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CUBIC BORON NITRIDE CRYSTALLINE POWDERS FOR DIELECTRIC AND HIGH THERMAL CONDUCTIVE THICK FILM LAYERS

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The authors present the results of investigating the c-BN micropowders sized in region 2-10 μm which were synthesized in high pressure/high temperature technique by themselves. The results of investigating the properties of the powders was carried with the use of SEM microscopy, Raman spectroscopy, X-ray analysis and grain size microscopic analysis, chemical analysis.

The powders were applied to prepare thick film dielectric pastes of high thermal conductivity. The pastes were screen printed onto different substrates. The properties of the layers such as microstructure, porosity, dielectric constant, resistance, thermal conductivity, etc. will be discussed.

1. Introduction

A wide band gap of 6.4 eV (the recent dates from private communication - 6.42 eV) of cubic boron nitride (cBN) has made the material to be very attractive for its application in semiconductor and optical devices [1,2]. It is very well known as closest analogues of diamond which suppresses the latter in band gap, thermal, electrical and radioactive resistance, in possibility to emit secondary electrons. As A_3B_5 semiconductor cBN can be easily transformed in n- and p-type (to compare to diamond) and because of very high thermoconductivity it can be used in microelectronics as passive element as well. CBN has been considered as a model material for A_3B_5 group compounds at last.

The real high pressure/high temperatures synthesis achievements of p- and n-type cBN doped by appropriate impurities [3-5] have showed promising prospects for fabrication of p-n junction and ultraviolet light emitting diodes based on the material [6,7]. However, because of technical difficulties of the crystals growth with stable and reproducible properties under HP/HT conditions and in films technologies cBN is still not available for wide practical use. Semiconducting, emitting, optical and electrical properties of real CBN samples are poorly known because of absence of reliable results of their characterization. There are some theoretical efforts in calculation of energetics of vacancies, interstitials and some impurities defects and their interactions in cBN [9-13]. Some methods have been applied for characterization of cubic boron nitride real micro-properties. Among them Raman. EPR and luminescence investigations are presented [14-23].

The application of cBN micropowders for high thermo-conductive thick film layers fabrication is described in present work. The properties of these layers are discussed.

2. Method of synthesis of the powders

The micropowders of cubic boron nitride sized in region 2-10 μm were synthesized in high pressure/high temperature technique. Large - tonnage presses (630 tons) were used.. High pressure apparatuses of "toroids" type (a modified form of the Bridgman-type anvil apparatus) with different reaction volumes were applied for the synthesis. The micropowders synthesis was carried out at temperatures about 1500 °C and pressures about 4-5 GPa via phase transformation in hBN (hexagonal boron nitride) precursors of different types in presence of different sorts of catalysts additionally to

nitrogen rich Li₃N. The light-yellow cBN powders were extracted from synthesis product by application of chemical methods and classified in grains size.

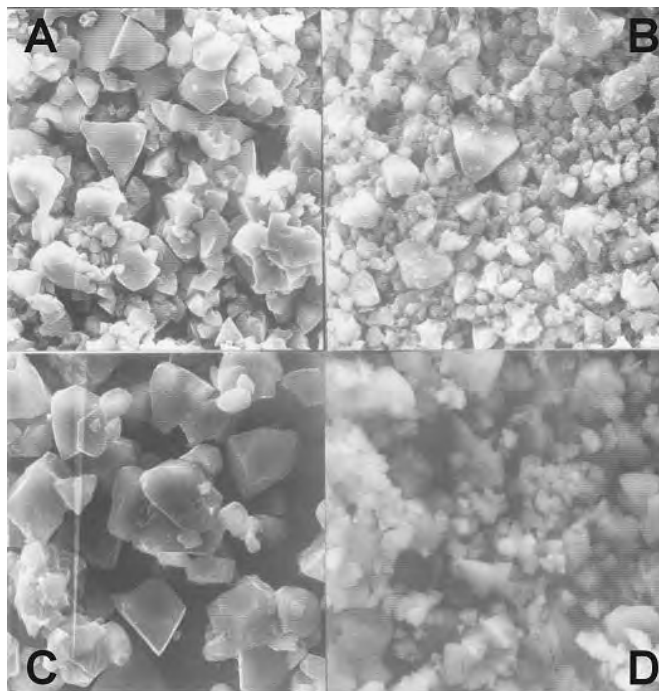
3. Properties of the powders

The grain size and the characterisation of the powders are presented in Table 1. SEM images of four (A,B,C,D) c-BN powder types are presented in Fig.1 which were synthesized in above mentioned technics. It is possible to see that powders are different in sizes and crystallinity. The powder A shows the best crystallinity and the powder D shows the worse one. It is important to notice, that initial precursor for the powder A synthesis was the purest about impurities hBN powder. All X-ray spectra of powders A,B,C,D show traces of hexagonal boron nitride (Fig.2). The powder A does not show traces of any others impurities confirming its the best quality. We managed also to register Raman spectrum of powders using RENISHAW 1000 spectrometer. The spectrum of powder A showed well resolved broadened lines of transverse and longitudinal optical phonons: TO = 1038 ($\Delta=16$) and LO = 1269 ($\Delta= 18 \text{ cm}^{-1}$) cm^{-1} . The positions of the lines are shifted to low wave numbers in full correspondence to micropowder's behavior to compare to a crystal of the same nature. In the powders B ,C and D TO and LO lines appeared as very broad and low intensive. EPR spectra of the powders showed some signals of known paramagnetic centres [18]. Among them signals with $g=2.0023$, $g=2.003$, $g = 2.0018$ ("diamond center") and $g = 2.0013$ („high temperature center") were presented from specimen to specimen. It should be noted that the powder A showed signals with $g = 2.0023$, $g = 2.0013$ and $g = 2.0018$. The centers were considered previously as vacancy, boron-divacancy and analog of P1 center in diamond correspondingly. The powders B,C and D showed the additional signal with $g = 2.003$ ($N = 2 \times 10^{16} - 3 \times 10^{17} \text{ cm}^{-3}$) assumed previously with boron micro inclusions. The results of chemical analysis is shown in Table 2.

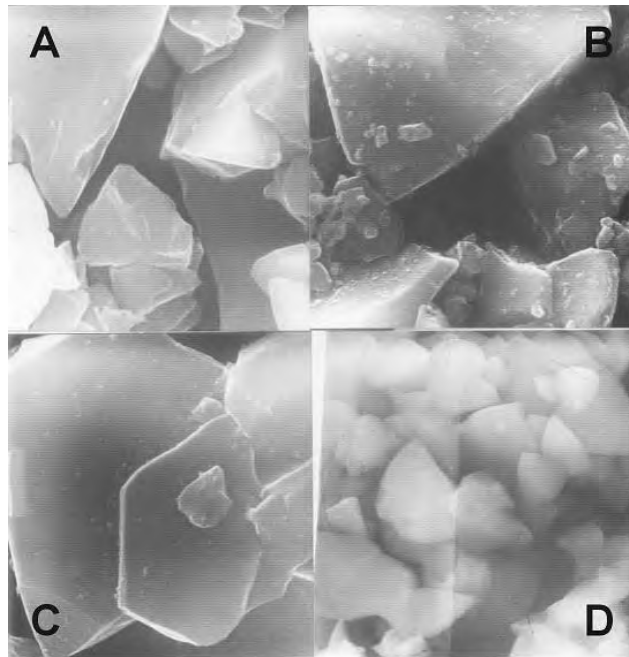
Table 1

The characterisation of elaborated powders

Symbol of powder	Grain size [μm]	Remarks
A	5-6	well defined grains
B	3 –5	not so well defined grains with inclusions
C	7-10	well defined grains
D	2-5	not so well defined grains with inclusions



Magnification 2000x



Magnification 10000x

Fig. 1. SEM pictures of powders A, B, C, D

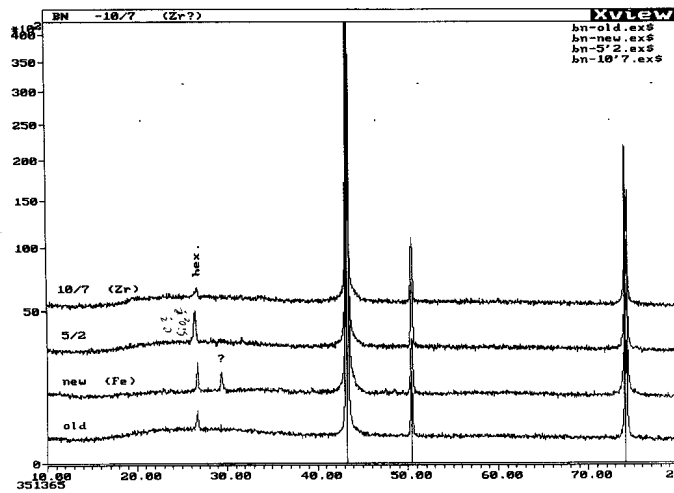


Fig. 2. X ray results for A, B, C i D powders

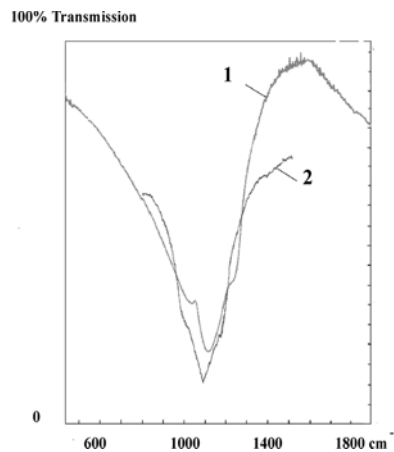


Fig. 3. The results of investigation of powder A with IR

Table 2

Chemical Analysis of c-BN powders

Rodzaj proszku c-BN	Impurities
A	Si, Cu, Fe, Mn, Ca, Ni
B	Mg, Si, Ca, Mn, Fe, Cu, Ni
C	Cu, Ca, P, Fe, Mg, Mn, Si
D	Ca, Fe, Mg, Mn, Si, Zr

2. The properties of obtained thick film layers

The elaborated thick films pastes are the mixture of c-BN powder, glass and standard organic vehicle ethylcellulose in terpeneol. The major component of the paste are particles of cubic boron nitride (c-BN) of different grain size, shape and obtained by different methods. Inorganic glass is supposed to bind together the particles of c-BN and good adhesion of the layer to the substrates. Several glasses have been tested. Most of them did not wet properly the c-BN powder, resulting in porous bulk structure with poor adhesion of the layer to the substrates. Thick films have been obtained by screen printing on (96%) Al_2O_3 substrates, dried and then fired in a belt furnace at 850°C .

The layers made of A, B, C and D powders are sintered much better and exhibit better dielectric properties, as well as better heat dissipation. However the layers of finer c-BN powder (1-3 μm) presented in Fig.4B are smoother than those shown in Fig.4A containing c-BN powder (3-5 μm). It explains why multilayer structures prepared from pastes based on c-BN powder 1-3 μm produce better dielectric properties to the contrast of their heat dissipation ability.

Image microscopic analysis showed that total porosity of the layer made of c-BN powder (BA) of 1-3 μm is 3.2 %, with the mean pores size is 1.61 μm and standard deviation 0.46 μm . Figure 5 presents the derivative (R) and integrate (C) distribution of pores size of the c-BN layer.

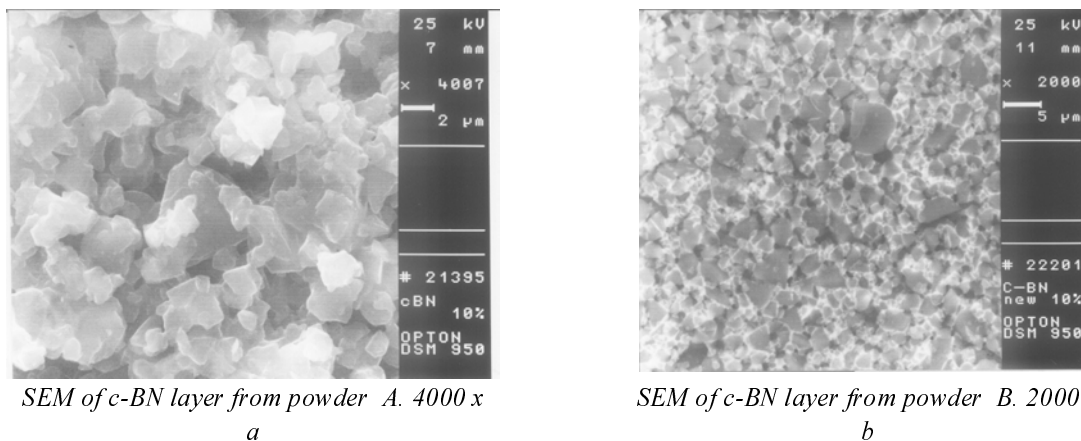


Fig. 4. SEM of c-BN layers made from powder A i B

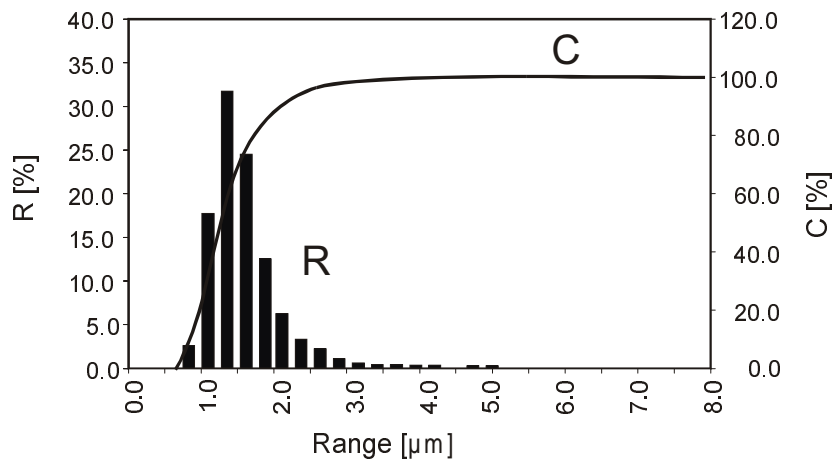


Fig. 5. Distribution of pores sizes of c-BN layer, R – derivative, C – integrate

Dielectric properties of the latter c-BN layer were tested using standard capacitor test . The electrodes were made of palladium silver paste P-202 (ITME). Results are presented in Table 3. The layers exhibit satisfactory dielectric properties.

Table 3

Electrical properties of c-BN layers (powder A)

Number of layers	Thickness μm	C_p , pF	ϵ	$Tg\delta$	Resistivity, $G\Omega$	ρ $\Omega^* \text{cm}$
Two layers, separate firing	74	720	30	0.12	13.0	2.8×10^{12}
Three layers, separate firing	119	410	32	0.12	4.8	3.9×10^{11}

The elaborated c-BN (BA) layers were applied on other than alumina substrates such as silicon, copper, stainless steel, and kovar. The pastes deposited on silicon were fired in air while those on metal substrates were fired in nitrogen with oxygen content below 100 ppm. All layers were fired at 850°C. Fig. 6A shows the c-BN layers on a single crystal Si wafer, (ground or polished) while Fig. 6 B shows the c-BN layers on copper, stainless steel and kovar. In all instances the layers exhibited good adhesion to the substrate. For the non-metallic cases, multiple firings caused no problems.

The elaborated c-BN layers exhibit better heat dissipation properties than alumina substrate. This is presented in Fig. 7. The heat was generated by a one square mm resistor placed on alumina substrate coated with 80 μm thick c-BN layer and on naked alumina, for comparison. The IR camera thermal distribution shows the spread of temperature. It can be observed that the heat is "travelling" much faster on the substrate covered with the c-BN layer.

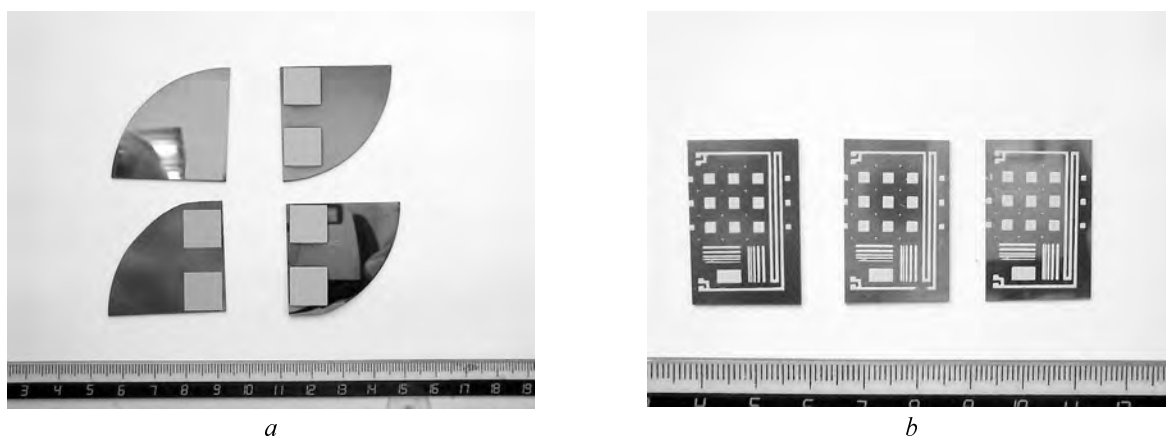


Fig. 6. c-BN thick films (squares) A - on silicon, fired at 850°C in air, B - on copper, stainless steel, and kovar

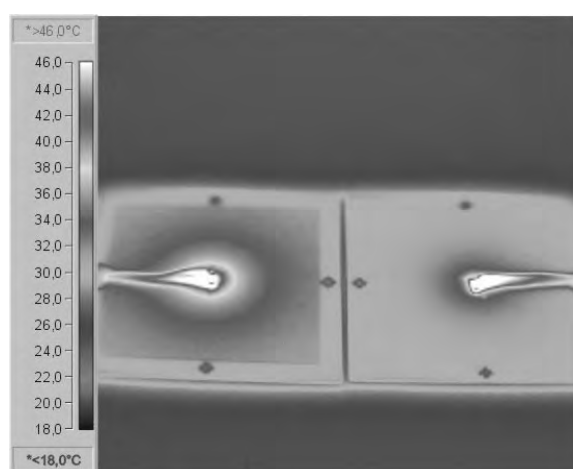


Fig. 7. IR camera thermal distribution generated by a one square mm resistor on the c-BN thick film coated Al_2O_3 substrate (left) and on an uncoated substrate (right)

5. Conclusions

Cubic boron nitride is a very promising material for thick film technology. It has been possible to develop and process a variety of new thick film pastes consisting of crystallites of the zincblende phase of boron nitride (c-BN), derived from HPHT synthesis processes, and a bismuth-silicate glass. The pastes could be readily printed on different substrates such as alumina, silicon and metallic: copper, stainless steel, and kovar. Bonding between the layers and the substrates appeared satisfactory. Initial thermal property evaluations of the films, using IR cameras clearly showed the ability of these prototype films to effectively spread and dissipate heat in semiconductor devices. It could be anticipated that c-BN will find applications not only in heat dissipating films, and as a thermal via material, but also in the engineering of embedded (integrated) passive components in MCIC's, preferably executed in low temperature co fired ceramic (LTCC) technology.

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ПРО КОРЕЛЯЦІЮ МІЖ АКУСТИЧНО СТИМУЛЬОВАНИМ ВІДГУКОМ ТА СТУПЕНЕМ СТРУКТУРНОЇ ДОСКОНАЛОСТІ ТВЕРДИХ РОЗЧИНІВ $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$

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Досліджена акустично стимульована зміна концентрації електронів та спектрів комбінаційного розсіювання світла для твердих розчинів $n\text{-Cd}_x\text{Hg}_{1-x}\text{Te}$. Встановлено кореляцію між значенням ефектів та ступенем структурної досконалості матеріалу.

Sonic-stimulated change of the electron concentration and Raman scattering intensity in $n\text{-Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys was investigated. It was determined that the value of such effects grows at increasing of dislocations and low-angle boundaries density in crystal.

Ультразвукові методи широко використовують у галузі технологічних обробок та неруйнівної діагностики напівпровідників [1]. Проте для того, щоби отримати прогнозований результат обробки кристала, необхідно чітко розуміти механізми індукованих процесів та визначити параметри зовнішнього впливу, які прямо залежать від вихідного стану матеріалу, який обробляється. Ця робота є продовженням дослідження впливу ультразвуку (УЗ) допорогової потужності в режимі динамічного навантаження (*in-situ*) на тверді розчини $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ [2,3]. Метою роботи є визначення впливу ступеня структурної досконалості на величину акустично стимульованого (АС) відгуку кристалів $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ($x \sim 0.2$), який проявляється у зміні параметрів зразків при ультразвуковому навантаженні. Зокрема, був досліджений вплив ультразвуку на спектри комбінаційного розсіювання світла (КРС) та концентрацію електронів.

Параметри досліджених зразків $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, які розділені на дві групи, наведено в таблиці. До першої групи були зараховані зразки з незначною густиною малокутових границь (МКГ), яка не перевищувала $N_{\text{МКГ}} \leq 3 \text{ см}^{-1}$, та густиною дислокацій в межах $N_{\text{дис}} = (10^5 \div 10^6) \text{ см}^{-2}$. До другої групи належать зразки з розгалуженою мережею МКГ $N_{\text{МКГ}} = 2 \div 50 \text{ см}^{-1}$ та густиною дислокацій $N_{\text{дис}} \leq 10^5 \text{ см}^{-2}$. Для виявлення структури поверхні та визначення густини протяжних дефектів зразки були оброблені в селективному травнику: 1ч. 50% розчину CrO_3 в H_2O + 1ч. HF + 1ч. HCl [4]. Час вихідної обробки поверхні становив 30 с при кімнатній температурі без перемішування. Величини $N_{\text{дис}}$ та $N_{\text{МКГ}}$ визначалися візуально за допомогою оптичного мікроскопа NV2E (Carl Zeiss Iena).

Концентрація електронів була визначена методом ефекту Холла та для всіх досліджених зразків знаходилася в межах $(3 \div 5) \cdot 10^{14} \text{ см}^{-3}$, якщо $T = 77\text{K}$. Акустично стимульована зміна концентрації електронів реєструвалася безпосередньо при УЗ-навантаженні зразків. Спектри КРС,