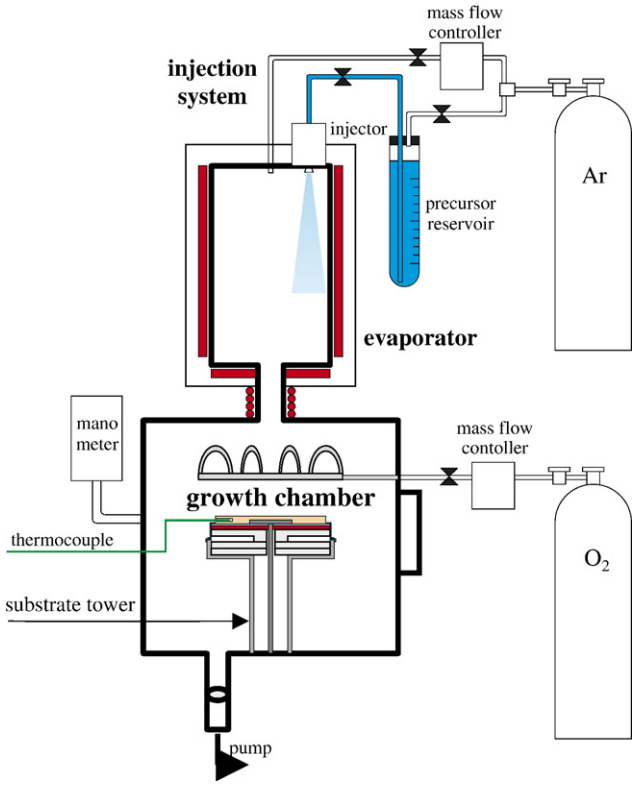

Fig. 1. A schematic design of the injection MOCVD setup.

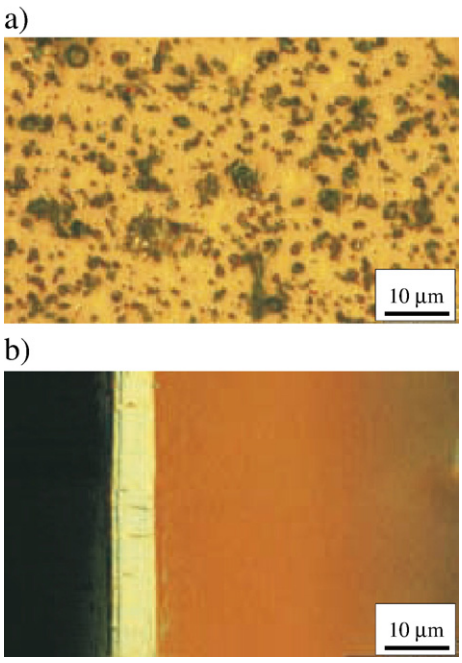

Fig. 2. (a) surface and (b) cross-section photos of β-BBO thin film grown at 700 °C.

computer-controlled injector. The solution itself consisted of the solvent triglyme and the barium and boron sources barium 2,2,6,6-tetramethyl-3,5-heptanedionate ($Ba(tmhd)_2$) and triisopropylborate, respectively. The droplets were injected during 1 ms by a high speed electromagnetic valve working typically at a frequency of 1 Hz. As the temperature of the evaporator was set to 250 °C, the droplets were flash evaporated immediately after leaving the valve. An argon carrier gas stream transported the vapours downstream into the growth chamber. Directly above the substrate holder oxygen gas was added through a shower inlet to prevent oxygen deficiency in the growing films. The deposition took place on the substrate that was fixed on its holder and heated to typically 600–700 °C by an internal resistance. The pressure in the evaporator and the growth chamber was held constant at a value of 133 Pa (1 Torr). Typical growth parameters for thin films deposited on silicon (100) substrates are summarized in Table 1. Optical microscopy served to characterise sample morphology and thickness by surface and cross-section analysis. The identification of the films was performed with the help of Raman spectra, recorded using a Jobin-Yvon Labram 010 spectrometer. Raman spectroscopy provides detailed information about molecular vibrations and therefore about the type and character of the molecular bonds in the sample. The excitation light source used was an IR laser with a wavelength of 784.7 nm and an output power of 500 mW. X-ray photoelectron Spectroscopy (XPS) was used to determine the surface chemical composition of the as-grown thin films. The spectra were obtained with MAC-2 (Riber) analyser using a monochromatic Mg Kα radiation source (1253.6 eV) with an output power of 300 W.

Table 1
The deposition conditions for the growth of β-BBO

Substrate temperature	600–700 °C
Evaporator temperature	250 °C
Argon flow	190 sccm
Oxygen flow	10 sccm
Total pressure	133 Pa (1 Torr)
Solution composition (Ba:B molar ratio)	1: 2
$Ba(tmhd)_2$concentration	1×10^{-2} mol/l
Solvent	Triglyme
Injector opening time	1 ms
Injection frequency	1 Hz

3. Results and discussion

β-BBO thin films deposited in the temperature range of 600–700 °C showed a typical growth rate of about 5 μm/h, i.e. about ten times higher than the growth rate achieved with the continuous injection-MOCVD experiment reported in [7]. Fig. 2a shows the typical morphology for sample deposited at 700 °C. The films were composed of a rather smooth matrix and some grains in the range of 0.5–4 μm diameter. When decreasing the growth temperature, an increase in grain density and a decrease of uniformity in grain size (0.5–10 μm diameter) was observed. The cross-section of the deposited film (Fig. 2b) shows a film thickness of around 7 μm.

The micro-Raman spectrum obtained by focussing onto a grain of a typical thin film is presented in Fig. 3 together with the spectrum of a single crystal grown in our laboratory by Maillard et al. using the Czochralski method [12]. Several