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Deposition rate optimization in SiH_4/H_2 PECVD of hydrogenated microcrystalline silicon

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Abstract

Intrinsic hydrogenated microcrystalline silicon films have been deposited by Plasma Enhanced Chemical Vapor Deposition using highly diluted SiH_4 in H_2 discharges, aiming at the increase of the deposition rate. Following a systematic optimization of the main process parameters, an increase of the film growth rate up to 7.5 Å/s has been achieved, from 1 Torr 6% SiH_4 in H_2 dust-free discharges at a frequency of 30 MHz. The experimental results are combined to a mass transfer model that can very well predict the deposition rate, for revealing the main reasons leading to the fast growth of μc-Si:H. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Microcrystalline silicon; Deposition rate; Hydrogen dilution; Frequency effect

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) thin films are usually deposited by Plasma Enhanced Chemical Vapor Deposition using highly diluted SiH_4 in H_2. The typical deposition rate in 13.56 MHz discharges is approximately 1 Å/s. However, due to the low optical absorption of μc-Si:H, thick films and thus higher deposition rates are required to further consider the use of μc-Si:H in industrial applications (solar cells and thin film transistors) [1]. Several studies can be found in literature concerning this issue and compatible and alternative CVD techniques have been proposed in order to overcome the problem. More precisely, a deposition rate of 16 Å/s has been achieved using Very High Frequency - Glow Discharge (VHF-GD) [2,3], 20 Å/s using fluorinated gases [4], while using hot wire CVD [5] and ECR-plasmas [6] rates of 15 and 8 Å/s respectively, have been reported. However, the industrial applicability of these techniques is still questionable due to electromagnetic emission and large area deposition limitations. Furthermore, the use of more compatible methods with the industrially established a-Si:H technology is desirable. Thus, the main purpose of this work is the systematic optimisation of the main parameters involved in the deposition process of μc-Si:H from highly diluted SiH_4 in H_2 discharges, with emphasis on the effects of frequency, from the conventional 13.56 MHz to the lower VHF range (50 MHz), silane partial pressure (2-6%), and power (10-70 mW/cm^2). Dust-free deposition rates up to 7.5 Å/s have been achieved, using 30 MHz, 1 Torr 6% SiH_4 in H_2 discharges, revealing that more conventional techniques can also be used successfully.

2. Experimental

Film deposition studies have been performed in a capacitively coupled Ultra High Vacuum (UHV) parallel plate reactor, with a base vacuum of 10^{-9} mbar. In all cases, highly diluted SiH_4 in H_2 (2%-6%) has been used at a substrate temperature of 250°C. The RF electrode was powered through an L-type matching network by a Dressler WLPG 101D wideband (5-125

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MHz) generator. The method used for the measurement of the real power consumed in the discharge and the determination of the discharge impedance has been presented in detail elsewhere [7]. Mass spectrometric measurements have been used for the calculation of silane depletion in the discharge, while in-situ Laser Reflectance Interferometry (LRI) was applied to monitor in-situ the deposition rate. Dust formation was monitored using a laser light scattering technique.

3. Results

3.1. Frequency effect

The effect of frequency on the film growth rate was examined, under conditions of constant power dissipation. Thus, presented in Fig. 1 is the variation of deposition rate as a function of frequency for 0.5 Torr, 2% SiH_4 in H_2 discharges, at the rather low, power density of 28 mW/cm^2. The deposition rate increases by 40% as frequency increases from 13.56 MHz to 30 MHz and remains almost constant to a further increase of frequency. An analogous increase has been reported for the case of a-Si:H deposition [8,9] and has been attributed to an enhanced radical production in the gas phase and to an enhanced surface reactivity due to the increase of the low energy ion flux towards the growing surface. For the present experimental conditions, both of the above-mentioned explanations fail to describe the dependence of the deposition rate with frequency. A detailed analysis of the present results has been performed [10], concerning the effect of frequency on the discharge electrical properties and electron induced processes, attributing the increase to a slight increase of the dissociation rate of silane, and to changes of the discharge structure. Namely, the 13.56 MHz due to the high voltage required to operate the discharge and the increase of the sheaths thickness, the contact of the discharge with reactor walls is more pronounced leading to an increase of the discharge volume. This increase is followed by production of film precursors far from the interelectrode space, having a minor probability to reach the deposition surface. These precursors either react in the gas phase producing stable molecules or contribute to undesirable deposition at the reactor walls. The higher values of the operation voltage at 13.56 MHz also induce strong electric fields between the RF electrode and the grounded shield, being responsible for the initiation of silane polymerization. In any case, the microcrystalline silicon deposition rate that can be achieved using the conventional frequency of 13.56 MHz under dust-free conditions is limited.

Instead, at 30 MHz, the operation voltage drops significantly, the sheath thickness decreases, the discharge spread-out is limited, and the primary dissociation of silane slightly increases, leading to the observed increase of the deposition rate. Thus, the frequency of 30 MHz has been chosen in order to optimize all other discharge parameters which influence the film growth rate, taking into account that a further increase of frequency at least up to 50 MHz does not produce any significant change to the film growth rate, and that it presents much lower electromagnetic emission problems, while it can easily be implemented in existing a-Si:H deposition reactors.

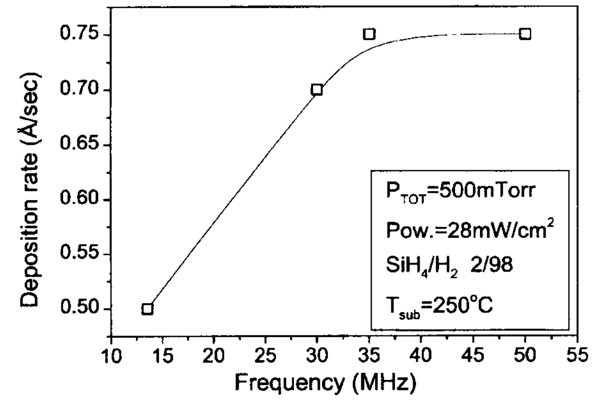

Fig. 1. Variation of film growth rate as a function of excitation frequency for 2% SiH_4 in H_2 discharges and constant power dissipation.

3.2. Silane partial pressure effect

The main reason for the low deposition rate of μc-Si:H is the extremely high dilution of SiH_4 in H_2 that leads to a very low concentration of radicals in the discharge [2]. Thus, the μc-Si:H growth rate for 2% SiH_4 in H_2 discharges at total pressures of 0.5 and 1 Torr despite the rather high power levels, leads to a deposition rate that cannot exceed 2 Å/s. On the other hand, a large increase of the silane percentage can deteriorate the film crystallinity [3]. Therefore, 2%–6% SiH_4 in H_2 gas mixtures have been used in order to avoid the undesirable transition to amorphous silicon. In Fig. 2 the variation of deposition rate as a function of silane percentage, at conditions of constant power dissipation (48 mW/cm^2) in 30 MHz, 0.5 Torr SiH_4/H_2 discharges is presented. The film growth rate is almost doubled increasing from 0.9 Å/s to 1.6 Å/s as the fraction of silane in the gas mixture increases from 2% to 6%. The results have been combined to an experimental measurements-based mass transfer model that has been described in Ref. [11] and an excellent agreement between experimental values and model deposition rate predictions has been found (Fig. 2). According to the model, the deposition rate, either for the low or for the high silane concentration, is determined from highly sticking at the surfaces-highly reactive in the gas phase radicals (SiH_2, Si_2H_4). Contribution of radicals having low film incorporation propability (SiH_3, Si_2H_5)

increases as the fraction of silane in the gas mixture increases but in all the cases remains lower than 20% of the total deposition rate. The variation of the contribution of Si_xH_{2x+1} compared to the Si_xH_{2x} radicals to the film growth as silane percentage increases, relates to their different gas-phase reactivity. Si_xH_{2x+1} have low gas-phase reactivity and thus the increase of silane concentration is expected to increase their production. In contrast, Si_xH_{2x} radicals undergo faster reactions with silane and thus the increase of silane concentration is expected to enhance their consumption, decreasing their relative contribution into film growth. This is also the reason that there is no simple one to one relation between the increase of silane concentration and deposition rate, i.e. although silane concentration is tripled deposition rate is less than doubled.

3.3. Discharge power effect

Another way to increase silane concentration is the increase of total pressure. Using a gas mixture of 6% SiH_4 in H_2 at a total pressure of 1 Torr and a frequency of 30 MHz, the effect of discharge power on the deposition rate has been studied. As shown in Fig. 3, the growth rate increases rapidly with power up to the value of 7.5 Å/s. As in the case of the increase of silane percentage, Si_xH_{2x} radicals determine the deposition rate. Therefore, the model slightly underestimates the deposition rate but it clearly indicates that the main reason for the rapid increase with power is the increase of the contribution of the Si_2H_4 radical. Si_2H_4 is one of the products of the SiH_2 insertion reaction into SiH_4 while it is also produced from disilane electron impact dissociation. The higher pressure and the increase of power enhance both reactions. Si_2H_4 radicals that reach the surface are directly incorporated into the growing film, offering two silicon atoms to the network thus leading to higher deposition rates.

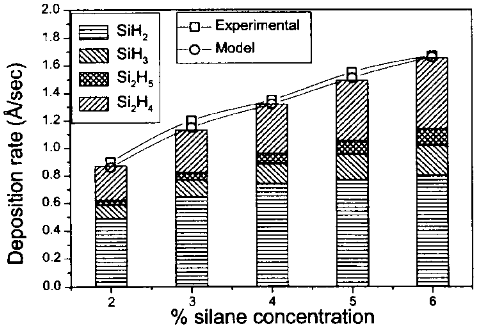

Fig. 2. Deposition rate as a result of silane percentage in 0.5 Torr SiH_4/H_2 mixtures and conditions of constant power dissipation (48 mW/cm^2). The deposition rate results of the mass transfer model and the contribution of the main radicals in film growth are also included.

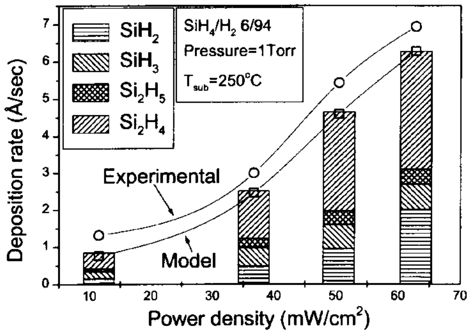

Fig. 3. Deposition rate as a function of power density for 1 Torr, 6% SiH_4 in H_2 discharges as measured and calculated from the model. Column bars represent the relative contribution of species to the calculated values of the deposition rate.

4. Conclusions

A systematic optimization of the main discharge parameters that influence the deposition process of μc-Si:H has been performed, aiming at the increase of the deposition rate. The increase of frequency from 13.56 MHz to 50 MHz has been found to enhance the deposition rate by 50%, mainly due to changes in the discharge structure and to prevent dust formation due to the rather low operation voltage. The increase of silane percentage in the gas mixture from 2% to 6% under low total pressure—low power conditions almost doubles the film growth rate with SiH_2 radicals being mainly responsible for the film growth. At higher total pressure—higher silane partial pressures the increase of RF power has been found to have the more pronounced effect on the deposition rate, with the main contribution to the film growth coming from Si_2H_4 radicals.

Rates up to 7.5 Å/s have been measured, with 1 Torr, 6% SiH_4 in H_2 discharges at the relatively low frequency of 30 MHz, while operating the discharge in dust-free conditions. These results reveal that high μc-Si:H growth rates can be achieved using conventional techniques.

References

[1] J. Meier, R. Fluckiger, H. Keppner, A. Shah, Appl. Phys. Lett. 65 (1994) 860.
[2] P. Torres, H. Keppner, J. Meier, U. Kroll, N. Beck, A. Shah, Rapid Res Notes: Phys. Status Solidi 163 (1997) R9.
[3] P. Hapke, F. Finger, J. Non-Cryst. Solids 227–230 (1998) 876.
[4] N. Shibata, K. Fukuda, H. Ohtoshi, J. Hanna, S. Oda, I. Shimizu, Jpn. J. Appl. Phys. 26 (1987) L10.
[5] A. Middya, J. Guillet, J. Perrin, J. Huc, J. Moncel, J. Parey, G. Rose, Mater. Res. Soc. Symp. Proc. 377 (1995) 119.
[6] M. Scheib, B. Schroder, H. Oeschner, Mater. Res. Soc. Symp. Proc. 420 (1996) 437.

[7] N. Spiliopoulos, D. Mataras, D. Rapakoulias, J. Vac. Sci. Technol. A14 (1996) 2757.

[8] A.A. Howling, J.L. Dorier, Ch. Hollenstein, U. Kroll, F. Finger, J. Vac. Sci. Technol. A10 (1992) 1080.

[9] M. Heintze, R. Zedlitz, G.H. Bauer, J. Phys. D 26 (1993) 1781.

[10] E. Amanatides, D. Mataras, D.E. Rapakoulias, to be submitted in J. Electroch. Soc.

[11] E. Amanatides, S. Stamou, D. Mataras, D. E. Rapakoulias, Proceedings of the Sixthteenth European Photovoltaic Solar Energy Conference, Glasgow (2000) in print.