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Effect of grain boundaries on iron distribution in polycrystalline cubic boron nitride

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Abstract

The influence of grain boundaries on local electronic states and the distribution of ^{57}Fe ions in cubic boron nitride (c-BN) polycrystals has been investigated as a function of technological processing. The study was performed on two sets of c-BN samples: (1) prepared by catalytic synthesis and (2) synthesized by direct phase transformation. It has been established that under catalytic synthesis iron ions are predominantly incorporated into the c-BN grain bulk in the Fe^{3+} charge state. In contrast, after direct phase transformation iron ions are distributed mainly along the grain boundaries in the Fe^{2+} state, probably due to the enhanced grain boundary diffusion of iron. Suppression of grain boundary diffusion of iron (and its incorporation mainly into the grain bulk) under catalytic synthesis can be attributed to interlocking of the movement of iron ions by precipitation of nitrides and borides of catalytic impurities (Al and Si) formed along the grain boundaries during c-BN synthesis.

1. Introduction

Cubic boron nitride (c-BN) with the sphalerite structure (ZnS type) and $F\bar{4}3m$ symmetry is well known for its extraordinary physical and mechanical properties such as a hardness second only to that of diamond, a high thermal stability and chemical inertness [1]. Recently, c-BN has been considered as a wide-gap semiconductor for potential application in high-temperature electronic devices.

It is noteworthy that most industrially grown c-BN, both in film and bulk form, possesses a substantial number of grain boundaries. For bulk polycrystalline samples this refers to the crystals synthesized by both catalytic synthesis and direct phase transformation of graphite-like boron nitride (h-BN). The availability of grain boundaries would obviously influence the distribution of doping impurities, the incorporation of which is necessary for assignment of the desired properties to c-BN and the preparation of semiconductor devices. In particular, the effects of segregation and enhanced diffusion of impurities along grain boundaries may cause inhomogeneous distribution of these impurities inside polycrystals, which, in turn, can have negative effects on the parameters of the material and electronic devices. In this case, knowledge of conditions under which the above-mentioned negative effects are compensated is very important with regard to the formation of a more homogeneous bulk impurity distribution.

The distribution of doping impurities has been studied by ^{57}Fe Mössbauer spectroscopy using ^{57}Fe ions as a model doping impurity. Previously ^{57}Fe Mössbauer spectroscopy has been successively applied to the analysis of iron states in semiconductors with a diamond structure such as C, Si and Ge [2–5]. This method allows for precise identification of iron-containing phases, estimation of their abundance and investigation of the crystalline and defect structure of c-BN. In these studies iron probes were incorporated either by ion implantation after c-BN preparation or directly during synthesis. Mössbauer spectroscopy at room temperature (RT) and liquid nitrogen temperature (LNT) allows us to establish some similarities in the behaviour of iron implants and dopants in the mentioned materials, depending on the iron concentration, the grain size of the host material and its lattice parameters. Some properties of c-BN, e.g. lattice parameters, bond strengths etc, are intermediate between those of diamond and Si [1–5]. On the other hand, only a few studies describe the Mössbauer study of ^{57}Fe as a model doping impurity in c-BN [6, 7].

As shown in [6, 7], iron ions in c-BN may exist in two different charge states (Fe^{2+} and Fe^{3+}) with different ion radii, and consequently occupying variable positions in the c-BN lattice. The aim of the present study was to investigate the influence of grain boundaries on local electronic states and the distribution and diffusion of iron ions (as a model doping impurity) depending on the technological processing of c-BN polycrystals prepared under high-pressure, high-temperature (HPHT) conditions from an h-BN precursor in the presence and in the absence of catalytic impurities.

2. Experimental details

The present study was performed with two sets of c-BN samples. Those of set 1 were polycrystalline c-BN samples synthesized by direct phase transformation (non-catalytic synthesis) from a mixture of pyrolytic h-BN and carbonyl iron ($\approx 10^{20}$ cm^{-3}). Polycrystalline c-BN samples of set 2 were prepared by catalytic synthesis from the mixture of pyrolytic h-BN, carbonyl iron ($\approx 3 \times 10^{19}$ cm^{-3} consistent with a ^{57}Fe ion content of about 10^{17} cm^{-3}) and also Si (1 wt%) and Al (1 wt%) as catalysts. The grain sizes of h-BN and iron were found to be about 2 and 3 μm respectively. In order to limit the oxide content (in particular, B_2O_3) in the pyrolytic h-BN precursor the latter was preliminary annealed in a vacuum at 800 °C for 2 h. Both sets of samples were prepared by the HPHT method at a quasistatic pressure $P = 7$–7.5 GPa and temperature $T = 2000$–2500 °C.

To study diffusion of iron impurities in c-BN, annealing of the samples at temperatures of 400, 600, 800 and 1000 °C in a vacuum of 10^{-3} Pa was carried out for 1 h.

The phase composition and structure of c-BN samples were analysed by x-ray diffraction (XRD) measurements with Cu Kα radiation using a DRON-3 diffractometer. The concentration of catalysts and technological impurities was verified by x-ray energy-dispersive microanalysis and has been reported elsewhere [8].

The local states of iron in c-BN were investigated by transmission Mössbauer spectroscopy (TMS) at RT and LNT. The thickness of the samples was chosen to be about 1 mm in order to obtain an optimal signal-to-noise ratio in TMS [9]. However, a small area of the sample limited the count rate. The spectra were recorded using a ^{57}Co/Rh source and proportional gas (Xe)

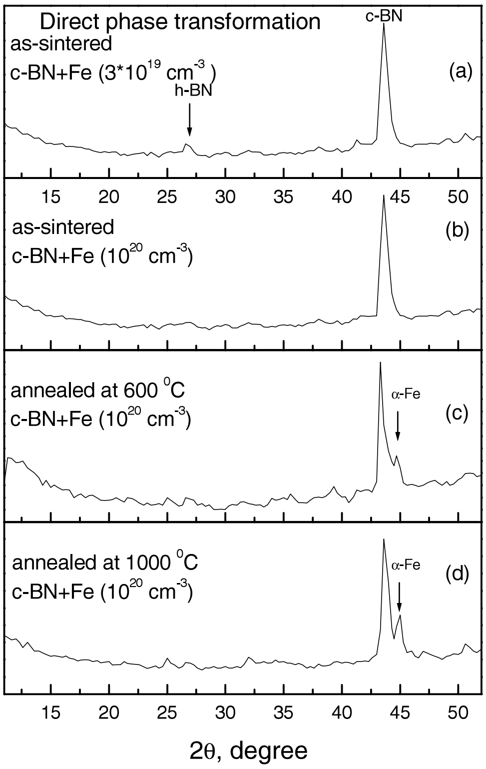

Figure 1. XRD patterns of as-sintered and annealed c-BN samples prepared by direct phase transformation.

counter. These spectra were evaluated by means of the MOSMOD program [10] taking into consideration the Gaussian distributions of hyperfine magnetic fields (H_{hf}) and quadrupole splittings (QS). All isomer shifts (IS) are given with respect to α-Fe.

3. Results

The phase composition of c-BN was studied by the XRD method with the angle ranging from 15° to 50°, a range that covers the most intense diffraction lines from the c-BN lattice. XRD patterns of c-BN from set 1 (see figure 1) are practically not affected by iron concentration. XRD patterns of both as-sintered c-BN samples show a dominating peak at 43.5° corresponding to (111) c-BN. An additional reflection at 44.8° arises in the pattern of c-BN with higher Fe concentration after subsequent annealing. Its contribution increases with temperature. This peak corresponds to the phase with an interatomic distance $d = 0.203$ nm coincident with (110) α-Fe.

XRD patterns of as-prepared and annealed c-BN formed by catalytic synthesis are presented in figure 2. In addition to a peak characterizing (111) c-BN, the pattern shows several reflections that can be assigned to nitrides, borides and oxides of Al and Si (shown by arrows in figure 2) [12]. The formation of these compounds is quite typical for HPHT catalytic synthesis of c-BN [11].

TM spectra of the as-prepared c-BN samples with different Fe concentrations and samples synthesized by direct phase transformation are shown in figure 3. Both spectra were

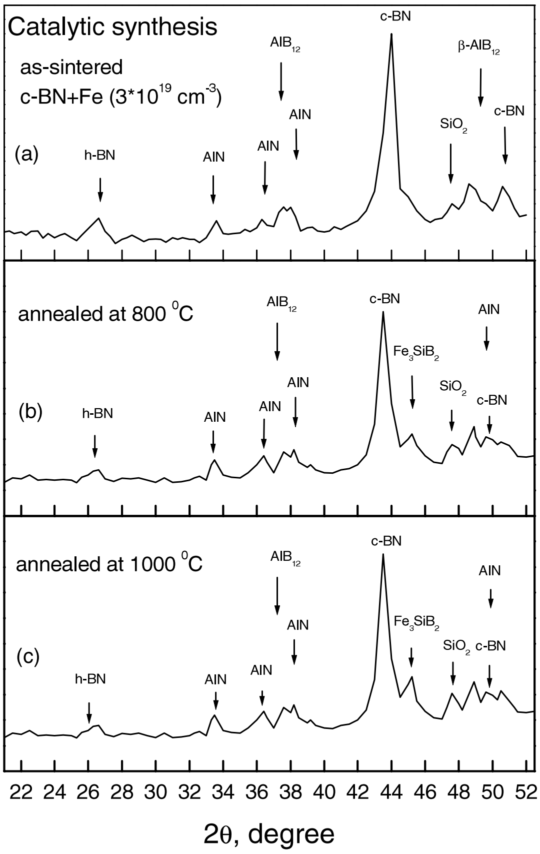

Figure 2. XRD patterns of as-sintered and annealed c-BN samples prepared by catalytic synthesis.

fitted assuming three sextets (H_{hf} = 33.0, 21.5 and 12.8 T) and one quadrupole doublet (IS = 0.8 mm s^{-1} and QS = 2.1 mm s^{-1}). This fact suggests that Fe has similar surroundings in both cases. The main difference between the two spectra in figure 3 is manifested as the abundance of metallic iron in as-prepared samples that is definitely higher in the case of c-BN with a lower Fe concentration.

In order to investigate the nature of the iron precipitates formed and iron diffusion in c-BN, the evolution of c-BN with an Fe concentration of 1×10^{20} cm^{-3} under annealing was studied. The obtained spectra are presented in figure 4. It is evident that thermal treatment of c-BN results in the transformation of the local surroundings of the iron. Obviously, the sextet characterized by H_{hf} = 33.0 T corresponds to large α-Fe inclusions [13]. Its contribution increases significantly with annealing temperature, in accordance with XRD results (see figure 1). The parameters of the second magnetic component with H_{hf} = 21.5 T coincide within experimental error (δH = 0.5 T) with those of ε-Fe$_3$N [13]. The sextet with H_{hf} = 12.8 T is characterized by a pronounced broadening of spectral lines, and its average H_{hf} is close to that of the amorphous a-(Fe–B) phase [14]. A decrease in its contribution with annealing temperature and its complete disappearance at 800 °C allows us to conclude that this fraction may be identified as the metastable (amorphous) a-(Fe–B) phase.

Mössbauer spectra of as-sintered and annealed c-BN also exhibited the presence of a quadrupole doublet whose parameters correspond to the Fe^{2+} state [15]. The Fe^{2+} state cannot

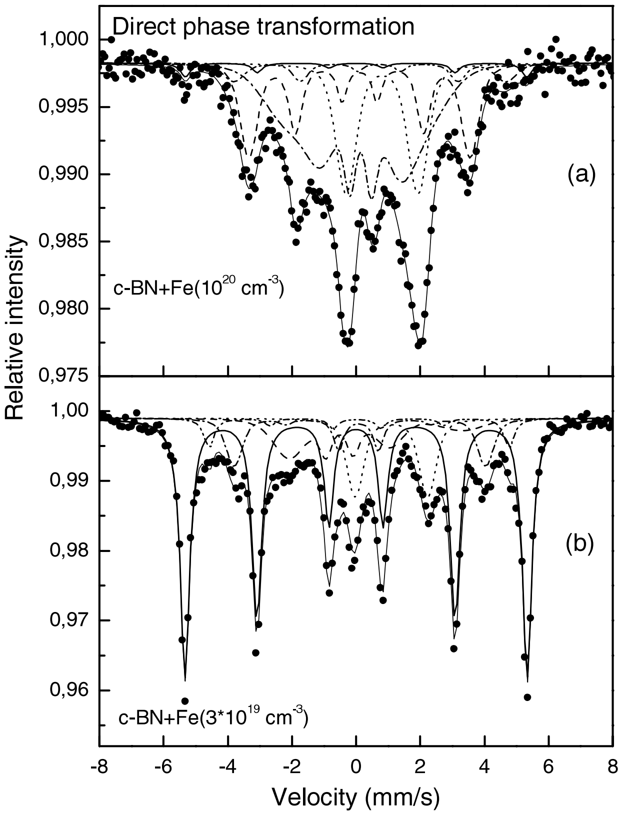

Figure 3. Transmission Mössbauer spectra of untreated c-BN samples prepared by direct phase transformation containing 10^{20} cm^{-3} (a) and 3×10^{19} cm^{-3} (b) of Fe.

be attributed to any known compound. In particular, the only iron oxide, which invokes Fe^{2+} in the octahedral sites is non-magnetic Fe$_{1-x}$O [15]. However, its IS and QS have lower values than those obtained by evaluation of the spectrum in figure 4(a). An increase in annealing temperature results in the successive growth of IS and QS which is evident from a decrease in the crystallographic imperfection of the local surroundings of Fe^{2+}. The configuration of Fe^{2+} demonstrates high thermal stability up to 900 °C and completely decomposes only at 1000 °C.

As seen in figure 4, annealing at $T = 800$ °C results in the appearance of an additional single line in the Mössbauer spectra. Its IS varies from -0.02 to -0.10 mm s^{-1} with increase in annealing temperature. Based on the data presented in [4], this line cannot be assigned to Fe at the substitutional sites in c-BN. Thus, the above discussion allows us to assume that most probably the single line in the spectra that appeared after annealing at 800 °C corresponds to a high-temperature bcc γ-Fe modification (see [16]) at the expense of decomposing a-(Fe–B) and ε-Fe$_{3+x}$N fractions.

TM spectra of as-sintered and annealed c-BN prepared by catalytic synthesis and containing 3×10^{19} atoms cm^{-3} of iron are shown in figure 5. The best fit of spectrum recorded for the as-sintered sample was obtained by assuming three components: a dominating quadrupole doublet (QS $= 0.56$ mm s^{-1}, IS $= 0.23$ mm s^{-1}) and two weak magnetic sextets with $H_{hf} = 23.4$ and 16.2 T. TM measurement of as-sintered c-BN at LNT shows some decrease in the doublet contribution at the expense of that of the sextets. This suggests the

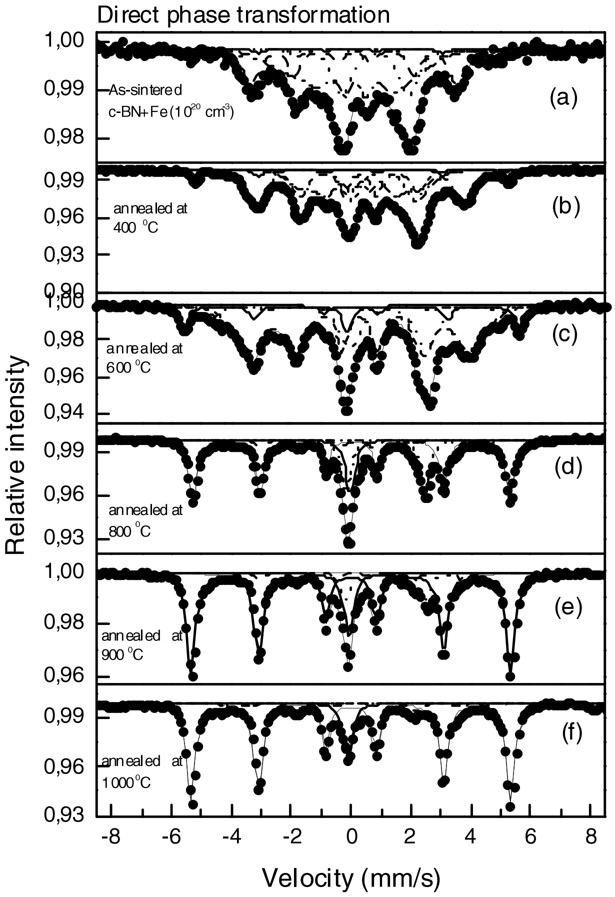

Figure 4. Transmission Mössbauer spectra of c-BN (10^{20} cm^{-3} of Fe) prepared by direct phase transformation: as-sintered (a), annealed at 400 °C (b), 600 °C (c), 800 °C (d), 900 °C (e) and 1000 °C (f).

presence of a certain amount of small iron-containing precipitate exhibiting superparamagnetic properties at RT. The quadrupole doublet observed in this case can be attributed to Fe^{3+} in strongly perturbed surroundings in the c-BN lattice [15]. Such a state was not observed in c-BN prepared by direct phase transformation (set 1). It is noteworthy that the contribution of the doublet under consideration was unchanged even at the highest annealing temperatures. Similar high-temperature stability of Fe^{3+} was found in Si and Ge implanted with ^{57}Fe, where the existence of deep Fe donors with point defects has been established [17, 18].

Two more sextets (S1 and S2) cannot be assigned unambiguously to any definite phase. The annealing behaviour of the S2 sextet analysed by XRD and TMS allows us to identify it as Fe$_3$SiB$_2$. This interpretation, however, needs additional study.

4. Discussion

The obtained TM results revealed at least one major difference between set 1 and set 2 c-BN polycrystals. For samples prepared by direct phase transformations (set 1) iron forms magnetically ordered aggregates with some fraction of paramagnetic Fe^{2+}, while in catalytically

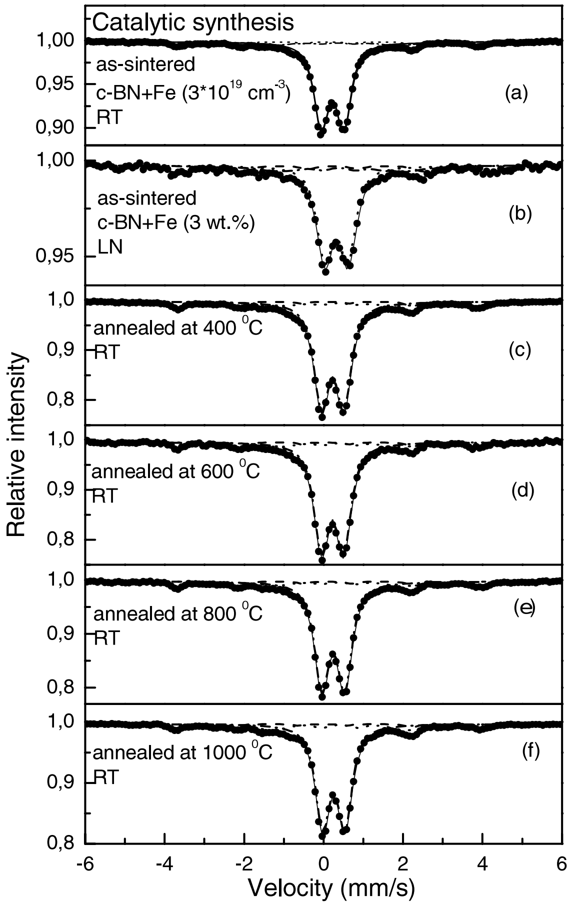

Figure 5. Transmission Mössbauer spectra of c-BN (3×10^{19} cm^{-3} of Fe) prepared by catalytic synthesis: as-sintered (recorded at RT) (a), as-sintered (recorded at LNT) (b), annealed at 400 °C (c), 600 °C (d), 800 °C (e) and 1000 °C (f). S_1—unidentified magnetically ordered phase, S_2—can be attributed to Fe_3SiB.

synthesized polycrystals (set 2) iron is mainly in the paramagnetic Fe^{3+} state. As has been shown in [11], application of catalytic impurities (Al, Si) during preparation of c-BN also leads to the formation of nitrides, borides and oxides of these elements on c-BN grain boundaries. It is also necessary to note that Fe^{2+} ions have a larger covalent radius (0.080 nm) than Fe^{3+} (0.067 nm) [19].

A phenomenological model to explain the obtained results is shown in figure 6. The initial state of samples at the beginning of sintering is represented in figure 6(a) as a mixture of h-BN (white) and Fe (black) grains. Taking into consideration the very strong bounding of atoms in the c-BN lattice and the large difference in effective radii of Fe^{2+} and Fe^{3+}, one may easily suppose that during c-BN polycrystal formation and subsequent annealing iron atoms prefer to locate predominantly along c-BN grain boundaries (figure 6(b)) that are most likely of the random (general) type. These possess enough defects to capture large Fe^{2+} ions, as shown in our previous paper [20]. Moreover, random grain boundaries are mainly considered as routes for enhanced migration of dopants [21] (thin arrows along grain boundaries in figure 6(b)). The final distribution of Fe^{2+} ions in directly synthesized polycrystals is presented in figure 6(d).

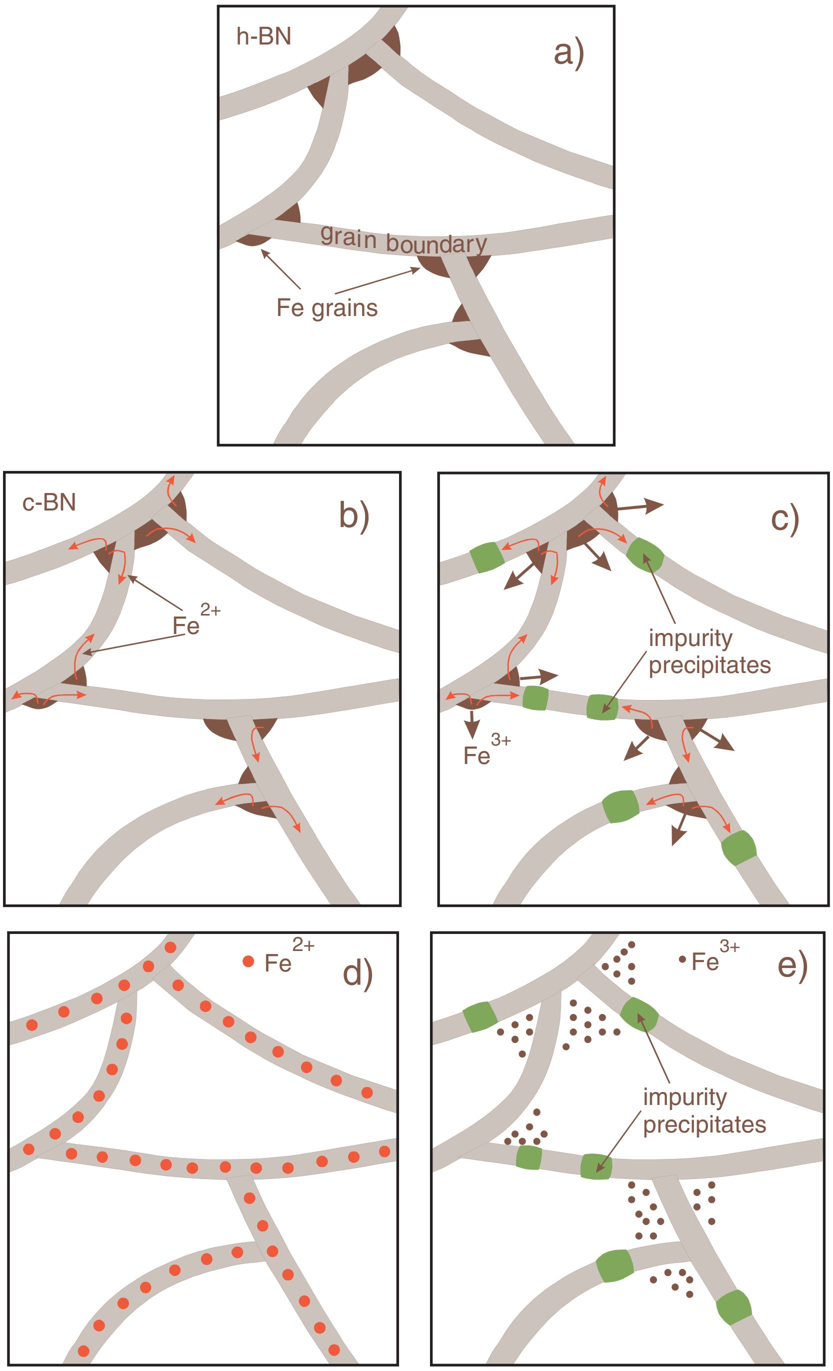

Figure 6. Phenomenological model of Fe diffusion in a c-BN polycrystal: initial mixture of h-BN and Fe grains (a); Fe diffusion in c-BN prepared by direct phase transformation (b) and prepared by catalytic synthesis (c); final distribution of iron ions in c-BN prepared by direct phase transformation (d) and prepared by catalytic synthesis (e).

(This figure is in colour only in the electronic version)

During catalytic synthesis the grain boundaries are blocked (at least, partially) as channels for enhanced Fe migration by nitrides and borides of catalytic impurities (such as AlN, SiB_2 etc; see figure 6(c)). That probably forces iron atoms to diffuse out of grain boundaries and to become incorporated into the bulk of the c-BN polycrystals (short bold arrows in figure 6(c)). However, considering the noticeable difference in the interatomic distances or volumes occupied by B and N atoms in the c-BN lattice and the volume of the Fe atom, the latter will preferably occupy positions in strongly perturbed environments and exhibit precisely the Fe^{3+} valence state which possesses a smaller covalent radius. The final distribution of Fe^{2+} ions in directly synthesized polycrystals is shown in figure 6(e).

5. Conclusions

Taking into consideration all the above results and discussion, the following conclusions were made about Fe interactions in c-BN, its defect structure and also about the influence of grain boundaries on the local electronic states and the distribution and diffusion of iron ions as a function of technological processing of c-BN polycrystals:

1. Configurations of iron ions diffused in c-BN prepared by direct phase transformation of c-BN samples can be attributed to Fe^{2+} charged states, ε-Fe_2N and a-(Fe–B). The relative contribution of the formed configurations of Fe ions is defined by their concentration but not the Fe valence state. Moreover, Fe^{2+} ions are distributed mainly along the grain boundaries due to enhanced boundary diffusion.

2. In the case of catalytically synthesized c-BN samples, iron atoms in the Fe^{3+} configuration are most probably embedded into strongly perturbed surroundings in the grain bulk. Fe^{3+} ions revealed a higher thermal stability than those formed in c-BN prepared by direct phase transformation. This may be due to the partial blocking of grain boundaries as effective diffusion channels for Fe atoms by nitrides, borides and oxides of Al and Si catalysts.

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