



Concentration and thermal release of hydrogen in amorphous silicon carbide films prepared by rf sputtering

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Abstract

Concentration and thermal release of hydrogen in hydrogenated amorphous SiC (a-SiC:H) films were studied. The films were prepared onto Si (111) wafers at room temperature by rf planer magnetron sputtering in a gas mixture of argon at partial pressures of 0.33 Pa and hydrogen from 0.065 to 1.3 Pa. The IR measurements conducted on the films annealed at various temperatures for 3600 s suggested that the hydrogen was released from Si–H and C–H bonds in the films at the temperatures above 600 and 850 K, respectively. In-situ isochronal annealing for 300 s at various temperatures from 323 to 1123 K in the ERDA (Elastic Recoil Detection Analysis) system was carried out for the specimen having the hydrogen concentration of 7.1×10^{27} atoms/m³. It was revealed that three types of hydrogen exist in the films; hydrogen bonded to Si or C atoms and unbonded hydrogen, with the concentrations of 2.8×10^{27} , 1.9×10^{27} and 2.4×10^{27} atoms/m³, respectively. The concentration of unbonded hydrogen decreases with increase of the hydrogen partial pressure. © 1997 Elsevier Science S.A.

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1. Introduction

Hydrogenated amorphous silicon carbide (a-SiC:H) films are used in the amorphous silicon solar cell [1,2], the tandem solar cell [3] and the electroluminescent device [4]. The structure, optical and electrical properties of the films depend on the deposition conditions [5,6]. Especially, the hydrogen atoms in the films give much influence on some electronic and optical properties [7,8]. Therefore, the measurement of hydrogen concentration and bonding structure in a-SiC:H films and their thermal stability are important for the devices. Hydrogen concentration is usually indirectly estimated by infrared (IR) absorption measurements [9] except for the unbonded hydrogen.

In this paper, we studied the variation of hydrogen in a-SiC:H film prepared by rf sputtering method in a gas mixture of argon and hydrogen by using IR spectroscopy and elastic recoil detection analysis (ERDA) [10,11]. In addition, we have carried out in-situ characterization of

hydrogen depth profiles during isochronal annealing of the specimen to obtain the activation energy for detrapping of hydrogen.

2. Experimental details

A-SiC:H films were prepared by diode-type rf planar magnetron sputtering on to Si (111) wafers at room temperature. A sintered silicon carbide disk 75 mm in diameter was sputtered at a power of 210 W in a gas mixture of argon at partial pressure (P_{Ar}) of 0.33 Pa, and hydrogen (P_{H_2}) from 0.065 to 1.3 Pa, where the background pressure before sputtering was 6.5×10^{-5} Pa. The distance from the cathode to the substrate was 50 mm. Under these conditions, the deposition rate obtained was about 0.5 nm s⁻¹. The component ratio of carbon to silicon determined by Auger electron spectroscopy was nearly unity.

IR spectra of as-deposited and annealed films were measured using a double beam IR spectrophotometer (Hitachi Perkin-Elmer 225). The annealing temperature was in the range of 373–1373 K for 3600 s in vacuum of 5×10^{-4} Pa.

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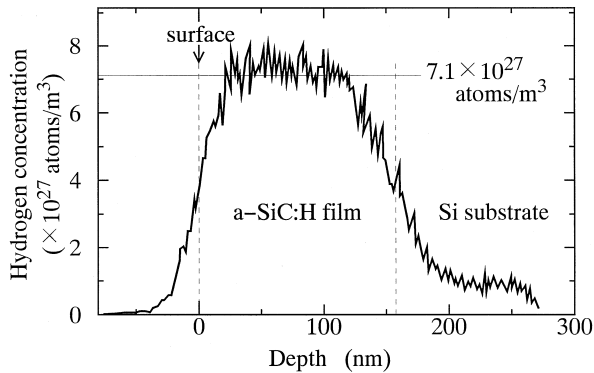


Fig. 1. Hydrogen depth profile in a-SiC:H film 154-nm-thick prepared at H_2 partial pressure of 0.33 Pa obtained by ERDA.

In ERDA [12,13], the recoiled hydrogen from elastic collisions with the bombarding 6.06 MeV $^{19}F^{3+}$ ions traverses through the $0.5 \times 2 \text{ mm}^2$ collimator and is at the fixed forward angle of 40° with an energy below 0.4 MeV. A 6.2- μm -thick Mylar absorber was used as a particle filter to shield the silicon surface barrier detector (SSBD) from the forward scattered analysis beam and other recoiled heavy ion beams. The typical beam current of $^{19}F^{3+}$ on the samples was 5–10 particle nanoampere (pnA). The depth scale applied to the sample was obtained using Bragg's law for stopping power based on the elemental values tabled by Ziegler [14,15] and Andersen and Ziegler [16]. In-situ isochronal annealing for 300 s at various temperatures from 323 to 1123 K was carried out in the ERDA system.

3. Results and discussion

3.1. Hydrogen depth profile by ERDA

A hydrogen depth profile in the 154-nm-thick a-SiC:H film prepared at P_{H_2} of 0.33 Pa obtained by ERDA is shown in Fig. 1. The surface of the a-SiC:H film and the interface between the film and silicon substrate are indi-

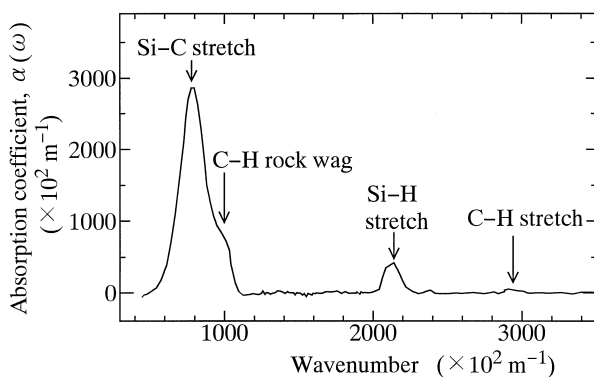


Fig. 2. Typical IR absorption spectrum of a-SiC:H film prepared at H_2 partial pressure of 0.33 Pa.

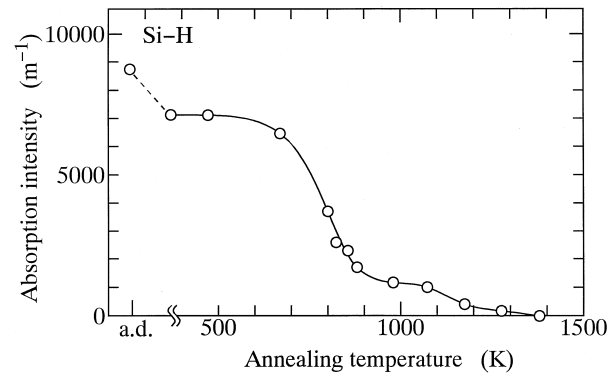


Fig. 3. Annealing temperature dependence of the integrated intensity ($\int(\alpha(\omega)/\omega)d\omega$), which is due to the vibrations of Si-H bonds.

cated by broken lines. The depth profile of hydrogen concentration in the film was uniform at 7.1×10^{27} atoms/ m^3 .

3.2. IR absorption results

Fig. 2 shows IR absorption coefficient $\alpha(\omega)$ vs. wavenumber for as-deposited a-SiC:H film prepared at P_{H_2} of 0.33 Pa. This figure shows broad absorption bands at around 800, 2100 and 2800 cm^{-1} , which are due to the stretching mode vibrations of Si-C, Si-H and C-H bonds, respectively [8]. In addition, a shoulder on the absorption band is shown at around 1000 cm^{-1} , which is due to the rocking and wagging mode vibrations of C-H bonds. The concentration of C-H bonds is estimated by using the absorption spectra at around 1000 cm^{-1} which was separated from the absorption at around 800 cm^{-1} .

Using the value of $\alpha(\omega)$, the concentration of bonds in the film, N_{IR} is given by [17]

$$N_{\text{IR}} = A_s \int \frac{\alpha(\omega)}{\omega} d\omega \quad (1)$$

where A_s is a conversion factor which depends on the bonding state, which will be estimated later, and the integration is over the absorption band. Thus the integrated

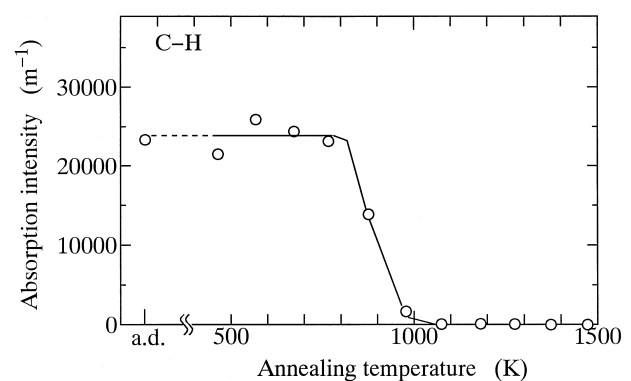


Fig. 4. Annealing temperature dependence of the integrated intensity ($\int(\alpha(\omega)/\omega)d\omega$), which is due to the vibrations of C-H bonds.

intensity ($\int(\alpha(\omega)/\omega)d\omega$) is directly proportional to the concentration of bonds in the films [8,18].

Figs. 3 and 4 show changes of the integrated intensities ($\int(\alpha(\omega)/\omega)d\omega$), which are due to the vibrations of Si–H and C–H bonds, with increase of annealing temperature for the samples prepared in the same condition in Fig. 2. These figures show the integrated intensities decrease with increase of annealing temperature from 600 to 1000 K and from 850 to 1100 K for Si–H and C–H, respectively. These results mean that the hydrogen which was bonded to Si or C atoms is released at different ranges of temperatures.

3.3. In-situ isochronal annealing in the ERDA system and the kinematical analysis of hydrogen release

In-situ isochronal annealing for 300 s at various temperatures from 323 to 1123 K in the ERDA system was carried out in order to measure a precise transition of hydrogen density in the film directly. Fig. 5 shows the variation of hydrogen depth profiles during the isochronal annealing. The surface of the film and the interface between the film and Si substrate are indicated by broken lines. In this figure, it is seen that the hydrogen does not diffuse into the Si substrate, but is released from surface of the sample with increasing temperature. At 1073 K, hydrogen is no longer detected. The average hydrogen concentrations deduced from Fig. 5 are plotted against annealing temperatures in Fig. 6. In Fig. 6, open circles and solid lines show the experimental results and the calculated, respectively. The hydrogen concentration decreases with

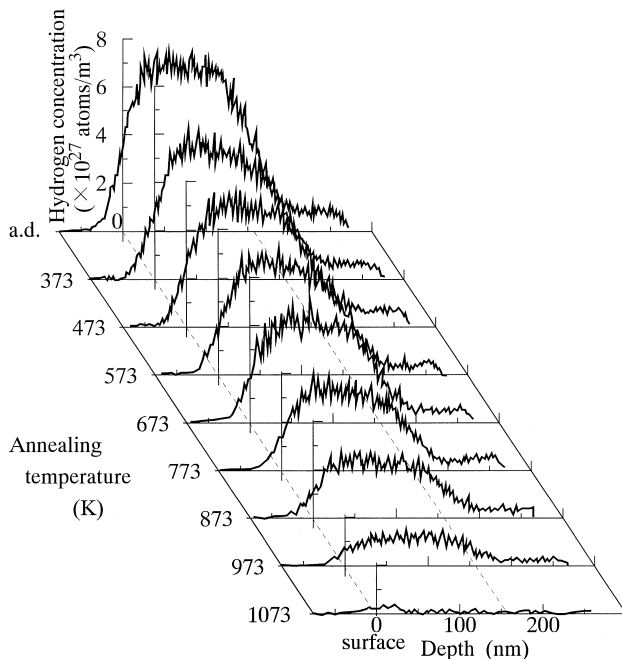


Fig. 5. Change in the hydrogen depth profile of a-SiC:H film prepared at H_2 partial pressure of 0.33 Pa during in-situ isochronal annealing for 300 s at the temperatures from 323 to 1123 K in ERDA system.

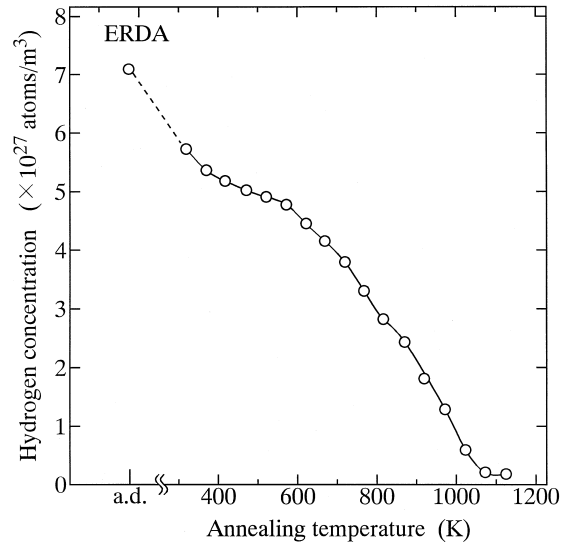


Fig. 6. Change in hydrogen concentration in a-SiC:H film with the annealing temperature, obtained from the hydrogen depth profiles seen in Fig. 5. Open circles and solid line show the experimental results and the calculated, respectively.

increase of annealing temperature. Three characteristic regions are seen where the hydrogen concentration decreases drastically at the annealing temperatures around 350, 700 and 950 K. These temperatures are in good agreement with the integrated intensities of IR absorption bands as shown in Figs. 3 and 4. Thus, it can be said that three types of hydrogen bonds are distributed in the films; the first type is the unbonded, which corresponds to the release around 350 K, the second and third types are the hydrogen bonded to Si or C atom, which correspond to the release at temperatures around 700 or 950 K, respectively.

The solid line in Fig. 6 was calculated under the assumptions [19] that the detrapping is a rate limiting process and that the release process obeys the first-order kinetics; the hydrogen atoms escape from the surface of the film, and diffusion is independent of the hydrogen concentration. In this case, the activation energy is expressed by a generalized form of the Arrhenius equation [20],

$$N = N_0 \exp \left[-t\nu \exp \left(\frac{-E_D}{kT} \right) \right] \quad (2)$$

where N is the hydrogen concentration in the film after annealing for a time t at a temperature T , N_0 is the initial hydrogen concentration, E_D is the activation energy for detrapping, ν is the detrapping attempt frequency and k is the Boltzmann constant. Since three types of hydrogen bonds are present in these films, three kinds of the initial hydrogen concentration N_1 , N_2 and N_3 , are to be considered. The experimental results in Fig. 6 were fitted by Eq. (2) where the activation energy E_D and the detrapping attempt frequency ν are obtained through the relation of $1/T$ vs. $\ln\{-\ln(N/N_0)\}$ in the three characteristic re-

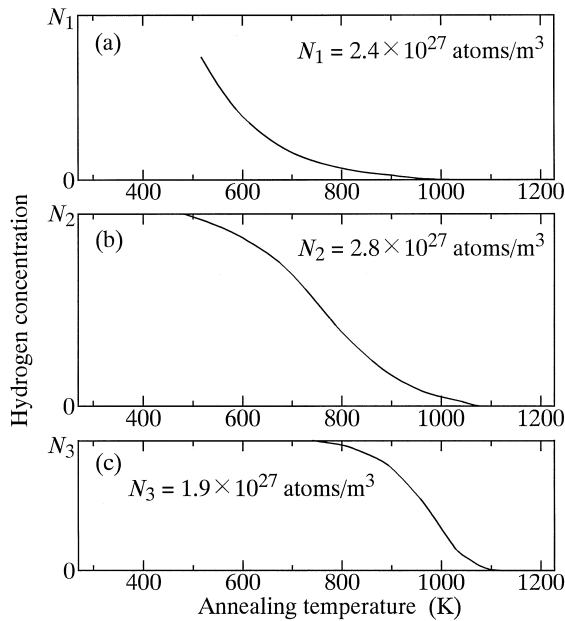


Fig. 7. Changes in the concentrations of three types of hydrogen in the film; (a) the unbonded hydrogen, (b) the hydrogen bonded to Si atom and (c) that to C atom. N_1, N_2 and N_3 indicate the initial hydrogen concentrations of such three types of hydrogen.

gions. The initial concentrations N_1 , N_2 and N_3 , were determined from iterative calculation. The initial hydrogen concentrations N_1 , N_2 and N_3 thus determined based on Eq. (2) are 2.4×10^{27} , 2.8×10^{27} and 1.9×10^{27} atoms/m³, respectively, and the activation energies are 0.079 eV (1.27×10^{-20} J), 0.44 eV (7.05×10^{-20} J) and 1.3 eV (2.08×10^{-19} J), respectively. Fig. 7a, b and c show the calculated concentrations of those three types of hydrogen as a function of annealing temperature. We determined the conversion factors A_s for Si–H and C–H bonds in a-SiC:H film based on Eq. (1) using the values of $\int(\alpha(\omega)/\omega)d\omega$ shown in Figs. 3 and 4 and N_2 , N_3 . The conversion factors A_s determined were 3.2×10^{23} and 6.4×10^{22} m⁻² for Si–H and C–H, respectively.

3.4. Concentrations of three types of hydrogen in a-SiC:H films prepared at various H_2 partial pressures

Fig. 8 shows the change of hydrogen concentration in a-SiC:H films with various hydrogen partial pressures P_{H_2} ranging from 0.065 to 1.3 Pa. In this figure, open circles indicate total hydrogen concentrations as measured by ERDA, and bar charts indicate the concentrations of Si–H and C–H bonds which were estimated from the IR absorption spectra, using the conversion factors estimated from the N_2 and N_3 values (Section 3.3). Hatched region then indicates unbonded hydrogen concentrations. It is seen that

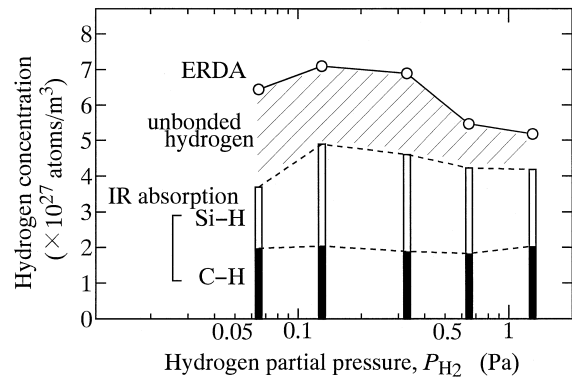


Fig. 8. Hydrogen concentrations in a-SiC:H films prepared under various H_2 partial pressures P_{H_2} ranging from 0.065 to 1.3 Pa. Open circles indicate total hydrogen concentrations as measured by ERDA, and bar charts indicate the concentrations of Si–H and C–H bonds which were estimated from the IR absorption spectra, using the conversion factors estimated from the N_2 and N_3 values (Section 3.3). Hatched region then indicates unbonded hydrogen concentrations.

the unbonded hydrogen concentration has peaked in the range of P_{H_2} from 0.13 to 0.33 Pa.

The radicals in the plasma during sample preparation were observed by optical emission measurements [21]. Fig. 9a, b shows the optical emission intensity of radicals of (a) Ar^* (415 nm) and (b) H_α^* (652 nm) and H_β^* (486 nm) for various hydrogen partial pressures P_{H_2} . In Fig. 9, it is seen

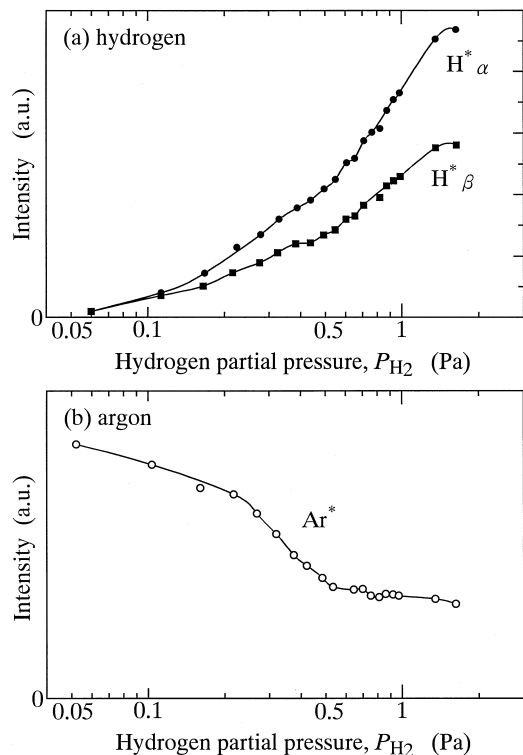


Fig. 9. The optical emission intensity of radicals of (a) Ar^* (415 nm) and (b) H_α^* (652 nm) and H_β^* (486 nm) for various hydrogen partial pressures P_{H_2} .

that the intensities of H_{α}^* and H_{β}^* increase and the intensity of Ar^* decreases with increase of P_{H_2} , respectively. The unbonded hydrogen concentration decreases in accordance with the increase of hydrogen radicals (H_{α}^* and H_{β}^*) in the plasma.

4. Summary and conclusions

Concentration and thermal release of hydrogen in the hydrogenated amorphous SiC (a-SiC:H) films were studied using IR spectroscopy and elastic recoil detection analysis (ERDA). The results obtained are as follows:

(1) Hydrogen depth profiles of as-deposited films by the ERDA method showed that the total hydrogen concentrations in the films ranged from 5.3 to 7.1×10^{27} atoms/m³.

(2) The IR measurements conducted on the films annealed at various temperatures for 3600 s suggested that the hydrogen was released from Si–H and C–H bonds in the films at the temperatures from 600 to 1000 K and from 850 to 1100 K, respectively.

(3) In situ isochronal annealing for 300 s at various temperatures from 323 to 1123 K in the ERDA system was carried out for the film having the hydrogen concentration of 7.1×10^{27} atoms/m³. Three types of hydrogen bonds exist in the film; the first type is the unbonded, the second and third types are the hydrogen bonded to Si or C atom. The initial concentrations and the activation energies for thermal release of three types of hydrogen were determined to be 2.4×10^{27} , 2.8×10^{27} and 1.9×10^{27} atoms/m³, and 0.079 eV (1.27×10^{-20} J), 0.44 eV (7.05×10^{-20} J) and 1.3 eV (2.08×10^{-19} J), respectively.

(4) The conversion factors A_s for the Si–H and C–H bonds in a-SiC:H film were 3.2×10^{23} and 6.4×10^{22} m⁻², respectively. The unbonded hydrogen concentration decreased in accordance with the increase of hydrogen radicals (H_{α}^* and H_{β}^*) in the plasma.

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References

- [1] G. Ganguly, A. Matsuda, Mater. Res. Proc. 258 (1992) 39.
- [2] S. Tsuda et al., Jpn. J. Appl. Phys. 26 (1987) 28.
- [3] G.A. Hirata, T. Nishimoto, H. Okamoto, Y. Hamakawa, IEEE Electron Devices 12 (1991) 41.
- [4] F. Demichelis, G. Crovini, C.F. Pirri, E. Tresso, G. Amato, U. Coscia, G. Ambrosone, P. Rava, Thin Solid Films 241 (1994) 274.
- [5] H. Shirai, D. Das, J. Hanna, I. Shimizu, Appl. Phys. Lett. 59 (1991) 1096.
- [6] Y. Suzuki, S. Inoue, I. Hasegawa, K. Yoshii, H. Kawabe, Thin Solid Films 173 (1989) 235.
- [7] C.H. Ling, C.Y. Kwok, K. Prasad, J. Vac. Sci. Technol. A5 (1987) 1874.
- [8] F. Demichelis, F. Giorgis, C.F. Pirri, E. Tresso, Phil. Mag. B 71 (1995) 1015.
- [9] W.A. Lanford, M.J. Rand, J. Appl. Phys. 49 (1978) 2473.
- [10] P.M. Read, C.J. Sofield, Thin Solid Films 110 (1983) 251.
- [11] A. Turos, O. Meyer, Nucl. Instr. Meth. b4 (1984) 92.
- [12] K. Umezawa, T. Kuroi, J. Yamane, F. Shoji, K. Oura, T. Hanawa, Nucl. Instr. Meth. b33 (1988) 634.
- [13] T. Kuroi, K. Umezawa, J. Yamane, F. Shoji, K. Oura, T. Hanawa, Jpn. J. Appl. Phys. 27 (1988) 23.
- [14] J.F. Ziegler, Stopping Cross-Sections for Energetic Ions in All Elements, Pergamon, New York, 1980.
- [15] J.F. Ziegler, Nucl. Instr. Meth. 168 (1980) 17.
- [16] H.H. Andersen, J.F. Ziegler, Hydrogen Stopping Powers and Ranges in All Elements, Pergamon, New York, 1977.
- [17] S. Inoue, K. Yoshii, M. Umeno, H. Kawabe, Thin Solid Films 151 (1987) 403.
- [18] F. Demichelis, C.F. Pirri, E. Tresso, G. Benedetto, Phil. Mag. B63 (1991) 1223.
- [19] F.M. Lord, J.S. Kittelberger, Surf. Sci. 43 (1974) 173.
- [20] A.H.M. Holtslag, A.V. Silfhout, Surf. Sci. 187 (1987) 36.
- [21] A. Matsuda, M. Matsumura, S. Yamasaki, H. Yamamoto, T. Imura, H. Okushi, S. Iizima, K. Tanaka, Jpn. J. Appl. Phys. 20 (1981) L183.