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Allotropic phase transformation induced by UV power laser irradiation of boron nitride

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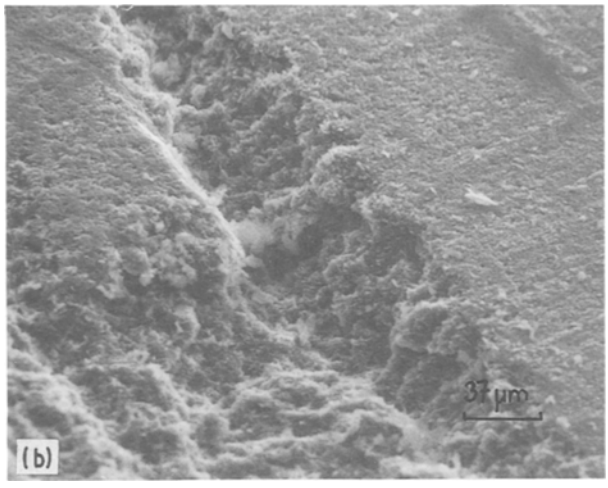
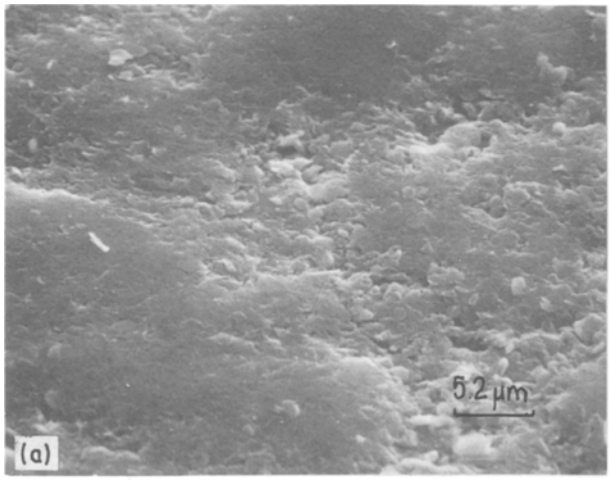
The optically induced allotropic phase transformations of boron nitride were studied. Under irradiation with laser beam of 337.1 nm wavelength, at energy density of 1.9 mJ per 0.1 mm^2 a hexagonal boron nitride transformed into the cubic form. The suggestion is made that the results obtained could be explained by the multiphoton excitation and recombination of electrons.

1. Introduction

Investigations on the effect of UV irradiation on boron nitride have not been published so far. The use of IR laser beam of $\lambda = 1060$ nm for evaporation of a BN target has been described [1]. The phase transformation of α-BN powder into β-BN has been achieved as a result of irradiation with IR laser beam [2]. This transformation was explained as a result of rapid heating followed by quenching. However, in our opinion this interpretation is in disagreement with the fact that the transformation α-BN to β-BN is monotropic, i.e. it should occur only under high pressure conditions. Due to the characteristic similarities and differences of boron nitride and carbon, we decided to examine the effect of irradiation with nitrogen-laser beam on the α-BN ceramics using analogous methods to graphite case (to be published).

As it is known boron nitride is isoelectronic with carbon and in its α-BN form differs from graphite only in the kind of bonds in the plane perpendicular to the σsp^2 plane. Namely, in the case of α-BN there is a polarized σsp^2 bond, not the πp bond as it is in graphite. As a result the α-BN has in its band structure the energy gap of 3.63 eV [3]. Irradiation of α-BN with





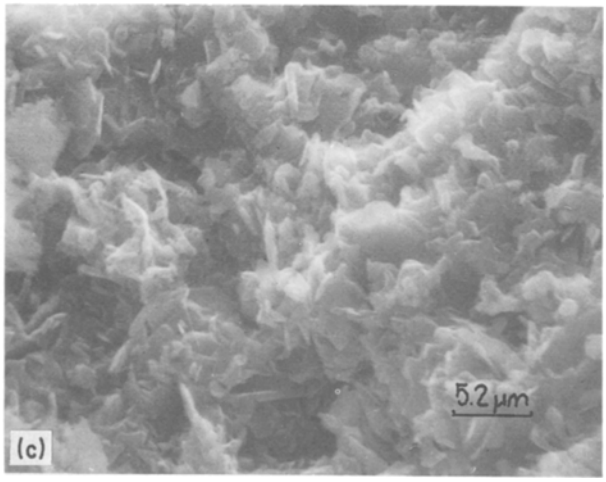


Figure 1 Scanning electronmicrographs of surface of BN sample (a) unirradiated, (b)(c) irradiated.

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the photon beam of energy $h\nu = 3.68\,eV$, emitted by nitrogen laser, may cause the single-photon interband transitions, in contrast to the transitions between π electrons bands, as in graphite. The cubic form of BN has the energy gap of 6.4 eV [4] corresponding with its $\sigma\,sp^3$ band.

2. Experimental

The irradiation was performed using a pulse, vacuum nitrogen laser. The laser generated light with $\lambda = 337.1\,nm$ (3.68 eV) at a repetition frequency, $\nu_r = 95\,Hz$, and pulse width $5\,\mu sec$. The energy of a single light pulse was 1.9 mJ and was measured using chemical actionometry. The laser light was focused on a spot of $0.5 \times 0.2\,mm^2$. The irradiated probe was moved perpendicularly to the light beam at a velocity of 5 to 6 $cm\,min^{-1}$.

A sintered BN plate, applied in semiconductor industry was used as the material to be irradiated. This

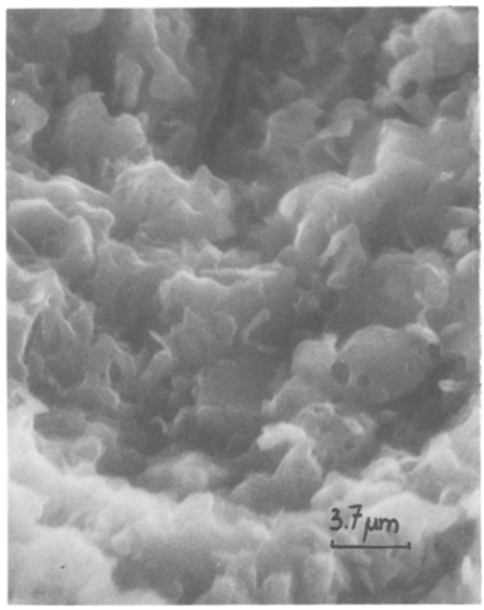


Figure 2 Scanning electronmicrographs of the holes in the lamellae of the BN sample after irradiation.

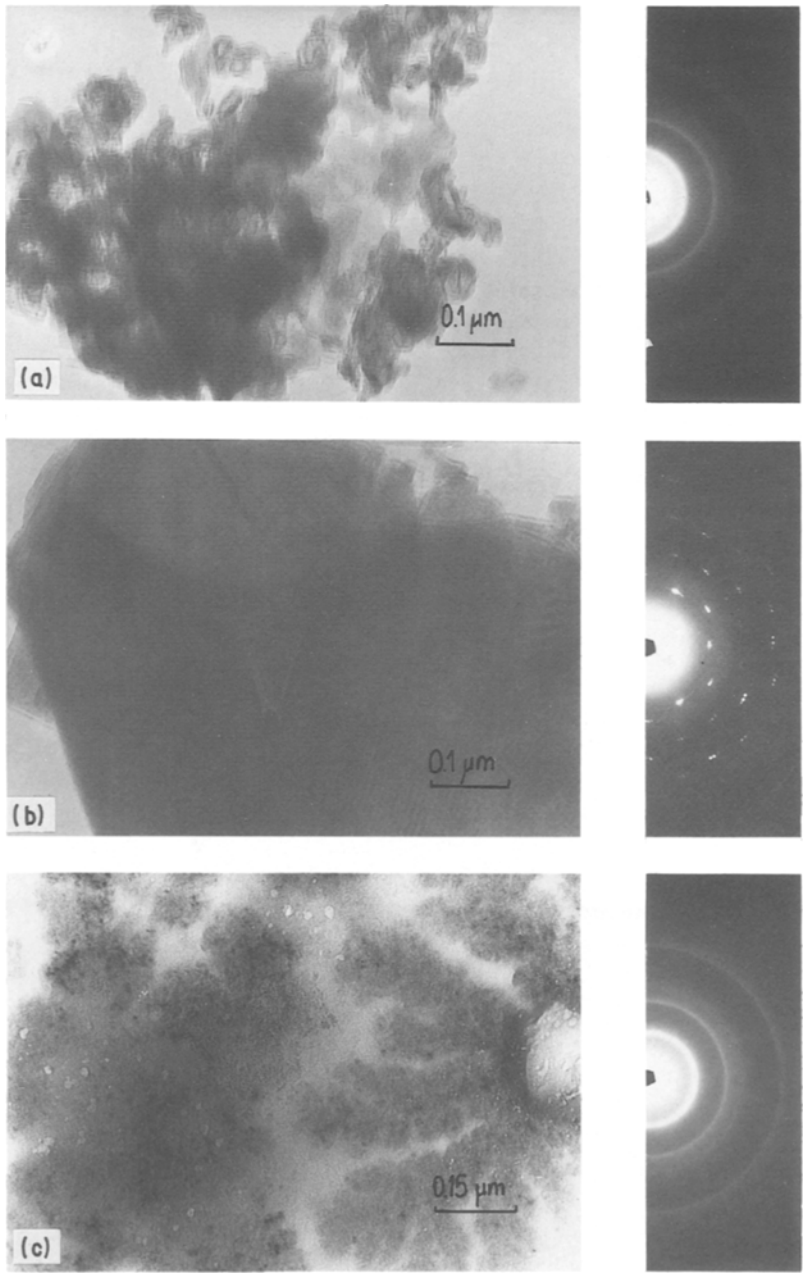


Figure 3 Transmission electronmicrographs of the components present in the BN sample before irradiation.

(a) α-BN

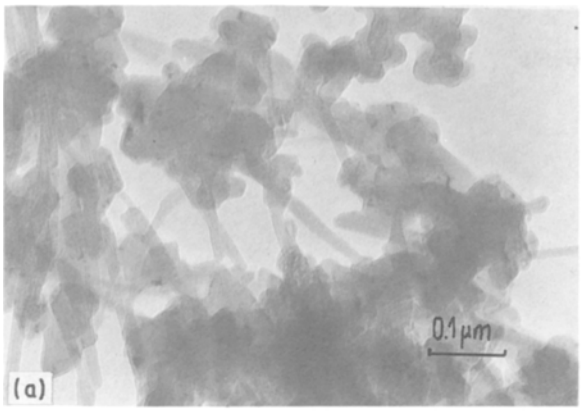
Exp. d(nm)	α-BN d(nm)
0.35	0.333
0.213	0.217
0.173	0.1817
0.123	0.1253
	0.173
0.107	0.1086
0.0816	0.083

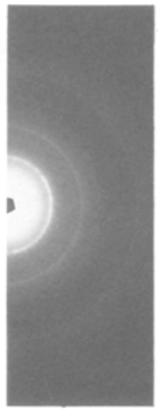
(b) h-B_2O_3

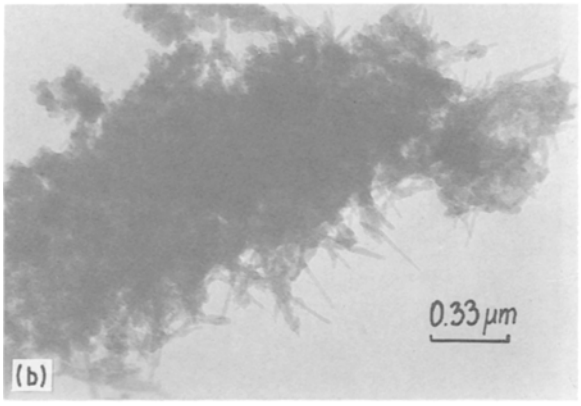
Exp. d(nm)	h-B_2O_3 d(nm)
0.353	0.342
	0.278
	0.223
0.210	0.2096
0.174	0.171
0.123	0.1197
0.107	0.108

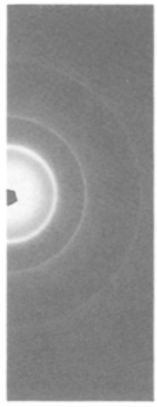
(c) B_7O

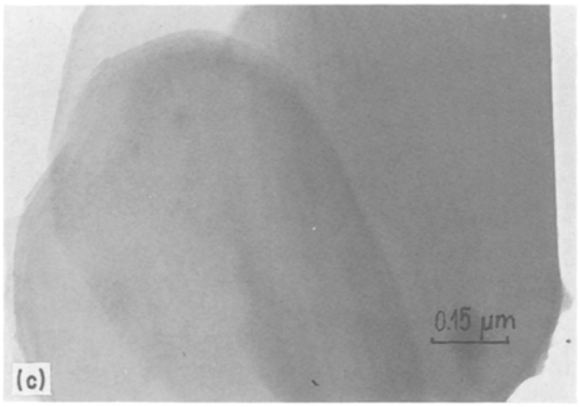
Exp. d(nm)	B_7O d(nm)
0.410	0.4114
0.264	0.2571
0.226	0.2284
0.170	0.1737
	0.1691
	0.1464
0.138	0.1340
0.122	0.1244
	0.1142
0.112	0.1121

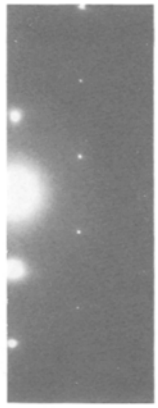


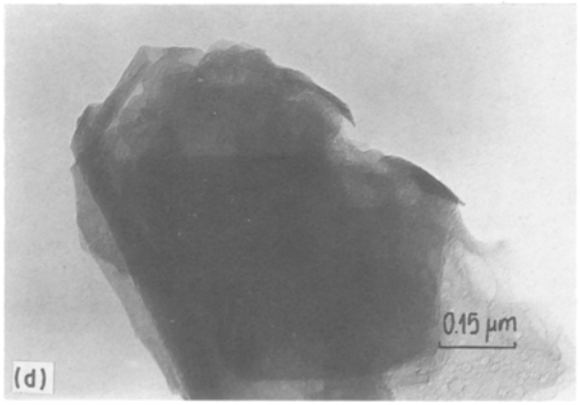












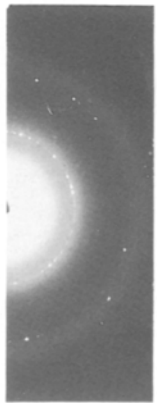


Figure 4 Transmission electronmicrographs of the BN sample after irradiation

(a) h-B_2O_3

Exp. d(nm)	h-B_2O_3 d_{nm}
0.341	0.342
	0.278
	0.223
0.207	0.2096
0.171	0.1710
	0.1403
0.122	0.1197

(b) α-BN

Exp. d(nm)	α-BN d(nm)
0.333	0.333
0.218	0.217
	0.206
0.172	0.1817
	0.1667
	0.1253
0.123	0.1173
0.107	0.1086
0.077	0.083

(c) γ-BN

Exp. d(nm)	γ-BN d(nm)
0.221	0.221
	0.210
	0.196
	0.152
0.124	0.1275
	0.1185
0.108	0.109
0.083	

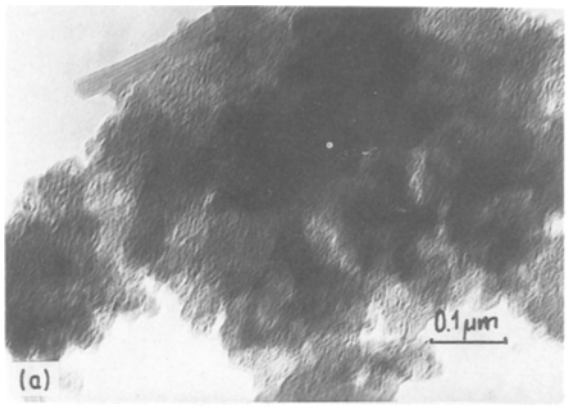
(d) β-BN

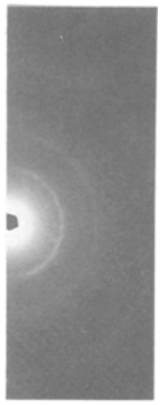
Exp. d(nm)	λ-BN d(nm)
0.208	0.209
	0.181
0.123	0.128
0.117	
0.165	0.1086
0.09	0.0904
	0.0823

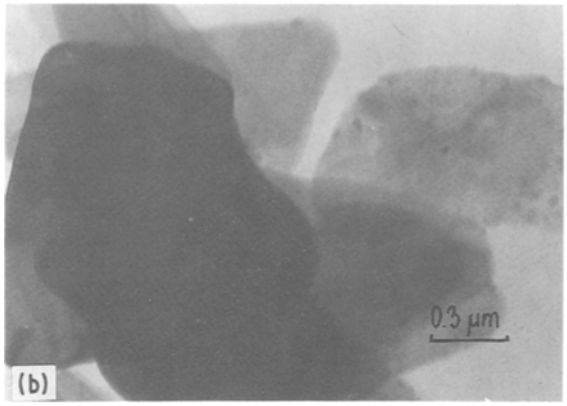
material, besides α-BN, consists also of h-B_2O_3 and B_7O. The plate dimensions were $10 \times 5 \times 1\,mm^3$. Samples were irradiated through a 20 mm thick quartz plate under normal pressure in air for 15 min.

3. Results

As a result of irradiation by a UV photon beam on the surface of the sintered BN sample the rows of ravine-like scratches appeared at the spots where the light was falling. The SEM images of the target surface prior to and after irradiation are presented in Fig. 1. During laser beam operation a small cloud of "smoke" was evident over the sample surface, At the edges, crests and the unevenesses of the "ravines"







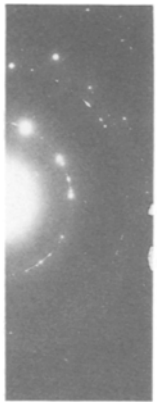


Figure 5 Transmission electronmicrographs of the deposit on the quartz-plate

(a) α-BN

Exp. *d*(nm)	α-BN *d*(nm)
0.331	0.333
0.202	0.206
0.121	0.1253
0.109	0.1086
0.103	0.1032
0.0794	0.083
0.0696	

(b) β-BN

Exp. *d*(nm)	β-BN *d*(nm)
0.21	0.209
0.123	0.128
0.107	0.1086
0.0812	0.0832
0.0726	

were observed, the material being only loosely connected with the substrate as could be deduced from its luminescence intensity during SEM observations. In the lamellae the sinter consisted of the holes seen at the spots being irradiated (Fig. 2). Fig. 3 presents the structural composition of the sample before irradiation observed using the TEM methods. At the spots submitted to the effect of UV photons some components appeared, not observed earlier, namely:

(i) fine polycrystalline fibres of h-B_2O_3 (Fig. 4a),
(ii) polycrystalline fibres of α-BN (Fig. 4b),
(iii) large γ-BN crystals (Fig. 4c),
(iv) large flat β-BN crystals (Fig. 4d).

The large flat B_7O crystals and numerous fine α-BN crystals which occurred in the sample before irradiation remained unchanged. Attention should be paid to the fact that after irradiation the h-B_2O_3 phase is not observed in the same form.

The surface of the quartz-plate, through which the sample was irradiated, became covered with a white deposit on the side in contact with the target. TEM structural examinations of this deposit revealed fine-crystalline h-B_2O_3, large single B_7O grains, fine crystalline α-BN of the same kind as in the starting sample and, not observed in the starting material, the α-BN phase in the form of polycrystalline fibres (Fig. 5a), and the β-BN phase in the form of single oval grains strongly differentiated in size (Fig. 5b). A scanning image of the material occurring on the quartz plate revealed some larger and smaller agglomerates of apparently plate-like grains, and also the single grains laying on the quartz surface and the relatively small spherules (Fig. 6). It could be seen that those agglomerates consisted of grains closely connected with the substrate and at different angles with respect to each other.

With reference to the shape of crystals, the plates were predominated by shapes identical to those observed in the "ravine" of the irradiated material as well as in the starting material.

4. Discussion of results

The B_2O_3 present in the sample could surely be melted (T_m = 850 K) under the light beam and rapidly evaporated. That is apparent by pores appearing in the material as well as by the occurrence of B_2O_3 on the quartz plate and by the "smoke" observed over the irradiated target. It is also likely that single α-BN microcrystals were melted and evaporated. Assuming

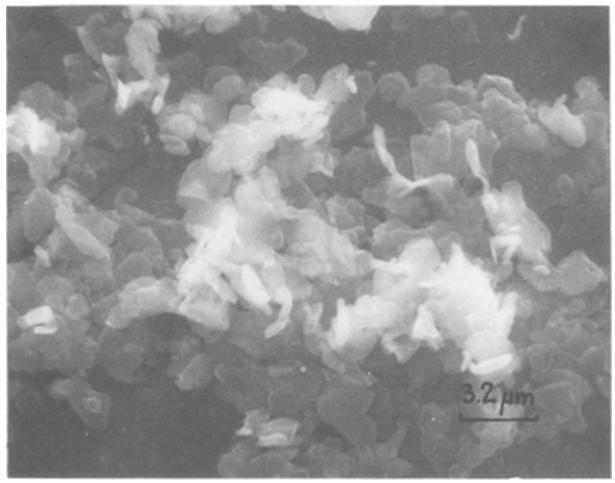


Figure 6 Scanning electronmicrograph of the deposit on the quartz-plate.

TABLE I

Energy of photon (eV)	Energy gap width (eV)	Phase of BN
3.68	3.6 [3]	α-BN
	6.4 + 0.5 [4]	β-BN

that the total energy of the light beam is used for heating the BN, it can be estimated that a mass of volume 3.83 μm^3 can reach the melting temperature of BN, i.e. 3273 K. However, B_2O_3 evaporation is the dominant process. It can be assumed that this process is so rapid that intensive evaporation of B_2O_3 causes the irradiated sample area to burst and capture the lamellae. Even the whole agglomerates of BN lamellae, which are next condensed on a quartz plate or at some cooler places on the sample; at the same time BN becomes "transported". The "ravines" observed on the BN sinter, of depth 0.1 mm, seem to be a result of dynamic transport of B_2O_3 vapours and of BN lamellae captured and then the collapse of the spatial structure of the plates after complete evaporation of B_2O_3. The effect of "swalling" of BN ceramics conventionally heated in order to remove B_2O_3 is well known.

The most important observation was the appearance of a β-BN phase under the influence of UV photons. This transformation could take place both in the solid state (which is indicated by the unchanged crystals) or as a result of condensation of vapours under irradiation with UV photons.

Our interpretation of the fact that the phase crystallization of the electron band structure is different to that of α-BN, is based on the concept of non-linear optics concerning excitation of electrons [5]. It is obvious that in the case of the high density power light field there is a possibility of multiphoton coherent absorption via virtual levels.

Table I shows the energy of photon, and the energy gap width for α-BN and for β-BN. As can be seen one-photon transitions may cause occupation of states in α-BN. Such excitations could only cause heating of the material due to recombination. Two-photon transitions may cause occupation of states in α-BN corresponding to the distribution of electrons in the excited β-BN phase. Thus, it can be accepted that the energetic structure of electrons "forces" formation of the corresponding phase, and the heat originating from recombination promotes the displacement of atoms.

It seems that obtaining the β-BN phase from the α-BN phase under the effect of irradiation with IR power laser described in [2] can also be interpreted as the result of multiphoton transitions.

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