Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 367–370 (2007) 692–697
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Analysis of recovery process of neutron-irradiation-induced defects in α-SiC by isothermal annealing up to 1400 °C

Saishun Yamazaki *, Kousuke Yamaya, Masamitsu Imai, Toyohiko Yano

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Abstract

The macroscopic length change of SiC due to neutron irradiation and recovery by subsequent annealing was examined. Samples were fast-neutron-irradiated to a fluence of 5.3×10^{24} n/m^2 ($E_n > 0.1$ MeV) at 470 °C, and 1.9×10^{23} n/m^2 at <200 °C. The length change did not saturate over 6 h at each isothermal annealing temperature between irradiation temperature and ~1200 °C. It was shown that the macroscopic length change could be fitted roughly as a straight line against the square root of total isothermal annealing time, indicating vacancy–interstitial recombinations are the main mechanisms for the recovery. Using recovery behavior during isochronal and isothermal annealing, the activation energy for the annealing of dilatation was estimated. The activation energy of length recovery increases with increasing annealing temperature, with several small stages.

1. Introduction

Monolithic SiC and SiC fiber-reinforced SiC composite are candidates for the first wall and blanket of advanced fusion reactors [1,2]. These components operate in an extremely high flux of fast neutrons generated by the nuclear fusion reaction, and must operate at high temperatures. Therefore, it is important to clarify the influence of the neutron irradiation on various physical properties of SiC. However, the details of the recovery process of irradiation-induced defects during post-irradiation heat-treatment are not fully understood [3–9]. This provides information on the thermal stability of each kind of defects in the crystal and is used in estimating the accumulation and stability of them, and consequently the life of the material can be estimated.

In ceramics, it is generally accepted that vacancy is a defect that can migrate only at relatively higher temperature while interstitial can migrate at relatively lower temperature. Primak et al. [10] first observed the neutron-irradiation damage of SiC irradiated at the Hanford reactor, and reported that SiC expanded as a result of irradiation and recovery on annealing, starting at a relatively low temperature and continuing monotonically up to ~1200 °C. Many later observations confirm the recovery behavior of SiC, namely, the recovery of length, volume or density starts near the irradiation temperature and continues monotonically up to around 1200 °C on isochronal annealing, for example by Pallentine [11] and Price [9]. One of the present authors [12] also reported that SiC ceramic neutron-irradiated at 280 °C started to recover at

* Corresponding author. Tel.: +81 3 5734 3380; fax: +81 3 5734 2959.
E-mail address: 04d19106@nr.titech.ac.jp (S. Yamazaki).

0022-3115/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2007.03.095

~300 °C. These results indicate that interstitial atoms introduced by neutron irradiation of SiC have mobility near room temperature. On the other hand, Price [13] reported that the length of SiC due to irradiation above 1200 °C expanded by the formation of voids. The result clearly shows that the vacancy has mobility at least at ~1200 °C. Recently, Katoh et al. [14] reported swelling behavior of ion-irradiated SiC, and suggested that vacancies can migrate at ~1000 °C.

The volume expansion produced by fast neutron irradiation and its recovery during post-irradiation heat-treatment is closely related to the concentration of crystalline defects such as interstitial atoms and vacancies. Therefore, it is plausible to measure changes in volume or macroscopic length to estimate the concentration of defects and their stability.

In this study, changes of the macroscopic length due to neutron irradiation and due to post-irradiation isothermal annealing up to 6 h between room temperature and 1400 °C were measured to clarify the thermal stability of neutron-irradiation induced defects. Isochronal annealing was also used to track defect behavior.

2. Experimental procedure

Two kinds of materials used in this study were pressureless sintered α-SiC (mainly 4H and 3C polytype) ceramics containing Al_2O_3 as a sintering additive (Asahi Glass Company, Ceraroi-C600) and pressureless sintered SiC containing B_4C as a sintering additive (α-SiC, mainly 6H polytype, Kyocera, SC-221). The polytype and the content of the sintering additive of the materials were measured with XRD and EDX. The specimens were rectangular bars $2 \times 4 \times 25\ mm^3$ in size. These specimens were neutron irradiated in the Japan Materials Testing Reactor (JMTR). The SiC specimens containing Al_2O_3 were irradiated to a fluence of 5.3×10^{24} n/m^2 ($E_n > 0.1$ MeV, ~0.5 dpa) at 470 °C (material A), and the SiC containing B_4C was irradiated to a fluence of 1.9×10^{23} n/m^2 ($E_n > 0.1$ MeV, ~0.02 dpa) at <200 °C (material B). The effects of glassy phase in the material A on recovery behavior are unknown at present. But usually, deformation or shrinkage due to grain boundary phase happens at higher temperature than 1200 °C. From our previous studies [15,16], the resemble SiC (SC-201, Kyocera) containing nearly the same amount of B and C, and irradiated in the order of 10^{24} n/m^2 using JMTR, showed bubble swelling if it was annealed higher temperature than 1200 °C. Therefore, at present, effects of the B_4C (i.e., He production) in the material B on the recovery of dilatation up to 1000 °C may be negligible due to much lower fluence and lower annealing temperature.

Two specimens of each irradiated material were isochronally annealed for 6 h in vacuum, from the irradiation temperature to 1400 °C with temperature interval of 50 °C. The other specimen, one of each material type, was isothermally annealed at each isochronal annealing temperature in series. They were heated up to 1000 °C in an infrared-heating vacuum furnace (~10^{-3} Torr), and above 1000 °C in a tungsten-heating element furnace (~10^{-6} Torr). The isothermal annealing was performed sequentially with measurements at annealing times of 2, 5, 10, 30, 60, and 240 min. Total duration of isothermal annealing at each temperature was 347 min. The specimen length was measured using a point-type micrometer at 25 °C using fixture jig. The accuracy of the measurement was better than 0.004% (±1 μm).

Experimental conditions and changes in length due to the neutron irradiation are summarized in Table 1.

3. Results and discussion

3.1. Recovery during isothermal annealing

Fig. 1 shows typical changes in length during isothermal annealing of the material B specimen. The

Table 1
Irradiation condition and swelling of the materials

Irradiation condition	Material no.	Linear swelling (%)	Sintering additives
5.3×10^{24} n/m^2 ($E > 0.1$ MeV)	A (isothermal)	0.379[a]	Al_2O_3
470 °C	A1, A2 (isochronal)	0.367[b]	2–5 wt%
1.9×10^{23} n/m^2 ($E > 0.1$ MeV)	B (isothermal)	0.464[a]	B_4C
<200 °C	B1, B2 (isochronal)	0.423[b]	0.2–0.3 wt%

[a] Average of A or B specimens.
[b] Independent value of the specimen.

isothermal annealing temperatures shown in this figure are 450 °C, 550 °C, 800 °C, 900 °C, and 1150 °C. The length change is given as a percentage of the pre-irradiation length of the specimen. The irradiation temperature for this specimen was less than 200 °C. There was only negligible change (−0.003%) after 6 h in macroscopic length due to isothermal annealing at 150 °C. At the isothermal annealing temperatures above 150 °C, the length decreased gradually as the annealing time increased up to 6 h, for annealing temperatures up to 1200 °C. The value of length change during any one isothermal annealing step (total 347 min) was nearly independent of the annealing temperature.

In the case of the material A specimen, there was no change in length due to the isothermal annealing at 450 °C. The irradiation temperature of the material A was reported to be 470 °C, therefore the length did not change by annealing at 450 °C, i.e., lower than the irradiation temperature. During the isothermal annealing at 550 °C, the length slightly decreased as the annealing time increased. A similar trend was observed for the isothermal annealing at 800 °C, but the total amount of change was larger than that at 550 °C. The degree of length change after one isothermal annealing step increased gradually from ~550 °C, and was the largest for anneals at 950–1200 °C, and decreased for annealing above 1250 °C.

During these isothermal annealing times up to 6 h, recovery of length in both materials continued for more than 2 h, and it was clear that the recovery at each temperature was not saturated completely even at 6 h.

As shown in Fig. 2, the length change of the material B specimen at each isothermal annealing temperature could be roughly fitted as a straight line against the square root of total isothermal annealing time, whereas some scatter of data was observed. The same tendency was observed for material A for all isothermal annealing temperature above 500 °C.

3.2. Recovery during isochronal annealing

Fig. 3 shows changes in length by isochronal annealing for 6 h at each temperature step. The length change of material A (two specimens) started to decrease near the irradiation temperature (470 °C), and decreased with increasing annealing temperature. The annealing curves of material A were somewhat rounded, i.e., not linear with annealing temperature. The length change of material B (two specimens) started to decrease near 150 °C, and decreased almost linearly with increasing annealing temperature.

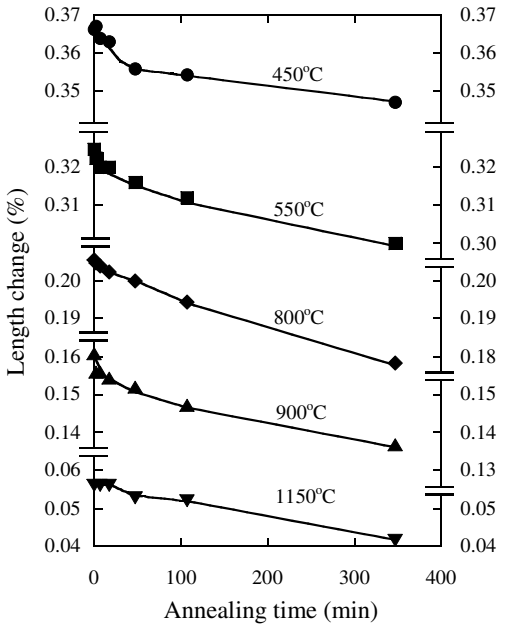

Fig. 1. Length change of the SiC material B as a function of the isothermal annealing time.

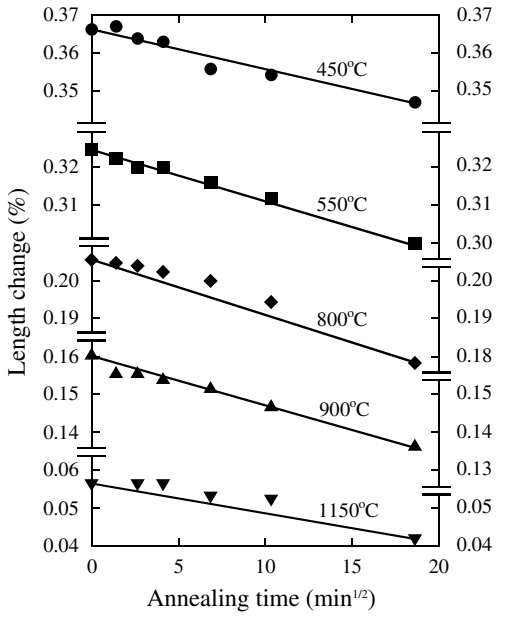

Fig. 2. Length change of the SiC material B as a function of the square root of total isothermal annealing time.

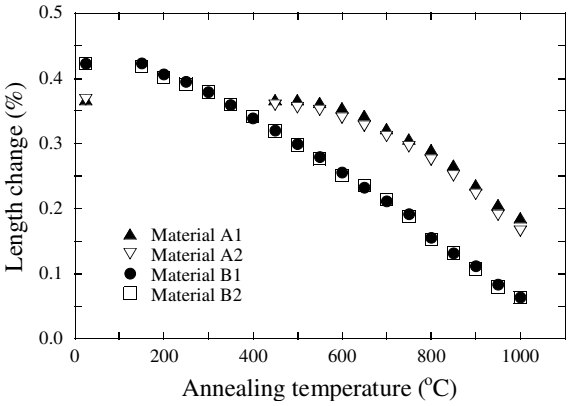

Fig. 3. Length changes as a function of isochronal annealing temperature, for annealing times of 6 h at each temperature step.

3.3. Discussion

If the neutron fluence is not too high (less than $\sim 1 \times 10^{26}$ n/m^2 ($\sim$10 dpa)), formation of defects clusters such as interstitial loops is limited [17], thus the irradiated SiC of the present study contains mostly point defects and their small clusters as irradiation induced defects. The effect of He production for length change in material B containing B_4C up to 1000 °C can be neglected due to very low fluence and low annealing temperature, as mentioned in experimental procedures. Thus, for the mechanism of length recovery during thermal annealing in the present specimens, it is suggested that interstitial atoms migrate to vacant sites as basic reactions, and then annihilate at temperatures lower than 1000 °C, based on the previously reported studies.

As shown in Fig. 2, it was observed that the length change can be roughly fitted as a straight line against the square root of total isothermal annealing time. Waite [18] discussed the diffusion-limited reaction of the simple A + B → AB type reaction. When a *V–I* Frenkel pair is produced from a single collision during electron irradiation, the defects locate on adjacent lattice sites, and they are uniformly distributed in the sample. The ratio φ that disappears by annealing to an initial density of vacancy and interstitial atom is given by,

$$\varphi = \kappa(Dt)^{1/2}, \tag{1}$$

$$\kappa = 8\pi^{1/2} r_0^2 N \exp(-1/\lambda^2), \tag{2}$$

where λ is a parameter shows the extension of the distribution of adjacent *V–I* pair, N is a normalization constant, and r_0 is a capture radius. This equation had been applied to the interpretation of the process of interstitial–vacancy pair recombination [18]. Although our specimens were irradiated by neutrons, most of the data points roughly lie on straight lines when plotted against the square root of total isothermal annealing time as shown in Fig. 2. Therefore annealing behavior of the present specimens can be expressed using Eq. (1), and it is suggested that the reaction should be proceeded in which interstitial atoms migrate to the vacant sites, and then annihilate. Since a continuous line without clear step was observed for the isochronal annealing above the irradiation temperature and up to $\sim$1200 °C, as shown in Fig. 3, it was suggested that the arrangement of point defects, i.e., the interstitial atoms, vacancies and anti-site defects, is not simple. A lot of complex interstitial states exist in the SiC lattice, consequently the dissociation temperature is distributed continuously up to high temperatures, and the activation energy for dissociation and migration of interstitial atoms is really a distribution of energies, different for each site and migration path. It is generally believed that covalent crystals, such as SiC, have a wide variety of stable positions including pseudo-stable topological positions [19].

Using a combination of isochronal and isothermal annealing, Meechan and Brinkman obtained the activation energy of the recovery stage that corresponds to a certain temperature [20,21]. If the initial defect concentration and profile are the same for each annealing experiment, the activation energy can be determined using the following expression:

$$\ln \Delta\tau_1 = \ln t_i + \frac{E}{kT_a} - \frac{E}{kT_i}, \tag{3}$$

where $\Delta\tau_1$ is the isothermal annealing time at temperature, T_a. T_a is needed to anneal the same amount of defects in the ith isochronal pulse of time t_i at a temperature, T_i. Where $\ln t_i$ and E/kT_a are constant, one obtains

$$\ln \Delta\tau_1 = C - \frac{E}{kT_i}. \tag{4}$$

A plot of $\ln \Delta\tau_1$ is linear in $1/T_i$ for a single activated process. From the slope, activation energy of the recovery at that temperature can be determined.

We applied this procedure to the recovery of length change of neutron-irradiated SiC. Fig. 4 shows the activation energy obtained for the materials A and B versus annealing temperature, using the data of the total isothermal annealing time from 30 min to 6 h. It is clear that the activation energy

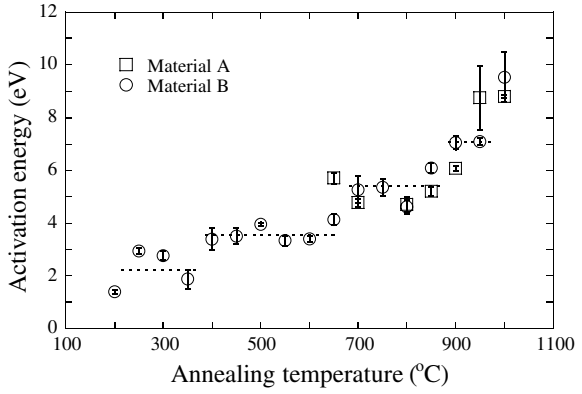

Fig. 4. The activation energy for recovery of dilatation as a function of annealing temperature.

of the recovery process increased gradually from 200 °C to ~1000 °C. The activation energies obtained from the materials A and B mostly overlapped. The data obtained from the material B covered wide range of annealing temperatures. We carefully examined the activation energies obtained from the material B, where small step-like increase of activation energy can be identified. There are steps at <200–350 °C, 400–650 °C, 700–850 °C, 900–950 °C, and higher than 1000 °C, corresponding to activation energies of ~2.2 eV, ~3.6 eV, ~5.3 eV, 7 eV, and ~9.5 eV, respectively. The material A shows almost the same activation energies.

Primak [10] reported the activation energies for annealing of dilatation of neutron-irradiated SiC, with a wide range of energy spectra from less than 1.5 eV up to 4.3 eV, with a maximum found at 3.4 eV, for the temperature range from 200 to 1200 °C. Recently, Weber et al. [22,23] investigated isochronal and isothermal annealing of Si^+ and C^+ ion-irradiation induced damage in SiC. Due to the ion-irradiation (550 keV C^+) at low temperature (−113 to −83 °C), the activation energy for recovery of the Si sublattice was found to be 1.5 ± 0.3 eV from 300 °C to 600 °C. Weber et al. [24] also reported three recovery stages at −100 to 30 °C (stage 1), 150–280 °C (stage 2), and 300–430 °C (stage 3) for Au^{2+} irradiated 6H–SiC, and corresponding activation energies of 0.3 ± 0.15 eV, 1.3 ± 0.25 eV and 1.5 ± 0.3 eV, respectively.

Recently, many attempts to estimate annealing kinetics of defects by theoretical approach using computational methods based on molecular dynamics (MD) or first-principles method. Gao et al. [23] indicated that activation energies for defect recombination processes range from 0.22 to 1.6 eV for C Frenkel pairs and from 0.28 to 0.9 eV for Si Frenkel pairs. The lower activation energies of the range indicated spontaneous recombination can happen on both Si and C sublattices below room temperature, corresponding above mentioned Weber's stage 1 recovery. The stage 2 can be explained as a recombination of interstitials separated from vacancies at distance longer than second nearest-neighbor distance. Bockstedte et al. [25] estimated several possibilities of annealing process of defects in 3C–SiC, including *I–V* recombination, diffusion to sinks, and formation of interstitial clusters. The recombination energy of C vacancies was reported to be 0.4–1.0 eV for $C_{sp\langle 100\rangle}$–V_C and 1.2–1.4 eV for $C_{spSi\langle 100\rangle}$–$V_C$, and that of Si vacancies was from ~0.2 eV for $Si_{sp\langle 1\,1\,0\rangle}$ to 3.2 eV for $Si_{TC,2}$–$V_{Si} \rightarrow C_{Si}$–$Si_C$ (anti-site pair formation). Furthermore, they provided dissociation energy of C atom from interstitial clusters. That is ranging from 0.4 to 5.7 eV depending on the cluster size and configuration. The Si vacancy migration barriers are reported as 3.2–3.6 eV, and those of Si interstitials are 1.4 or 3.5 eV. The C migration energies also varied 0.5–1.4 for $C_{sp\langle 1\,0\,0\rangle}$ or 3.5–5.2 eV for V_C, depending on the charge state. Whereas lots of energies are estimated by the theoretical calculations, the observed first (<200–350 °C) and second (400–650 °C) stages can be attributed to $C_{spSi\langle 100\rangle}$–$V_C$ recombination, and $Si_{TC,2}$–$V_{Si} \rightarrow C_{Si}$–$Si_c$ recombination (anti-site pair formation) or Si interstitial migration, respectively. A part of the stages higher than 700 °C may be attributed for the dissociation of C atom from carbon clusters, at present. It is necessary to obtain more accurate activation energy to attribute each step for corresponding annealing processes, and reassignment should be necessary.

The activation energies obtained in the present study were about twice those of the experimentally observed values for the corresponding temperature range. In this study, isothermal annealing was conducted serially, using the same specimen with increasing isothermal temperature. It means that the initial defects concentration and profile were not the same, and gradually changed toward higher energies with increasing temperature. Whereas these changes are expected, since we only used annealing data for long duration (30 min to 6 h) in each annealing step, the effect of annealing at previous (lower) temperatures should be mostly negligible. Therefore, activation energies at each temperature represent thermal stability of defects at that temperature, but slightly higher values might be obtained.

There were some differences in isochronal annealing rate (Fig. 3) between material A and B. The material B showed a relatively straight line against annealing temperature for the beginning of recovery, just beyond the irradiation temperature, as reported for SiC previously. On the other hand, material A showed more moderate shrinkage close to the irradiation temperature, therefore the annealing curve was not straight, but rounded. It indicated the rate of recovery in dilatation around 600–800 °C in the material A was smaller than that of the material B. There are some reasons that contribute to this difference, for example, difference in polytype of SiC, different kind and amount of sintering additives, or total neutron fluence. Further research is necessary to define the reason for the difference.

4. Conclusions

The results of precise isothermal and isochronal annealing studies on length measurement for the neutron-irradiated SiC during post-irradiation annealing are summarized as follows:

(1) The recovery of length during the isothermal annealing does not saturate at 6 h. It was shown that the length change becomes roughly a straight line when plotted as the square root of total isothermal annealing time, indicating that vacancy–interstitial recombinations, including many processes, are mainly responsible for length recovery.
(2) The activation energy for the recovery of dilatation increases with increasing annealing temperature. Several recovery stages up to 1000 °C, which were not seen in the isochronal annealing curves, were recognized by careful analysis of the data, suggesting several mechanisms should be included for recovery of dilatation.

References

[1] P. Rocco, H.W. Scholz, M. Zucchetti, J. Nucl. Mater. 191–194 (1992) 1474.
[2] R.F. Mattas, M.C. Billone, J. Nucl. Mater. 233–237 (1996) 72.
[3] P. Fenici, A.J. Frias Rebelo, R.H. Jones, A. Kohyama, L.L. Snead, J. Nucl. Mater. 258–263 (1998) 215.
[4] R.H. Jones, L. Giancarli, A. Hasegawa, Y. Katoh, A. Kohyama, B. Riccardi, L.L. Snead, W.J. Weber, J. Nucl. Mater. 307–311 (2002) 1057.
[5] L.H. Rovvner, G.R. Hopkins, Nucl. Technol. 29 (1976) 274.
[6] R.J. Price, J. Nucl. Mater. 33 (1969) 17.
[7] R.J. Price, J. Nucl. Mater. 46 (1972) 268.
[8] J.C. Corelli, J. Hoole, J. Lazzaro, C.W. Lee, J. Am. Ceram. 66 (7) (1983) 529.
[9] R.J. Price, Nucl. Technol. 35 (1977) 320.
[10] W. Primak, L.H. Fuchs, P.P. Day, Phys. Rev. 103 (1956) 1184.
[11] J.E. Palentine, J. Nucl. Mater. 61 (1976) 243.
[12] T. Suzuki, T. Yano, T. Maruyama, T. Iseki, J. Nucl. Mater. 165 (1989) 247.
[13] R.J. Price, J. Nucl. Mater. 47–57 (1973) 47.
[14] Y. Katoh, H. Kishimoto, A. Kohyama, J. Nucl. Mater. 307–311 (2002) 1221.
[15] T. Yano, K. Sasaki, T. Maruyama, T. Iseki, M. Ito, S. Onose, Nucl. Technol. 93 (1991) 412.
[16] T. Suzuki, T. Yano, T. Maruyama, T. Iseki, T. Mori, J. Nucl. Mater. 165 (1989) 247.
[17] T. Yano, M. Akiyoshi, K. Ichikawa, Y. Tachi, T. Iseki, J. Nucl. Mater. 289 (2001) 102.
[18] T.R. Waite, Phys. Rev. 107 (1957) 463.
[19] C. Kinoshita, J. Nucl. Mater. 191–194 (1992) 67.
[20] C.J. Meechan, J.A. Brinkman, Phys. Rev. 103 (1956) 1193.
[21] A.C. Damask, G.J. Dienes, Point Defect in Metals, Gorden and Breach, New York, 1971, p. 145.
[22] W.J. Weber, W. Jiang, S. Thevuthasan, Nucl. Instrum. and Meth. B 166–167 (2000) 410.
[23] F. Gao, W.J. Weber, J. Appl. Phys. 94 (2003) 4348.
[24] W.J. Weber, W. Jiang, S. Thevuthasan, Nucl. Instrum. and Meth. B 175–177 (2001) 26.
[25] M. Bockstedte, A. Mattausch, O. Pankratov, Phys. Rev. B 69 (2004) 235202.