Excited states density measurements in a radio-frequency Ar-SiH$_4$ discharge using optical emission spectroscopy

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Abstract

Hydrogenated polymorphous silicon (pm-Si:H) thin films have been shown to be interesting for the production of new generation electronic devices. We study such films produced in a pulsed plasma enhanced chemical vapor deposition (PECVD). These films are deposited by using an argon-silane gas mixture in dust-forming plasma conditions. In this paper we will present results concerning time-resolved optical emission spectroscopy of the plasma. We have measured the absolute density of excited states for different species in the plasma and their evolution in time. Optical spectroscopy measurements allow a better understanding of the role of the excited species and their role during the chemical kinetics. This understanding is primordial not only for the films growth but also for the powder production in the bulk of the plasma. In this work, we particularly focused our interest on the excited states of H$_2$, H, Si, Ar and SiH.

1 Introduction

For a few years, plasmas produced by radio-frequency (RF) discharges are more and more studied for the production of hydrogenated polymorphous silicon (pm-Si:H) thin films deposition. These films present optoelectronic properties which particularly interest electronic device industry. For example, it has been shown that the use of such material for solar cells gives higher and stable photovoltaic conversion rate.

These films are produced using RF discharge in an Argon-Silane gas mixture. Nevertheless, it has been shown that the kinetics allowing film growth induces also the production of dust particles with a nanometer range size. These particles formation and their

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1369
behavior in plasma reactors have been widely studied[2]. The principal consequences of these powders that they grow and diffuse to the film where they are incorporated. It results a modification of film properties.

Many studies have been published using optical spectroscopy to characterize the chemistry and the kinetics in the plasma processes. They allow a better understanding to the role of excited species produced in the discharge. Furthermore, one can correlate the temporal excited states evolution with the powder formation. In this paper, we present results concerning emission spectroscopic observation of Si, H, Ar, SiH species. We have measured absolute densities of some excited states. Finally we used these results to determine the time evolution of electron temperature and density.

2 Experimental setup

A scheme of the experimental benchmark is presented on the figure 1. The reactor has been largely presented in previous work [1]. The plasma is produced in cylindrical box of 13 cm diameter enclosed in a vacuum chamber with a residual pressure of about $8 \times 10^{-6}$ torr. The gas mixture (96% of Ar) is injected to the reactor by mass flow controllers at a pressure of 0.1 torr. The gap between the two electrodes is 3.3 cm. They are placed at the top and the bottom of the cylindrical box. The RF power supply delivers a 13.56 MHz sinusoidal voltage and the RF power is varied up to 10 W. This corresponds to a power density of $1.5 \times 10^{-2}$ W.cm$^{-3}$ in the plasma. The RF signal is modulated by a square wave signal for which we adjust the duty cycle. The use of a pulsed plasma is chosen for a better chemical kinetic control. Indeed, the discharge is turned off just before the beginning of the coalescence of the formed primary crystallites.

Optical measurements were performed through a vertical slit of 2 mm width in the cylindrical box and a quartz window as interface between reactor and room. The plasma image was formed on the entrance slit of 0.8-meter double monochromator (Jobin Yvon) coupled to an intensified charged coupled device (ICCD) detector (Princeton model 576/RB-E). This configuration allows us to perform spectra acquisition with time-, space- and spectral resolution of 10 ms, 4 mm and 0.1 nm respectively.

Measurements have been performed at temperature of 300 K and 400 K. The delay $\tau_D$ between the start of the RF discharge and the measurement gate of the ICCD detector has been varied from 10 ms to 10 s in a logarithmic scale.

3 Results and discussion

Typical plasma emission spectra are shown on figure 2 for $\tau_D = 1$ s and $T = 400$ K for the spectral ranges from 481 to 489 nm and from 408 to 421 nm. Both spectra show several spectral lines of neutral argon atoms which dominate the plasma emission in the entire spectral range from near ultraviolet to the red independently of the experimental
conditions. The domination of Ar I spectral lines is a consequence of the fact that the argon carrier gas represents 96% of the mixture. In addition to Ar I line, we have also measured hydrogen (H₂) line, ionized argon (Ar II) line and molecular band of SiH (0,0).

On the figure 3-a, we have plotted the time evolution of the excited level corresponding to H₂ line for both temperatures. The two curves present the same aspect: first, the curves are relatively flat and then increase linearly. The gas temperature influence is materialized by a shift of the beginning of the increase. For room temperature, the increase start around τD = 200 ms and τD = 1.5 s at T = 400 K.

On figure 3-b) we have plotted the Si line corresponding to the wavelength 390.5 nm. The curves have the same appearance that H₂ one. Indeed we can observe the temperature shift but we can also observe a drop mainly visible on the curve corresponding to 300 K. This drop occurs at about τD = 1 s for T = 400 K.

The SiH molecular band (see figure 3-c) belongs to the A²Δ - X²Π system. For such a system, it has been noted that for a vibrational temperature much lower than 1000 K, only the (0,0) band can be observed. Beside the characteristic peak at 414.2 nm, two shapes corresponding to the R-branch between 410 and 412.8 nm and the Q-branch between 412.8 and 414.2 nm are identified on this figure 2-b. The overall shape of the SiH (0,0) band is characteristic for low rotational temperature.

To interpret the increase of different excited state densities, we have to consider the particle formation and their evolution. The flat zone of the curve correspond to the formation of nanometer size crystallites. Indeed, at this moment, the crystallite density reaches a critical value and they start to agglomerate to form larger size particles. As the particles grow they attach electrons. Rapidly, the particle charge increase inducing an electron density drop. At the same time, the electrical neutrality of the plasma (i.e.
equilibrium between negative and positive charge densities) is changing. Then the
electrical field in the plasma increase according to Maxwell-Gauss equation \((\nabla \times E = \rho/\varepsilon_0)\).
The electronic temperature changes from 2 eV to 8 eV (see section 4). As a consequence,
the excitation rates of excited states increase leading to higher excited state population
levels. The curve shift when gas mixture change to 400 K is due to delay concerning
nucleation process. As the gas kinetic temperature is higher the VT relaxation process
increase and then leading to slow the growth of the crystallites. Those optical results are
in good agreement with others methods used to study the plasma [3].
The drop observed on the Si lines (see figure 3-b) could be due to atoms incorporation
in the particles during the growth process.

4 Electron temperature and density

Spectroscopic measurements on atomic lines to determinate the temperature and the
density of the electrons can be used. Our model is based on equilibrium between excitation
processes by electronic impact and radiative deexcitation. We assume that the plasma is
weakly excited: thus atoms are essentially excited from the ground state. This can be
resume by the following formula:

\[
\frac{dn_u}{dt} = k_{0u} (T_e) n_0 n_u - \frac{n_u}{\tau_u}
\]

where \(n_u\), \(k_{0u}\), \(n_0\), \(n_u\), \(\tau_u\) are respectively the excited state population density, the
excitation rate from the ground level to the \(u\)-level, the ground state density, the electron
density and the lifetime of the level \(u\). We used experimental values for excited
rate densities. The excitation rate \(k\) are determined assuming that the Electronic Energy
Distribution Function (EEDF) is Maxwellian. The collisions cross-section are computed
Figure 3: H₂ (a), Si (b) lines and the head of SiH molecular band (c) evolution for both temperatures (25 and 100°C).
using the Born-Soth approximation. The results are shown on figure 4 for the room temperature ($T = 300$ K). These results agree rather well with other measurement methods like Langmuir probe [2] and microwave resonant cavity. We observe that the electron density decreases during the coalescence process ($\tau_D > 200$ ms). In the same time, electron temperature increases from 2 eV to 6 eV.

5 Conclusion

In this paper, we have presented basic results obtained by optical spectroscopy emission in a dust-forming Ar-SiH$_4$ plasma. These measurements allowed us to determine the temperature and the density of the electrons. In future work, we hope to extend our model to calculate the hydrogen concentration in fundamental state. This contributes to a better understanding in powder formation and pm-Si:H films growth (and also for its role in surface passivation).

References

