A NOVEL COMMERCIAL PLASMA SOURCE FOR ULTRA HIGH-RATE DEPOSITION OF SILICON NITRIDE FOR c-Si SOLAR CELLS

P.J. van den Oever[1], W.M.M. Kessels[1], B. Hoex[1,2], R.C.M. Bosch[2],
A.J.M. Van Erven[2], M.D. Bijker[2], and M.C.M. van de Sanden[1]
[1]Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven,
The Netherlands, email: w.m.m.kessels@tue.nl
[2]OTB Solar B.V., P.O. Box 7108, 5605 JC, Eindhoven, The Netherlands

ABSTRACT:
Recently, a new inline tool for high rate deposition of silicon nitride for (multi) crystalline silicon solar cells, the "DEPx", was introduced. This tool uses the so called expanding thermal plasma (ETP) technique operated on an Ar-NH_3 gas mixture to dissociate SiH_4. We will discuss some of the important properties of this remote and high density plasma in terms of ion densities, radical densities (N, NH, NH_2) and the NH_3 consumption degree.

Keywords: PECVD, Silicon-Nitride, Antireflection Coating

1 INTRODUCTION

Nowadays, silicon nitride deposition processes are present in almost every state-of-the-art production line of (multi-) crystalline silicon solar cells. The silicon nitride films serve as multifunctional antireflection coatings as they reduce optical losses and provide surface and bulk passivation (in multicrystalline or ribbon silicon). In most cases, the silicon nitride is deposited using a PECVD type of process using radiofrequency parallel plate reactors or microwave plasmas. These plasma techniques, characterized by a deposition rate < 1 nm/s, generally results in relatively long reactor chambers to maintain the required throughput.

Recently however, a more efficient plasma source which can deliver very large fluxes of reactive species (radicals, ions, etc.) was introduced in a commercial inline deposition tool by OTB Solar [1,2]. The implementation of three expanding thermal plasma (ETP) sources [3,4,5] in the "DEPx" inline PECVD deposition tool has resulted in silicon nitride deposition rates up to 20 nm/s, while the nominal deposition rates range from 4 to 7 nm/s [1,2]. The nominal throughput of the "DEPx" is 960 cells/hour (15.7×15.7 cm^2), while the footprint of the production equipment is only 12 m^2.

In this contribution we describe the basic properties of the ETP plasma operated on an Ar-NH_3 gas mixture, which is used to dissociate the SiH_4 in the downstream deposition reactor. Section 2 briefly descibes the basics of the ETP technique and the plasma diagnostics that were used in this study. Section 3 discusses the role of different ion species in the plasma, while Sec. 4 shows the typical radical densities in the plasma. In Sec. 5 we discuss the NH_3 consumption degree and finally, we end with conclusions in Sec. 6.

2 THE EXPANDING THERMAL PLASMA

2.1 The ETP technique: The basics

The ETP technique combines a high-pressure plasma source with a low-pressure processing (deposition) reactor. The plasma source (see Fig. 1) is a cascaded arc in which a dc voltage is applied between one or more cathodes and a grounded anode. A discharge is created in a non-depositing carrier gas (often Ar, but also N_2 and H_2 can be used) flowing through a narrow channel. The current flowing through the plasma channel is typically set between 30 and 70 A and the voltage is approximately 40 V. Due to the narrow channel, the high gas flows and the plasma itself, the pressure in the plasma source is sub-atmospheric (typically 300 mbar). The plasma expands through a nozzle into the low-pressure reactor and the electron temperature is reduced to ~0.1-0.3 eV in the downstream region due to the expansion behavior. Therefore electron-induced dissociation and ionization reactions can be neglected in the downstream region in contrast to conventional plasma techniques. The downstream ion density on the other hand is relatively high (10^{13} cm^{-3} for pure Ar down to 10^{10} cm^{-3} for molecular plasmas) compared to other plasma techniques, which can be attributed to the fact that plasma creation takes place at high pressure with consequently a much higher ionization degree (typically 10% in the source) than in low-pressure plasmas.

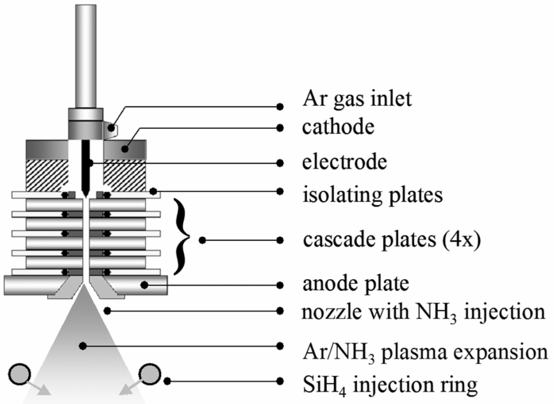

Figure 1: Schematic of the novel commercial Expanding Thermal Plasma (ETP) source used for silicon nitride deposition at ultrahigh rates.

For the deposition of silicon nitride antireflection coatings, the plasma source is operated on pure Ar with NH_3 injected into the nozzle, while SiH_4 gas is injected further downstream through the injection ring [6]. The reactive species generated from the Ar-NH_3 mixture lead to the dissociation of SiH_4 creating new species that can contribute to the silicon nitride growth. A more detailed description of the source and its operating principle can be found elsewhere [7].

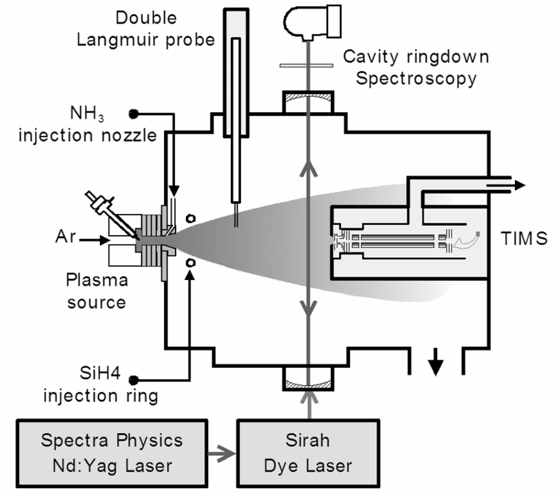

Figure 2: Schematic representation of the expanding thermal plasma lab reactor with the different plasma diagnostics that are used to study the Ar-NH_3 plasma.

2.2 Plasma diagnostics

Figure 2 gives an schematic overview of the experimental setup used to characterize the Ar-NH_3 plasma emanating from the source. The ion and electron density in the plasma was measured using the double Langmuir probe technique [8] at 36 cm from the plasma source for different arc currents and for different Ar-NH_3 mixtures. Furthermore, we used cavity ringdown absorption spectroscopy at 36 cm from the source [9] to measure the densities of the NH and NH_2 radicals in the plasma. The N radical density was measured using threshold ionization mass spectrometry [10] at a distance of 56 cm from the source. Furthermore, the ion composition and the dissociation degree of the injected NH_3 were also measured by mass spectrometry.

3 IONS IN THE Ar-NH_3 PLASMA

Operated on pure argon, the ETP plasma source produces primarily ions as reactive species. Figure 3 shows the ion density in the downstream region for 4 different arc currents. The ion density in the plasma is in the order of 10^{13} cm^{-3} and increases linearly when the arc current increases from 30 A to 70 A. For a pure Ar plasma, the ion density remains high due to the fact that

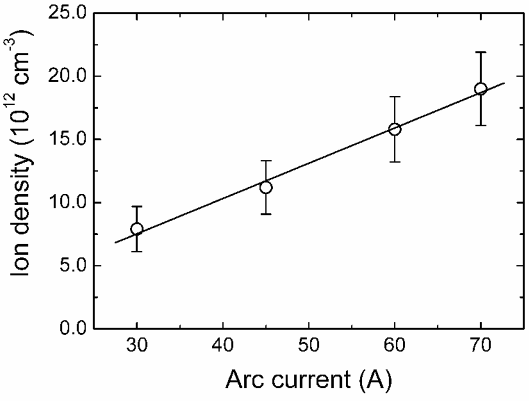

Figure 3: The ion density in a pure Ar plasma versus the arc current measured at 36 cm from the plasma source.

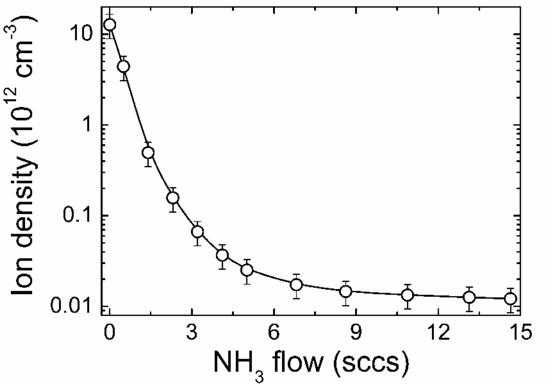

Figure 4: The ion density at 36 cm from the plasma source versus the NH_3 flow for an arc current of 70 A.

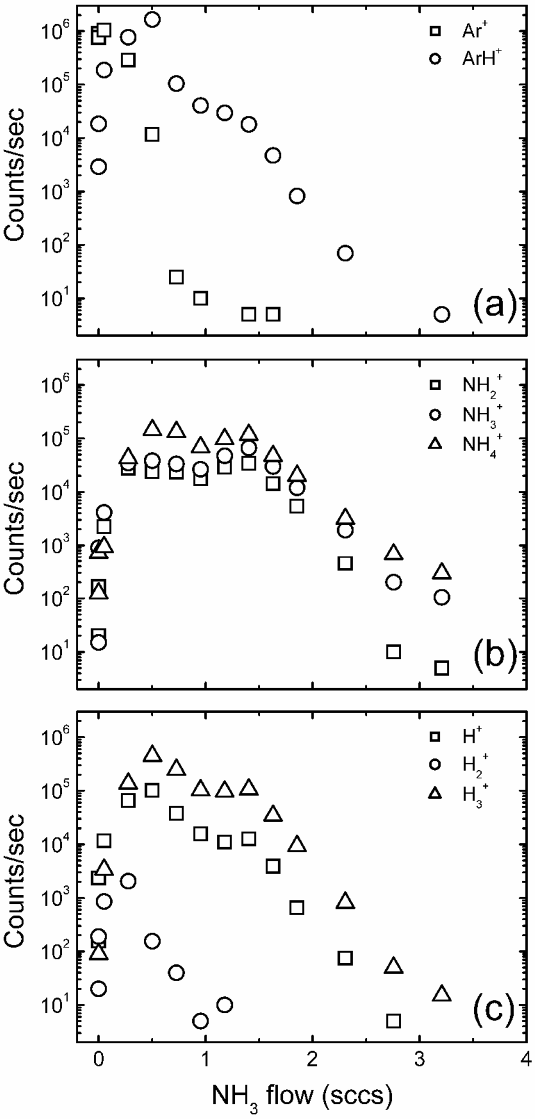

Figure 5: The ions in the plasma versus the injected NH_3 flow as measured by ion mass spectrometry: (a) Ar^+ & ArH^+, (b) NH_4^+, NH_3^+ & NH_2^+, (c) H_3^+, H_2^+ & H^+. The arc current was 70 A.

recombination of Ar ions can only take place by three particle recombination:

$$Ar^+ + 2e \rightarrow Ar + e,$$

a reaction, that is very slow under the present conditions. However, when molecular gases such as NH_3 are injected in the plasma a new loss mechanism for the Ar ions is accessible [10]. Figure 4 shows the ion density in the plasma versus the injected NH_3 flow for an arc current of 70 A. The ion density decreases very fast from ~ 10^{13} cm^{-3} to ~ 10^{10} cm^{-3} when NH_3 is injected in the plasma. The strong decrease of the ion density can be explained by a mechanism that starts with a charge transfer reaction of the Ar^+ ion with NH_3 [9]:

$$Ar^+ + NH_3 \rightarrow Ar + NH_3^+.$$

Subsequently, the molecular ion that is created recombines dissociatively with an electron, reducing the ion density drastically:

$$NH_3^+ + e \rightarrow NH_x \text{ products} + H.$$

Due to the dissociative nature, this process is much faster than the recombination of an Ar^+ ion with an electron. Therefore the ion density decreases very fast when NH_3 molecules are injected into the Ar plasma. As a consequence a relative high radical density is created (see below).

To obtain insight into the dominant ions that are created in the Ar expanding plasma upon injection of NH_3, we have employed line-of-sight mass spectrometry. Figure 5 shows the signal for the Ar^+ and ArH^+ (a), NH_4^+, NH_3^+ and NH_2^+ (b), H_3^+, H_2^+ and H^+ (c) ions versus the injected NH_3 flow in the plasma. In the flow regime from 0 to 0.75 sccs the charge is transferred from the Ar^+ ions to the other ions, as can be seen by the decrease of the Ar^+ signal [Fig. 4 (a)] while the signals of all other ions increase [Fig. 4 (a-c)]. For flows greater than 0.75 sccs NH_3, the ion density decreases due to dissociative recombination and the plasma is dominated by the ArH^+, NH_4^+, NH_3^+, NH_2^+, H_3^+ and H^+ ions. At an injected NH_3 flow of 3 sccs, almost no ions are detected anymore, except for the NH_4^+ ion and to a lesser extend the NH_3^+ ion. This observation corresponds to earlier observations that the NH_4^+ ion is a relatively stable ion [11].

To summarize, when NH_3 gas is injected in the plasma, the charge is transferred from the Ar^+ ion to various molecular ions. These ions are subsequently lost from the plasma by dissociatively recombination causing the total ion density to decrease very fast.

4 RADICALS IN THE Ar-NH_3 PLASMA

Radical species such as N, H, NH and NH_2 are created in dissociative recombination processes of molecular ions, such as ArH^+, NH_4^+, NH_3^+, NH_2^+, and H_3^+. Figure 6 shows the density of N, NH and NH_2 radicals versus the NH_3 flow injected in the plasma. The density of N radical is in the order of 10^{11} cm^{-3}, while the densities of the NH and NH_2 radicals are in the order of 10^{12} cm^{-3}. No information on NH_x radical densities is available for other NH_3 and NH_3-SiH_4 processing plasmas, however, it is expected that these radical densities are relatively high, considering also the high deposition rate obtained by the ETP technique. Furthermore, the trend as a function of the NH_3 flow is different for the N and NH radical on one side, and the NH_2 radical on the other side. This suggests a different production mechanism for N and NH radicals compared to NH_2 radicals [9].

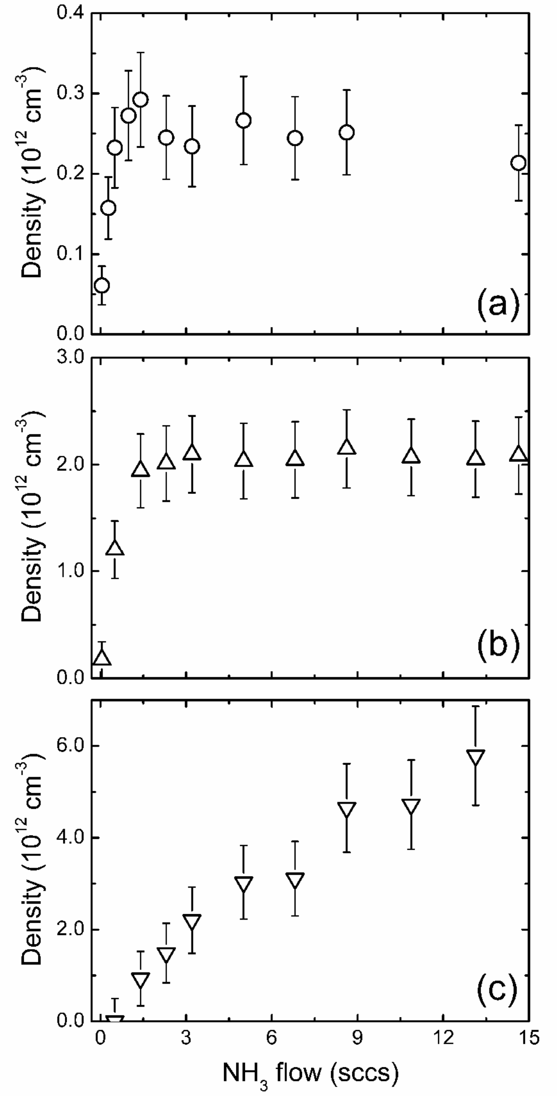

Figure 6: The density of the N (a), NH (b) and NH_2 (c) radicals in the ETP plasma as a function of the NH_3 flow. The arc current was 45 A.

5 NH_3 CONSUMPTION IN THE Ar-NH_3 PLASMA

In the previous sections, the characteristics of the Ar-NH_3 plasma have been described in terms of ions and radicals densities. But also the consumption degree of NH_3 is of importance while it can also give valuable information into the dissociation mechanism of NH_3. Figure 7 shows the consumption of NH_3 in a Ar-NH_3 plasma. The consumption of NH_3 decreases from ~ 75% for small NH_3 flows to ~ 20 % for a NH_3 flow of ~15

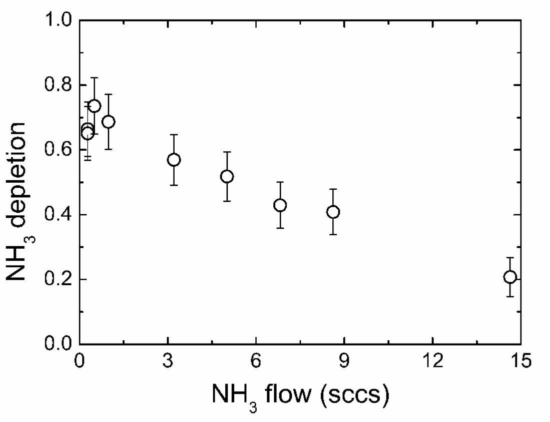

Figure 6: The consumption of NH_3 in an Ar-NH_3 plasma for an arc current of 45 A.

sccs. The decrease in the consumption of NH_3 indicates that the amount of reactive species (Ar^+ ions) from the plasma source is not sufficient to dissociate all the injected NH_3. This is supported by the linear relation between arc current and NH_3 consumption measured when NH_3 is abundantly present in the plasma [9].

When the plasma source operated on an Ar-NH_3 mixture is used for silicon nitride deposition, 60 % to 90 % of the injected SiH_4 is consumed, depending mainly on the SiH_4 flow and the arc current.

6 CONCLUSIONS

In this contribution we describe the basic properties of the Ar-NH_3 ETP plasma that has recently been implemented in a commercial inline PECVD tool ("DEPx") for silicon nitride deposition. The ETP plasma has been characterized in detail in terms of ion and radical species emanating from the source. The ion densities found range from 10^{10} to 10^{13} cm^{-3} depending on the arc current and gas mixture used. The typical density of the radicals in the plasma is very high (mostly > 10^{12} cm^{-3}), which makes the plasma well suited for high rate deposition processes where high flows of precursor gases (e.g., SiH_4) need to be dissociated. Furthermore, it was concluded that the NH_3 consumption in the plasma is mainly determined by the amount of reactive plasma species (ions) from the ETP source and consequently by the arc current.

ACKNOWLEDGMENTS

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