Mechanical properties of boron nitride thin films prepared by atomic layer deposition

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SI 1 : Experimental section

Atomic Layer Deposition of Boron nitride

All depositions have been carried out in a horizontal, low pressure hot-wall (home-built) ALD reactor. More details about this reactor can be found elsewhere.[30] Boron tribromide (BBr_3) precursor was purchased from Sigma Aldrich and used as received. The co-reactant was ammonia gas. The precursor and co-reactant lines were heated at 110°C to avoid condensation and the deposition chamber was set at a temperature of 750°C. If not stated otherwise, the typical ALD cycle consisted of 0.1 s pulse of BBr_3, 2 s exposure, and 5 s purge, followed by a 3 s pulse of NH_3, 5 s exposure and 5 s purge with Argon. The p-type (100) silicon wafers substrates were purchased from MEMC Korea Company. To remove the organic contaminants, the substrates were pre-cleaned in acetone, ethanol and de-ionized water for 5 min in ultrasonic bath before the depositions.

Physico-chemical and mechanical characterization

To evaluate the BN film thickness after the ALD depositions, ex-situ spectroscopic ellipsometry (SE) measurements were carried out using a Semilab GES5E visible ellipsometer (1.2–5.0 eV) at an angle of incidence of 70.2°. The empirical Cauchy dispersion formula has been adopted to model the optical properties and the thicknesses. The composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS) on a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Aluminum Kα line of 1486.6 eV energy) and a power applied of 300 W and calibrated using the $3d_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 1.1 eV. Samples were measured after a short etching (5 minutes) with a 3 kV energy Ar^+ beam. In the fittings Gaussian-Lorentzian functions were used (after a Shirley background correction) where the FWHM of all the peaks were constrained while the peak positions and areas were set free. Surfaces were analyzed using

(AFM –ICON Bruker), the analyzed roughness was determined over a 5 μm^2 surface, and the images analysis has been achieved with the WSxM 5.0 software. The microstructure and the density of the films were determined by X-ray diffraction and reflectometry (GiXRD-XRR) using a Panalyitical X'pert 3 system. A JEOL ARM 200F high-resolution transmission electron microscope at 200 kV has been used for the HR-TEM studies. Raman scattering measurements were performed using a Renishaw micro-Raman spectrometer equipped with a confocal microscope (Leica) with the excitation wavelength 488 nm.

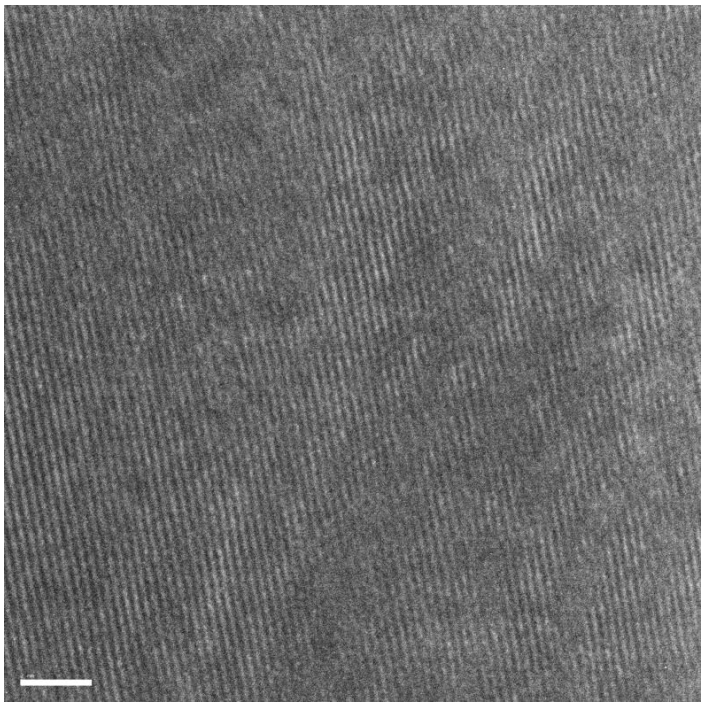
The nanoindentation measurements were performed with a Hysitron TI 950 TriboIndenter using a Berkovich diamond indenter, at a maximum load of 7500 µN. Hardness(*H*) and elastic modulus(*Er*) values were determined from the load−displacement curves by the Oliver−Pharr and Korsunsky methods using the experimentally measured *H*(5,5±0,7 GPa) and Er(90±30 GPa) of as received Si(100). The tests were performed using the CMX (constant strain mode) with an overlapping frequency of 200Hz. The E(indenter) and V(indenter) considered were 1140 GPa and 0.07, respectively, with Poisson's ratio between 0 and 0.5 for the material. The minimum penetration depth was set as 25 nm, in order to ensure the proper reproducibility of the calibrated Berkovich tip; moreover, long periods of drift correction were used in order to and avoid artifacts arising from the measurement.

Table S1: Properties of BN films prepared by ALD using BBr_3 as precursor and NH_3 as co-reactant at 750°C. The substrates were Si(100) wafers and the substrate temperature was 750°C. Growth-per-cycle, C and O contents, mass density, and roughness values of BN films of 25 nm thickness prepared by ALD.

In situ spectroscopic ellipsometry (SE), X-Ray reflectometry (XRR), atomic force microscopy (AFM), X-Ray photoelectron spectroscopy (XPS) and sessile drop technique (SDP) measurements were used for the analysis.

Properties	**Value**	**Analysis technique**
Growth-per-cycle (Å/cycle)	0.8±0.1	SE
Mass density (g/cm^3)	2.2±0.3	XRR
RMS roughness (nm)	3.5±2	AFM
C content (at.%)	4±3	XPS
O content (at.%)	7±3	XPS
Wetting (°)	81±3	SDP

SI 2 : TEM image of an annealed sample



High resolution TEM image of a BN film prepared on carbon fibers using an ALD process at 750°C and an annealing step at 1350°C under nitrogen atmosphere. The lattice fringes of BN are clearly visible. The scale bar corresponds to 2 nm.