Spectroscopic investigations of a SiH₄ – NH₃ microwave plasma

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Abstract

Gas mixtures of silane (SiH₄) and ammonia (NH₃) are used for plasma enhanced chemical vapor deposition of silicon nitride films. These films were deposited in a low-pressure microwave plasma device, called PLASMODUL®. The plasma is excited by microwaves with a frequency of 2.45 GHz at a pressure between 0.1 and 10 mbar. By changing the gas mixtures and plasma parameters (e.g. pressure and microwave power) it is possible to vary the properties of the films over a wide range. To get informations about the involved processes, spectroscopic investigations of the plasma with a high resolution wide range spectrometer (Mechelle 7500) and an Echelle spectrometer with ultra high resolution were performed. For a control of the plasma parameters, the ratios of selected atom lines and molecular bands are applied.

1. Introduction

Silicon nitride films (SiN) are widely used in microelectronics, optoelectronics and optics and have important applications in photovoltaic systems [1]. For instance, for the production of highly effective silicon solar cells. Reflection losses and surface recombinations have to be minimized. Thin SiN films can improve both, the reflection behaviour by adjusting the refractive index of the antireflection coating and a surface passivation to avoid surface recombination processes [2].

Recently, much work has been done to deposit SiN films using plasma enhanced chemical vapor deposition processes. This technique produces films of good quality at relatively low deposition temperatures. However, it is still not known in detail how these plasmas interact with the substrates, and which chemical processes eventually lead to higher or lower quality deposited layers. For a better understanding of these processes measurements of e.g. the plasma composition and the particle fluxes to the substrates are highly desirable. In order to determine plasma parameters different diagnostic methods, such as electrical probe measurements, infrared absorption spectroscopy and emission spectroscopy of atom lines and molecular bands were applied to these plasmas.

The present paper deals mainly with spectroscopic diagnostics of a microwave heated plasma. The plasmas were generated in NH₃, N₂-NH₃ and N₂-SiH₄ gas mixtures in the pressure range from 0.1 to 2 mbar.
2. Experimental

Stationary plasmas were generated in various gases (N₂, NH₃ and SiH₄) in a low-pressure microwave plasma device, called PLASMODUL® [3]. Details of the experimental set-up are shown in Fig. 1. The PLASMODUL® is a modular device, mainly consisting of a plasma source, two gas inlet systems and a reaction chamber with a heatable substrate holder. The whole device has a diameter of 35 cm and a height of 40 cm.

The plasma is produced by 4 plasma lines. Each plasma line consists of a copper rod as inner conductor centered in a quartz tube. The inside of the tubes is cooled with air at atmospheric pressure and the outside is at low pressure. The microwave power is 2 x 600W supplied by two magnetron sources at the frequency of 2.45 GHz. The microwaves are fed from both sides into the copper rods via waveguide transmission lines. When the electric field strength exceeds the breakdown field strength the discharge ignites outside the tubes in the low pressure regime. If adjusting only a low microwave power (e.g. 50-100 W) the plasma is mainly concentrated at the ends of the tubes. With increasing microwave power the plasma grows from both ends of the tubes resulting in a linearly extended, homogeneous plasma.

Fig. 2 shows the plasma source in action driven with higher pressure so that the plasma is concentrated mainly around the tubes.

![Figure 2: Photograph of the plasma source in action.](image)
The device is continuously pumped by a turbo molecular pump and a forepump. The gases were supplied to the plasma chamber by means of two gas inlet systems. In the case of the N\textsubscript{2}-SiH\textsubscript{4} gas mixtures, the N\textsubscript{2} gas was fed via a calibrated mass flow controller (MFC) to the first gas inlet and the SiH\textsubscript{4} gas via a further MFC to the second gas inlet. The special arrangement allows a film deposition remote from the plasma source and prevents a contamination of the plasma source.

The plasmas were investigated spectroscopically observing through a quartz window at the top plate (see Fig. 1). Two spectrometer systems were used: A high resolution wide range spectrometer (Mechelle 7500) and an Echelle spectrometer with ultrahigh resolution. In the case of the Mechelle 7500 the spectra were taken simultaneously over the spectrum range from 200 nm to 1050 nm. The spectral resolution of $\lambda/\Delta\lambda=7500$ over the whole spectrum range is sufficient to distinguish even the rotational structure of molecular bands. To determine the Doppler width of the H\textsubscript{\alpha} line and to calculate the H gas temperature the high resolution ($\Delta\lambda=2$ pm at 650 nm) Echelle spectrometer was used.

3. Results and Discussion

3.1 Wide range spectra with the Mechelle 7500

For wide range overview spectra the Mechelle 7500, a newly developed high resolution spectrometer was used. Fig. 3 shows a spectrum of a pure ammonia plasma in the spectral range between 200 nm and 1050 nm.

![NH\textsubscript{3}-Plasma](image)

**Figure 3:** Wide range spectrum of a pure NH\textsubscript{3} plasma.

The spectrum is dominated by the H\textsubscript{\alpha} and H\textsubscript{\beta} lines at 656.28 nm and 486.13 nm, respectively. The atomic lines of nitrogen and the molecular bands of N\textsubscript{2}, N\textsubscript{2}\textsuperscript{*} and NH are also visible, however, with a much lower intensity. Fig. 4 shows a spectrum obtained from a plasma with a mixture of 50 % SiH\textsubscript{4} and 50 % N\textsubscript{2}. Concerning the SiH\textsubscript{4} molecule [4], the species which could be measured with the spectroscopic set-up are the silane dissociation products SiH, Si, H and H\textsubscript{2}. The emission of molecular hydrogen is represented by the
Fulcher band in the spectral range of 590nm to 615nm. In the UV region the emission lines of atomic Si (251nm – 253nm) and 288nm can be observed.

**Figure 4:** Wide range spectrum of a N$_2$-SiH$_4$ plasma.

Radiation from e.g. SiH$_3$ molecules, Si$^+$ ions and Si$_2$ molecules could not be detected. From this, we conclude that the number densities of these species were too small in the plasma. The relative intensities of several atomic lines and molecular bands were investigated in order to get informations about the influence of parameters like gas mixture ratio, pressure and input microwave power on relative densities of these species. Fig. 5 shows the changes of some species by varying the silane rate in a nitrogen plasma. An increase of the SiH$_4$ concentration in the plasma leads to an increase of the Si atom intensity and to a corresponding decrease of the N intensity.

**Figure 5:** Normalized intensities of various plasma species in dependence on the SiH$_4$ rate.
On the other hand the intensity of atomic hydrogen first shows a strong increase when adding only 10% of SiH₄ to the N₂ gas, then it reaches a maximum and as soon as the SiH₄ rate exceeds 35% the H intensity decreases. The decrease of H may be due to H-H reactions to H₂ or to molecule-molecule and molecule-ion reactions, like for example SiH₂ + H → SiH₃. Another possibility is the decrease of the hydrogen gas temperature (discussed in the following chapter) which may lead to a corresponding decrease of the H concentration.

The influence of the pressure in a N₂-NH₃ plasma on the relative densities of the species is shown in Fig. 6.

![Figure 6: Normalized intensities of various plasma species in dependence on the pressure.](image)

The intensity of N₂ increases while the intensity of N₂⁺ decreases. This can be explained by a decreasing mean free path with increasing pressure and therefore a decreasing kinetic energy of the colliding particles. Hence the ionisation degree of the N₂ molecules also decreases.

3.2. Gas temperatures of atomic hydrogen

The H gas temperature was determined from the Doppler width of the H₆ line using the high resolution Echelle spectrometer.

![Figure 7: Example for a measured H₆ line.](image)
In addition to the 3d-2p transition at 656.281 nm there is further emission from the 3p-2s transition at 656.274 nm. The two transitions are emitting with an intensity ratio of approx. 7:4. Fig. 7 shows an example of a measured Hα line together with the calculated lines for the 2 relevant transitions and the resulting fit curve.

The gas temperature of atomic hydrogen was measured for a variation of the silane ratio in a nitrogen plasma at a constant microwave power of 2x360 W and a pressure of 0.1 mbar. The results are shown in Fig. 8.

![Figure 8: H gas temperature in dependence on the SiH₄-N₂ mixture ratio.](image)

The temperature decreases from 800 K at a SiH₄ rate of 5% to 650 K at a SiH₄ rate of 40%. The reason for this behaviour is the increasing amount of energy that is needed for the dissociation of the silane molecules.

3. Conclusions

The main results can be summarized as follows:
- The spectrum of a NH₄ plasma is clearly dominated by the Hα and the Hβ lines.
- In a N₂-SiH₄ plasma a considerable amount of H₂ can be detected.
- By varying the silane rate within a N₂ plasma the ratio of H and H₂ can be varied.
- With increasing pressure in a N₂-NH₄ plasma discharge the equilibrium between N₂ and NH₄ moves towards N₂.
- Adding silane to a N₂ plasma cools the H gas.

References