

EVOLUTION OF MICROSTRUCTURAL PROPERTIES OF HYDROGENATED PROTOCRYSTALLINE SILICON (PC-SI:H) THIN FILMS DEPOSITED BY HW-CVD

¹V. S. Waman, ²M. M. Kamble, ³S. W. Gosavi, ⁴S. R. Jadkar

¹Assistant Professor, ²Assistant Professor, ³Professor, ⁴Professor,

¹Department of Physics,

¹Modern college of Arts, Science and Commerce, Pune, India

²Department of Physics,

²Anantrao Pawar College, Pirangut, Pune, India

^{3,4}Department of Physics,

^{3,4}Savitribai Phule Pune University, Pune, India

Abstract : Demand for an efficient intrinsic layer for a-Si:H based solar cells in terms of microstructure is ever increasing since the inception of single junction and tandem solar cells. In this paper, we report synthesis of high quality hydrogenated protocrySTALLINE silicon (pc-Si:H) thin films by HW-CVD using the mixture of silane (SiH₄) and hydrogen (H₂). Variation in film characteristics with filament-to-substrate distance (d_{s-f}) was studied, and revealed that the structural changes occur in film structure. The filament-to-substrate distance was varied in between 6 cm - 10 cm. The structural properties were studied by Raman and FTIR spectroscopy. Raman spectroscopy results shows with decrease in filament-to-substrate distance the structural changes occurs in thin films. The bond angle variation ($\Delta\theta_b$) of the films is in between 7.34 - 8.43 degrees. Fourier transform infrared spectroscopic analysis showed that the hydrogen mainly bonded with monohydride (Si-H) bonding configuration in all the films deposited at different filament-to-substrate distance. The hydrogen content (C_H) in the films increases with increasing filament-to-substrate distance and was found to be ~ 10.5 at. % over the entire range of filament-to-substrate distance studied. The microstructure parameter (R^*) was found to be decreases 0.19 - 0.16 for the films deposited at higher filament-to-substrate distance and increases upto 0.43 at lower filament-to-substrate distance. The low value of microstructure parameter (R^*) at $d_{s-f} = 8$ cm, suggesting that there is an enhancement of structural order and homogeneity in the film also revealed by Raman spectroscopy. The results obtained by FTIR and Raman suggests that the films deposited at the onset of nanocrystallization i. e. at $d_{s-f} = 8$ cm called protocrySTALLINE nature of the film. From the present study it has been concluded that the filament-to-substrate distance is a key process parameter to decrease structural disorder in thin films deposited by HW-CVD. The obtained film can be used as an intrinsic layer in p-i-n solar cell and Tandem solar cell.

IndexTerms - Hot wire chemical vapor deposition, Hydrogenated protocrySTALLINE silicon, FTIR spectroscopy, Raman spectroscopy, Microstructural properties.

I. INTRODUCTION

Thin film silicon solar cells are based on abundant and non-toxic materials which makes this technology very promising for mass production. Silicon can appear in several forms. The best known is probably crystalline form. The material applied for PV cells is polycrystalline or monocrystalline silicon. In thin film technology there is another form of crystalline silicon called nanocrystalline because of the grain dimension in the nanometer range. In addition, there is amorphous form of silicon where all crystalline symmetries are broken. In recent years, hydrogenated protocrySTALLINE silicon (pc-Si:H) has gained much attention over amorphous silicon (a-Si:H) due to its potential application in opto-electronic devices such as thin film solar cells. ProtocrySTALLINE silicon is the transition phase between amorphous and microcrystalline silicon having high bandgap. The concept of protocrySTALLINE silicon as first described by Koh et al. (Koh, 1998). The important characteristic of protocrySTALLINE thin film growth regime has described by Wronski et al. (Wronski et al., 2002). The intermediate material between hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ c-Si:H) has attracted great attention from many researchers as a promising active layer material for a-Si:H based solar cells due to its relatively high stability against the Stabler-Wronski effect (Stabler and Wronski, 1977). The high stability may be due to the increasing order of the material just onset of the amorphous-to-microcrystalline phase transition (Koh et al., 1998, 1999). The improved medium range order of the amorphous thin films observed by x-ray diffraction (Guha et al., 1999). The position shift of the amorphous silicon (a-Si) transverse optical (TO) band of 480 cm⁻¹ to a higher wavenumber transverse optical (TO) band of nanocrystalline silicon (nc-Si) at 520 cm⁻¹ is also observed in Raman spectroscopy (Tsu et al., 1997).

Several conventional methods have been used for the deposition of Si:H based thin films. These include electron cyclotron resonance chemical vapor deposition (ECR-CVD) (Garcia-Hernansanz et al., 2016), conventional plasma enhanced chemical vapor deposition (PE-CVD) (Nardes et al., 2003), magnetron sputtering (Cerqueira et al., 1995), photo chemical vapor deposition (Photo-CVD) (Ahn et al., 2003), laser ablation (Khan et al., 2015) etc. Each deposition method has its own advantages and limitations. In recent years, hot wire chemical vapor deposition (HW-CVD) technique has emerged as a promising technique to deposit such films at relatively low substrate temperature (Wang et al., 2008, Mahan et al., 2001, Mahan, 2006, Schropp, 2004). The HW-CVD has high gas-decomposition efficiency, large area fabrication, deposition rate etc. over other conventional PE-CVD. Furthermore, the microstructure of Si:H thin films can easily be tuned by manipulating the deposition parameters. However, capabilities of HW-CVD for obtaining device quality pc-Si:H have not been fully established and only few reports on

pc-Si:H films exist in the literature. With this motivation we have initiated the detail study of synthesis of intrinsic pc-Si:H by HW-CVD method. In this paper, we present investigation of influence of filament-to-substrate distance on microstructural properties of pc-Si:H films deposited by HW-CVD method. It has been found that the filament-to-substrate distance is a critical parameter in HW-CVD to obtain pc-Si:H films. The results obtained by FTIR and Raman suggests that the pc-Si:H highly stable at the onset of nanocrystallization.

II. EXPERIMENTAL DETAILS

In this study intrinsic hydrogenated protocrystalline silicon (pc-Si:H) thin films were deposited simultaneously on Corning #7059 glass and c-Si wafers (111) in a hot-wire deposition system, details of which have been described elsewhere (Waman et al., 2011). Films were prepared by using silane (Matheson Semiconductor Grade) and hydrogen (Matheson Semiconductor Grade) mixture. The silane and hydrogen flow rate was kept constant (5 sccm) while filament-to-substrate distance was varied from 6 cm to 10 cm in the step of 1 cm. Other deposition parameters are listed in Table 1. Prior to each deposition, the substrate holder and deposition chamber were baked for 2 h at 100 °C to remove any water vapor absorbed on the substrates and to reduce the oxygen contamination in the film. After that, the substrate temperature was brought to the desired value by appropriately setting the inbuilt thermocouple and temperature controller. The deposition was carried out for the desired period of time and films were allowed to cool to room temperature in vacuum. Then films were taken out for characterization.

Table 1: Deposition parameters employed for the synthesis of pc-Si:H films by HW-CVD

Filament temperature	1900 °C
Deposition pressure	25 mTorr
Substrate temperature	200 ±5 °C
Filament- to- substrate distance	6 - 10 cm
Deposition time	20 min
SiH ₄ flow rate (F _{SiH4})	5 sccm
H ₂ flow rate (F _{H2})	5 sccm

Fourier transform infrared (FTIR) spectra of the films were recorded in transmission mode by using FTIR spectrophotometer (JASCO, 6100-type A) in the range 400-4000 cm⁻¹. Bonded hydrogen content (C_H) was calculated from wagging mode of IR absorption peak using the method given by Brodsky et al. (Brodsky et al., 1977). The microstructure parameter (R*) can be

estimated by formula, $R^* = \frac{I_{2100}}{(I_{2000} + I_{2100})}$, Where, I₂₀₀₀ and I₂₁₀₀ are the integrated intensities of the absorption bands at 2000

cm⁻¹ and 2100 cm⁻¹ respectively (Schropp et al., 1998). Raman spectra were recorded with micro-Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the wavelength range 200-700 nm. The spectrometer has backscattering geometry for detection of Raman spectrum with the resolution of 1 cm⁻¹. The excitation source was 632.8 nm line of He-Ne laser. The power of the Raman laser was kept less than 5mW to avoid laser induced crystallization on the films. The Raman spectra were deconvoluted in the range 410-560 cm⁻¹ using Levenberg-Marquardt method (Marquardt, 1963). The structural disorder or the band angle deviation can be estimated using the relation (Beeman et al., 1995), $\Gamma = 15 + 6 \Delta\theta_b$, Where Γ is the full width at half maximum (FWHM) of the 480 cm⁻¹ peak and $\Delta\theta_b$ is the average bond angle deviation in degrees.

III. RESULTS AND DISCUSSION

Micro-Raman spectroscopic analysis:

Raman spectroscopy is a very powerful non-destructive technique that gives a fast and simple way to determine the phase of the material, whether it is amorphous, crystalline or nanocrystalline. Fig. 1 shows the Raman spectra of pc-Si:H films deposited at various filament-to-substrate distances (d_{s-f}). The films deposited at filament-to-substrate distances (d_{s-f} ≤ 8, 9, 10 cm) show only a broad peak near 480 cm⁻¹ which corresponds to typical a-Si:H material. The broad peak ranges from 415 cm⁻¹ to 560 cm⁻¹ of a-Si:H TO band which indicates the structural order of the films improves with decrease in filament-to-substrate distance. However, the film deposited at d_{s-f} = 7 cm, shows the broad Transverse Optic (TO) phonon peak at ~ 480 cm⁻¹ corresponding to the amorphous phase and another Transverse Optic (TO) phonon peak start to appear at ~ 519 cm⁻¹ originating from nanocrystalline phase (Xu et al., 2000). It shows that films deposited at d_{s-f} = 7 cm shows amorphous-to-nanocrystalline phase transition. This indicates that the improvement of structural order in thin films. Before the onset of amorphous-to-nanocrystalline phase transition is called protocrystalline phase. The film deposited at d_{s-f} = 8 cm shows protocrystalline nature. Further decrease in d_{s-f} at 6 cm, the peak centered at 519 cm⁻¹ shows small enhancement in intensity indicates nucleation of smaller size of crystallites are start to appear in amorphous matrix.

The bond angle deviation ($\Delta\theta_b$) determined from the model given by Beeman et al. (Beeman et al. 1995) are shown in fig. 2. It can be seen that $\Delta\theta_b$ decreases from ~ 8.16° to ~ 7.43° with decrease in filament-to-substrate distance 10 cm to 8 cm and it again increases to 8.01° when filament-to-substrate distance decreases to 6 cm. The decrease in $\Delta\theta_b$ which shows that improvement of structural order at the onset of amorphous-to-nanocrystalline phase transition. The film deposited at d_{s-f} = 8 cm having low value of $\Delta\theta_b$ indicates the protocrystalline nature of thin films. Again increase in $\Delta\theta_b$ which shows nucleation start to occur in amorphous phase increases structural disorders in amorphous network. Thus, Raman scattering study clearly indicates that the Si:H films synthesized by HW-CVD shows improvement in structural order. The film deposited at d_{s-f} = 8 cm having protocrystalline in nature.

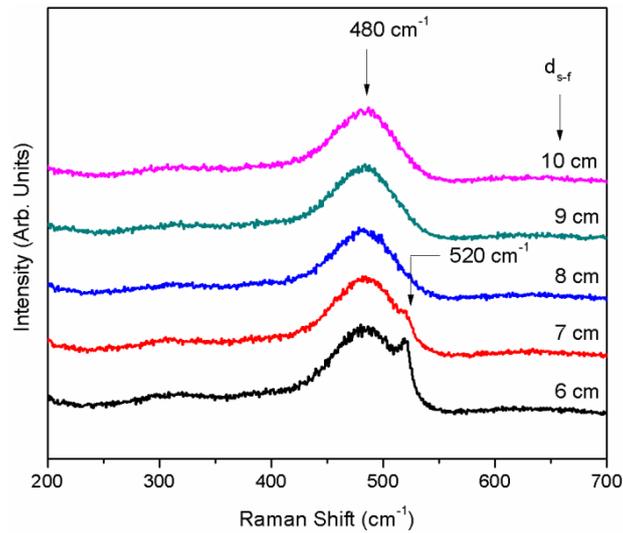


Figure 1: Raman spectra of Si:H films deposited at various filament-to-substrate distances (d_{s-f}).

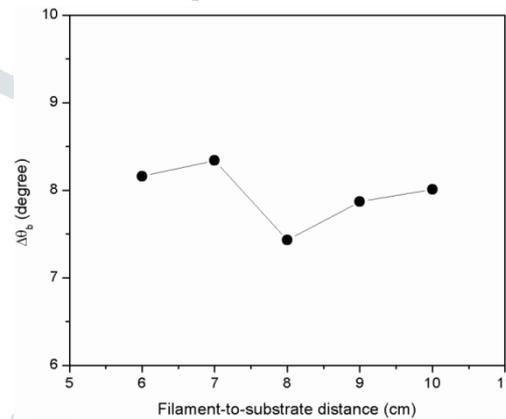


Figure 2: Bond angle variation of Si:H films deposited at various filament-to-substrate distances (d_{s-f}).

Fourier Transform Infrared (FTIR) spectroscopic analysis

To reveal the hydrogen bonding configuration, total hydrogen content and the microstructure parameter, Fourier transform infrared spectroscopy (FTIR) spectroscopy was used. The FTIR spectra of the films (normalized to thickness) deposited by hot-wire deposition method at various filament-to-substrate distances (d_{s-f}) are shown in Fig. 3.

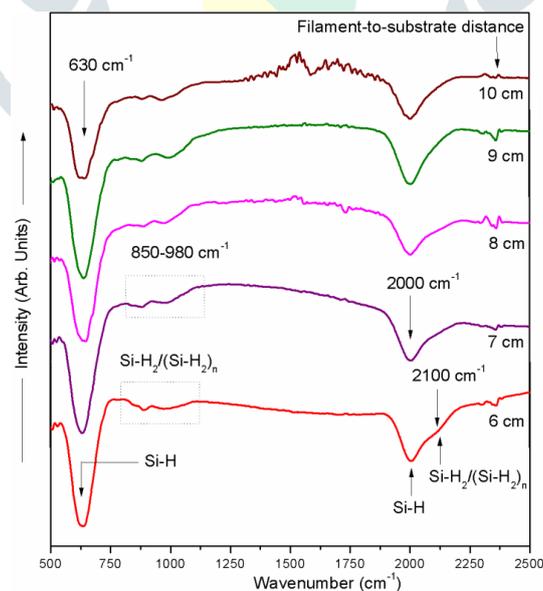


Figure 3: The normalized FTIR spectra of Si:H films deposited at different filament-to-substrate distance (d_{s-f}).

It can be seen from the FTIR spectra for all the films has strong absorption bands at $\sim 630 \text{ cm}^{-1}$ and at $\sim 2000 \text{ cm}^{-1}$, which correspond to the wagging/stretching vibrational modes of mono-hydride (Si-H) bonded species respectively (Lucovsky, 1980). The absorption band at $\sim 850\text{-}980 \text{ cm}^{-1}$ has been also observed and assigned to the bending vibrational modes of di-hydride (Si-H₂) and poly-hydride (Si-H₂)_n complexes having relatively lesser intensity (Knights et al., 1970). Thus, the films deposited at different filament-to-substrate distances, the hydrogen incorporated in the films mainly in Si-H bonded species. However, the films deposited at $d_{s-f} = 7$ and 6 cm , the absorption at $\sim 2100 \text{ cm}^{-1}$ emerges in the FTIR spectrum. This absorption band

corresponds to stretching vibrational modes of Si-H₂ and (Si-H₂)_n species (Shanks et al., 1980). These results clearly indicate that the films deposited at different filament-to-substrate distances the hydrogen in Si:H films is predominantly incorporated in Si-H bonding configuration.

Fig. 4 shows the dependence of hydrogen content (C_H) for the films deposited at various filament-to-substrate distances (d_{s-f}). It is seen from the figure that C_H in the film increases 5.2 to 10.5 at. % with an increase in d_{s-f}. The decrease in C_H with decrease in d_{s-f} can be attributed to the increase in structural order in the film. The emergence of absorption band ~ 2100 cm⁻¹ for the films deposited at lower filament-to-substrate distance also indicates the clustered Si-H at the grain boundaries due to the nanosize Si crystallites embedded in a-Si:H as revealed from the Raman results and microstructure parameter (R*). Han et al. (Han et al., 2003) and Itoh et al. (Itoh et al., 2000) have also observed the increase in intensity of absorption band at 2100 cm⁻¹ for HW-CVD and PE-CVD grown nanocrystalline films due to increase in volume fraction of crystallites. They attributed this peak to the clustered Si-H at the grain boundaries due to the nanosize Si crystallites embedded in a-Si:H.

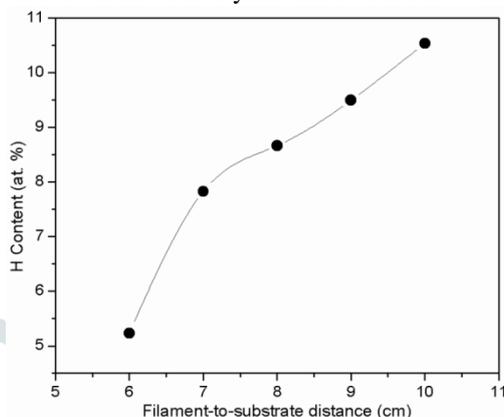


Figure 4: Variation in hydrogen content as a function of filament-to-substrate distance (d_{s-f}).

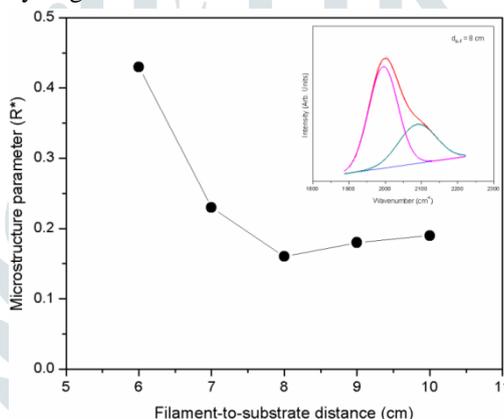


Figure 5: Variation in microstructure parameter as a function of filament-to-substrate distance. The inset show the de-convolution of FTIR spectra in the range 1850 cm⁻¹ - 2150 cm⁻¹ for the film deposited at d_{s-f} = 8 cm to calculate microstructure parameter.

Fig. 5 shows the variation in microstructure parameter as a function of filament-to-substrate distance. The microstructure parameter R* reflects the structural quality of the material. In good quality material R* has a low value, whereas in bad quality, void rich material its value is higher. For device-quality film the value of R* should not be larger than 0.1 (Feenstra et al., 1999). The band ~ 1800-2200 cm⁻¹ is de-convoluted into two peaks one centered ~ 2000 cm⁻¹ and the other centered ~ 2100 cm⁻¹ and the microstructure parameter (R*) is calculated using the formula described in experimental section. As seen from the figure, R* decreases 0.19 - 0.16 for the films deposited at filament-to-substrate distances 10 - 8 cm while the films deposited at lower filament-to-substrate distances i.e. 7 and 6 cm, R* increases upto 0.43. Thus, the film deposited at d_{s-f} = 8 cm having low value of R* indicates that at the onset of nanocrystallization the structural order improvement in film structure. Again, the increase in microstructure parameter (R*) indicating that the hydrogen-bonding configuration in the films changes from Si-H group to Si-H₂ group with decrease in filament-to-substrate distance 7 and 6 cm. The crystallite growth start to occur in the films, the crystallites push out the hydrogen from the growing structure is confirmed by FTIR and Raman result.

CONCLUSIONS

Intrinsic hydrogenated protocrystalline silicon (pc-Si:H) thin films have been deposited by HW-CVD method. The effect of filament-to-substrate distance on the microstructure has been studied. An improvement in structural order in Si-H films has been observed in Raman spectroscopic analysis. The bond angle variation ($\Delta\theta_b$) of the films decreases from ~ 8.16° to ~ 7.43° with decrease in d_{s-f} and it again increases to 8.01° when d_{s-f} decreases to 6 cm. The low value of $\Delta\theta_b$ at d_{s-f} = 8 cm which shows that improvement of structural order at the onset of amorphous-to-nanocrystalline phase transition also correlate with microstructure parameter (R*). The results obtained from FTIR analysis clearly indicate that at all filament-to-substrate distances the hydrogen is mainly incorporated in Si-H bonding configuration. The hydrogen content in the films was found to be < 10.5 at. % over the entire range of filament-to-substrate distance studied. The microstructure parameter (R*) was found to be < 0.43 at different filament-to-substrate distance. The low value of microstructure parameter (R*) at d_{s-f} = 8 cm, suggesting that there is an enhancement of structural order and homogeneity in the film also revealed by Raman spectroscopy. In summary, we observed that film deposited at filament-to-substrate distance, d_{s-f} = 8 cm shows protocrystalline nature at the onset of nanocrystallization.

From the present study it has been concluded that filament-to-substrate distances is a key process parameter to improve structural ordering in the pc-Si:H films deposited by HW-CVD method.

IV. ACKNOWLEDGMENT

The author VSW is thankful to the School of Energy Studies, Savitribai Phule Pune University for using the facility. VSW is also thankful to Ministry of New and Renewable Energy (MNRE), Government of India for financial assistance.

REFERENCES

- [1] Ahn, J. Y. et al. 2003. Stable protocrystalline silicon and unstable microcrystalline silicon at the onset of a microcrystalline regime. *Applied Physics Letters*, 82: 1718-1720. Koh, J. et al. 1998. Optimization of hydrogenated amorphous silicon p-i-n solar cells with two-step i layers guided by real-time spectroscopic ellipsometry. *Appl. Phys. Lett.*, 73(11): 1526-1528.
- [2] Beeman, D. et al. 1995. Structural information from the Raman spectrum of amorphous silicon. *Phys. Rev. B*, 32(2):874-878.
- [3] Brodsky, et al. 1977. Infrared and Raman spectra of the silicon hydrogen bonds in amorphous silicon prepared by glow discharge and sputtering. *Phys. Rev. B*, 16: 3556-3571.
- [4] Cerqueira, M. F. et al. 1995. Microcrystalline silicon thin films prepared by RF reactive magnetron sputter deposition. *Vacuum*, 46(12): 1385-1390.
- [5] Feenstra, K. F. et al. 1999. Deposition of amorphous silicon films by hot-wire chemical vapor deposition. *J. Appl. Phys.*, 85(9): 6843-6852.
- [6] Guha, S. et al. 1999. Structural, defect, and device behavior of hydrogenated amorphous Si near and above the onset of microcrystallinity. *Appl. Phys. Lett.*, 74: 1860-1862.
- [7] Garcia-Hernansanz, R. et al. 2016. Deposition of intrinsic a-Si:H by ECR-CVD to passivate the crystalline silicon heterointerface in HIT solar cells. *IEEE Journal of Photovoltaics*, 6(5): 1059-1064.
- [8] Han, D. et al. 2003. Hydrogen structures and the optoelectronic properties in transition films from amorphous to microcrystalline silicon prepared by hot-wire chemical vapor deposition. *Journal of Applied Physics*, 93(7): 3776-3783.
- [9] Itoh, T. et al. 2000. Characterization and role of hydrogen in nc-Si:H. *Journal of Non-Crystalline Solids*, 266-269: 201-205.
- [10] Knights, J. C. et al. 1979. Defects in plasma-deposited a-Si:H. *Journal of Non-Crystalline Solids*, 32(1-3): 393-403.
- [11] Koh, J. et al. 1999. Evolutionary phase diagrams for plasma-enhanced chemical vapor deposition of silicon thin films from hydrogen-diluted silane. *Appl. Phys. Lett.* 75, 2286-2288.
- [12] Khan, M. A. et al. 2015. Structural, electrical and optical properties of nanocrystalline silicon thin films deposited by pulsed laser ablation. *Materials Science in Semiconductor Processing*, 30: 169-173.
- [13] Lucovsky, G. 1980. Vibrational spectroscopy of hydrogenated amorphous silicon alloys. *Solar Cells*, 2(4): 431-442.
- [14] Mahan, A. H. et al. 2001. Saturated defect densities of hydrogenated amorphous silicon grown by hot-wire chemical vapor deposition at rates up to 150 Å/s. *Appl. Phys. Lett.*, 78 (24): 3788-3790.
- [15] Mahan A. H., 2006. An update on silicon deposition performed by hot wire CVD. *Thin Solid Films*, 501(1-2): 3-7.
- [16] Marquardt, D.W. 1963. An algorithm for least-squares estimation of non linear parameters. *J. Soc. Ind. Appl. Math.*, 11: 431-441.
- [17] Nardes, A. M. et al. 2003. Low temperature PECVD deposition of highly conductive microcrystalline silicon thin films. *Journal of Materials Science: Materials in Electronics*, 14(5/7): 407-411.
- [18] Stabler, D. L. et al. 1977. Reversible conductivity changes in discharge-produced amorphous Si. *Appl. Phys. Lett.*, 31(4):292-294.
- [19] Schropp, R. E. I. 2004. Present status of micro- and polycrystalline silicon solar cells made by hot-wire chemical vapor deposition. *Thin Solid Films*, 451(452): 455-465.
- [20] Schropp, R. E. I. et al. 1998. Amorphous and microcrystalline silicon solar cells: Modeling materials and device technology. (Kluwer, Boston) 47.
- [21] Shanks, H. C. et al. 1980. Infrared spectrum and structure of hydrogenated amorphous silicon. *Physica Status Solidi B*, 100(1): 43-56.
- [22] Tsu, D. V. et al. 1997. Effect of hydrogen dilution on the structure of amorphous silicon alloys. *Appl. Phys. Lett.*, 71:1317-1319.
- [23] Wang, Y. et al. 2008. Stability of microcrystalline silicon solar cells with HWCVD buffer layer. *Thin Solid Films*, 516(5):733-735.
- [24] Waman, V. S. et al. 2011. Nanostructured hydrogenated silicon films by hot-wire chemical vapor deposition: the influence of substrate temperature on material properties. *J. Nano.-Electron. Phys.* 3 (1): 590-600.
- [25] Wronski, C. R. et al. 2002. *Mater. Res. Soc. Symp. Proc.* in press
- [26] Xu, G.Y. et al. 2000. Raman spectra of nanocrystalline silicon films. *Chin. J. Semicond.*, 21: 1170-1176.