

Supporting Information for

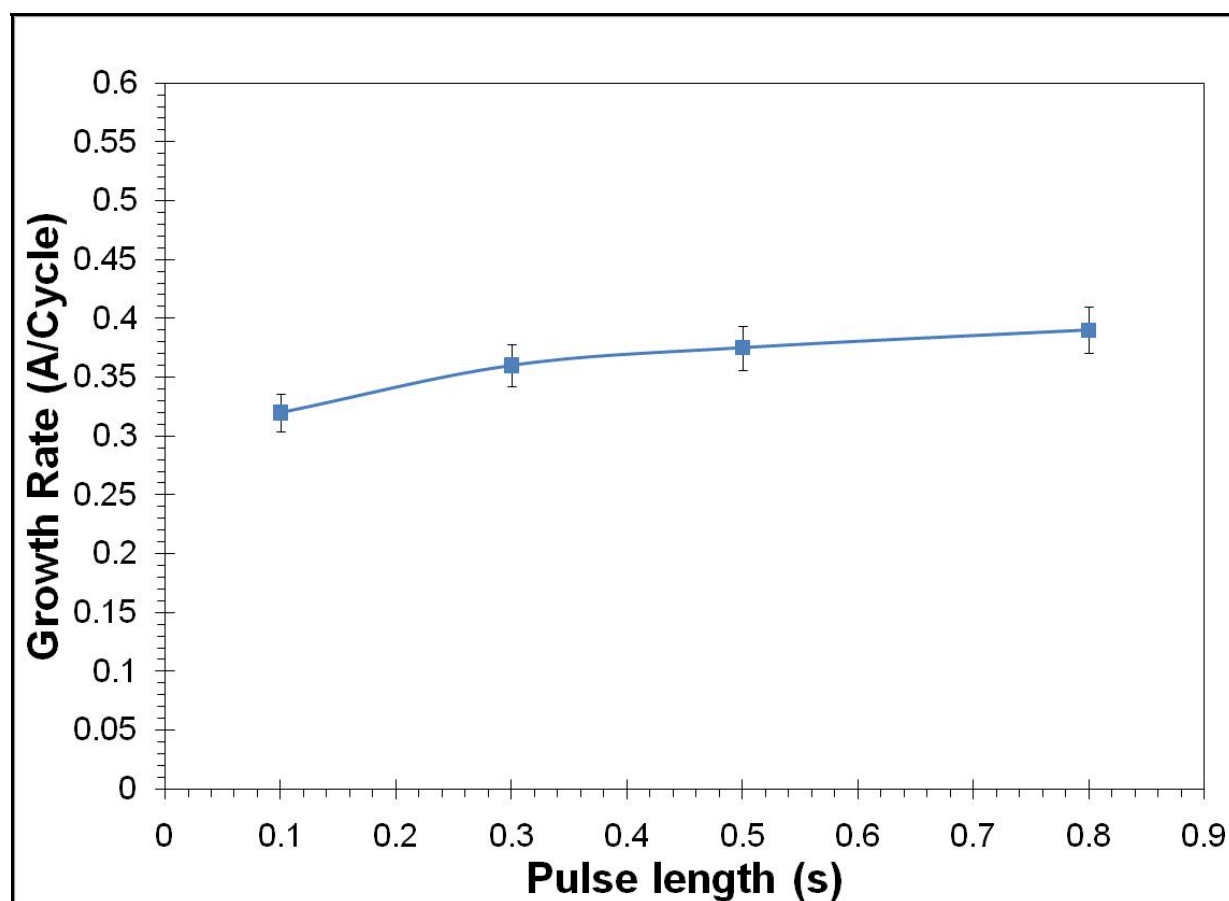
**Atomic Layer Deposition of CaB<sub>2</sub>O<sub>4</sub> Films Using Bis(tris(pyrazolyl)borate)calcium  
as a Highly Thermally Stable Boron and Calcium Source**

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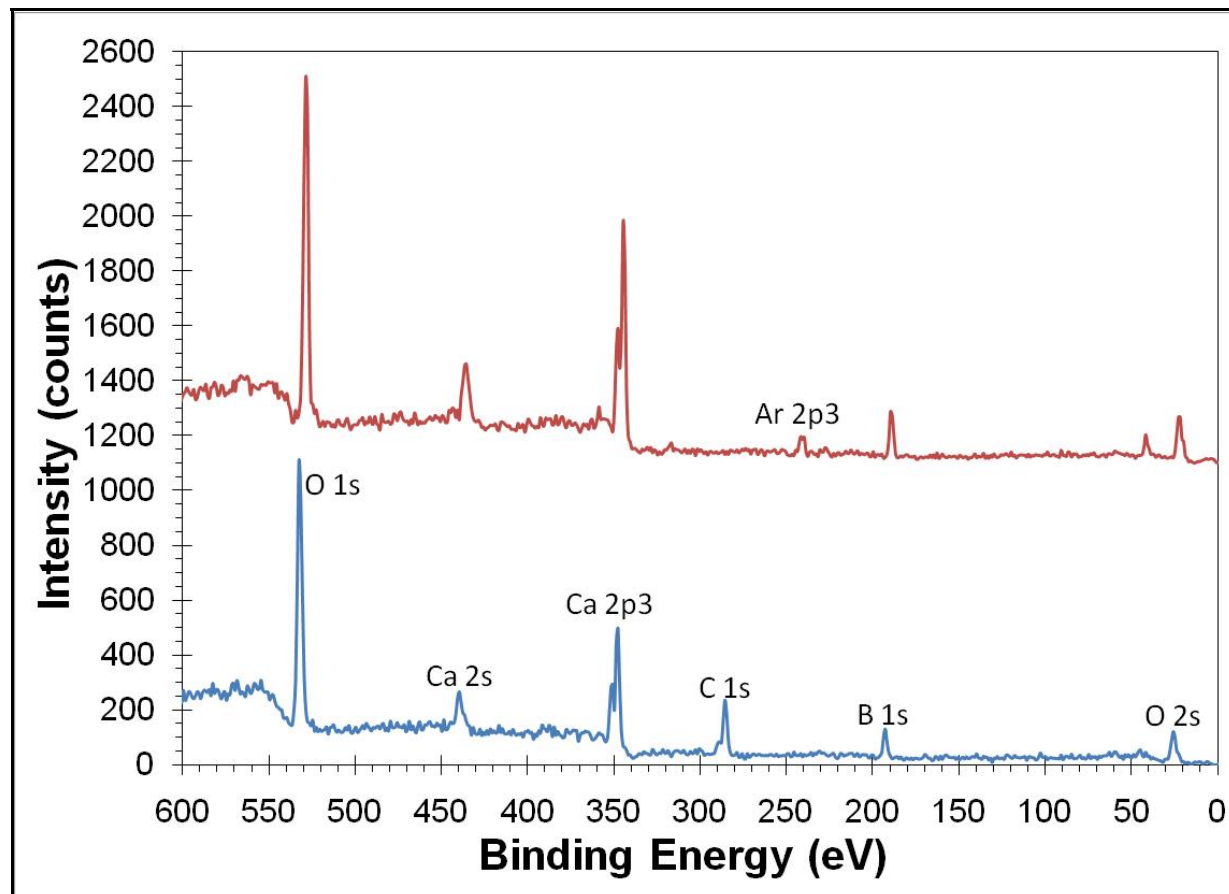
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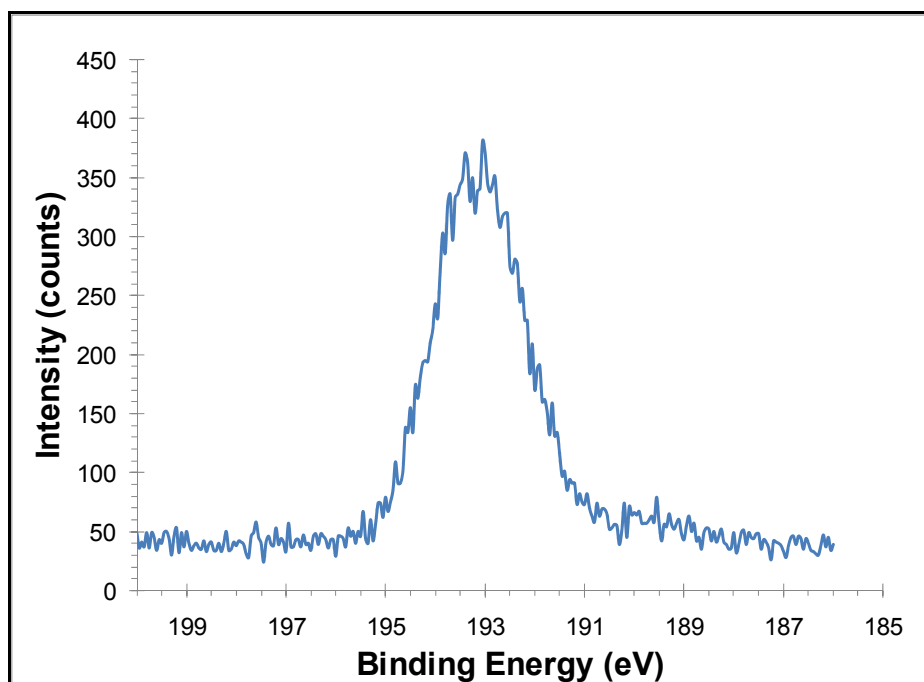
**Figure S1.** Growth rate as a function of water pulse length. The deposition temperature was 350 °C.



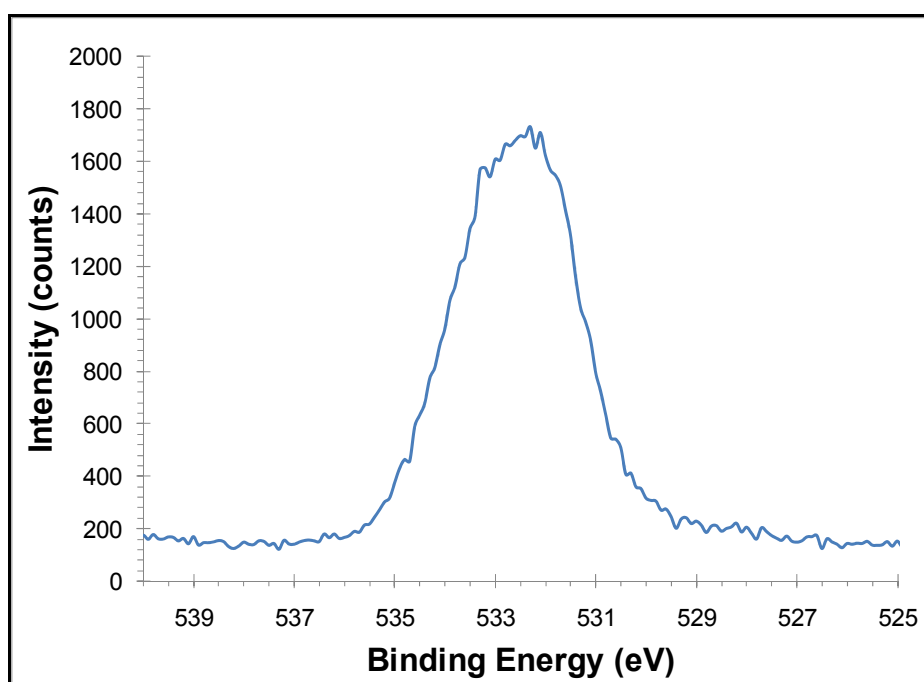
**Figure S2.** X-ray photoelectron spectrum of a 72 nm film deposited at 350 °C before (blue) and after 2 minute argon ion sputtering (red).



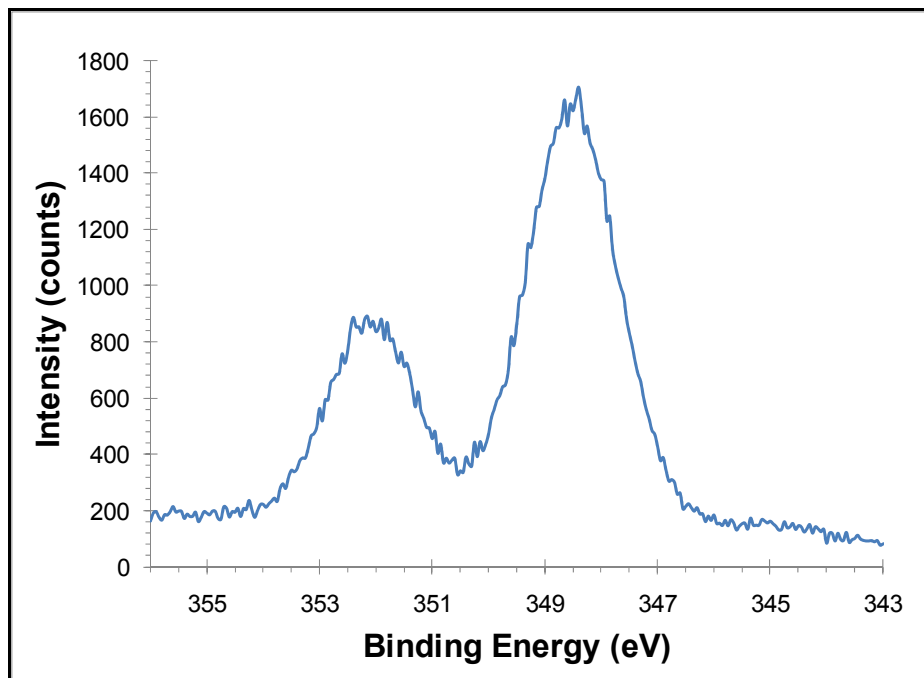
**Figure S3.** X-ray photoelectron spectrum of a film grown at 325 °C after 2 minute argon ion sputtering, showing the B 1s ionization.



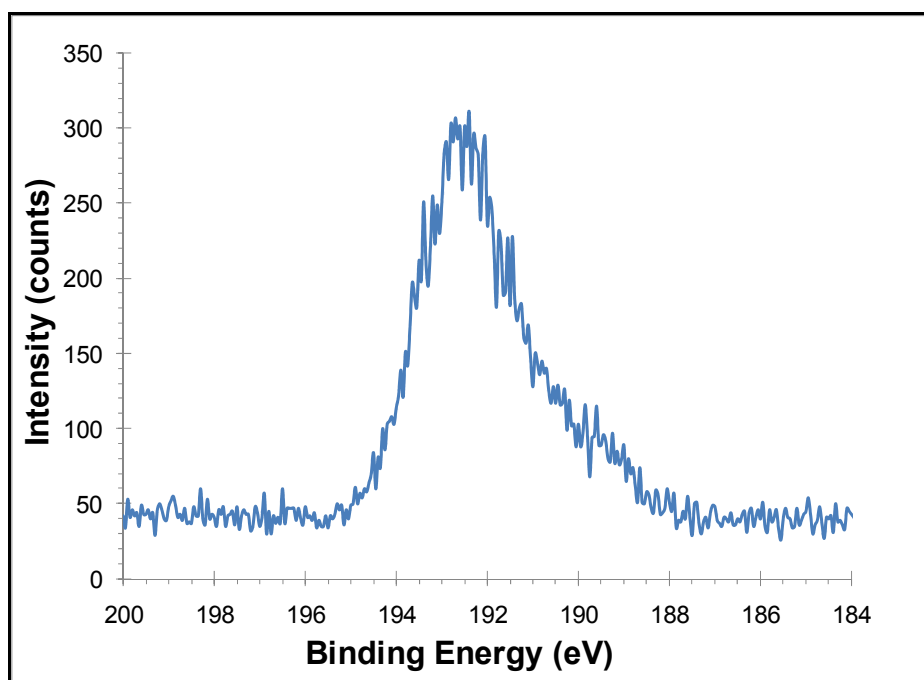
**Figure S4.** X-ray photoelectron spectrum of a film grown at 325 °C after 2 minute argon ion sputtering, showing the O 1s ionization.



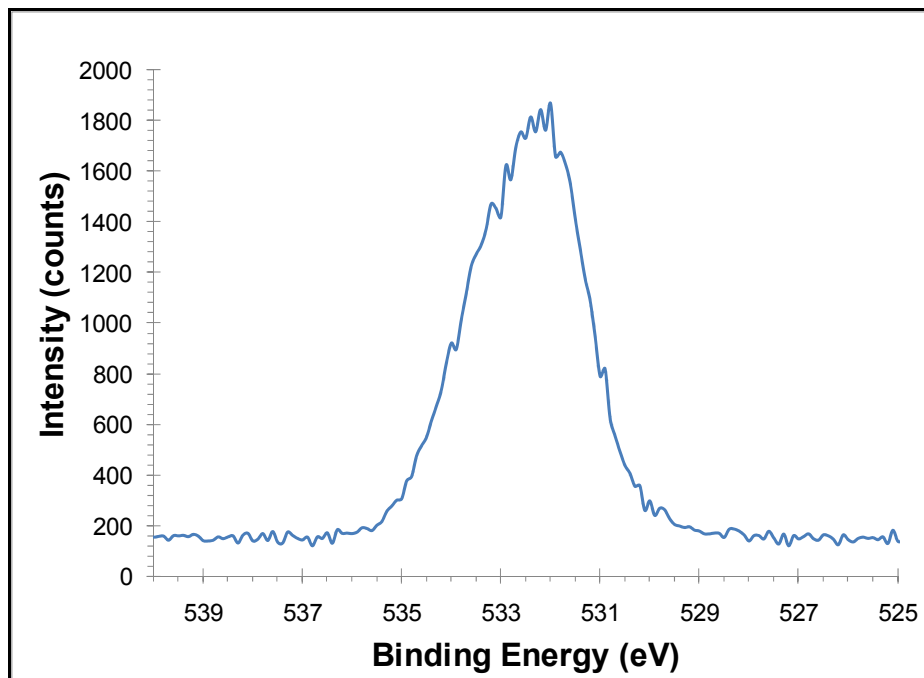
**Figure S5.** X-ray photoelectron spectrum of a film grown at 325 °C after 2 minute argon ion sputtering, showing the Ca 2p<sub>1/2</sub> and Ca 2p<sub>3/2</sub> ionizations.



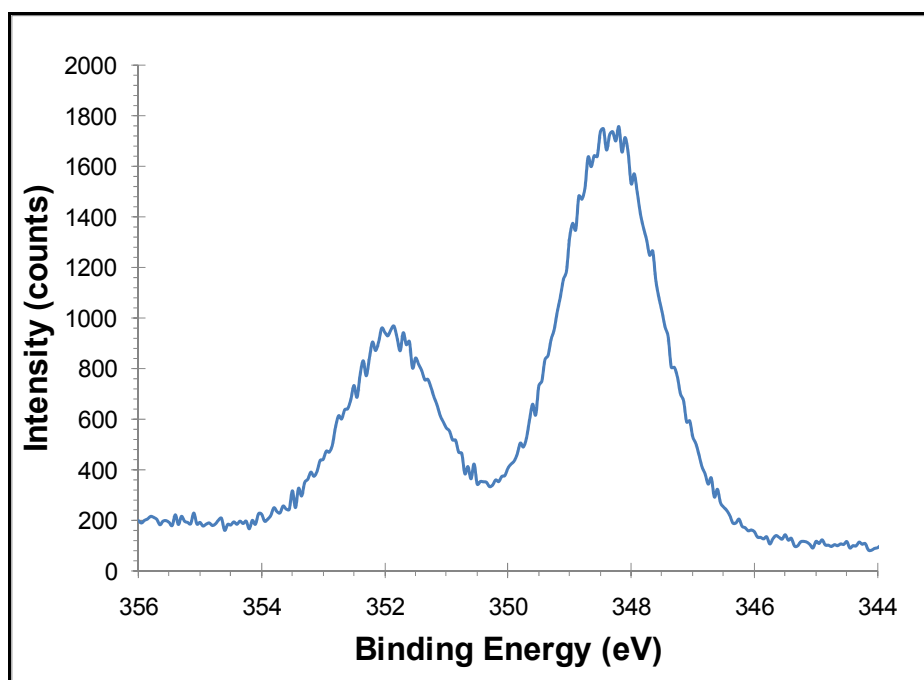
**Figure S6.** X-ray photoelectron spectrum of a film grown at 350 °C after 2 minute argon ion sputtering, showing the B 1s ionization.



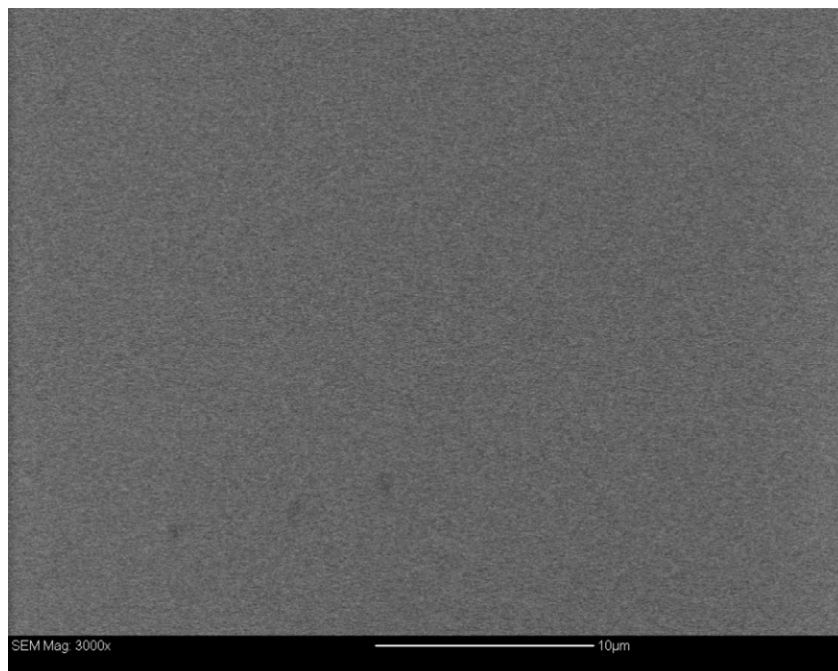
**Figure S6.** X-ray photoelectron spectrum of a film grown at 350 °C after 2 minute argon ion sputtering, showing the O 1s ionization.



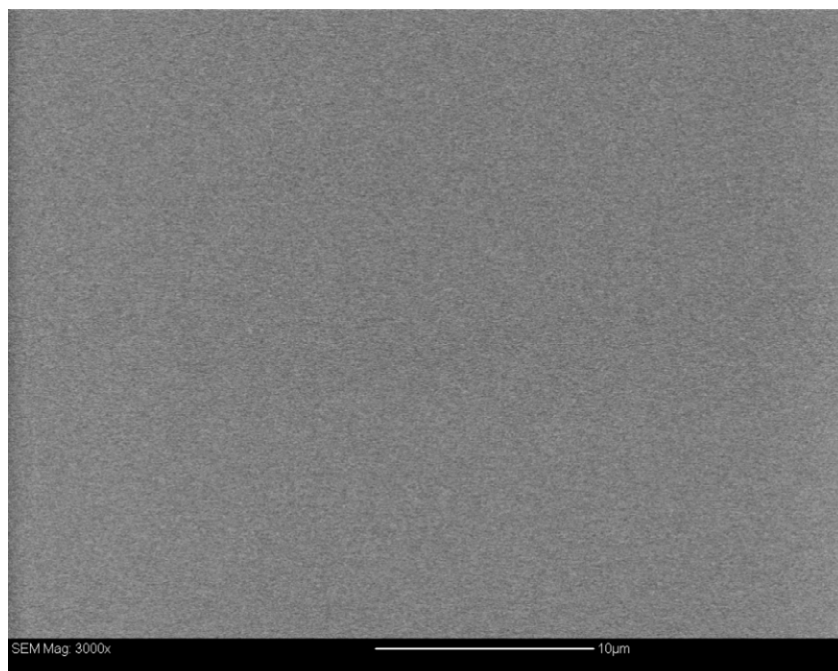
**Figure S7.** X-ray photoelectron spectrum of a film grown at 350 °C after 2 minute argon ion sputtering, showing the Ca 2p<sub>1/2</sub> and Ca 2p<sub>3/2</sub> ionizations.



**Figure S8.** Scanning electron micrograph of a 72 nm thick  $\text{CaB}_2\text{O}_4$  deposited at 325 °C on a silicon substrate.



**Figure S9.** Scanning electron micrograph of a 72 nm thick  $\text{CaB}_2\text{O}_4$  deposited at 350 °C on a silicon substrate.



Full report of the CaB<sub>2</sub>O<sub>4</sub> ERDA:

**Analysis Report**

Forschungszentrum Dresden-Rossendorf

**Client:**

Wayne State University

Prof. Charles H. Winter

Author: Dr. F. Munnik

Date: 15-Mar-2010

**Purpose:**

The analysis of four samples with a “CaB<sub>2</sub>O<sub>4</sub>” layer to determine the sample composition.

**Experimental:**

The samples have been analysed with ERDA (Elastic Recoil Detection Analysis) using a 35 MeV Cl<sup>7+</sup> ion beam. The angle between the sample normal and the incoming beam is 75°, the scattering angle is 31°. The analysed area is about 1½ x 1½ mm<sup>2</sup>. The recoil ions have been detected with a Bragg Ionisation Chamber using one standard amplification circuit for the full energy and one fast timing circuit to obtain a Z dependent signal to separate ion species. H has been detected with a separate solid state detector at an angle of 38° preceded by an Al foil to stop other scattered and recoiled ions.

The samples showed elemental loss during the measurements. In order to correct for the element loss, intermediate files were saved after each 1/20th portion of the total dose. The total counts for Ca (from the scattered Cl ions), B, O and H were determined for each section of the dose and plotted, see Figure 1 for an example. The curves were fitted using a linear function and extrapolated to zero dose for each element to obtain a correction for the loss, see Table 1. The element loss was not so large as for previous measurements. It can be noticed that the rate of loss is slightly different for different elements. On average it is larger for O than for B and for Ca it is lowest.



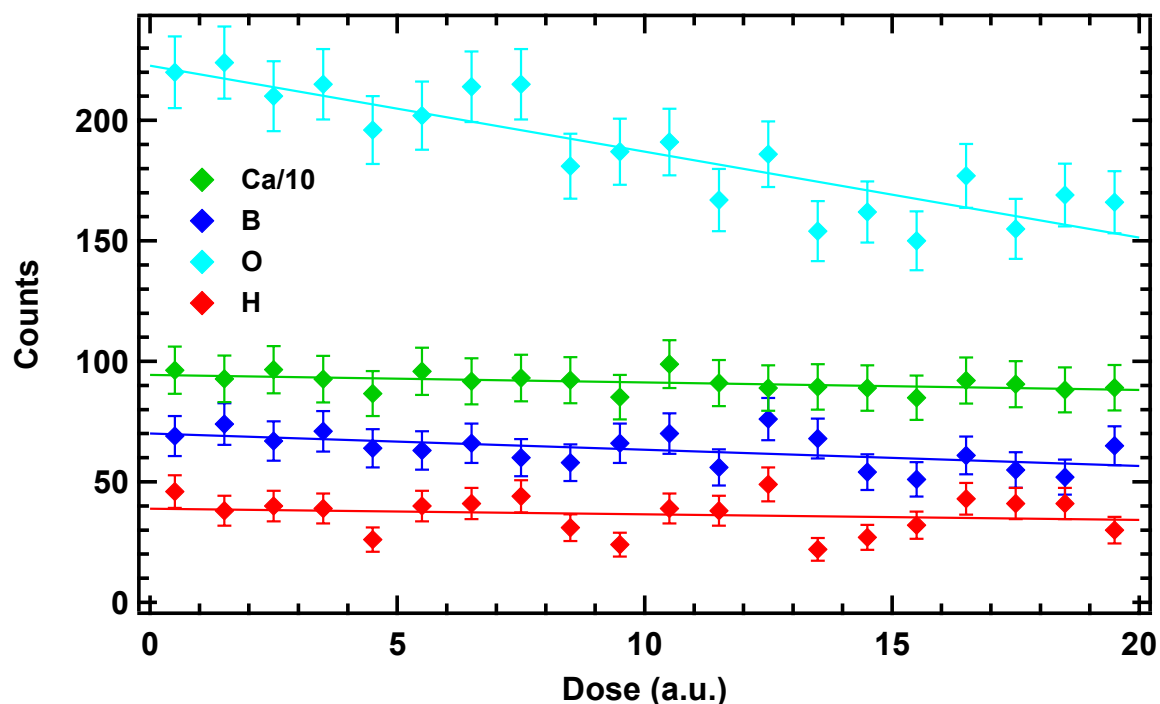


Figure 1: Elemental loss as a function of the measurement dose for a sample grown at 350 °C. The points are measured and the lines are fits. The results for Ca are reduced by a factor of 10.

**Table 1:** Correction factors for elemental loss. The correction factors are between the measured number of counts and the extrapolated counts at zero dose. Sd is the standard deviation in % for the correction factor.

Sample	Ca cor	B cor	O cor	H cor	Ca sd	B sd	O sd	H sd
MJS 640 (275 °C)	1.04	1.10	1.14	1.00	2.6	5.5	3.7	8.7
MJS 641 (325 °C)	1.02	1.10	1.08	1.23	1.5	6.4	4.2	7.9
MJS 643 (350 °C)	1.03	1.11	1.19	1.06	1.8	5	2.9	9.9
MJS 645 (400 °C)	1.12	1.10	1.19	1.25	1.7	4.9	3.6	4.6

## Results and Discussion:

The results are presented in the table below:

<i>Sample</i>	$t$ $10^{15}$ at/cm <sup>2</sup>	$t$ nm	$\rho$ g/cm <sup>3</sup>	<i>Ca</i> at. %	<i>B</i> at. %	<i>O</i> at. %	<i>H</i> at. %
<i>MJS 640</i> (275 °C)	643	72	2.7	15.1±0.4	28.5±1.8	56.2±2.3	0.22±0.02
<i>MJS 641</i> (325 °C)	649	76	2.7	18.2±0.3	25.9±1.8	54.5±2.5	0.48±0.04
<i>MJS 643</i> (350 °C)	639	71	2.7	14.3±0.3	26.5±1.5	57.6±1.9	0.35±0.04
<i>MJS 645</i> (400 °C)	542	61	2.6	14.2±0.3	26.1±1.5	57.9±2.3	1.13±0.06

The following remarks concerning the analysis can be made:

- A correction has been made for the presence of O in the native SiO<sub>2</sub> layer. It is estimated that 1.5 nm of SiO<sub>2</sub> constitutes about  $8 \cdot 10^{15}$  at/cm<sup>2</sup> O and this has been subtracted from the corrected total amount of O.
- All ERDA spectra and the RBS spectrum (Cl scattering) are fitted simultaneously using the program NDF<sup>1</sup>.
- The concentrations are based on a sample model that is fitted to the measured spectra. The model consists of a number of layers with for each layer a thickness and concentrations of all elements.
- The thickness in at/cm<sup>2</sup> is directly obtained from the measurements and the thickness in nm is obtained from the accompanying letter. The density is calculated from these two values and the composition using the equation in the note.
- The results are corrected for elemental loss using Table 1. The elemental loss is likely to be caused by “electronic sputtering” not by direct sputtering due to ion-atom collisions. The latter process is not very likely since the energy of the ions is very high. For electronic sputtering, the target atoms disappear due to localised heating although the mechanism is not yet very clearly understood<sup>2</sup>. It strongly depends on the target.
- The uncertainties in the table are based on the statistical uncertainty in the measurement and the uncertainty in the correction factor presented in Table 1. No other sources of error have been considered.
- Some other minor elements have also been found:
  - For sample grown at 400 °C: C with 0.66±0.15 at. %,
  - for sample grown at 350 °C: F with 1.26±0.12 at. %,

### References:

<sup>1</sup> N.P. Barradas, C. Jaynes, R.P. Webb, Appl. Phys. Lett. 71 (1997) 291

<sup>2</sup> W.M. Arnoldbik, N. Tomozeiu, F.H.P.M. Habraken, Electronic sputtering of thin SiO<sub>2</sub> films by MeV heavy ions, Nucl. Instr. Meth. B 203 (2003) 151-157

- for sample grown at 325 °C: F with 0.84±0.10 at. %.
- No C, N and F could be detected in the other samples above the detection limit of about 0.3 at. %.

Notes:

- The equation below can be used to calculate the density from the measured thickness in at/cm<sup>2</sup> and the thickness in nm obtained from some other source. The formula for the conversion is:

$$t = \frac{N_M \cdot \langle M_Z \rangle}{\rho \cdot N_A}$$

with  $t$  the thickness in cm,  $N_M$  the areal density in at/cm<sup>2</sup>,  $\langle M_Z \rangle = \sum f_Z \cdot M_Z$  the average atomic mass in g/mol (with  $f_Z$  and  $M_Z$  the atomic fraction and the atomic weight of element  $Z$  respectively),  $\rho$  the density in g/cm<sup>3</sup>, and  $N_A$  Avogadro's number (mol<sup>-1</sup>).

### Conclusions:

Four samples have been analysed and the results are presented in the previous section. The films have been damaged by the measurements necessitating a correction as described in the experimental section. The ratios between O and Sr, and B and Sr are presented below:

<i>Sample</i>	<i>B / Ca</i>	<i>O / Ca</i>
<i>MJS 640</i> <i>(275 °C)</i>	1.84±0.11	4.08±0.18
<i>MJS 641</i> <i>(325 °C)</i>	1.85±0.11	4.03±0.15
<i>MJS 643</i> <i>(350 °C)</i>	1.89±0.13	3.73±0.18
<i>MJS 645</i> <i>(400 °C)</i>	1.42±0.10	2.99±0.14