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Attempts of boron nitride deposition on different substrates under the influence of the electric field present in the reaction zone

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Abstract

Attempts were undertaken to obtain deposits of hexagonal boron nitride under the influence of either the electric field or current of various frequency flowing through the substrate. It was demonstrated that magnetic field as well as electrical potential difference created in the reaction zone both influence the way BN layers are formed. The layers grow with the formation of fine crystallites in the center of the substrate with their size increasing while moving from the center of the substrate to its edges. Distinct correlation between the electric fields line density and the sizes of the crystallites was observed. The distribution of the crystallites depends on current frequency used. It was found that there is an optimal current frequency for which the substrate is covered with the homogeneous layer of BN. The adhesion of this deposit depends strongly on the kind of the substrate used. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Boron nitride is an inorganic compound possessing a number of interesting physicochemical properties [1,2], which in turn result from its several crystallographic modifications. Two

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of them seem to be potentially most useful: hexagonal and cubic BN structure. Boron nitride is chemically a very stable compound (even at a high temperature), it exhibits high and strongly anisotropic thermal conductivity (similarly to graphite), and being an excellent dielectric is highly insulating. That's why hexagonal BN was proposed as a good dielectric for the use in the III-V semiconductors. Attempts have been made to deposit BN on InP in order to develop new technology for insulator formation during the fabrication of semiconductor devices at a low temperature [3–5]. Being chemically inert it can be used as a protective layer resistant against high temperature corrosion. For example, the incorporation of silicon during the GaAs crystals growth from crucibles and ampoules made of silica can be avoided if this process is conducted in BN crucibles or if BN is deposited on SiO_2 as a film to prevent direct contact with the silica wall [6]. Hexagonal BN may also be used in ceramic protective coatings while mixed with B_4C. Since B_4C is an exceptionally hard material, the introduction of softer hexagonal BN phase should increase the fracture toughness and may act as a solid lubricant [7,8]. It can be also introduced into ceramic-matrix composites replacing carbon matrix. Studies of infiltration of porous substrates were undertaken to produce BN coatings on fibers [9,10].

In turn cubic boron nitride is the second hardest material known after diamond. Apart from the possibility of using it as cutting tool material it can be deposited as an insulator on Si. Having high thermal conductivity it may be superior to the other known epitaxial insulators on silicone [11].

Our investigations which we carried out over the last several years using different substrates and $NH_3 + BCl_3$ gas mixtures let us determine conditions necessary to deposit hexagonal boron nitride from the gas phase. These investigations were carried out in an open system. It was found [12–13] that temperature, pressure ratio of the reagents, amount of argon and hydrogen added, as well as the geometry of the reaction zone, may influence the process of the deposition. Thermodynamic analysis of this process was conducted in our previous paper [12]. Theoretical efficiency of the process was calculated as well as the rate of the deposition. Both of these parameters depend strongly on the temperature and partial pressure of reagents in the gas phase. Results showed that the amorphous BN phase formed during deposition process at a low temperature disappears above 1400 K. This result is in agreement with the conclusions of Takahashi's *et al.* [14] work.

Deposition of the homogeneous layer of BN requires lower flow rates, mainly BCl_3, while keeping the ratio of BCl_3 / NH_3 in the range 0.2–0.5. Under higher flow rates the layer becomes nonhomogeneous. In general, the adhesion of the deposit depends on the kind of the substrate used.

In the present paper we report the attempts of hexagonal BN deposition under the influence of either electric or magnetic fields present in the reaction zone. It was decided to check if such external force can influence the structure of the deposit formed on the surface of the substrate.

2. Experimental

The scheme of the apparatus and the experimental procedure were described in the previous paper [13]. The main part consists of the reaction tube in which the reaction zone is placed. From

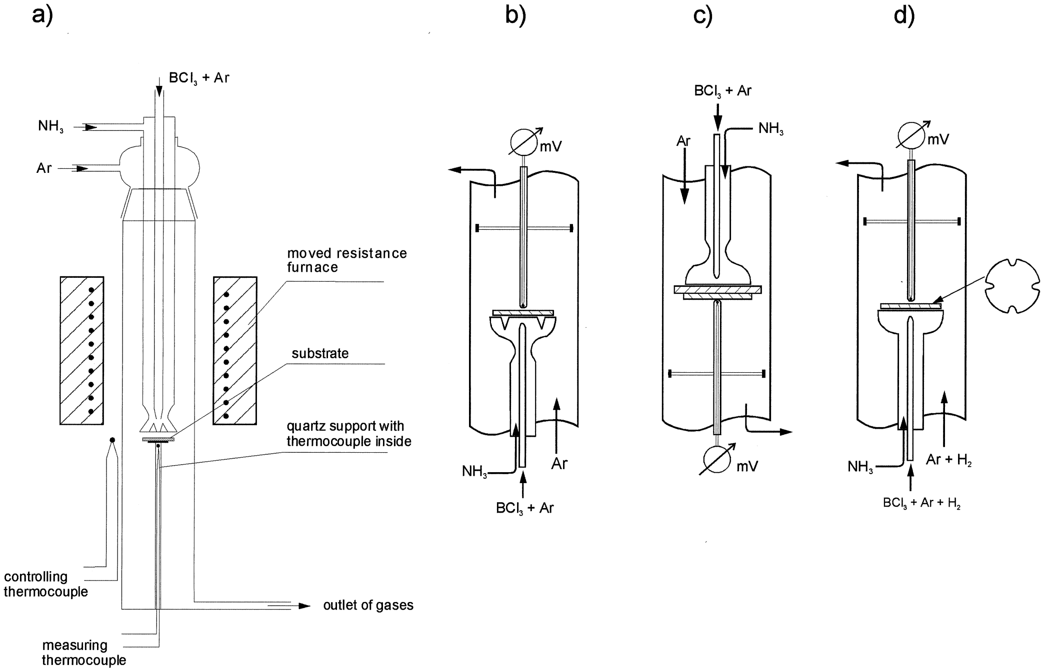

Fig. 1. The schematic diagram of the experimental arrangement (a). (b) gases introduced separately from below. (c) gases introduced separately from above. (d) hydrogen addition into the gas mixtures.

the previous study it was clear that mutual position of radially placed nozzles which introduce gases into the zone, may influence the structure of the deposit. That's why the scheme of the reaction zone shown in Fig. 1 displays several modifications of the gas-inlet system.

Experiments were run under identical conditions of temperature and pressure. The gas mixture with the ratio $P_{BCl3}/P_{NH3} = 0.5$ flowed through the system with the rate 140 cm^3/min and under total pressure of 1 atm. The temperature was kept constant at 1323K. The substrates made of pure nickel and 18/8 stainless steel were cleaned and polished in order to obtain clean and flat surface. Then the sample was placed inside the tube at constant distance from the nozzle which introduced the mixture of gases into the reaction zone. For all the experiments the time of deposition varied from 3,5 to 4.5 min. After this time the flow of BCl_3 was stopped while the obtained deposit was further kept at constant temperature under the stream of Ar + 7% H_2 gas mixture (with NH_3 flow reduced by half) for another 30 min. Then, the total flow rate was reduced and the furnace with the sample was cooled to the room temperature. X-ray diffraction of the deposit obtained in this way is shown in Fig. 2. It demonstrates that hexagonal boron nitride was formed under given experimental conditions. Motojima *et al* [15] suggested that the heat treatment performed at 1273K for 5h in argon stabilized the hexagonal structure of CVD deposits obtained in the temperature range 873–973K. It seems however, that under these conditions only impurities are entirely removed and the transition into hexagonal structure cannot be completed.

Having experimental conditions of hexagonal BN deposition determined, the influence of an external field on CVD process may be investigated. At first, AC current source (I = 0.2A)

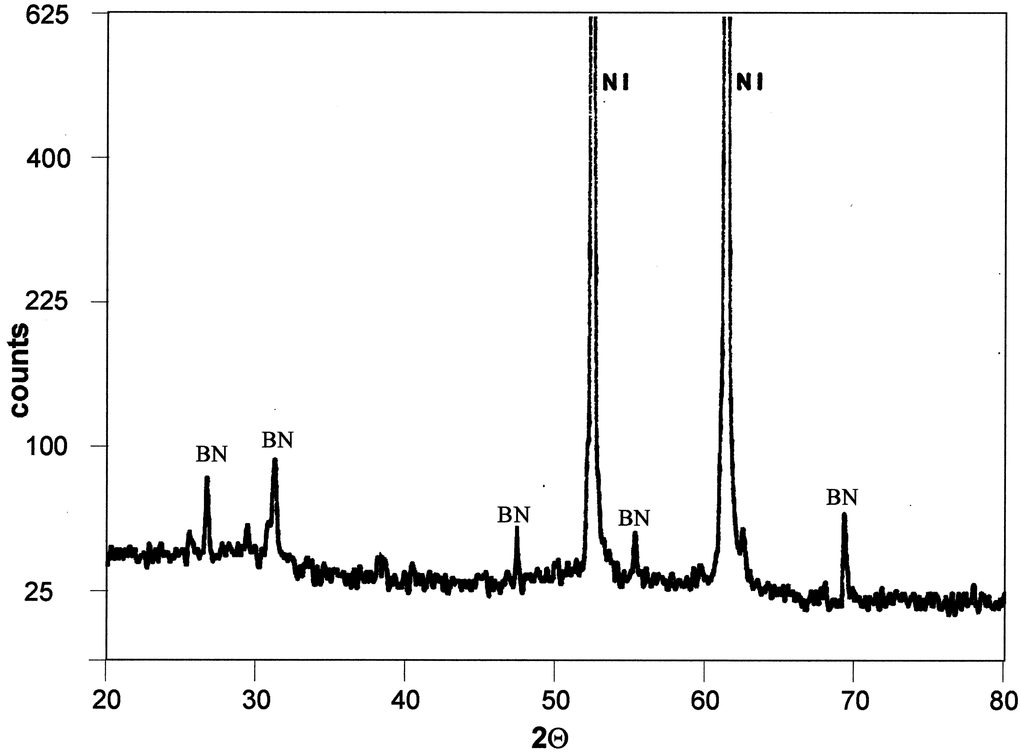

Fig. 2. X-ray diffraction pattern of the vapor deposition BN on Ni substrate at 1323K.

was connected with the nickel substrate. The expected effect was not visible except in the area of the connections of the electric leads to the substrate. The obtained deposit showed weak stripes in this region of the substrate. This effect suggested that the structure can be modified by external factor not directly connected with the chemistry of CVD process itself.

Next, the electric potential difference was imposed upon the substrate. Schematic arrangement of the reaction zone is shown in Fig. 3. Negative potential was connected to the substrate against the positive potential which was connected to the metallic ring introduced into the reaction zone in such a way that the created electric field was perpendicular to the surface of the substrate. Since the current may bring about glowing, and moreover the current flow through imperfect silica insulation is not known, one cannot suggest the direction of the magnetic field in this case. The estimated field density under potential difference of 500V and given electrodes distance is about 60000V/m. In this case the magnetic field effect can be neglected.

Finally, alternating current was used, and the arrangement of the experimental setup is shown in Fig. 4. Maximum current was 0.5A, while substrate resistance is negligibly small. The resulting potential drop across the substrate is of the order of tens of millivolts. This field is not strong since the current is small and there is only one conductor. The current used had the frequency of 50Hz as well as the acoustic frequency. The direction of the field was changing according to sin - function. The deposition process was carried out with the current frequency of: 50, 530, 1060 and 1670Hz. An electronic device assembled and connected to

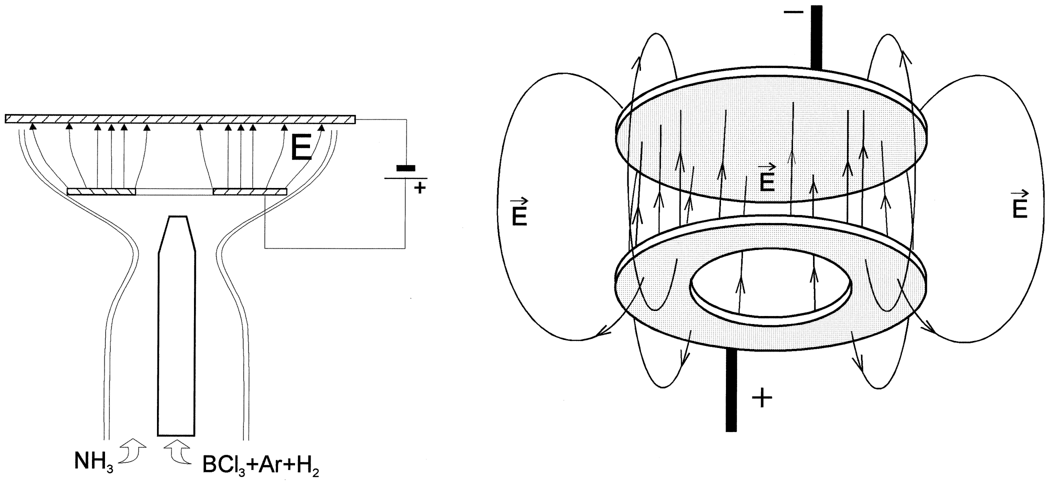

Fig. 3. Distribution of the electric field lines perpendicular to the surface of the substrate.

the circuit let the frequency be changed from 30Hz to 3000Hz with the amplitude changing from sin to step-function. One can assume that electric field has no influence on the process, while created magnetic field acts parallel to the surface of the substrate.

3. Results

All experiments were run at constant temperature of 1323K. Also, the flow of the gas mixture was kept the same for all experiments. Attempts have been made to keep the distance between electrodes identical for all experiments.

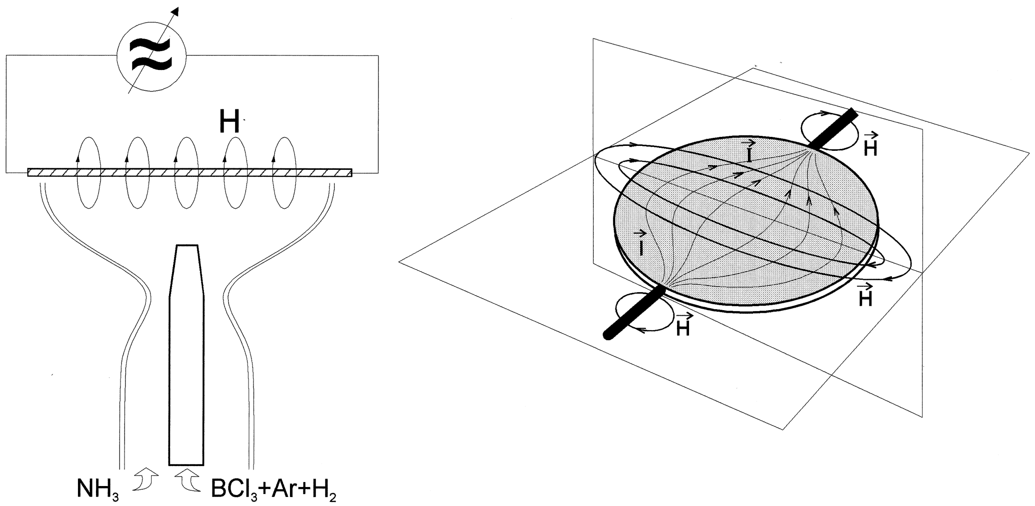

Fig. 4. Distribution of the magnetic field lines perpendicular to the axis of the substrate placed in the reaction zone.

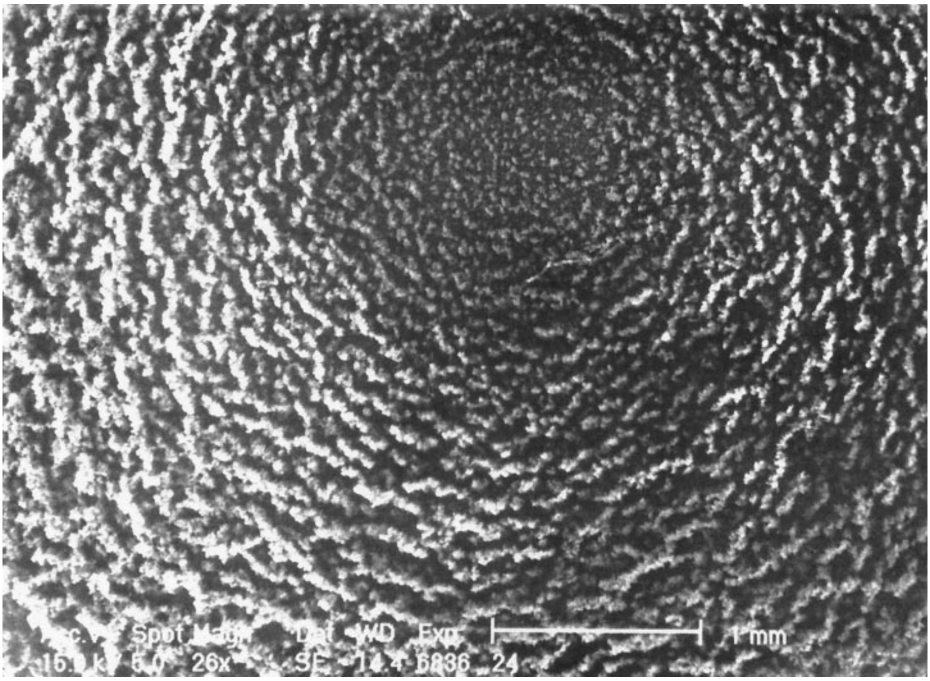

Fig. 5. Scanning electron micrograph of vapor-deposited BN on Ni surface obtained in the presence of the electric current.

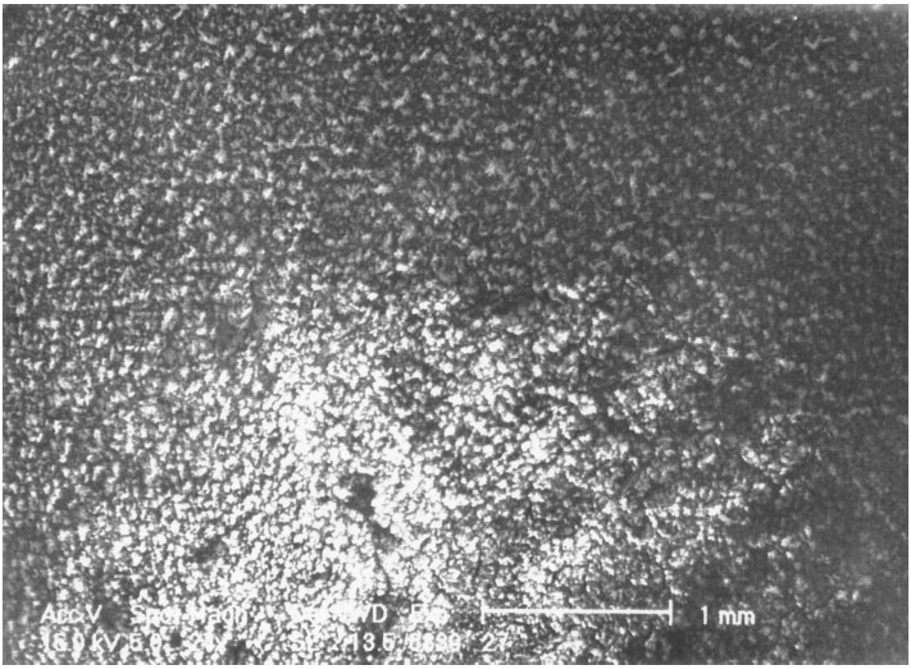

Fig. 6. Surface of the BN deposit obtained at AC current of the frequency 530Hz.

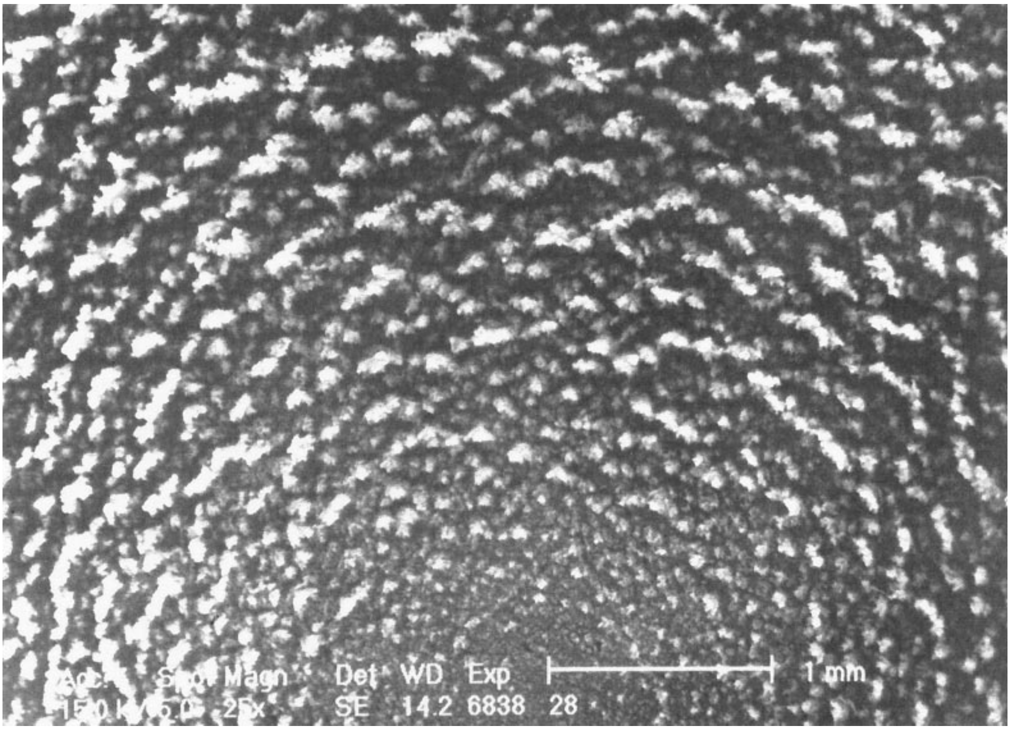

Fig. 7. Surface of the BN deposit obtained at AC current of frequency 1070Hz.

Deposit shown in Fig. 5 was obtained under the electric field perpendicular to the surface of nickel substrate. Minus sign potential was connected to the substrate. It is seen that this deposit is distributed in the shape of coaxial circles with greater amount of deposit concentrated in the region with higher density of field lines. Change in the potential sign on the substrate (i.e. plus connected to nickel) gave no visible effect on the deposit.

Deposits obtained under AC current flowing through nickel substrate are shown in Figs. 6 and 7. The frequency of the current was 530 and 1070 Hz, respectively. Deposit obtained on stainless steel with the current of 50 Hz is shown in Fig. 8. The surface of all samples was prepared in the same manner prior to experiments. In all cases the influence of the field is visible. Deposits grow in the similar centrifugal manner and the current with higher frequency tends to introduce a less uniform distribution of deposit's grains. It was also observed that deposit adheres better to steel than to nickel and its grains are smaller. It seems that there exists optimal field's frequency which yields uniform distribution of the deposit over the surface of the substrate.

The obtained results indicate that there is a possibility to influence the structure of the deposit using external field. It is also clear that the field exerts influence on the mechanism of the reaction of BN formation. Since the effects of the field are seen with minus potential connected to the substrate one may speculate that at least one of elementary steps causing BN formation must involve positively charged particles. Perhaps, it is a radical formation with positive charge.

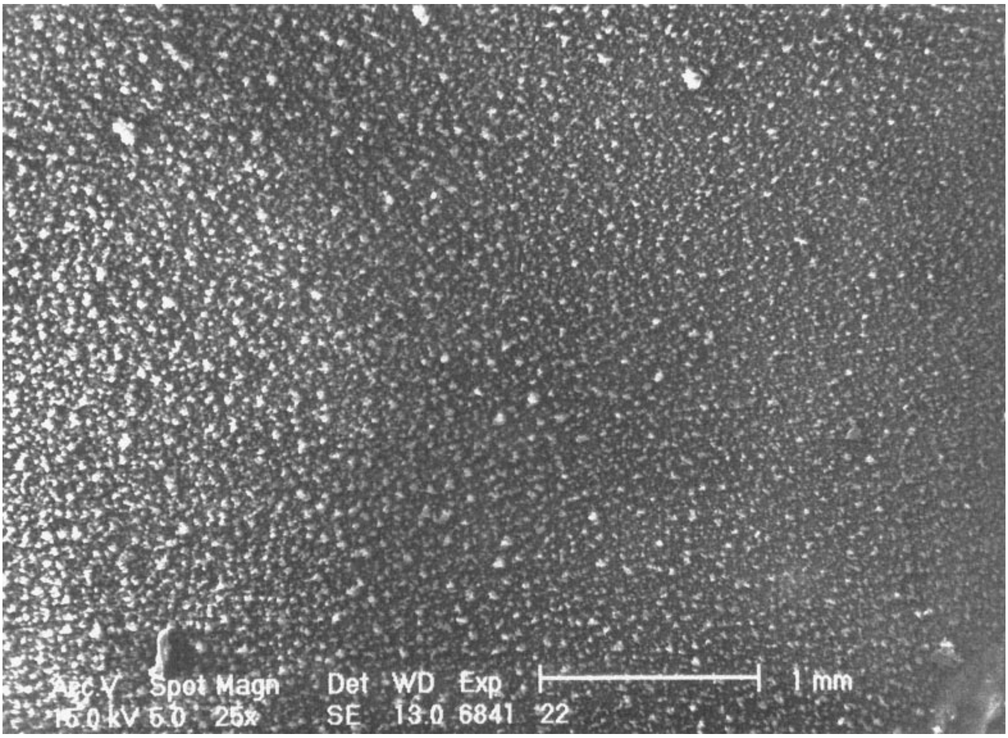

Fig. 8. Scanning electron micrograph of vapor-deposited BN surface obtained on the stainless steel substrate in the presence of the current (50Hz).

The application of the field with variable frequency may cause mechanical vibrations of the substrate and resulting acoustic vibrations in the reaction zone. This may also be the reason of nonuniform deposit distribution. However, since the acoustic wave length is at least several times longer than the distance between grains, it does not seem likely that this wave is responsible for the created structures. It seems that the electric as well as magnetic field are indeed responsible for their formation.

4. Conclusions

a) Attempts to deposit boron nitride in an open system from the gas phase containing the mixture $BCl_3 + NH_3$ showed that the structure of the deposit may be influenced by an external field.
b) The shape and distribution of this deposit depends on the frequency of the current. It seems that there exists an optimal frequency which yields uniform distribution of the deposit over the substrate.
c) Results obtained under electric field may suggest the mechanism of the reaction leading to the formation of the deposit.
d) It was observed that stainless steel substrate is characterized with better adhesion than nickel.

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