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Doping and electrical properties of cubic boron nitride thin films: A critical review

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ABSTRACT

Cubic boron nitride (c-BN) is a promising material for high-power and high-temperature electronic devices operating in harsh environments due to its outstanding properties including a wide band-gap, good chemical stability, high thermal conductivity, and high breakdown field. The electronic applications of c-BN have received considerable attention, benefiting from the progress in c-BN thin film deposition techniques during the last few years. The present article reviews the latest developments in doping and electrical properties of c-BN thin films. Following a brief introduction on film growth, we present calculated theoretical results on electronic structure as well as the energies of native defects and impurity dopants in c-BN. In recent experimental research, several dopants, including Be, Mg, Zn, S, and Si, have been incorporated into c-BN thin films during deposition or by post ion implantation, resulting in both *n*- and *p*-type conduction. These results are summarized and discussed in Section 3. In addition, results on c-BN/metal-contacts and *p*–*n* junctions based on intrinsic or doped c-BN thin films are discussed in Section 4. Finally, current status and future prospects for doping and electrical properties of c-BN thin films are discussed.

1. Introduction

Boron nitride (BN) is a compound isoelectronic with carbon, and like carbon, can possess sp^2- and sp^3-bonded phases which are the analog of graphite and diamond. BN crystallizes in the sp^2-bonded hexagonal (h-BN), rhombohedral (r-BN), and turbostratic (t-BN) phases, and in the sp^3-bonded cubic (c-BN) and wurtzite (w-BN) phases [1–3]. Hexagonal BN is comprised of sp^2 bonds forming planar hexagonal networks which are stacked along the *c*-axis in an AA′AA′A configuration. Because of the weak interplanar bonding in h-BN, the planes easily slide against each other; thus, these materials are excellent lubricants. In the r-BN structure, B and N atoms are also arranged in a planar hexagonal network, but the hexagons are stacked along the *c*-axis in an ABCABCA configuration. For t-BN, the two-dimensional in-plane order of the hexagonal basal planes is largely retained, but these planes are stacked in a random sequence and with random rotation around the *c*-axis. Accompanying this decrease in stacking order is a general increase in the (0002) interplanar spacing.

Wurtzite BN is comprised of sp^3 bonds in which the atoms are arranged in a buckled hexagonal configuration and stacked along the *c*-axis in an AA′AA′A arrangement. Another phase of sp^3-bonded BN has the cubic zinc-blend structure (i.e. c-BN), which consists of tetrahedrally-coordinated B and N atoms with {111} planes arranged in a three-layer ABCABC stacking sequence. Cubic BN has a crystal structure similar to diamond, except that while the diamond structure is comprised of two face-centered cubic (FCC) carbon cells, c-BN has one B FCC cell and one N FCC cell. The lattice constant for c-BN is $a = 0.3615$ nm [4], which is very similar to that of diamond, $a = 0.3567$ nm. The bonding between atoms is entirely covalent in the case of diamond, while c-BN exhibits ionicity between 0.26 and 0.48, depending on the ionicity scale used [5].

Cubic BN is a highly attractive material as a hard and protective coating for cutting tools and optical elements because of an extreme hardness (70 GPa) second only to diamond, good chemical and thermal stabilities, and excellent oxidation resistance [1–3]. Much attention has been paid to the outstanding physical properties of c-BN such as a wide band-gap ($E_g \approx 6$ eV), high thermal conductivity (13 W cm^{-1} K^{-1}), low dielectric constant (7.1), and a high breakdown field (8 MV cm^{-1}); all of which make it a good candidate material for high-power and high-temperature electronic devices operating in harsh environments.

1.1. Growth of c-BN thin films

Cubic BN has been available since the 1960s as bulk material formed by the high pressure and high temperature (HPHT) synthesis technique established by Wentorf [6], but the equipment of the HPHT synthesis is considerably complicated, and the resulting crystallites are too small for most industrial applications. Therefore, great efforts have been made to grow c-BN thin films [1–3] since the synthesis of c-BN thin films under low pressure was firstly reported by Sokolowski [7] in 1979. Since the 1990s, successful growth of c-BN films has been reported using a variety of ion-assisted deposition techniques including ion-assisted pulsed laser deposition (PLD) [8], radio frequency (RF) sputtering [9,10], ion

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beam assisted deposition (IBAD) [11,12], mass-selected ion beam deposition [13], and plasma enhanced chemical vapor deposition (PECVD) [14]. A review of c-BN preparation methods and their parameter spaces was presented by Kulisch and Ulrich [15].

Energetic-ion bombardment during film growth, by irradiation with an ion beam or substrate biasing, has been found necessary to obtain the cubic phase irrespective of the method of film synthesis. However, such ion bombardment is inevitably accompanied by the build-up of strong compressive stresses (5–20 GPa) until eventually, at a critical thickness, the c-BN films peel off. The maximum thickness of c-BN films is typically limited to a few hundred nanometers, and consequently, the application of c-BN coatings has been severely hindered. During the last decade, some post-deposition or sequential processes, such as annealing at temperatures above 800 °C [16,17] and ion irradiation [18,19], have been proposed to reduce the stress of c-BN films. More preferably, some attempts such as high temperature deposition [12,20], simultaneous ion implantation [21], the addition of a third element [22–24], and a two-step deposition process [24,25] have been undertaken to keep stress as low as possible during film growth. Although several groups have made important progress in reducing the stress, allowing the deposition of c-BN films with thickness above 1 μm, most of these approaches are rather complicated and not compatible with industrial needs. Furthermore, the deposition rate of BN films is too slow because of the high ion-to-atom ratio in the synthesis of c-BN films.

Recently, fluorine was found to be effective as an additional reaction precursor for c-BN thin film deposition and it can selectively etch the non-cubic BN phase [3,26,27]. Introducing fluorine into the gas phase dramatically reduces the substrate bias voltage required for c-BN deposition. Fig. 1 shows a scanning electron microscopy (SEM) cross-sectional image of the morphology of a 3-μm-thick c-BN film deposited on Si(001) substrates at 1040 °C using direct current (DC) jet plasma CVD with an Ar–N_2–BF_3–H_2 gas mixture [26]. Due to a low bias voltage and a large precursor supply, a rather high deposition rate of 0.3 μm/min was obtained. The residual stress in such c-BN films is 1–2 GPa and the largest film thickness achieved is over 20 μm. However, during fluorine-based CVD processing, very high temperatures up to 800 °C are required [3,27] which is incompatible with many substrate materials.

Besides high compressive stresses, it has been found that the majority of c-BN films possess a three-layer structure starting with an amorphous intermixed layer at the substrate interface, switching into preferentially oriented t-BN, and followed by the topmost c-BN layer [1]. Furthermore, these c-BN films are of poor crystalline quality, and composed of very small grains containing a high density of defects and grain boundaries which essentially prohibit electronic applications. A significant improvement in film quality was achieved by the fluorine-based CVD technique, resulting in a columnar film structure with grain sizes extending up to micrometers in the normal direction and up to 50–100 nm in the lateral direction [26,27]. However, the presence of a t-BN interlayer and the polycrystalline structure of c-BN were directly revealed by high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) results [26,27].

For electronic device applications, single crystalline c-BN films appear necessary, demanding epitaxial growth on top of a suitable substrate. Nucleating nanocrystalline c-BN thin films directly onto monocrystalline w-AlN(0001) films of 220 nm thickness without the t-BN interlayer was firstly demonstrated in 2001 by Feldermann and co-workers using mass-selected ion beam deposition (MSIBD) [28]. Nanocrystalline BN grains with the cubic, and, more frequently, with the wurtzitic structure were found in direct contact with the AlN substrate. However, on many areas of the substrate, the well-known t-BN/c-BN layer sequence was present. Direct growth of c-BN onto the AlN substrate without t-BN interlayer was observed on only one-third of the total substrate surface.

In view of similar properties and excellent lattice matching between c-BN and diamond, the latter appears to be a promising candidate as a substrate material for epitaxial c-BN growth. Recently, direct growth of c-BN thin films without any intermediate t-BN layer has been demonstrated on CVD diamond substrates using both IBAD [29,30] and electron cyclotron resonance microwave plasma (ECR-MP) CVD [31]. An HRTEM image from a c-BN/diamond sample is shown in Fig. 2. The interface between the two materials is nearly undistinguishable, since the atomic planes are perfectly aligned in that region. Films consisting of 100% pure c-BN phase grow heteroepitaxially on diamond substrates with a relative orientation given by c-BN(001)[100]//diamond(001)[100] [29]. High substrate temperature (900 °C) was considered to be a key factor for epitaxial growth of c-BN in order that the ion-induced damage is sufficiently annealed out to maintain an ordered substrate surface during nucleation of the c-BN layer [32]. By adopting a single-crystalline diamond(001) substrate, large-area, single crystal c-BN thin films are obtained. Epitaxially grown, 500-nm-thick c-BN films are mechanically stable even under ambient conditions, though they still exhibit a compressive stress of 5 GPa, which opens exciting possibilities for electronic applications of c-BN films.

Besides diamond, direct growth of c-BN on commonly used Si(001) substrates has been attempted as well. Yang and coworkers [33,34] observed that elimination of amorphous and t-BN layers is possible even on Si(001) substrates by preheating the substrate in hydrogen

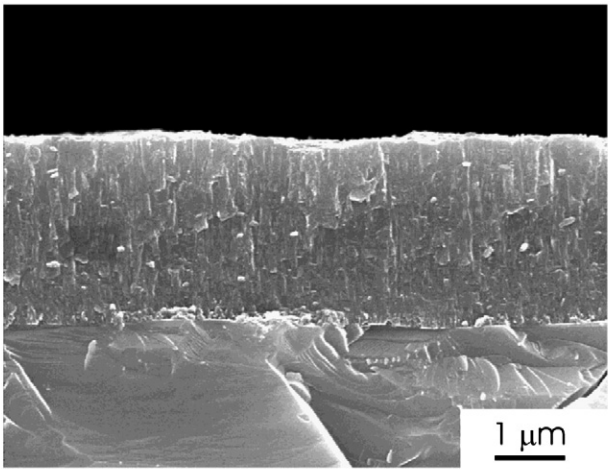

Fig. 1. A 3-μm-thick c-BN film deposited under DC substrate bias of −85 V at 1000 °C by DC jet plasma CVD [26].

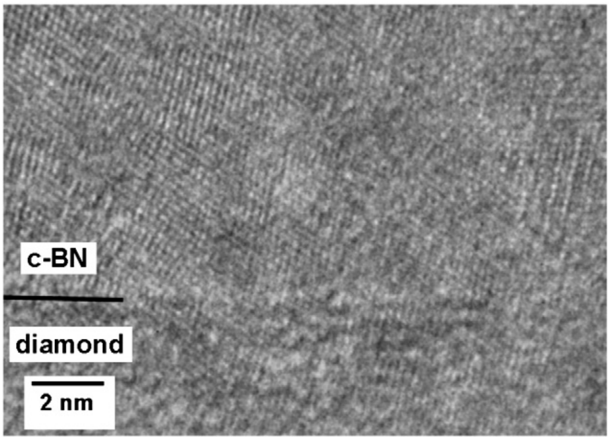

Fig. 2. A characteristic HRTEM image of a c-BN/diamond interface from a 20-nm-thick c-BN film deposited on a 200-nm-thick CVD diamond film by IBAD at 900 °C [29].