Original Article

Effect of catalysts on BN NanoParticles production

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BNNP of (Boron Nitride) nanoparticlese thick films were grownup on the substrates of silicon and glass through a catalytic hybrid vapor deposited technique (PVD and CVD) in a horizontal electric tube furnace. Which that performed by a growth vapor catching access as guided by the nucleation theory. B-N film was deposited within an 0.5 h at the temperature (950°C) under the mixture of nitrogen N₂ and ammonia NH₃ flow gases. The effect of growth temperature and catalysis surface (TiO₂, Ni, multilayer of TiO₂-Ni and graphene) on the structure and morphology for the powdered films of separate BNNPs were in a systematic investigated. XRD patterns evident the crystal formation phases C-BN as well as phases related to interaction of coating materials with substrates, catalyst of TiO₂ was reflected growth and have highly intensity peaks diffracted for phase C-BN. Scherer and W-H calculations are employing to estimate particle size which that be in range of nanoscale, in addition to compressive and expansion micro strain which that to be (0.00132−0.00027) and (0.0011) respectively. SEM refereed BNNP films grown comprised of dispersed homogeneously with distinct nanoparticles in directions randomly. The BN thick film growth was conducted by the root growth pathway. These nanoparticles existed in a crowded web-like an configuration for the glass substrate, where the substrates whole surfaces were topped of this thick layer nanoparticles, indicating a big output quantity, characteristic of h-BN and C-BN peaks were evidences in the infrared spectra of both Si/TiO₂ and Si/TiO₂-Ni films for the existence of crystalline B-N film.

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1. Introduction

(BN) Boron nitride is fully known as one of the most significant technique ceramic materials with interesting characteristics, like, low density, high strength, great melting point, elevated mechanical strength, respectable resistance of corrosion, superior chemical stability, and distinguish properties of thermal and electric. These give BN an attractive applicant for a wide range of technical uses, especially for requests under conclusive conditions [1–3]. In recent times, a number of works have been informed on the preparation of materials boron nitride with specific morphologies, such as, nanostructures of one-dimensional, hollow spheres, nano capsules, nano cages, structures of porous to gain new remarkable properties and promising applications [4–6]. Furthermore, BNNPs are great more thermally and chemically stable be comparable to CNPs. Up to now, BNNPs have been synthesized through a
2. Experimental set-up

Dissimilar powders of metals were utilized to synthesize the thick films of B-N. In brief, the precursor powders of boron, (Merck), iron oxide Fe$_2$O$_3$ and magnesium oxide MgO (Sigma Aldrich), which that mixed at the molar ratio of (B: Fe$_2$O$_3$:MgO) 2:1:1 mechanically. Then positioned in an alumina burning boat and covered with substrate, and with using of ammonia NH$_3$ as a reactive gas at a relatively high deposition temperature (950 °C) in the (HWCVD) hot - wall - chemical – vapor - deposited system apparatus. A mixture of gas phase deposition procedure technique of physical vapor deposition and chemical vapor deposition (PVD and CVD) which seen Fig. 1 were carried out in the work by a new condition for the deposition as severe film, wherein the precursors were provided in the phase of gas was created by powders which that vaporized with thermal energy, i.e., Reactive Evaporation Process (PVD), during deposition path was fixed on technique of CVD. Mainly the system includes four units along these lines: 1. Powder evaporation unit utilized in present work make up from vacuum tube furnace of high temperature type of (GSL-1600-60X-MTI) that supplied of metal gases to deposition development, 2 and 3. System of gas delivery, is employed to provide all necessary gases toward chambers in a well-ordered mode, (its contains of three feeding lines that is: B0 Base vapor, nitrogen N$_2$ and ammonia NH$_3$ gases). 4. Chamber of deposition, is reactor of deposit thick powdered B-N film. 5. System of exhaust gas to liberate all non - reacted chemical ingredients and with production of reaction various metal powders. The substrates also were cleaned by ultrasonic tool with ethanol for 25 min prior to the process of deposition. Temperature of reaction and flow rating of the carrier gas were exactly controlled. B-N films were deposited through evaporation of the powders with NH$_3$ as reactive gas in this hybrid deposition system. The B-N films were deposited at the same deposition temperature (950 °C) and time duration about 0.5 h, under the similar nitrogen flow rating equal to 2.5 SLPM (Standard Litter Per Minute) under vacuum to about ~10 mTorr. Different coated and uncoated substrates materials were used in this work to determine the catalytic surface effect on the production of the BN Nano. Silicon wafer (100) substrate, Silicon wafer (100) substrate which coated of thin layer from TiO$_2$ powder, thin layer of Ni powder, thin multilayer of TiO$_2$-Ni powders, that were produced by thermal evaporation process, and glass substrate coated graphene which also was produced by thermal evaporation process. (XRD) X-ray diffraction technique for crystal structural study, XRD investigation was achieved with a diffractometer supplied of a X-ray tube Cu – Kα (Shimadzu XRD – 6000), at angular range of 2θ = 10–80 (degree). In addition to the morphology of produced thick film nanoparticles was examined utilizing a (SEM) Scanning Electron Microscope (FEI Company Inspect S50 – Model) joined with an (EDS) Energy Dispersive Spectrometer (x-ray) of (Burker Company - Germany XFlash 6110 – Model).

3. Results and discussions

X-ray diffraction (XRD) results were obtained for evaluating the crystalline phases of the prepared samples which produced from the gas mixtures. Phases detected in the diffractogram are identical and homogenous, as well as proven of presence catalyst materials (coating). Fig. 2a illustrates sample 4 which that clear main phase of silicon Si with peak was identified at angle 2θ = 28 reflected from plane (111) [ICSD card no.53782]. From pattern it can be concluded that the phase diffraction peaks belong to C-BN (cubic Boron Nitride) at position 2θ = 74.32 with Space Group: F-43m (216) of plane (220) and at angle 2θ = 30 of Space Group: F which related to (220) crystal direction, both are in a good agreement with those published in the [ICCD card no.00-035-1365] and [ICCD card no.00-050-1075] respectively. Furthermore, there are reflected deducted peaks (001), (000) and (002) for intermetallic compound phase (titanium boride nitride) TiB$_2$N$_{0.33}$ at diffraction angles 2θ = 26.02, 34.2 and 57.02 [ICSD card no.614878] respectively. Another phases of compound (nickel boride) Ni$_4$B$_3$[ICCD card no. 187403] and (silicon boride) Si1.04B5.82[ICCD card no. 63554] which presence at positions 2θ = 33.6 and 13.2 (as indicated by the inset to Fig. 2a) in the order given. It is worth noticing that the pattern contains of two broadening diffracted peaks centered around angle 2θ = 26.2 and 43.7, it related to planes (200) [ICCD card no.01-076-8389] and (101) [ICCD card no.01-070-7312] for phase BCN (boron carbontiired) are revealed from (Fig. 2b) related to sample10 which have amorphous nature related silicon dioxide (glass substrate). It is probably overlapped by diffraction peak of SiO$_2$ [ICPD Card No.7631-86-9] and layered graphen at the same position 2θ = 26.2. When graphene was loaded on glass substrate, some diffraction peaks from pure SiO$_2$ were overlapped as its surface was covered by graphene particles. The crys-
tallinity of structured materials graphite-like might be valued from the d-spacing along with value of full width at high maximum (FWHM) in XRD spectra. Consequently, it was estimated that the average diameter of prepared powder (sample10) is about to 31.605 nm. Low crystallinity could be owing to various between bonds of B–N and C–C, which forbid complex (BCN) crystal by accomplishing distances of interlayer which similar with those of the pure components parts of carbon and boron nitride. In the other hand, it is reflect which that gained born nitride powder have a low size of crystallite comparable with others. Moreover, it reveals structure of the turbostratic, which the base planes that have glided sideways relation one another, affecting spacing among the planes become larger than ideal. Commonly, this type for structure is described with a lower size of crystallite [3]. Two dominant explanation that might clarify the shaping of that type structure throughout synthesize of BCN powder. First which that (B and N) atoms in a graphite structure are arbitrarily wedged due to variance in radii of atomic among B (0.67Å), C (0.67Å), and N (0.6Å), which that induced glass substrate to curvature and congruently creating of distortion in symmetry of hexagonal. Second is reduced fluidity of structural about the growing tempera-
ture 950 °C. In this situation, constitutive atoms of B, C, and N have dissimilar diffusion grades to the accurate positions of lattice, then are stacking confused or bonding with each other outside of plane.

It was well-known that this crystallinity of the turbostratic BCN may be improved through treatment with a high temperature 2000 °C [6]. Furthermore, small peaks which presence at 2θ = 33.6 with plane (101) reflected to phase β-Si3N4 [JCPDS Card No.12033-89-5]. Sample 6 revealed consequence multiple phases reflected from X-ray diffraction spectra in Fig. 2c (with inset fig) at position 2θ = 30 related to phase cubic BN with crystal orientation of (220) and 2θ = 35.7 of plane (311). Angles 2θ = 14.28 and 25.8 are diffraction peaks positions for (1-2-1) and (05-1) plans, which both display interaction between substrate with coating was noticed through the existing of intermetallic phase of chemical formula Si1.04 B0.82 and phase of Ni4 B3 which identified at 2θ = 47.38 with plane (004).

Fig. 2d (with inset fig) shows the sample 1, it is clearly from X-ray diffraction spectra, the effect of substrate with coating which is unfurl for intermetallic compound phases at positions 2θ = 44.6 for Ti B2 N0.33, 17.38 and 14.2 of Si1.04 B0.82 and 58.9 respect to β-Si3N4 with crystal orientations (00-1), (03-1), (1-2-1) and (311) respectively. Obviously, produced compound phase of cubic boron nitride (C-BN) related to sample 1 was growth (extension of the reaction) and have highly intensity peaks diffraction at angles 2θ = 30.01, 43.1, 50, 76.5 and 26. These phases appear and increase with temperatures greater than 1300 °C [9]. Clearly, all peaks in diffractogram get well clarified during the intensity. Put on heat treatment usually might cause the synthesized materials to reorganize and reoriented their selves, which then give to well evident structure.

Scherer’s equation, a familiar equation in estimating crystallite size which expressed as [10],

\[ B = \frac{k\lambda}{L \cos \theta} \]  

(1)

Where L is the average crystallite size, k is a shape factor dimensionless (typical value of 0.9), \( \lambda \) the wavelength of X-ray (Cu Kα cathode \( \lambda = 1.5405 \) Å), B is (FWHM) broadening of full width at half maximum at the peak after instrument correction and \( \theta \) denote the Bragg’s angle in degree unit.

crystallite size and internal stress are estimated applying Williamson hall’s methodology [8–10],

\[ B \cos \theta = B_\alpha + B_\varepsilon = \frac{k\lambda}{L} + 2\varepsilon \sin \theta \]  

(2)

where \( B_\alpha \) and \( B_\varepsilon \) are FWHM reasoned with small grain size and internal strain respectively, \( \varepsilon \) is an internal strain. Broadening of location coherent scatter was referable to internal stress and predictable size in the synthesize crystals. Simplifying, using W–H calculations to detect induced peaks broaden resultant for size or strain established on relationship between width of peak and 2θ. Influenced broadening because strain of lattice for powders which reason crystal disfiguration and deficiency:

\[ \varepsilon = \frac{B}{4\tan \theta} \]  

(3)

Through Eqs. (1) and (3) it could be noticed that size of crystal was indirectly portion with \( \cos \theta \) where strain was indirectly portion to \( \tan \theta \). Accordingly, total broaden could be describe with equations of W–H (4) and (5):

\[ B = \frac{k\lambda}{L \cos \theta} + 4\varepsilon \tan \theta \]  

(4)

\[ B \cos \theta = \frac{k\lambda}{L} + 4\varepsilon \sin \theta \]  

(5)

Eq. (5) known as Williamson–hall (W–H) equation in the form of \( Y = m X + c \). Strain and crystal size could be estimation value through linear fitting graph. Slope in addition intercept for plot give from the relative between \( B \cos \theta \) and \( 4\varepsilon \sin \theta \) for prepared nanoparticles. Final estimated results were tabulated in Table 1.

The nature of isotropic for BN crystal is proposed, the strain was uniform in varied directions conducting to crystal with independent characteristics. Size and micro-strain of the experimental clarified broadening for numerous peaks are computed concurrently by least squares manner. As, size of particles go smaller, related to effect of size, then the peaks go broaden and widths bigger. Broadening for peak can also happen due to micro-strains of crystal origin from defects such as twinning and dislocation [8], causing to decrease in grain size. Reasons of that variation can be mentioned to this point which that increasing heating time, hard deformation happen particles of powders put on and leading for increase defects of crystalline like dislocations, point defects, porosity and vacancies of oxygen etc. [11–16]. Absolutely, existence of defects made an increasing of energy of system and than lattice strain. In order to balance mentioned effects dislocations motivate to create new orientations with lesser energy, supposed sub-grain boundary. Heat treatment reasons particles to forming larger grains, so that suggests that particles go larger. Therefore, the large size of particle for sample 1 which have powder deposited on substrate with catalyst coating TiO2. This also accept with advanced crystallinity, with bigger grains denote more of (long range order), and thus more the crystallinity. On other word, crystallite size of ceramic was increased, can be because of recrystallization and crystallite grown which that could have been existence for large quantity of energy. Parameters of crystal lattice are regarded such as equilibrium with distance of inter-atomic whereas that attractive forces for metal ions of nuclear charges are stable via charges with negative for ions of metal. Active charge of nuclear on ions of metal were lessen with in large distances from the nucleus. As forces of compressive have been functional above atoms then the clouds of electron are probably to be derived to nucleus, which that leading to added decreasing in atoms size and causing an increasing with nuclear charges per unit of volume [4–7]. All samples in a average particle size (Sch) 41–36 nm which release negative slop referred to lattice strain are due to fact that deformations in microstructure were compressive, where reverse can occur in case of tensile stress for expansion of lattice. Source of an expansive stress for a nano particles solid is owing to surface layer containing of dangling bonds. Ions of catalyst on the surface substrate for such a nanoparticle are partly coordinated and have un-paired electron orbitals. Each of the dangling bonds forms an electric
dipole resultant in attractive electrostatic interaction among ions increases. When nanocrystalline BN in sample 10 was heated at about 950 °C for period of time 0.5 h exhibit positive strain. Owing to strong oxidation condition which an excess of oxygen may happen on surface layer. This excess oxygen can be provide in interstitial positions, which that in order would leading to an expansion of lattice. Crystallite size it is not a direct technique and not based on observation of any individual crystallites or particles, so the results are only estimated. The reliability of this method is a frequent and questionable subject [11–13]. All estimated results in Table 1 are comparable and identical, which that close to before reported results. Broadening and narrowing for diffracted peaks display the increase and decrease for crystallite size in addition to lattice strain.

Scanning electron microscopy SEM of synthesis films and calculated size distribution are observed in Figs. 3–6 with inset figs. Different coated and uncoated of substrates materials were used to determine the catalytic surface effect on the production of the Boron Nitride nano Particles (BNNPs). Alloying multiple transition metal, Non-metal, and oxide-based materials catalysts have been investigated as catalysts in CVD nanoparticles synthesis. Since such materials remain solid at typical CVD temperatures and exhibit lower catalytic activity (compared to transition metal catalysts), it was conceiving of that these materials would minimize catalyst contamination and were potential candidates for controlled growth. The majority of theoretical investigations into Boron Nitride (BN) growth have attentive on the structural and energetic look of BNNPs cap structures. In our work, all samples treated under the same deposition conditions and the same process sequences to produce the BNNPs thick film by using of the hybrid deposition system equipment’s [2,4]. This was made to eliminate any other parameter that can affect the BN films production. In Fig. 3(a,b) the SEM images reveal the surface topography of the BN thick film that was produced on Silicon wafer (100) substrate (Sample 9). In this figure the surface is characterized by the exissive growth of the Boron Nitride Particles to reach the range of the nanometer size as there is evidences of some of the Boron Nano Particles. Extensive studies show that Nano Particles growth during CVD with supported catalysts occurs via one of two pathways, depending on the catalyst-substrate interaction strength. When the catalyst-substrate interaction is weak, growth occurs by the “tip-growth mode”, where Nano Particles diffuses from the top of the catalyst to the catalyst-substrate interface causing the catalyst to lift off from the substrate; as the BNNPs grows longer, the catalyst continues to move further away from the substrate. When the catalyst-substrate interaction is strong, growth occurs via the “base-growth mode”, where the catalyst remains anchored to the substrate during growth. Smaller particles about 100–20 nm were suggested to grow via a root growth pathway, as closed, flat BN caps were observed [15–20]. Conversely, particles with diameters greater than 100 nm were suggested to produce via tip growth pathway.

In Fig. 4(a,b) the SEM images disclose the surface topography of the BN thin film that was produced on Silicon wafer (100) substrate that coated of thin layer Titanium oxide(TiO₂) (Sample1) was found to be in the range of the 24.0331 nm which suggested that the BN thick film growth was conducted by the root growth pathway.

The catalytic TiO₂ thin layer was produced by thermal evaporation process on the Si substrate. In these experiments, the proposed growth mechanism involved the formation of vapor phase B₂O₃, BO and B that form clusters before reacting with NH₃ to form solid-phase BNNPs. Here boron nanoparticles act as solid-phase catalysts and subsequently confine the particle Nano size. Small amount of non-tubular forms of hexagonal BN, preferably BN flakes [5–7], may also be produced simultaneously due to the lack of catalyst surface film in these samples. Some of BN nanoparticles self - crowd up to several hundred micrometers long on top of the nanoparticle layer. Reactions of chemical and require of catalyst suggesting a new mechanisms of formation BN nanoparticles. In Fig. 5 (a,b) the BN thin film was produced on Silicon wafer (100) substrate coated with thin multilayer of TiO₂-Ni (sample 4) that was produced by thermal evaporation process. As a number of substrates have been shown to be catalytically active using this approach, Ni is one of the most popular substrates for CVD of high-quality h-BN production. In Fig. 5 small amounts of the produced Boron Nitride nanoparticles are the main characteristic of this sample, where the BN particles were in the size of 16.31021 nm which suggested that the BN thin film growth was conducted by the root growth pathway. The glass substrate (Sample 10) coated with thin layer of graphene surface is shown in Fig. 6(a,b). This surface was homogeneously topped with a thick layer of a large number of Boron Nitride Nanoparticles. These nanoparticles were existed with a dense of (web-like) shape. As seen in this figure, the entire surface of the substrates have been covering with this thick nanoparticle layer, signify a large quantity production. Obtained layer with thickness of the was around 12μm. SEM image in Fig. 6 revealed that nanoparticles have a regular diameter about ~16.40475 nm.

So that additional access chemical compositions of prepared samples, and special distinguishing chemical of bonding with the types which that have indirectly evidence through XRD pattern. FTIR investigations were achieved on
the BN thick film samples. Fig. 7 shows typical IR spectra in the infrared region of the BN films produced in the hybrid deposition system at 950 °C, with using of NH₃ as a reactive gas, and under the same nitrogen flow rate that is equal to 2.5SLPM. A transparent Si wafer substrate were used in IR test, which were measured utilizing the transmission manner. Si sample without catalytic surface layer shows the effect of poor catalytic surface film that results in poor not homogeneous IR spectra, where our BN films do not product C-BN peak but then product peaks for B–O–Si, B–O and B–OH that appears at 921, 1193 and 1450 cm⁻¹ respectively [11–14,21]. The infrared spectra of both samples Si/TiO₂ and Si/TiO₂-Ni films showed the existence of crystalline B-N peak that was modified by the catalytic surface film mechanism as it can be used for both situations, IR peaks at about 1400 and 800 cm⁻¹, characteristic of h-BN, and the C-BN peaks at about 1100 cm⁻¹ that can be seen in Fig. 7. One important note is that all the prepared films exhibited two IR bands clarified characteristic for boron nitride, with a high band at around 1375 cm⁻¹, which that as a resulting through stretch of B–N plane bond, and a feebler band at about 800 cm⁻¹, which is referable from plane of B–N–B bending mode. Also, for the glass substrate that was coated with thin layer of graphene surface, the IR spectrum show distinctive peaks at 1065, 1138, 1247 and 2150 cm⁻¹ could be analogous with bond of C–N. FTIR spectrum propose to presence of the C–C bond at 1357, 1589, and 1863 cm⁻¹ for the glass sample as it can be seen in Fig. 7
4. Conclusions

BN Nanoparticles have been deposited on different catalytic substrates utilizing a mixed gas phase for technique of deposition synthesize through PVD with CVD using a new procedure for hard films production. Depending on the catalyst–substrate interaction strength. The effect of growth temperature and catalysis surface materials (TiO₂, Ni, multilayer of TiO₂/Ni and graphene) on the structure and morphology of the particular BNNPs films were investigated systematically. XRD patterns evident the crystal formation phases related to coating substrates kind. Catalyst of titanium oxide TiO₂ was revealed growth and have high intensity diffraction peaks for phase C-BN. Scherer and W–H calculations are employing to estimate size of crystallite which that be in range of nanoscale, as well as compressive and expansion micro strain (0.0013–0.0002) and (0.0011) respectively. SEM show BNNP films grown comprised of dispersed homogeneously as clear nanoparticles in directions randomly. The BN thick film growth was conducted by the root growth pathway. That existed in a crowded web-like an shape for the glass substrate, where the substrates whole surfaces were topped of this thick layer nanoparticles, indicating a big output quantity. The FTIR spectra suggest the presence of both the C–C and the C–N bonds along with characteristic of h-BN and C-BN peaks for the deposited samples.

Conflict of interest

The authors have declared no conflict of interest.

REFERENCES


