Thermal chemical vapor deposition of epitaxial rhombohedral boron nitride from trimethylboron and ammonia

Laurent Souqui, Henrik Pedersen and Hans Högberg

The self-archived postprint version of this journal article is available at Linköping University Institutional Repository (DiVA):

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-155543>

N.B.: When citing this work, cite the original publication.

Souqui, L., Pedersen, H., Högberg, H., (2019), Thermal chemical vapor deposition of epitaxial rhombohedral boron nitride from trimethylboron and ammonia, *Journal of Vacuum Science & Technology. A. Vacuum, Surfaces, and Films*, 37(2), 020603. <https://doi.org/10.1116/1.5085192>

Original publication available at:

<https://doi.org/10.1116/1.5085192>

Copyright: AIP Publishing

<http://www.aip.org/>

Thermal chemical vapor deposition of epitaxial rhombohedral boron nitride from trimethylboron and ammonia

Running title: CVD of epitaxial r-BN from $B(CH_3)_3$ and NH_3

Running Authors: Souqui et al.

Laurent Souqui^{a)}, Henrik Pedersen, Hans Högberg

Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83, Linköping, Sweden.

^{a)} Electronic mail: laurent.souqui@liu.se

Epitaxial rhombohedral boron nitride films were deposited on $\alpha-Al_2O_3(001)$ substrates by chemical vapor deposition, using trimethylboron, ammonia, and with a low concentration of silane in the growth flux. The depositions were performed at temperatures from 1200 to 1485 °C, pressures from 30 to 90 mbar and N/B ratios from 321 to 1286. The most favorable conditions for epitaxy were: a temperature of 1400 °C, N/B around 964, and pressures below 40 mbar. Analysis by thin film X-ray diffraction showed that most deposited films were polytype-pure epitaxial r-BN with an out-of-plane epitaxial relationship of $r-BN[001] \parallel w-AlN[001] \parallel \alpha-Al_2O_3[001]$ and with two in-plane relationships of $r-BN[110] \parallel w-AlN[110] \parallel \alpha-Al_2O_3[100]$ and $r-BN[110] \parallel w-AlN[110] \parallel \alpha-Al_2O_3[\bar{1}00]$ due to twinning.

I. INTRODUCTION

The trialkylboron triethylboron (TEB, $\text{B}(\text{C}_2\text{H}_5)_3$) is commonly used as boron precursor in chemical vapor deposition (CVD) of boron-based thin films as it is less corrosive than the halides BF_3 and BCl_3 , and less poisonous than diborane (B_2H_6). In a seminal study, Lewis *et al.*¹ compared the trialkylborons TEB, trimethylboron (TMB, $\text{B}(\text{CH}_3)_3$) and tributylboron (TBB, $\text{B}(\text{C}_4\text{H}_9)_3$) and suggested that TEB was the most suitable for depositing boron carbon films, judged mainly by the high B/C ratio obtained. A recent study on the thermal gas phase chemistry of TEB in CVD² confirmed that the molecule is an efficient boron source at temperatures below 1000 °C. TEB has been employed for CVD of boron carbides^{2,3}, phosphides and arsenides⁴ and, of particular interest for this study, boron nitrides.^{5–13} TEB decomposes primarily by β -hydride elimination, offering a low-temperature synthesis route for boron-rich films^{1,2}. On the contrary, a drawback is that the ethyl ligands are suggested to form C_2H_4 upon β -hydride elimination², which will be reactive as CVD precursors at the high temperatures needed for the growth of boron nitride (around 1500 °C)^{5,9} and can therefore lead to carbon impurities in the BN films. From this perspective, TMB with only three carbon per boron is seemingly a promising alternative to TEB. In addition, TMB was recently shown to be an efficient boron precursor for high temperature deposition and suggested to form less reactive CH_4 in an α -elimination decomposition.¹⁴ However, fundamental studies on CVD of boron-based compounds using TMB are scarce. Manasevit *et al.* successfully deposited boron monophosphide and boron subarsenide from TMB⁴. For boron-nitride-based neutron detectors, Maity *et al.* deposited films from ^{10}B -enriched TMB and ammonia in a nitrogen ambient,¹⁵

but did not report on any characteristics of the process. Here, we present a fundamental CVD study for deposition of epitaxial rhombohedral boron nitride (r-BN) using TMB and ammonia in hydrogen ambient at temperatures ranging from 1200-1485 °C, pressures from 30 to 90 mbar, N/B ratios ranging from 321 and 1286. We have added minute amounts of silane, as discussed in our previous study, a small partial pressure of silicon during CVD of sp^2 -BN from TEB was shown to improve the crystalline quality.¹⁶

II. EXPERIMENTAL DETAILS

BN films were deposited on α -Al₂O₃(001) for 120 min at temperatures of 1200, 1300, 1400, and 1485 °C in a hot-wall CVD reactor kept at a base pressure below 10^{-7} mbar. The substrates were cut in 10x10 mm² pieces and were cleaned according to the following procedure: 3 min in an ultrasonic bath in acetone at 80 °C, 3 min in an ultrasonic bath in ethanol at 80 °C, followed by standard clean 1 (SC1, NH₃:H₂O₂:H₂O with relative concentrations 1:1:26 at 80 °C)¹⁶ and standard clean 2 (SC2, HCl:H₂O₂:H₂O with relative concentrations 1:1:22 at 80 °C)¹⁷. The substrates were placed in the center of a tantalum-carbide-coated elliptical susceptor. Prior to BN deposition, the α -Al₂O₃ substrates were heated to 1100 °C during 5 min in palladium membrane purified hydrogen gas (H₂), after which ammonia (NH₃, 99.999 %, further purified with respect to water by a getter filter) was introduced and the temperature ramped up to the selected growth temperature for 10 min to form an in-situ aluminum nitride buffer layer as previously reported in ^{8,9,12}. H₂ was used as carrier gas for the boron precursor TMB (99.99 % purity, Voltaix/Air Liquide Advance Materials, FL) as well as the nitrogen source NH₃. TMB was flowed in a separate quartz liner to avoid the formation of the H₃N:B(CH₃)₃ adduct¹⁸. The N/B

ratio was varied between 321 and 1286. From previous works¹⁶, silane (SiH_4 , 99.999 % purity, 2000 ppm diluted in 99.9996 % H_2) was inserted 2 min prior to growth. The process pressure was in the range of 30 to 90 mbar and regulated by a throttle valve. The growth temperature was monitored by a pyrometer (Heitronics KT81R, calibrated by silicon melting).

The deposited films were characterized by thin film X-ray scattering, electron microscopy and ion beam analysis. All diffractograms and reflectograms were PANalytical X'Pert PRO, using a Bragg-Brentano HD mirror with $1/2^\circ$ divergence and anti-scatter slits as primary optics and an X'Celerator detector with a 0.5 mm anti-scatter slit, 0.04 rad Soller slits and nickel $\text{K}\beta$ filter as secondary optics. In plane measurements, as azimuthal scans (ϕ -scans) and Glancing-Incidence Diffraction (GID) were acquired with a Phillips X'Pert MPD, using cross-slits ($2 \times 2 \text{ mm}^2$) with nickel $\text{K}\beta$ filter as primary optics and a proportional detector (PW1711/96) equipped with a parallel plate collimator. The thickness of the film was estimated from scanning electron microscopy (SEM) using an accelerating voltage of 5 kV and an in-lens secondary electron detector. The analysis of the composition was performed by time-of-flight energy elastic recoil detection analysis (ToF-E ERDA). The measurements were carried out with a 36 MeV 127 iodine ion beam. The incident angle of primary ions and exit angle of recoils were both 67.5° to the sample surface normal giving a recoil angle of 45° . The measured ToF-E ERDA spectra were converted into relative atomic concentration profiles using the Potku code¹⁹.

III. RESULTS AND DISCUSSION

A. *Structural characterization of the BN films*

Figure 1 shows $2\theta/\omega$ diffractograms recorded from sp^2 -BN films deposited at 1200, 1300, 1400, and 1485 °C. At 1400 °C there are clear peaks positioned at 26.5° and 54.5° originated from the diffraction of sp^2 -BN(00 ℓ) and the second order diffraction (002 ℓ), suggesting highly-oriented pyrolytic BN²⁰ or textured h-BN²¹ or r-BN²² on the nitridated α -Al₂O₃(001). We note that the growth temperature of 1400 °C is 100 °C lower than the temperature previously reported for TEB at similar growth conditions⁹. Increasing temperature to 1485 °C or decreasing it to 1300 °C, decreases the intensity of the 00 ℓ peak and the second order diffraction peaks are no longer visible. At 1200 °C, no diffraction peak is visible. As for deposition with TEB⁹, the deposition of high-quality sp^2 -BN films seems to be constrained to a narrow temperature window, albeit at 100 °C lower temperature. In addition, to the high-intensity 006 peak from the sapphire substrate in all investigated films, the 002 diffraction peak of w-AlN was detected from 1200 °C and with 100 and 110 peaks visible for growth at 1485 °C. SEM measurements of cross sections showed that the average film thickness increased from 896 ± 87 nm at 1200 °C to 1308 ± 194 nm at 1485 °C, corresponding to an average growth rate from 7.5 ± 0.7 nm/min to 10.9 ± 1.6 nm/min. This is nearly three times faster than the growth rate of around 3.7 nm/min obtained with the same concentration of TEB at 1500 °C. The films also presented a high roughness as in²³.

Using a combination of glancing incidence diffraction (GID) and ϕ -scans, we concluded that the films deposited on AlN/ α -Al₂O₃(001) were epitaxial already at 1300 °C. The films deposited 1400 °C were most cases polytype-pure rhombohedral BN. The epitaxial relationships were $\text{sp}^2\text{-BN}[001] \parallel \text{w-AlN}[001] \parallel \alpha\text{-Al}_2\text{O}_3[001]$ (Figure 1) out-plane and, $\text{sp}^2\text{-BN}[110] \parallel \text{w-AlN}[110] \parallel \alpha\text{-Al}_2\text{O}_3[100]$ in-plane as shown by the GID diffractogram in Figure 2.(a).

The {110} planes of sp²-BN cannot be used to determine the BN polytype. By rotating the sample by 30°, it is possible to use GID to investigate the presence of the {100} planes of h-BN, as this family of planes is extinct in the case of r-BN.^{22,24} The

result is shown in Figure 2.(b), where only diffraction from the aluminum nitride buffer and the sapphire substrate is detected. This shows that it is possible to obtain polytype-pure r-BN films from TMB. In a few films, diffraction of h-BN inclusions could be detected by GID, as previously reported in²⁵.

The twinning of the r-BN films was also investigated by acquiring azimuthal scans of the {101} of planes of r-BN. These planes have a three-fold symmetry as dictated by rhombohedral crystal system, whereas the ϕ -scan in Figure 3 shows six peaks for r-BN{101}. This originates from the presence of twin crystals that are rotated by 60°. From this result, two in-plane epitaxial relationship can be determined to: r-BN[110] $\parallel$ w-AlN[110] $\parallel$ α -Al₂O₃[100] and r-BN[110] $\parallel$ w-AlN[110] $\parallel$ α -Al₂O₃[$\bar{1}$ 00]. Twinning of r-BN has been reported in previous works for films deposited on sapphire⁹ and SiC¹⁰ and is to be expected due to the 6-fold symmetry of the AlN buffer layer and of the hexagonal polytypes of silicon carbide, respectively.

B. Deposition process

In contrast to r-BN deposited from TEB⁹, epitaxial films were obtained in a wider range of N/B ratios and lower pressures using TMB at 1400 °C.

At fixed pressure, NH₃/TEB ratios below 460 and above 770 were shown to strongly affect r-BN epitaxy⁹, whereas NH₃/TMB between 321 and 1286 resulted in epitaxial r-BN, without having any influence on the crystal quality from 2 θ / ω scans for N/B ratios above 643, as shown in Figure 4 (a) by the full width at half maximum (FWHM) values from θ /2 θ scans of r-BN(003). For comparison, the FWHM of 2 θ / ω diffractograms of α -Al₂O₃(006) was 0.06° and the FWHM of epitaxial r-BN deposited from TEB on nitridated sapphire was reported to be 0.3° in⁹. Figure 4 (b) indicates an optimal N/B ratio of 964. This is higher than the value observed for decomposition of TEB (N/B around 615-640) and can be explained by the fact that at a lower process temperature the activation of the NH₃ molecule is less favorable²⁶. In Figure 4 (c), the crystal quality is shown to increase while decreasing the process pressure as illustrated by the proportional decrease in FWHM of θ /2 θ scans of r-BN(003) from 0.43 to 0.29 with decreasing process pressure from 90 to 30 mbar. Interestingly, Figure 4 (d) shows that at fixed N/B ratios, the pressure does not affect the total amount of coherently diffracting domains along the c-axis, *i.e.* the proportion of crystallites is independent of the total pressure at these experimental conditions.

From our previous studies on CVD of B-C film from TEB² and TMB¹⁴, we note that TEB deposits B-C:H films at 400 °C while TMB deposits films only at 700 °C. This points to slower decomposition kinetics of TMB compared to TEB. In CVD of BN films, we speculate that the slower kinetics of TMB is then better matched to the slow decomposition kinetics of ammonia leading to a more well-matched deposition chemistry for B and N at the growth zone in the reactor, as discussed in the literature²⁷. This allows a reduction of the overall deposition temperature and a wider

N/B range for epitaxial growth. However, the optimal N/B ratio is then also shifted to a higher value.

Regarding the composition of the films, ToF-ERDA gives 44.5 at% B, 46.1 at% N (B:N ratio of 1:1.04), 4.3 at% C, 3.8 at% O and 1.1 at% H in an r-BN film deposited at 1400 °C, 40 mbar, 0.9 sccm TMB and NH₃/TMB ratio of 643. This can be compared to the B:N ratio of 1:0.98; O, H of 0.1 at%, 1 at%, respectively, and C being less than 0.1 at% (below detection threshold) for a film deposited at 1500 °C, 70 mbar, 0.7 sccm TEB and NH₃/TEB = 643.⁸ As for films deposited from TEB, silicon was below the detection limit of the technique (at best 0.1 %).¹⁶ From our previous studies on CVD of B-C films from TEB² and TMB¹⁴, we note that the B-containing species, active for the film growth, are different when TMB and TEB are used. When TMB yields boron species with methyl groups while TEB yields boron species with ethyl groups. This renders different surface chemistry for the removal of carbon from the surface. Ethyl groups can undergo β -elimination while methyl groups must be removed by the more energetically demanding α -elimination or by assistance of another species like hydrogen radicals. This can explain the higher carbon content in the BN films deposited by TMB. Similar trends have been observed for the pairs trimethylaluminum/triethylaluminum and trimethylgallium/triethylgallium for Al_xGa_{1-x}As²⁸, GaAs²⁸, In_xGa_{1-x}As²⁹ and GaN³⁰. We speculate that the oxygen content is due to contamination due to air exposure after deposition.

Similarly as reported for TEB¹⁶, the deposition process using TMB is dependent on the background silicon concentration. In the absence of silane, the intensity of the (003) diffraction peak of r-BN is significantly reduced and the peak broadens as shown in Figure 5.

IV. CONCLUSIONS

We demonstrate a deposition process for epitaxial r-BN on α -Al₂O₃(001) from a reaction between TMB and NH₃ in hydrogen. Epitaxial growth was achieved at 1300 °C and with the best conditions at a deposition temperature of 1400 °C. The epitaxial relationships are: r-BN[001] $\parallel$ w-AlN[001] $\parallel$ α -Al₂O₃[001] out-of-plane and in-plane r-BN[110] $\parallel$ w-AlN[110] $\parallel$ α -Al₂O₃[100] and r-BN[110] $\parallel$ w-AlN[110] $\parallel$ α -Al₂O₃[$\bar{1}$ 00] due to twinning. At 1400 °C, the deposition process is shown to have a more favorable process window for epitaxy at investigated N/B ratios and process pressures and where the crystal quality of the films was the highest for a N/B ratio of 964 and a deposition pressure below 40 mbar. ToF-ERDA gives 44.5 at% B, 46.1 at% N, 4.3 at% C, 3.8 at% O and 1.1 at% H, where the C and the O contents in the investigated film are higher compared to a film deposited with TEB under similar conditions.

ACKNOWLEDGMENTS

This work was supported by the Swedish Foundation for Strategic Research (SSF) and contract IS14- 0027. H.P. and H.H. acknowledge financial support from the Swedish Government Strategic Research Area in Materials Science on Advanced Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971). Dr. Carina Höglund is acknowledged for her assistance with the ion beam analysis. The authors are grateful for access to the Tandem Laboratory at Uppsala University.

SUPPLEMENTAL INFORMATION

See supplementary material at [URL will be inserted by AIP Publishing] for Fourier Transform Infrared Spectroscopy (FTIR)

References

- ¹ J.S. Lewis, S. Vaidyaraman, W.J. Lackey, P.K. Agrawal, G.B. Freeman, and E.K. Barefield, *Mater. Lett.* **27**, 327 (1996).
- ² M. Imam, K. Gaul, A. Stegmüller, C. Höglund, J. Jensen, L. Hultman, J. Birch, R. Tonner, and H. Pedersen, *J. Mater. Chem. C* **3**, 10898 (2015).
- ³ H. Pedersen, C. Höglund, J. Birch, J. Jensen, and A. Henry, *Chem. Vapor. Depos.* **18**, 221 (2012).
- ⁴ H.M. Manasevit, W.B. Hewitt, A.J. Nelson, and A.R. Mason, *J. Electrochem. Soc.* **136**, 3070 (1989).
- ⁵ K. Nakamura, *J. Electrochem. Soc.* **133**, 1120 (1986).
- ⁶ Y. Kobayashi, T. Akasaka, and T. Makimoto, *J. Cryst. Growth* **310**, 5048 (2008).

- ⁷ Y. Kobayashi, H. Hibino, T. Nakamura, T. Akasaka, T. Makimoto, and N. Matsumoto, *Jpn. J. Appl. Phys.* **46**, 2554 (2007).
- ⁸ M. Chubarov, H. Pedersen, H. Högberg, V. Darakchieva, J. Jensen, P.O.Å. Persson, and A. Henry, *Phys. Status Solidi - R* **5**, 397 (2011).
- ⁹ M. Chubarov, H. Pedersen, H. Högberg, J. Jensen, and A. Henry, *Cryst. Growth Des.* **12**, 3215 (2012).
- ¹⁰ M. Chubarov, H. Pedersen, H. Högberg, Z. Czigany, and A. Henry, *CrystEngComm* **16**, 5430 (2014).
- ¹¹ N. Coudurier, R. Boichot, F. Mercier, R. Reboud, S. Lay, E. Blanquet, and M. Pons, *Physcs. Proc* **46**, 102 (2013).
- ¹² M. Chubarov, H. Pedersen, H. Högberg, A. Henry, and Z. Czigány, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 061520 (2015).
- ¹³ R. Dahal, J. Li, S. Majety, B.N. Pantha, X.K. Cao, J.Y. Lin, and H.X. Jiang, *Appl. Phys. Lett.* **98**, 1 (2011).
- ¹⁴ M. Imam, L. Souqui, J. Herritsch, A. Stegmüller, C. Höglund, S. Schmidt, R. Hall-Wilton, H. Högberg, J. Birch, R. Tonner, and H. Pedersen, *J. Phys. Chem. C* **121**, 26465–26471 (2017).
- ¹⁵ A. Maity, T.C. Doan, J. Li, J.Y. Lin, and H.X. Jiang, *Appl. Phys. Lett.* **109**, 072101 (2016).
- ¹⁶ M. Chubarov, H. Pedersen, H. Högberg, and A. Henry, *CrystEngComm* **15**, 455 (2013).
- ¹⁷ W. Kern, *J. Electrochem. Soc.* **137**, 1887 (1990).
- ¹⁸ G.S. Ross, D. Enagonio, C.A. Hewitt, and A.R. Glasgow, *J. Res. NBS. A Phys. Ch.* **66A**, 59 (1962).
- ¹⁹ K. Arstila, J. Julin, M.I. Laitinen, J. Aalto, T. Konu, S. Kärkkäinen, S. Rahkonen,

- M. Raunio, J. Itkonen, J. Santanen, T. Tuovinen, and T. Sajavaara, Nucl. Instrum. Meth. B **331**, 34 (2014).
- ²⁰ D. Belforti, B. Bovarnick, and S. Blum, Nature **190**, 901 (1961).
- ²¹ R.S. Pease, Acta Crystallogr. **5**, 356 (1952).
- ²² T. Sato, P. Japan Acad. **61**, 459 (1985).
- ²³ M. Chubarov, H. Pedersen, H. Högberg, S. Filippov, J.A.A. Engelbrecht, J. O'Connel, and A. Henry, Phys. B Condens. Matter **439**, 29 (2014).
- ²⁴ M. Chubarov, H. Högberg, A. Henry, and H. Pedersen, J. Vac. Sci. Technol. A **36**, 030801 (2018).
- ²⁵ M. Chubarov, H. Pedersen, H. Högberg, Z. Czigány, M. Garbrecht, and A. Henry, Chem. Mater. **27**, 1640 (2015).
- ²⁶ K. Rönby, S.C. Buttera, P. Rouf, S. Barry, L. Ojamäe, and H. Pedersen, Preprint DOI: 10.26434/chemrxiv.7067687.v2 (2018).
- ²⁷ P. Stenberg, Ö. Danielsson, E. Erdtman, P. Sukkaew, L. Ojamäe, E. Janzén, and H. Pedersen, J. Mater. Chem. C **5**, 5818 (2017).
- ²⁸ T.F. Kuech, E. Veuhoff, T.S. Kuan, V. Deline, and R. Potemski, J. Cryst. Growth **77**, 257 (1986).
- ²⁹ R.W. Glew, K. Grim-Bogdan, N. Tzafaras, and S. Nakahara, J. Electron. Mater. **29**, 146 (2000).
- ³⁰ Q. An, A. Jaramillo-Botero, W.G. Liu, and W.A. Goddard, J. Phys. Chem. C **119**, 4095 (2015).

FIG. 1. $2\theta/\omega$ diffraction patterns from BN films deposited at (from top to bottom) 1485, 1400, 1300, and 1200 °C for 120 min, using a process pressure of 70 mbar and N/B = 643. The bulk of the carrier flow consisted of 5000 sccm H₂, the TMB flow

was set to 0.7 sccm diluted in 150 sccm H₂ and the Si/B ratio was 0.037. The NH₃ flow applied for nitridation of the α -Al₂O₃(001) substrate was 500 sccm.

FIG. 2. (a) GID diffractogram aligned on r-BN(110) ($\phi = 124.48^\circ$, $\psi = 89.43^\circ$) revealing the epitaxial relationship of a sp²-BN film deposited at 1400 °C and 55 mbar. The bulk of the carrier flow consisted of 6400 sccm H₂, the TMB flow was set to 0.9 sccm diluted in 191 sccm H₂ and the N/B and Si/B ratios were 707 and 0.037, respectively. (b) GID diffractogram of the same film as in Figure 2.(a), but rotated 30° ($\phi = 154.48^\circ$, $\psi = 89.39^\circ$), showing extinction of the (100) planes of sp²-BN.

FIG. 3. XRD ϕ -scans of r-BN{101} ($2\theta = 42.6835^\circ$, $\psi = 77.61^\circ$) and α -Al₂O₃{202} ($2\theta = 46.161^\circ$, $\psi = 72.20^\circ$). Diffraction from crystals oriented -30° with respect to the substrate is indicated by circles, diffraction from crystals oriented +30° is indicated by crosses.

FIG. 4. (a, b) Dependence of the FWHM (a) and of the normalized intensity (b) of 2 θ / ω diffractograms from r-BN(003) for films deposited at 1400 °C, 50 mbar and N/B ratios ranging from 321 to 1286. The carrier gas flow was changed to keep the same residence time inside the hot zone. To discard the effects of the buffer layer, the NH₃ flow during nitridation was adjusted so that the partial pressure of NH₃ was the same for each sample. (c, d) Evolution of the FWHM (c) and of the normalized intensity (d) of 2 θ / ω diffractograms of r-BN(003) for films deposited at 1400 °C, N/B = 643 and pressure from 30 to 90 mbar. The nitridation conditions were the same for each film *i.e.* 636 sccm NH₃ in 6400 sccm H₂ at 40 mbar. The TMB flow was 0.9 sccm and mole fractions were the same as in Figure 1. Lines are guide for the eyes.

FIG. 5. (00 l) diffraction peak of BN films deposited at 1400 °C, N/B = 643 and 50 mbar with minute amounts of SiH₄ (Si/B = 0.037, in red) and without (in black).