

Transistor Package's Boron Nitride Film Microstructure and Roughness: Effect of EPD Suspensions' pH and Binder

Jayaganasan Narayanasamy¹, Kok-Tee Lau², Muhammad Zaimi Bin Zainal Abidin²

¹*Infineon Technologies (Malaysia) Sdn Bhd, Free Trade Zone, Batu Berendam, Melaka, Malaysia.*

²*Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Durian Tunggal, Melaka, Malaysia.*

Jayaganasan.Narayanasamy@infineon.com

Abstract— Boron Nitride (BN) film is increasingly used in various applications like lubrication, releasing agent, thermosetting insulator material, thermal enhancer etc. Limited studies were done on electrophoretic deposition (EPD) using BN particles for industrial application. EPD is potential coating method for automotive, appliance and general industrial parts, because of its capable to do deposition on the complex geometry shape, achievable controllable thickness, easy setup, and low cost process set-up. BN stability in EPD suspension is important to produce repeatability and reproducibility deposition result. EPD process was characterized by evaluate dispersion medium (water, Acetic acid, Sulphamic acid & Ammonia) and binder (PEG, Silane Coupling Agent, Poly cationic 1 – PC 1, Poly cationic 2 – PC 2). Dispersion medium was evaluated suspension stability at different level of pH, acid (pH 2-pH 6), neutral and base (pH 8 – pH 11). Binder was used to enhance bonding strength of the deposited micron size particle on the substrate. The study was used sedimentation test to identify suitable dispersion medium and binder (charging agent) for BN particles. Stability of dispersion and binder medium was selected based on the particles dispersion and settling rate was evaluated by sedimentation test. Our result indicates combination of water medium and polycationic 2 gave the high BN suspension stability and compact EPD film. It also found that Polycationic 2 concentration from 0.2 - 0.7 wt% was increased the surface roughness of the deposited BN film and optimum roughness was achieved 825 nm with 0.7 wt%.

Index Terms— Thermal conductivity; Dielectric strength; Sedimentation test; Transistor outline package.

I. INTRODUCTION

Boron Nitride is a synthetically manufactured ceramic substance with the chemical formula BN. Boron nitride (BN) is the less investigated III-nitride materials, now it has gathers researchers' interest due to its interesting properties and close similarities with carbon [1]. BN can be existed in various forms; it can form crystals with either sp³-hybridized (cubic (c-BN) or wurtzite (w-BN) phase) or sp²-hybridized (hexagonal (h-BN) or rhombohedral (r-BN) phase) bonds [1]. Hexagonal boron nitride (h-BN) has a similar structure like graphene [2, 13]. No functional group is present on the surface of the basal plane of BN particles. It has functional groups

such as hydroxyl and amino groups on the edges planes [4]. BN has a very good chemical stability, which is a drawback for a filler as it could not form chemical bonding with the matrix easily. Therefore, despite the large number of amino groups, further surface treatment is necessary to make reaction sites available on the particle surface [5, 6].

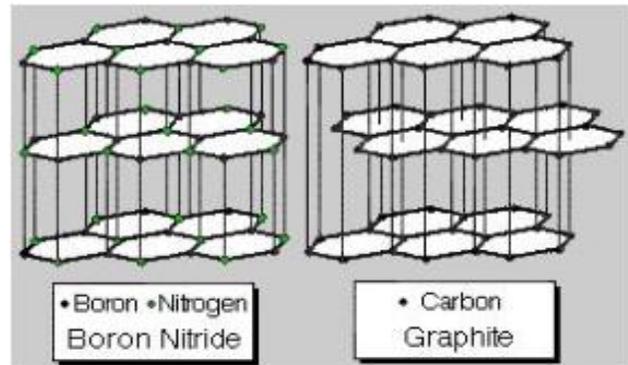


Figure 1: Structure of Boron Nitride (Left) and Graphite (Right) [1]

Table 1
Below listed typical benefits and applications of Boron Nitrides [7-10]

Benefits	Applications
Thermal conductor	As an additive to various types of heat radiation material
Electrical insulator & Low dielectric constant /loss	Electronics as substrate for semiconductors, microwave transparent windows, seals, electrodes and catalyst in fuel cell and batteries.
High temperature stability	Aeronautics and Space applications
Lubricious	as mold release agent for Plastic Injection and Metal Injection Molds
Inert and chemically stable	used in manufacture of crucibles, boats, molten metal carrier pipes, pumps, thermocouple protection sheaths and lining for reaction vessels
Non-wetting	widely used in glass manufacturing process

II. METHODOLOGY

Electrophoretic deposition is a coating method that uses colloidal suspension (i.e. suspension particles are either polymer, glass or ceramic particles) and applied electric field [11]. During the EPD process, the particle is deposited at anode if the surface charge is negative (known as anodic process) and, deposited at cathode if the particle is positive charged (known as cathodic process) [12]. The advantage of EPD is capable to do deposition on the complex geometry shape, achievable controllable thickness, easy setup, and low cost process [14]. The main characteristic of the EPD process is determined by two groups' parameters: i) those related to suspension and ii) those related physical parameters such as electrodes, voltage intensity, deposition time etc. [15].

An electrical isolation and thermal dissipation is one of the key performances that required in miniaturization of semiconductor parts in order to meet technology development. Most of the semiconductor parts manufacturers focus on thermal management or thermal dissipation improvements to extend the product life cycle [16]. Currently, electrical isolation feature is made at the printed circuit board (PCB) stage [17]. The miniaturizations and technology development of semiconductor parts requires the thermal dissipation and electrical isolation features to be implemented at the package development stage. Toshikastu Tanaka [18] claimed that Boron Nitride is the one of the best option engineering materials which is can give high thermal conductivity compare to Alumina. Besides that, conglomerated hexagonal Boron Nitride is the best option to achieved high dielectric strength, but it has low solids loading limit in epoxy composite. Therefore, interest growth to investigate on the deposition of hexagonal boron nitride by using electrophoretic disposition method to achieve compact deposition on the substrate. This paper mainly focuses on the material microstructure, morphology, suspension and binder of electrophoretic deposition on Nickel plated-Copper alloys substrate.

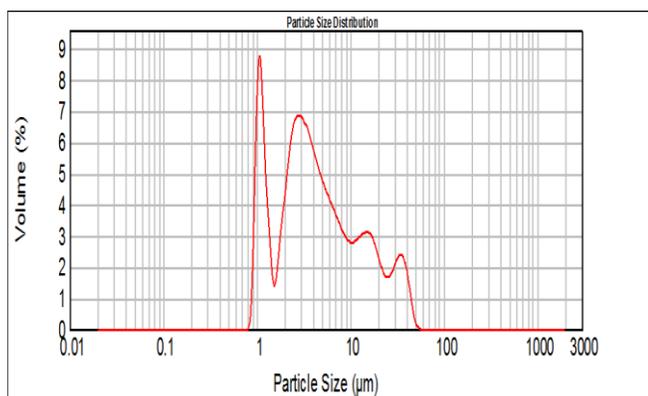


Figure 2: BN Particle Size Distribution

A. Sedimentation Tests of as-Received BN Particles Suspension at Different pH Levels

Boron Nitride (BN) particle with purity of 99.8 wt% was purchased from Nova Scientific. Figure 2 shows the BN particles size distribution with average particle size of 3.8 micron (obtained using Malvern sizer 2000).

BN particles suspension was prepared by agitating (i.e. for 15 min) 0.5 gram as-received BN particles in the 100 mL solutions of acetic acid, sulphamic acid or ammonia. Prior to the particles mixing, the solutions' pH values were controlled at respective ranges: 2.5-6 (for acidic), 8-11 (for basic), 7 (for neutral) by varying the acid or/and base additional volumes. Then, 15 mL of the suspensions were transferred into sealed test tubes. Sedimentation monitoring was performed until 5 days period.

B. NaOH Treatment of BN Particles

BN particles were heated in 5 M NaOH solution at 120°C for 24 hours to form hydroxyl functional groups on the particles surface [12]. The functional groups was necessary for chemical bonding with additives and polymer matrix. After that, the particles suspension were diluted with water and then particles were extracted through filtering process. The rinsing processes (i.e. dilution and filtration) were repeated until pH is reduced to pH 7, with purpose to remove excess NaOH chemicals from the particles. Finally, the particles were air dried at 80°C in oven for 5 hours.

C. Sedimentation Tests for Binder Selection and Suspension Reusability Study

0.1 grams treated BN particles was initially ultrasonicated in 100 mL water for 15 min. Then, different binders were added separately into the treated suspensions. This was followed by 20 min stirring and 15 min ultrasonication. The binders' concentrations were fixed at 0.3 wt% of the BN particles basis [13]. Finally, 15 mL of the suspensions were transferred into test tubes for sedimentation monitoring for 1 day period. Untreated (as-received) and treated (i.e. no binder was added) particles suspensions were also prepared as controlled samples. Details of the compositions of the suspensions are tabulated in Table 2.

Table 2
Chemical compositions of BN suspensions for both sedimentation test and EPD process

Suspension	Solids Loading (mg/mL)	Binder	Binder Concentration
Non treated	1	Nil	NA
Treated	1	Nil	NA
Treated	1	PEG	0.3 wt%
Treated	1	Polycationic 1	0.3 M
Treated	1	Polycationic 2	0.3 wt%
Treated	1	Silane Coupling Agent	0.3 wt%

D. Electrophoretic Deposition of NaOH treated and Binder- added BN Particles Suspensions

EPD was performed on transistor package of Ni-plated Cu alloy substrate at 100 V for 5 min. Ti plate was used as counter electrode at electrode separation of 1 cm. After cleaned with DI-water, the substrate was dried at 50°C for 30 min.

E. Characterizations of BN Film

Sedimentation tests for binder selection and suspension reusability study was performed by measuring pH of the solution using Eutech PC 700 pH meter. The electrode was

cleaned using DI water before and after the measurement. Reading of pH was measured before and after EPD process. After that, 15 mL of suspension was transferred to test tube to perform sedimentation test. The surface roughness parameters (Sa & Sq) were measured by the light source method (SENSOFAR PLu2300). The micro-structural analysis of the samples was performed by scanning electron microscopy (FESEM, Hitachi SU8230).

III. RESULT AND DISCUSSION

A. Sedimentation Tests Results of BN Particles Suspension at Different pH Levels

Table 3 compares the as-received BN particles suspensions' stabilities in neutral, acidic and basic solutions at different pH levels. Stability of the suspension were determined by the sedimentation (viz. settling) rate. Previous study showed that pH levels of suspension controls the stability of particles suspension [19]. This in turns affects the EPD deposition yield. Meanwhile, less reactive weak acids and alkaline were chosen as pH additives because they are more chemical-friendly for BN particles-polymer composite deposition by EPD.

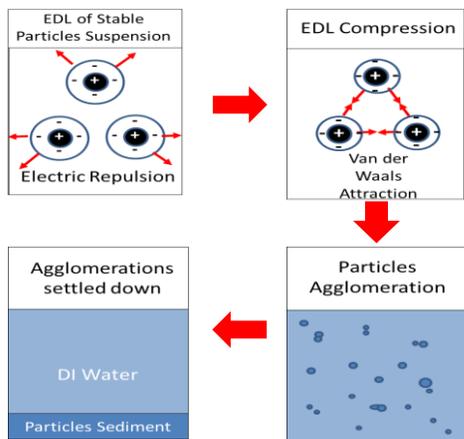


Figure 3: Schematic diagram of the described sedimentation mechanism.

The sedimentation results shows the as-received BN particles have poor stability with the presence of the acid or/and alkaline, as compared to blank BN suspension (i.e. prepared with DI water only). It is speculated that the as-received BN particles have relatively low surface charge and were sensitive to pH change. It is although it was sufficient to produce relatively stable suspension particles in pure DI water after 45 days (as seen in Figure 3). An increase of acid or/and alkaline electrolytes in the water media compressed electric double layer (EDL) of BN particles [15], caused a drastic drop in the suspension particles' electrical repulsion in liquid medium. The decrease in the suspensions' stability accelerated the particles sedimentation process.

Figure 4 shows particles sediment of suspensions with pH additive were thicker and less dense than that of blank suspension (i.e. without acid and/or alkaline). It seems that particles agglomeration occurred immediately after particles were suspended in the acid or/and alkaline electrolytes

environment. When the agglomerated particles settled at the tube base, they formed disorder particles arrangement. This creates highly porous sediment, and raised the sediment height. Agglomeration of particles occurs when individual particles coalesce to form heavier particles. This happens when attractive van der Waal forces overcame the weakening electrical repulsion of suspension particles resulted from EDL compression. The particles agglomerations increase gravity pull on the particles, forcing the particles to settle down at faster rate. Thus, the particles agglomeration was another possible cause of the poor particles suspension stability. Schematic diagram of Figure 3 illustrates mechanism of the particles sedimentation, as per earlier discussion.

Table 3

Sedimentation test results of BN particles suspension at different pH levels

Solution	pH	Sedimentation Rate - Time	Suspension Stability
DI Water (Blank)	Not measurable	Slow	High
Acetic Acid	2.5-6.0	Fast -15 min	Low
Sulphamic Acid	2.5-6.0	Fast -15 min	Low
Acetic Acid + Ammonia	7.0	Fast -15 min	Low
Ammonia	8.0-11.0	Fast -15min	Low

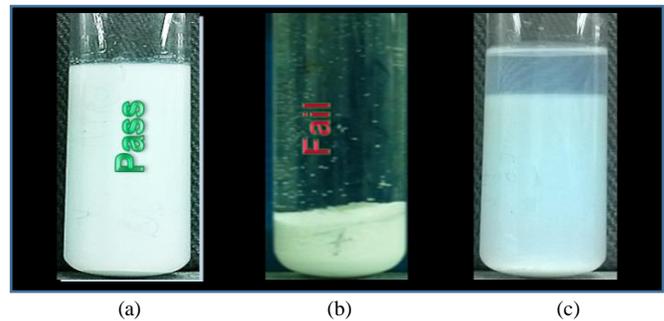


Figure 4: Images of suspensions or/and sedimentation of BN particles in: (a) DI water (after 5 day) (b) acetic acid solution (after 5 days), and (c) DI water (after 45 days)

B. Sedimentation Tests for Binder Selection and Suspension Reusability Study

The addition of chemical binder in the particles suspension was to increase adherence strength of EPD film and to prevent cracking after drying process [20]. However, type of binder used in suspension preparation had a significant influence on the suspension stability. In addition, sedimentation results of post-EPD suspension indicate reusability of post-EPD suspension for subsequent EPD processes. The reusability study of EPD suspensions is an important indicator for manufacturability of coated product through EPD process. In other word, the study is a measure of whether EPD technique can be scaled up to manufacturing level.

Before underwent EPD process, suspensions which had been treated by different chemicals, were stable (i.e. for a day period) and were not distinguishable between the suspensions. All the suspensions did not show particles sedimentation. However after EPD process, their stability (i.e. turbidity) became distinguishable. The highest stability was observed in suspension using PC 1, then was followed by PC2, PEG and silane coupling agent. These suspensions were also had higher

stability than the as-received and blank (i.e. without binder) suspension particles.

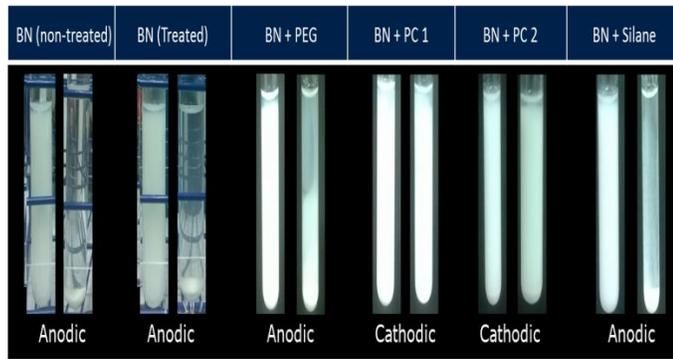


Figure 5: Sedimentation test results (i.e. after one day period) of suspension produced using different binders before (LEFT tube) and after (RIGHT tube) EPD process

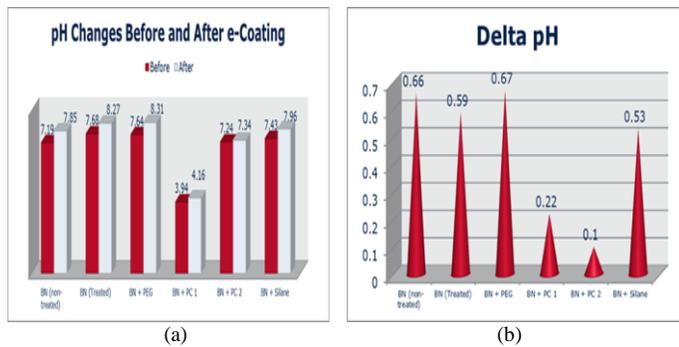


Figure 6: (a) pH Changes, (b) Delta pH, before and after EPD

pH values of suspensions at before and after EPD processes were compared in order to investigate change of ionic properties in the suspensions. Figure 6 shows that the two most stable suspensions (i.e. that added with PC 1 and PC 2 binders) recorded the least changes in their pH values after EPD process (i.e. delta pH). Their pH increased by 0.22 and 0.1 respectively than during before EPD. The suspensions with higher pH increase showed lower suspension stabilities.

Before EPD, pH values of all of the suspensions were located at slightly basic regions, except for suspension added with PC 1 (i.e. at 3.94). As-received BN particles is naturally a basic chemicals, thus their suspension's pH was placed at basic region. NaOH treatment on the BN particles may cause slightly increased in the basicity of the suspension particles. This was illustrated by blank treated BN suspension. Addition of PC 1, PC 2 and silane appear to reduce the basicity of NaOH treated suspensions, and subsequently mitigated the pH increase. Thus, their pH values before EPD were slightly lower than the untreated and binderless suspensions.

After EPD, the observed pH changes in all suspensions were likely due to occurrence of chemical leaching during EPD process. This in turns introduced more basic ions into suspensions. The pH changes in the suspensions had negative impact on the suspension stability, except for suspensions using PC 1 and 2. Any small changes in pH of the suspensions, BN particles tend to lose their stability.

Suspension stability with binder addition appeared to deteriorate less. Zhitomirsky et al. reported that organic binder macromolecules could be utilized to induce steric stabilization, where the macromolecules are attached to the particle surface, or depletion stabilization, in which the macromolecules are free in suspension [21]. The current results showed the steric stabilization increased the stability of the binder-added suspensions (i.e. PEG, PC 1, PC 2 and silane added suspensions).

However, the suspensions with PC 1 and PC 2 had significantly higher stability than the other binder-added suspensions. It is hypothesized that the PC 1 and PC 2 also had the capability to reduce free ions in the suspension media, probably through adsorption by the PC 1 and 2 binder molecules. This may avoid EDL compression of suspension particles, which indirectly increased the suspension stability after EPD process.

C. EPD Results of Surface Treated BN Particles Suspension

Deposition of particles happened at anode (anodic process) for the as-received or binderless treated suspensions, as well as PEG and silane coupling agent added suspensions. While, suspension particles using polycationic 1 and polycationic 2 binders were deposited at cathode electrode (cathodic process). It seems that the EPD yield results were inversely correlated with the stability of the post-EPD suspensions (see Figure 7 for the surface coverage morphology of deposited substrate). Suspensions using polycationic 2 binder produced very smooth and dense BN film as compared to polycationic 1 related suspensions, which produced very rough and incomplete surface coverage film. Whereas, thin layer and incomplete surface coverage particles deposit were deposited using none or binderless treated suspensions, as well as PEG and Silane-added suspensions.

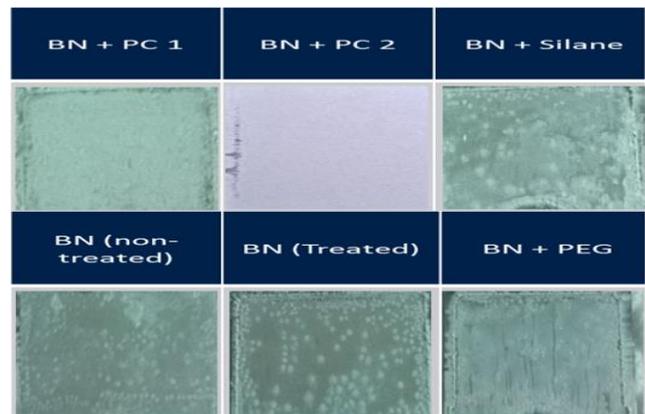


Figure 7: Boron Nitride particles deposited on Nickel plated Copper base material

SEM images of Figure 8 show the suspension with varies range of PC 2 concentration (i.e. 0.2–1.0 wt %) is capable to produce BN particles. It appears that an increase of PC 2 addition level until 1 wt%, improved the density (i.e. reduced porosity) and surface microstructure of the deposited films.

Suspension using 1.0 wt% PC 1 produced smooth and dense films.

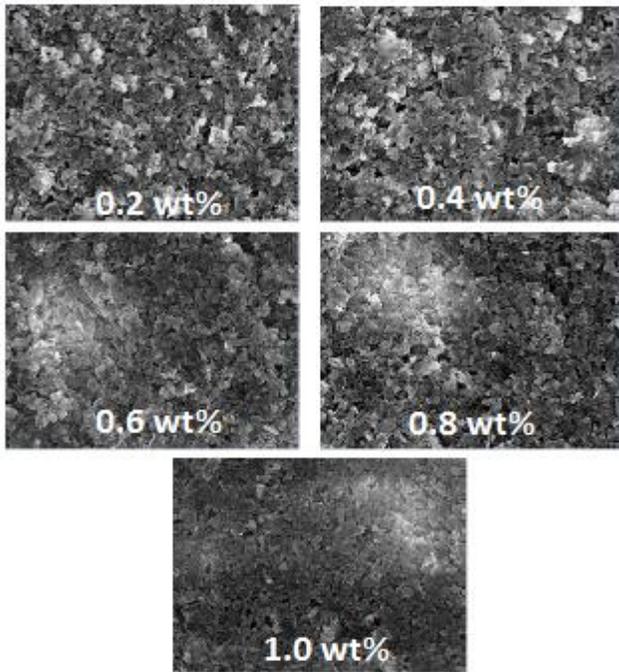


Figure 8: Surface microstructure (10000x) of Boron Nitride after EPD with different Polycationic 2 concentrations (0.2 wt% from BN particles basis)

Surface roughness of deposited BN film (Figure 9) was characterized versus PC 2 addition concentration. The surface roughness increased with polycationic 2 concentration increases at 0.2–0.7 wt% range. At higher concentration until 1.0 wt% PC 2, surface roughness of deposited films decreased. It was found in the previous study that thicker deposition correlates positively with the films' surface roughness [22].

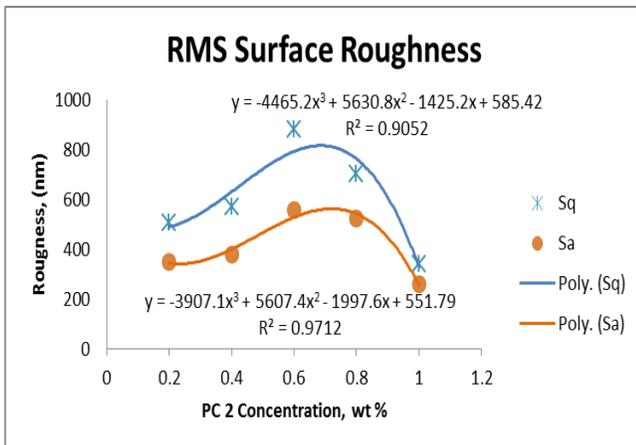


Figure 9: RMS Surface Roughness at different range of polycationic 2 concentrations

IV. CONCLUSION

Sedimentation test and electrophoretic deposition results were assessed to determine the effect of dispersing media,

NaOH treatment and binder additions on the EPD of h-BN ceramic particles. h-BN particle suspensions are very sensitive to the pH changes of dispersing media. Polycationic 2 addition formed fully coverage film and dense as compared to other binders. Surface roughness of the deposited film increased until 0.7 wt% addition level, but then reduced at higher addition level.

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