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Pulsed reactive magnetron sputtering of high-temperature Si–B–C–N films with high optical transparency

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ABSTRACT

Multifunctional Si–B–C–N films with exceptionally high thermal stability are becoming increasingly attractive because of their potential applications in coating technologies, and in high-temperature electronics and optoelectronics. In the present work, amorphous Si–B–C–N films were deposited onto SiC and Cu floating substrates using pulsed dc magnetron co-sputtering of a single $(B_4C)_{25}Si_{75}$ target in a 50% Ar + 50% N_2 gas mixture. High-quality defect-free films with smooth surfaces (average roughness $R_a = 4$ nm) were produced. The films, possessing a composition (in at.%) of $Si_{30–32}B_{10–12}C_{2–4}N_{49–51}$, exhibited a hardness of 22 GPa, an effective Young's modulus of 170 GPa and an elastic recovery of 75%. The oxidation resistance of the Si–B–C–N films in air was found to be very high up to 1600 °C. The film materials retained their amorphous structure after annealing in inert gases (He and Ar) up to 1600 °C. Annealing of the as-deposited films in He from room temperature to 1400 °C led to a slight decrease in the refractive index from 1.92 to 1.91 and to an accompanying increase in the extinction coefficient from 3×10^{-4} to 3×10^{-3} (both at the wavelength of 550 nm).

1. Introduction

Amorphous Si–B–C–N films are becoming increasingly attractive because of their potential applications in coating technologies [1–5], and in high-temperature electronics [2,6] and optoelectronics [7,8]. They can provide a unique combination of properties, such as exceptionally high thermal stability in inert gases [9–12] and oxidation resistance in air [10,13], high hardness [3–5,10,14,15], low electrical [16] and thermal [12] conductivity, low thermal expansion coefficient [17], low internal stress [2,3,14] and good adherence to various substrates [1–3]. In addition, the Si–B–C–N films can exhibit high optical transparency [10,15], high photodetection sensitivity [7] and strong photoluminescence [8].

The physical characteristics of Si–B–C–N materials make them suitable for thermal barrier applications such as non-oxide based ceramic coatings for high-temperature protective systems of aircraft and spacecraft, as well as surfaces of cutting tools and optical devices. Moreover, the Si–B–C–N coatings with a low thermal expansion coefficient ($2.2–2.4 \times 10^{-6}$ K^{-1} in Ref. [17] and 2.0×10^{-6} K^{-1} in Ref. [18]), being close to that of carbon fibers, are a possible candidate for a high-temperature protection of novel materials based on carbon fibers, nanowires and nanotubes with the temperature limit of about 500 °C owing to their low oxidation resistance [18]. The multifunctional Si–B–C–N films have also potential to be used in microelectronics where the requirement for high thermal stability, low dielectric constant [19], low electrical leakage [20] and good wet etch resistance, together with high optical transparency [10,15] and optoelectronic properties [7,8], are of key importance.

In our recent papers, a high-temperature behavior of amorphous Si–B–C–N films was investigated up to 1700 °C in flowing air [9,13] and inert gases [9,11]. The films there were deposited by a continuous reactive dc magnetron co-sputtering using a single C–Si–B or B_4C–Si target in argon–nitrogen gas mixtures. The Si–B–C–N films prepared under optimized conditions (B_4C–Si target with a 75% Si fraction in the target erosion area, 50% Ar + 50% N_2 gas mixture, total pressure of 0.5 Pa, rf induced negative substrate bias voltage of −100 V and substrate temperature of 350 °C) exhibited very high oxidation resistance in air and extremely high thermal stability in inert gases (helium and argon) up to 1600 °C. The negative substrate bias voltage of −100 V and the substrate temperature of 350 °C were found to be optimum at the total pressure of 0.5 Pa for preparation of hard densified amorphous silicon-rich Si–B–C–N films with the use of the same deposition system [3,14].

In the present paper, we report on a pulsed reactive dc magnetron sputtering of high-temperature Si–B–C–N films with very high optical transparency. Motivation for this study came from the requirement to avoid micro arcing at the target and thus, to produce high-quality defect-free films with low surface roughness needed, for example, for their applications in optics and microelectronics. Note that Si–B–C–N materials can exhibit very high electrical resistivity [4,14,16,20] (particularly at low C [14] and high N content [16], i.e. including the most transparent and thermally stable compositions), required e.g. for system-on-chip applications. In addition, the pulsed magnetron

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sputtering makes it possible to deposit the films onto floating substrates due to increased kinetic energies of sputtered target material and process gas ions at the substrates. This is of key importance for industrial applications (particularly for production of large-area films).

2. Experimental details

The Si–B–C–N films were deposited on 6H–SiC(0001) and Cu substrates using pulsed dc magnetron co-sputtering of silicon, boron and carbon from a single B_4C–Si target (127×254 mm^2) in a 50% Ar + 50% N_2 gas mixture. A Balzers BAS 450 PM sputtering system was used with a planar rectangular unbalanced magnetron and a stationary circular substrate holder (125 mm in diameter). The B_4C–Si target was formed by a B_4C plate (thickness of 6 mm) overlapped by p-type Si stripes with fixed 25% B_4C + 75% Si fractions in the target erosion area [3]. The magnetron was driven by a pulsed dc power supply (Rübig MP 120) operating at a repetition frequency of pulses of 10 kHz and an average target power of 500 W in a period with a voltage pulse length of 85 μs, leading to a fixed 85% duty cycle. The base pressure was 3×10^{-3} Pa. The total pressure of the gas mixture was 0.5 Pa at a constant total gas flow of approximately 25 sccm. The substrate temperature was set to 350 °C by an Ohmic heater during the depositions onto the substrates at a floating potential. The target-to-substrate distance was 100 mm.

The film thickness was 2.1 μm as measured by profilometry (Dektak 8 Stylus Profiler, Veeco). The elemental composition of the films was determined by the Rutherford backscattering spectrometry (RBS) and the elastic recoil detection (ERD) methods [21], as described in Ref. [3]. The contents of Si, B, C, N, O and Ar were measured by RBS while the content of H was measured by ERD. The RBS and ERD spectra were evaluated by computer codes GISA [22] and SIMNRA [23], respectively. The accuracy of the measurements is approximately 0.1–0.2 at.% for hydrogen and 1–2 at.% for the other elements detected. For structural investigation of the film material, X-ray diffraction (XRD) measurements were carried out at room temperature on a PANalytical X'Pert PRO MPD diffractometer working in the Bragg–Brentano geometry using a CuKα (40 kV, 40 mA) radiation and an ultra-fast semiconductor detector [13].

Surface morphology was determined by atomic force microscopy (AFM) using a Metris 2001A-NC Microscope (Burleigh Instruments) with a Silicon Nitride Supertip (nominal radius of 10 nm) in the contact mode. Film hardness, effective Young's modulus and elastic recovery were determined using an ultramicroindenter (Fischerscope H-100B) according to the ISO 14577-1:2002 E standard. The measurements were performed with a preset maximum load of 30 mN. The refractive index, n, and the extinction coefficient, k, in the visible and near infrared regions were determined by variable angle spectroscopic ellipsometry (VASE) using the J.A. Woollam Co. Inc. instrument. The measurements were performed using angles of incidence of 65°, 70° and 75° in reflection. The optical data were fitted using the WVASE software and an optical model consisting of a SiC(6H) substrate, a Si–B–C–N layer described by a Cauchy dispersion formula and a surface roughness layer (5 nm only for the as-deposited sample). A Cody–Lorentz dispersion formula (leading to the same n, and the same or lower k) was used for cross-check purposes. Thus, the k values shown below should be regarded as an upper bound for this quantity.

Annealing of the Si–B–C–N films on SiC substrates was performed using a symmetrical high-resolution Setaram thermogravimetric (TG) system TAG 2400 in a helium atmosphere (flow rate of 1 l/h) from room temperature to 1400 °C (a limit for thermal stability of the SiC substrate in inert atmosphere [11]) in order to investigate thermal stability of the films and in pure air at the same flow rate from room temperature to 1700 °C (a limit imposed by the TG analysis in oxidative atmospheres, given by properties of a corundum tube which envelopes the heating element) in order to investigate high-temperature oxidation resistance of the films, as described in Ref. [9]. The samples were heated at a rate of 10 °C/min, and then cooled down at 30 °C/min (with no dwell time at the highest temperature). A Setaram Labsys DSC 1600 system was used for differential scanning calorimetry (DSC) in flowing argon (1 l/h) from room temperature to 1600 °C (a limit imposed by the DSC analysis). Dynamic heating and cooling were carried out at the same rate of 40 °C/min. To obtain a sufficient DSC signal and to exclude an influence of a substrate, the Si–B–C–N films were deposited onto polished and ultrasonically pre-cleaned Cu substrates ($25 \times 40 \times 0.5$ mm^3), which were subsequently chemically removed using a 25% nitric acid. After filtering, washing in water and drying, freestanding film fragments were mechanically ground in an agate mortar to prepare a specimen for using in the calorimeter [11]. The film fragments (not ground) were also tested in the TG system in flowing helium (1 l/h) from room temperature to 1700 °C. The heating and cooling rates were the same as in the aforementioned TG measurements.

3. Results and discussion

In the following, we present the results obtained for amorphous Si–B–C–N films prepared using pulsed reactive dc magnetron sputtering onto floating substrates. The as-deposited films, possessing a composition (in at.%) of $Si_{30–32}B_{10–12}C_{2–4}N_{49–51}$ with low contamination level (H + O + Ar < 4 at.%), exhibited a hardness of 22 GPa, an effective Young's modulus of 170 GPa and an elastic recovery of 75%. First, we explain and show the choice of the pulsed discharge parameters (Fig. 1). Then, we evaluate the high-temperature oxidation resistance of these films in air (Figs. 2 and 3) and the thermal stability of the film materials in inert gases (Figs. 5 and 6). In addition, we show defect-free surfaces of the films with low surface roughness (Fig. 4) and their very high optical transparency even after annealing in helium up to 1400 °C (Fig. 7).

3.1. Discharge characteristics

When a dielectric compound is deposited using reactive dc magnetron sputtering, layers of the same dielectric compound or even

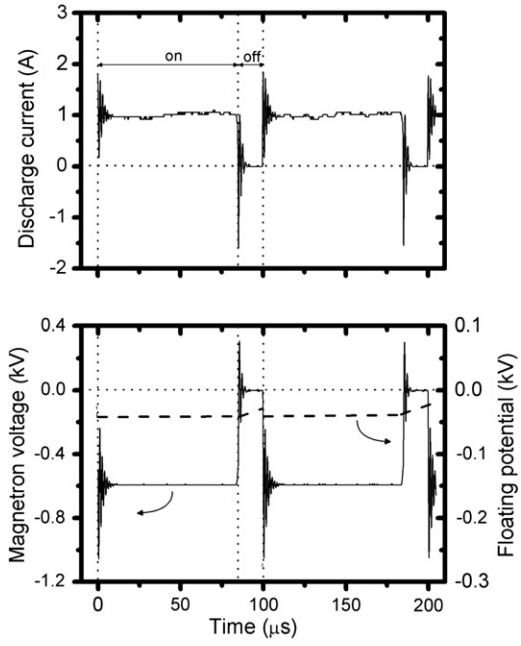

Fig. 1. Time evolutions of the magnetron voltage, the discharge current and the floating potential at the substrate during pulsed reactive magnetron deposition of Si–B–C–N films at an average target power of 500 W in a period, a voltage pulse length of 85 μs and a repetition frequency of 10 kHz for a substrate distance of 100 mm.