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Atomic layer deposition of B_2O_3 thin films at room temperature

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Abstract

Atomic layer deposition of boron oxide thin films was demonstrated at room temperature using BBr_3 and H_2O as precursors. Crystallinity of the films was characterised by X-ray diffraction while time-of-flight elastic recoil detection analysis (TOF-ERDA) and X-ray fluorescence were used to analyse stoichiometry and possible impurities. As-deposited films were amorphous and reacted readily with the atmosphere if not protected by an alumina overlayer. Boron oxide deposition rate of 0.76 Å per cycle was obtained at 20 °C. If the deposition temperature was increased to 50 °C and above, almost no film growth could be obtained. According to the TOF-ERDA, hydrogen and carbon contents in the films were very low being less than 0.2 and 0.1 at.%, respectively.

Keywords: Boron oxide; Thin film; Atomic layer deposition; ALD

1. Introduction

Binary undoped boron oxide has only been studied to a limited extent as thin films whereas other boron-containing thin film materials, such as various nitrides, carbides and metal borides, have received considerable attention as optical and hard coatings (e.g. BN) as well as superconductors (MgB_2). Due to the instability of B_2O_3 in contact with the ambient atmosphere, its uses as such are limited. Nevertheless, chemical vapour deposition (CVD) or infrared heating of elemental B and B_2O_3 have been employed for the preparation of B_2O_3 nanowires [1,2]. In addition, boron oxide thin films react with air to form boric acid (H_3BO_3) which finds uses as solid lubricant [3] or as self-assembled boric acid nanostructures [4]. Moreover, boron oxide is a constituent of borophosphosilicate [5,6] and glassy B_2O_3–Li_2O–PbO [7] thin films as well as a dopant for diamond [8,9] and Si:H [10] thin films. In addition to nanowires, chemical vapour processing has been used for the deposition of some other boron-containing materials as well. However, CVD deposition of binary B_2O_3 thin films has only been performed at 500–650 °C by using $[(CH_3)_2CHO]_3B$ as a single-source precursor [11].

Atomic layer deposition (ALD) [12,13] is a variant of CVD which has previously been employed for the deposition of various oxide, nitride and sulfide as well as metallic thin films. [12,14–16]. Typically in ALD the metal-containing precursors have been applied either as volatile halides, β-diketonates or organometallics with optimum deposition temperatures around 300 °C [14,16]. Unfortunately, the suitable precursors become fewer as the deposition temperature is decreased. This is most often due to low reactivity of the precursors leading to increased impurity contents as well as to a decrease in the overall film quality and growth rate. If deposition temperature is still further lowered to below 100 °C, insufficient volatility of most solid precursors restricts their use in ALD. In the literature, there are some examples of ALD processes working around 100 °C; these include the deposition of Al_2O_3 [17], SiO_2 [18], MgO [19], ZrO_2 [20], HfO_2 [20], V_2O_5 [21], Ge [22] and Pd [23]. In some processes however, special measures need to be taken to initiate or maintain the ALD growth. For instance, the deposition of palladium thin films even at 80 °C was initialised by a seed layer of Pd or Ir which was deposited at higher temperatures by ALD or by e-beam deposition [23]. In this context it should be noted that an ALD-related deposition process, namely molecular layer deposition, has been demonstrated to yield polymer thin films at 50–65 °C [24]. Still lower ALD deposition temperatures, i.e. close to room temperature have been demonstrated for only a few materials, namely Al_2O_3

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Table 1
Atomic layer deposition of boron-containing thin films

Precursors	Film	Dep. *T*/°C	Ref.
$B_2H_6+Et_2Zn+H_2O$	B:ZnO	105–165	[30,31]
BBr_3+NH_3	BN	250–750	[27]
BCl_3+NH_3	BN	227	[28]
$SiH_2Cl_2+BCl_3+NH_3$	SiBN	630	[29]
$WF_6+NH_3+Et_3B$	WN_xC_y	300–350	[32,33]
BBr_3+H_2O	B_2O_3	20	This study

[17], SiO_2 [25] and CdS [26]. In was observed, however, in the case of the well-known $(CH_3)_3Al/H_2O$ process for Al_2O_3 that impurity contents of films significantly increase as the deposition temperature is decreased. In low-temperature ALD processes in the absence of sufficient thermal activation the reactions sometimes need to be promoted by plasma [18], laser [27] or catalysts [25].

Previously, ALD has been utilised for the deposition of some boron-containing thin films (Table 1). These studies have focused mainly on the growth of BN [27,28] but also SiBN [29] and boron-doped ZnO [30,31] have successfully been deposited. For ALD of boron-containing thin films, volatile halides and hydrides have been traditionally applied, but in some cases also organometallic boron precursors have been used. For example, organometallic boron compounds, such as triethylboron, have been employed as reducing agents in the ALD of WN_xC_y thin films from WF_6 and NH_3 precursors [32–34]. Also BBr_3 and NH_3 have been recently used for ALD of BN thin films at 600 °C [27]. The suitability of boron tribromide for self-limiting reactions with water has been earlier demonstrated on the surface of bulk silica gel powders at 180 °C [35]. Although the initial sequential reactions of B_2O_3 for the thin film preparation by ALD have been studied [35], the actual thin films of B_2O_3 have not been deposited nor their properties reported. Consequently, our interest in B_2O_3 films stems from the need to exploit the possibilities ALD offers for the processing of binary boron oxide thin films. In this paper, we report the results of boron oxide thin film growth by ALD at low deposition temperatures using BBr_3 and H_2O as precursors.

2. Experimental details

Commercial BBr_3 (>99%, Cerac Inc., USA) was used as a precursor. Estimated from the vapour pressure data [36], it was evaporated at a source temperature of −5 °C. BBr_3 was transported from external cylinder into the reactor without carrier gas. Distilled H_2O was used as the oxygen source. Water vapour was generated in a cylinder kept at 20 °C without additional bubbling system. Source material pulsing was achieved by inert gas valving with pure nitrogen (>99.999%, Schmidlin UHPN 3000 N_2 generator) as a carrier and purging gas. Due to the hygroscopic nature of B_2O_3 films, they were covered in the same pump-down with Al_2O_3 deposited from $(CH_3)_3Al/H_2O$ [37] (98%, Strem Chemicals, USA). All thin film depositions were carried out in a commercial F-120 ALD reactor manufactured by ASM Microchemistry Ltd. (Helsinki, Finland). For B_2O_3 thin films the deposition temperature range of 20–400 °C was explored. The films were deposited onto 5×10 cm^2 soda lime glass and Si(100) substrates.

Film thicknesses were measured by using the optical fitting method as described by Ylilammi and Ranta-aho [38]. Reflectance and transmittance spectra were measured in a Hitachi U-2000 double beam spectrophotometer. Crystallinity and crystallite orientations of the films were determined by X-ray diffraction (XRD) with CuKα radiation (Philips MPD 1880). Some B_2O_3 thin films were annealed in a PEO 601 rapid thermal annealing (RTA) furnace (ATV Technologie GmbH, Germany). N_2 atmosphere and annealing temperatures of 300–900 °C were employed. Adhesion of the deposited films was evaluated by tape test [39].

The boron and oxygen content as well as possible impurities were determined by TOF-ERDA (time-of-flight elastic recoil detection analysis) [40]. TOF-ERDA enables the probing of the B_2O_3 films encapsulated by Al_2O_3 without exposure to the ambient atmosphere. For these TOF-ERDA studies, a 16 MeV ^{35}Cl ion beam was used. Samples were measured at 19° tilt and the recoils were detected at 38° with respect to the incoming beam. The amount of possible bromine impurities in selected samples were evaluated by X-ray fluorescence (XRF) in a Philips PW 1480 WDS spectrometer using Rh excitation and the results were verified by TOF-ERDA. Data were analysed with the Uniquant 4.34 program (Omega Data Systems, Netherlands), which is based on fundamental parameters and experimentally determined instrumental sensitivity factors [41,42].

Deposited films were also analysed by Fourier transform infrared (FTIR) spectroscopy. The FTIR transmission spectra of the films were obtained in a Nicolet Magna-750 spectrometer equipped with a deuterated-triglycine-sulfate detector. The silicon substrate contribution was subtracted from the measured sample spectra.

Preliminary capacitance–voltage (*C–V*) characteristics of the Al_2O_3-coated B_2O_3 thin films were determined for samples deposited onto native oxide covered Si(100) substrates. Measurements were carried out for the as-deposited stacks at room temperature and under normal pressure. Aluminium dots (0.204 mm^2) for ohmic contacts were e-beam evaporated onto the sample surface. Backside contact of the silicon substrates were made at the same time. Native silicon dioxide layer on the backside was removed by HF-etching before evaporation of aluminum. *C–V* measurements on the resulting $Al/Al_2O_3/B_2O_3$/native SiO_2/p-Si(100)/Al structures were performed using a HP 4284A. In the *C–V* measurements, ac signal frequency of 500 kHz and voltage step size of 0.05 V were applied.

3. Results and discussion

At first, thin film deposition was attempted in the temperature range of 100–400 °C. Precursor pulsing times were kept sufficiently long in order to achieve surface saturation and ALD-type film growth. Typically 1.0–3.0 s pulse times were used for the metal precursors as well as for H_2O. However, regardless of the pulsing time or substrate, no film growth was observed. This behaviour of the BBr_3/H_2O precursor system on