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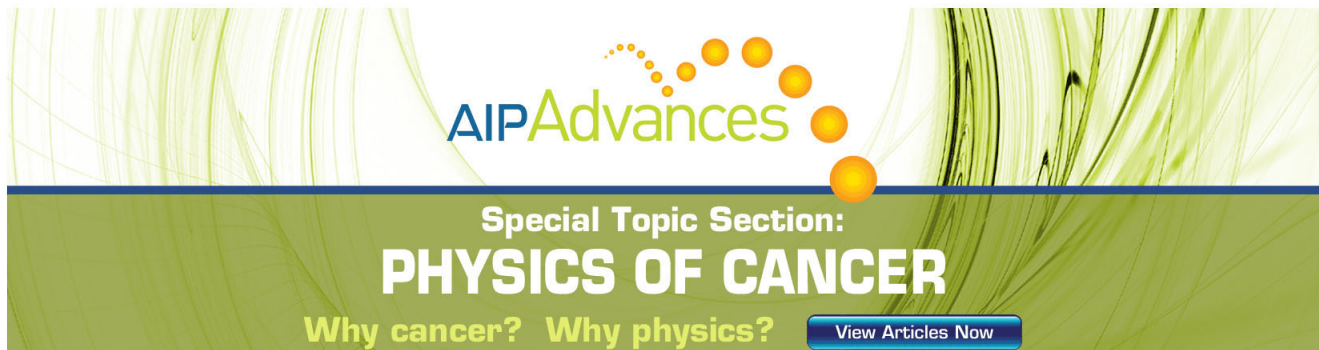
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An optical analysis tool for avoiding dust formation in very-high frequency hydrogen diluted silane plasmas at low substrate temperatures

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Control of the formation of dust particles in a silane deposition plasma is very important for avoiding electrical shunts in devices, such as thin film silicon solar cells. In this work we present a noninvasive *in situ* method for identification of the plasma regime, based on optical emission spectroscopy (OES), which can be applied to silane/hydrogen plasmas at low substrate temperatures. By monitoring the OES spectra as a function of the position perpendicular to the plasma electrodes we developed a method to identify the transition of a plasma from the dust free to a dusty regime, which was confirmed by TEM images of layers deposited in both regimes. Using this technique we mapped this transition as a function of applied forward very-high frequency (VHF) power and hydrogen dilution at different substrate temperatures. The advantage of this technique is that the experiment is insensitive to optical transmission loss at the viewport due to deposition of silicon films. As the transition from the dust free to the dusty regime is substrate temperature dependent and the transition from amorphous to nanocrystalline growth mainly depends on hydrogen dilution, a limited parameter window has been defined in which dust-free amorphous silicon can be deposited at low substrate temperatures. A single simple OES technique can be used for *in situ* monitoring of amorphous to nanocrystalline transition as well as the onset of the dusty regime in a thin film silicon cell fabrication process. © 2012 American Institute of Physics. [doi:10.1063/1.3683559]

A low cost approach for fabrication of flexible electronics or thin film solar cells is to deposit silicon layers directly onto plastics. This will reduce material and processing costs, due to the feasibility of roll-to-roll processing of flexible cheap substrates. Low cost plastics are sensitive to temperature and cannot withstand temperatures above 125 °C (PEN, PC) or only 100 °C (PET).¹ Therefore manufacturing processes need to be developed to deposit device quality layers at these low substrate temperatures. During plasma deposition, a major problem in low temperature depositions is the formation of dust particles. When these particles are incorporated in the silicon layers, they can introduce voids which will increase the disorder in the amorphous network and will thus introduce electronic defects. Because the particles can be large compared to the film thickness, the dust particles can also cause electrical shunts through the layers.² Recent research shows that controlled dust formation in the plasma can be beneficial for device performance when the layers are deposited at high rate.³

In a silane containing plasma, through polymerization reactions, negatively charged clusters may form. Due to the positive potential of the plasma bulk, these negative clusters are trapped within the plasma. When these clusters collide with (abundantly available) positively charged ions, they will become neutrals and will leave the plasma. When these neutral clusters collide with electrons before they leave the plasma, they will collect negative charge and will remain trapped. Because the electron-capture cross section depends strongly on the size of the clusters,⁴ only clusters that are large

enough (>2 nm) will be trapped inside the plasma bulk. Because the polymerization rate inversely depends on gas temperature,⁴ the formation of dust particles within the plasma will be more pronounced at low temperatures. When the gas temperature decreases because of the decrease in the substrate temperature, the critical cluster concentration is reached much quicker. When these clusters reach a critical size, the dust particles will coagulate and dust will start to form.^{5,6} After coagulation, dust particles can be larger than the thickness of the deposited layers and thus cause shunting in a thin film silicon solar cell. Therefore, especially at low substrate temperatures, it is important to monitor the dust formation in the plasma during the deposition process and to identify parameter windows for the deposition of dust free silicon. Laser light scattering experiments have shown to be a powerful tool to study the dust formation process.^{7,8} Recent investigations show nanoparticle characterization using white light.⁹ However, one of the drawbacks of these optical techniques is the deposition of silicon films on the viewports.⁷ A method that uses no optical detection is spectral analysis of the radio-frequency current to monitor to study dust formation.^{10,11} In this letter we present a non invasive *in situ* diagnostic tool for monitoring dust formation, based on optical emission spectroscopy (OES). By recording the optical emission lines for several species in the plasma as a function of the vertical position between the electrodes we construct the emission profile of the optical emission of the plasma. Using these profiles we are able to identify the plasma regime.

Whether dust is produced in a plasma depends on the condition under which the plasma is maintained. It has been

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shown before that increasing power density input, decreasing hydrogen dilution, increasing gas pressure or lowering the substrate temperature can change a dust free plasma into a dust producing plasma.^{12–14} Using this method we have investigated the influence of applied VHF power, hydrogen dilution and substrate temperature on the formation of dust in hydrogen diluted silane plasmas.

The plasmas under investigation are generated in our ultra-high vacuum deposition system ASTER,¹⁵ with reactors that have a background pressure of around 10^{-8} mbar. For all plasmas we used a process pressure of 1.1 mbar, an excitation frequency of 60 MHz, a total applied power P ranging from 5 to 20 W and a hydrogen to silane flow ratio R ranging from 20 to 60. The hydrogen flow was kept constant at 100 sccm and the hydrogen dilution was changed by adjusting the silane flow. The distance between the horizontal powered lower electrode and the upper grounded electrode was 27 mm. To measure the coupled power into the plasma, the system is fitted with an MKS VI-probe, which measures RMS voltage over the plasma, RMS current through the plasma and the phase difference between voltage and current. The OES measurements were made with an Avantes MC2000 spectrometer, through a quartz window to ensure transparency in the ultraviolet, through an assembly of two horizontal slits. The spectral range of the spectrometer is 200 nm to 900 nm. The system is mounted on a stage that can be moved in the vertical direction. Using this system we recorded horizontal slices of the optical emission from the plasma. The spatial resolution of this system is 1 mm. The position is measured from the upper grounded electrode downwards. Before recording the spectra, we waited for the emission to become stable. From the recorded spectra we derive the relative intensity of the lines associated with different plasma species, by subtracting a local background and fitting Gaussians to the peaks found in the spectra. In this way we obtained the relative signal intensity of Balmer-alpha (H_α), Balmer-beta (H_β), excited SiH (SiH^*), and excited Si (Si^*) as a function of vertical position. We used substrate temperatures T_s of 100, 150, and 200 °C, which were reached through resistive heating of the substrate holder. Heating of the substrate due to power dissipation from the plasma is measured to be less than 3 °C for a 20 W plasma at typical conditions. Because all powers used in our experiments are well below 20 W, the plasma heating does not have a significant contribution to the substrate temperature.

If we fix the plasma parameters; pressure, hydrogen dilution and substrate temperature, we can control the plasma regime by changing the applied power. If we start a plasma in the α -regime and increase the applied power, eventually dust particles will start to form and the plasma will transit to the so called γ' -regime. The dust particles will capture free electrons, causing a decrease in electron density. This causes a change in a number of physical properties of the plasma that can be monitored through a change in plasma impedance or a change in the optical emission of the plasma. Figure 1 shows a typical optical emission profile for various emission lines of a plasma in the α -regime. The plasma parameters were $P=13$ W, $R=45$, and $T_s=200$ °C. This axial emission distribution is very typical for particle-free plasmas: Maxima in emission in the plasma sheath near both electrodes and a minimum in the

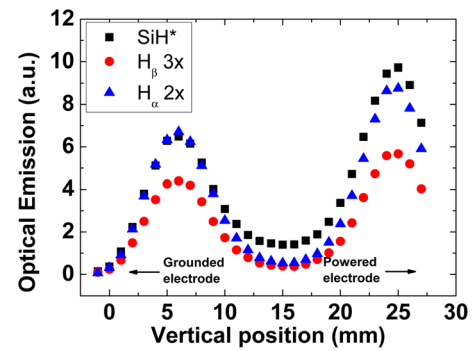


FIG. 1. (Color online) Vertical optical emission profile of a plasma in the α -regime. Shown are the SiH^* , H_α , and H_β lines. The position is measured from the upper grounded electrode downwards.

centre.^{16,17} The somewhat higher emission near the bottom powered electrode can be ascribed to the asymmetric design of our reactor where the powered (bottom) electrode has a smaller area than the grounded (upper electrode+chamber wall) electrode. Figure 2 shows the optical emission profile for a plasma using the same parameters but at an applied power of 16 W. This plasma is in the (dusty) γ' -regime, which is confirmed by a shift in the impedance towards a more resistive plasma.¹⁸ The profile changes from two rather symmetric peaks at the plasma sheaths and low bulk emission to a large peak in emission at the sheath near the lower powered electrode and a smaller peak at the upper grounded electrode, along with higher bulk emission. Pulled by gravity, the dust particles accumulate near the bottom electrode, where gravity is counteracted by the force that the negatively charged particles experience from the potential drop near the electrode. The increase in optical emission in this lower region of the plasma in the γ' -regime can be ascribed to the presence of dust particles. Because the dust particles act as electron traps, the electron density decreases and therefore the energy per electron increases, which in turn enhances the emission. The emission intensity is proportional to the rate constant of emission by the relation; $I_{\text{Si}} = K_{\text{SiH}_4} N_e N_{\text{SiH}_4}$, where N_e and N_{SiH_4} are the electron concentration and silane concentration, respectively, and K_{SiH_4} is the rate constant that depends on the electron temperature. The increase of electron temperature in the gamma regime, therefore, increases the optical emission, specifically at the powered electrode.

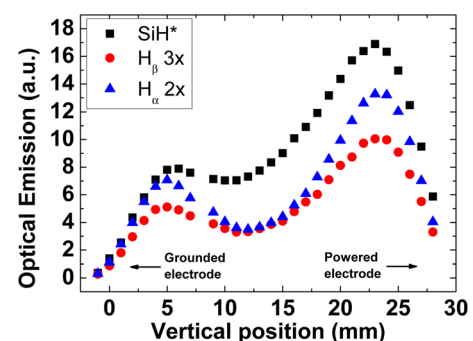


FIG. 2. (Color online) Vertical optical emission profile of a plasma in the γ' -regime. Shown are the SiH^* , H_α , and H_β lines. The position is measured from the upper grounded electrode downwards.

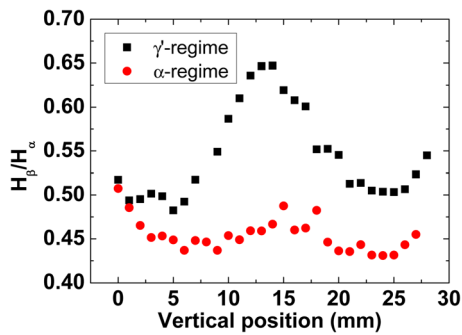


FIG. 3. (Color online) The intensity ratio H_{β}/H_{α} as an indication of electron temperature as a function of position between the electrodes in the α -regime (squares) and in the γ' -regime (circles). The position is measured from the upper grounded electrode downwards.

For large monodisperse injected particles in a non-reactive plasma, this effect is limited mainly to the region close to the bottom electrode.¹⁶ Because in our reactor the dust is grown rather than injected, we expect a variety in size and therefore a broader axial distribution of the dust. Some of the lighter dust particles will be located near or in the plasma bulk, thereby also enhancing the optical emission from the bulk of the plasma.

Because we can assume a Maxwell-Boltzmann distribution for the electron energy for a low-pressure plasma¹⁹ and because the electron temperature is well below the minimum electron energy to excite hydrogen for emission in the Balmer series, the H_{α} and H_{β} emission can be ascribed to excitation of hydrogen by electrons in the high energy tail of the electron energy distribution. Because of the differences in excitation energies (16.0 eV for H_{β} and 16.6 eV for H_{α} (Ref. 20)), the ratio of the intensities H_{β}/H_{α} can be used as a qualitative measure for the electron temperature.²¹ Figure 3 shows the spatially resolved H_{β}/H_{α} emission ratio for a plasma in the α -regime and for a plasma in the γ' -regime at the two above mentioned conditions. We observe an increase in electron temperature throughout the plasma reactor, which is most pronounced in the bulk of the plasma. This again reveals the presence of trapped dust particles in the plasma.

In both regimes we deposited amorphous silicon layers to investigate the presence of dust in the deposited layers. Figure 4 shows transmission electron microscopy (TEM) images of a layer deposited in the α -regime (a) and a layer deposited in the γ' -regime (b) and (c). In the layer deposited

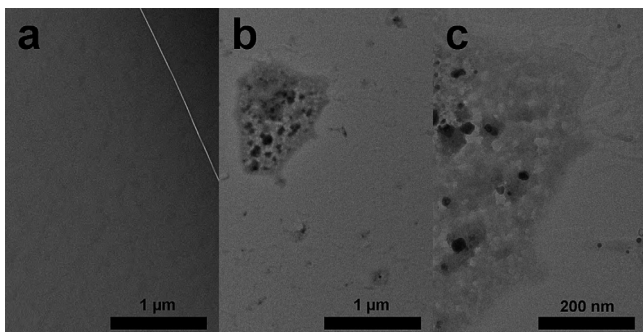


FIG. 4. TEM image of an a-Si layer deposited in the α -regime (a) and of an a-Si layer deposited in the γ' -regime (b), (c), as identified by analysis of the optical emission profile.

in the γ' -regime we observe particles with sizes ranging from several tens of nanometers up to micrometer sizes, whereas in the layers deposited in the α -regime we observe no particles in the layers. The transition from the α -regime to the γ' -regime was induced by a small increase in the forwarded power into the plasma, whereas all the other plasma parameters were kept constant.

Using this optical technique of estimating the asymmetry of the optical emission distribution, we mapped the transition from the α -regime to the γ' -regime as a function of hydrogen dilution, applied power and substrate temperature. The advantage of this technique is that the state of the plasma (dust free or dusty) is marked by the asymmetry of the OES intensity profile and not by the absolute intensity value. Therefore this technique is insensitive to the loss of transmittance of the viewport due to silicon film deposition. Figure 5 shows the results from these investigations. Apart from applied power and hydrogen dilution, we clearly see that the transition depends on substrate temperature. This implies that depositing at low substrate temperature limits the parameter space for dust-free deposition. The parameter window for dust-free amorphous silicon growth at a substrate temperature of 100 °C is indicated in gray in the figure. Similar windows can be identified for depositions at higher substrate temperatures. Also shown is the transition from amorphous to nanocrystalline growth, which mainly depends on hydrogen dilution. Together, the two transitions define a parameter window in which we can grow dust-free amorphous silicon, which is very limited at low substrate temperatures. The limitations on forward power will limit the maximum achievable deposition rate.

We have presented a noninvasive *in situ* technique to determine whether a deposition plasma is in the dust free α -regime or in the dusty γ' -regime by recording a spatially resolved optical emission profile perpendicular to the electrodes. In the γ' -regime we observe an increase in electron temperature in the bulk, which indirectly confirms the presence of dust particles. We mapped the transition from the α - to the γ' -regime as a function of hydrogen dilution, applied power, and substrate temperature. This method can generally be used to determine the processing window in which dust free silicon

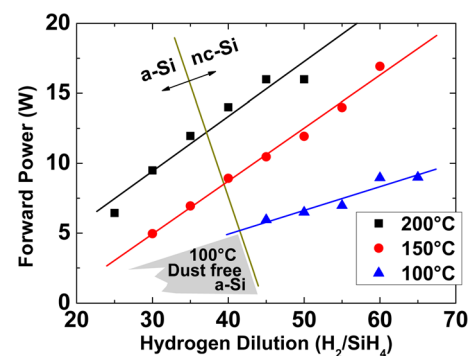


FIG. 5. (Color online) Map of the transition from the α -regime to the γ' -regime as a function of hydrogen dilution and forward power at substrate temperatures of 200 °C (squares), 150 °C (circles), and 100 °C (triangles). The amorphous to nanocrystalline transition also depends on forward power and hydrogen dilution. The parameter window for dust free amorphous silicon growth at 100 °C is shown in gray.

can be deposited. This study shows that a single technique can be used as an *in situ* plasma diagnosis tool for monitoring of the amorphous to nanocrystalline transition as well as the transition of the dust-free to the dusty regime without a supplement technique. We have presented a simple plasma monitoring tool for process control in “micromorph cell” manufacturing.

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