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Journal of Crystal Growth 153 (1995) 97–102

JOURNAL OF **CRYSTAL
GROWTH**

Boron nitride coating on fused silica ampoules for semiconductor crystal growth

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Received 21 October 1994; manuscript received in final form 6 February 1995

Abstract

Fused silica ampoules for use in Bridgman growth of semiconductor crystals were coated with boron nitride films by chemical vapor deposition from borazine. Ampoules coated for 20 h at 1100°C yielded uniform, small grain hexagonal boron nitride films about 10 μm thick. The coatings were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), contact angle measurements, and thickness measurements by profilometer. The coatings contained no hydrogen, appeared to possess a very uniform morphology, and showed high contact angles with molten CdTe. The low wetting nature of the coating makes it a promising container material for crystal growth.

1. Introduction

Boron nitride has attracted considerable attention in the past few years as a promising container material for crystal growth of semiconductors such as GaAs [1], and CdTe [2]. Pyrolytic boron nitride (PBN) is chemically inert. It is the surface least wetted (high contact angle) by molten CdTe and GaAs compared to other common crucible materials such as fused silica, carbon-coated fused silica, sandblasted fused silica etc. [3,4]. The low wetting of PBN has important implications for crystal growth, since adhesion of solidified crystal to the crucible can be the major cause of stress in crystals [5,6]. It is thought that the greater the wetting by the melt, the greater is

the sticking by the resulting solid. Another application of a low wetting ampoule material is its use in crystal growth in space. It has been often observed in directional solidification experiments performed under microgravity that the diameter of the ingot is smaller than the inner diameter of the ampoule in which the experiment was carried out (even after accounting for thermal contraction) [7,8]. This is thought to be due to the low wetting of the ampoule by the melt, that enhances the tendency of the melt and the resulting solid to have reduced contact with the ampoule in space.

Solid PBN ampoules for crystal growth are very expensive. Also, PBN has anisotropic properties due to its hexagonal layered structure (thermal conductivity in the direction along the layers is ~20 times greater than across the layers). The anisotropic properties and the high thermal conductivity of solid PBN are thought to

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make obtaining the desired interface shape difficult in vertical gradient freeze or Bridgman techniques [12,13]. Coatings of boron nitride on fused silica ampoules have the advantage of preserving the desirable properties of PBN without the difficulties associated with anisotropy. The BN-coating should prevent silicon or oxygen contamination of the melt from the silica crucible. It will reduce wetting of the melt and subsequent sticking of the crystal to the crucible. The particulate amorphous carbon coating commonly used in crystal growth is often found to contaminate melts and introduce carbon impurities and precipitates in crystals [14,15]; these could be avoided with BN-coatings.

In this paper we report a method for coating fused silica ampoules with boron nitride. Borazine was chosen as the precursor for BN film deposition. Borazine has the chemical formula $B_3N_3H_6$ with a hexagonal ring structure analogous to benzene. It undergoes decomposition at high temperatures, involving stepwise intermolecular dehydrogenation and ring cleavage to form boron nitride as shown in Fig. 1 [9]. Complete decomposition of borazine to BN and H_2 is thought to occur at temperatures above 900°C [10]. BN films prepared at lower temperatures tend to contain hydrogen and adsorb atmospheric

moisture [17,18]. Films prepared by chemical vapor deposition from gases such as BCl_3 and NH_3 , become more crystalline at higher growth temperatures: amorphous at $900\text{--}1000^\circ\text{C}$, mixture of crystalline and amorphous phases at $1000\text{--}1150^\circ\text{C}$ and crystalline hexagonal boron nitride at 1200°C [11]. With the use of borazine as the only precursor, impurities are minimized. For example, this avoids the carbon commonly found in solid PBN crucibles due to deposition on graphite.

The use of borazine for preparation of BN films has been reported by several workers [16-19]. The films were usually deposited on silicon substrates at temperatures not exceeding 700°C . In this work, deposition was carried at temperatures up to 1100°C . Cylindrical fused silica ampoules with conical bottoms were coated with boron nitride for subsequent use in crystal growth of cadmium telluride. The coatings were characterized by films deposited on silicon wafers and quartz slides placed inside the ampoule.

2. Experimental procedure

A method similar to that used to coat quartz ampoules with carbon for Bridgman growth was tried initially. Borazine was introduced into an evacuated ampoule through a smaller diameter tube running inside the larger diameter ampoule. The ampoules were 28 mm inner diameter (ID), 32 mm outer diameter (OD), and had a conical bottom approximately 50 mm long. About 250 to 300 mm of the ampoule from the conical bottom was to be coated for subsequent use in crystal growth. After letting in a certain amount of gas, the borazine valve was closed and the ampoule was held at the pyrolysis temperature ($800, 1000$ or 1100°C) for about an hour and then cooled. This method did not yield uniform coatings on the ampoule. The product tended to be flaky or powdery, did not adhere to the ampoule, and deposited mostly on the bottom half of the ampoule. The whitish powder indicates that the reaction occurred in the gas phase. A new apparatus was therefore designed to allow for continuous flow of borazine through the ampoule. A schematic of this apparatus is shown in Fig. 2.

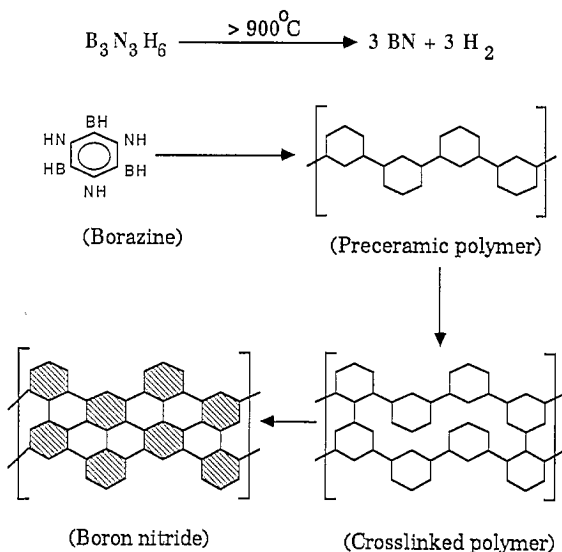


Fig. 1. Mechanism for formation of BN from borazine [9].

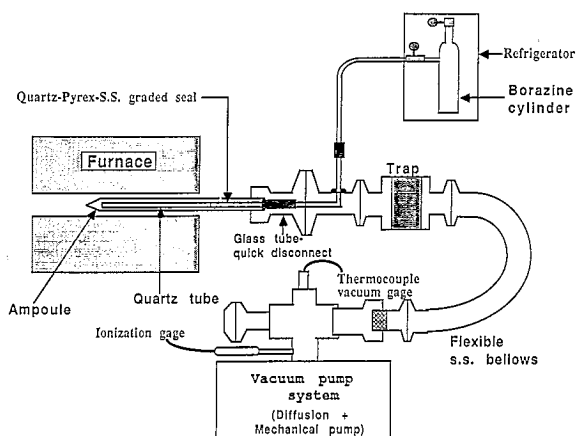


Fig. 2. Schematic of BN-coating apparatus.

Several different schemes were tried for introducing borazine into the ampoule in order to obtain deposition along its entire length. A smaller diameter tube (4 mm ID, 6.3 mm OD), with seals graded from stainless steel to Pyrex and then to quartz, was found to work best as a borazine feed tube. This tube ran along the length of the ampoule up to about 25 mm from the conical tip. The ampoule was connected to a vacuum pump system through a quick disconnect vacuum fitting, a coaxial trap and a stainless steel bellows connector. The vacuum system consisted of a diffusion pump backed by a mechanical pump.

The borazine was stored in a refrigerator at $< 0^{\circ}\text{C}$ to prevent its decomposition. Borazine is a liquid at room temperature, but has a high vapor pressure [20]. During an experimental run, the ampoule to be coated was cleaned in an ultrasonic bath, first with Micro glass cleaning agent, and then with deionized water. It was then soaked for an hour in a mixture of 5% HF/35% HNO_3 /60% H_2O , and washed again with deionized water. The cleaned quartz ampoule was fitted into the vacuum system and the part of the ampoule to be coated was placed inside a horizontal, split tube furnace, as shown in Fig. 2. The ampoule was evacuated to below 10^{-5} Torr. The furnace temperature was then raised to the deposition temperature. After allowing for thermal equilibration, borazine was introduced into the ampoule through the smaller diameter tube. Pure borazine was used without any

diluent gas. With borazine flow, the pressure in the system increased to $\sim 10^{-4}$ Torr. A very small flow was maintained so as to achieve a uniform deposition. To use in characterization of the films, quartz microscope slides and pieces of silicon wafer were placed inside the ampoule. Four different pyrolysis temperatures were tried: 500, 800, 1000, and 1100°C . The deposition time was varied from 1 to 20 h. No significant deposition was observed at 500 or 800°C , as inferred by the absence of characteristic peaks in the FTIR spectrum obtained with the silicon wafers. Most experiments were performed at 1100°C , since this would be near the temperature the ampoules would be subjected to during CdTe crystal growth. After deposition, the furnace was cooled while still holding a vacuum of $(6-8) \times 10^{-6}$ Torr. Coatings were usually thicker on silicon wafers, and tended to peel off more easily.

3. Results

The coatings on the ampoules deposited at 1100°C varied from almost transparent when deposition was carried out for 1 h, to a slightly whitish translucent film at deposition times of more than 10 h. Coatings also appeared very uniform over the portion of the ampoule placed inside the furnace.

The identification of the coatings was mainly based on the FTIR spectra of the films deposited on silicon wafers placed inside the ampoules. Fig. 3 shows such an IR transmittance spectrum of a

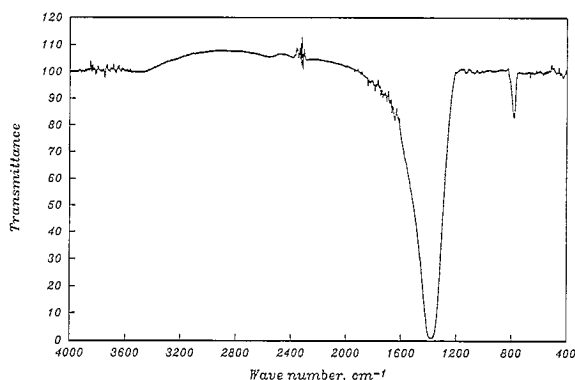


Fig. 3. IR spectrum of a BN film deposited at 1100°C for 1 h.

film deposited at 1100°C for 1 h. Absorption peaks are evident corresponding to B–N stretching vibration at $\sim 1380 \text{ cm}^{-1}$ [16,21,22] and to B–N–B bending vibration at $\sim 780 \text{ cm}^{-1}$. There are no other distinct peaks corresponding to B–H or N–H bonds, proving that the films contained no hydrogen.

The X-ray energy dispersive spectrum of the films obtained with a scanning electron microscope also showed only boron and nitrogen peaks.

Films were characterized by X-ray diffraction for crystallinity. Fig. 4 shows the X-ray diffraction spectrum of a film deposited at 1100°C for 20 h on a fused quartz slide. There is a wide peak corresponding to (002) reflection of small grain hexagonal boron nitride. The interplanar spacing calculated from the position of the peak maximum is 3.35 \AA compared with the powder diffraction file value of 3.33 \AA for reflection from the (002) plane of hexagonal boron nitride. The grain size calculated using Scherrer's relation [23] is approximately 70 \AA .

The film thickness was measured using a Dektak profilometer on a quartz slide masked partly during deposition. The thickness of the film was about $1 \text{ }\mu\text{m}$ when deposition was carried out at 1100°C for 1 h. The thickness increased to about $5 \text{ }\mu\text{m}$ in 10 h at the same temperature of 1100°C, and to about $10 \text{ }\mu\text{m}$ in 20 h.

Fig. 5a shows the scanning electron micrograph of a BN film deposited on quartz, and Fig. 5b that of solid PBN for comparison. The BN

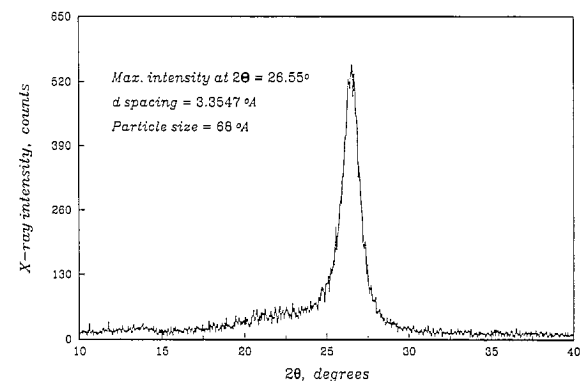


Fig. 4. X-ray diffraction spectrum of a BN film deposited at 1100°C for 20 h.

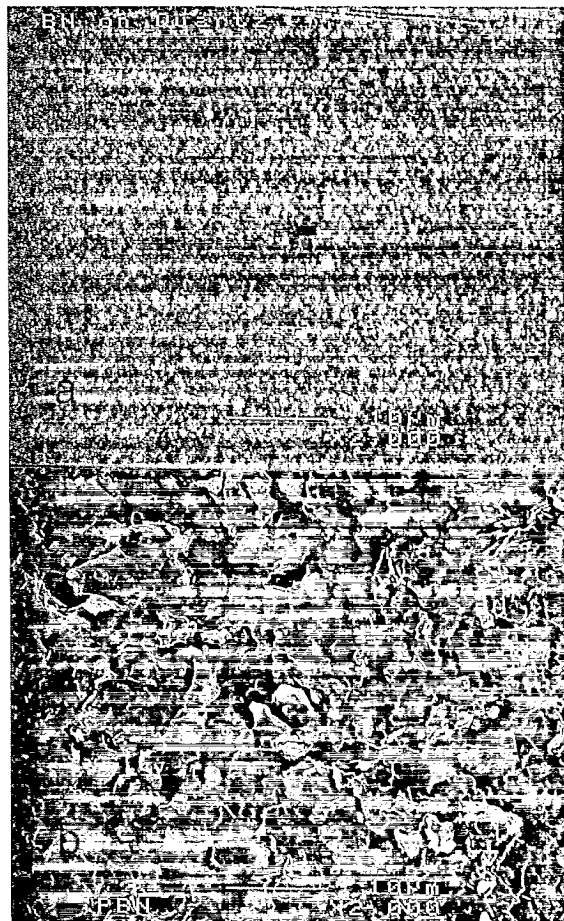


Fig. 5. Scanning electron micrograph of (a) BN film on quartz, (b) solid PBN.

film appears to have a very fine granular morphology compared to the rougher surface texture of PBN.

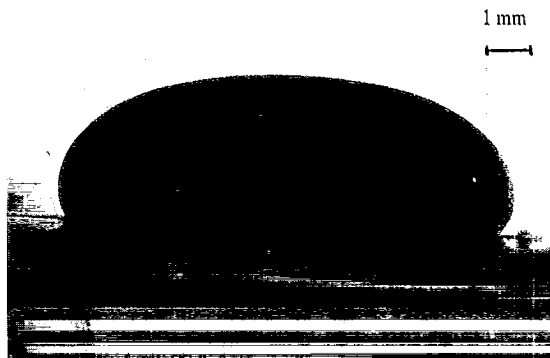


Fig. 6. Drop of molten CdTe on BN-coated quartz.

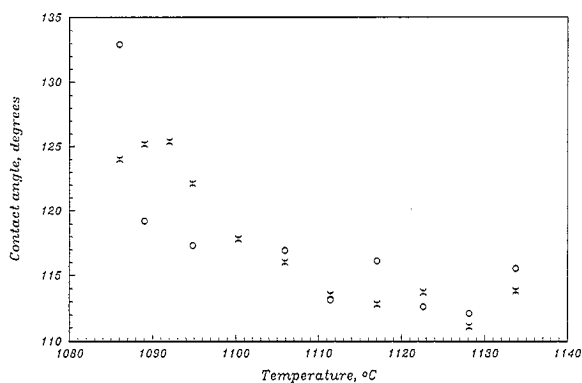


Fig. 7. Contact angle of molten CdTe on BN-coated quartz. The two symbols represent two measurements.

The contact angle of molten CdTe was measured on films deposited on fused quartz microscope slides. The contact angle was measured by the sessile drop technique described previously [3]. Fig. 6 shows a drop of molten CdTe on a BN-coated quartz slide, and Fig. 7 shows the contact angle data from two measurements. For comparison, the contact angle of molten CdTe measured on other surfaces is shown in Fig. 8 [3]. The contact angle on BN-coated quartz is higher than on most of the other common ampoule surfaces; it is, however, slightly less than on solid PBN. This is probably due to the rougher surface

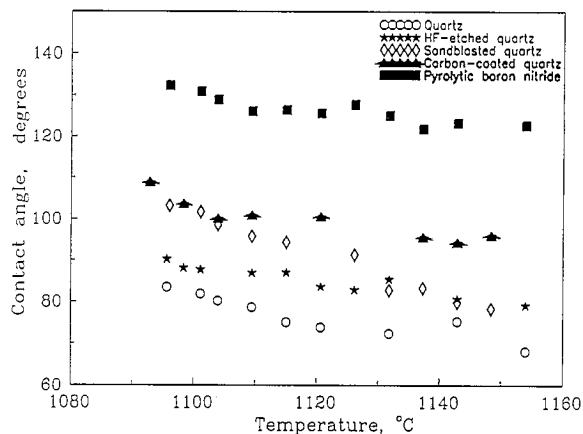


Fig. 8. Contact angle of molten CdTe on different ampoule surfaces.

morphology of solid PBN compared to the smooth polycrystalline film of BN.

Acknowledgements

This research was supported by the Consortium for Commercial Crystal Growth, the New York State Science and Technology Foundation through the Center for Advanced Materials Processing, and Clarkson University.

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