ECWR plasma enhanced chemical vapour deposition of microcrystalline silicon thin films.

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Abstract. An ECWR plasma source was used in order to deposit microcrystalline silicon thin films. The effect of input power and silane content on the deposition rate and the materials properties was investigated. Deposition rates, up to 25Å/sec, and high crystallinity degree were achieved using high silane content which is in contrast to the conventional CCP method. The amorphous to crystalline transition zone was determined revealing that in ECWR discharges microcrystalline silicon growth is favoured in a wide range of experimental conditions.

1. Introduction
Hydrogenated microcrystalline silicon thin films are widely applied in a variety of optoelectronic devices such as thin film solar cells and thin film transistors. Industrially, the material is produced by silane/ hydrogen discharges in capacitively coupled plasma (CCP) reactors, although the deposition rate achieved by this method does not exceed 1 nm/sec. In order to increase the deposition rate and the gas conversion to film, several deposition techniques have been proposed such as high pressure depletion method (HPD), very high frequency method (VHF) and use of alternative precursors [1-3]. Moreover, high density methods such as Inductively Coupled Plasmas, microwave plasmas, Electron Cyclotron Reactors and Hollow cathode discharges have been suggested [4-7]. The aim of this work is to use an Electron Cyclotron Wave Resonance (ECWR) plasma reactor in order to deposit microcrystalline silicon thin films and determine the process parameters leading to high deposition rate and device grade materials.

ECWR plasma sources are inductively coupled sources in a weak superimposed magnetic field. The rf magnetic field is usually produced from a single sector coil whose axis is perpendicular to the stationary magnetic field and its frequency is lower than the electron cyclotron frequency (ωc) corresponding to the static magnetic field. Depending on the value of the static magnetic field, plasma dimensions and the radiofrequency, ECWR sources present a resonant-like increase of plasma density. In order to describe the ECWR effect, B. Pfeiffer proposed a theory according to which when the magnetic field enters the plasma region, it splits into a right-hand polarized wave and a left-hand polarized wave [8, 9]. When the wave frequency is higher than the cut-off frequency (which depends on the plasma frequency and the ωc) both waves penetrate the plasma region. On the other hand for wave frequency lower than the cut- off frequency, the refractive index of the left- hand polarized wave is imaginary and the wave does not propagate into the plasma region. However, when the wave frequency is lower than the electron cyclotron frequency (ωc), the refractive number of the right hand polarized wave becomes higher than unity and this wave penetrates the plasma region. These right hand polarized waves, which can propagate in the plasma, are called Electron Cyclotron Waves, or
whistler waves. Resonant plasma excitation by whistler waves is possible when an odd number of the wavelength of the propagating waves fits the plasma thickness in the direction of the wave vector. Experimentally this can be achieved by varying the static magnetic field for a specific radiofrequency. Thus the electron density can reach values more than one order of magnitude higher than that of conventional ICP and CCP discharges [8-11]. The enhancement of the electron density allows the ECWR sources to be used for ionization processes and for plasma enhanced chemical vapour deposition of various films such as hydrogenated Si and Ge, boron and carbon nitride films and amorphous carbon films [12-15].

In this work the deposition of hydrogenated microcrystalline silicon thin films by ECWR discharges is examined. More precisely, the effect of process parameters, such as silane content and input power on the deposition rate and the materials properties is investigated. Laser Raman Spectroscopy was used in order to calculate the crystallinity of the materials and to define the transition zone from amorphous to crystalline phase, while Fourier Transform Infrared Spectroscopy measurements were performed in order to estimate the hydrogen to silicon bonding. Atomic force microscopy measurements were also performed to monitor the morphology of the films and to calculate the materials roughness.

2. Experimental

The experimental set-up is illustrated in figure 1. The ECWR source (COPRA DN250 by CCR Technology) is placed vertically in a high vacuum chamber. The source consists of a single turn copper coil which surrounds the plasma region. The coil is powered via a matching network by RF power of 13.56 MHz. Helmholtz coils are placed around the source in order to create the necessary static magnetic field, for the ECWR effect. The substrate holder is grounded and it is placed at a distance of 10 cm from the plasma source. An external heating system allows the sample heating up to 200°C, which is the typical temperature for μc-Si depositions. A system of flow meter controllers and valves is used in order to feed the reactor with the precursor gases. The hydrogen is fed directly in the plasma source while silane enters the reactor in the region between the substrate holder and the source. The pumping system, which consists of a rotary pump, a roots pump and a turbomolecular pump, is capable to maintain low pressure, in the range of 10⁻² mbar, even for high flow rates. All experiments presented in this work, were performed by keeping the process pressure equal to 10⁻² mbar, while the input power and the silane content varied. Corning glass and c-Si wafers were used as substrates. Just after the depositions, all materials were characterized by Laser Raman Spectroscopy, Fourier Transform Infrared Spectroscopy and Atomic Force Microscopy while the deposition rate was estimated by optical methods.

![Figure 1. Experimental set-up.](image-url)
Raman spectra, excited with the 441.6 nm line of an air-cooled HeCd laser (Kimmon Electric Co.), were measured with the UV-Vis Labram HR-800 spectrograph (Jobin Yvon). A narrow-bandpass interference filter was used for the elimination of the laser plasma lines. The excitation beam was directed to the sample compartment of a confocal open microscope attachment for punctual analysis. The microscope was used for the delivery of the excitation laser beam on the sample and the collection of the backscattered light through a notch-filter and the objective lens adapted to the aperture of the microscope. The focusing objective was a Long Working distance (8 mm) 50x/0.55 Olympus lens. The spectra were obtained using fixed 0.07 mW laser power on the specimen for a total integration time of 200 s. The Raman scattered radiation was focused on a confocal entrance slit (200 μm width) of an achromatic flat field spectrograph with 800 nm focal length. A 1800-grooves/mm grating and a two-dimensional CCD detector cooled at 140K were used for the dispersion and detection of the Raman photons, respectively.

Infrared spectra of films deposited on Si-wafers were measured in the transmission mode on a Bruker Equinox 55 Fourier transformed mid-IR spectrometer with sealed and desiccated optics. All spectra were measured at room temperature and represent the average of 50 scans at a resolution of 2 cm⁻¹.

A NTEGRA Prima by NTMDT, Atomic Force Microscope was used for imaging the materials surface. All films were investigated at semi-contact mode and the RMS roughness was calculated using appropriate software.

3. Results and discussion

3.1 Deposition Rate

The effect of the input power on the deposition rate was examined for silane content equal to 20 and 43%. In order to keep the process pressure constant at 10⁻² mbar both silane and hydrogen flow rates were adjusted. The experimental results are presented in figure 2. The deposition rate in all cases studied here is higher than the rates observed for conventional capacitively coupled reactors. A maximum value ~25 Å/sec is achieved for the highest silane content which is 5 times higher than the industrial rate.

![Figure 2. Deposition Rate as a function of the input power for silane content equal to 20 and 43%.](image-url)

As the input power increases, the deposition rate also increases for both mixtures. Within ECWR discharges the electron density varies linearly with the input power, thus the silane dissociation and the SiHₓ (x<4) radicals production are promoted [16]. Moreover the pressure dependent reactions which lead to radicals consumption, silane polymerization and powder formation in the gas phase are suppressed as the process pressure is very low and the secondary gas phase reactions are not favored. Even highly reactive radicals can travel long distances and reach the surface rather than consumed in
the gas phase. The enhancement of radicals production and the limitation of secondary reactions establish an efficient silane conversion to Si-H thin film.

3.2 Materials Characterization
The Raman spectra of films deposited on glass substrates at input power ranging from 300 to 700 W and constant silane content are illustrated in figure 3. The spectrum at the lowest power is dominated by a broad band around ~480 cm\(^{-1}\) attributed to amorphous silicon. At higher input power a band near ~517 cm\(^{-1}\) appears assigned to crystalline phase of the material. The c-Si phonon peak position in all materials is shifted from its position at 520 cm\(^{-1}\) to lower wavenumbers which is related to the crystallite size and the film stress [17-19].

![Figure 3. Raman spectra of Si-H thin films deposited at different input power.](image)

Crystallinity calculations were performed using spectrum deconvolution in three Gaussian peaks: one at 480 cm\(^{-1}\) assigned to a-Si, one at 517-520 assigned to c-Si and one at 505 assigned to grain boundaries and crystallite sizes below 5nm [20]. The results are presented in figure 4 for materials deposited on glass substrates by varying the silane content and the power input. All materials deposited at the highest silane content (66%) appeared amorphous while an increase of Raman crystallinity with power is observed for silane content 30 and 43%. This is a significant difference compared to conventional CCP method where the microcrystalline silicon deposition is usually achieved when silane mole fraction in the mixture with H\(_2\) is lower than 10% [21].

![Figure 4. Raman crystallinity as a function of the input power on glass substrates for silane content 30, 43 and 66% and pressure 10\(^{-2}\) mbar.](image)

The deposition of highly crystalline materials in ECWR discharges, even for high silane content, is achieved due to the enhancement of silane and hydrogen dissociation and the increase of atomic hydrogen density in the reactor. Atomic hydrogen reaching the film surface has an important role on...
microcrystalline silicon growth. The models that have been proposed in order to explain the beneficial role of atomic hydrogen on the crystallinity of Si: H thin films are summarized in ref [22]. In silane – hydrogen discharges, atomic hydrogen can be produced by both gases. Thus as the input power increases and the dissociation of gases is enhanced, a discharge rich in H is established which in turn leads to higher film crystallinity. As expected, the crystallinity enhancement is more pronounced for the lowest silane content and it reaches a value up to 60% at power 500W. On the other hand, the transition zone from amorphous to crystalline materials is more extended for the intermediate silane content (43%) making possible the microcrystalline silicon deposition in a wider range of input power.

Figure 5 illustrates the Raman crystallinity as a function of input power for materials deposited on glass and c-Si wafers for silane content 43%. Raman crystallinity shows the same trend for both substrates but the transition zone for materials deposited on c-Si wafers is shifted to lower values of the input power. Crystalline silicon wafers offer higher nucleation sites density [23], allowing the crystallization at lower power.

Materials deposited on c-Si wafers were used in order to examine the hydrogen to silicon bonding by means of Fourier Transform Infrared Spectroscopy. A typical spectrum of hydrogenated silicon films consists of three absorption regions: 600-700 cm\(^{-1}\), 850-910 cm\(^{-1}\) and 1850-2250 cm\(^{-1}\) assigned to Si- H\(_x\) wagging, Si-H\(_2\) bending and Si-H\(_x\) stretching vibrations [24]. In this work the analysis is focused on the range of hydrides stretching mode (SM). Figure 6 illustrates the FTIR absorbance spectra of materials deposited by varying the power and for constant silane content 20%. The deposition rate was estimated between 10 and 12 Å/sec and the crystallinity for all samples was calculated between 50 and 60%. The thickness of the films was kept at \(\sim\)600 nm.

![Figure 6. FTIR absorbance spectra of materials deposited by varying the input power.](image)

In the SM region of the spectrum two bands at 2000 and 2090 cm\(^{-1}\) can be observed for all materials. The Low Stretching Mode (2000 cm\(^{-1}\)) is attributed to hydrogen bonded in vacancies while the High Stretching Mode (2090 cm\(^{-1}\)) to hydrogen bonded on voids surfaces [25]. However the relative intensities of LSM and HSM bands vary significantly with the deposition conditions. The LSM is dominant for the film deposited at the lowest power, while the HSM intensity increases as the input power and the deposition rate increase, regardless the crystalline volume of the material. The enhancement of HSM intensity is indicative for porous materials and it has been correlated to post oxidation phenomena [26].
In order to examine if post oxidation phenomena take place, the materials were exposed in ambient conditions for 1 month and FTIR measurement were repeated. Figure 7 illustrates the SM region of the spectrum for films after the exposure in the atmosphere. For samples deposited at power range 500-700 W two bands arise in the spectrum at 2190 and 2250 cm\(^{-1}\), assigned to O\(_2\)Si-H\(_x\) and O\(_3\)Si-H\(_x\) [27], indicating materials oxidation. However, O\(_y\)Si-H\(_x\) bands are barely indentified for the film deposited at the lowest input power suggesting that high quality crystalline materials can be deposited at high deposition rates in ECWR discharges.

Figure 8 illustrates the AFM images of films deposited on glass substrates crossing the transition zone from the amorphous to the crystalline phase. All materials, even the amorphous, show a fine structure and the grain size is of several nm. However as the crystallinity increases the material becomes compact due to grains coalescence. This is also illustrated in figure 9, where the Rms roughness and Raman Crystallinity are plotted. The Rms roughness increases significantly in the
transition zone of the material, while the roughness drops when conditions of crystalline materials deposition are established.

![Rms roughness and Raman crystallinity as a function of the input power.](image)

**Figure 9.** Rms roughness and Raman crystallinity as a function of the input power.

4. Conclusions

Hydrogenated silicon thin films have been deposited by Electron Cyclotron Wave Resonance discharges. The effect of the silane content and input power on deposition rate and materials properties was investigated.

The deposition rate shows a significant increase as silane content and input power increases and can reach a value up to 25Å/sec for silane content 43%. The enhancement of the deposition rate is related to the high dissociation degree of silane. The production of SiH$_x$ (x<4) radicals, which are the building blocks of the film, is more pronounced in ECWR discharges. Moreover, secondary reactions, which promote the silane consumption in the gas phase, are suppressed at the process pressure ($10^{-2}$ mbar). The combination of the above mentioned phenomena leads to effective utilization of the precursor gas.

At constant silane content, Raman Crystallinity increases with the input power due to high flux of atomic hydrogen which is produced by silane and hydrogen dissociation. The high dissociation degree of silane provides sufficient atomic hydrogen, so microcrystalline materials can be deposited for silane content up to 43%. It is worth noticing that for ECWR discharges the experimental conditions which lead to crystalline materials are wider than for conventional ccp discharges.

Furthermore, FTIR analysis revealed that highly crystalline materials deposited at deposition rates ~12 Å/sec are porous and oxidation can take place as the material is exposed in ambient conditions. On the contrary, crystalline materials deposited at intermediate rates (~10 Å/sec) do not show significant post oxidation phenomena.

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References
[1] Roschek T, Repmann T, Muller J, Rech B and Wagner H 2002 J. Vac. Sci. Technol. A 20 492
[2] Fukawa M, Suzuki S, Guo L, Kondo M and Matsuda A 2001 Sol. Energy Mater. Sol. Cells 66 217
[3] Hammad A, Amanatides E, Mataras D and Rapakoulias D 2004 Thin Solid Films 451-452 255
[4] Kosku N and Miyazaki S 2006 Thin Solid Films 511 265
[5] Jia H, Saha JK, Ohse N and Shirai H 2007 Thin Solid Films 515 6713
[6] Roca i Cabarrocas P, Bulkin P, Daineka D, Dao TH, Leempoel P, Descamps P, Kervyn de Meirendre T and Charlaic J 2008 Thin Solid Films 516 6834
[7] Dimitrakellis P, Amanatides E, Mataras D and Rapakoulias DE 2011 J. Phys. : Conf. Ser. 275 012014
[8] Pfeiffer B 1965 J. Appl. Phys. 37 4 1624
[9] Pfeiffer B 1965 J. Appl. Phys. 37 4 1628
[10] Oechsner H 1974 Plasma Physics 16 835
[11] Oechsner H, Scheib M and Goebel H 1999 Thin Solid Films 341 101
[12] Oechsner H 2009 Vacuum 83 727
[13] Scheib M, Schroder B and Oechner H 1996 J. Non-Cryst. Sol 198-200 895
[14] Rodil S, Morrison NA, Milne WI, Robertson J, Stolojan V and Jayawardane DN 2000 Diamond and Related Materials 9 524
[15] Weiller M, Lang K, Li E and Robertson J 1998 Appl. Phys. Lett. 72 1314
[16] Schreiber SJ 2001 Plasma Deposition Of Microcrystalline Silicon For Thin Film Transistors (Cambridge University)
[17] Iqbal Z and Veprek S 1982 J. Phys. C 15 377
[18] Viera G, Huet S and Boufendi L 2001 J. Appl. Phys. 90 3276
[19] Paillard V, Puech P, Sirvin R, Hamma S and Roca i Cabarrocas P 2001 J. Appl. Phys., 90 3276.
[20] Veprek S, Sarott FA and Iqbal Z 1987 Phys. Rev. B 36 3344
[21] Matsuda A 2004 J. Non-Cryst. Solids 338-340 1
[22] Matsuda A 1999 J. Non-Cryst. Solids 337 1
[23] Collins RW, Ferlauto AS, Ferreira GM, Chen C, Koh J, Koval RJ, Lee Y, Pearce JM and Wronski CR 2003 Sol. Energy Mater. Sol. Cells 78 143
[24] Brodski MH, Cardona M and Cuerno JJ 1977 Phys. Rev. B 16 3556
[25] Smets AHM, Matsui T and Kondo M 2008 Appl. Phys. Lett. 92 033506
[26] Bronneberg AC, Smets AHM, Creatore M and Van de Sanden MCM 2011 J. Non-Cryst. Solids 357 884
[27] Niwano M, Kageyama J, Kurita K, Kinashi K, Takahashi I and Miyamoto N 1994 J. Appl. Phys. 76 2175