In this study, triethylboron (TEB) was used as single source CVD precursor to deposit boron carbide thin films. The initial experiments focused on low reaction rate deposition by depositing in a kinetically limited regime. The films deposited at ≤450°C in an 8:1 aspect ratio micro-trench structures were highly conformal and show a stoichiometry of about B$_5$C$_2$. The depositions carried out on the prototype detector chips for neutron detector application show promising results. We expand our studies to investigate a new strategy with the prospect of improving the step coverage at higher temperatures for better film properties. We hypothesize that adding a suitable heavier molecule, diffusion additive, with an appropriate partial pressure can enhance the step coverage by pushing the lighter precursor molecule via competitive co-diffusion. It was tested by adding Xe gas to the boron carbide CVD from TEB. The result shows that with this diffusion additive the step coverage was improved. The CVD process is further validated by depositing onto carbon nanotube membranes. The initial results show that the process was able to afford evenly deposition around the individual nanotubes in the carbon nanotube membrane. Raman spectroscopy measurements show a similar D-band to G-band intensity ratio before and after the deposition.
Conformal chemical vapor deposition of boron carbide thin films

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Cover images:

Front side: Schematic illustration showing an exploded view of a 3D solid-state neutron detector. More details can be found in chapter 5.2.

Rear side: SEM micrographs of the boron carbide deposited high aspect ratio prototype neutron detector-chip. More details can be found in chapter 5.2.
Abstract

The sustainability goals of the modern world and the fascinating properties of sub-micron scale materials promote development of materials in thin film form. Thin films are materials that have thicknesses ranging from sub-nanometer to several micrometers, synthesized by various deposition techniques. They are used for diverse applications, such as light emitting diodes, solar cells, semiconductor chips, etc. The primary objective of this research project is to develop a chemical vapor deposition (CVD) process for conformal boron carbide thin films. Since boron carbide is a promising neutron converter material for solid-state neutron detectors, the process was validated by depositing on prototype detector chips.

In this study, triethylboron (TEB) was used as single source CVD precursor to deposit boron carbide thin films. The initial experiments focused on low reaction rate deposition by depositing in a kinetically limited regime. The films deposited at ≤450 °C in 8:1 aspect ratio micro-trench structures were highly conformal and show a stoichiometry of about B$_{3.2}$C. We attribute this observed conformality to the slow reaction kinetics of the TEB at the low deposition temperature enabling the diffusive transport of the precursor molecule down the trench. The depositions carried out on the prototype detector-chips show promising results.

We expand our studies to investigate a new strategy with the prospect of improving the step coverage at higher temperatures for better film properties. We hypothesize that adding a suitable heavier molecule, diffusion additive, with an appropriate partial pressure can enhance the step coverage by pushing the lighter precursor molecule via competitive co-diffusion. It was tested by adding Xe gas to the boron carbide CVD from TEB. The result shows that with this diffusion additive the step coverage was improved from 0.71 to 0.97. From our experimental results, we suggest a competitive diffusion model that can be adapted to other CVD processes to enhance the film step coverage.

The CVD process is further validated by depositing onto carbon nanotube membranes. The initial results show that the process was able to afford evenly deposition around the individual nanotubes in the carbon nanotube membrane. Raman spectroscopy measurements show a similar D-band to G-band intensity ratio before and after the deposition indicating that no defects were induced in the nanotubes.
**Populärvetenskaplig sammanfattning**


Det finns flera olika tekniker för att skapa tunna filmer, några av de vanligaste utnyttjar atomer eller molekyler i gasfasen. Denna avhandling har använt en sådan teknik, som kallas CVD, från engelskans chemical vapor deposition, vilket betyder ungefär kemisk ångdeponering. Huvudsyftet med forskningsprojektet är att utveckla en CVD-process för materialet borkarbid, som består av grundämnen bor (B) och kol (C). CVD-processen ska styras mot helt konforma filmer, alltså filmer som är helt jämntjocka på objekt med en komplex topologisk struktur. Eftersom isotopen $^{10}$B är bra på att omvandla neutroner till partiklar som är lättare att detektera, är borkarbid ett bra val som neutronomvandlarskikt i neutrondetektorer. Forskningens första mål var därför att utveckla en process som kan ge konforma filmer på chips med djupa spår och hål. När en passande CVD-process hade utvecklats verifierades den genom att neutrondetektorer tillverkades med processen i ett internationellt samarbete.

En utveckling av projektet kom med idén att man borde kunna styra hur källmolekylerna rör sig ner i hålen och spåren genom att använda sig av tyngre molekyler som knufflar ner källmolekylerna. Denna idé har verifierats och patenterats i projektet. Båda CVD-processerna kommer i vidare forskning användas för att belägga väldigt utmanande strukturer, som till exempel kolnanorör för att öka deras prestanda i tuffa miljöer.
Preface

This licentiate thesis is a part of my Ph.D. studies in the thin film physics division at the Department of Physics, Chemistry and Biology (IFM), at Linköping University. The area covered in this research is chemical vapor deposition of boron carbide thin films and its applications include neutron converter layer in solid-state neutron detectors and capping of carbon nanotubes. It was achieved by synthesizing boron carbide films with desired micro or nano structures. Novel strategies were introduced to make the chemical vapor deposition process suitable for the applications. The thesis has two major segments, the first one contains the overview of the research field and scientific concepts and methodologies used. The second segment provides the outcomes of this research in the form of scientific papers.

Financial support by the Swedish Research Council (VR) and from the Swedish Government Strategic Research Area in Materials Science on Advanced Functional Materials at Linköping University have supported my studies and are gratefully acknowledged.

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List of included publications

Paper 1  Conformal chemical vapor deposition of boron-rich boron carbide thin films from triethylboron

_Arun Haridas Choolakkal, Hans Högberg, Jens Birch and Henrik Pedersen_


My contribution:
I have done the depositions, planned the analysis, done the cross section scanning electron microscopy measurements, performed X-ray reflectivity measurements and data fitting, performed the analysis of ToF-ERDA data, I wrote the first draft of the manuscript and coordinated the writing of the article.

Paper 2  3D silicon detectors for neutron imaging applications


My contribution:
I have optimized the conformal boron carbide CVD process, carried out boron carbide depositions on high aspect ratio Si substrates, and performed cross section SEM measurements. I also participated in the writing of the article.

Paper 3  Competitive diffusion as a route to enhanced step coverage in chemical vapor deposition

_Arun Haridas Choolakkal, Pentti Niiranen, Jens Birch and Henrik Pedersen_

_In manuscript_

My contribution:
I conceived the experiment and carried through the depositions, planned the analysis, carried out cross section scanning electron microscopy measurements, performed X-ray reflectivity measurements and data fitting, and performed the analysis of ToF-ERDA data, I wrote the first draft of the manuscript and coordinated the writing of the article.
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1. Introduction

Materials science is a dynamic and evolving discipline that study properties and applications of materials for construction, manufacture, or electronics, such as metals, ceramics, organic materials, and composites. It draws on knowledge from the fundamental science branches such as physics, chemistry, and biology. The fascinating properties of sub-micron scaled materials promote thinner materials known as thin films\textsuperscript{2,3} which have thickness ranging from sub-nanometer to several micrometers. They are used for various applications, such as light emitting diodes (LEDs)\textsuperscript{4}, solar cells\textsuperscript{5}, and micro electronics\textsuperscript{6}.

An evolving technique to study materials in general, and thin films in particular, uses neutrons as a probe to advance scientific research. Since neutrons can probe through the electron cloud around an atomic nucleus, it has access to the tiniest universe. The ability of neutrons to interact with the nuclei and magnetic moments of atoms makes them suitable to study atomic and molecular arrangements, the residual stress and strain, the texture and orientation and magnetic order of materials. A few examples of neutron techniques are neutron imaging, neutron diffraction, neutron reflectometry, small angle neutron scattering and neutron spectroscopy.

There are several large-scale neutron facilities around the world which includes the Oak Ridge National Laboratory in Tennessee, USA, the ISIS neutron and muon source in the United Kingdom, the Paul Scherrer Institute in Switzerland, the Budapest Neutron Centre in Hungary, and the Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan. Research is ongoing to make even more powerful and efficient neutron instruments.\textsuperscript{7} The European spallation source (ESS) which is being built in Lund, Sweden, will be able to deliver higher energy and higher intensity neutron flux to study materials than any present neutron facility. However, to enable the advanced next generation neutron techniques we also require better instrumentation. Efforts are required to improve the performance of neutron detectors, polarizers, neutron mirrors etc. For instance, the technique of neutron imaging is suffering from poor resolution due to the lack of suitable detectors. Although it was proposed a few years ago, we have not started using solid-state semiconductor neutron detectors in neutron facilities. In this work, we address the need of a suitable neutron converter material for the next generation solid state neutron detectors from a materials science perspective.

The purpose of this research project is to develop a chemical vapor deposition process to deposit boron carbide thin films on substrates with high aspect ratio morphologies. Film conformality and boron rich elemental composition were the major objectives.
2. Neutron detection

Neutron detectors are classified into three types, scintillators, proportional counters, and solid-state detectors. Scintillators sense neutrons by detecting photons produced during the neutron interaction with hydrogen or during a neutron capturing event. Whereas in proportional detectors, the ionization caused by neutron interaction with a gaseous medium is amplified by secondary ionization with an external voltage bias to get the signal output. Solid-state neutron detectors convert neutrons into energetic detectable ions in a solid conversion layer. These energetic ions further reach a semiconductor medium and create electron-hole pairs causing an electric output signal through a device, such as a PiN diode. Since detection of neutrons is made possible by converting them into detectable ions, the isotopes with high neutron capture cross section such as $^{155}$Gd, $^3$He, $^{10}$B and $^6$Li are used for neutron converters. Fig. 1 shows the neutron capture cross section for these elements for the neutron energy ranging from $10^{-5}$ to $10^7$ eV.

![Neutron Capture Cross Section](image)

**Fig. 1:** showing neutron absorption cross section for $^{155}$Gd, $^3$He, $^{10}$B and $^6$Li for the neutron energy ranging from $10^{-5}$ to $10^7$ eV. It shows comparable neutron capture cross section between $^3$He and $^{10}$B. Plotted using data from Nuclear energy agency database ENDF/B-VII.0.

2.1. Conversion of neutrons into detectable particles

Unlike protons, neutrons are subatomic particles with zero net electric charge making them difficult to detect. The detection of neutrons is made possible mainly by detecting nuclear

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$^1$The neutron capture cross section is the measure of probability of capturing a neutron by a nucleus. **$^{81}$**
fission fragments produced during the interactions with the nuclei of suitable elements or by detecting the high energy photons. Basically, these reactions convert the nuclei of certain elemental isotopes having high neutron capture cross sections into lighter nuclei resulting in detectable charged ions together with high energy radiation. A few examples are given below.

\[
n + ^{3}\text{He} \rightarrow ^{4}\text{H} + ^{1}\text{H} + 0.765 \text{ MeV} \quad (1)
\]

\[
n + ^{6}\text{Li} \rightarrow ^{4}\text{He} + ^{3}\text{H} + 4.78 \text{ MeV} \quad (2)
\]

\[
n + ^{10}\text{B} \rightarrow ^{7}\text{Li}^{*} + ^{4}\text{He} \rightarrow ^{7}\text{Li} + ^{4}\text{He} + ((2.31 \text{ MeV} + \text{ gamma } 0.48 \text{ MeV}) \text{ or } 2.79 \text{ MeV}) \quad (3)
\]

\[
n + ^{14}\text{N} \rightarrow ^{14}\text{C} + ^{1}\text{H} + 0.625 \text{ MeV} \quad (4)
\]

\[
n + ^{155}\text{Gd} \rightarrow \text{Gd}^{*} \rightarrow \text{gamma-ray spectrum} + \text{ conversion electrons spectrum} \quad (5)
\]

\[
n + ^{157}\text{Gd} \rightarrow \text{Gd}^{*} \rightarrow \text{gamma-ray spectrum} + \text{conversion electron spectrum} \quad (6)
\]

\[
n + ^{235}\text{U} \rightarrow \text{xn} + \text{fission fragments} + \sim 160 \text{ MeV} (x \sim 2.5) \quad (7)
\]

\[
n + ^{239}\text{Pu} \rightarrow \text{xn} + \text{fission fragments} + \sim 160 \text{ MeV} (x \sim 2.5) \quad (8)
\]

The most used neutron detection element is $^3\text{He}$ according to the nuclear reaction (1). $^3\text{He}$ based neutron detectors require filling of neutron transparent tubes with $^3\text{He}$ gas, allowing neutrons to pass through the tube wall and interact with $^3\text{He}$ nuclei. $^3\text{He}$ nuclei convert the neutron flux into detectable charged particles of $^3\text{H}$ and $^1\text{H}$. These ions cause secondary ionization of the gas medium and form more electron-ion pairs. With a suitable bias voltage, one can amplify and accelerate these ions and electrons towards their respective electrodes resulting in an electric current. Although this is an effective way of detecting neutrons, it is becoming difficult to procure $^3\text{He}$ gas due to its world over short supply. It is mainly produced as a byproduct during nuclear weapon manufacturing. Alternative detection techniques are therefore investigated. It has been proposed that solid-state detectors can be realized to replace $^3\text{He}$ filled proportional detectors in neutron facilities especially for the techniques where large area detectors are used. Both $^6\text{Li}$ based and $^{10}\text{B}$ based solid-state detector models have been proposed, but the $^{10}\text{B}$ based solid-state detectors have this far been most explored due to the abundance of $^{10}\text{B}$ isotope and the stability of converter material made from $^{10}\text{B}$.

$^{10}\text{B}$ has a high capturing cross section against thermal neutrons according to the nuclear reaction (3), as illustrated in Fig. 3, which makes it a promising converter element for solid-state neutron detectors. Also, the ions produced by $^{10}\text{B}$ and neutron interaction are in a convenient energy range, as shown in Fig. 2. Nevertheless, boron in its pure elemental form will not be ideal for neutron detectors due to poor electrical conductivity and a vulnerability to oxidation and corrosion.
Fig. 2: Schematic showing thermal neutron and Boron-10 interaction. It produces 0.84 MeV Li ion, 1.47 MeV He ions and 0.48 MeV gamma in 94 % of the events.

2.2. Solid state neutron detectors

The multiblade detector concept, made up of several $^{10}$B$_4$C coated Al or Ti cassettes, has already been introduced as a replacement for $^3$He detectors.21,22,23 Especially, for the techniques where large area detectors are required. They are assembled from Al or Ti blades, coated with $^{10}$B$_4$C by magnetron-sputtering. Drawbacks of multi-blade detectors are moderate spatial feasibility, inconvenient geometry, and a lack of directional information. Solid-state semiconductor neutron detectors are therefore investigated to overcome these limitations. The detector efficiency using a planar thin film neutron converter configuration is limited by self-absorption of the conversion products in the layer. A 3D configuration, as illustrated in Fig. 3, which allows the conversion products to exit the converter, offers possibility for higher detection efficiency.9,11 A suggested evolution of a solid-state neutron detector will require filling of high aspect ratio vertical holes with neutron converter material. This 3D architecture increases the probability of interactions between the charged reaction products and the semiconductor material.

Fig. 3: Schematic showing comparison between Planar and 3D detector architecture. Adapted from: illustration by Marco povoli in: M. Povoli et al. J. Instrum. 18, C01056 (2023)9.
A pixelated detector using $^{10}\text{B}_4\text{C}$ deposited onto a Si sensor-chip is a promising concept to push the limitations of the current generation neutron detectors for imaging application. One of the principal differences between $^3\text{He}$ filled proportional counter and $^{10}\text{B}_4\text{C}$ solid state detector is the difference in the signal generation. While $^3\text{He}$ proportional counter produces current signal by forming electron-ion pairs, solid-state detector generates signals by creating electron-hole pairs. Electron-hole pair generation is more energy efficient than electron-ion pair generation. Furthermore, detectors for neutron imaging applications are characterized by their spatial resolution. In principle, solid-state detector design using boron carbide deposited pixelated sensor chips can offer higher spatial resolution. To achieve a high efficiency and high spatial resolution, filling of vias structures of minimum pitch in a Si chip-substrate with boron-rich boron carbide is required, see Fig. 3. The efficiency of such a detector depends also on the aspect ratio of the vias structure and the conformality of the boron carbide film deposition.

2.3. Boron carbide

Boron carbides are very hard, durable, and thermally stable materials that finds applications in various fields.\(^{24}\) It has a chemical formula of approximately B$_4$C, however, it can also be written as B$_{12}$C$_3$ or B$_4$C depending on the carbon content and the structure of the boron icosahedra.\(^{25}\) The total structure is rhombohedral.\(^{26}\) It also has amorphous phases with superior properties. Boron carbide in bulk exhibits a hardness of about 40 GPa,\(^{27}\) making it the third hardest known material after diamond and cubic boron nitride. It is a very good abrasion, wear, and impact resistant material.\(^{28}\) Boron carbide is a lightweight material with a bulk density of about 2.52 g/cm$^3$,\(^{27}\) which makes it suitable for armor and aerospace applications. It has a high melting point of about 2427 °C\(^{28}\) with good thermal conductivity and thermal shock resistance\(^{26}\). Also, it can withstand high temperatures without losing its strength or hardness. It exhibits a strong chemical resistance and stability to most acids, bases and solvents, and resist oxidation and corrosion. Since $^{10}\text{B}$ isotope exhibits high neutron capture cross section, boron carbides can absorb neutrons and moderate their energy, making it suitable for nuclear reactors\(^{26}\) and neutron detectors\(^{29,30}\). Compared to bulk the thin film counterpart of boron carbide is also fascinating.

The thickness of the boron carbide converter layer in the 3D solid-state detectors is decided mainly by the range of the conversion products, i.e., $^4\text{He}$ and $^7\text{Li}$ ions, in the as synthesized boron carbide material. Stopping and Range of Ions in Matter (SRIM) is a widely used code to calculate ion range in matter.\(^{31}\) The SRIM simulation using the properties of the as deposited material on flat substrate shows a maximum ion range of about 2 and about 3.8 µm for the 0.84
MeV Li and 1.47 MeV He ion, respectively, see Fig. 4. It shows that the B₅.₂C converter layer thickness should be below 2 µm to collect maximum ions in the semiconductor medium. This means that a deposition technique that can deposit boron carbide thin film with a thickness between 1 and 2 µm onto a high aspect ratio sensor-chip is required to realize solid-state neutron detectors. This shows that the boron carbide material in thin film form needs to be deposited uniformly in trenches or vias structures of a few micrometres wide and a few tens of micrometers deep.

Fig. 4: The range of 1.47 MeV He and 0.84 MeV Li ions in the as deposited material simulated using SRIM program shows a depth of about 3.8 and 2 micrometers, respectively.
3. Thin film deposition

Thin film deposition techniques which use some sort of vapor phase are broadly classified into Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) with different pros and cons. As mentioned above, the conformality of the thin film in a recessed feature is of great importance to the work done in this thesis. As the conformality of film deposition on 3D objects by PVD is very limited, due to its line-of-sight behavior, CVD, which can be designed to cover 3D objects to a great extent is chosen for applications requiring conformal coverage. Therefore, the work done in this thesis focuses on using CVD to conformally deposit boron carbides.

One subclass of CVD is known as atomic layer deposition (ALD), which is a time-resolved form of CVD where the different precursors are prevented from interacting in the gas phase by supplying them to the reactor in discrete pulses separated in time by pulses of inert gas. This renders a deposition chemistry fully governed by surface reactions, which are ideally self-limiting. The hallmark of ALD is the ability to deposit perfectly conformal films on topologically very complex objects. On the other hand, the typical ALD method is not always useful due to limited throughput and lack of good process recipes for materials such as silicon carbides and boron carbides. This since carbon is typically a surface leaving group, making carbon precursors that exhibit self-terminating surface chemistry difficult to design. Hence, the present project cannot use ALD.

CVD is one of the core techniques for thin film deposition in the semiconductor and hard coatings industries. The deposition rate in CVD depends on the activation energy and incident flux of reactive species to the surface. Although it is better than PVD techniques for conformal film deposition, it needs to be further tuned to afford highly conformal depositions. The thin film conformality is typically characterized by the step coverage (SC), Fig. 5. It is the ratio between the film thickness at the bottom surface of a high aspect ratio feature and the film thickness at the top surface of a high aspect ratio feature. It has been reported that with effective strategies CVD conformality can be improved to higher than even one which is called super-conformal, i.e., SC > 1.
3.1. Thermal chemical vapor deposition

Thermal CVD uses heat energy to activate the chemical reaction that deposits thin films. Depending on the application and temperatures needed, the CVD reactor is either heated by resistive heating elements in an oven surrounding the reaction chamber, or by using an inductor coil and radio frequency (RF) power supply. For the latter, the magnetic field fluctuations created by the inductor coil and RF power heat up the core material, susceptor, kept inside the reactor cell. Quartz tubes are typically used as the cell body for this type of reactor and the Cu windings around the tube as the inductor coil. A focused pyrometer monitors real time temperature if thermocouples cannot be inserted in the reactor. The susceptor is typically made of graphite. However, it is coated with materials such as SiC or TaCx to prevent the etching of graphite by hydrogen.

My CVD experiment typically starts with loading the substrates inside the reactor cell. The hollow susceptor block provides room for the substrates. Subsequently, the reactor is pumped to rough vacuum. Then it is back filled with H\textsubscript{2} gas, or Ar in experiments with Ar. The steady process-gas flow keeps the reactor pressure constant with the help of a throttle valve connected on the vacuum pump mouth. The substrates were heated to the deposition temperature by enabling RF current through the inductor coil. Upon reaching the temperature set point, a few minutes of soak time is typically provided. This will help to outgas the substrate and the temperature to stabilize. Reactive gases are then admitted to the reaction zone. The hot-wall configuration prevents the condensation of precursor gases on the reactor walls near to the reaction zone.

The reactant molecules, often called precursor molecules, diffuse through the boundary layer from the main gas stream to the substrate surface as illustrated in Fig. 6. Although surface-reaction results in film formation some fraction of the reaction can occur in the gas phase. Upon arriving at the substrate surface precursor molecules and reaction intermediates from the gas
phase reaction get adsorbed onto the surface sites. Subsequently, they absorb thermal energy and undergo surface reactions resulting in film deposition. The volatile byproducts will diffuse through the boundary layer back up to the main gas stream and get pumped out of the reactor. However, it is possible that a fraction of the reaction byproducts can go under further decomposition and contribute other elements into the film.

![Fig. 6: Schematic illustration of CVD reactions that enable film deposition (inspired by schematic by Jensen KF In: Ref. 43).](image)

CVD deposition rate varies with the incident flux of reactive species and the rate of reaction. If the surface receives enough incident flux, then the deposition is characterized as kinetics limited. If the surface sites have sufficient energy for reaction to occur but lack incident flux of reactive species, then the deposition is characterized as gas transport limited. Fig. 7 schematically illustrates the various thermal CVD regimes. The kinetics-limited regime can be accessed by operating a CVD process at lower temperatures. In kinetics-limited regime the sticking probability of a CVD precursor molecule can be tuned. Sticking probability is defined as the probability that a precursor molecule reacts and sticks to a substrate surface. If \( \Theta_i \) is the incident flux of reactive species over a unit area of a substrate surface and \( \Theta_r \) is the flux of reactive species per unit area, a fraction of incident flux, coming out of that surface. Then the sticking probability, \( \beta \), is given by the following equation:

\[
\beta = 1 - \frac{\Theta_r}{\Theta_i}
\]  

(9)
The lower the $\beta$ is, the higher the chance that the molecules can bounce back a few times before they stick and decomposes into solid product, i.e., film. CVD in the kinetics limited regime can take advantage of lower $\beta$ which will enable more gas phase diffusion and even distribution of reactive species over a 3D surface.

\[ \text{Deposition rate [arb. unit]} \]
\[ 1/\text{Temperature [K$^{-1}$]} \]

\begin{itemize}
  \item Thermodynamics limited
  \item Gas transport limited
  \item Kinetics limited
\end{itemize}

\textit{Fig. 7: Schematic illustration of the various CVD reaction regimes. Adapted after: Ref. 45.}

\section*{3.2. Deposition in high aspect-ratio features}

Modern semiconductor device architecture requires deposition of materials inside high aspect-ratio structures.\textsuperscript{46,47} Sometimes it demands even filling of the entire vias or trench structure.\textsuperscript{48,49,50} Since CVD is an economically feasible industrial scale process, the solution lies on surface-reaction controlled CVD process recipes. It has been reported that CVD conformality can be improved by using different strategies.\textsuperscript{51} One effective strategy is to use precursors with low sticking coefficient\textsuperscript{52} or reaction coefficient. This will enhance the diffusive transport of precursor molecules in a high aspect ratio feature resulting in an increase in the deposition rate at the bottom surfaces, consequently, an increase in the step coverage. Another method is to add a surface inhibitor which can passivate the surface sites and bring down the deposition rate.\textsuperscript{53,54,55} The passivated surface-sites will cause the precursor to bounce back from the surface to the gas phase instead of binding to the surface and subsequently deposit one or several atoms. If this happens in a trench or a hole, the precursor can diffuse further down in
the feature and instead deposit film further down. This will result in an increased diffusion of precursor molecules and more evenly distributed film deposition.

Another approach is partial pressure tuning of precursor molecules where more than one precursor is used.\textsuperscript{56} In this method, we lower down the partial pressure for lighter co-reactant and supply excess amount of heavier co-reactant. This will result in a deficiency in the partial pressure for lighter co-reactant at the opening of the high aspect ratio feature. It pushes the deposition process to partial pressure limited regime where deposition rate is controlled by one of the precursors partial pressures. An increased reaction rate at the bottom surface results in deposition in a super-conformal fashion. However, this approach can affect the compositional homogeneity of the film over the high aspect ratio depth as the reactants flux ratio varies.

All the above-described methods manipulate the reaction kinetics thus the diffusive transport of reactants in a high aspect ratio structure to enhance the step coverage. An alternative strategy to obtain a conformal film deposition is to operate the CVD process in deposition rate saturated regime by maintaining a high partial pressure for the precursor gas.\textsuperscript{57} Since the deposition rate is independent of precursor partial pressure, the process exhibits a deposition rate saturation. However, this approach requires an excess amount of precursor gas to break the partial pressure dependency of deposition rate which will results in inefficient precursor utilization.

The approach of pulsed CVD can also deposit films in high aspect ratio features with improved step coverage.\textsuperscript{58,59} Although it does not self-limit the growth likewise in the case of ALD deposition, it enhances the transport of reactants through the narrow openings of the high aspect ratio features results in an increased step coverage.

3.3. CVD of boron carbide thin films

Since boron carbide prevails over other materials as a choice for neutron converters, conformal deposition of boron-rich boron carbide thin films has a great demand. The prime objective of this research project is to develop a conformal CVD process that can deposit boron-rich boron carbide thin films in micro features made in a Si-chip. CVD of boron carbide thin films has been reported. Triethylboron (TEB) and trimethylboron (TMB) are the most studied CVD precursors. Both were validated as single source precursor to deposit boron carbide thin films.\textsuperscript{54,60,61,62} The thermal decomposition of these metal organic molecules leaves boron and carbon atoms on the substrate surface. The film properties can be tuned by varying the process parameters. M. Imam et al. report that elemental composition of B-C film deposited from TMB varies with ambient gas and deposition temperature.\textsuperscript{62}
Although processes for boron carbide deposition on flat substrates have been studied, conformal deposition of boron carbide thin films are less explored. L. Souqui et al. report conformal deposition of boron carbide thin films from trimethylboron as a single-source precursor and atomic hydrogen or dihydrogen as surface inhibitor at or above 700 °C. This process resulted in 0.5 boron to carbon ratio in the film. Nevertheless, this process-temperature was higher than the thermal budget for the solid-state detector fabrication. In addition, even higher boron concentration is always favored. The alternate path was to study CVD of boron carbide from TEB. Since the ligand group attached to the boron atom in a TEB molecule is larger than the same in TMB, it must show a different decomposition pathway. Furthermore, the boron to carbon ratio in the film shall be different.

The thermal decomposition of TEB molecule follows two major pathways, i.e., β-hydride elimination and hydrogen-assisted ethane elimination. While the former gives ethylene (C\(_2\)H\(_4\)) as the reaction byproduct the later gives ethane (C\(_2\)H\(_6\)) gas. C\(_2\)H\(_6\) will likely decompose to two methyl radicals (CH\(_3\)) which would, in hydrogen ambient, further form CH\(_4\). CH\(_4\) is rather nonreactive\(^{61}\) at lower CVD temperatures while the C\(_2\)H\(_4\) molecules, produced in β-hydride elimination, are rather reactive species which can add C into the film.

### β-hydride elimination pathway\(^{61}\)

\[
\begin{align*}
B(C_2H_5)_3 & \rightarrow B(C_2H_5)_2H + C_2H_4 & (9) \\
B(C_2H_5)_2H & \rightarrow B(C_2H_5)H_2 + C_2H_4 & (10) \\
B(C_2H_5)H_2 & \rightarrow BH_3 + C_2H_4 & (11)
\end{align*}
\]

### Hydrogen-assisted ethane elimination pathway\(^{61}\)

\[
\begin{align*}
B(C_2H_5)_3 + H_2 & \rightarrow B(C_2H_5)_2H + C_2H_6 & (12) \\
B(C_2H_5)_2H + H_2 & \rightarrow B(C_2H_5)H_2 + C_2H_6 & (13) \\
B(C_2H_5)H_2 + H_2 & \rightarrow BH_3 + C_2H_6 & (14)
\end{align*}
\]

It has been reported that carbon composition in the boron carbide films deposited from TEB varies with the deposition conditions. Also, previous studies show that TEB can thermally decompose at lower temperatures compared to TMB. M. Imam et al. report that at 50 mbar pressure in H\(_2\) ambient TEB molecule decomposes at above 400 °C.\(^{62}\) It was of interest for us to further study this process to synthesis a boron-rich boron carbide thin film from TEB.
4. Characterization techniques

The boron carbide thin films were characterized using various characterization techniques. The film conformality in high aspect ratio substrates were the most demanding. This was measured using cross sectional Scanning Electron Microscopy (SEM). Since boron and carbon were the elements in the film and hydrogen and oxygen were the major impurities, it was important to use a technique that can separate these elements and quantify the composition with good accuracy. Time-of-Flight Elastic Recoil Detection Analysis (ToF ERDA) was chosen for quantifying the elemental composition in the films since boron and carbon, which come next to each other in the periodic table, can be well separated using this technique. X-ray photoelectron spectroscopy and X-ray reflectivity techniques were also used to study the chemical environment and the film density, respectively.

4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) is a very powerful characterization technique. It can offer a magnification level up to 20,000 – 130,000 times depending on the resolving power of the instrument and resolve topographical features with enormous detailing. In this technique, samples are scanned using a focused electron beam under a high vacuum environment. The interaction between atoms in the sample surface and the electron beam gives information of the sample. It is mainly used to study the surface morphology of the sample. However, it can also be used to study elemental compositions, grain texture and cathodoluminescence of the sample material.

A SEM apparatus (Fig. 8) typically consists of electron gun, electron condenser lens, focusing lens, scan coils, objective lens, sample stage and detectors. High energy electrons are used to scan the specimen. Depending on electron energy and electron optics used, SEM can offer various resolutions. The interaction of electrons with the surface atoms in the specimen generates diverse signals such as secondary electrons, back scattered electrons, X-rays and cathodoluminescence. The detection of these signals reveals information such as topography and elemental composition.
Fig. 8: Schematic illustration of a scanning electron microscope apparatus together with probing volume with various signal types. It shows a maximum probing volume with cathodoluminescence and a minimum with Auger electrons.

To produce micrographs of a sample morphology, secondary electron imaging is a commonly used technique. It is done by detecting the secondary electrons emitted from the surface atoms of the sample. Scattered electrons can also be detected for imaging. Since back scattered electrons are elastically scattered form the heavy elements, it can carry information about the compositional contrast. The characteristic X-rays emitted from the sample is used to perform energy dispersive spectroscopy (EDS). In this study, secondary electrons, which provide the highest resolution and surface sensitivity, were used for imaging. The thin films deposited on patterned Si substrates were broken to micrograph the cross section (Fig. 9). The thickness of the films was estimated from the SEM micrographs. EDS mapping was used to trace the boron and carbon distributions qualitatively.

Fig. 9: Cross section SEM micrographs of a B,C deposited Si microstructure.
4.2. **Time-of-flight elastic recoil detection analysis**

Time-of-flight ERDA is a widely used technique for elemental analysis with the capacity to quantify even the lightest element H.\(^\text{64,65}\) It is a nondestructive technique for estimating elemental concentrations in a sample. Although it cannot see chemical information of the specimen, it has a great accuracy in quantifying elements, especially if there are lighter elements in the sample. The interesting feature of ToF-ERDA is that it can even separate isotopes and quantify the concentration. Compared to most of the other analytical techniques, it is not limited to the sample surface. It is capable of probing from different depths. That means this technique can measure the elemental composition as a function of film depth.

The typical ToF-ERDA measurement setup consists of an ion beam, a vacuum chamber, collimator, and time-of-flight detector. Basically, we irradiate the sample with a known ion beam with appropriate energy level, see Fig. 10. The projectile ions are typically heavier than the elements in the sample. It knocks out recoil atoms from the sample by elastic collisions with a kinematic factor depending on the mass of the element and the probing depth. From the recoil energy based on the kinematic factor the elements of the sample can be identified. The recoil trajectory can be extracted from histograms, representing recoiled energy loss, and converted into depth profile.\(^\text{66}\) The mass separation depends on the energy and mass of the projectile ion used. The transferred kinetic energy of the recoil atom \(E_r\) can be expressed as:

\[
E_r = \left( \frac{4M_iM_r \cos^2 \Theta}{(M_i + M_r)^2} \right) E_i
\]

(15)

Where \(M_i\) and \(M_r\) are the mass of the primary ion and the recoiled species, respectively. The \(E_i\) is the initial kinetic energy of the primary ion and \(\Theta\) is the recoil angle.
4.3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive spectroscopic technique used for studying the chemical environment in the sample. The apparatus (Fig. 11) typically consists of X-ray source, sample stage, electron optics, hemispherical analyzer, and detectors.
XPS technique works with the principle of photoelectric effect. The core level electrons in an atom can be ejected by exciting them with photons of suitable energy level. The transferred energy to the electron is partially utilized to overcome the electron binding energy and the rest of the energy is utilized as kinetic energy. Upon arrival at the detector, one part of the energy is converted as the work function of the detector medium. XPS can detect almost all the elements except H and He. These two elements are not detectable due to its low photoelectron cross section and the incompatibility of their core electrons for XPS detection. Let $h\nu$ be the X-ray energy, $\delta$ be the work function and $E_{KE}$ be the measured kinetic energy. Then binding energy ($E_{BE}$) is given by:

$$E_{BE} = h\nu - (E_{KE} + \delta)$$

(16)

By measuring the kinetic energy and number of electrons that escape from the surface of a material, XPS core level spectra can be produced. By analysing this spectrum, information such as elemental composition, chemical state and electronic state of the elements that exist in the sample material can be obtained. While peak position, binding energy of the core electron, tell us about the element and the chemical state of the atom, peak intensity reflects the amount of the element present on the sample surface. The chemical shift in the core level spectra depends on the electrostatic potential experienced by the core electron. Typically, the more electronegative the ligands are, the higher the binding energy of the core electron will be, resulting in a positive shift. A data fitting software can be used to deconvolute the background and obtain the information about the peak position and intensity. Fig. 12 shows the fitting obtained for the B 1s and C 1s core level spectra of the boron carbide film using CasaXPS software. It can be observed from the figure that bonding with C causes positive shift in the B 1s and bonding with B causes negative shift in the C 1s spectra.

![Fig. 12: XPS B 1s and C 1s core level spectra obtained for the boron carbide film.](image-url)
4.4. X-ray reflectivity

X-ray reflectivity (XRR) is a characterization technique used to study the structure and properties of surfaces and interfaces which are typically in thin film form. In this technique a flat surface is irradiated by a beam of X-ray with a very small incident angle and measure how much of the X-ray is reflected, as schematically illustrated in Fig. 13. The amount of reflection varies with electron density of the material also changes across different layers and with different depths. When an X-ray beam hits a surface with an angle smaller than the critical angle, all the X-rays are reflected which is called the total external reflection. This is determined by the ratio of refractive indices of the materials and the ambient. Typically, X-ray reflectivity measurements are done by varying the incident angle ranges from below the critical angle of the material to a few degrees above the critical angle.

Fig 13: Schematic illustration of the X-ray reflections at thin film interfaces.

Slightly above the critical angle, the X-ray beam is partially transmitted and partially reflected at the interface between two different materials with various electron densities. This transmitted X-ray can transmit and reflect again at subsequent interfaces causing multiple beams that interfere with each other. The interference can be constructive or destructive depending on the phase difference between these beams results in oscillation. By measuring the oscillating reflected X-ray intensity as a function of incidents angle, the characteristics of the thin films or the structural information can be estimated, see Fig. 14. While the critical angle and the amplitude of the oscillation mainly gives information on density contrast and the period of the oscillation mainly depends on the thickness of the films, these effects are inter-related and therefore require simulations to yield accurate results. In this work XRR technique was used mainly to study density evolution of the boron carbide films in response to variations in the deposition conditions. The reflectivity curves were fitted for thin film density using PaNalytical X’pert software.
Fig 14: X-ray reflectivity curves obtained for the boron carbide thin films of various thicknesses deposited on polished Si substrates.
5. Summary and contribution to the field

The demand for boron carbide materials and deposition processes for conformal and uniform thin films of boron carbide are well pronounced. In our research studies, we addressed some of the associated challenges. We chose a CVD process route for synthesizing boron carbide films and investigated different strategies for improving film conformality and uniformity. Since boron carbide materials are a good choice as neutron converter layer in solid-state neutron detectors, one of the motivations was to develop a process that can afford conformal film deposition on high aspect ratio detector-chips. We further expanded our studies and investigated strategies to improve film characteristics and extend potential applications of the deposition process and the boron carbide films.

5.1. Low reaction rate deposition

In order to achieve a good conformality, two different strategies were evaluated. The first method was to operate the CVD process in a kinetically limited regime. It was explored by depositing at various substrate temperatures ranging from 425 to 550 °C in steps of 25 °C, using TEB as single source precursor. The film thickness at the bottom and the top of a micro trench structure in Si substrates as a function of substrate temperature was studied. It shows that at 450 °C and below the process can afford highly conformal film deposition with a step coverage of 1 in 1:8 aspect ratio micro-structures. Above 450 °C film thickness at the top and the bottom surfaces become two independent functions of temperature, as shown in Fig. 15. Also, the films deposited ≤ 450 °C exhibit a boron-rich elemental composition, i.e., about B₅₋₇C.

Since the mass transport of TEB molecules through the narrow trench structure mainly is by diffusion, a lower deposition rate allows molecules to bounce back and diffuse down to the bottom surfaces. This will reduce the partial pressure gradient of the precursor gas over the trench depth and results in improved step coverage. Whereas, at higher temperatures the probability of molecules decomposing at the surface site where they hit for the first time is higher. Consequently, the deposition rate at the bottom surface goes down and shows no proportional increase with that of the top surface for various temperatures.

A high conformality achieved by operating CVD in kinetics limited regime often compromises film density as shown in figure 16. Also, in the boron carbide CVD, the film density shows an inverse proportionality with the step coverage. The chemical environment does not change much though. A new strategy that can push this limitation and improve film
conformality at higher deposition temperature would be useful to restore the density without losing conformality. The concept of adding a diffusion additive can overcome this limitation and enable even higher step coverage at higher deposition temperature.

Fig. 15: film thickness at the top and bottom of an 8:1 aspect ratio Si chip as a function of deposition temperature. It can be noted from the figure that step coverage decreases with an increase in the deposition temperature.

Fig. 16: X-ray reflectivity curves fitted for film density for the samples deposited on polished flat Si substrates at various temperatures ranging from 425 to 550 °C. It can be observed from the figure that the film density increases with an increase in the deposition temperature.
5.2. Deposition on prototype detector-chips

As schematically illustrated in Fig. 17, the detector sensor requires three different layers of coatings on a semiconductor chip namely, passivation layer, neutron converter layer and metal contact layer. The passivation layer is typically deposited using Al₂O₃ by atomic layer deposition. Physical vapor deposited aluminum is typically used as metal contacts. The critical layer is the neutron converter layer. In this work we validate nat.B₃C films deposited by CVD as converter material.

![Fig. 17: Schematic illustration shows exploded view of the solid-state neutron detector together with the photograph of prototype Si chip with patterned side facing up.](image)

The fundamental challenge with a 3D solid state detector architecture is to deposit the converter material in high aspect ratio features of a pixelated sensor-chip with a good conformality. In addition, a low temperature process is required since the detector requires ohmic contacts which need to be established before the converter layer deposition. Thus, the CVD process developed in this work and described above is suitable for depositing the neutron converter layer on the chips. The cross-section SEM micrographs presented in Fig. 18 show conformal film of boron carbide on sensor chip substrates deposited by the as developed CVD process.
Fig. 18: SEM micrographs showing conformal film deposition in high aspect ratio Si sensor-chip substrate; a) Top view, b) opening of the high aspect ratio feature, c) coating inside the microstructure, d), e) and f) magnified cross sectional view, and g), f) and i) metal contacts on the rear side after deposition.

The elemental composition obtained by time-of-flight ERDA measurement shows a stochiometry of about B$_3$C which is good for neutron detector application. In addition, the films were characterized using XRR. Thinner films on polished flat Si substrates were prepared for the measurement. The reflectivity curves fitted for film density shows a density of about 2 g/cm$^3$, see Fig. 19. It can be noted from Fig. 18 c) that the material is dense enough to retain the shape.
Fig. 19: XRR curve obtained for the sample deposited at 450 °C on polished flat Si substrate fitted for film density shows a density of 2 g/cm³. In the top right corner, the depth profile of elemental concentration is presented.

Since the CVD process is highly conformal meaning that it deposits wherever gas diffuses into, the metal contacts were masked before the boron carbide deposition. A slurry of graphite and ethanol was applied and waited to get it dried to form the mask. The mask was inhouse developed at Linköping university. The SEM studies show that the masking was effective, see Fig. 18 g), h) and i). The Al contacts were protected from boron carbide deposition. The graphite mask withstood the CVD process condition and did not cause any damage to the chip.

The cross-sectional scanning electron microscopy study shows that the process can afford a highly conformal film deposition. Also, plan view measurements carried out on the metal contact side show no damage after the deposition process. These results show that the conformal CVD process is one of the ways forward to fabricate solid-state neutron detectors.

5.3. Concept of diffusion additive

As noted in Fig. 15 and 16, the kinetically limited growth regime is a compromise between achieving film conformality at a relatively low temperature and obtaining high density at higher temperature. We propose the concept of using a diffusion additive that can overcome this limitation and enable even higher step coverage at higher deposition temperature. The principle is based on competitive co-diffusion as described in the following.

If we assume a local thermodynamic equilibrium at and around the substrate surface, the particles in the near surface should have the same kinetic energy. This means that the heavier
particles exhibit lower velocities, and the lighter particles exhibit higher velocities. For a binary mixture of two gases, A and B, this can be expressed as:

\[
\frac{1}{2}M_AV_A^2 = \frac{1}{2}M_BV_B^2
\]  

(17)

Where \(V_A\) and \(V_B\) are the average molecular velocity of gas A and B, respectively and \(M_A\) and \(M_B\) are the molecular mass of gas A and gas B, respectively. Eq. (1) can be rearranged and written as follows.

\[
\frac{\text{Diffusion rate of gas A}}{\text{Diffusion rate of gas B}} = \sqrt{\frac{\text{Molecular mass of gas B}}{\text{Molecular mass of gas A}}}
\]

(18)

We hypothesize that this phenomenon can be used to improve film conformality in CVD. If we add a heavy inert molecule together with a lighter precursor molecule and allow them to co-diffuse through narrow trenches or vias structures, it exhibits a competitive diffusion behavior (Fig. 20). It means that the lighter precursor molecules diffuse faster than the heavier molecules added to enhance the diffusion. By maintaining a high enough partial pressure for the diffusion additive, the precursor gas concentration can be diluted at the top surfaces of a high aspect ratio feature. Taking the flux conversion into solid film into account, there will be a continuous mass transport towards the substrate surface from the higher flow stream during deposition process.

**Fig. 20: Mass transport in high AR feature with and without a diffusion additive.**
The gas of choice as a diffusion additive must not participate in chemical reactions in an undesirable manner and it should be heavier than the precursor molecule. Since Xe is inert and heavier than TEB, we have investigated the possibility of using Xe as a diffusion additive in the single source CVD process of boron carbide. The film step coverage in 1:10 AR microstructure at 550 °C deposition temperature was improved from 0.71 to 0.97 when the Xe coflow was added. The elemental composition obtained by time-of-flight elastic recoil detection analysis shows 82.14 at. % B, 17.30 at. % C, 0.50 at. % O and 0.16 at. % H giving a stoichiometry of about B₄.7C. We note that the film density remains unchanged, as seen from densities of 2.23 and 2.26 g/cm³ for the films without and with Xe addition, respectively. We performed control experiments by replacing Xe with its lighter counterpart Ar, to test if it was the mass of the additive or the inertness of the additive that caused this effect. Since Ar is lighter than TEB molecule, a similar co-diffusion profile is not expected. Our experimental results agreed with these attributes.
6. Outlook

We foresee that the conformal CVD process of boron carbide thin films solves many research challenges. Apart from neutron converter layer, one of the potential areas where it can be applied is the capping of carbon nanotubes in CNT membranes which enables better performance and durability in harsh environments. Carbon nanotube membranes are used for various applications such as radiation filter in X-ray detectors in space\textsuperscript{70} and extreme ultraviolet lithography pellicles\textsuperscript{71,72}.

6.1. Capping of carbon nanotubes in a CNT membrane

The conformal boron carbide CVD process was tested on carbon nanotube membranes. It has been reported that the durability of carbon nanotube membrane can be improved by depositing them with a very thin layer of suitable material. Although carbides are one of the suggested material types\textsuperscript{73,71} depositing a boron carbide caping layer evenly around each individual nanotube is challenging. We report a deposition of boron carbide thin films evenly around carbon nanotubes in a membrane structure with very precise thickness control. The SEM micrographs in Fig. 21 show that the deposition is highly conformal, continuous, and uniform. There is no clogging of boron carbide material at the intersections.

![SEM micrographs of the carbon nanotube membrane before and after B$_4$C deposition. It shows that the film deposition is highly conformal, continuous and the nanotube intersections are sharp.](image)

Further characterization of the membranes using Raman spectroscopy (Fig. 22) show similar D-band to G-band intensity ratio before and after the deposition\textsuperscript{74,75} It is evident from the Raman spectroscopy measurements that the CVD process does not cause defects in the carbon nanotubes. These initial results are very promising and motivating to explore further.
Fig 22: Raman spectroscopy measurements of bare and $B_{4.7}C$ deposited carbon nanotube membranes. It shows a similar peak position for G, D and 2D bands. The similar D-band to G-band intensity ratio before and after the $B_{4.7}C$ deposition indicates that the CVD process did not cause any structural defects in the nanotubes.

6.2. **Diffusion enhanced deposition**

The concept of a diffusion additive can be further explored by depositing on more challenging substrates, for example mesostructured particles. Mesoporous substrates are used for various applications ranging from catalysis\(^76\) to drug delivery\(^77\). J. Yim et al. report ALD of ZnO on mesoporous Zirconia as an example for a catalytic application.\(^78\) The boron carbide CVD process that we developed can deposit not only conformal but also homogeneous films in high aspect ratio structures. Therefore, it would be interesting to test if it can afford a conformal deposition on porous materials. Deposition on mesoporous substrates would be one of the potential areas where diffusion enhanced deposition process can find applications.

The concept of adding a diffusion additive to enhance the conformality by regulating the diffusive transport inside a high aspect ratio structure can also be tested in ALD processes, especially, in the processes which are operated in the diffusion-limited-regimes\(^79\). The diffusion of ALD precursors and the penetration depth in high AR structures are often studied using lateral high aspect ratio pillar-hall structures.\(^80\) We foresee that it would be interesting to look at these studies with the additional approach of diffusion additive. ALD on pillar-hall substrates with a diffusion enhancement agent can be experimented.
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Papers

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In this study, triethylboron (TEB) was used as single source CVD precursor to deposit boron carbide thin films. The initial experiments focused on low reaction rate deposition by depositing in a kinetically limited regime. The films deposited at \( \leq 450 \) °C in an aspect ratio micro-trench structures were highly conformal and show a stoichiometry of about \( \text{B}_5\text{C}_2 \). The depositions carried out on the prototype detector chips for neutron detector application show promising results.

We expand our studies to investigate a new strategy with the prospect of improving the step coverage at higher temperatures for better film properties. We hypothesize that adding a suitable heavier molecule, diffusion additive, with an appropriate partial pressure can enhance the step coverage by pushing the lighter precursor molecule via competitive co-diffusion. It was tested by adding Xe gas to the boron carbide CVD from TEB. The result shows that with this diffusion additive the step coverage was improved.

The CVD process is further validated by depositing onto carbon nanotube membranes. The initial results show that the process was able to afford evenly deposition around the individual nanotubes in the carbon nanotube membrane. Raman spectroscopy measurements show a similar D-band to G-band intensity ratio before and after the deposition.