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Radiation resistance of amorphous silicon in optoelectric properties under proton bombardment

N. Kishimoto *, H. Amekura, K. Kono, C.G. Lee

High-Resolution Beam Research Station, National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Abstract

Optoelectronic properties of semiconductors are generally affected by radiation damage. To possibly improve the radiation resistance, an amorphous phase of Si (a-Si:H) has been tested and compared to crystalline Si(c-Si). Photoconductivity spectra and radiation-induced conductivity (RIC) have been measured in situ, under 17 MeV proton irradiation, as a simulation of fusion environments. In c-Si, crucial deterioration of the optoelectronic properties is caused by radiation-induced defects, produced in the ordered lattice. On the contrary, a-Si:H shows remarkable radiation resistance against the proton bombardment. The stable photoconductivity in a-Si:H is accompanied by enhanced structural metastability under the irradiation. The stability does not result from stiffness, but from soft flexibility inherent in the amorphous structure. The good radiation resistance is also due to characteristics of high-energy protons, i.e., electronic excitation dominant over structural displacement damage formation. The mechanism is ascribed to spontaneous recombination of displaced atoms, promoted by the electronic excitation.

1. Introduction

Plasma diagnostics in fusion reactors require optical monitoring over a wide wavelength range, from far-infrared light up to X rays. The optical sensors and electronics primarily consist of semiconductors. Some semiconductors are inevitably subject to fusion neutron irradiation. As is well known, optoelectronic properties of semiconductors are very sensitive to radiation-induced defects, which promptly capture photo-carriers and promote non-radiative recombination. Although radiation resistance of the semiconductors is desired for the stable diagnostics, an extensive material development for semiconductors is not possible, because of few changeable parameters.

Material development of radiation-resistant semiconductors is rather advanced for space applications. Some of the results may be applied to semiconductors for fusion reactors. Performance of solar cells, i.e., photovoltaic effects, have been extensively studied under the space environment and particle irradiation, i.e. proton [1,2] alpha [3,4] and neutron [4]. Among various crystalline semiconductors, some compounds, e.g., InP [5] and GaAs [6], have been found to have better radiation resistance than crystalline Si (c-Si). Moreover, it has been occasionally [1,2,4] found that amorphous materials tend to have a better radiation resistance than single crystals. The mechanism relevant to amorphous semiconductors was explained in terms of radiation-induced generation and passivation of defects [7]. On the contrary, there were other cases where the cell performance greatly degraded under particle irradiation. For instance, 2 MeV alpha irradiation degraded the photoconductivity of hydrogenated amorphous Si (a-Si:H) by five orders of magnitude, with a fluence of 10^{15} cm^{-2} [3].

Since the irradiation testing for space applications is mostly conducted for photovoltaic effects of the solar-cell structures or p–n junctions, the bulk radiation resistance cannot be simply evaluated. Also, the total displacements, presumed for fusion environments, are much larger than those induced by the cosmic rays, and radiation damage of a-Si:H at high fluences has not been well understood, except for amorphization with heavy ions. Recently, we have found stable photoconductivity

* Corresponding author. Tel.: +81-298-59-5059; fax: +81-298-59-5010; e-mail: kishin@nrim.go.jp.

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of the bulk a-Si:H up to considerable fluences of protons [8], but also that the relevant phenomena are not simple.

Consequently, further studies of radiation damage, simulating the fusion environments, are requisite. One of the most important testing aspects for the optoelectronic materials is in situ measurement, particularly for this metastable amorphous Si. The purpose of the present research is to investigate the bulk radiation resistance of a-Si:H and to discuss the mechanism relevant to characteristics of the proton irradiation.

2. Experimental procedures

Specimens used are hydrogenated amorphous Si (a-Si:H), fabricated by glow-discharge of SiH_4 onto silica substrates (0.3 mm thick). The a-Si:H film ($\sim$1 μm thick) was deposited at 500 K, where the quantum efficiency was highest. The film does not include any intentional dopants. Ohmic electrodes, 1 mm distant, were formed by vacuum deposition of Al.

A He-circulating cryostat, integrated with the target chamber, enabled low-temperature irradiation down to 20 K. The present irradiation was carried out at 200 K. A monochromator was connected with the chamber and the specimen was illuminated with monochromatic light ($h\nu = 0.7$–2.4 eV). A 17 MeV proton beam and the light were intermittently irradiated at a separate angle of 45°, to either a-Si:H or c-Si. In situ measurements of photoconductivity (PC) and radiation-induced conductivity (RIC) were carried out. The beam-current density was about 20 nA/cm^2, while the photon flux was about 1×10^{14} photon/cm^2 s at $h\nu = 2.1$ eV. Damage conditions were evaluated with the TRIM-code [9], using a displacement energy, $E_d = 15.8$ eV (for c-Si) [10] and mass density of 2.1 g/cm^3 for a-Si:H. The proton fluence was translated into units of dpa (displacement per atom). The conversion ratio is 20 nA/cm^2 (1.25×10^{11} ions/cm^2 s) $= 6.2 \times 10^{-10}$ dpa/s, for 17 MeV protons in Si.

3. Results and discussion

3.1. Radiation regime of proton irradiation

Depth profiles of defect-production rate $d\phi/dt$ and electronic excitation per unit volume Q_B of 17 MeV protons were calculated by the TRIM-code [9]. Projectile ranges of 17 MeV protons were 1.9 mm in a-Si:H and 1.7 mm in c-Si. The radiation effects calculated is almost identical between a-Si:H and c-Si. The profiles of $d\phi/dt$ and Q_B were uniform over the specimen thickness. The present damage rate $d\phi/dt$ of 6×10^{-10} dpa/s is accompanied by electronic excitation Q_B of 7×10^{18} eV/cm^3 s.

Here, it should be noted that "point defect" or "dpa" may not be well-defined concepts for the metastable a-Si:H. The covalent bonding, of the same short-range order, should give a similar nuclear-deposition energy, but does not necessarily mean equal resultant defects. Therefore, the dpa-value for a-Si:H is hereafter given for intuitive convenience, and is regarded as a measure of the instantaneous displacements.

Electronic excitation is a key aspect to consider radiation effects on semiconductors, as well as displacement collisions. Fig. 1 shows stopping powers, i.e., electronic energy loss per unit thickness, as a function of proton energy, where S_e and S_n are electronic and nuclear stopping powers, respectively. With increasing the proton energy, the collision cross-section decreases and both stopping powers steadily descend. However, a ratio of electronic- to nuclear stopping power, S_e/S_n, keeps increasing with the proton energy. A characteristic feature of protons is a large value of S_e/S_n over the whole MeV region, as compared to heavy ions. The ratio is $S_e/S_n = 2 \times 10^3$ for 17 MeV protons. For comparison, the stopping power of a heavier ion, phosphorus, is also given in Fig. 1. The ratio, S_e/S_n, of P increases faster but the absolute value is much smaller than that of protons, over the MeV region. The large ratio of S_e/S_n indicates that, for the protons, electronic excitation dominates displacement damage formation.

3.2. Photoconductivity of a-Si:H in comparison with that of c-Si

Photoconductivity (PC) spectra of a-Si:H at 200 K, before and after the 17 MeV proton irradiation, are given in Fig. 2. The PC spectra in the visible-light region consist of a wide tail-spectrum and the band-to-band transition above the band gap, $E_g \sim 1.5$ eV. Unlike c-Si, the tail-spectrum is characteristic of amorphous semiconductors, associated with sub-gap states below E_g. The band-to-band PC saturates in the higher energy region. As an optical sensor, such a wide spectrum is preferable to apply for the wide energy region. Similarity among these spectra demonstrates the superb PC stability against the proton irradiation. At the fluence of 10^{-7} dpa, the PC of c-Si already degrades by 3–4 orders of magnitude (as will be seen in Fig. 3), but the spectrum of a-Si:H does not degrade and rather shifts upward. Even at 10^{-6} dpa, the spectral shape of a-Si:H is almost unchanged as compared to the unirradiated one. The same spectral shape, irrespective of the fluence, indicates that the band structures of a-Si:H do not significantly change. It is furthermore important that defects acting as deep recombination-centers are not produced by the proton irradiation.

Fig. 3 shows fluence dependence of PC intensity $\Delta\sigma_L$ of a-Si:H, in comparison with those of non-doped (N.D.) and P-doped c-Si (3×10^{15} cm^{-3}). The PC

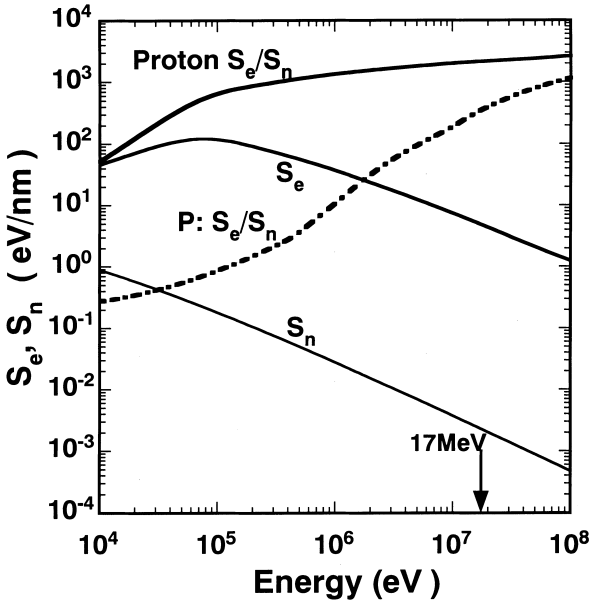

Fig. 1. Electronic stopping power S_e, nuclear stopping power S_n and their ratio S_e/S_n in Si, as a function of proton energy. A corresponding ratio for phosphorus ions is also plotted for comparison.

intensity of $\Delta\sigma_L$ is taken at a given wavelength above each band gap, i.e., at 2.1 eV for a-Si:H and at 1.3 eV for c-Si, both at 200 K. At the proton fluence of 2×10^{13} ions/cm^2 (10^{-7} dpa), the PC of c-Si drastically decreases by 3–4 orders of magnitude. The former work on c-Si [11] clarified that the PC deterioration by protons resulted from a decrease in lifetime of charge carriers. Namely, a small number of defects degrades the PC, enhancing non-radiative recombination of photoexcited carriers. In contrast to c-Si, the PC of a-Si:H does not deteriorate but rather increases up to 6×10^{13} ions/cm^2 (3×10^{-7} dpa) and gradually decreases beyond the fluence.

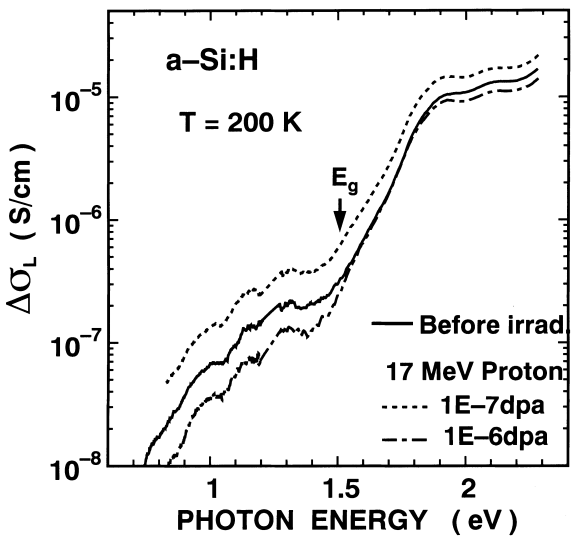

Fig. 2. Photoconductivity spectra of a-Si:H at 200 K, before (solid line) and after (dashed lines) the 17 MeV-proton irradiation. The energy gap, E_g, is given by an arrow. The photon flux is about 1×10^{14} photon/cm^2 s at $h\nu = 2.1$ eV.

It is worthwhile comparing these results with those for specially doped c-Si, where free carriers are supplied from the shallow impurities. Previously, we reported [12] that radiation-resistant photoconductivity could be accomplished by the shallow-impurity doping. An example of such doped c-Si is also plotted in Fig. 3. The radiation tolerance of doped c-Si is prolonged up to ϕ_C, improving over the practically zero tolerance of non-doped Si. This improvement of radiation resistance is ascribed to passivation of radiation-induced recombination-centers. The mechanism is not merely conductivity survival by excess carriers, as seen in dark conductivity, but mainly the passivation of photo-carrier traps. Therefore, the PC drops very rapidly, as soon as free carriers become exhausted above the ϕ_C. These phenomena in c-Si are well-understood in terms of stable-defect formation in the rigid crystalline lattice.

On the other hand, a-Si:H is radiation-resistant, even better than doped c-Si. The PC stability indicates that the proton irradiation does not produce active deep recombination centers. Since a-Si:H used is of intrinsic type, the doping effect above is not expected. As previ-

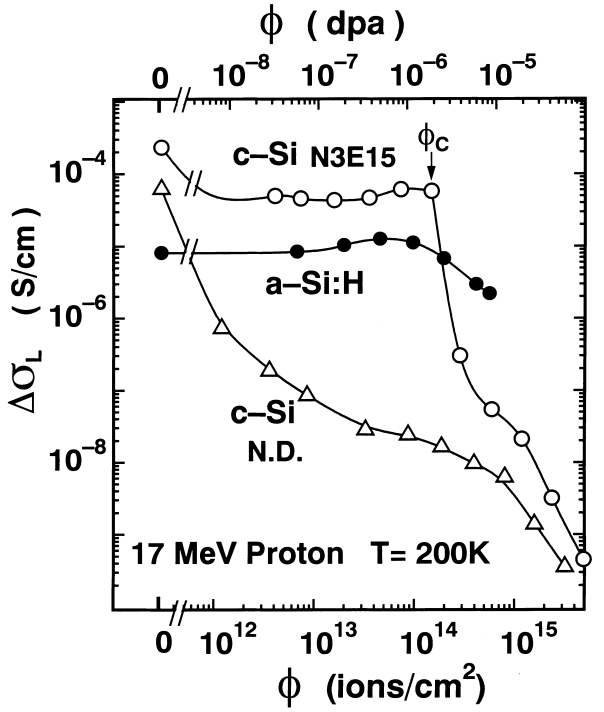

Fig. 3. Proton-fluence dependence of photoconductivity $\Delta\sigma_L$ of a-Si:H, in comparison with non-doped (N.D.) and doped c-Si. The PC intensities of a-Si:H and c-Si are values at 2.1 eV and 1.3 eV, respectively, as their band-to-band transitions.

ously discussed, the collision events which break the covalent bonds are essentially not different between a-Si:H and c-Si. Consequently, subsequent processes after the collision events must differ from each other. The PC stability is therefore attributable to structural flexibility inherent in a-Si:H. The metastable flexibility is enhanced during the proton irradiation, as will be described, and results in the high radiation resistance of a-Si:H.

The PC decrease above 6×10^{13} ions/cm^2 (3×10^{-7} dpa) is most likely caused by a decrease in carrier lifetime, due to eventual failure of annihilation of the displaced atoms, i.e., dangling-bond formation. The superb radiation resistance of a-Si:H is again exhibited even after the degradation around the highest fluence, 5×10^{14} ions/cm^2. Namely, the degraded PC is recovered by annealing at 450 K where dangling bonds are annealed out [13,14]. It is in contrast to c-Si, where defect clusters remain after the annealing. The reversible recovery of a-Si:H also confirms that the PC variation is not associated with loss of hydrogen passivation.

3.3. Radiation-induced conductivity (RIC) in a-Si:H

Radiation-induced conductivity (RIC) has been observed in a-Si:H. Fig. 4 shows the time-dependent conductance of a-Si:H at 200 K, during and after the proton irradiation. To verify the net RIC of the a-Si:H film, RIC of the silica substrate is also given. As shown in

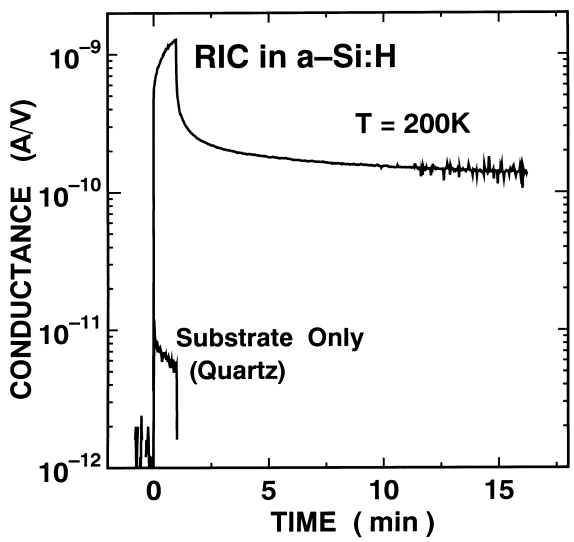

Fig. 4. Conductance signals of radiation-induced conductivity (RIC) in a-Si:H at 200 K. A signal of the silica substrate only is also given for comparison.

Fig. 4, the conductance signal of the a-Si:H film is 10^2 times as large as that of the substrate. It is again noted that the projectile range of 17 MeV protons is much larger than the substrate thickness (0.3 mm). This experimental simplicity is important to evaluate the net RIC and the radiation resistance of the film. Otherwise, bypass current and damage of the substrate may affect the total performance. Such false effects could occur, if photovoltaic devices and/or ions of a short projectile range were used.

As seen in Fig. 4, the RIC of a-Si:H occurs very slowly, in response to the proton irradiation ($\phi \sim 8 \times 10^{12}$ ions/cm^2). The time-constant of on-beam RIC is about 60 s and that of off-beam decay is roughly 2×10^3 s [15]. The RIC for the repetitive irradiations is reversible, except the initial change in the dark conductivity. It should be noted that the PC of a-Si:H has a quick response. The RIC variations of a-Si:H are also quite different from those of c-Si where the responses are instantaneous. The sluggish RIC-variations in a-Si:H indicate that significant structural changes occur with the proton irradiation.

3.4. A mechanism of the radiation resistance of a-Si:H

As an experimental result, the structural metastability in a-Si:H, enhanced by the proton irradiation, causes a good radiation resistance. Accordingly, the structural rearrangements, like collective atomic motions, would recombine displaced atoms and prevent the creation of deep centers. Fig. 5 shows schematic diagrams to illustrate a mechanism for the radiation resistance. The essential points of the mechanism are both the structural flexibility of a-Si:H and the predominant electronic excitation by the high energy protons. An incident proton collides with a target Si atom, either directly or via cascades, and displaces the atom from the original site of the covalent network. This collision process should be similar

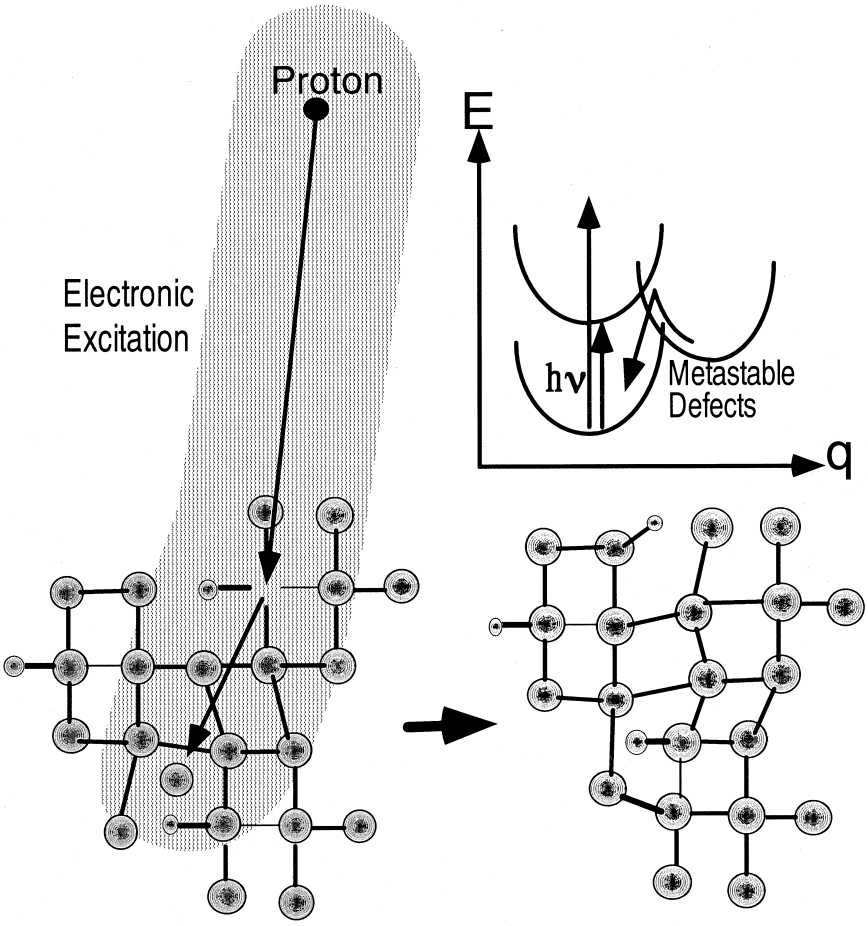

Fig. 5. Schematic diagrams of a mechanism for the radiation resistance of a-Si:H under proton irradiation. A hatched area illustrates electronic excitation along the proton track. Large and small circles express Si and H, respectively. A schematic energy diagram of coordination-coordinate is also depicted.

to the case of c-Si, though some of the covalent bonds of a-Si:H are a somewhat weaker than the other Si–Si bonds [16]. If the network were rigid, the displaced "vacancy" gives rise to persistent defects. In the case of a-Si:H, the displacements could be relaxed via a collective rearrangement, by virtue of the structural metastability.

Here, it should be reminded that the atomic rearrangement requires a certain activation energy, because the dangling-bond states are fairly stable [16]. Moreover, we have to solve an apparent paradox that the band-to-band photons causes more effective damage (i.e., the Staebler–Wronski effect [17]), than this proton irradiation.

The energy diagram of configuration-coordinate is also illustrated in Fig. 5. The dangling-bonds form as a metastable state, displaced from the network site [16]. To recover to the ground states, an activation energy to overcome the barrier is necessary. The strong electronic excitation of protons supplies the activation energy for the atomic rearrangement. In contrast, a photon absorbed is consumed just as to break a covalent bond.

The high-energy proton induces strong electronic excitation along its track. This electronic excitation allows a-Si:H to rearrange the atomic bonds and anneals the instantaneous displacements.

4. Conclusion

In situ measurements of PC and RIC were carried out for a-Si:H under 17 MeV proton irradiation. The PC of a-Si:H showed remarkable radiation resistance in both the spectral shape and the intensity, while that of c-Si drastically degraded at low fluences. The a-Si:H maintained good optoelectronic performances, even after the proton irradiation. The stable PC was accompanied by the metastable RIC, indicating the structural rearrangements. A mechanism of the radiation resistance was proposed, on the basis of the structural flexibility of a-Si:H and the electronic excitation of protons. The collision displacements are accommodated by local rearrangements, by virtue of the structural flexibility of a-Si:H, activated by the electronic excitation of protons. It is further necessary to clarify dynamic interactions between photo- and particle-excited carriers, and to study whether the radiation resistance of a-Si:H is still valid for 14 MeV neutrons which dominate structural damage over electronic excitation.

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References

[1] J.J. Hanak, E. Chem, A. Myatt, J. R. Woodyard, Conference Record of the 19 IEEE Photovoltaic Specialists Conference (Cat. No. 87CH2400-0), IEEE, New York, 1987, p. 630.
[2] J.R. Woodyard, J.J. Hanak, in: A. Madan, M. Thompson, D. Adler, Y. Hamakawa (Eds.), Amorphous Si Semiconductors – Pure and Hydrogenated (Symposium), Mater. Res. Soc, Pittsburgh, 1987, p. 533.
[3] J.S. Payson, J.R. Woodyard, Conference Record of the 20th IEEE Photovoltaic Specialists Conference (Cat. No.88CH2527-0), IEEE, New York, 1988, p. 990.
[4] V. Perez-Mendez, S.N. Kaplan, W. Ward, S. Qureshi, R.A. Street, Nucl. Instr. and Meth. A 260 (1987) 195.
[5] S. Yoshida, K. Mitsui, T. Oda, Y. Yukimoto, Jpn. J. Appl. Phys. 21 (Suppl.) (1982) 27.
[6] M. Yamaguchi, J. Appl. Phys. 78 (1995) 1476.
[7] J.R. Woodyard, G.A. Landis, Solar Cells 31 (1991) 297.
[8] N. Kishimoto, H. Amekura, K. Kono, T. Saito, Mater. Res. Soc. Symp. Proc. 439 (1997) 679.
[9] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, ch. 8, Pergamon Press, New York, 1985.
[10] J.A. Van Vechten, Inst. Phys. Conf. Ser. 31 (1977) 441.
[11] H. Amekura, N. Kishimoto, K. Kono, T. Saito, J. Appl. Phys. 77 (1995) 4984.
[12] N. Kishimoto, H. Amekura, K. Kono, T. Saito, J. Nucl. Mater. 233–237 (1996) 1244.
[13] M. Stutzmann, W.B. Jackson, C.C. Tsai, Phys. Rev. B 32 (1985) 23.
[14] N. Kishimoto, H. Amekura, K. Kono, C.G. Lee, 17th Int. Conf. on Amorph. and Microcryst. Semicond., J. Non-Cryst. Solids, in press.
[15] H. Amekura, N. Kishimoto, K. Kono, Mater. Sci. Forum 258–263 (1997) 599.
[16] For example, K. Shimakawa, A. Kolobov, S.R. Elliot, Adv. in Phys. 44 (1995) 475.
[17] D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292.