Proceedings of the IX International Conference ION 2012, Kazimierz Dolny, Poland, June 25–28, 2012

EPR Investigations of Electrons and Neutrons Irradiated Cubic Boron Nitride

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Microcrystals of cubic boron nitride powders synthesised under different conditions and further irradiated with neutrons and electrons have been investigated. It was found that some changes of the samples' paramagnetic properties depend on the electron irradiation dose. It was also shown that the initial boron type defects growth occurs under thermal neutron, as well as under fast neutrons irradiation. The nitrogen-containing defects concentration changes in a threshold manner.

DOI: 10.12693/APhysPolA.123.923
PACS: 76.30.–v, 81.05.Ea, 61.72.J–

1. Introduction

Cubic boron nitride (cBN) is of a great interest as a multifunctional material possessing some properties resistant to the extreme external stress. Nevertheless, the nature of its impurity and self-defects have not been sufficiently studied until now. At the same time, even some insignificant changes of the synthesis conditions lead to the formation of cBN crystals different in their physical characteristics. The diversity of the defects and their complexes play an important role in this. On one hand, further irradiation of the crystals complicates the identification of the crystals' structure, but on the other hand, there may appear some conditions, such that some types of the original structural defects become either more pronounced or on the contrary get muted which may simplify the understanding of the whole picture of the cBN crystalline lattice defects.

A special role among the defects belongs to a nitrogen vacancy. According to [1] it creates a completely filled *s*-like state near the upper level of the valence band and partially filled resonance *p*-type state on the edge of the conductivity band. The importance of the nitrogen vacancy and its complexes in formation of activation, recombination, absorption and photosensitivity levels in original and irradiated cBN crystals was confirmed in paper [2]. An interpretation of the X-ray spectra of those crystals is presented in [3]. The authors of the latter paper have also calculated the electronic state, charge density and total energy distribution in cubic and hexagonal boron nitride. It is shown in [4] that the cBN crystals may contain some part of dissolved hydrogen, but these structures are very unstable under an external influence.

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The faulted structure of the initial and radiation modified super hard materials can be well identified by the EPR method studies. Previously we have shown [5, 6] that the irradiation of cBN micropowders at pulsed fast reactor causes an increase of the paramagnetic centers (PC) concentration, while the irradiation of diamond crystals with thermal neutrons of the nuclear reactor fission spectrum causes their strength improvement. Now we present the results of the neutron and electron irradiation of cubic boron nitride micropowders.

2. Experiment

We have studied the samples of cBN microcrystalline powders grown under the pressure of 5.5 GPa and at the temperature of 1620 K, identical to those studied in [6]. The studies of the samples grown from the mixture of the hexagonal BN and multi-component additive Ca–Mg–Fe–Si–Al–O (in the amounts from 1 to 5%) were performed before the electron irradiation of the micropowders. Thus prepared powders were separated from the impurities using step-by-step etching in the mixture of alkalies and acids. The samples were processed further using the planetary mill and ranged by the size and strength criteria after washing. Some samples were obtained from the spliced crystals.

In our work we investigated the cBN micropowders having the grain size from 1 to 40 μm, which were irradiated with neutrons and electrons. The irradiation by neutrons of fission spectrum was conducted with the flux density of 1×10^{13} cm^{-2} s^{-1} in the horizontal channel of the reactor during 120–360 s, the doses varied from 1.2×10^{15} to 3.6×10^{15} cm^{-2}. The energy and the doses of the electron irradiation was 4 MeV and from 1×10^{16} to 2.2×10^{17} cm^{-2}, respectively. The annealing of the samples was conducted additionally in the temperature range from 300 to 600 °C during 30 min.

The specimens were investigated using the standard electron paramagnetic resonance (EPR) spectrometer at X-band in the temperature range 77 to 473 K. Basic standards of Mn^{2+} in the MgO powder and DPPH were used for the EPR spectral parameters and the concentration of PC determination. The paramagnetic centers content in cBN powders was registered by the "Varian E112" spectrometer in the same samples, before and after the irradiation.

3. Results and discussion

The EPR signals registered at three fixed temperatures of 77, 273, and 473 K have been studied in order to evaluate the role and extent of the neutron and electron irradiation influence on the cBN micropowders structural changes.

It is estimated for the original samples of the cBN micropowders that the concentration of high-temperature paramagnetic centers possesses a linear dependence on the crystal growth duration in the case of the furnace containing Ca–Mg–Fe–Si–Al–O. The irradiation of the samples with electrons as well as with neutrons does not affect the qualitative state of the paramagnetic system structure of the cBN powders, as after the irradiation of the samples, so after their further annealing. Relatively wide EPR-signal dominates at the measurement temperature of 77 K, its g-value remains constant and equals to 2.006, being independent of the irradiation influence. Figure 1 presents the EPR-line width dependence on the annealing temperature of the cBN microcrystals irradiated with electrons.

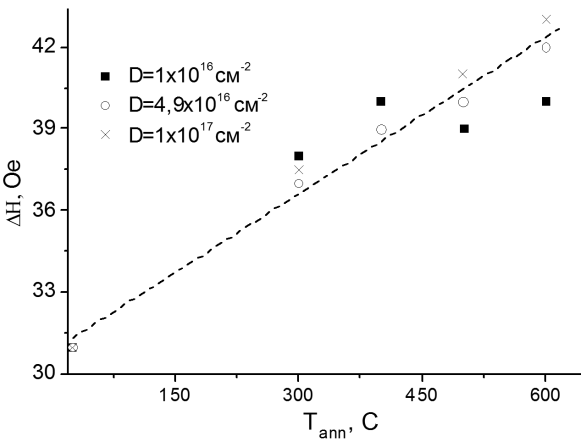

Fig. 1. The EPR-line width dependence on the annealing temperature of the cBN microcrystals irradiated with electrons.

We observed increase of the line width along with the paramagnetic centers concentration increase in the cBN samples irradiated with neutrons. However, the studies of the cBN samples irradiated with the electron dose of 2.2×10^{17} cm^{-2} showed that the concentration of PC with the g-factor equal to 2.006 increased, while the line width remained unchanged. Figure 2 presents the dependence of that paramagnetic centers concentration on the irradiation dose. It should be noted that the PC concentration showed a slight dependence on the annealing temperature.

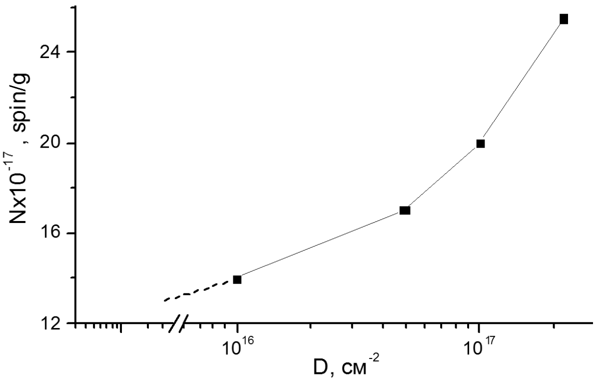

Fig. 2. Dependences of PC relative concentrations on the electron irradiation doses for the cBN samples measured at 77 K.

Let us consider further studies of the EPR spectra of the cBN micropowders registered at room temperature. The samples irradiated in the horizontal channel of the reactor with the fission spectrum neutrons show an increase of the amount responsible for the signal PC, besides the line with $g \geq 2.003$ becoming wider. At that the line width increases by about one third of its magnitude, while the PC concentration increases by 2.5 times at the irradiation dose $D = 1.2 \times 10^{15}$ cm^{-2} and by 8 times in the case of $D \geq 2.4 \times 10^{15}$ cm^{-2}. The electron irradiation of the cBN samples does not cause the paramagnetic centers concentration increase. It was estimated that the PC concentration does not also change after the samples further annealing, although the EPR line width of the samples increases after thermal treatment. Thus it is established that some defects do not express the paramagnetic properties at room temperature but show a switch to the paramagnetic state, as the temperature decreases. This fact does not contradict the earlier assumption made in [5] that the boron atoms, being relatively light, undergo a sufficient displacement from the centers of the crystalline lattice and form some separate precipitates. We also registered an increase of paramagnetic centers concentration at low measurement temperatures. It occurred in the case of neutron irradiation of the cBN samples, as well as in the case of an increase of the amount of boron in the furnace compared to its stoichiometric composition.

The high temperature defects are usually registered in the crystals of cBN with an increased number of nitrogen-originated defects. Such micropowders were studied further and we registered the EPR-spectra at 150 °C. There we found the signals with g-value equal to 2.0012 and the line width of 1 Oe. It was found that neither the electron irradiation itself nor the irradiation with further thermal annealing of the samples in the study caused an increase of the PC concentration or the EPR-line widening. At the same time, the concentration of the nitrogen-originated defects in question decreases as a result of the neutrons of fission spectrum irradiation with the doses from 2.4×10^{15} cm^{-2} and higher. This may be due to the effective under neutron irradiation process of boron atoms displacement from the lattice centers. The excess nitrogen atoms placed in the interstitials take the thereby formed vacancies and thus the total nitrogen-defects concentration decreases.

4. Conclusion

It is established that the EPR characteristics of the cBN micropowders depend on their synthesis and further neutron and electron irradiation conditions as well as on the annealing temperature. Some features of these dependences are studied. It is revealed that regardless of the prehistory of the cBN crystals synthesis (specifically the furnace catalytic mixture composition) the process of the boron containing defects formation effectively proceeds in the samples after their exposure to irradiation. The electron or neutron irradiation of the cBN micropowders up to the irradiation doses of 2.2×10^{17} cm^{-2} causes the EPR-line widening at room temperature, as well as at 77 K. The temperature annealing of the irradiated samples results in almost linear widening of the EPR-line having the g-value equal to 2.006, which may be due also to the increase of the total number of defects in the samples structure. It seems quite obvious that since the paramagnetic nitrogen vacancies may produce similar EPR signals as boron ones do [6], we cannot specify whether some signals originate only from boron defects. This matter needs some further studies which may clarify the question.

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