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DEPOSITION AND CHARACTERIZATION
OF
BORON CARBIDES

BY

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GRADUATE COLLEGE
UNIVERSITY OF NEBRASKA

DEPOSITION AND CHARACTERIZATION OF BORON CARBIDES

AHMAD A. AHMAD, Ph.D.

University of Nebraska 1996.

Advisors: N.J. Ianno and P.G. Snyder

This work compares the physical properties of boron carbides, B_5C in particular, fabricated by plasma enhanced chemical vapor deposition (PECVD) and r.f. magnetron sputtering techniques. In the former technique, icosahedral closo-1, 2-dicarbadodecarborane ($C_2B_{10}H_{12}$; orthocarborane) was used as a single source compound to fabricate the boron carbide films. In the latter technique, a pure and dense boron target, flushed with Argon/Methane glow discharge prior to the sputtering process was used to deposit boron carbides. Although sputtering boron from a boron target and boron carbide from a boron carbide target (of the same stoichiometry) are well known methods, this sputtering methodology is considered to be unique. The optical properties, microstructure and surface morphology of the films were investigated by UV, visible and near infrared probing techniques. Other properties due to carrier traps inside the band gaps were investigated by Raman scattering and FTIR spectroscopic ellipsometry. Electrical properties such as heterojunction diodes characteristics, and film resistivity of the materials were investigated as well.

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CONTENTS:

CHAPTER 1

INTRODUCTION

The fact that boron is a low atomic-weight element and can be combined with high atomic-weight elements makes multilayer thin film fabrication potentially attractive for protective coating applications in the nuclear industry and in rocket technology. It can be used in high-temperature thermoelectric conversion and metallurgical applications. [1-8] Also, the extreme hardness and high-refractory properties of boron thin films makes them useful in mechanical coatings [2].

Historical interest in boron and boron-based semiconductors has led to the attention given to the compound boron-carbide. The interest in boron carbide microelectronic devices and high-temperature thermoelectronic conversion devices started in the 1950's [3,4]. Many deposition techniques were used to fabricate boron carbide thin films [3-27] for various purposes.

The compound stoichiometry (B_xC) as well as other physical properties, such as optical band gap, thin film resistivity and microstructure, of deposited boron carbide material can be controlled by the deposition parameters.

Boron carbide thin films have not yet been deposited in single crystal form, however, an attempt to produce epitaxial B_4C thin films on single crystal NaCl (100) and sapphire mono-crystals, using the method of laser spraying [25],

resulted in a polycrystalline material. Also, polycrystalline boron carbide material and high resistivity boron carbide thin films were grown successfully by plasma enhanced chemical vapor deposition (PECVD) [9-14] and synchrotron radiation-induced chemical vapor deposition (SR-CVD) [9,15-18,27] techniques. Also, ion beam deposited boron carbide (B_4C) thin films used in coatings for the extreme ultraviolet were fabricated by high energy argon ion beam sputtering of a hot pressed B_4C target [26].

In almost all the previous attempts to fabricate microelectronic boron carbide material, the thin films exhibited relatively low resistivity [20] and therefore their use in the microlectronic applications was limited. The electronic properties of boron carbide thin films have been attributed to the free non-bonded carbon atoms on the lattice sites of the material microstructure [1] which ultimately contribute to film degradation and peal off phenomena. In 1990 Mazurowski et. al [10] used a novel PECVD method to fabricate high quality boron carbide thin films with controllable electrical properties and optical band gaps. Thereafter, heterojunction devices, such as diodes and field effect transistors (FET) [9-11,13,14,27] have been fabricated by synchrotron radiation induced chemical vapor deposition (SR-CVD) [15,18] as well as plasma enhanced chemical vapor deposition (PECVD). This was a result of the high resistivity of the boron carbide thin films which are ten orders of magnitude greater than the other known boron carbide alloys [3] developed by conventional CVD [19,20,24,28-43], hot pressed [21,22,44-50] or electron beam [23-26] techniques. The advances made by using these methods were due to a better

control over the boron carbide stoichiometry, band gaps and microstructure [12,13,51-56], computerized theoretical models for boron compound sources [15-18,57] and technical improvements in fabrication methodologies and thin film characterization techniques.

Since boron carbide material is so resistive to corrosion and has a large neutron capture section, boron carbide cermets were successfully used, with a volume percentage fraction of copper as a high thermal conductive and high melting point material, as an inner gamma shield and outer neutron radiation shield for nuclear reactors. The boron carbide cermets were fabricated by either vacuum hot pressing, involving one dimension pressing, which resulted in undesirable low density cermets or hot isostatic pressing, which involves three dimensional pressing, which successfully met the standard for neutron detector shield layers. [58-62]

Boron carbides fabricated via sputtering have received very little attention and were limited to applications for protective coatings, [44-50,58-63] in particular, for materials subject to erosion, corrosion or high temperature. The major advantage of this process is that temperature-sensitive substrates which couldn't be used in conventional CVD or other relatively high-temperature techniques, can now be used in this process at room temperature. In addition to that, sputter deposited boron carbide thin films were known to have an amorphous texture which contains no morphological growth features. It is worth it to mention that the B_{12} icosahedral compounds, in boron-rich borides, are classified into eight different types, α-rhombohedral boron is one type which has

a similar basic rhombohedral structure to boron carbides. [43,64] The structure consists of icosahedral units (B_{12} and possible carbon substitution) bonded together with direct B-B bonds as well as other covalent structural linkage units (such as CBC). Boron carbides crystallize and may fill the space by either using a primitive rhombohedral unit cell of dimensions near a_R = 5.2 Å and α_R = 65° or a hexagonal unit cell near a_h = 6.1 Å and c_h = 12.0 Å. Detailed reviews of literature on the boron and boron carbide microstructure are given in references 43 and 64.

A dense boron target is necessary for the reproducible deposition of high quality films. The unavailability of commercially fabricated high density and high purity boron and boron carbide sputter targets limited the use of sputter deposition for this material. In 1988 Hoenig et. al. [46] developed a high density (2.34 g/cm^3) and low porosity (less than 15%) boron target which made the sputtering technique practical. The targets were developed by hot isostatic pressing at 1700 C ^{0} in argon gas at 0.21 GPa for 2-4 hours.

High quality magnetron sputtered boron thin films on different substrates (quartz, fused silica, sapphire and silicon) using a dense boron target and argon as a sputtering gas have been reported [45,47]. For the d.c. sputter deposition of boron carbide thin films, a laminated target design was necessary to prevent the boron carbide target from cracking or sudden failure. In this process, in addition to the thermal insulating nature of the boron carbide target, the high deposition rate and the constant non-uniform ion bombardment caused by the balanced or

unbalanced magnetron sputter sources are the major factors causing the thermal gradient and stress throughout the target, and hence, physical cracking.

No reports on the use of a pure, dense boron target coupled with a reactive carbon-source gas, such as CH_4 or C_2H_4, relating to the sputter deposition of boron carbide thin films have been found. A dense boron carbide target (B_4C), however, was used to sputter deposit B_4C thin films and a dense boron target (B) was also used to sputter deposit boron (B) thin films [44-46] using argon as the sputtering gas in both cases. Therefore, this work is the first to use balanced magnetron sputtering of a high density boron target [44-46] coupled with methane (CH_4) as a carbon-source gas and argon (Ar) as a sputtering gas, to deposit boron carbide ($B_{1-x}C_x$) thin films. It was our intention to provide a general relationship between the selected deposition parameters and the compound stoichiometry, film resistivity, band gap and other physical properties of $B_{1-x}C_x$. The boron target was supplied by Kurt J. Lesker Company. It has been bonded and framed with a copper plate to insure good thermal contact and uniform heat distribution. This protection method was also meant to save the target from physical cracking due to the heat gradient caused by non uniform ion bombardment.

One of the goals of this work is comparative analysis of the physical properties of boron carbide samples fabricated by plasma enhanced chemical vapor deposition (PECVD) and balanced magnetron sputtering techniques. The recent development of boron carbide materials, deposited by PECVD and synchrotron radiation induced chemical vapor deposition (SR-CVD) with high

resistivity (10^{10} Ω-cm) and the fabrication of p-n heterojunction diodes and field effect transistors (FET) is extremely promising. It is not completely understood why these films exhibit high resistivity compared to those made by other methods. The main explanation is the fact that more incorporated hydrogen in the compound may substantially reduce the free unbound carbon atoms by filling the polycrystalline lattice empty sites and, therefore, limit the film electrical conductivity. According to these predictions, we developed our own unique method to sputter deposit high quality electronic boron carbide thin films with high resistivity.

In chapter 3, the new sputtering method as well as the similarities in the microstructure and control of fabrication of the sputter deposited and PECVD $B_{1-x}C_x$ films will be presented. If the quality of sputter deposited material is comparable to the quality of the PECVD material, it should possess a similar role hydrogen content and hence high electrical resistivity regardless of the method of deposition. A qualitative investigation to the hydrogen concentration and its role in the sputter deposited and PECVD B_5C films, at the microstructural level, are presented in chapter 4. In chapter 5, we present the electrical resistivity measurements as well as an application to the device fabrication based on the sputter deposited boron carbide films. A comparison between the electrical resistivity and the device fabrication based on the PECVD and the sputter deposited materials are presented too. The optical properties of the PECVD and the sputter deposited B_5C deposited on silicon and transparent substrates are presented and compared in chapter 6. The effect of film composition (boron to

carbon ratio) on the optical band gaps are presented for the sputter deposited boron carbide films and compared to that for the PECVD films. A short summary and brief conclusion are given in chapter 7.

Our study includes optical and Raman characterization of thin B_5C films fabricated by plasma enhanced chemical vapor deposition (PECVD) as well as deposition and physical characterization of $B_{1-x}C$ films fabricated by the reactive balanced magnetron sputtering technique. The main purpose of this study is to form a better understanding of the physical characteristics of boron carbide material by developing a new deposition method for high resistivity films. Therefore, we focus on comparing the two semiconducting materials via probing of their band gaps and the traps inside their band gaps. The former characterization process was accomplished by X-ray diffraction, Spectrophotometry, UV, visible and near infrared spectroscopic ellipsometry in addition to Auger Electron Spectroscopy . The later characterization process was accomplished by infrared spectroscopic ellipsometry and Raman scattering processes as well as four point probe resistivity measurements. Heterojunction (p-n and p^+-p) devices were also fabricated. Current-voltage (I-V) and capacitance-voltage (C-V) measurements were used to characterize the devices and the interface effects.

The phase diagram of B_4C is given in appendix A. [65] More information about the phase diagrams and numerical data on other boron carbides and their microstructure may be found in reference 66.

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