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Recovery of neutron-induced damage of Si analyzed by thermal expansion measurement

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ABSTRACT

Single-crystal silicon was neutron-irradiated up to a fluence of 3.0×10^{23} n/m^2 ($E_n > 0.1$ MeV) at 120–150 °C, and up to a fluence of 6.9×10^{23} n/m^2 at 300 °C. Changes in macroscopic length and FT-IR spectra were observed after irradiation and after post-irradiation isochronal annealing up to 1000 °C. Irradiation-induced swelling was 0.01% in both specimens. Up to 1000 °C, relatively large shrinkage was observed around 600 °C in both specimens by precise dilatometric method. There was a difference of the recovery rate between two irradiation conditions. From the FT-IR spectra, it is supposed that the Si irradiated at 120–150 °C includes more small vacancy clusters than the Si irradiated at 300 °C, thus recovery of the former Si was faster than that of the latter Si.

1. Introduction

For the future fusion reactor materials, fine ceramics have a lot of advantages on account of several excellent properties such as high temperature stability, high strength, high corrosion resistance and high electrical resistivity. Furthermore, they are relatively stable under severe radiation environment, and thus they are considered to be necessary components as electric insulators, dielectric windows, diagnostic windows, optical fibers and breeder materials [1].

Within several ceramics, silicon carbide (SiC) is expected as a candidate of blanket structural material for advanced fusion reactors [2,3]. However, SiC is a typical covalent-bond crystal and have relatively complicated crystal structure, consisted from stacking of SiC_4 tetrahedral layers, to understand property changes due to neutron irradiation [4]. Therefore, it is suggestive to study irradiation effect of Si, of which crystal structure is similar to SiC and consisted from single element. Both in SiC and Si crystal, bond nature between atoms are mostly covalent and the structures consisted from tetrahedral configuration. Therefore, geometry and distribution of interstices for interstitials are same. Neutron-irradiated SiC may include many kinds of defects, which make difficult to analyze the neutron irradiation effects. If a kind of defect is limited, analysis of the recovery process of irradiation-induced defects in SiC should be easier.

Whereas large number of researches on irradiation effects of Si was reported, most of them concentrated on the influence on electrical properties since Si is a typical semiconductor material. The volume change induced by fast neutron irradiation into single-crystal Si was rarely reported [5]. The volume change of a crystal is reflected by the concentration and type of crystalline defects. Neutron-irradiation-induced crystalline defects are generally consisted from interstitials and vacancies or their clusters, and they migrate to lower energy sites depending on the irradiation temperature and post-irradiation heat-treatment.

A lot of studies were reported on kinds and structures of defects in Si using various techniques. When Si is irradiated with charged particles such as electrons, single isolated defects are reported to be generated, otherwise irradiation with neutrons various kind of clusters are created [6]. Meng et al. [7,8] reported that radiation-induced silicon interstitials (I_{Si}) can be annihilated with monovacancies (V) at −130 °C. Therefore, generally, V-type defects such as vacancies, vacancy clusters, and vacancy-impurity complexes like vacancy–oxygen complexes (V_n–O_m) are stable at RT. Trace amounts of impurity such as oxygen and hydrogen cannot be avoided during manufacturing stages. Based on the positron annihilation investigation with annealing treatment, the defect type of neutron-irradiated Si was reported to be divacancy-type below 200 °C [9], and some bigger vacancy clusters appeared with increasing annealing temperature up to 550 °C [7]. Li et al. [10] reported that the value of activation energies for the donor decomposition was decreasing with increasing the annealing temperature up to 640 °C using resistivity measurements of neutron-irradiated Si (6.0×10^{21} n/m^2, 40 °C, and 7.8×10^{21} n/m^2, 100–150 °C). It was suggested that defects induced by neutrons up to this fluence (10^{21} n/m^2) could be annihilated over 640 °C. With using Fourier transform infrared spectrometry (FT-IR), Chen et al. [11,12]

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reported that vacancy–oxygen complex (VO) in neutron-irradiated Si (5.0×10^{21} and 1.17×10^{23} n/m^2, 45 °C) trapped more oxygen interstitials (O_i) and V to form V_nO_m defects with increasing annealing temperature.

The volume expansion of Si by fast neutron irradiation and the recovery by post-irradiation heat-treatment are deeply related to the behavior of induced crystalline defects and its mobility. The dimensional change by isochronal annealing was conventionally measured at room temperature using a micrometer. However, due to repetition of annealing in a furnace and measurement at room temperature, the length change as a function of temperature was not continuously obtained. Furthermore, ambiguousness of temperature effect of cyclic increase and decrease temperature or setting reproducibility of specimen become causes of data scatter for the micrometer measurement. Compared with the conventional measurement, precise dilatometric (DIL) method can measure the dimensional change continuously and more precisely in situ at high temperature. Up to the present, there is no report on dimensional change in neutron-irradiated Si by annealing, because neutron-induced volume change of silicon is strictly small [5]. In this study, we try to detect dimensional change of neutron-irradiated Si during annealing using the DIL method, and then coupled with FT-IR measurements, annealing behavior of irradiated Si was discussed. Our objective of the present study is to obtain basic information of the nature of any defects in Si. In this case, lower irradiation temperature and not so heavy irradiation fluence is better to clarify/identify defects. Furthermore, wider range of temperature stability information can be obtained during course of annealing if the irradiation temperature is low. The fundamental understanding obtained in this study should be valuable not only to understand the nature of defects in Si but also those in SiC.

2. Experimental procedures

High purity semiconductor-grade single-crystal silicon specimens were neutron-irradiated under two irradiation conditions. The crystal growth direction is [1 1 1] by Czochralski (CZ) method fabricated in 1993 (Komatsu Electric. Co.). The amount of oxygen was determined by a commercial hot-gas-extraction analyzer (TC-436, LECO), and the concentration of oxygen was obtained to be 1.4×10^{18} atoms/cm^3 (16 ppm). These specimens were neutron-irradiated in the Japan Materials Testing Reactor (JMTR). One group of the Si specimens was irradiated up to a fluence of 3.0×10^{23} n/m^2 ($E_n > 0.1$ MeV) at 120–150 °C, and the other group of Si specimens was irradiated up to a fluence of 6.9×10^{23} n/m^2 ($E_n > 0.1$ MeV) at 300 °C. Hereafter, irradiation condition was mentioned only by irradiation temperature, since fluences were not so largely different. The specimen for the dilatometer experiment was a rectangular bar $2 \times 2 \times 25$ mm^3 in size.

Length change of specimen was measured in situ using a precision dilatometer (DIL 402C, NETZSCH) from the irradiation temperature up to 1000 °C with a step-heating temperature interval of 50 °C in helium atmosphere (He purity: >99.99995 vol.%). Between each step, heating rate was 5 °C/min. Specimen length change was detected by a differential transformer via pushrod movement. The temperature of the furnace was controlled using a control thermocouple (Type-S; Pt–10%Rh) located beside the heating element (SiC-heating element). Specimen temperature was measured beneath the specimen using another thermocouple (Type-S). Temperature of specimen was kept constant for isochronal annealing up to 1 h within ±0.5 °C. Observed length change using the dilatometer includes both the sample holder expansion and the length change of the specimen. Therefore, data were corrected by measuring a suitable reference material, in the present study single-crystal Al_2O_3 (sapphire). To extract the net recovery of neutron-irradiated damage, an unirradiated specimen was measured first and the data were subtracted from the data of the neutron-irradiated specimen. The temperature profile of both measurements was precisely adjusted. The minimum detection sensitivity of the present dilatometer is 10 nm, corresponding 0.0001% of the specimen of 10 mm in length.

The specimens for FT-IR (FTIR460plus, JASCO) were annealed at each isochronal annealing temperature in a series. They were heat-treated in an infrared-heating vacuum furnace ($\sim 10^{-3}$ Torr). The isothermal annealing was performed for 1 h at each temperature. After each annealing treatment, IR absorption spectrum was collected by reflection mode at room temperature (25 °C) with resolution of 1 cm^{-1} and accumulation of 1000 scans. The spectrum was corrected first for background to subtract signals from air such as H_2O and CO_2, then corrected for inclination and undulation caused by scattering of light, and finally smoothened for small noise reduction. Only the peaks more than a certain value were detected. The specimen was measured twice, and reproducibility was confirmed.

Irradiation condition and changes in length due to the neutron irradiation are summarized in Table 1. The length change was measured at room temperature by a micrometer with 1 μm precision on total 10 bars using the calibrated-length standard block before and after irradiation.

3. Results and discussion

The macroscopic length expansion of both specimens was 0.01% in average after the neutron irradiation. Considering the specimen length (long direction, 25 mm), the change was close to the detection limit of the micrometer. No amorphization of silicon crystal is expected in the present irradiation fluences [13].

Fig. 1 shows length change of the neutron-irradiated Si due to the isochronal annealing for 1 h at each temperature step measured by the DIL method. Length of the as-irradiated specimen was set as a standard. Two specimens for each irradiation condition were measured, and reproducibility was confirmed. Length change of the Si irradiated at 120–150 °C started from 150 °C, which is close to the irradiation temperature. Around 600 °C, the change was steeper than that of the Si irradiated at 300 °C, and it reached −0.008% at annealing temperature of 800 °C. Although length change of the Si irradiated at 120–150 °C was continued up to 1000 °C, the change related to recovery of defects by thermal annealing may be almost finished at around 800 °C, since the length of the specimen at 850 °C did not decrease during isothermal treatment for 1 h. On the other hand, there was no sharp shrinkage up to 1000 °C in the Si irradiated at 300 °C. The length change started to decrease from 250 to 350 °C, near the irradiation temperature, and it decreased relatively linearly with increasing annealing temperature up to 1000 °C. At 1000 °C, the length change of the Si irradiated at 300 °C reached −0.008%, thus the change of neutron-induced defects was almost finished at this annealing temperature. It is observed that recovery of Si irradiated at 300 °C is slower than that of the Si irradiated at 120–150 °C. Chelyadinskii [14] reported that lattice parameter of the neutron-irradiated Si (5×10^{22} and 4.3×10^{23} n/m^2, <70 °C) by isochronal annealing for 15 min decreased up to ~250 °C, and then kept up to ~400 °C, and again decreased gradually above 400–700 °C in both specimens. After annealing at 700 °C, the lattice parameter was mostly recovered. The large decrease between 400 and 700 °C is coincided with the present results.

Fig. 2 shows the FT-IR absorption spectra of the Si irradiated at 120–150 °C and subsequently annealed at 200, 400, 600, 800 and 1000 °C for 1 h. Due to low neutron irradiation fluence, every absorption spectrum was weak except for absorption peaks related

Table 1
Irradiation condition and swelling of the single-crystal silicon.

Fluence	Irradiation temperature (°C)	Average length change (%)
3.0×10^{23} n/m^2 ($E_n > 0.1$ MeV)	120–150	0.01
6.9×10^{23} n/m^2 ($E_n > 0.1$ MeV)	300	0.01

to VO-complex observed around 830 cm^{-1}. In the present study, all wave numbers of peaks were referred from Yang et al. [12]. From Fig. 2, it was observed that VO (829 cm^{-1}) annealed out gradually with increasing annealing temperature, and V_2O_2 at 825 cm^{-1} and V_2O at 840 cm^{-1} were observed at 400 °C. Then VO (829 cm^{-1}) was observed at 600 °C again. The existence of V_3O_2 (833 cm^{-1}) at 600 °C is corresponded to disappearing of V_2O_2 (825 cm^{-1}), which trapped O_i to form V_3O_2 (833 cm^{-1}). It is also considered that reap-

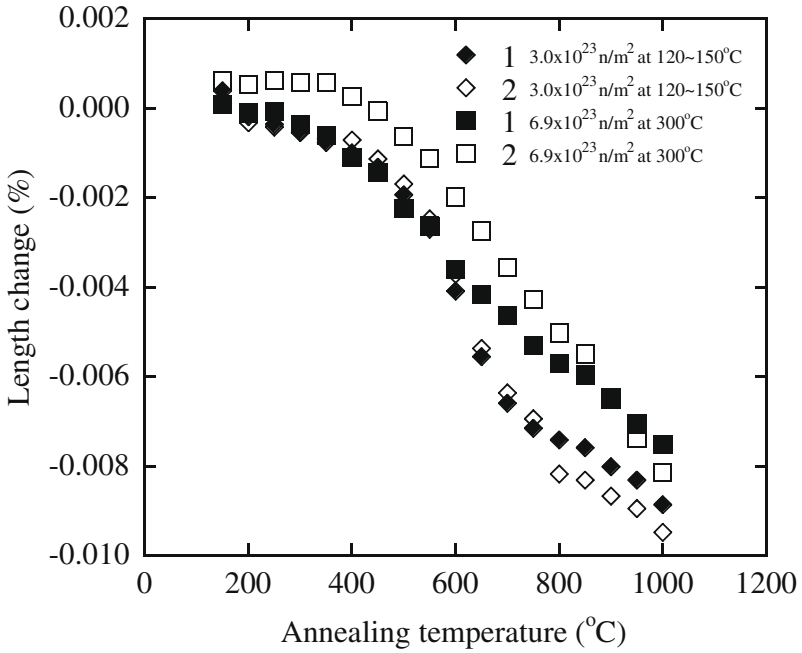

Fig. 1. Length changes as a function of isochronal annealing temperature for an annealing period of 1 h at each temperature step.

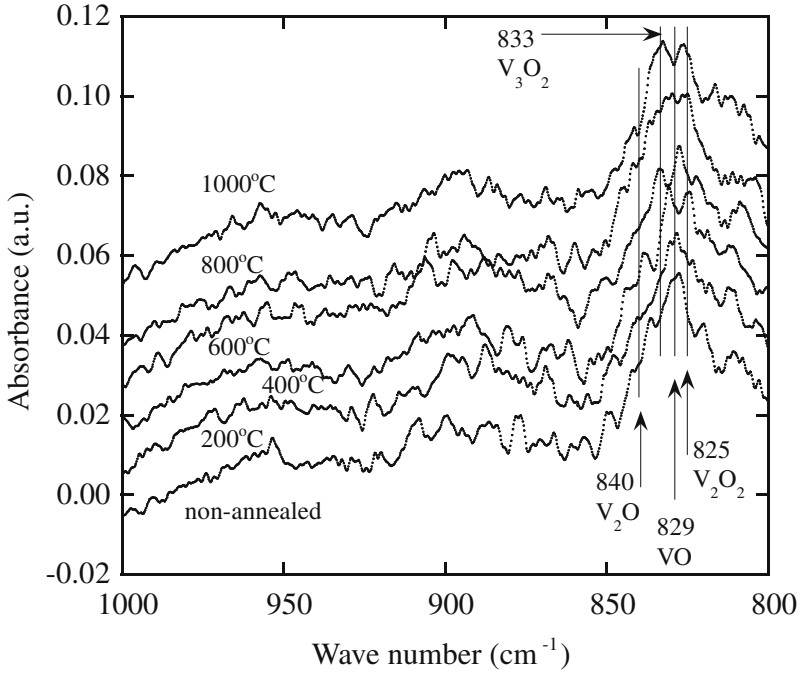

Fig. 2. FT-IR spectra for the Si irradiated 3.0×10^{23} n/m^2 at 120–150 °C after isochronal annealing for 1 h, and measured at room temperature.

pearing of V_2O_2 (825 cm^{-1}) at 800 °C is corresponding to reduction of VO (829 cm^{-1}), which trapped O_i and V to form V_2O_2. After annealing at 1000 °C, V_3O_2 (833 cm^{-1}) and V_2O_2 (825 cm^{-1}) were dominant. In these defects-creation mechanisms about the Si irradiated at 120–150 °C, small V–O complexes tend to trap more O_i and V, and to form larger size V–O complexes like V_2O_2 and V_3O_2. This tendency continued up to 800 °C.

Fig. 3 presents FT-IR spectra of the Si irradiated at 300 °C and subsequently annealed at 200, 400, 600, 800 and 1000 °C for 1 h, which suggesting slightly different defects creation scheme from the Si irradiated at 120–150 °C. The difference was that, VO (829 cm^{-1}) and V_2O_2 (825 cm^{-1}) is mostly dominant up to 600 °C and V_2O at 840 cm^{-1} were observed at 800 °C. Not only V_2O_2 (825 cm^{-1}) and VO (829 cm^{-1}) but also V_3O_2 (833 cm^{-1}) are probably co-existed at 800–1000 °C. Generally, change in the kind of defects shifted higher temperature than these in the Si irradiated at 120–150 °C.

Oshima et al. [15] reported the formation of vacancy-type clusters in the Si neutron-irradiated at 200 °C up to 2.5 × 10^{23} n/m^2. It is also reported that vacancy-type defect clusters were observed in 14 MeV neutron-irradiated Si at less than 350 °C, and in the case of above 450 °C, it was associated with oxygen impurity [16]. Meng [8] reported that kind of defects depended on irradiation temperature. Considering the irradiated condition of the present specimen, it is suggested that the Si irradiated at 300 °C had larger size defect clusters than the Si irradiated at 120–150 °C after neutron irradiation. Li et al. [17] reported that the oxygen precipitation in Si was found at annealing temperature between 400–600 °C, 700–800 °C and 1070–1130 °C. Furthermore, Watkins and Corbett [18] reported that the divacancy in Si disappeared quickly between 300 and 400 °C in electron-irradiated Si by annealing. Schröder et al. [13] mentioned conductance of neutron-irradiated Si changed quickly at around 500 °C and all defects were annealed at ~600 °C.

In the range of annealing temperature at 400–800 °C of the present study, there was a difference of the length change between the Si irradiated at 120–150 °C and the Si irradiated at 300 °C. FT-IR spectra of both Si in this annealing temperature range indicated presence of V–O complex. Based on the FT-IR observation, it was also indicated that the Si irradiated at 120–150 °C showed higher tendency to generate larger size defects than the Si irradiated at 300 °C. Therefore, it is suggested that length of the Si irradiated at 120–150 °C showed rapid decrease at lower temperature due to the decrease in number of smaller size defects, such as V, O_i or V_2.

On the other hand, the Si irradiated at 300 °C contained already larger size defects (V–O complexes) than the Si irradiated at 120–150 °C due to higher irradiation temperature. These complexes did not transform into larger complexes such as V_3O_2 by absorbing vacancies with increasing temperature. It was suggested that amount of smaller defect such as V_2 in the Si irradiated at 300 °C was less than the case of the lower irradiation temperature specimen. Therefore, there was not steep decrease in length regarding to the decrease in smaller size defects. Jones et al. [19] reported that I_3 (three interstitial Si atoms cluster) was formed and stable until 350 °C, and I_4 evolved with disappearing of I_3 and was stable until about 500 °C. Libertino et al. [20] reported that the dissociation of vacancy pairs produced free vacancies, and they migrated to interstitial-type complexes, resulting in their dissociation. These reports suggested that the length recovery of the Si irradiated at 300 °C should be attributed mainly to the dissociation of clusters. This process would result in difference of the length change. Reduction of smaller size defects makes relatively rapid shrinkage at ~600 °C than the dissociation of interstitial clusters.

Compare to the length recovery of neutron-irradiated SiC [21] with the present results, the recovery of length of SiC relatively resembles to that of the Si irradiated at 300 °C. In both cases, the macroscopic length started to decrease from nearly the irradiation temperature, and then decreased monotonously up to higher temperature without clear steps. From the present analysis, length recovery of the Si irradiated at 300 °C may be resulted by annihilation of vacancy complexes with interstitials dissociated from Si interstitial clusters. In this case interstitials are supplied from various kinds of interstitial clusters, those dissociation energies should be varied widely. Presence of similar interstitials clusters or variety of interstitials with different dissociation energies should be suggested in neutron-irradiated SiC.

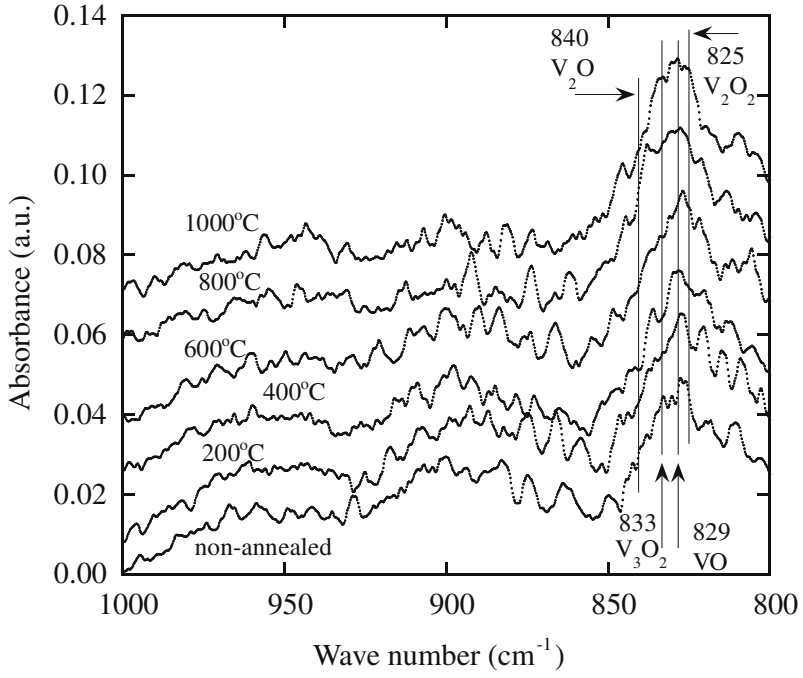

Fig. 3. FT-IR spectra for the Si irradiated 6.9 × 10^{23} n/m^2 at 300 °C after isochronal annealing for 1 h, and measured at room temperature.

4. Conclusions

Single-crystal silicon specimens were neutron-irradiated up to a fluence of 3.0×10^{23} n/m^2 ($E_n > 0.1$ MeV) at 120–150 °C, and irradiated up to a fluence of 6.9×10^{23} n/m^2 at 300 °C. Changes in macroscopic length and FT-IR spectra were observed after irradiation and after post-irradiation annealing. Very small length change during annealing could be detected by the precise dilatometric method. The Si irradiated at 120–150 °C showed rapid decrease in length at around 600 °C, whereas the Si irradiated at 300 °C showed relatively monotonous decrease in length up to 1000 °C. From the FT-IR spectra, the Si irradiated at 120–150 °C had more VO and smaller vacancy clusters than the Si irradiated at 300 °C. The difference of the recovery process between the Si irradiated at 120–150 °C and the Si irradiated at 300 °C can be attributed to the concentration of smaller defects such as divacancy due to difference in irradiation temperature.

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References

[1] P. Rocco, H.W. Scholz, M. Zucchetti, J. Nucl. Mater. 191–194 (1992) 1474.
[2] G.R. Hopkins, R.J. Price, Nucl. Eng. Des. Fusion 2 (1985) 111.
[3] Y. Katoh, N. Hashimoto, S. Kondo, L.L. Snead, A. Kohyama, J. Nucl. Mater. 351 (2006) 228.
[4] T. Yano, T. Iseki, Philos. Mag. A 62 (1990) 421.
[5] T. Yano, Y. Yamamoto, T. Iseki, J. Nucl. Mater. 307–311 (2002) 1102.
[6] M. Kuhnke, E. Fretwurst, G. Lindstroem, Nucl. Instrum. and Meth. Phys. Res. B 186 (2002) 144.
[7] X.T. Meng, B.Z. Zhang, Y.C. Du, Y.F. Zhang, Semicond. Tech. 3 (1984) 31.
[8] X.T. Meng, Nucl. Instrum. and Meth. Phys. Res. B 95 (1995) 65.
[9] S. Dannefaer, G.W. Dean, D.P. Kerr, B.G. Hogg, Phys. Rev. B 14 (1976) 2709.
[10] H. Li, R. Wang, H. Zhang, J. Zhao, G. Liu, Y. Chan, S. Duan, Mater. Sci. Eng. B 107 (2004) 119.
[11] G. Chen, Y. Li, L. Liu, P. Niu, S. Niu, D. Chen, Trans. Nonferrous Met. Soc. China 16 (2006) s113.
[12] S. Yang, Y. Li, Q. Ma, L. Liu, X. Xu, P. Niu, Y. Li, S. Niu, H. Li, J. Cryst. Growth 280 (2005) 60.
[13] B. Schröder, H. Wild, E. Minninger, J. Nucl. Mater. 108&109 (1982) 685.
[14] A.R. Chelyadinskii, Sov. Phys. Solid State 18 (1976) 506.
[15] R. Oshima, T. Kawano, R. Fujimoto, J. Nucl. Mater. 212–215 (1994) 293.
[16] R. Oshima, M. Mori, G.C. Hua, S. Honda, M. Kiritani, F.E. Jujita, Mater. Sci. Forum. 38–41 (1989) 1199.
[17] Y.X. Li, H.Y. Guo, B.D. Liu, Q.Y. Hao, C.C. Liu, D.R. Yang, D.L. Que, J. Cryst. Growth 253 (2003) 6.
[18] G.D. Watkins, J.W. Corbett, Phys. Rev. 138 (1965) A543.
[19] R. Jones, T.A.G. Eberlein, N. Pinho, B.J. Coomer, J.P. Goss, P.R. Briddon, S. Öberg, Nucl. Instrum. and Meth. Phys. Res. B 186 (2002) 10.
[20] S. Libertino, J.L. Benton, D.C. Jacobson, D.J. Eaglesham, J. M Poate, S. Coffa, P. Kringhøj, P.G. Fuochi, M. Lavalle, Appl. Phys. Lett. 71 (1997) 389.
[21] T. Yano, K. Sasaki, T. Maruyama, M. Ito, S. Onose, Nucl. Technol. 93 (1991) 412.