Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 6912–6918
www.elsevier.com/locate/tsf

# Effect of substrate bias on the plasma enhanced chemical vapor deposition of microcrystalline silicon thin films

X.D. Zhang [b], F.R. Zhang [b], E. Amanatides [a], D. Mataras [a,*], Y. Zhao [b]

[a] *Plasma Technology Laboratory, Department of Chemical Engineering, Patras University, Patra, 26504, Greece*
[b] *Institute of photo-electronics thin film devices and technique of Nankai University, Tianjin, 300071, China*

## Abstract

The effects of substrate bias voltage on the growth rate and structure of silicon thin films, deposited from highly diluted 13.56 MHz $SiH_4/H_2$ discharges at elevated pressures (2.5 Torr) are presented. More precisely, the possibility to increase the deposition rate by exciting the substrate holder with positive or negative dc bias mixed with a low frequency voltage (20 kHz) was investigated. The results are compared to those obtained using grounded and floating substrate configurations. Significant effects were observed concerning both the deposition rate and the film crystallinity. Plasma diagnostics were implemented in order to understand if the changes are purely due to ion bombardment and to identify other plasma parameters that are affected as well. Namely, plasma electrical measurements were used to maintain constant power consumption and to monitor changes in the discharge current and impedance. In addition, spatially resolved emission spectroscopy was applied for recording changes in the discharge structure. The results are discussed and the main problems related to the application of bias together with the best configuration allowing fast deposition of μc-Si:H thin films are presented.

*Keywords:* PECVD; Microcrystalline silicon; Substrate bias; Plasma diagnostics

## 1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) thin films produced in low temperature plasma processes have found application in thin film solar cells [1–3]. However, due to the low optical absorption of μc-Si:H higher deposition rates are required to further consider the use of μc-Si:H in industrial applications [4]. The main macroscopic discharge parameters controlling the deposition of μc-Si:H are RF power, frequency, gas composition, substrate temperature, discharge geometry and total gas pressure. The variation of any of these parameters can significantly alter the discharge properties by affecting the charged particle kinetics, gas phase chemistry, and finally plasma–surface interaction.

Among the above-mentioned parameters, an increase of the plasma excitation frequency and high pressure together with high power are mostly used to optimize the film deposition rate [5–8]. A common indirect conclusion from these studies is that for a certain $SiH_4/H_2$ gas mixture a proper combination of frequency, pressure and power may optimize ion bombardment on the growing film surface, resulting to device quality material deposited under high growth rates. This assertion is mainly based on theoretical and experimental studies dealing with the contribution of ion flux and energy to the deposition rate [9] and film properties [10].

The most straightforward method to alter the flux and energy of the ions that strike the surface of the growing film is through the application of an RF or dc bias on the substrate holder. Recently, N. Kosku et al. [11] have investigated the effect of substrate bias on the microcrystalline film growth from inductively-coupled plasma (ICP) of $H_2$-diluted $SiH_4$. By applying a dc bias, the crystallinity is significantly improved even though the deposition rate has almost no evident variation. In addition, H.J. Jia et al. [12] also demonstrated the effect of dc substrate bias on high-rate deposition of microcrystalline silicon films using a high-density microwave plasma source. Their results proved that microcrystalline silicon films deposited under appropriate negative dc

---

* Corresponding author. Plasma Technology Laboratory, Department of Chemical Engineering, University of Patras, P.O. Box 1407, Patras 26504, Greece. Tel.: +30 2610969525; fax: +30 2610993361.
*E-mail address:* dim@plasmatech.gr (D. Mataras).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.12.060

substrate bias exhibit improved film crystallinity and reduced defect density along with thinner amorphous silicon incubation layer at the initial growth stage. Concerning the low density capacitively-coupled glow discharges that are widely used to deposit this material, several attempts have been made to investigate the role of the application of an external bias voltage in amorphous and microcrystalline silicon deposition [13–17]. However, these studies include controversial conclusions concerning the effect of ion bombardment. In some cases negative values of dc bias appears to be beneficial for the initial growth stage and the films crystallization. In other cases a positive bias and a reduction of plasma potential is reported to improve the film growth rate, morphology and electronic properties, while there are also studies that have found almost no effect of the bias voltage on the deposition process.

The present work has two main targets: The first one is to investigate if it is possible to improve the deposition rate of μc-SI:H thin films through the application of an external bias voltage and the second one is to clarify if biasing of the substrate can be beneficial for the films crystallinity. The study was performed in high pressure–high power capacitively-coupled $SiH_4/H_2$ discharges under different substrate holder configurations (positive, negative ac and dc biasing, grounded, and floating) with a subsequent monitoring of the film deposition rate and crystallinity. All the experiments were performed in conditions known to be close to the transition from a-Si:H to μc-Si:H growth and the interpretation of the results was supported by the application of in situ plasma diagnostics as electrical measurements and 2D spatially resolved plasma emission spectroscopy.

## 2. Experimental

Film deposition studies have been performed in a capacitively-coupled ultrahigh vacuum (UHV) parallel plate reactor, with a base vacuum of $10^{-9}$ mbar. The reactor is equipped with a load lock system for transportation of the substrates and with four quartz windows suitable for spectroscopic observations. The usually grounded (deposition) electrode is mounted on an UHV linear motion feedthrough, allowing for continuous variation of the interelectrode distance. In the present study the distance between the two electrodes was fixed at 1.5 cm. In all cases 4% silane mole fraction ($[SiH_4]$ / $[SiH_4+H_2]$) has been delivered to the reactor at a total pressure of 2.5 Torr. Pressure and flow rate are independently adjusted by a downstream throttle valve controller and an upstream mass flow controller, respectively.

One important issue in the application of a bias voltage, especially when insulating substrates need to be used, is to ensure that the potential applied to the electrode is also distributed across the insulating surface [18,19]. Actually, the value of the dc voltage that is measured behind the substrate does not correspond to the one in the surface of the insulator, which strongly depends on the configuration of the surrounding mask or the shield of the substrate [18]. It is then the plasma induced conduction or the electric field conduction that drives the voltage across the insulating surface. Fig. 1 shows the substrate holder that we have used for substrate biasing. A conductive (316L Stainless Steel) electrode holds the glass substrate and it is also used for the development of the desired voltage at the surface. In the left and right side of the glass there is a small gap of 1 mm promoting substrate biasing through plasma induced conduction (Ref. [18], configuration Y). At the top and bottom side of the substrate there is a conductive shield covering 2 mm of the substrate and favoring the development of a surface voltage through electric field conduction ((Ref. [18], configuration Z). Points 1, 2 and 3 in Fig. 1 denote the spots where Raman measurements were performed in order to check the film crystallinity. These measurements were then used as a guide for the effectiveness of the two substrate biasing modes.

Moreover, special precautions have been taken to isolate the dc generator from the low (10–110 kHz, ENI AT3200) and high (13.56 MHz, ENI ACG-5) frequency generators and also from the grounded walls of the reactor. For this purpose we have used a high frequency–high voltage 1:100 transformer. The voltage in the conductive part of the substrate holder was monitored with a 1:10 passive probe (Lecroy, PPE 1:10. The substrate holder voltage conditions that are presented in this paper are positive ($100+200\sin\omega_1 t$), grounded, floating, and negative ($-100+200\sin\omega_1 t$). The frequency $\omega_1$ was 20 kHz in order the time period of the applied frequency to be about 4 times higher compared to the ion transit time through the sheath. This condition ensures that the ions will follow the alteration of the low frequency field, thus being able to acquire the highest amount of energy during the cathodic phase of the 20 kHz cycle. For the specific set of conditions, the transit time of the heaviest silane ions was estimated to $\sim 2.5\times10^{-6}$ s assuming an average sheath length of 0.002 m and mean ion energy of 1 eV. The high frequency power (13.56MHz) actually consumed in the discharge and the discharge impedance was determined by using Fourier transform voltage and current analysis. The voltage and current waveforms

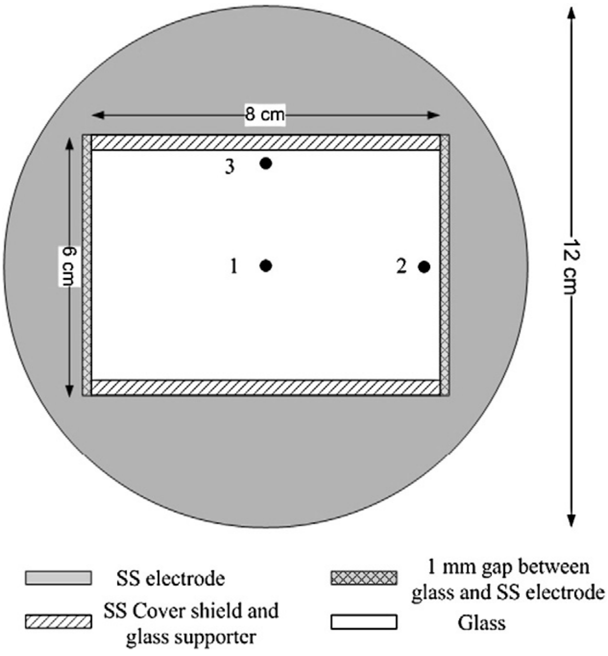

Fig. 1. The configuration of the substrate holder used for biasing the glass substrate. Points 1, 2 and 3 where Raman measurements were performed.

were measured on the powered electrode, using a high impedance 1:1000 attenuation voltage probe (Lecroy PPE 1:1000), an 0.1 Ω transfer impedance RF current probe (FCC model F-35-1). The detailed method used for the measurement of the power consumed in 13.56 MHz discharges can be found in Ref. [20]. The setup used to record the emission spectra and spatially resolved emission profiles consists of a cylindrical or a focusing achromatic lens, an imaging spectrograph and an iCCD detector (Andor, iStar734) [21]. Emission profiles were recorded for SiH*, $H_\alpha$ and $H_\beta$ by using suitable interference filters.

The films were deposited on common glass substrates, heated at a temperature of 250 °C. The deposition rate was measured in situ using laser reflectance interferometry. The structural properties of the films were measured with the JY T-64000 Raman system, which was excited by the 514.5 nm line of an air-cooled $Ar^+$ laser. The details for the Raman measurement can be found in Ref. [22].

## 3. Results and discussion

The main targets of the present study were to investigate if it is possible to enhance the μc-Si:H thin film deposition rate and/or the film crystallinity through the application of an external bias voltage to the surface. So, the starting point of the study was to find the plasma conditions that lead to the transition from μc-Si:H to a-Si:H growth, when the substrate holder is grounded. A set of experiments was then performed with variable % $SiH_4$ fraction and discharge power in order to determine the values that lead to the transition at reasonably high deposition rate. The parameters found were 4% $SiH_4$ in $H_2$ mole fraction, 35 W 13.56 MHz power. At these conditions, the deposition rate was 7.3 Å/s and a very small shoulder appeared in the Raman spectra appeared at long wavenumbers around 518 $cm^{-1}$. Then, using the same parameters we have successfully applied a positive bias ($+100+200\sin\omega_1 t$), a negative bias ($-100+200\sin\omega_1 t$), while in the last experiment the substrate holder was floating. Special care was taken to maintain constant real power dissipated in the discharge through the different substrate excitation modes. Fig. 2 (a), (b), (c) and (d) present the variation of RF voltage, discharge current, discharge phase impedance and RF electrode self-bias voltage respectively leading to the same power dissipation as the substrate holder bias conditions change. Any change from the grounded conditions imposes an increase of the applied 13.56 MHz voltage amplitude to maintain the same power and this increase is higher for the negative biasing conditions (Fig. 2 (a)). On the other hand, the discharge current presented in Fig. 2

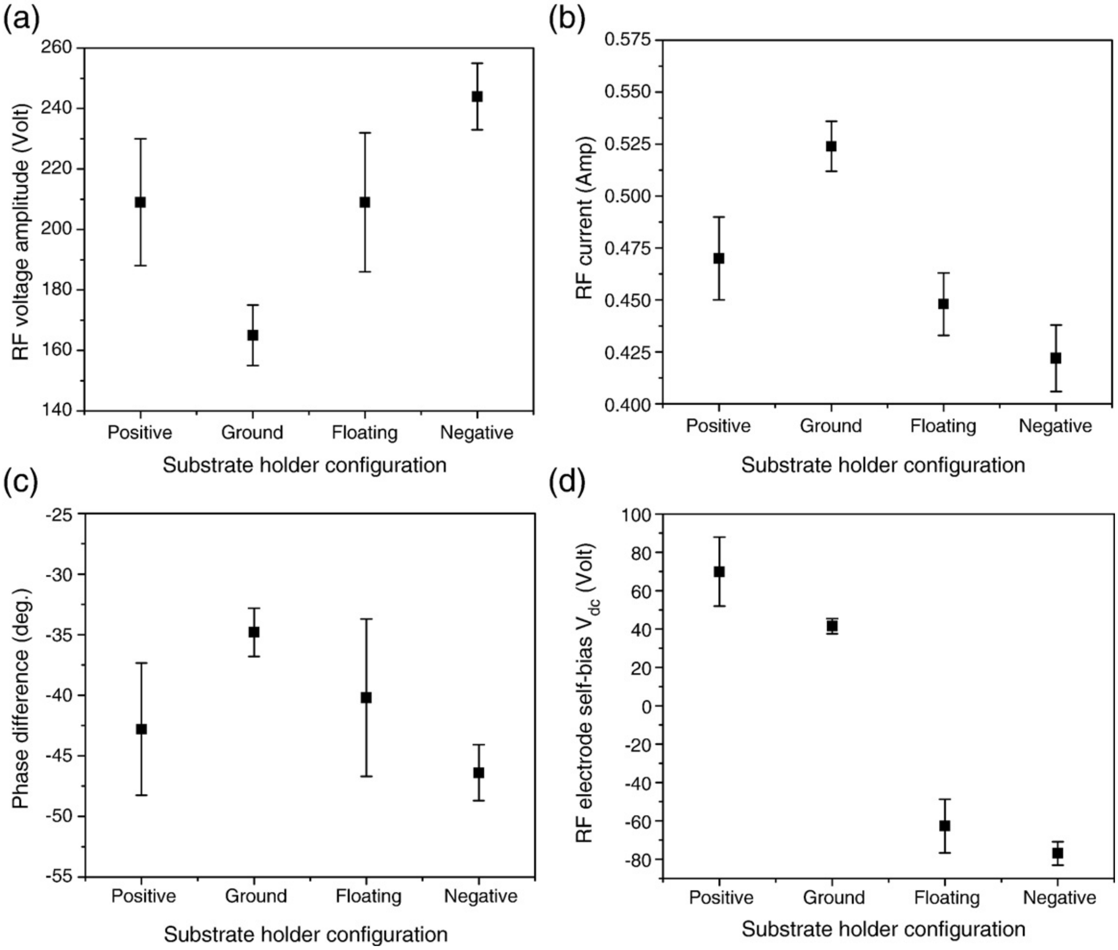

Fig. 2. (a) The applied RF voltage amplitude (b) total discharge current (c) dc self-bias of the RF electrode and (d) phase difference between RF voltage and current that correspond to conditions of constant RF power dissipation in positive and negative biasing, grounded and floating conditions of the conductive part of the substrate holder.

(b) shows an opposite relation compared to voltage and drops in any configuration different than the grounded one. Again, the drop is stronger for the negative biasing conditions. In addition, the discharge phase impedance, which is plotted in Fig. 2(c) indicates that in the grounded conditions the discharge exhibits the most resistive character as the phase is reduced in absolute value. Finally, the self-bias voltage $V_{dc}$ that is developed on the RF electrode is strongly affected by the application of an external bias voltage on the substrate holder. Actually, the application of a positive bias leads to an increase of the $V_{dc}$ to more positive values, while the application of a negative voltage to more negative values of $V_{dc}$. The floating conditions lead to similar values of $V_{dc}$ with the case of negative biasing, indicating that in these conditions the substrate holder is also negatively charged. It is also noticeable that in the grounded conditions the value of $V_{dc}$ is positive which means that at these conditions of relatively high gas pressure and power, the discharge has an electronegative character. The errors bars in the figures were obtained from about 10 measurements performed in different days. The exhaustive check of reproducibility is very important because the application of the external bias voltage introduces a distortion on the voltage and current waveforms measured at the RF electrode.

To summarize the results of the electrical measurements, we can conclude that in the case of grounded substrate holder, a lower voltage, a higher current flow and a more resistive discharge is required to maintain the same discharge power with the other configurations. Typically, these are conditions of higher plasma density and lower electron temperature, identified in previous studies [22] to be beneficial for the precursor species production, the deposition rate and the film crystallinity. In addition, the variation of the $V_{dc}$ clearly indicates that the application of the substrate bias reconstructs the voltage distribution in the discharge in such a manner that the time-averaged plasma potential is always the most positively charged part of the discharge. Finally, the results of the electrical measurements have clearly pointed out that the application of substrate biasing affects all the plasma properties and the influence cannot be limited to the sheath of the substrate holder and the ion bombardment.

Thus, besides the changes of the electrical properties of the discharge, variations in the production of film precursor species are also expected. In order to follow these changes, spatially resolved emission spectroscopy was applied and profiles of excited silylylidene radical SiH ($A^2\Delta \rightarrow X^2\Pi$) and α- and β-balmer lines of atomic hydrogen were recorded. Fig. 2(a) and (b) present the absolute and the relative spatial distribution of $H_\beta$ line for the different substrate holder modes. The spatial profiles were obtained by averaging the radial emission intensity from the center of the plasma to electrodes edges. As we can observe the change in the substrate holder modes affect both the rate of production and the spatial distribution of the excited species. The change in the production rate is more clearly seen in Fig. 3(a) where the absolute values of emission intensity are plotted. The grounded condition is by far the most efficient in species production everywhere in the discharge and is followed by the positive biasing configuration. The negative and floating modes present almost the same rate of $H_\beta$ production. The results for SiH* and $H_\alpha$ were about the same despite the differences between grounded and positive bias conditions were not so strong. As for the changes in the spatial distribution of species, these are better reflected in Fig. 3(b) where the normalized values of $H_\beta$ emission intensity are plotted. The first observation is that for the positive, negative and floating conditions the optimum of the emission intensity is located closer to the RF electrode compared to the grounded configuration. In addition, a second peak close to substrate holder appears in these configurations. The appearance of this peak indicates that the plasma potential is enhanced in these conditions in relation to the grounded conditions where the highest voltage drop seems to take place in the sheath of the RF electrode. The positive biasing condition gives the more symmetric profiles compared to all other cases.

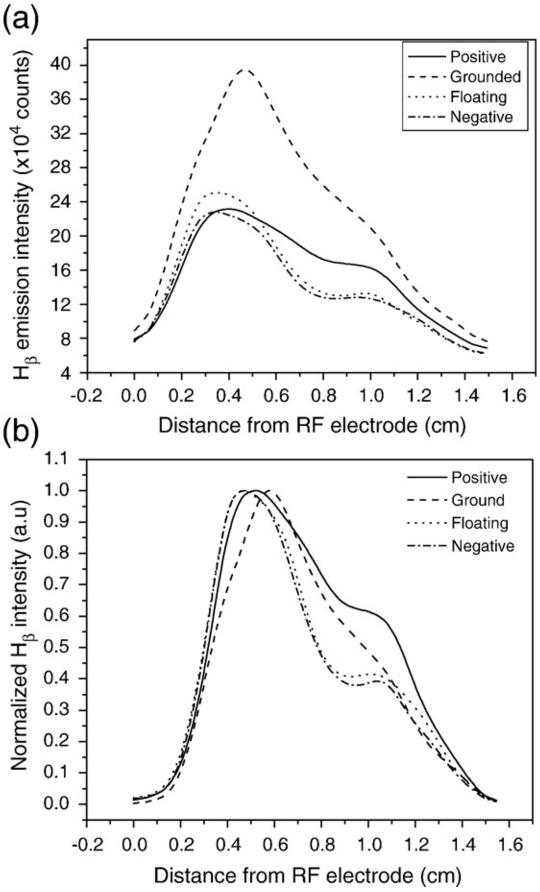

Fig. 3. Spatial distribution of the normalized $H_\beta$ emission intensity at different substrate holder conditions.

The variations in the production and distribution of species in the discharge lead also to changes in the film growth rate, as presented in Fig. 4(a). The modification of the substrate holder mode, from positive biasing to grounded, floating and finally to negative biasing, results in a continuous drop of the deposition rate. Actually, the fact that the deposition rate is higher in the case of positive biasing compared to the grounded conditions is not an expected result according to the previous discussion concerning the electrical properties and the lower rate of species

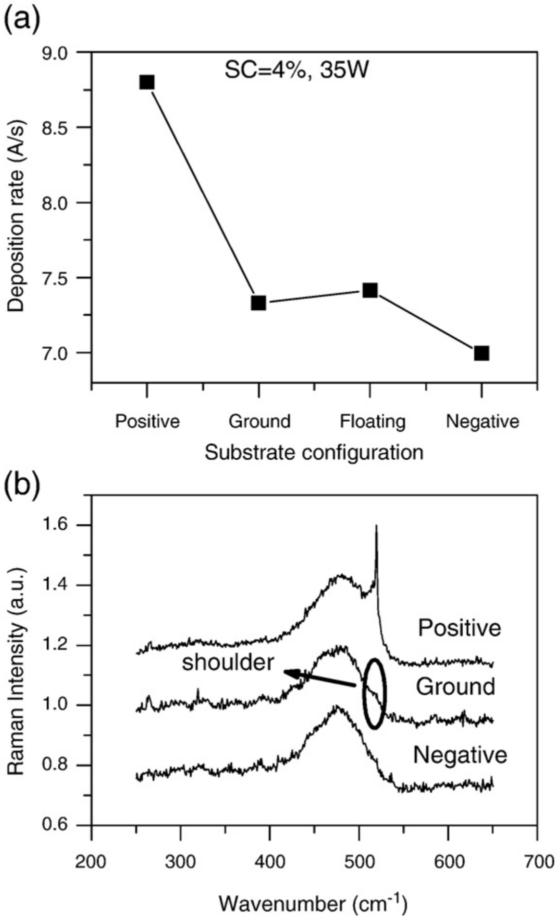

Fig. 4. (a) Deposition rate and (b) Raman spectra of the films deposited in different substrate holder conditions.

production (Fig. 3(a)). This enhancement is due to the more symmetric discharge in the case of positive biasing, which in turn favors the production of species closer to the substrate, increasing thus their probability to reach the growing surface. The increase of plasma potential, which was also predicted from the emission profiles for the case of positive biasing will result to an increase of the ion flux towards the substrate and this may also contribute to the enhancement of the deposition rate either through direct incorporation of the ions or through the enhancement of the mobility of the physisorpted species.

Moreover, the structure of the films deposited at the different conditions was estimated by using Laser Raman Spectroscopy and the results are shown in Fig. 4(b). As already mentioned, the films deposited under grounded conditions were in the transition from μc-Si:H to a-Si:H growth. So, for this film only a small 'shoulder' appeared at long wavenumbers around 518 $cm^{-1}$. In addition, the films deposited under negative biasing and floating conditions are purely amorphous and only one peak around 480 $cm^{-1}$ appears in the Raman spectra. On the other hand, the film deposited with a positive bias presents a sharp peak at ~ 519.6 $cm^{-1}$ due to the TO phonon mode, which means that the crystalline phase is significantly enhanced. Thus, the application of positive biasing seems to improve the deposition rate while at the same time favoring film crystallinity.

It must be noted that the Raman spectra presented in Fig. 4(b) were obtained from the middle of the glass (point 1, Fig. 1). As already discussed in the experimental section, the application of an external bias on an insulator like glass and the achievement of the desired voltage drop in the sheath of the substrate holder is a difficult task and depends on the setup around the substrate. In order to check the effectiveness of the configuration applied in inducing the desired voltage drop across the glass we have used Raman spectroscopy as a probing tool. Thus except of the spectra obtained from the center of the samples two more measurements were done: one close to right edge of the substrate (point 2, Fig. 1) and one close to the cover shield of the substrate (point 3, Fig. 1). These measurements are presented in Fig. 5(a) and (b) for the films deposited under positive and grounded conditions, respectively. Measurements for the films deposited under negative and floating modes were also performed but these films in all positions were purely amorphous. On the other hand, the Raman measurements of the film deposited under positive biasing have shown that the crystallinity varies with position and for point 2 that corresponds to the area of the substrate biasing through plasma induced conduction [18], the amorphous phase is reduced. Moreover, for the point 3, which matches to the area of substrate biasing through electric field conduction, the deposited film present almost no amorphous

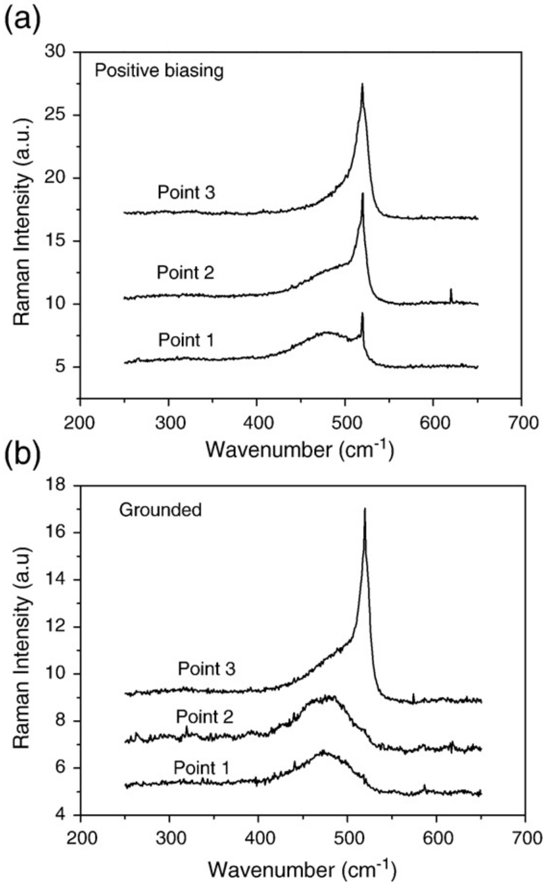

Fig. 5. Raman spectra at three different points of the films deposited (a) under positive biasing and (b) grounded configurations of the conductive part of the substrate holder.

phase. The same trend is maintained also for the film deposited under grounded conditions of the conductive part of the electrode although the crystallinity of this film at each of the measured points is lower compared to the one in Fig. 5(a).

The variation of the crystalline volume fraction in the films can be either a result of non-uniform species flux or/and a result of the charged species transport. A possible explanation can be that a strong radial field is developed between the conductive part of the holder and the insulator and this drives the motion of charged species near the surface, enhancing their role in the film growth. Due to the large number of collisions as the total gas pressure is relatively high, the field intensity decays gradually resulting to the observed spatial changes in the film structure. In addition, as the electric field conduction is more effective compared to the plasma induced conduction, the developed electric field intensity is expected to be higher in the top and bottom compared to the left and right side of the glass and this seems to be beneficial for the film crystallinity. The fact that this is observed only for the films deposited under positive biasing and grounded conditions and not in the case of floating and negative biasing clearly indicates that the glass surface and the deposited film is always negatively charged independently of the biasing conditions due to the higher electron mobility. Thus, only the positive biasing and the grounded conditions can induce the necessary charge difference for the development of a strong electrostatic field. Further work is in progress with different and more complicated masks and substrate holders to improve the structure uniformity of the deposited films, to confirm the effectiveness of positive substrate biasing in the deposition process of μc-Si:H thin films and to further clarify the reasons for the observed effects on the deposition rate and crystallinity.

## 4. Conclusions

A study of the effect of the substrate bias on the deposition process of μc-Si:H thin films was performed with the purpose to investigate the possibility to enhance the deposition rate and/or the film crystallinity.

Positive and negative biasing together with grounded and floating conditions of the conductive part of the substrate holder has been tested. The other experimental parameters as power, total gas flow, pressure and $SiH_4$ mole fraction have been chosen to be in the transition from μc-Si:H to a-Si:H growth.

The results of the electrical measurements have shown that in order to maintain constant power dissipation as the substrate holder configuration changes, all the electrical parameters need to be modified. In fact, the grounded configuration required the lowest applied voltage, the highest discharge current and presented the higher resistive character. In addition, the results of the spatially resolved emission profiles of excited species in the discharge have shown that the rate of species production in the discharge is higher for the grounded configuration. On the other hand, the positive biasing mode resulted in more symmetric species production, indicating also an important enhancement of the plasma potential.

Moreover, the deposition rate and the film crystallinity were favored by the positive biasing conditions. A deposition rate increase of ~20% was recorded as we changed from the grounded to positive biasing conditions, while the film crystallinity was also improved. The negative biasing and floating configuration gave in both cases worst results. Raman measurements at different points of the deposited films show structure non-uniformities and higher crystalline volume fractions in the areas close to the conductive part of the substrate holder for both the positive and grounded configuration. This result indicates that the development of a strong electrostatic field across the glass substrate can be beneficial for the deposition rate and the film crystallinity. So, we can conclude that an appropriate positive substrate biasing during the film growth can improve both the deposition rate and crystallinity of μc-Si:H thin films. An important issue for further application of this technique and a subject under investigation is the possibility to avoid the structural non-uniformities with the proper application of more complicated setups of the substrate holder.

## Acknowledgements

Project supported by International cooperation project between China–Greece Government, National Natural Science Foundation of China (60506003), the State Key Development Program for Basic Research of China (Grant No.2006CB202602, No.2006CB202603), Natural Science Foundation of Tianjin of China (05YFJMJC01600), the starting project of Nankai University (J02031), and the Program for New Century Excellent Talents in University of China (NCET). Two of the authors (E. Amanatides and D. Mataras) wish also to thank the European Social Fund (ESF) Operational Program for Educational and Vocational Training II EPEAEK II, and particularly the Program PYTHAGORAS for partly funding this work.

## References

[1] O. Vetterl, A. lamberts, A. Dasgupta, F. Finger, B. Rech, O. Kluth, H. Wagner, Sol. Energy Mater. Sol. Cells 66 (2001) 345.

[2] L. Feitknecht, O. Kluth, Y. Ziegler, X. Niquille, P. Torres, J. Meier, N. Wyrsh, A. Shah, Sol. Energy Mater. Sol. Cells 66 (2001) 397.

[3] F. Finger, P. Hapke, M. Luysberg, R. Carius, H. Wagner, M. Scheib, Appl. Phys. Lett. 65 (1994) 2588.

[4] U. Kroll, J. Meier, P. Torres, J. Pohl, A. Shah, J. Non-Cryst. Solids 227–230 (1998) 68.

[5] L. Guo, M. Kondo, M. Fukawa, K. Saitoh, A. Matsuda, Jpn. J. Appl. Phys. 37 (1998) L1116 Part2.

[6] T. Roschek, T. Repmann, J. Muller, B. Rech, H. Wagner, J. Vac. Sci. Technol. A 20 (2002) 492.

[7] K. Yamamoto, M. Yoshimi, T. Suzuki, Y. Tawada, Y. Okamoto, A. Nakajima, Mater. Res. Soc. Symp. Proc. 507 (1998) 131.

[8] M. Kondo, M. Fukawa, L. Guo, A. Matsuda, J. Non-Cryst. Solids 266–269 (2000) 84.

[9] E.A.G. Hamers, A. Fontcuberta i Morral, C. Niikura, R. Brenot, P. Roca i Cabarrocas, J. Appl. Phys. 88 (2000) 3674.

[10] P. Roca i Cabarrocas, P. Morin, V. Chu, J.P. Conde, J.Z. Liu, H.R. Park, S. Wagner, J. Appl. Phys. 65 (1991) 2942.

[11] N. Kosku, H. Murakami, S. Higashi, S. Miyazaki, Appl. Surf. Sci. 244 (2005) 39.

[12] H.J. Jia, J.K. Saha, N. Ohse, H. Shirai, J. Phys. D: Appl. Phys. 39 (2006) 3844.

[13] S. Hajime, T. Nakamura, T. Arai, J. Non-Cryst. Solids 227–230 (1998) 53.

[14] A. Gordijn, L. Hodakova, J.K. Rath, R.E.I. Schropp, J. Non-Cryst. Solids 352 (2006) 1868.

[15] S. Lebib, P. Roca i Cabarrocas, J. Appl. Physi. 97 (2005) 104334.

[16] B. Kalache, A.I. Kosarev, R. Vanderhaghen, P. Roca i Cabarrocas, J. Non-Cryst. Solids 299–302 (2002) 63.

[17] P. Roca i Cabarrocas, P. Morin, V. Chu, J.P. Conde, J.Z. Liu, H.Fi. Park, S. Wagner, J. Appl. Phys. 69 (1991) 1.

[18] C.A.M. De Vries, W.G.M. Van Den Hoek, J. Appl. Phys. 58 (1985) 2074.

[19] E.V. Johnson, N.P. Kherani, Stefan Zukotynski, J. Mater. Sci., Mater. Electron. 17 (2006) 801–813.

[20] N. Spiliopoulos, D. Mataras, D. Rapakoulias, J. Vac. Sci. Technol. A 14 (1996) 2757.

[21] E. Amanatides, P. Gkotsis, Ch. Syndrevelis, D. Mataras, Diam. Relat. Mater. 15 (2006) 904.

[22] E. Katsia, E. Amanatides, D. Mataras, A. Soto, G.A. Voyiatzis, Sol. Energy Mater. Sol. Cells 87 (2005) 157.