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Optical characterization of BCN films deposited at various N_2/Ar gas flow ratios by RF magnetron sputtering

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ABSTRACT

We present the deposition and optical characterization of amorphous thin films of boron carbonitride (BCN). The BCN thin films were deposited in a radio frequency magnetron sputtering system using a B_4C target. Films of different compositions were deposited by varying the ratio of argon and nitrogen gas in the sputtering ambient. X-ray photoelectron spectroscopy was used to perform surface characterization of the deposited films and a change in composition with nitrogen flow ratio was observed. The effect of gas flow ratios on the optical properties of the films was also investigated. It was found that the transmittance of the films increases with nitrogen incorporation. The optical band gap of the films ranged from 2.0 eV to 3.1 eV and increased with N_2/Ar gas flow ratio except at the highest ratio.

1. Introduction

Binary, ternary and quaternary compounds formed through combinations of silicon, boron, carbon and nitrogen are gaining importance due to possible applications in harsh environments. Vijayakumar et al. have presented results on one such quaternary compound of silicon boron carbon nitride that demonstrated good thermal stability and improved performance at high temperature, thus, allowing the compound to be used in low cost and easy-to-fabricate high temperature photodetector applications [1,2]. Similarly, a ternary compound of boron carbonitride (BCN) has gained increased attention due to its potential applications in electronic, optoelectronic and luminescent devices [3,4]. The boron–carbon–nitrogen phase diagram contains interesting phases, such as diamond, graphite, fullerene, cubic-BN, B_4C and there is also a hypothetical C_3N_4 [5]. Carbon nitride (C-N) thin films are predicted to have hardness comparable to diamond due to the small bond length and low ionicity of this material [6]. Boron nitride (BN) films have high hardness and wide band gap but typically have poor adhesion due to high internal stress [7]. There exist atomic bonding similarities amongst boron, carbon, and nitrogen that allow the formation of compounds with a wide compositional range. BCN compounds have been expected to combine the excellent properties of B_4C, BN and C_3N_4, with their properties adjustable, depending on composition and structure [8–10]. For example, Morant et al. have reported BCN films with hardness > 20 GPa [11]. The BCN alloy has been regarded as a promising candidate for novel super hard materials to be used as protective coatings. Moreover, recent efforts have been devoted to develop a low dielectric constant BCN film in order to reduce the stray capacitance induced signal delay of interconnections in Si ultra large scale integrated circuits (ULSI). Dense (pore-free) BCN films with a low dielectric constant in the range of 1.9–2.1 have been successfully demonstrated [12,13]. It has already been reported that the band gap energy of BCN films decreases with increasing carbon ratio [14]. The control of band gap energy and refractive index may make it possible to develop optical components such as filters and mirrors for use in the UV wavelength region. Polymer films have gained significant attention for industrial applications but their low wear and low scratch resistance limit their use. These limits can be overcome by coating the polymers with ceramics. For optical applications, the deposition of BCN coatings on polymers is a promising method for protecting the polymer surface [15]. Montasser et al. have reported the transparent BCN films to light of wavelength of 200–1000 nm using plasma assisted CVD [16]. Weber et al. reported that the BCN films can be used as mask substrates for X-ray lithography due to their optical transparency [17]. Lei et al. studied the optical properties with respect to the deposition temperature and observed the films deposited at higher temperature to have better optical properties [3].

Several methods of preparing boron carbon nitride films have been reported, such as chemical vapor deposition (CVD) [9,18,19], plasma assisted CVD [20,21], pulsed laser ablation [22,23], ion beam deposition [24], and sputtering [25–27]. However, it is still not easy

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to synthesize boron carbon nitride compounds with controllable composition by changing deposition parameters. The sputtering technique provides unique advantages over other techniques such as freedom to choose the substrate material and a uniform deposition over relatively large area. Furthermore, it is possible to control the deposition parameters to prepare BCN films of various compositions. A more detailed analysis of the complex bonding structure in the films obtained by sputtering is thus necessary to understand and improve the technique further. Some work has been reported on BCN films produced by sputtering. Sputtered BCN films with excellent mechanical properties, such as adhesion, high hardness and good wear resistance, have been reported [28,29]. However, there is a lack of knowledge on the optical properties of BCN films produced by sputtering. Hence, in this paper, we report on the optical properties of amorphous BCN thin films prepared by radio frequency (rf) magnetron sputtering. Optical properties are studied with respect to the composition of the gas mixtures during film deposition.

2. Experimental details

The rf sputtering was carried out in a multi-gun ultra-high vacuum sputtering system manufactured by AJA International. The system was evacuated to a base pressure in the 10^{-8} Torr range. The BCN films were deposited by sputtering from a high purity B_4C target (99.95%). The radio frequency used for sputtering was 13.56 MHz. The N_2 to Ar gas flow ratio was varied from 0 to 1 in steps of 0.25 by varying the individual gas flow rates, while the sum of gas flows was kept constant at 20 sccm and a constant deposition pressure of 4 mTorr was maintained. Since we focus on the optical properties of BCN films in this paper, minimal change in optical properties was observed with respect to power density and deposition pressure. Moreover, the deposition power of 4 mTorr was optimized as we had problem with the plasma sustainability at deposition pressure of less than 4 mTorr. At the same time we saw significant change in the optical properties of the BCN films with respect to N_2/Ar gas flow ratios.

The AJA sputtering system used for the deposition is equipped with substrate rotation which was used for uniform deposition. The distance between the substrate holder and the target was optimized to get a consistent deposition rate and the distance was kept at 25 cm. Sputtering power was maintained at 200 W for the B_4C target for all of the depositions and the target was sputter cleaned in argon ambient for about 45 min before each deposition. For each deposition, films were deposited simultaneously on optical grade quartz slides and on oxidized silicon wafers which had been subjected to standard cleaning procedures before deposition. The quartz slides were used for optical measurements using UV visible spectrophotometer only. The oxidized silicon wafers were used for other measurements namely profilometer, SIMS and XPS. The duration of all depositions was 3 h. The films were deposited at room temperature. However, with the deposition run of 3 h the temperature of the substrate was found to be ~100 °C. The films obtained were amorphous in nature and their thickness was measured to be in the range of 75–135 nm using a Veeco optical profilometer and confirmed with a stylus profilometer.

A Cary-100 UV–Visible spectrophotometer was used to study the optical characteristics of the thin film samples. This is a double beam instrument controlled by a microprocessor and has a measurement range of 800–185 nm. The ratio of the transmitted light to that of the incident light (%*T*) and absorption data were collected and a base line correction was applied prior to collection of spectral data. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5400 ESCA system. The base pressure during analysis was in the 10^{-9} Torr range and Mg Kα X-ray source ($h\nu$ = 1253.6 eV) at a power of 300 W was used for the analysis. The surface analytical studies were typically performed on 5 mm × 5 mm pieces cut from silicon wafers coated with the film of interest. SIMS analysis was performed using a PHI Adept 1010 Dynamic quadrupole SIMS system capable of depth resolution up to 1 nm. A cesium (Cs^+) ion source operated at 3 kV and 25 nA was used so that oxygen detection can be possible. For depth profile the depth scale was quantified by measuring the analysis craters with a stylus profilometer.

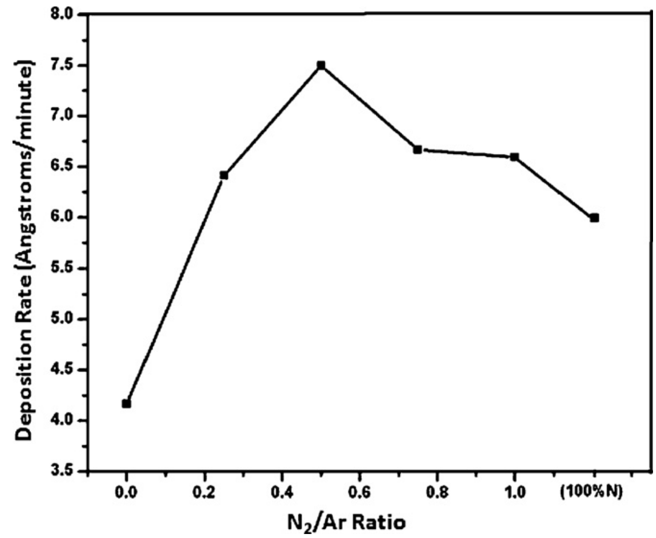

Fig. 1. Deposition rate v/s N_2/Ar gas flow ratio.

3. Results and discussion

Fig. 1 shows the deposition rate of BCN films as a function of N_2/Ar gas flow ratio during sputtering. It is observed that the deposition rate initially increases to 7.5 Å/min when the N_2/Ar ratio increases up from zero to 0.5. Further increase in N_2/Ar ratio causes the deposition rate to reduce to ~6.5 Å/min. This trend can be attributed to the nitridation of the target during sputtering processes. Nitridation of the target refers to poisoning of the target with the incorporation of nitrogen. Initially, with low nitrogen flow the boron and carbon sputtered from the target forms a layer of BCN on the substrate and the thickness of this layer increases with the increased nitrogen incorporation for the gas phase. During this period the rate of formation of a BCN layer of the target surface is less than the removal rate by argon ions thereby maintaining a constant sputtering rate of boron and carbon. As the nitrogen ratio is increased above 0.5, the removal rate drops below the rate of formation, resulting in the formation of a stable BCN layer in the target surface and a reduced overall deposition rate on the substrate. Moreover, when the sputtering was performed in pure nitrogen ambient, a further decrease in deposition rate to 5.8 Å/min was observed. The variation in deposition rate due to poisoning of the target has been reported earlier by Sundaram and Garside [30]. In this paper, they discussed the changes in deposition rate with respect to oxygen content in the sputtering ambient and the trend in deposition rate was attributed to target poisoning with incorporation of oxygen. Aita et al. observed similar behavior for reactively sputtered ZnO films using ZnO target [31].

The elemental compositions of the films were obtained from XPS surface scans. The relative atomic concentrations of boron, carbon, and nitrogen are shown in Table 1. Once nitrogen is intro-