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Dielectric barrier discharge assisted chemical vapor deposition of boron nitride phosphide films on a quartz substrate

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ABSTRACT

Boron nitride phosphide films were deposited on a quartz substrate by dielectric barrier discharge assisted chemical vapor deposition. From results of X-ray photoelectron and UV–Vis absorption spectral measurements, the chemical composition of the films may be defined as $BN_{1-x}P_x$, where the mole number (x) is variable between 0.25–0.58, through modifying the PH_3 flow rate in the film deposition process, and the corresponding optical band gap may be modulated between 4.17–3.25 eV. From measurements of X-ray diffraction and high resolution transmission electron microscopy, an amorphous matrix embedded with a hexagonal crystalline phase of BNP with a crystal lattice spacing of 0.35 nm and a textured pattern is observed. The $BN_{1-x}P_x$ films are smooth, well-adhered to the quartz substrate, and display dark resistivities on the order of 10^{11} Ω cm and ultraviolet light photo/dark conductivity ratios higher than 10^3, with negligible sensitivity in the visible region, indicating a potential application in visible/blind UV detectors.

1. Introduction

Cubic boron nitride (c-BN) has received much attention due to its wide bandgap, superior hardness, and chemical and thermal stabilities [1]. The ternary boron nitride phosphide (BNP) compound predicts a tuneable band gap within the ultraviolet (UV) region by adjusting the BP/BN ratio in the ternary compound, due to the suggestion that phosphorus belongs to the same subgroup as nitrogen, acting as an equal-electron center that modifies the optical band gap [2]. Potential applications of BNP for UV photoelectronics are accordingly anticipated.

BNP films have been deposited on an opaque GaAs substrate using a traditional pyrolytic chemical vapour deposition (CVD) method [3], but were unsuccessfully deposited on a transparent substrate such as quartz wafer, due to serious cracking or peeling. For the latter case, more potential practical applications, especially for visible/blind UV detectors, would be predicted for the growth of BNP films on an ultraviolet-infrared transparent ($\lambda > 190$ nm) quartz substrate. In addition, BNP films are difficult to grow using common methods that have proven to be effective for preparing boron nitride films. This is probably due to the difference of their lattice constants and thermal expansion coefficients with those of c-BN, caused by partial substitution of P for N in the BN lattice [4]. Therefore, it is important to develop a practical method for deposition of BNP films on a UV transparent substrate that is favorable for UV photoelectric measurements and UV photoelectric devices.

In our previous report, BNP films were deposited on a UV transparent quartz substrate using a hot filament (HF) and r.f. plasma co-assisted CVD method [5]. Both the high energy from r.f. plasma sources and hot filament- emitted electrons activate the reactants, dramatically decreasing the threshold for chemical reaction and structural modification. However, the metal contamination from very hot filaments seriously deteriorates the deposited films in the HF-CVD process [6]. The film growth rate is considerably restricted due to the low working gas flow pressure suitable for r.f. plasma maintenance, and the complicated processing parameters give poor reproducibility of the resulting BNP films. These disadvantages seriously impede the industrial utilization of the present process on a commercial scale.

In the present publication, we report our results for the deposition of BNP films on a quartz substrate by a novel CVD process. This process is enhanced by a dielectric barrier discharge (DBD) [7,8], which activates the reacting precursors to a higher energy level (1–10 eV) to rapidly achieve chemical reactions for thin film depositions. This process is called the dielectric barrier discharge enhanced chemical vapor deposition (DBD-CVD) method and has received growing attention in recent years [9,10]. The DBD-CVD process may function under a wide range of working pressures (from low pressure of tens of Pa to atmospheric pressure) without fear of forming electric arcs. Thus the necessity for an expensive vacuum system may be eliminated and the workplace size need not be restricted to that of a vacuum chamber. In addition, the allowable high pressure of the working gas flow permits a high concentration of reactive species, so that a rapid reaction rate is possible. The DBD mechanism permits the generation of an excellent source of energetic electrons with 1–10 eV energy in high density. At such high energies, the chemical bonds of reaction

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precursors are easily broken and a lower reaction temperature is accordingly possible.

In the present paper, the chemical composition of BNP films was determined, along with the relationship between their dark and photo conductivities and the corresponding optical band gap. The textured crystalline microstructure of BNP films was also examined. Technical parameters of the DBD-CVD process were optimized in order to achieve BNP films with high dark resistivities, wide optical band gap variation, and high ultraviolet light photo/dark conductivity ratio. A potential application for these BNP films in visible/blind UV detectors was also explored.

2. Experimental details

The dielectric barrier discharge chemical vapor deposition system, which was designed by our research group, is shown in Fig. 1. The DBD power source is capable of supplying a pulse wave output with 0–20 kV peak voltage at an AC frequency of 0–20 kHz. The impulse voltage rise time is below 2 micros (μs). The DBD plasma is produced between two parallel-plane aluminum electrodes with an adjustable spacing of 2–10 mm. Both of the plates have an area of about 5000 mm^2 and a thickness of 2 mm. The upper aluminum electrode is tightly covered and sealed by a piece of silica glass with a thickness of 2 mm (acting as a dielectric barrier layer), and is connected to the DBD power source. The lower aluminum electrode is connected to the ground without dielectric cover. Quartz substrates are placed onto the surface of the lower electrode. All of above components are placed in a vacuum chamber with a vacuum maintained by a vacuum pumping system.

In a typical experimental case, the DBD power source provided a pulse wave output with 15 KV peak voltage at an AC frequency of 12 KHz, with an estimated plasma power per surface unit (Ws) of about 0.35 W/cm^2 through calculation from measurements of current and voltage. The impulse rise time was 1 μs. The spacing between two parallel-plane aluminum electrodes was fixed at 5 mm.

The reaction precursor was a mixture of high purity gases including N_2 (800 sccm), H_2 diluted B_2H_6 (260 sccm; 1.01%,), and H_2 diluted PH_3 (100–300 sccm; 1.01%). The substrate was quartz glass, with working temperatures at 100–400 °C. The background vacuum was 10^{-3} Pa and the working pressure was 200 Pa. A series of film samples was prepared, with temperature changing from 100 to 400 °C, and with PH_3 flow rate changing from 100 to 300 sccm. Most samples had a film thickness of about 1.2 μm with a growth rate of about 1.7 μm/h.

Surface morphologies and cross-sectional patterns of the films were observed using atomic force microscopy (AFM) and scanning electron microscopy (SEM, Hitachi S570). The composition of the films was determined by X-ray photoelectron spectroscopy (XPS: Omicron EAC2000-125X), using monochromatized Mg Kα X-ray (1253.6 eV). The samples were cleaning by dipping in ethanol for at least 1 h, without Ar$^+$ sputtering pre-treatment. It was necessary to use a charge neutralizer as all the samples were insulating. This tends to shift the peak positions by about 2 eV so the binding energies were calibrated to the C 1s peak at 284.8 eV of the surface adventitious carbon. The film compositions were estimated from the relative area intensities of the different high resolution peaks after normalizing with their respective relative sensitivity factors in the XPS software package. The dark conductivity and photoconductivity were measured using a 6517 Keithley electrometer, using planar indium electrodes and a 400 W mercury lamp with the peak intensity at 254 nm as the ultraviolet light source. A Lambda 20 UV/Vis spectrometer was used for optical absorption measurements. Phase composition of the films was analyzed by X-ray diffraction (XRD, Rigaku D/max 2550). The microstructures of the films were observed by high-resolution transmission electron microscopy (HRTEM, JEOL-200CX), together with the selective zone electron diffraction pattern.

The electron energy (electron temperature) of the DBD plasma was deduced from Langmuir double probe measurements [11] as a function of the parameters applied peak voltage (U_p), working pressure (vacuum degree) (P), and discharge gap (d). The estimated electron energy in our typical experimental case is 4.5 eV, which renders a high energy level for rapidly achieving chemical reactions for thin film deposition. Detailed diagnosis of these DBD plasmas is beyond scope of the present report and will be published in the near future.

3. Results and discussion

Fig. 2 shows the cross-sectional SEM and AFM images of BNP films (with a PH_3 flow rate of 100 sccm in the process). Good continuity is evident across the quartz/BNP film interface in Fig. 2a; no cracking or peeling appears, indicating good adherence between quartz substrate and the deposited BNP film. In fact, the value of the adhesive strength obtained by the nano-scratching instruments is 40.5 N, verifying a satisfactory adhesive strength. Fig. 2b reveals a smooth BNP film surface with estimated RMS roughness of 0.74 nm. The kinetic energy of the DBD generated plasma charged particles may efficiently eliminate voids, asperities and rough particles by their surface atomic mobility during the film growth [12]. Thus, we believe that these BNP films with smooth surfaces and good adherence on ultraviolet-infrared (λ > 190 nm) transparent quartz substrates may be favorable for ultraviolet photo-electronic applications, such as for visible/blind UV detectors.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the BNP films. Fig. 3 shows the XPS spectrum for a BNP film with PH_3 flux of 100 sccm in the process. In addition to the constituent elements B, N, and P, the presence of C and O are also evident, which are introduced from the air or sample treatment procedures. Fig. 3a presents the XPS B 1s spectrum. It is observed that the position of the XPS B1s peak in the BNP film is 189.5 eV, which is a chemical shift of about 0.8 eV compared to the standard position (190.3 eV) of B 1s in pure BN film. This phenomenon may be explained

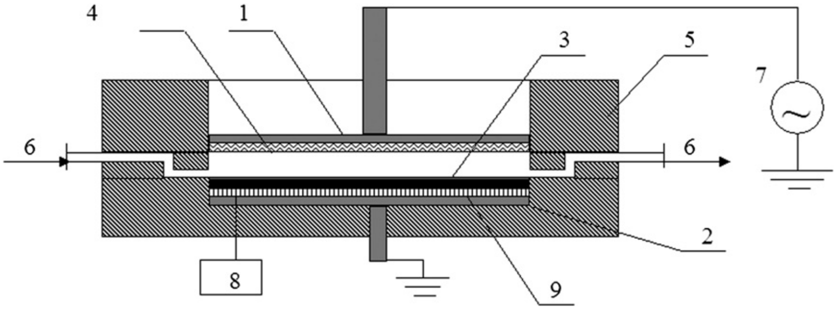

Fig. 1. Schematic diagram of DBD-CVD reactors: 1,2) parallel-plane aluminum electrodes; 3) quartz substrate; 4) silica dielectric plane; 5) stainless steel chamber; 6) planar spacing; 7) DBD power source; 8) temperature controller; (9) heater.