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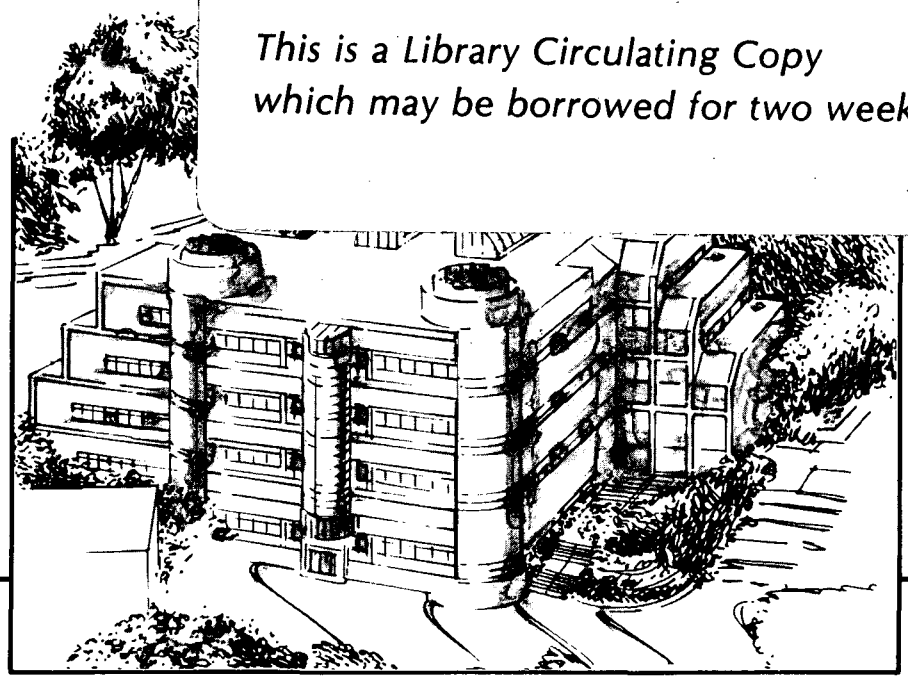

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Polycrystalline hexagonal boron nitride films on SiO_2 for III-V semiconductor applications

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ABSTRACT

Isotropic hexagonal BN (h-BN) films were deposited on SiO_2 crucibles used for synthesis of GaAs. Deposited films were analyzed for composition, morphology, and growth rates using proton resonant scattering, optical absorption, X-ray and electron diffraction, and transmission electron microscopy. The silicon concentration of GaAs synthesized in BN coated crucibles was approximately one order of magnitude higher than that for GaAs synthesized in uncoated crucibles under identical synthesis conditions.

I. INTRODUCTION

Advances in the synthesis of GaAs with low concentrations of electrically active impurities has led to the large scale integration of GaAs devices. The incorporation of silicon during gradient freeze (GF) growth of GaAs remains a significant obstacle to the use of these crystals for device applications despite their advantageously low dislocation densities (~500 cm^{-2}). The purpose of this investigation was to explore the growth and use of boron nitride films as a barrier to the incorporation of silicon in the GaAs melt during synthesis from elemental Ga and As in SiO_2 crucibles. The use of boron nitride films may have application to GF growth and other III-V crystal growth processes such as liquid encapsulated (LEC) growth when a solid pyrolytic boron nitride crucible is normally used.

SiO_2 is typically used as crucible and ampule material for GF GaAs crystal growth. Reduction of SiO_2 by reaction with gallium[1,2] during growth leads to high enough concentrations of silicon donors to preclude the growth of semi-insulating crystals[3] necessary for high-speed device applications. Vapor-phase transport reactions increase the incorporated silicon beyond the contribution from crucible dissolution.[4] To obtain semi-insulating behavior, Ga_2O_3 has been added to the melt[2,5,6] to oxidize free silicon and reduce the donor concentration. Solid pyrolytic boron nitride (PBN)[5,7,8,9] has been used as a crucible material in horizontal and vertical configurations of GF crystal growth to eliminate direct contact of the melt to silica with the intent of reducing the silicon incorporation rate. Silicon incorporation in GaAs, however, has been seen to be enhanced for growth configurations where SiO_2, PBN, gallium vapor, and the GaAs melt can react with each other near the growth temperature.[10] Boron and nitrogen each prefer sp^2 hybridization causing a planar distribution of three bonds about each atom in the (001) basal planes with Van der Waals bonding between these planes. This results in a lower

thermal conductivity in the <001> direction and may complicate the thermal control of the GF crystal growth process if a bulk PBN crucible is used. The use of isotropic BN films on SiO_2 crucibles is expected to reduce the silicon incorporation from the crucible without requiring significant modification of the thermal growth configuration or control parameters from those for uncoated crucibles. Modifications to the crucible environment may be necessary to reduce the vapor transport of silicon to the melt.

Hexagonal BN film growth by chemical vapor deposition (CVD) using BCl_3 and NH_3 below 700 °C and at 1 atm on flat copper substrates has been reported.[11] These films were characterized by X-ray diffraction to yield a single diffraction peak for the (002) reflection. Films grown by an analogous process on flat Al_2O_3 and SiO_2 substrates below 1100 °C were studied[12] by optical absorption for band gap energy determination, and by photoluminescence.

This paper describes the growth of hexagonal BN on SiO_2 crucibles by CVD at 1030 to 1125 °C and 1 atm. pressure using BCl_3 and NH_3 reactant gases. An analysis of the structure and morphology of films grown by this method is presented. The composition and thickness of sample films were characterized by proton resonant scattering (PRS).[13] The band gap energy was determined by optical absorption. The structure and morphology were analyzed by X-ray diffraction, electron diffraction, and transmission electron microscopy (TEM) lattice imaging. BN coated crucibles were used in the synthesis of two GaAs ingots from elemental Ga and As. These ingots were subsequently analyzed by 300 K Hall effect. The net free carrier concentration was compared with the silicon concentration obtained through SIMS analysis of a sample from one of the ingots.

II. EXPERIMENTAL

Fig. 1 illustrates the horizontal hot-wall reactor and gas delivery system used for the CVD growth of h-BN thin films. The furnace was a 65 mm bore diameter and 46 cm long tube furnace with platinum resistance heaters. The furnace ends were insulated with quartz wool and Zircar ZAL-15 alumina ceramic outside the furnace tube. A control thermocouple was placed through the insulation to contact the furnace tube about 5 cm from the furnace exit end. Crucibles used in synthesis were 33 cm long x 50 mm I.D. half-cylinder shaped boats. The lengthwise midpoint of the crucible was positioned to coincide with the reactor maximum temperature (~1125 °C). The crucible ends were ~50 °C cooler. The crucible was inverted (to avoid settling on its surface of BN formed in the vapor) and supported by the BCl_3 and NH_3 reactant gas distribution manifolds. These were made from 4 mm I.D. fused silica tubing sealed at one end, with 2 mm drilled and fire-polished holes spaced at

2.5 cm intervals to direct the gas flow to the inside crucible surface. Fig. 2 shows a crucible and gas distribution manifolds within the 57 mm I.D. fused silica ampule shortly after film growth. All fused silica parts were etched in 5% HF solution and rinsed in deionized water prior to assembly.

The silica crucibles were sandblasted prior to BN film growth. Sandblasting avoids wetting and subsequent sticking of the GaAs to the crucible during crystal growth or synthesis. To avoid contamination from SiC particles the crucibles were rinsed alternately with methanol and deionized water until all visible particulates were eliminated. The crucibles were then placed for 5 min in a methanol ultrasonic bath. This was followed by a 5 min aqua regia etch ($HCl:HNO_3$, 3:1) and rinsing 20 times in deionized H_2O.

The BCl_3 (99.9%) and NH_3 (99.998%) were each diluted with argon prior to their introduction into the reactor. A separate argon line for purging the reactor was connected through the gas manifold at the entrance end of the furnace tube. A flow ratio of $NH_3/BCl_3=2$ was maintained during each growth run. Typical flow rates for crucible coating were 1.2 l/hr BCl_3 diluted with 4.8 l/hr Ar, 2.4 l/hr NH_3 diluted with 3.6 l/hr Ar, and 3.0 l/hr Ar purge.

In addition to the abraded SiO_2 crucibles, a separate run utilized two flat 1x3 cm^2 SiO_2 test plates mounted in a surrogate crucible holder perpendicular to the gas streams. The plates were used as deposition substrates to facilitate subsequent film characterization.

Film characterization by optical absorption measurements for band-gap determination were performed with a Perkin-Elmer Lambda-9 spectrophotometer. For the proton resonant scattering we used a 1.67 MeV proton beam with a 165° backscatter angle. The X-ray diffraction was carried out with a Seeman-Bohlin diffractometer[14] using Cu K_α (λ=1.54 Å) radiation at a 6° incident angle. TEM observations utilized a JEOL-JEM200CX electron microscope operating at 200 kV and equipped with an ultra high resolution pole piece for lattice imaging.

III. RESULTS AND DISCUSSION

BN film 1 was grown on a silica test crucible that had been previously sandblasted on 50% of its width. Gas flow rates were 1.2 l/hr BCl_3 diluted with 4.8 l/hr Ar, 2.4 l/hr NH_3 diluted with 3.6 l/hr Ar, and 6.0 l/hr Ar purge. The film was grown for 15 min.at 1070 to 1120 °C. The resulting film was colorless, transparent and insoluble in water. The presence of optical reflection fringes indicated a film thickness near 1 μm. The film adhered to the silica, but could be scratched off with metal tweezers. A significant quantity

of BN formed in the vapor, settling on the furnace liner surface and in the exit tube. Deposits were seen that had clogged some of the downstream gas manifold openings. All the coatings were continuous over the inside surface of the crucibles.

Film 2 was grown on a flat unabraded silica test plate mounted perpendicular to the gas flow at the downsteam end of a crucible for 1 hr at 1030 ± 5 °C with gas flow rates: 0.36 l/hr BCl_3 diluted with 0.96 l/hr Ar, 0.75 l/hr NH_3 diluted with 0.72 l/hr Ar, and 1.2 l/hr Ar purge. This film also showed optical reflection fringes and was used for the subsequent X-ray and PRS characterization.

Film 3 was obtained from the silica furnace liner surface underneath a crucible with a 16 μm BN coating. The gas flow rates were the same as for film 1 with the exception of a 3.0 l/hr Ar purge. The temperature in the growth region of the furnace was approximately 1100 °C. The film was separated from the liner by etching with 5% HF solution, rinsed with deionized H_2O, picked up on a Cu mesh grid, and ion milled for TEM observation. Film 4 was a ~0.1mm white BN deposit from the same crucible located above the first two upstream gas manifold openings and it was deposited at 1050 ± 5 °C.

Optical absorption measurements revealed a sharp absorption edge for films 1 and 2 beginning at 0.21 μm, corresponding to the 5.8 eV direct bandgap of hexagonal BN.[15,16] Proton resonant scattering on film 2 yielded B and N peaks superimposed on the Si and O peaks of the substrate (see Fig. 3). The BN thickness of film 2 was found to be about 0.9 μm through proton energy loss calculations, confirming the estimated thickness based on the presence of reflection fringes.

An X-ray diffractometer spectrum was recorded for the SiO_2 substrate material of film 2 with and without the BN film. The near-grazing angle of incidence yielded a 9 μm path length through the film. Fig. 4 is the resultant spectrum after subtracting the substrate spectrum. A wide peak corresponding to the (002) reflection of small grain hexagonal boron nitride is present. The apparent interplanar spacing derived from the position of the peak maximum is 3.72 Å. A single broad peak was also observed for the films grown by Motijima et. al.[11] after annealing at 1000 °C for 5 hr. The small grain size causes a broad peak that is shifted from the (002) reflection (3.33 Å interplanar spacing) of crystalline BN. The crystallite size corresponding to the degree of line broadening seen for the (002) peak was calculated to be ~30 Å using a correlation by Scherrer.[17,18] The upper corner of Fig. 5 shows a TEM electron diffraction pattern of film 3. Table 1 is a comparison of the interplanar spacings measured by 1) X-ray diffraction of film 2, 2) X-ray diffraction of film 4, and 3) electron diffraction of film 3. These are compared with the card file values[19] for crystalline hexagonal BN.

A TEM lattice image of film 3 is shown in Fig. 5. The grouping of (002) planes is clearly evident, but the groups twist and interweave which is quite uncharacteristic for a crystalline material. There can be very little order to planes other than (002) in this morphology and this consequently explains the weakness of diffraction lines other than (002). The average thickness of planar groups in the <002> direction is ~30 Å confirming the calculation of grain size due to X-ray line broadening. The morphology is isotropic down to ~100 Å, indicating that the film thermal conductivity is also isotropic.

Film thickness could not be measured on sandblasted crucibles. Based on PRS energy loss data for film 2 and the presence of reflection fringes for films 1 and 2, we estimated the film thickness (a) for growth in the range 1030 to 1120 °C, and in this configuration to be limited by the BCl_3 flow rate as follows:

$$a\ (\mu m) \cong 2.6 \times f \times t$$

where $f =$ BCl_3 flow rate (l/hr)

$t =$ growth time (hr).

This expression is used to calculate the film thickness on abraded silica crucibles used for GaAs synthesis and growth. It is assumed to be valid only within the small range of flow rates used here.

Hall measurements at 300 K on two samples cut from a GaAs ingot synthesized in a silica crucible with a ~1.4 μm BN coating revealed net ionized donor concentrations N_D-N_A of 5.0×10^{15} cm^{-3} and 9.6×10^{15} cm^{-3}. In a sample from an ingot grown with a 16 μm BN coating there were N_D-N_A = 2.1×10^{16} cm^{-3} ionized donors. This represents an increase of ionized donor concentration from that for ingots synthesized in uncoated silica crucibles (1 to 6×10^{15} cm^{-3}). Variable temperature Hall effect measurements on these samples revealed no freeze-out of carriers above 16.5 K. This is to be expected for silicon impurities that have a 5.9 meV ionization energy, but it does not rule out the presence of shallow donors due to impurities other than silicon. However, there is no reason to assume that any other donor impurity is present in major concentrations. Boron dissolved from the crucible is expected to occupy the gallium site isovalent with gallium and without an electronic effect at low concentrations. The same is true for nitrogen on the arsenic site.

A synthesis ingot sample analyzed by SIMS had a silicon concentration $[Si]=2.6 \times 10^{16}$ cm^{-3} which is close to N_D-N_A=2.1×10^{16} cm^{-3} from Hall effect measurements. The SIMS value is ~20% higher than the net donor concentration determined by Hall effect. Taking into account the amphoteric nature of Si in GaAs, we

expect self-compensation to some degree bringing the SIMS and Hall results in close agreement. This confirms the major donor is silicon on gallium sites.

IV. CONCLUSIONS

It has been demonstrated that the CVD process using BCl_3 and NH_3 can be used for the coating of silica crucibles with 1 to 16 μm thick BN films. These films exhibit optical absorption and the X-ray diffraction characteristics of h-BN, but TEM lattice imaging of thin films reveal an isotropic structure that is expected to result in isotropic physical properties. Hall effect and SIMS concentration measurements show a silicon concentration in GaAs ingots synthesized in BN coated crucibles that was larger than the silicon concentration found in those synthesized in uncoated crucibles. The source of this additional silicon may in part stem from impurities in the BCl_3 source gas, or from decomposition of the silica parts used during BN film growth. The silicon concentration in the BN films has not been measured. The major contribution to silicon incorporation was by vapor phase transport of silicon from the SiO_2 ampule during synthesis.

In summary, it has been shown that CVD BN-coated crucibles can be used for synthesis of GaAs since they do not adhere to the GaAs charge or decompose in contact with it. However, to take advantage of the process, sources of silicon contamination other than the crucible must be eliminated both during the CVD process for deposition of the BN film and during subsequent synthesis and growth.

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TABLE I. X-ray and electron diffraction data for CVD-BN films in comparison with X-ray powder diffraction data.

Hexagonal Boron Nitride X-ray powder diffraction card file data			Film 2 (film - substrate) X-ray	Film 4 thick deposit X-ray	Film 3 separated film TEM
h k l	I/I_1	d (Å)	d (Å)	d (Å)	d (Å)
002	100	3.33	3.72	3.46	3.68
100	16	2.17			
				2.09	2.23
101	6	2.06			
102	14	1.817		1.73*	
004	6	1.667			
				1.69*	
103	2	1.552			
104	4	1.322			
110	6	1.253			
				1.24*	1.29
112	8	1.173			1.18*
.	.	.			
.	.	.			
.	.	.			
204	2	0.910			
					0.87*
008,116	6	0.83			
					0.75*

* weak intensity

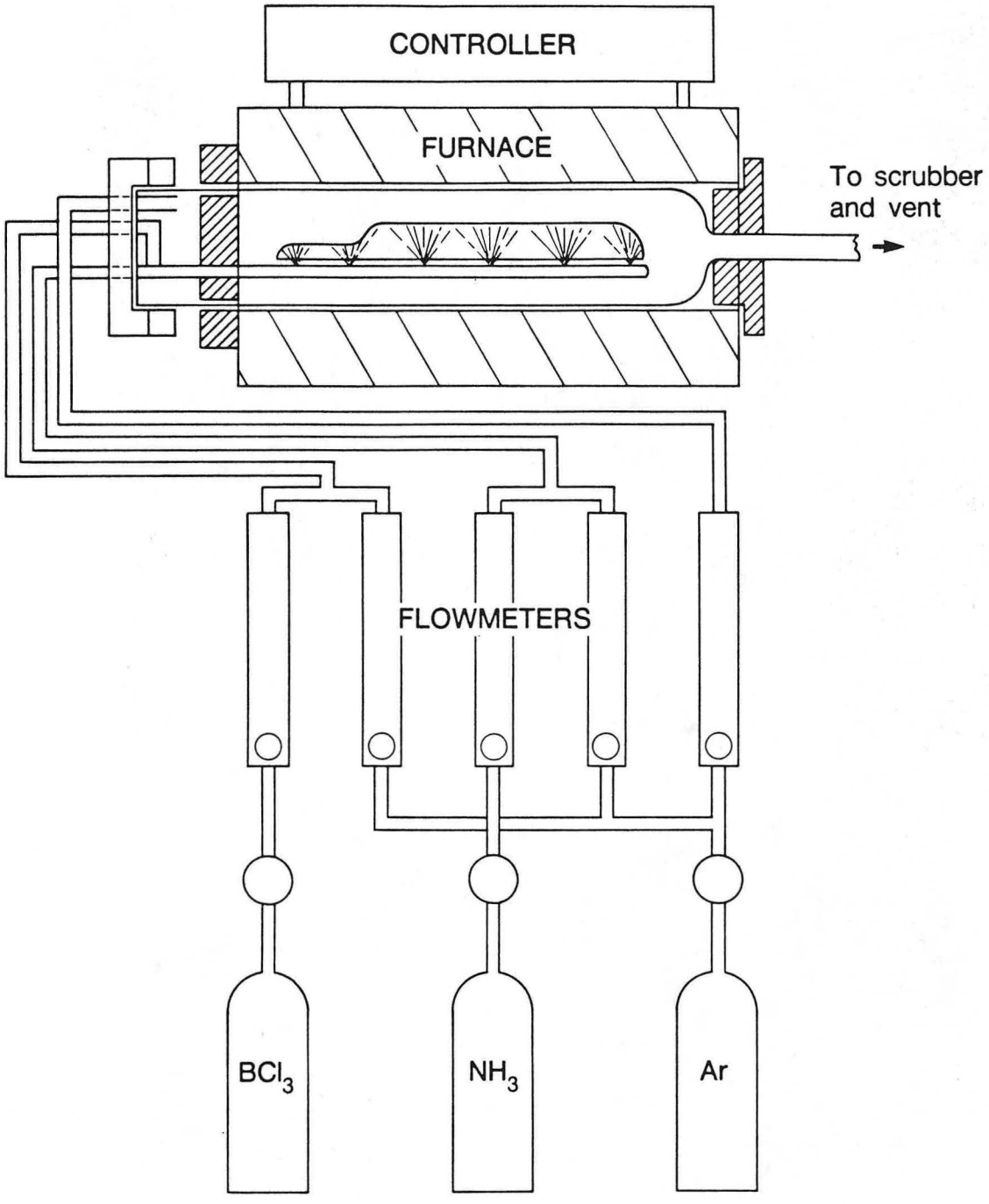

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FIG. 1. Schematic of the CVD system used for boron nitride deposition on SiO_2 crucibles.

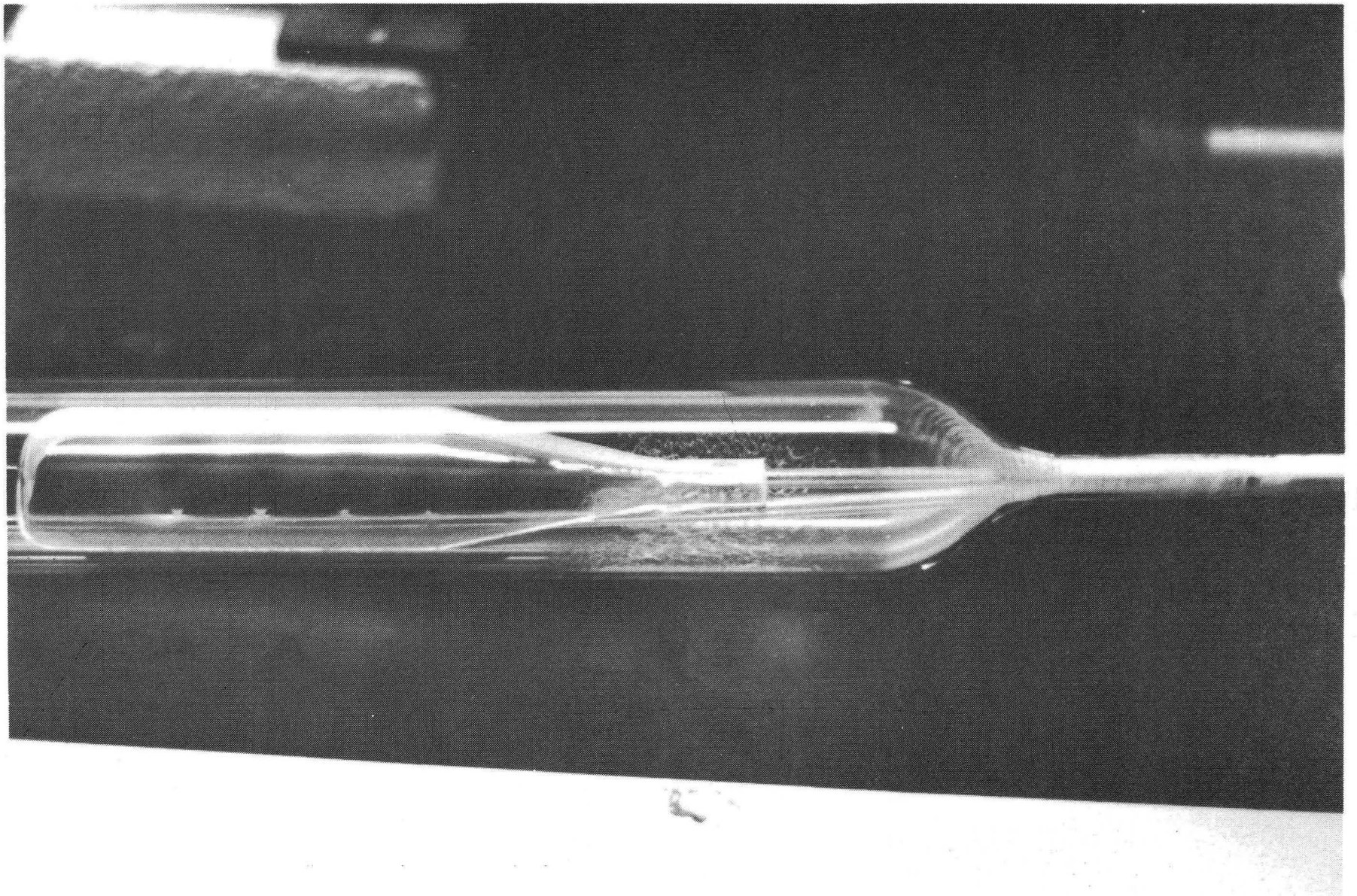

FIG. 2. A BN coated crucible within a furnace tube after film growth. The crucible is supported by the gas distribution manifolds.

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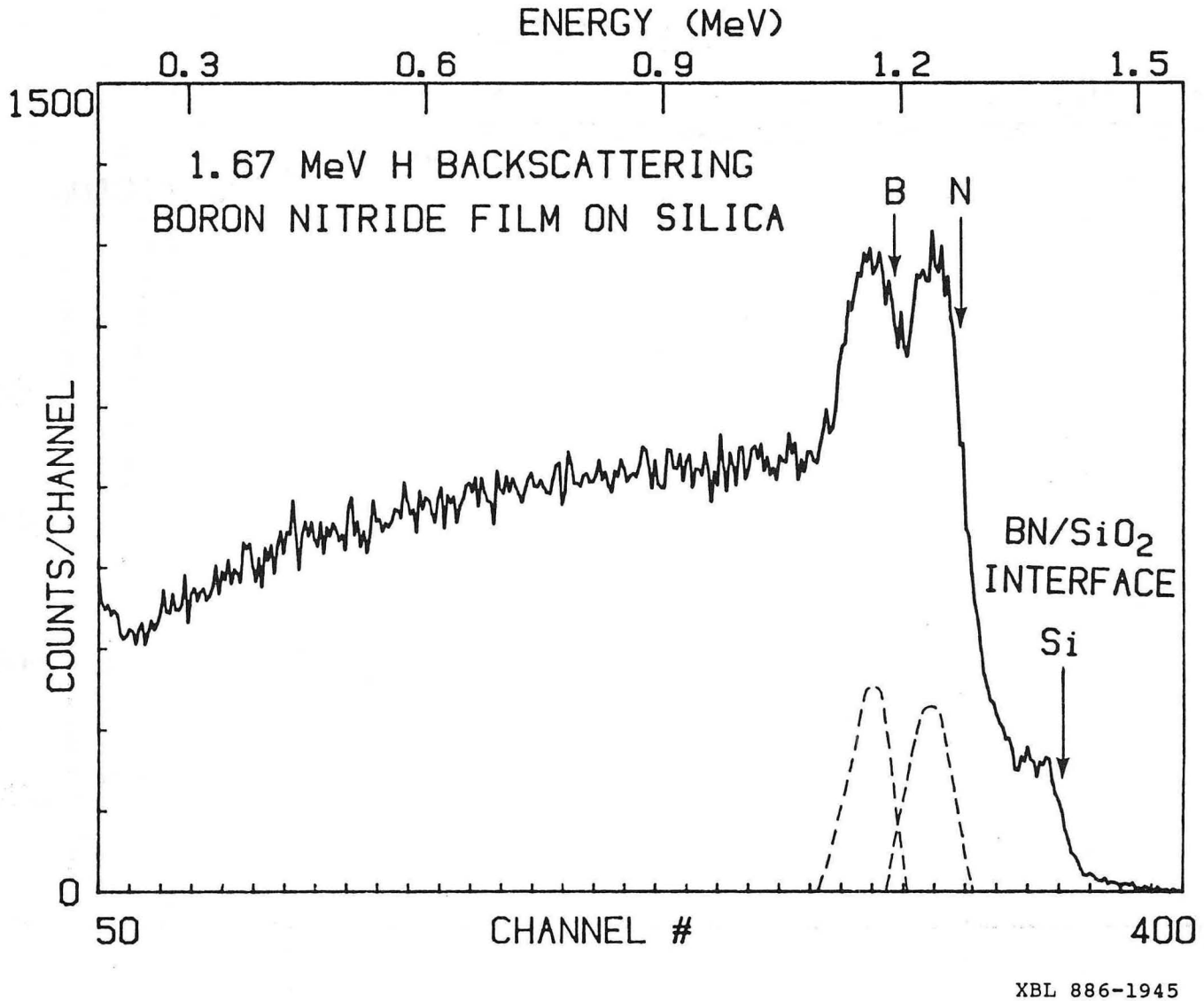

FIG. 3. Proton resonant scattering spectrum of a 1 μm BN film.

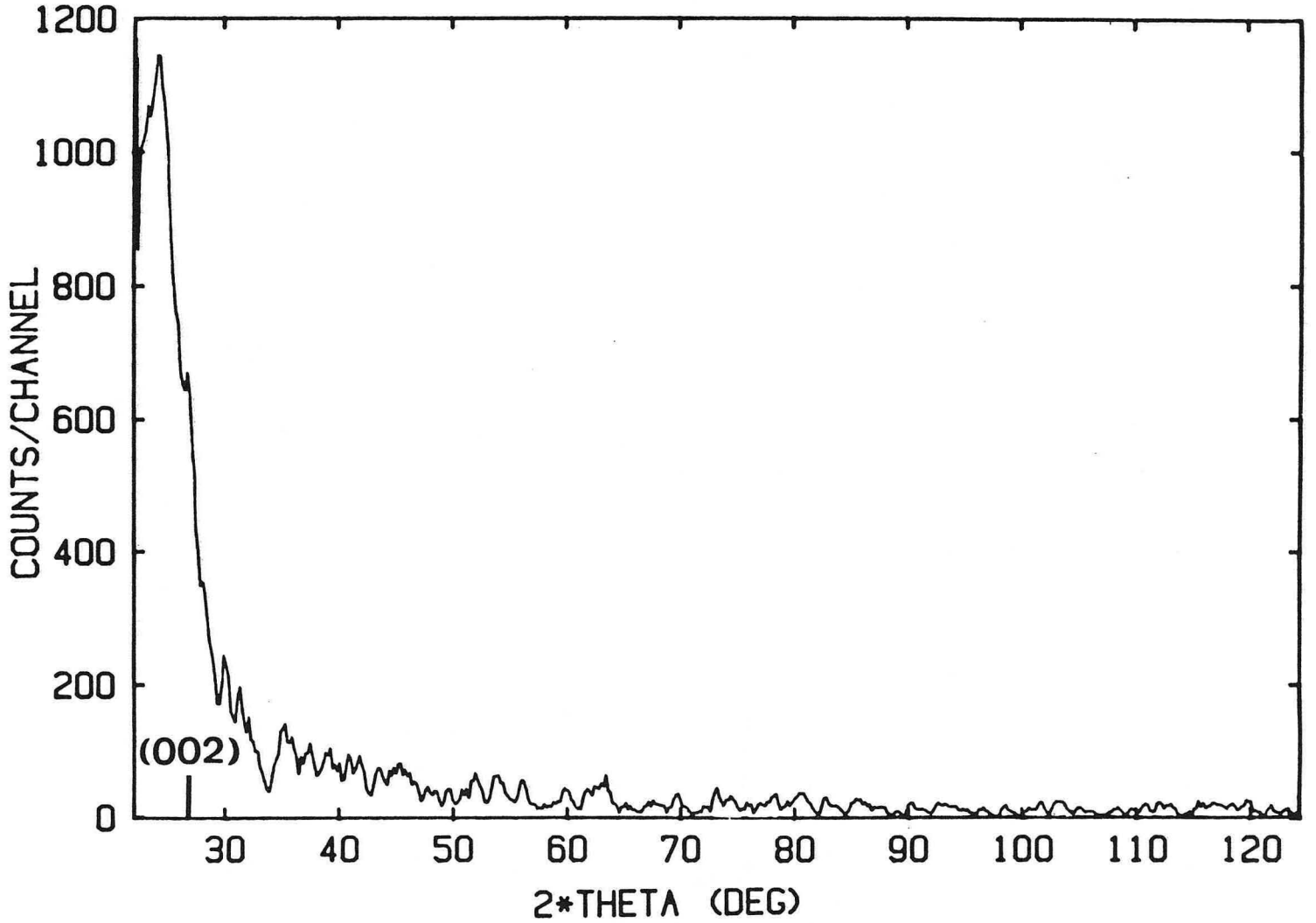

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FIG. 4. X-ray diffraction spectrum of a 1 μm BN film.

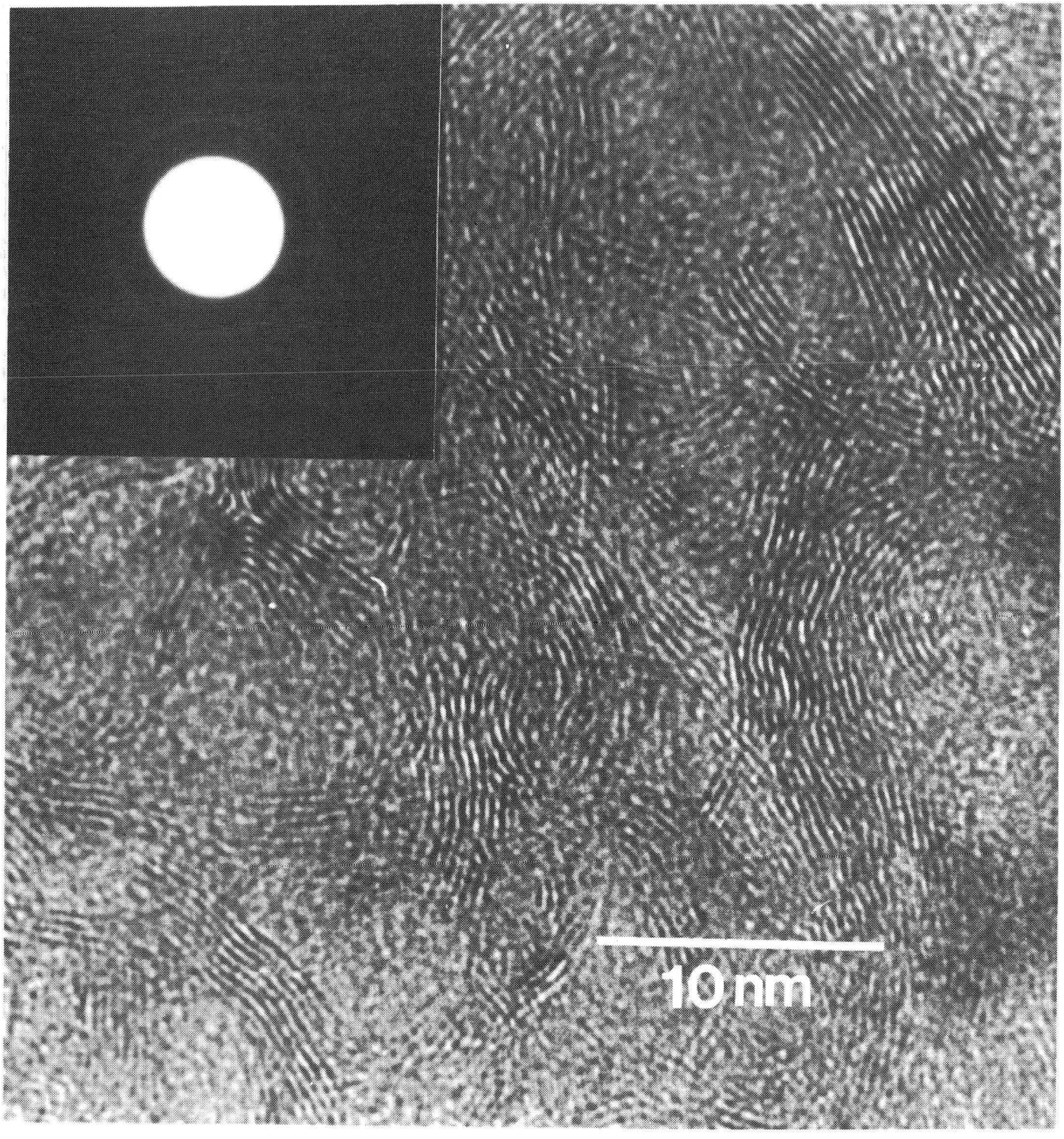

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FIG. 5. Transmission electron micrograph: lattice imaging and diffraction pattern of a CVD-BN film

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