

## Ion beam analysis of SiC<sub>x</sub> thin films using a deuterium beam

E. Andrade<sup>a,\*</sup>, A. Mahmood<sup>b</sup>, S. Muhl<sup>b</sup>, E.P. Zavala<sup>a</sup>, J.C. Pineda<sup>a</sup>, L. Huerta<sup>a</sup>

<sup>a</sup>Instituto de Física, UNAM, Apartado Postal 20-364, México D.F. 01000, Mexico

<sup>b</sup>Instituto de Investigaciones en Materiales, UNAM, Apartado Postal 70-360, México D.F. 04510, Mexico

Received 25 January 2001; accepted in revised form 25 October 2001

### Abstract

SiC<sub>x</sub> thin films have been prepared using RF reactive magnetron sputtering. The deposition parameters were varied over a wide range to optimise the quality of the films. The film atomic density per unit area (atoms/cm<sup>2</sup>) and composition were obtained by NRA and RBS techniques by bombarding the samples with a low energy deuterium beam. The films were also characterised by X-ray diffraction, FTIR spectroscopy, profilometry and ellipsometry to supplement the RBS and NRA results. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Silicon carbide; Thin film RF; RBS; NRA; Characterisation films

### 1. Introduction

Crystalline silicon carbide is a large bandgap semiconductor (> 2 eV) with high thermal stability (melting point ~ 2800 °C), good mechanical properties, large thermal conductivity (~ 3.9 W/cm per °C), high electric breakdown field (~ 4 × 10<sup>6</sup> V/cm) and a saturation drift velocity of approximately 2 × 10<sup>7</sup> cm/s [1,2]. This combination of properties makes this material an attractive candidate for many high temperature and power applications in the electronics industry.

Unfortunately, the high melting point and the diversity of crystal structures adopted by SiC means that it is very difficult to prepare good quality single crystal or polycrystalline samples. Crystalline films have been made using high temperature chemical vapour deposition but this inevitably leads to unintentional doping and a high concentration of lattice defects. To overcome these problems several lower temperature methods have been used, such as thermal or laser recrystallisation [3,4], plasma or hot-filament enhanced chemical vapour deposition [5,6], low pressure chemical vapour deposition [7], gas source molecular beam epitaxy [8] and UHV reactive DC magnetron sputtering [9,10].

In this paper we present results of the preparation of SiC films by reactive RF magnetron sputtering using conditions that are similar to those used in the DC sputtering study and which resulted in the formation of crystalline SiC. The films were grown on (100) orientated high resistivity silicon at temperatures between 700 and 1000 °C. The structure and composition of the films were obtained using X-ray diffraction (XRD) and ion beam techniques, including both Rutherford back-scattering (RBS) and induced nuclear reaction analysis (NRA).

### 2. Experiment

A turbomolecular-pumped stainless steel UHV vacuum system with a base pressure of less than 1.3 × 10<sup>-5</sup> Pa was used for film preparation. The deposition chamber is equipped with a 4-inch diameter magnetron source and stainless steel substrate stage/heater. Fine wire thermocouples were used to calibrate the temperature of the surface of the P-etched silicon substrates to the temperature of the sample holder. Sputtering was performed using different argon/methane gas mixtures, Ar/CH<sub>4</sub> of 80:20, 70:30, 50:50 and 40:60 (the purity of both gases was 99.999%), at RF plasma powers of 100 and 200 W and a gas pressure of 0.4 Pa. The gas pressure and flows were measured using a MKS capacitance manometer and mass flow controllers. The cham-

\* Corresponding author. Tel.: +52-5-622-5055; fax: +52-5-622-50-46.

E-mail address: andrade@fenix.ifisicacu.unam.mm (E. Andrade).

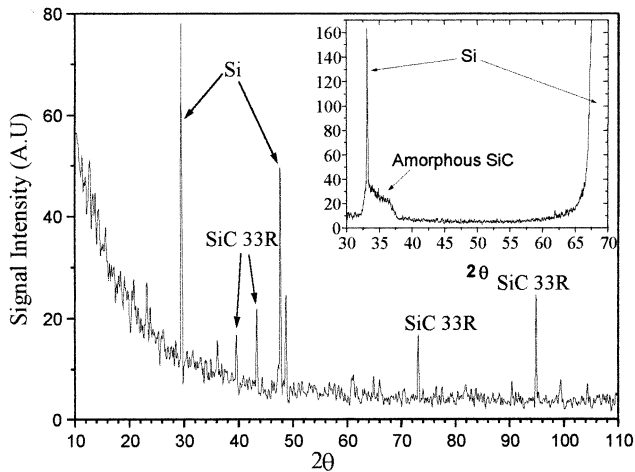


Fig. 1. A typical X-ray diffraction spectrum at glancing angle showing the peaks from the crystalline phase of silicon carbide. The insert shows a spectrum from an amorphous sample using the powder diffractometer.

ber gas pressure was controlled by manually adjusting the position of the gate valve between the chamber and the turbomolecular pump. The substrate to target distance was maintained at 5 cm for all experiments.

The following preparation procedure was used to both clean the target and carbonise the surface of the substrates: after the required substrate temperature was attained 0.08 Pa of  $\text{CH}_4$  was introduced for 10 min, the chamber pressure was then increased to 0.4 Pa through the addition of the argon and the plasma was ignited with a shutter covering the substrate. The shutter was then removed to deposit the film. After growth the substrates were moved to the loadlock chamber using the substrate manipulator, and only when the substrate temperature was less than 100 °C was the gas flow turned off and the substrate removed from the system.

Pieces of silicon, 1 mm wide, were used to mask part of the substrate to facilitate the film thickness measurement using the Dektak IIA profilometer. The samples were analysed using a Nicolet 510P FTIR spectrophotometer, a Gartner model L117 ellipsometer and a Siemens D500 X-ray powder diffractometer using  $\text{CuK}\alpha$  radiation.

The ion beam (IBA) facilities at the University of Mexico [11] based on a vertical single ended 5.5-MV Van de Graaff accelerator was used to obtain the areal density (atoms/ $\text{cm}^2$ ) and the composition of the  $\text{SiC}_x$  films. A low energy  $^2\text{H}^+$  beam instead of the  $^4\text{He}^+$  RBS standard technique was chosen to analyse the samples because the carbon areal density can be obtained from both the  $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$  nuclear reaction (NR) peak and the  $^2\text{H}^+$  elastically backscattered part of the spectrum. A 1140-keV deuterium beam incident perpendicular to the sample with a laboratory detector angle of  $\theta_{\text{lab}} = 165^\circ$  was used. At this energy the Coulomb barrier

for the Si nuclei is high and the elastic cross-section is approximately three orders of magnitude larger than the possible  $^{28}\text{Si}(\text{d},\text{p})$  and  $^{28}\text{Si}(\text{d},\alpha)$  nuclear reactions and therefore their contribution to the particle spectrum is negligible. A 300- $\mu\text{m}$  surface barrier detector with standard electronics was used to measure the energy of the emitted particles. The particle energy spectra collected from the samples were analysed using the more recent SIMNRA program [12]. This computer code is more versatile than the more often used RUMP program [13], because it includes NR cross-sections, non-Rutherford cross-sections, and multiple and plural scattering, etc.

### 3. Results

The standard 2- $\theta$  X-ray diffraction measurements indicated that the majority of the films were amorphous. Only films prepared using the conditions of 100 W, Ar/ $\text{CH}_4$  60:40, 800 °C showed indications of diffraction peaks related to silicon carbide. Typical spectra from both the normal and glancing angle measurements are shown in Fig. 1, including the (1025) and (0216) planes of 33R SiC.

The FTIR spectra of the films contained the expected absorption peak centred between 780 and 790  $\text{cm}^{-1}$  from the silicon carbon bond. No peaks were observed in the 2000 and 3000  $\text{cm}^{-1}$  regions indicating that the films contained very low concentrations of hydrogen bonded to either silicon or carbon.

Fig. 2 shows the variation of the deposition rate as a function of the methane concentration in the gas mixture for plasma powers of 100 and 200 W and for substrate temperatures of 800 and 900 °C. The rate is always higher for the 200-W plasma and tends to decrease for higher methane concentrations. At the lower plasma

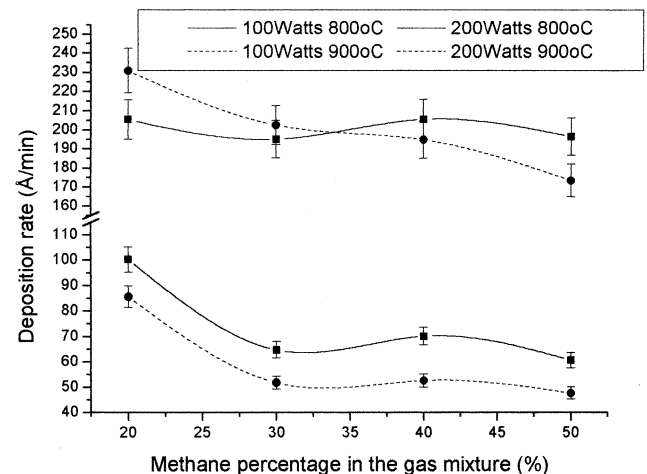


Fig. 2. A graph of the variation of the deposition rate as a function of the methane concentration in the gas mixture for both 100 and 200 W of plasma power and for substrate temperatures of 800 and 900 °C.

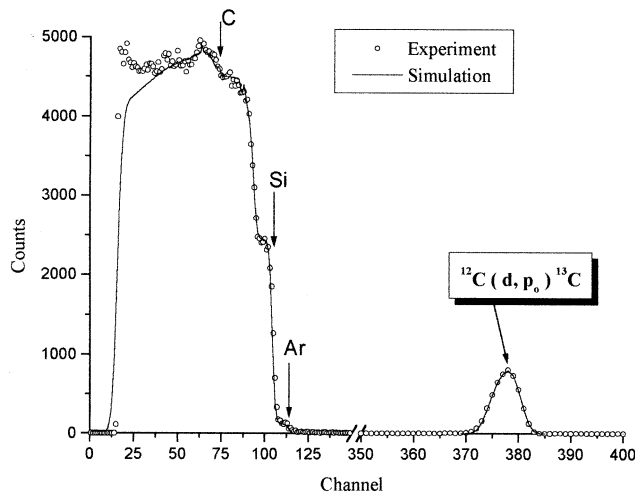


Fig. 3. A typical 1140-keV deuterium spectrum showing the signals from carbon, silicon and argon in the film and substrate, as well as the peaks from the protons produced from the induced nuclear reaction  $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$ . The scattering angle was  $165^\circ$ . The dots are the experimental data points and the solid line is the SIMNRA simulation.

power an increase in the substrate temperature causes a decrease in the deposition rate. However, at 200 W the effect of the temperature appears to depend on the methane concentration but even so the observed variation of 800 and 900 °C data is of the order of the experimental uncertainty.

Fig. 3 shows a typical particle energy spectrum (dots) produced from a sample bombarded with the 1140-keV deuterium beam. The low energy part of the spectrum is from  $^2\text{H}^+$  elastically scattered from the Si, C and Ar nuclei in the film and the Si in the substrate. The spectrum shows that Ar is incorporated in to the film during growth, at a low concentration of  $\approx 2\text{--}4\%$ . The high energy region of the spectrum shows just one peak which corresponds to protons from the  $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$  NR. The presence of oxygen in the films was not observed; no signals from the  $^{16}\text{O}(\text{d},\text{p}_0)$  or  $^{16}\text{O}(\text{d},\text{p}_1)$  NRs were seen for any of the samples. The solid line in the figure is the SIMNRA fit to the spectrum. For this case the spectrum fit was obtained using a  $7.5 \times 10^{18}$  atoms/cm<sup>2</sup> thick layer of  $\text{SiC}_x\text{Ar}_y$  on a 100% Si layer representing the substrate. The percent concentrations were: 48% C, 50% Si and 2% Ar. The SIMNRA error in the atomic concentration values is normally estimated to be approximately 10%. It was expected that this level of error could be improved by simultaneously fitting both the elastic and NR parts of the spectrum. This was true for the film thickness where an uncertainty of better than 5% was found. However, in order to fit the  $^{12}\text{C}(\text{d},\text{p}_0)^{13}\text{C}$  NR peak with  $7.5 \times 10^{18}$  atoms/cm<sup>2</sup> of carbon, it was found necessary to introduce a correction factor,  $f \approx 1.3$ , to the Bragg stopping power rule. Similar experiments on solid compounds, such as oxides,

nitrides and hydrocarbons have also shown comparable deviations from Bragg's rule [14]. Once the best value of this factor was established small variations in the carbon content were used to establish the detectable simulation uncertainty. This error was again estimated to be approximately 5%, however, since the exact value of 'f' is not known this is the relative error in the composition for the films with similar Si/C ratios, and the absolute error in the composition remains at 10%.

Fig. 4 shows the variation of the film composition, expressed as  $R = \text{C}/\text{Si}$ , as a function of the methane content in the gas mixture for plasma powers of 100 and 200 W and substrate temperatures of 800 and 900 °C. The films become less silicon rich as the methane content is increased, but stoichiometric films are only found for the highest methane concentrations at the lower substrate temperature. For the plasma power of 200 W the value of  $R$  is almost constant between 0.47 and 0.67 for all gas mixtures and substrate temperatures.

Fig. 5 presents the film density against the substrate temperature for two methane concentrations at 100 and 200 W. The film density was calculated from the ion beam analysis and the thickness,  $t$ , from the profilometer data, using the formula  $\rho = sA/(N_0t)$ , where  $A$  is the molecular mass of the compound in grams and  $N_0$  is Avogadro's number. The general trend seen is that the density increases as the substrate temperature increases, similar general tendencies are also seen for the rest of the experimental conditions used.

The variation of the refractive index with the substrate temperature for various methane concentrations at both 100 and 200 W is shown in Fig. 6. In most cases the refractive index decreases towards the value expected for SiC,  $n = 2.6\text{--}2.7$ , as the temperature increases and,

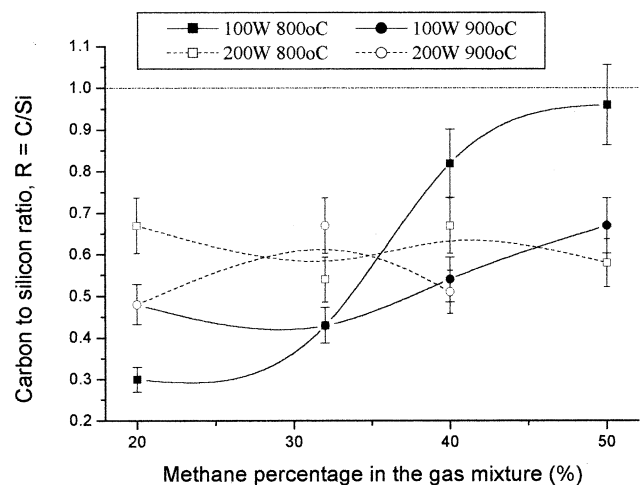


Fig. 4. A graph of the variation of the film composition, expressed as  $r = \text{C}/\text{Si}$ , as a function of the methane content in the gas mixture for a plasma power of 100 W and substrate temperatures of 800 and 900 °C.

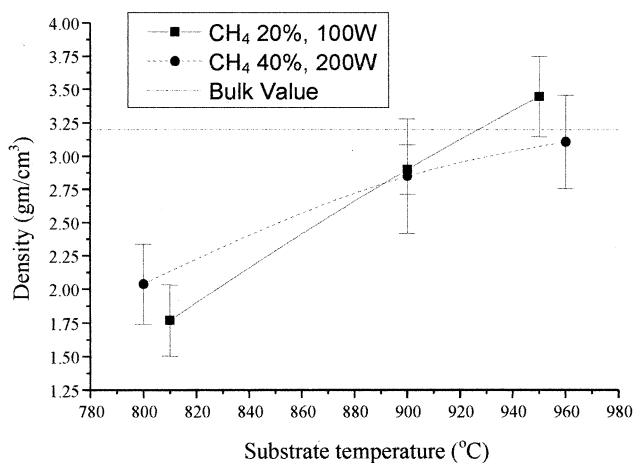


Fig. 5. The film density, calculated from the areal density obtained from the ion beam analysis and the thickness from the profilometer data, against the substrate temperature for two methane concentrations at 100 and 200 W.

in general, is higher for the larger concentrations of methane in the gas mixture.

#### 4. Discussion

The properties of the films depends on the formation process of SiC<sub>x</sub>, and a priori, we do not know if the silicon and carbon atoms arrive at the substrate independently with the compound being formed by a chemical reaction on the surface of the growing film (case A), or if the compound is created on the target and then sputtered as molecular species (case B). Furthermore, given the stability of the methane molecule it is probable that the carbon supplying species for either of the above processes are CH<sub>x</sub> molecules created within the plasma ( $0 \leq x < 4$  with the reactivity increasing for smaller values of  $x$ ). If the degree of decomposition of the methane within the plasma is very high then the amount of CH<sub>x</sub> molecules will be supply limited and will change with the percentage of methane in the gas mixture (case I). If the degree of decomposition is much less than complete then the concentration of CH<sub>x</sub> will be almost independent of the CH<sub>4</sub> percentage but will be controlled by a combination of the electron temperature and plasma density (case II). The plasma density and electron temperature generally increase as the plasma power increases, although changes in the gas composition can also be of importance. Additionally, since atomic hydrogen is created in the plasma the net deposition rate will also depend on the etching of the growing film by these atoms. Moreover, since this is a chemical process it will be thermally activated, and the variation of the amount of atomic hydrogen will be the same as that described for the CH<sub>x</sub> molecules. However, the etch rates for the

elemental silicon, carbon and silicon carbide will not be the same and can be expected to have different thermal activation rates. At temperatures above 700 °C the etch rate for carbon is higher than silicon and both are probably higher than SiC.

The expected variation of the arrival rates of the different species to the substrate for the cases described above as a function of the plasma power and methane gas concentration is described in Table 1.

In summary, with increasing plasma power, the carbon to silicon ratio in the deposit, C/Si, can be expected to decrease for case A I, remain almost constant for case A II, be constant or slightly decrease for case B I and increase for case B II, and the total deposition rate is expected to increase for cases B I and B II. With increasing methane concentration in the gas mixture, the C/Si ratio is expected to increase for cases A I, A II and B I, and remain almost constant for case B II, and the deposition rate will decrease for cases B I and B II.

The results shown in Fig. 4 indicate that case B II can be excluded since C/Si does not increase with increasing plasma power. The results shown here and in Fig. 2 show the importance of the etching of the deposit by hydrogen and reinforces the idea that the etch rate of carbon is greater than that of either silicon or SiC. The data from Fig. 2 also indicate that case B I is probably not operative since an increase in the deposition rate would have to be accompanied by a significant change in the C/Si ratio as the plasma power increased. Similarly from Fig. 2 we can exclude case A II. In this figure it is clear that thermally activated etching of the deposit is occurring (see the data for 100 W, 800 and 900 °C), therefore if the CH<sub>x</sub> and H concentrations increased with increasing power, enhancement of the etch rate would be likely, but this is not observed. Therefore we can conclude that the film formation

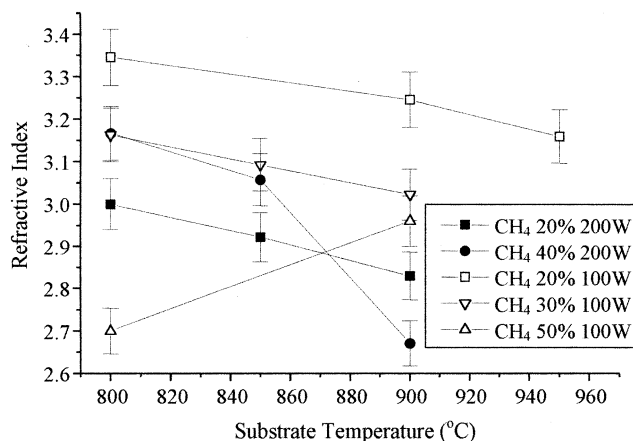


Fig. 6. The variation of the refractive index for different substrate temperatures for various methane concentrations at both 100 and 200 W.

Table 1

Variable	Case	Variation of the arrival rate of species to the substrate	Comments
Increasing plasma power	(A+I) SiC formed on subs. and	Si increases	Target sputtering rate increases
	Methane flow constant	CH <sub>x</sub> supply limited	CH <sub>x</sub> and H remain almost constant
Increasing methane flow	(A+II) SiC formed on subs. and	Si increases	The target sputtering rate increases
	CH <sub>x</sub> not supply limited	CH <sub>x</sub> and H both increase	The increased plasma power increases the decomposition of CH <sub>4</sub>
	(B+I) SiC formed on target and	SiC remains almost constant or slightly increases, Si rate increases.	The arrival rate of CH <sub>x</sub> is constant therefore the sputtering rate of SiC cannot increase greatly without increasing the flux of Si atoms.
	CH <sub>x</sub> supply limited	CH <sub>x</sub> and H remain almost constant or slightly decrease	The CH <sub>x</sub> and H production rates are limited by the supply of CH <sub>4</sub>
	(B+II) SiC formed on target and	SiC increases, Si rate decreases.	The target sputtering rate increases, but the increased arrival of CH <sub>x</sub> reduces the area of unreacted Si.
	CH <sub>x</sub> not supply limited	CH <sub>x</sub> and H both increase	The increased plasma power increases the decomposition of CH <sub>4</sub>
	(A+I) SiC formed on subs. and	Si decreases	The concentration of Ar decreases therefore the sputtering rate decreases
	CH <sub>x</sub> supply limited	CH <sub>x</sub> and H both increase	The CH <sub>x</sub> and H production rates are dependent on the supply of CH <sub>4</sub>
	(A+II) SiC formed on subs. and	Si decreases	The concentration of Ar decreases therefore the sputtering rate decreases
	CH <sub>x</sub> not supply limited	CH <sub>x</sub> and H remain almost constant	The CH <sub>x</sub> and H production rates are not dependent on the supply of CH <sub>4</sub>
Plasma power constant	(B+I) SiC formed on target and	SiC and Si rates decrease, but the Si more both than the SiC	The concentration of Ar decreases therefore the sputtering rate decreases but the increased arrival of CH <sub>x</sub> reduces the area of unreacted Si available.
	CH <sub>x</sub> supply limited	CH <sub>x</sub> and H both increase	The CH <sub>x</sub> and H production rates are dependent on the supply of CH <sub>4</sub>
	(B+II) SiC formed on target and	SiC decreases	The concentration of Ar decreases therefore the sputtering rate decreases
	CH <sub>x</sub> not supply limited	CH <sub>x</sub> and H remain almost constant	The CH <sub>x</sub> and H production rates are not dependent on the supply of CH <sub>4</sub>

process occurs, mainly, by the independent arrival of Si and CH<sub>x</sub> species, and that these react on the surface of the substrate/growing film to form SiC. Furthermore, that the degree of decomposition of the methane in the plasma is high such that the concentration of CH<sub>x</sub> and H is independent of the plasma power and controlled by the methane flow rate. Finally, we see that etching of the deposit by atomic hydrogen is of considerable importance and in particular the preferential etching of carbon from the deposit strongly affects the film composition. However, the etching process helps to optimise the density of the deposits.

## 5. Conclusions

The properties of silicon carbide films made by reactive RF magnetron sputtering of silicon in a mixed atmosphere of argon and methane depend on the experimental conditions in a complicated way, in part because of the formation of atomic hydrogen in the plasma which etches the deposit during growth but with different etch rates for carbon, silicon and silicon carbide phases of the deposit.

From a comparison of a phenomenological model of the film formation process and the variation of the film

properties with the experimental conditions we propose that the deposit is formed by a chemical reaction on the surface of the growing film with the silicon and carbon atoms arriving independently at the substrate. Furthermore, we consider that the results can be best explained if we consider that the degree of decomposition of the methane within the plasma is very high such that the amount of  $\text{CH}_x$  molecules are supply limited and therefore mainly change only when the percentage of methane in the gas mixture is altered.

One of the main differences between RF and DC sputtering is that ion bombardment of the growing film with a RF plasma is normally much reduced and this is probably the reason why the films produced in this study were almost completely amorphous.

### Acknowledgments

This work was partially supported by the following project grants DGAPA IN114998 and IN108798, and CONACyT 27676E. We also wish to take the opportunity to thank Ernesto Sanchez and Leticia Baños for their help with the FTIR and X-ray diffraction measurements.

### References

- [1] CRC, CRC Handbook of Chemistry and Physics, 76th ed., CRC Press, West Palm Beach, FL, 1996.
- [2] H.J. Kim, R.F. Davis, *J. Electrochem. Soc.* 133 (1986) 2350.
- [3] K. Sagra, E. Murakami, *Appl. Phys. Lett.* 54 (1989) 2003.
- [4] T. Matsuyama, T. Baba, T. Takahama, S. Tsuda, S. Nakano, *Solar Energy Mater. Solar Cells* 34 (1994) 285.
- [5] S. Veprek, *Mater. Res. Solar Symp. Proc.* 164 (1990) 39.
- [6] T. Sugil, T. Aoyama, T. Ito, *J. Electrochem. Soc.* 3 (1990) 989.
- [7] C.A. Dimitriadis, J. Stoemenos, P.A. Coxon, S. Friligkos, J. Antonopoulos, N.A. Economou, *J. Appl. Phys.* 73 (1993) 8402.
- [8] S. Motoyama, H. Mitsui, Y. Tarui, T. Fuyuki, H. Matsunami, *J. Appl. Phys.* 68 (1990) 101.
- [9] Q. Whab, R.C. Glass, I.P. Ivnaov, J. Birch, J.E. Sundgren, M. Willander, *J. Appl. Phys.* 74 (1993) 1663.
- [10] Q. Whab, M.R. Sardela, J.L. Hultman, et al., *Appl. Phys. Lett.* 65 (1994) 725.
- [11] E. Andrade, *Nucl. Instrum. Meth. B* 57 (1991) 799.
- [12] M. Mayer, SIMNRA User's Guide, Technical Report IPP 9/113, Max-Planck-Institut für Plasmaphysik, Garching, Germany.
- [13] R. Doolittle, *Nucl. Instrum. Meth. B* 15 (1986) 227.
- [14] J.F. Ziegler, J.M. Manoyan, *Nucl. Instrum. Meth. B* 35 (1988) 215.