Ellipsometric study of *a*-Si:H thin films deposited by square wave modulated rf glow discharge

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Thin films of hydrogenated amorphous silicon (*a*-Si:H), deposited by square wave modulated (SQWM) rf silane discharges, have been studied through spectroscopic and real time phase modulated ellipsometry. The SQMW films obtained at low mean rf power density (19 mW/cm^2) have shown smaller surface roughness than those obtained in standard continuous wave (cw) rf discharges. At higher rf powers ($\geqslant$56 mW/cm^2), different behaviors depending on the modulating frequency have been observed. On the one hand, at low modulating frequencies ($<$40 Hz), the SQWM films have shown a significant increase of porosity and surface roughness as compared to cw samples. On the other, at higher modulating frequencies, the material density and roughness have been found to be similar in SQWM and cw films. Furthermore, the deposition rate of the films show more pronounced increases with the modulating frequency as the rf power is increased. Experimental results are discussed in terms of plasma negative charged species which can be relatively abundant in high rf power discharges and cause significant effects on the deposited layers through polymers, clusters, and powder formation.

I. INTRODUCTION

In recent years, some effects of square wave amplitude modulation (SQWM) radio-frequency (rf) glow discharges, for *a*-Si:H deposition, and for plasma etching have been reported.[1–7] Such a plasma technique compared to standard continuous wave (cw) discharges, increases deposition or etch rates, improves *a*-Si:H film quality, and eliminates powder generation in the plasma volume. Published studies of this technique for *a*-Si:H deposition, include those using rf discharges in silane-hydrogen[1] and silane-helium mixtures[2–5] and for etching using rf discharges in SF_6,[6] CF_4, and F_2-He.[7]

Except in the case of pulsed silane-hydrogen discharge, in which no effect on the deposition rate is reported, all other silane-helium plasmas show a clear increase of deposition rate. This increase apparently follows the plasma electron density for modulation frequencies below 10 kHz.[2] In Ref. 2, it is also suggested that the increase of the *a*-Si:H deposition rate may be attributed to the deposition of negative ions (normally confined by the plasma potential sheath) during the afterglow period.

Effects of low-frequency modulation (lower than 5 kHz), such as the improvement of *a*-Si:H deposition rate and film quality, and powder suppression, are also explained[3,4] by an increase of SiH_3 radical density due to the electron density enhancement observed in the rf power on periods. Furthermore, the lifetime of SiH_3 radicals is much longer than those of SiH_2 and SiH radicals. This proposed model is developed in Ref. 5 which adds that the dissociative recombination of ions and the dissociative attachment could explain the reported distinctive temporal evolutions of electron and ion densities during the on-period. A modification of the energy distribution by the modulation is then suggested.

Studies of modulated SF_6 rf plasma etching have reported a very high etch rate of silicon.[6] A mass spectrometry study[7] shows that in CF_4 and F_2-He rf discharges, the negative ions flux can be dramatically enhanced by a square wave amplitude modulating (10 Hz–100 kHz) glow. This enhancement depends, in particular, on the modulating frequency.

It is now normally admitted that the powder formation in the silane rf glow discharge region is one of the most important factors limiting the quality of *a*-Si:H using large deposition rate regimes. In etching plasmas, macroscopic particles or clusters producing serious contamination are also observed. Cluster formation has been studied[8] by measuring light scattering and two-photon laser-induced fluorescence (LIF) signals in the interelectrodes region of a CCl_2F_2 in Ar plasma for etching applications. A signal, attributed to cluster and powder formation, was observed in plasma sheath boundary regions. These signals increase with the elapsed time after the start of etching.

All mentioned authors report that powder generation is largely suppressed in modulated rf plasmas. It is therefore of great interest to investigate the mechanisms which create the powder and its effective consequences on the material performance. General effects due to negative ions and particles in plasmas have been estimated for strongly electronegative gas discharges,[9] so attachment reactions are often considered as being the dominant electron loss process. One of the consequences of silane discharge modulation is the generation of interfaces in *a*-Si:H films. Artificially generated interfaces in *a*-Si:H was first studied

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using ellipsometry[10,11] and later using other characterizations,[12] such as hydrogen content, electronic density of states, and transport properties measurements.

In order to better understand the effects of modulated rf discharge on the growth of *a*-Si:H films, spectroscopic and *in situ* kinetic ellipsometry measurements were performed. From that SQWM discharges were compared to those obtained from standard cw glows. Ellipsometry has therefore been used in the present work as a method to optimize *a*-Si:H growth processes in silane rf glow discharges.

II. EXPERIMENT

A. Deposition process

Thin films of hydrogenated amorphous silicon were prepared by rf glow discharge decomposition of pure silane. The deposition reactor[13] consists of two vertical electrodes with a 40 mm gap. A capacitively coupled rf source works at 13.56 MHz, and is equipped with an automatic matching network, which minimizes reflected power coming from the load impedance of the discharge.

The output rf power was varied from 10 to 80 W, and the amplitude was square wave modulated (SQWM) by a function generator. This corresponds to a cathode power density of 25–200 mW/cm^2. In the present study, the modulating frequencies (f_{mod}) were in the range 0.2–4000 Hz with duty cycles, D of 50% and 75%. The rf matching network was adjusted during a preliminary cw plasma while the substrate was protected by a shutter. During the modulated plasma deposition, the automatic rf matching was turned off.

Films of *a*-Si:H were deposited on Ni-Cr coated glasses, crystalline silicon wafers, and Corning 7059 glass substrates at 300 °C. The pressure of silane was measured by an absolute pressure capacitive meter, and the usual values were set in the range of 20–50 Pa with a flow rate of 30 sccm. The pressure was kept nearly constant during the deposition time.

B. Ellipsometer

The reactor chamber is equipped with a fast phase modulated ellipsometer (PME) which can operate in the uv-visible range in two ways: the real time mode and the spectroscopic mode.[14,15] Ellipsometry measures the angles (Ψ, Δ) as a function of wavelength. These angles are obtained from a Fourier analysis of the detected signal which is modulated at 50 KHz, and are related to the complex reflectance ratio ρ by:

$$\rho = \tan \Psi e^{i\Delta}. \quad (1)$$

The complex pseudodielectric function ε is related to ρ through the relationship:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = \sin^2\Phi\{1 + [(1-\rho)/(1+\rho)]^2 \tan^2\Phi\} \quad (2)$$

where Φ is the incidence angle of the light on the sample surface.

The real time mode provides the evolution of the complex reflectance ratio during the growth process of the films. This permits the monitoring of the growth kinetics of the *a*-Si:H films at a given wavelength. From this evolution, the deposition rate and the film microstructure can be determined by fitting the experimental trajectories (Ψ, Δ) to theoretical growth models.[16–18] In the present study, real time ellipsometric Ψ and Δ values were measured during the growth of *a*-Si:H films on NiCr and *c*-Si substrates. For the NiCr substrates, a 7.08-ms time resolution was used, whereas for *c*-Si substrates, the time interval between two experimental points were 0.53 s (low rf power conditions) and 0.35 s (high rf power conditions). In this latter case (Ψ, Δ) pairs were calculated by integrating 75 and 50 consecutive measurements, respectively, for each rf power condition. The background signal was measured at the beginning of the deposition process and then subtracted from the measured signal. This procedure is permissible because of the optical arrangement used,[15] which minimizes the plasma light variations (the spectrometer is placed after the analyzer). In spite of that, a variation of Ψ is observed at low frequency modulation levels due to the background variations. In the used optical elements orientation (configuration II in Ref. 19) a background variation perturbs Ψ but not Δ.

The spectroscopic mode of the ellipsometer gives the dependence of the complex pseudodielectric function ε on the photon energy. The maximum ($\varepsilon_{2\max}$) of the imaginary part of ε is related to the Si—Si bond packing density as well as the surface roughness and oxidation.[20,21]

III. RESULTS

A. Effects of modulating rf plasmas on *a*-Si:H deposition rate

The deposition rate was calculated by using two independent procedures: by *in situ* ellipsometry, at a fixed wavelength, during the growing process, and by measuring the film thickness with a visible ir optical transmittance spectrophotometer. Both methods give close values (10% variation).

In cw glows and constant substrate temperature, the *a*-Si:H deposition rate (v_d) depends on the silane dissociation yield, which is a function of the rf power, gas pressure, and plasma-surface reactions. The rf power dependence of v_d, at constant 30 Pa pressure, is shown as the solid line in Fig. 1.[22,23] When rf power is increased, v_d increases up to saturation due to gas consumption.

The growth rate values of films deposited in SQWM discharges are plotted in Fig. 1 for $f_{\text{mod}} = 2$, 40, 400, and 4000 Hz and duty cycle $D = 0.75$. The mean rf power densities, $\langle W_{\text{rf}} \rangle = DW_{\text{rf}}$ were 19, 56, and 150 mW/cm^2.

It is interesting to note in Fig. 1 that v_d(SQWM) values roughly follow the cw curve and increase with the modulating frequency at a fixed rf power. This latter effect is more marked at high rf power discharges as can be observed in Fig. 2 where v_d is plotted versus f_{mod} for two rf power values.

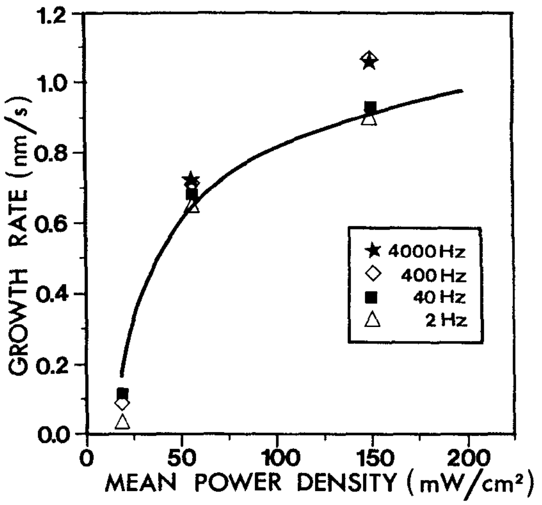

FIG. 1. Dependence of the deposition rate with the mean rf power density of *a*-Si:H films grown on *c*-Si at 30 Pa silane pressure and 300 °C substrate temperature by SQWM rf discharges with 75% duty cycle. Symbols correspond to different modulating frequencies. Solid line corresponds to samples obtained in cw rf discharges (see Ref. 23).

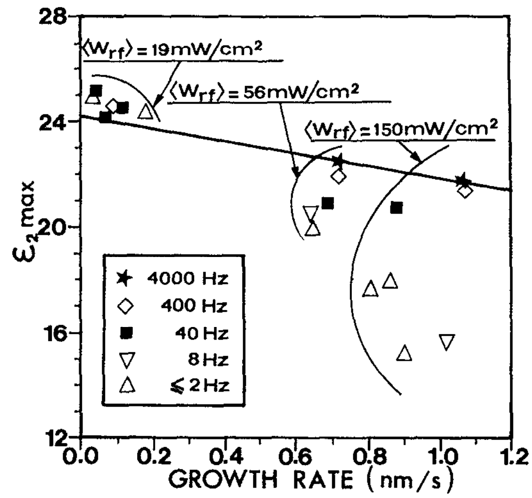

FIG. 3. The maximum of the imaginary part of dielectric function ($\varepsilon_{2\max}$) vs the *a*-Si:H growth rate. Symbols correspond to different modulating frequencies (duty cycle = 75%). Solid line corresponds to the empirical relation (3) for samples obtained in cw rf glows. Three mean rf power conditions have been studied.

B. Effects of modulating rf plasmas on *a*-Si:H films studied by ellipsometry

Spectroscopic ellipsometry measurements (ε versus the photon energy) were performed on *a*-Si:H samples obtained, with native oxide, in cw and SQWM rf discharges. Figure 3 shows the correlation between $\varepsilon_{2\max}$ and v_d in the studied v_d range (0–1.2 nm/s). The solid line corresponds to samples produced in cw discharges[22,23] with the same experimental conditions as SQWM ones. For these cw samples, obtained at different values of silane pressure and rf power, an empirical linear correlation was found:[23]

$$\varepsilon_{2\max} = -2.27 v_d \text{ (nm/s)} + 24.2. \qquad (3)$$

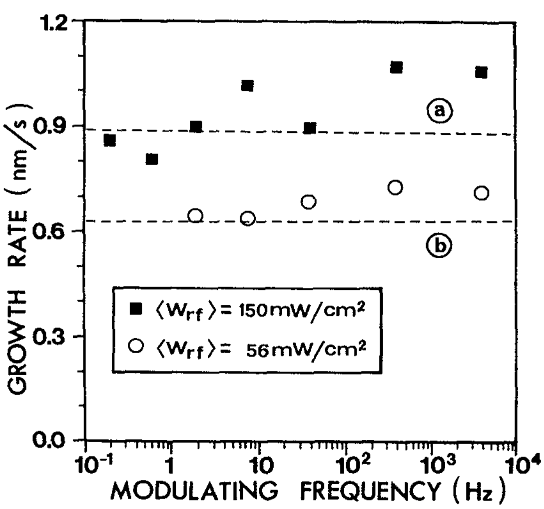

FIG. 2. *a*-Si:H deposition rate vs rf modulating frequency for two mean rf powers. Dotted lines indicate the corresponding deposition rate values of samples obtained in cw rf glows: (a) at 150 mW/cm^2 and (b) at 56 mW/cm^2

The cw films grown at low deposition rate ($v_d < 0.2$ nm/s) have the highest $\varepsilon_{2\max}$ values and therefore the highest material density value and the smallest surface roughness.

Depending upon the discharge conditions, the relation (3) can be strongly disturbed for samples obtained in SQWM rf glows (Fig. 3). Measurements of v_d(SQWM) and $\varepsilon_{2\max}$(SQWM) of samples produced at low rf power ($\langle W_{\rm rf}\rangle = 19$ mW/cm^2) show that for all samples grown with different $f_{\rm mod}$:

$$\varepsilon_{2\max}(\text{SQWM}) \geqslant \varepsilon_{2\max}(\text{cw}).$$

No significant variation of $\varepsilon_{2\max}$(SQWM) with the modulating frequency is observed. In contrast, at higher rf powers, there is a clear $\varepsilon_{2\max}(\text{SQWM}) - f_{\rm mod}$ dependence. In the case of $\langle W_{\rm rf}\rangle = 150$ mW/cm^2, $\varepsilon_{2\max}$(SQWM) presents a strong dependence on the modulating frequency (Fig. 4): $\varepsilon_{2\max}$ values first drop from cw to 2 Hz SQWM samples, then increases with $f_{\rm mod}$ in such a way that for $f_{\rm mod} \geqslant 40$ Hz, they are compatible with the cw empirical law.[3]

The plasma modulation process at $f_{\rm mod} = 0.2$ Hz, 50% duty cycle, $\langle W_{\rm rf}\rangle = 100$ mW/cm^2 and 30 Pa, has been monitored by means of the real time evolution of the Ψ, Δ ellipsometric angles, during the *a*-Si:H growth (Fig. 5). In the present experimental conditions, the modulation of the plasma follows correctly the modulation of the rf power and, although there is a shift of Ψ angle to lower values when the plasma is switched off, due to the difference between the dc background levels of plasma on with respect to plasma off, the on–off switching of the plasma does not modify the normal ellipsometric trajectory at the beginning of the deposition. Nevertheless, after a few cycles, a progressive anomalous behavior of Δ ellipsometric angle is

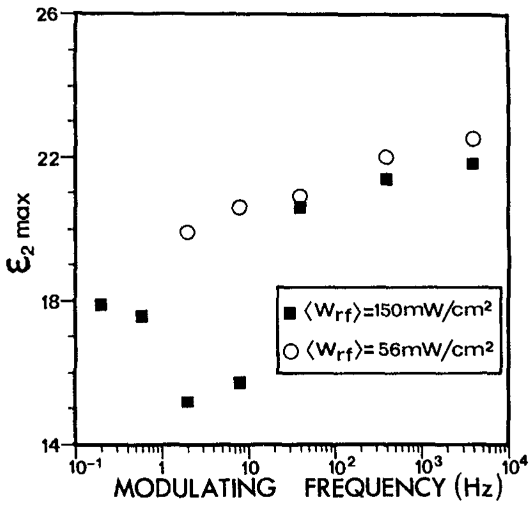

FIG. 4. The maximum of the imaginary part of dielectric function (ε_{2max}) vs the rf power modulating frequency.

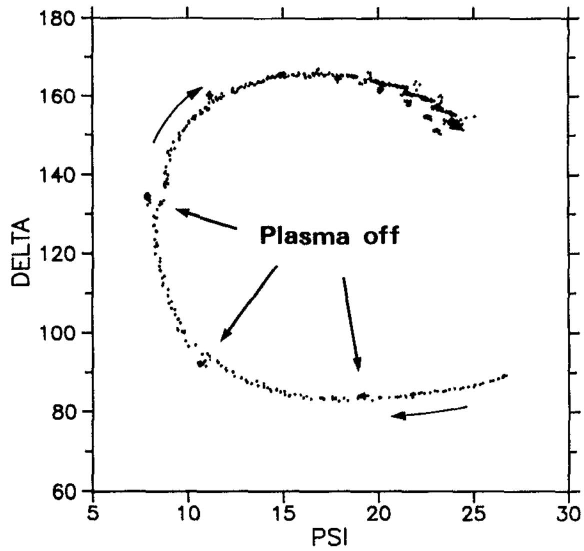

FIG. 5. Ellipsometric angles (Ψ, Δ) evolution during the growth of an a-Si:H film on a Ni-Cr substrate at 0.2 Hz and 50% duty cycle modulated rf discharge ($\langle W_{rf}\rangle = 100$ mW/cm^2, 30 Pa, 30 sccm). The used photon energy was 3.1 eV. The time interval between two experimental points is 7.08 ms. The experimental points shifted about 1° from the trajectory correspond to the plasma off periods. The arrows indicate the growth direction. The trajectory endpoint corresponds to a film thickness of about 20 nm.

observed in the trajectory, suggesting an increase of roughness. This is in agreement with the fact that at low modulating frequency, ε_{2max} values are small [ε_{2max}(SQWM) = 19.7 for $f_{mod} = 2$ Hz in the same experimental conditions]. The same study with higher f_{mod} cannot be done with the present ellipsometer performances.

In order to get information on the growth and microstructure of cw and SQWM samples, a real time ellipsometric analysis has been done at a photon energy $E\gamma = 3.40$ eV. At this energy, $\langle\varepsilon_2\rangle$ is near its maximum value, so the ellipsometric results are only related to the surface of the samples. On the other hand, the spectroscopic ellipsometric analysis provides information about the bulk material and surface roughness.

The ellipsometric trajectories, at fixed energy $E\gamma$, were fitted using a theoretical model[17] which supposes a homogeneous growth below a surface roughness overlayer, with a void fraction of 0.395, corresponding to a hemispherical representation of surface roughness.[24]

The spectroscopic measurements were fitted assuming a two layers structure, namely, a surface roughness overlayer (with a void fraction of 0.395) and a bulk material constituted by dense a-Si:H and voids.[24] The a-Si:H reference is a high density material having $\varepsilon_{2max} = 28.8$ at 3.74 eV.

Tables I and II collect the ellipsometric results corresponding to low and high rf power deposition conditions, respectively.

1. Low rf power samples

It is interesting to note that, at low rf power, the films obtained in SQWM plasmas have a significantly smaller roughness than that of cw films (Table I). This roughness change is clearly shown in Fig. 6 where the ε_2 vs ε_1 for cw and SQWM growing films, measured *in situ* at $E\gamma = 3.40$ eV, have been plotted together with the fitted theoretical curves. Each fitted trajectory starts from the end of the coalescence phase (6.5 nm of thickness), up to reach the semi-infinite media condition (70 nm of thickness).[17] In these trajectories, the relative position of the endpoints (Fig. 6), indicates a difference in surface roughness, whereas the bulk parameters, such as refractive index and extinction coefficient remain practically unchanged.

2. High rf power samples

At high modulating frequencies ($f_{mod} \geqslant 40$ Hz), the surface roughness and bulk void fraction show similar values to the cw sample. In contrast, for $f_{mod} = 2$ Hz, the

TABLE I. Results of the real time ellipsometry analysis for a-Si:H films grown in cw and SQWM plasmas at low rf power. Discharge parameters were: $P = 30$ Pa, $W_{rf} = 25$ mW/cm^2, and duty cycle of 50% for the SQWM sample. Real time ellipsometry measurements were done at 3.4 eV of photon energy. The final roughness values were deduced from *ex situ* measurements of a-Si:H films with its native oxide.

Sample No.	Modulating frequency (Hz)	Deposition rate (nm/s)	Initial roughness (nm)	Final roughness (nm)	Refractive index n	Extinction coefficient k
1	0	0.25	1.7	3.2	4.91	2.65
2	400	0.03	1.6	2.0	4.92	2.64

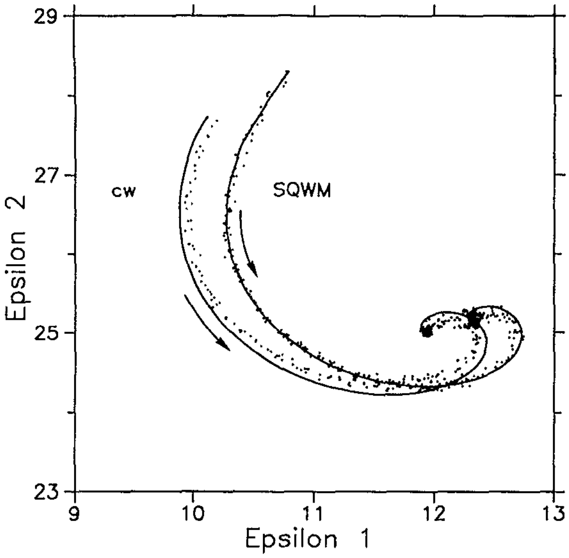

FIG. 6. ε_2 vs ε_1 evolution (points), measured at 3.4 eV photon energy, corresponding to *a*-Si:H growth on *c*-Si substrates for cw and 400 Hz SQWM in a low rf power discharge ($\langle W_{rf} \rangle$ = 19 mW/cm^2). The solid lines correspond to a fitted model. The arrows indicate the growth direction. The trajectory starting points in the figure correspond to the end of the nucleation and coalescence phases (6.5 nm of film thickness). The time intervals between two experimental points in the initial stages, displayed in the figure, are 0.52 s for cw trajectory and 2.65 s for SQWM trajectory.

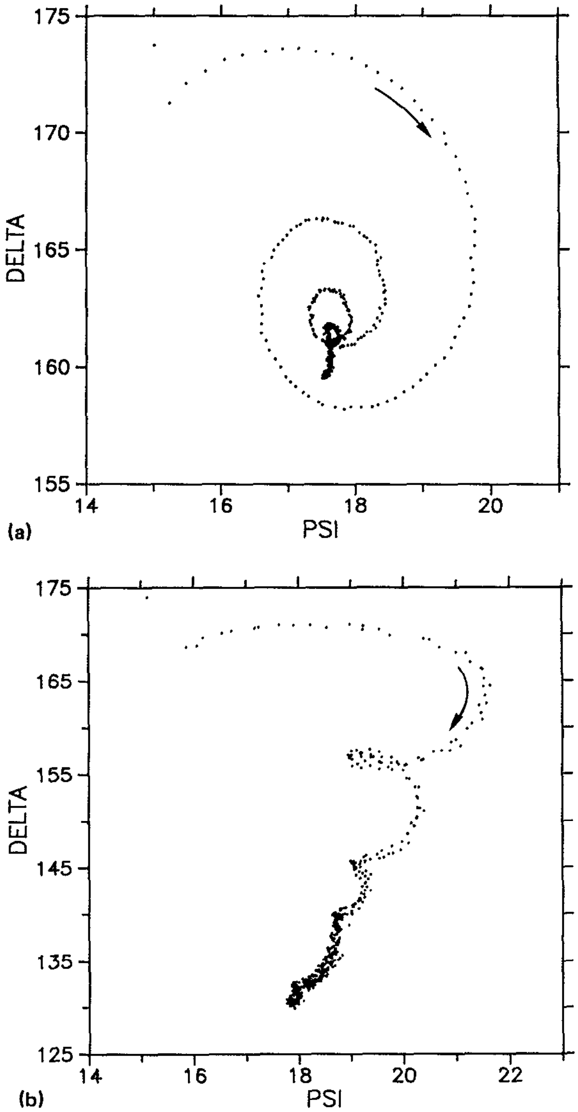

FIG. 7. Ellipsometric angles (Ψ, Δ) evolution recorded at 2.48-eV photon energy, during the growth of *a*-Si:H films on *c*-Si substrates in a 4000 Hz (a), and 2 Hz (b) high SQWM rf power discharges ($\langle W_{rf} \rangle$ = 150 mW/cm^2). The arrows indicate the growth direction. The film thickness reached at the endpoints of the trajectories is 400 nm. The time interval between two experimental plotted points is 0.71 s.

situation appears quite different, since the surface roughness and bulk void fraction increase strongly (Table II). This behavior can also be observed in the real time evolution of the Ψ, Δ ellipsometric angles (Fig. 7). In Fig. 7(a) the decrease of Δ at the trajectory endpoint corresponding to the sample grown with f_{mod} = 4000 Hz, can be attributed to an increase of about 2 nm in thickness of the surface roughness during the growth.[18] A similar behavior has been found for cw depositions,[25] where a decrease of the pseudodielectric function $\langle \varepsilon_1 \rangle$ has been related to a surface roughness thickness increase. The dramatic evolution shown in Fig. 2(b), corresponding to the sample grown with f_{mod} = 2 Hz, can also be attributed to the surface roughness thickness and/or bulk density changes. If no variation of the bulk density is assumed, the overall surface roughness increase is estimated to be 15 nm.

TABLE II. Results of spectroellipsometric analysis for *a*-Si:H films grown in cw and SQWM glows at high rf power (W_{rf} = 200 mW/cm^2). SQWM samples were deposited with a duty cycle of 75%. The final roughness and void volume fraction values were deduced from *ex situ* measurements of *a*-Si:H films with its native oxide.

Sample No.	Modulating frequency (Hz)	Pressure (Pa)	Deposition rate (nm/s)	Final roughness (nm)	Void volume fraction (%)
3	0	25	0.80	3.4	3.6
4	2	25	0.75	21.9	17.7
5	400	30	0.70	4.1	6.4
6	4000	30	1.0	4.1	6.1

All these effects must be related with the ε_{2max} measurements plotted in Fig. 3 that show an important degradation of the *a*-Si:H film quality in samples grown at low modulating frequency and high rf power. They are also in agreement with the anomalous behavior of Ψ, Δ trajectory reported in Fig. 5.

To summarize, it clearly appears that by modulating the rf power, the growth and the quality of the films can be very disturbed, depending on f_{mod} and W_{rf}.

C. Production of silicon powder

For high pressure and high rf power cw and SQWM discharges, a yellow silicon powder has been observed on the wall close to the exhaust apertures of the plasma chamber. A visual evaluation of this powder produces the following remarks: (a) an increasing of the rf power or pressure enhances the powder production, (b) at low modulating frequencies ($f_{mod} < 40$ Hz), the powder was more abundant than at higher frequencies, for identical pressure and rf power conditions, and (c) at higher modulating frequencies, the powder production is close to the observed in cw glows.

It must be pointed out that the powder has never been observed on the substrates and some have been found stuck to the cathode surface, particularly at low f_{mod} conditions. This can be attributed to the vertical arrangement of the electrodes, to the gas flow downstream along the electrode gap, and to temperature effects.

IV. DISCUSSION

A global explanation of the observed effects of plasma modulation must be found in the correlations between the modulation of silane rf discharges and the kinetics of plasma components as well as the induced film microstructure. Plasma modulation can modify the plasma itself by changing the applied rf power, the gas pressure, the electronic density, the electronic temperature, the active species composition in the plasma volume, the plasma sheath, and the film ion bombardment.

We propose, following the ideas suggested in Refs. 2, 7, and 9, a discussion based on a qualitative model that assumes that the negative ions in modulated silane rf glows, have a dominant role with respect to the other parameters on the film growth properties. When the rf power is switched off, the plasma sheath potential disappears allowing the negative ions, normally confined in the plasma volume, to reach the walls of the discharge chamber. The layer microstructure and the plasma negative ion density can therefore be modified.

Primary negative ions are essentially produced in silane discharges by attachment reactions. The most important one is

$$e^- + SiH_4 \rightarrow SiH_3^- + H.$$

The production of SiH_2^- and SiH^- is close to 3 times less. Another negative ion production that can be important in the case of high electron plasma density is the anion-cation pair formation from highly excited molecular states.[26] The amount of primary negative ions in the plasma depends essentially on the rf power which is responsible for the plasma electronic energy and density distribution for a defined gas pressure, and on the residence time. The residence time depends on the probability of negative ion loss and it is clearly larger than that of positive ions, because of the confinement effect of the negative potential sheath near the electrodes. If a negative ion is neutralized, it diffuses as a normal radical, and disappears contributing to the deposition. The processes responsible for negative ion neutralizations in the plasma region are ion-molecule detachment reactions (a pressure-dependent process) or photodetachment reactions, and anion-cation neutralizations.

Primary negative ions can strongly polymerize in ion-molecule reactions and grow into clusters or powder. Two factors modify its polymerization yield: pressure and residence time.

In cw glows, there are other processes contributing to a residence time decrease. The gas stream between electrodes and gravitation effects can contribute to eliminate negative ions and, of course, clusters and powder from plasma region.

In SQWM discharges there is also another possibility. The periodical sheath demolition contributes to eliminate, from the plasma chamber, negative ions and clusters which are allowed to reach the layer. In this case the growth rate should increase due to negative ion or cluster contribution when f_{mod} increases. The corresponding increase rate will also depend on cluster size. Furthermore the fact that the increasing rate of v_d with f_{mod} is more important at high rf power than at the low one, should be originated by the negative ions production yield, which increases with the rf power.

The interpretation of the present results about deposition rate, material density, and surface roughness needs to introduce the fact that, because of their long residence time, negative ions can strongly polymerize. When rf glows are modulated at low frequency (i.e., 2 Hz), the time of discharge is very long with respect to the residence time. The plasma polymer or cluster density is then expected to be close to that of cw glows, and each time the plasma is stopped, the substrate receives strongly polymerized negative ions. The material density and roughness can therefore be strongly affected.

The low ε_{2max}(SQWM) values, measured at $\langle W_{rf} \rangle = 150$ mW/cm^2 and $\leqslant 8$ Hz f_{mod} (Figs. 3 and 4) confirm this layer degradation by a surface roughness and porosity increase, produced by clusters issued from negative polymers.

While the rf power-on time is long enough to allow the maximum cluster size, the detrimental effects must increase with f_{mod}. Therefore, for increasing very low f_{mod}, ε_{2max}(SQWM) values are expected to decrease until a minimum. This behavior is observed in the present results where a minimum ε_{2max}(SQWM) is reached at ~ 2 Hz (Fig. 4).

The situation is dramatically changed at high f_{mod}. The rf power-on time (the cluster formation available time), can then be smaller than the residence time, and even too small to allow polymerized silicon molecule formation. When f_{mod} is increased, the size of the clusters becomes then smaller and even if polymer composition becomes negligible, incident negative ion flux on the substrate is essentially constituted by SiH_3^-, which is beneficial to a-Si:H film quality.[27]

At $\langle W_{rf} \rangle = 56$ mW/cm^2 there are the same effects but less important because the negative ions production is smaller. Finally at $\langle W_{rf} \rangle = 19$ mW/cm^2, where negative ion density in the plasma is still smaller, no effect of degradation is observed.

It is interesting to note that at low rf power, and consequently at the low deposition rate, ε_{2max}(SQWM) $\leqslant \varepsilon_{2max}$(cw) for all f_{mod}. Ellipsometric real time measurements reveal that the surface roughness is small in films obtained in these modulated plasmas.

It should also be mentioned that the obtained final roughness values are greater than the usual values reported in the literature for the optimum rf discharge material. The reported values are typically between 1 and 2 nm.[11,16,28] The reason for this difference could arise from the fact that the present values have been deduced from *ex situ* measurements of a-Si:H films with its native oxide.

The arguments, used to explain the $\varepsilon_{2\max}$ values, also concern the deposition rate. High modulating frequency involves a high number of post-glow depositions of small size particles whereas low f_{mod} involves a small number of post-glow depositions of great size clusters. Measurements presented in Figs. 1 and 2 are the consequence of these effects.

V. SUMMARY AND CONCLUSIONS

A. The experimental results in SQWM rf glows

(i) The silicon powder stuck on the cathode or outside the plasma chamber decreases as modulating frequency rises. At $f_{\text{mod}} = 2$ Hz the powder production is very important. (ii) The growth rate increases with the modulating frequency. The increased rate is magnified at high rf power. (iii) The spectroscopic ellipsometry shows that $\varepsilon_{2\max}$ changes with modulating frequency and rf power.

At low mean rf power (19 mW/cm^2), for all studied modulating frequencies, the roughness is smaller for the SQWM samples than for the cw ones.

At high mean rf power (56 mW/cm^2), for $f_{\text{mod}} < 40$ Hz, the roughness and porosity are much higher in SQWM samples than in cw ones [$\varepsilon_{2\max}(\text{SQWM}) \ll \varepsilon_{2\max}(\text{cw})$]. For $f_{\text{mod}} \geqslant 40$ Hz, the roughness and material density are similar in SQWM and cw samples [$\varepsilon_{2\max}(\text{SQWM}) \approx \varepsilon_{2\max}(\text{cw})$].

B. Interpretation

Present results can be understood on the basis that, in SQWM rf glows, the plasma negative species have a dominating role, with respect to the other plasma parameters, on a-Si:H film formation. As negative ions have a long residential time in the plasma, they are able to strongly polymerize, to form clusters, and to originate the usually observed powder.

When the rf power is switched off, the plasma potential sheath disappears and negative ions and clusters are allowed to reach the layer. Therefore the growth rate must increase with the modulating frequency in agreement with the precedent results.

At low rf power such that there is a small plasma negative ion density, cluster and powder formation is small. The plasma modulation therefore produces a beneficial effect by decreasing the roughness, for all f_{mod} studied. This property could be of great interest in the a-Si:H industrial applications.

At higher rf power and for $f_{\text{mod}} < 40$ Hz, the layer receives all kinds of negative monomers and especially polymers and clusters. Therefore the roughness and film porosity are increased. On the contrary, for $f_{\text{mod}} \geqslant 40$ Hz the polymerization probability and cluster size become smaller, and therefore the negative species contribution does not modify the a-Si:H layer with respect to the one obtained in standard cw rf discharges.

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