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# The influence of electric field on the microstructure of nc-Si:H films produced by RF magnetron sputtering

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**Abstract:** Hydrogenated nanocrystalline silicon thin films were prepared by RF magnetron sputtering. Different bias fields (no bias–no ground, grounded and negative bias) were applied to the substrate. The effect of the ion bombardment on the structure, chemical composition and optical property were studied by Raman spectroscopy, X-ray diffraction, Rutherford backscattering (RBS) and optical transmission spectroscopy. The deposition rate and the optical bandgap decrease as the bias voltage increases from 0 to -50 V. The structural characterization indicates that compressive stress is developed in plane and tensile stress is induced in the growth direction. No significant variation on the chemical composition was observed.

Keywords: nc-Si; Stress; Optical properties; Thin films

## 1. Introduction

Thin films of hydrogenated nanocrystalline silicon find wide applications in optoelectronic devices such as solar cells, flat panel displays, image sensors and printer heads. Improved optical properties of these devices are due to the saturation of silicon dangling bonds (DB) by hydrogen incorporation during growth, leading to considerable reduction in the defect density in the film. In addition hydrogen passivation of defects also helps to relieve strain and provides the possibility of doping the material [1].

RF magnetron sputtering is one of the techniques by which hydrogen can be incorporated during film growth. This technique allows the possibility of choosing and controlling the hydrogen content by varying the hydrogen proportion in the gas mixture. The microstructure of the grown films is a function of growth parameters such as (a) deposition temperature, (b) RF power, (c) hydrogen/argon atmosphere, (d) distance between target and substrate and (e) bias field applied to the substrate.

The influence of a negative bias field applied to the substrate on the microstructure has been reported for TiN films [2,3]. For these films it was shown that the presence of negative bias field led to a more compact structure due to the reduction of voids between the crystallites. This has been attributed to the influence of ion bombardment on the sputtered material. Re-sputtering of the grown film and selective removal of impurities also caused decrease in the deposition rate and average crystallite size [2,3]. Moreover during the growth under biased conditions, the films were found compressively stressed (shot peening model) in the direction parallel to the substrate surface [4]. In order to keep the unit cell volume unaltered due to the compressive stress, expansion in the direction normal to the substrate surface was observed [5].

To our knowledge, the application of bias field during the growth of hydrogenated nanocrystalline silicon has not been reported in the literature. Hence a detailed investigation on the influence of bias fields (grounded – GND, no bias–no ground – NBNG, and negative) was carried out during growth of nc-Si:H films. In this communication the influence of different bias field conditions on the structure (crystal size, crystalline fraction, microstrain) and optical properties is reported.

## 2. Experimental

Thin films of nc-Si:H were grown using reactive RF magnetron sputtering technique. The target material was a crystalline Si wafer (99.99%). The distance between the substrate and target was fixed at 50 mm. A mixture of hydrogen and argon gas was used in the chamber. The substrate temperature, RF power and partial gas pressure were kept as constants and the values were 400$^{o}$C, 80W, $P_{H2}$ = 0.156 Pa and $P_{Ar}$ = 0.117 Pa, respectively. Different bias fields (grounded, no bias–no ground, negative bias) were applied to the substrate.

The microstructure of the thin films was studied by the conventional techniques as Raman spectroscopy and X-ray diffraction. Raman scattering experiments were carried out using Ar-Laser ($\lambda$= 514.5 nm) radiation. X-ray spectra were obtained using Cu K$\alpha$ ($\lambda\alpha1$=1.54056 Å and $\lambda\alpha2$ =1.54439 Å) in a standard ($\theta/2\theta$) geometry.

All the experiments were carried out at room temperature and at atmospheric pressure. Chemical composition of the films was determined by Rutherford backscattering (RBS) technique.

## 3. Results and discussion

### *3.1. Optical and chemical study*

Thickness and optical bandgap of films obtained from the near IR transmission spectra using the Swanepoel method [6] and Tauc's [7] plot are given in Table 1. The deposition rate determined from the thickness measurements is also shown in Table 1.

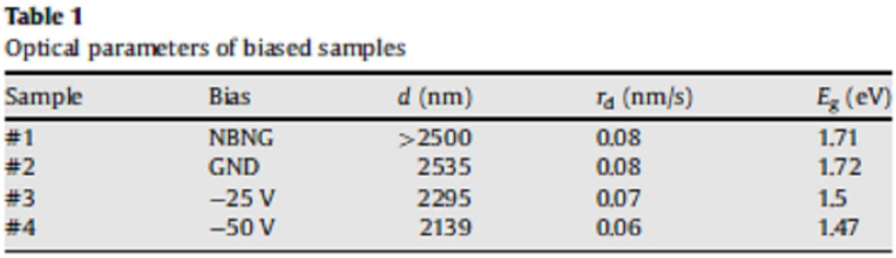

**Table 1**

Optical parameters of biased samples

| Sample | Bias | d (nm) | $r_d$ (nm/s) | $E_g$ (eV) |
|---|---|---|---|---|
| #1 | NBNG | >2500 | 0.08 | 1.71 |
| #2 | GND | 2535 | 0.08 | 1.72 |
| #3 | −25 V | 2295 | 0.07 | 1.5 |
| #4 | −50 V | 2139 | 0.06 | 1.47 |

We can see that the deposition rate is higher for films grown under grounded substrate condition. The absence of ion bombardment can be attributed to a high deposition rate. For negative bias conditions (0 to -50 V), the deposition rate decreases with increasing negative bias voltage. Due to ion bombardment, resputtering of the growing film occurs resulting in a decrease in the deposition rate.

The optical bandgap values obtained for the GND and NBNG samples are similar/close to the amorphous silicon value (around 1.7 eV). For an increase in negative bias voltage, the optical bandgap decreases towards crystalline silicon value (around 1.2 eV).

The chemical composition was determined using Rutherford backscattering (RBS) technique. The results show that the composition (Si, Ar and $H_2$) is independent of bias voltage. Similar result has been observed in Ref. [18] where $H_2$ content in the film is unaltered by the bias field.

### *3.2. Structural characterization*

#### *3.2.1. Raman spectroscopy*

It is well known that the Raman spectra of nanostructured silicon material shows a broad band near 480 cm$^{-1}$ and a peak in the vicinity of 520 cm$^{-1}$, which is attributed to the amorphous matrix and to the transverse optical mode (TO) of crystalline silicon, respectively.

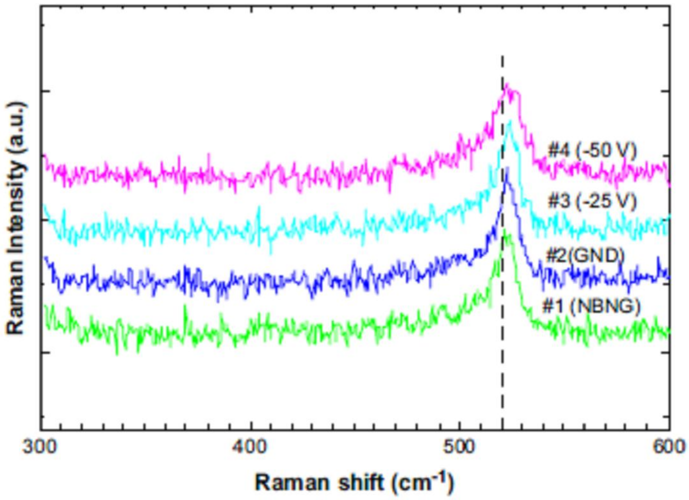

**Fig. 1.** Raman spectra of different biased samples.

To obtain the structural information the experimental spectra was analysed using a Lorentzian profile for the amorphous matrix and the crystalline contribution was obtained on the basis of the strong phonon confinement (SPC) model [9,10] described as follows:

$$I(\omega) \approx \int_0^{\frac{2\pi}{a_0}} \frac{\exp\left(-\frac{q^2L^2}{16\pi^2}\right) 4\pi q^2 dq}{(\omega - \omega(q) - \omega_s)^2 + \left(\Gamma_{0/2}\right)^2} \qquad (1)$$

where $\Gamma_o$ is the line width of the c-Si including the instrumental contribution ($\Gamma_o$ =4.0 cm$^{-1}$), $\omega(q) = \omega_0 - 120(q/q_0)^2$ is the phonon dispersion relation where $\omega_0$ =521 cm$^{-1}$, $q_o = 2\pi/a_o$, $a_o$ is the lattice constant of c-Si ($a_o$ = 0.54308 nm), D is the average size of the crystals and $\omega_s$ is the Raman shift due to the strain ($\varepsilon$) given by

$$\omega_s = -3\gamma\varepsilon\omega_0 \qquad (2)$$

where $\gamma$ is the Gruneisen constant and takes the value 1 for c-Si. Fig. 1 shows the Raman spectra of the samples studied, obtained in backscattering geometry. It is apparent that the Raman peak frequency is higher than 521 cm$^{-1}$ for all the samples. Moreover the Raman peak frequency is higher than the expected value based on crystal size by SPC that correlates halfwidth value with peak position. This suggests that the crystals in the films are stressed and the induced stress is compressive due to the blue shift observed [9].

This blue shift was small and remained constant for grounded and NBNG samples, and increased when the negative bias voltage was increased.

The total stress value was estimated according to Ref. [11] and is given by

$$\sigma(\mathrm{Pa}) = \left(-2.6 \times 10^{8}\right)\Delta\omega\left(\mathrm{cm}^{-1}\right) \qquad (3)$$

where Δω is the induced wavenumber shift compared to stress free bulk crystal Raman line.

The total stress in the thin films consists basically of two components: one component is the thermal stress due to the different thermal expansion coefficients of the film and the substrate, and the other component is the intrinsic stress ($\sigma_{in}$). The thermal stress was calculated according to

$$\sigma_{\mathrm{th}} = (E/1 - \nu)\Delta T(\alpha_{\mathrm{f}} - \alpha_{\mathrm{s}}) \qquad (4)$$

where $\alpha_f$, $\alpha_s$ are the thermal expansion coefficients of the film (f) and substrate (s) and ΔT is the temperature difference between substrate temperature during the film deposition and room temperature [12]. Hence the intrinsic stress was calculated based on the relation:

$$\sigma_{\mathrm{in}} = \sigma - \sigma_{\mathrm{th}} \qquad (5)$$

where σ is the measured total stress using Raman spectroscopy.

For the growth temperature employed in this work, the calculated thermal stress was tensile and the value was found to be 0.03 GPa. Total and intrinsic stress values are given in Table 2.

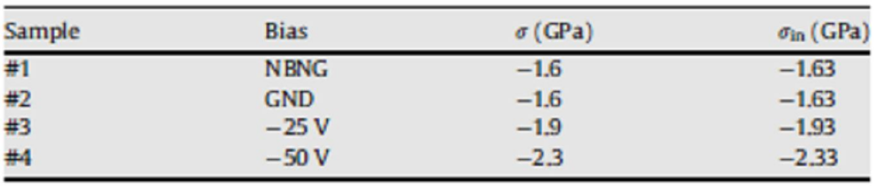

**Table 2**
Calculated total stress ($\sigma$) and intrinsic stress ($\sigma_{in}$) values of nc-Si:H films

| Sample | Bias | $\sigma$ (GPa) | $\sigma_{in}$ (GPa) |
|---|---|---|---|
| #1 | NBNG | −1.6 | −1.63 |
| #2 | GND | −1.6 | −1.63 |
| #3 | −25 V | −1.9 | −1.93 |
| #4 | −50 V | −2.3 | −2.33 |

Using the strong phonon confinement model, the crystal size (D) and strain values (ε) were calculated using Eqs. (1) and (2), respectively. The crystalline fraction (C) was estimated from the integrated intensities of the amorphous and crystalline components [13]. The behavior of these structural parameters on the bias voltage is shown in Figs. 2–4. From Fig. 2 we see that the crystal size computed from Raman measurements decreases with increasing substrate bias voltage. This decrease is more pronounced when the bias voltage is -50 V.

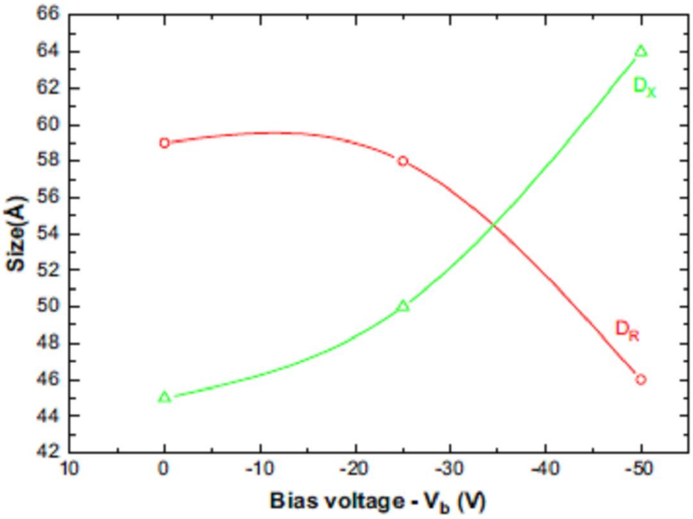

**Fig. 2.** Size of crystallites as a function of bias voltage. $D_R$ – crystal size from Raman analysis. $D_X$ – mean crystal size from X-ray analysis.

Otherwise the behavior of the strain values (Fig. 3) and crystalline fraction (Fig. 4) is the opposite; this means these parameters increase with increasing substrate bias voltage (from 0 (GND) to -50 V). This behavior suggests that the increasing of the negative bias voltage leads to the development of fine grains and a more dense structure. Indeed ion bombardment promotes the selective removal of impurity atoms leading to a decrease in crystal size.

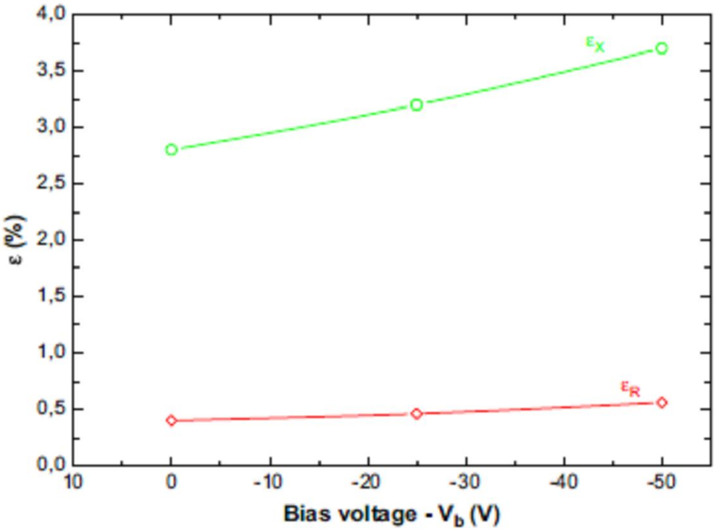

**Fig. 3.** Relationship between strain and bias voltage. $\varepsilon_R$ – strain obtained from Raman spectrum. $\varepsilon_X$ – strain obtained from X-ray diffraction.

Defects induced by ion bombardment can serve as secondary nucleation sites that promote crystallization for negatively biased samples to a larger extent than in the grounded sample [2]. Since the crystalline fraction increases with increasing substrate bias voltage it cannot release the strain in the amorphous matrix/grain boundary [14] and then we observe an increase in strain with bias.

### *3.2.2. X-ray diffraction*

According to Shot Peening model, compressive stress is created parallel to the substrate surface during the growth under bias conditions. This leads to tensile stress in the growth direction. In order to identify the presence of tensile stress, X-ray diffraction was carried out. The analysis of the X-ray diffraction was performed using pseudo-Voigt function [15] to (111) c-Si peak. The apparent crystallite or domain size, D, is given by D= $\lambda/(\beta_C^f \cos\theta)$ and the strain, ε, by ε= $\beta_G^f/(4\tan\theta)$ where l is the wavelength of the k$\alpha_1$ component and θ is the angular position.

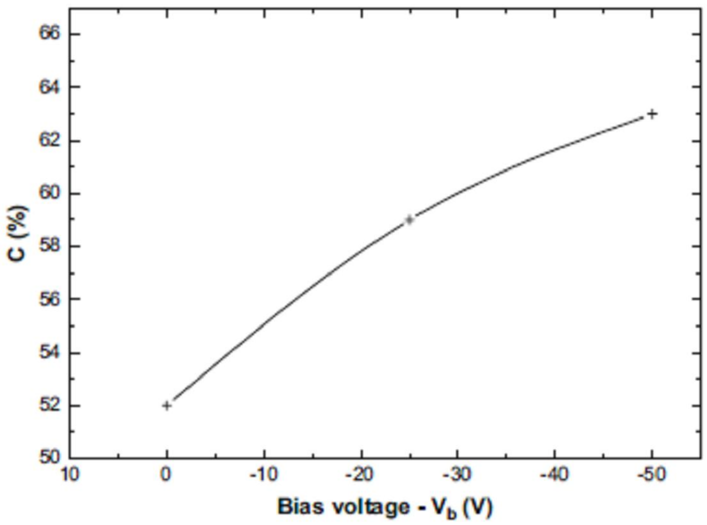

**Fig. 4.** The dependence of crystalline fraction as obtained by Raman study on bias voltage.

The size and strain dependence, by X-ray, on the substrate bias voltage is shown in Figs 2 and 3, respectively. The strain is directly proportional to bias voltage from 0 to -50 V and the stress is tensile, since the diffraction angle (2θ) is less than 28.4° (value for c-Si free of strain). The dependence of crystal size on the applied bias voltage calculated from X-ray diffraction is opposite to that obtained from Raman spectroscopy.

## 4. Conclusions

Thin films of nc-Si:H were deposited by reactive magnetron sputtering under different bias field conditions. Deposition rate and optical bandgap values decrease for an increase in bias voltage 0 to -50 V. Decrease in deposition rate is due to the re-sputtering effect of growing film. Improvement in crystalline fraction may cause decrease in optical bandgap. Raman results indicate that films are compressively stressed in plane and this is directly proportional to bias voltage. Moreover fine grains and more compact structure are developed by ion bombardment for negatively biased samples compared with grounded sample. However, XRD measurements show that tensile stress is developed in the growth direction. The different crystal size behavior obtained by Raman and XRD analysis is related with the fact that $D_X$ (from X-ray) is not the average crystal size but a measure of the correlation length on the growth direction.

No significant difference in the structure and optical properties has been observed between grounded (V= 0) and no bias–no ground samples (NBNG).

## Acknowledgment

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