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Probing periodic oscillations in a silane dusty plasma in a very high-frequency plasma enhanced chemical vapor deposition process

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Abstract: To estimate the dust formation time scale in a silane–hydrogen plasma, optical and electrical plasma diagnostics are performed. We report a periodic fluctuation in emission intensity and electric current in a dusty plasma. The trends of the frequency of fluctuations with varying substrate temperatures and gas flows are studied. However, no such fluctuation is observed in the nondusty plasma. It is hypothesized that this fluctuation arises from the periodic formation and ejection of a dust cloud via the void formation when a critical dust size is reached.

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Résumé : Nous effectuons des diagnostiques optiques et électriques dans des plasmas de silane–hydrogène, afin de déterminer l'échelle de temps de la formation de poussière dans ce plasma. Nous observons une fluctuation périodique de l'intensité d'émission et de courant électrique dans un plasma poussiéreux. Nous étudions les tendances de la fréquence des fluctuations selon différentes températures du substrat et différents écoulements gazeux. Nous n'observons aucune fluctuation de ce genre dans le plasma non poussiéreux. Notre hypothèse est que cette fluctuation vient de la formation périodique et de l'éjection d'un nuage de poussière, causant la formation d'un vide (cavitation), lorsqu'un volume critique de poussière est produit. [Traduit par la Rédaction]

1. Introduction

Plasma enhanced chemical vapor deposition (PECVD) is a widely used technique for thin film silicon depositions. Nanoparticle and dust formation in a silane–hydrogen discharge in PECVD can have a beneficial or deleterious effect on the deposited layer depending on the growth conditions of silicon material. Plasma dust leads to voids and defects in the deposited layers and degrades the performance of the solar cell; incorporating silicon nanoparticles in photovoltaic amorphous layers, called polymorphous material, on the other hand delivers high open circuit voltage and has claimed to have better stability against light soaking [1]. Moreover, the use of a layer of silicon quantum dots in a multijunction solar cell would allow to surpass the Shockley–Queisser efficiency limit [2] by trapping light from a wider solar spectrum, while reducing losses associated with nonabsorption of below bandgap photons and lattice thermalisation loss. Quantum dot (QD) is a way to engineer the bandgap, and theoretically, 42.5% and 47.5% for two- and three-cell tandem stacks, respectively, can be achieved compared with 29% for a single junction Si cell according to S–Q limit [3]. This research attempts to find precise control of plasma processes to obtain the desired particles to be embedded in the layer or removed from the gas phase depending on the choice of the material for the device.

The different phases in the growth phenomena from precursors to powder in a silane-based discharge have been extensively described elsewhere [4]. Here, we emphasize two plasma regimes, the nature of which depends on the condition in which the plasma is maintained.

As is illustrated in Fig. 1, charging and growth of clusters to a certain critical size and density leads to the formation of multiply charged aggregates with sizes of 10–100 nm [5]. The formation of larger aggregates offers a greater capture cross section for electrons [6]. Powders act as electron traps resulting in negatively charged particles with charges of the order of 10–3000 elemental charges (proportional to the dust radius) [7]. The Debye shielding becomes less effective because of this drastic loss of electrons and the electric field penetrates deeper into the plasma, raising the electron temperature and causing an important plasma transition from the so-called α (nondusty) to the γ (dusty) regime. This transition to a more dissipative regime is accompanied by significant changes in plasma characteristics, such as higher bulk emission, reduction in self-bias voltage, and increase in ionization and deposition rates. A dust-free plasma can be made into a dusty one by increasing one or more of the deposition parameters, such as the applied power density, process gas pressure, or interelectrode distance, and decreasing one or more parameters, such as the $\text{H}_2/\text{SiH}_4$ fraction and the substrate temperature [8–13].

Our interest in dusty plasmas originates from our particles of interest, a special class of semiconductors called QDs that appear during the transition from the nondusty to dusty regime [14]. Time evolution of particle density and size by Boufendi et al. [15] by transmission electron microscope studies has shown that when the cluster size becomes higher than 6 nm, the transition from α to γ regime takes place. At the onset of this transition, the density of particles drops and their radius increases by aggregation [14]. Using a pulsed plasma, our particles of interest (size less
than 5 nm) could be generated, as already shown by a few other groups [16, 17].

QDs are the polymerization precursors to dust, and a thorough understanding of their formation and growth is the key to control dust. QDs are materials with size less than the exciton Bohr radius, spatially confining the electrons and holes. The exciton Bohr radius of silicon is 4.2 nm when quantum confinement effects come into play, rendering size dependent optoelectronic properties. Our materials of interest are silicon and silicon germanium QDs. Thus with a judicious combination of different QDs a wide variety of materials with different bandgap can be made to harvest a wider solar spectrum.

With this goal in mind, we have designed a new plasma chamber to grow and extract QDs in the gas phase in a single step for implementation in a solar cell. This chamber is a part of the ultrahigh vacuum multichamber very high frequency PECVD deposition system ASTER (amorphous silicon thin film experimental reactor). But prior to this, it is crucial to have utmost control over particle formation in the plasma to strengthen our understanding on the dynamics of dusty plasma processes, which is presented in this paper.

2. Methods

The experiments described here are performed in chamber 1 of ASTER, which is equipped with a view port for optical diagnostics and a MKS current voltage (VI) probe for electrical diagnostics as shown in Fig. 2. More technical details on ASTER can be found in [18]. Because the QDs are formed before the transition of the plasma to the dusty phase, a thorough understanding of the behavior of the nondusty and dusty plasmas is necessary. We probe the plasma with noninvasive techniques: optically with in situ optical emission spectroscopy (OES) and electrically with a built-in VI-probe.

The emission of photons from the large number of excited species in the plasma leads to characteristic lines in the emission spectrum, which is monitored with OES. The agglomeration of dust particles leads to a transition from the a to γ’ regime where the particles have a higher electron capture cross section, in turn decreasing the electron density and increasing the electron temperature. These properties are reflected in the enhanced emission of the plasma as more electrons have higher energy to excite different plasma species, hence having a broader emission profile and higher bulk emission [19, 20].

The optical emission spectrometer Avantes Avaspec-2048-USBl2, equipped with a grating, was used to record axial emission profiles from the plasma. The light from the plasma chamber was focused on an optical fiber, which subsequently led the light into the spectrometer. This system is mounted on a stage that can be moved in the vertical direction, perpendicular to the plane of the electrode.

For the electrical measurements of the plasma, the electrode potential (V), plasma current (I), and relative phase (ϕ) were measured directly using an MKS VI-probe attached between the matchbox and the powered electrode. The plasma impedance (Z = V/I) and delivered power (P = VI cos ϕ) can also be calculated.

Optical and electrical measurements were performed in both nondusty and dusty regimes in very high frequency PECVD process by altering the plasma parameters according to the regime we desired as given in Table 1. The nondusty regime is our standard deposition condition of device quality a-Si:H. Decreasing the inter-electrode distance from 27 to 10 mm will decrease the probability of dust formation, but in our case, the combination of increasing power and pressure counteracts this effect and the plasma is in the dusty regime. The transition from the nondusty to the dusty regime was observed by a change in emission profile and higher bulk emission and also by the shift in plasma impedance towards a more resistive plasma. More details on dusty plasma
and OES can be found in ref. 20. For each measurement the plasma was switched on, left to stabilize for 60 s, before doing the optical and electrical measurements for 100 s. The data were then subjected to discrete Fourier transform (DFT).

3. Results and discussion

The optical emission lines of SiH*, Balmer Hα, and Balmer Hβ at 413.8, 656, and 486 nm, respectively, and the plasma current from VI-probe were recorded from nondusty and dusty regimes. Output parameters of both optical and electrical measurements probed with OES and VI-probe, respectively, showed a stable periodic oscillation in the dusty regime. However, for the same measurements performed in the nondusty regime, there was no fluctuation in either optical or electrical measurements, but a weak signal at 50 Hz, which is the line frequency. No fluctuation of the ratio $H\beta/H\alpha$, which is related to the electron temperature [21] could be detected with OES in both regimes. This could be masked by its low signal to noise ratio at the required acquisition times. Some examples of the fluctuation are displayed in Fig. 3.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Frequency (MHz)</th>
<th>Power (W)</th>
<th>Pressure (mbar)</th>
<th>Substrate temperature (°C)</th>
<th>SiH4:H2 flow (sccm)</th>
<th>Electrode distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dusty plasma</td>
<td>60</td>
<td>17.5</td>
<td>3</td>
<td>180</td>
<td>5:100</td>
<td>10</td>
</tr>
<tr>
<td>Nondusty plasma</td>
<td>60</td>
<td>5</td>
<td>0.16</td>
<td>180</td>
<td>35:175</td>
<td>27</td>
</tr>
</tbody>
</table>

### Table 1. Plasma parameters for dusty and nondusty regime.

Fig. 3. (a) Emission intensity of SiH* in the dusty regime. (b) Current through the plasma in the dusty regime. (c) DFT of emission intensity of SiH* in the nondusty regime. (d) DFT of SiH* emission intensity in the dusty regime.

Fig. 4. Combined peaks from (crosses) emission of SiH* and (circles) current frequencies.
As the VI-probe has a sampling frequency of approximately 133 Hz, the DFT has a maximum frequency of 67 Hz. Frequencies above this limit are displayed as mirror images of the below frequency. So the DFTs were cropped to a range of 5–60 Hz, and Lorentzian peaks were fitted after averaging over the stable plasma period. The resulting peak positions from emission and current are combined in Fig. 4. Here it should be noted that the synchronously recorded DFTs in both plasma current and emission overlapped each other perfectly at 38 Hz, which is the dominant frequency.

The frequencies of both SiH* and H$_2$ showed similar trends. For a deeper understanding of these periodic fluctuations, variation of frequencies of H$_2$ at different substrate temperatures and flows are studied. As it can be seen in Fig. 5a and 5b, an increase in substrate temperature was observed to have an inverse effect on fluctuation frequency, whereas increasing the gas flow has an opposite effect.

The effect of substrate temperature and gas flow rate on dusty plasma is complex. Ions get accelerated outwards in the sheath, while in the bulk they are completely screened and affected by the thermal energy only; increasing the gas temperature increases the thermal energy of bulk ions and neutral species. For the same thermal energy only; increasing the gas temperature increases the ion scattering cross section decreases with ion temperature, which may be attributed to slower polymerization reaction in gas phase [27]. For the same dust size and charge, the ion scattering cross section decreases with ion temperature: ion drag becomes less when ion temperature increases. This could also contribute to the slower fluctuation at higher temperature.

### 4. Conclusion

We studied the fluctuation of plasma in a dusty regime of silane–hydrogen gas mixture in a very high frequency PECVD process. Our study thus may lead to a method to precisely control the particle size in a dusty plasma for our experimental condition, by pulsing the plasma to time scales less than the fluctuations that we observe. In this way, we could disrupt the particle growth before the critical size is reached and extract them to be implemented in a quantum dot solar cell.

Periodic fluctuations observed in the dusty regime manifests itself in the overall plasma emission intensity as well as in its electrical behavior. Increased temperatures have an inverse effect on the pulsing frequency, however, increasing the gas flow increased the pulsing frequency. No such fluctuation in the non-dusty regime could be detected. It can be hypothesized that these fluctuations arise from periodic formation and ejection of dust clouds via void formation in the plasma bulk when a critical dust size is reached [24, 27]. The driving force of this instability is the dust growth rate and the ion drag force. The experimental results shown in Fig. 5a and 5b support such a hypothesis; the frequency of fluctuation increased with silane flow rate, which may be attributed to faster growth of dust with increased precursor flux, whereas it decreased with increase in substrate temperature, which may be attributed to slower polymerization reaction in gas phase [27]. For the same dust size and charge, the ion scattering cross section decreases with ion temperature: ion drag becomes less when ion temperature increases. This could also contribute to the slower fluctuation at higher temperature.

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References