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Deposition of device quality silicon nitride with ultra high deposition rate (>7 nm/s) using hot-wire CVD

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Abstract

The application of hot-wire (HW) CVD deposited silicon nitride (SiN_x) as passivating anti-reflection coating on multicrystalline silicon (mc-Si) solar cells is investigated. The highest efficiency reached is 15.7% for SiN_x layers with an N/Si ratio of 1.20 and a high mass density of 2.9 g/cm^3. These cell efficiencies are comparable to the reference cells with optimized plasma enhanced (PE) CVD SiN_x even though a very high deposition rate of 3 nm/s is used. Layer characterization showed that the N/Si ratio in the layers determines the structure of the deposited films. And since the volume concentration of Si-atoms in the deposited films is found to be independent of the N/Si ratio the structure of the films is determined by the quantity of incorporated nitrogen. It is found that the process pressure greatly enhances the efficiency of the ammonia decomposition, presumably caused by the higher partial pressure of atomic hydrogen. With this knowledge we increased the deposition rate to a very high 7 nm/s for device quality SiN_x films, much faster than commercial deposition techniques offer [S. von Aichberger, Photon Int. 3 (2004) 40].

Keywords: Silicon nitride; Hot-wire CVD; Multicrystalline solar cells; High deposition rate

1. Introduction

Hydrogenated silicon nitride (SiN_x) is an intensively studied material with many applications. For most of these applications Plasma Enhanced (PE) chemical vapor deposition (CVD) is used in commercial device manufacturing. However, in recent years a more gentle deposition technique, hot-wire (HW) CVD, has attracted much interest. With this deposition technique the source gasses are catalytically decomposed at heated wires to radical species only. This deposition takes place with very high efficiency without any plasma, which gives HWCVD the benefit that substrate damage by ion bombardment is prevented.

For this research, HW deposited SiN_x is studied as top layer on multicrystalline silicon (mc-Si) solar cells where it simultaneously acts as antireflection coating (ARC) and induces bulk and surface passivation. The thin SiN_x films are able to act as good ARC because of their high and tunable refractive index in combination with a low extinction coefficient. However, the passivating properties of the SiN_x are at least as important. During a short anneal, atomic hydrogen is released from the SiN_x layer and diffuses partially to the mc-Si wafer. This hydrogen causes passivation of defects enabling an important enhancement in cell performance.

Next to good performance as passivating ARC, for commercial SiN_x application the deposition rate is also important. From a cost-perspective point of view, an easy way to reduce the production costs of module manufacturing is by decreasing the throughput time. The simplest way to achieve this is by an increase of the deposition rate. We will show that high quality SiN_x films can be deposited at a very high deposition rate of 7 nm/s, using HWCVD.

2. Experimental details

Various SiN_x films were deposited on highly resistive monocrystalline Si wafers and 1737 Corning glass. We made use of a four-filament hot wire reactor, which is part of an ultra high vacuum multi-chamber system (PASTA) [2]. Pure silane (SiH_4) and ammonia (NH_3) were used as source gasses, which are

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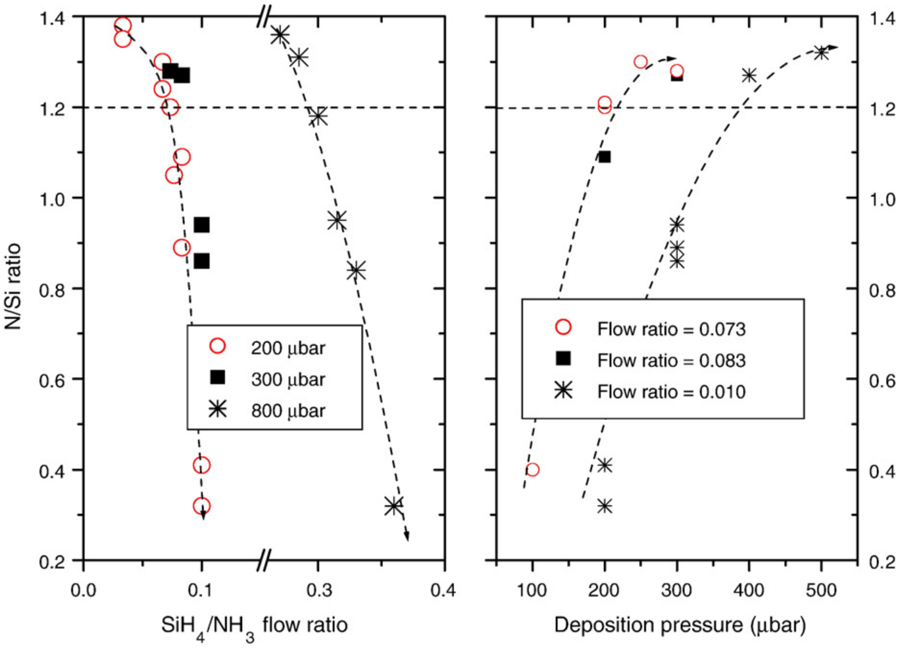

Fig. 1. The effect of silane flow and deposition pressure on the composition of the layers. Higher silane flows lead to more Si-rich layers whereby a higher deposition pressure results in higher N-incorporation. The lines are a guide to the eye.

decomposed on heated tantalum filaments (~2300 °C). No hydrogen dilution is used. The substrate was heated by radiation from the filaments only and reached a temperature of about 450 °C. A shutter is located between the sample and the wires to control the growth and to let the substrates thermally equilibrate before the start of the deposition.

The effects of process pressure and gas-flow ratio on the composition of the deposited SiN_x layers are studied. In all cases the ammonia flow was kept constant and the silane flow was altered to obtain different flow ratios. The structure of the samples is investigated with elastic recoil detection (ERD) [3] and Fourier transform infrared spectroscopy (FTIR) whereby corrections for coherent and incoherent reflections are used [4]. The layer-thicknesses are determined by reflection/transmission measurements [5,6]. To evaluate the passivating properties of the SiN_x coatings, HW SiN_x was deposited on mc-Si texture-etched wafer as supplied by ECN Solar Energy [7]. After completion of the depositions the wafers were transported back to ECN Solar Energy for front- and backside metallization. For comparison and reference, solar cells with optimized microwave (MW) PECVD SiN_x ARC were made using neighboring wafers.

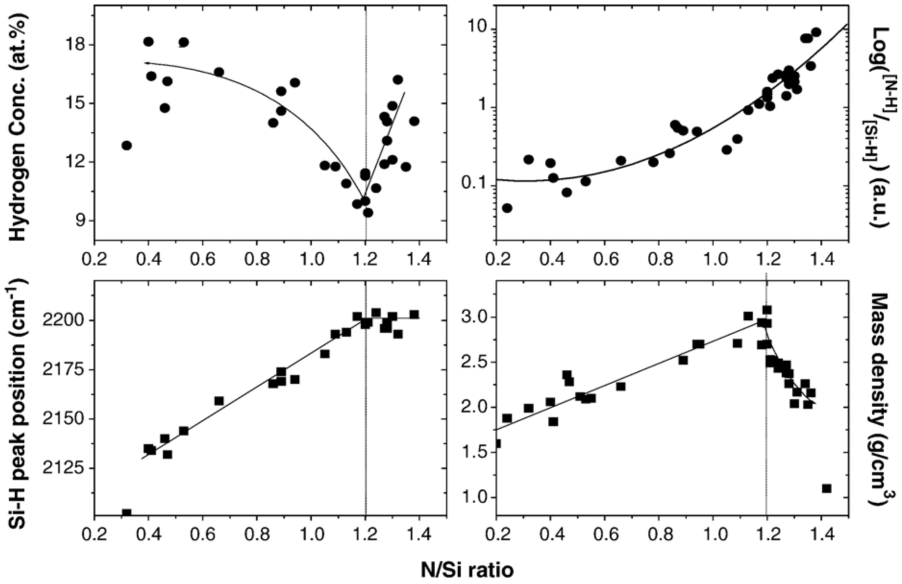

Fig. 2. Structural properties of SiN_x layers deposited with process parameters. Clear trends can be observed as a function of the N/Si ratio in the layers. The lines are a guide to the eye.

3. Hot-wire CVD deposition process

The effect of silane flow on the composition of the deposited films can be observed in Fig. 1. As expected, with increasing silane flow smaller N/Si ratios are obtained since more SiH_4 molecules are exposed to the wires. Secondly, when depositing with a constant flow ratio using different deposition pressures, higher pressures produce higher N/Si ratios in the films. This means that apart from the flow ratio also the deposition pressure has a strong influence on the composition of the layer.

Although the effect of an increase in the SiH_4 flow can be explained relatively simply, the effect of deposition pressure is more complex. The influence of atomic hydrogen on the deposition process has been intensively investigated by the addition of H_2 as a source gas [8–10]. All these studies have shown that atomic hydrogen increases the ammonia decomposition and enhances the nitrogen incorporation. Since an increase of the deposition pressure results in an increase in the partial pressure of atomic hydrogen, originating from the SiH_4 and NH_3 decomposition. This higher partial pressure of atomic hydrogen causes higher nitrogen concentration in the deposited layers.

This means that an increase of the SiH_4 flow results in more Si-rich samples and that a raise in deposition pressure results in more efficient N incorporation. As a result, SiN_x films deposited with totally different combinations of gas flow ratio and pressure can result in equal N/Si ratios. To see if the structural properties depend on the deposition parameters, Fig. 2 shows structural properties of samples deposited with *different combinations* of deposition parameters (pressure and flow ratio) versus the composition of the films.

A good indication for the internal structure of the films is the FTIR Si–H peak position, which is dependent on the back bonding of the hydrogenated Si-atom [11]. The shift of the FTIR Si–H peak position is proportional to the layer composition up to 2200 cm^{-1}. It is interesting that the back bonding of the films does *not* change for films with an N/Si ratio higher than 1.20. Just like the Si–H peak position, also the mass density of the deposited films shows a linear increase for films with N/Si up to 1.20. For samples with higher N/Si ratios a sharp decrease in mass density is observed. Both trends are (indirectly) also reported for conventional PE CVD silicon nitride, though with that significant difference that with PE CVD the maximum in mass density is reached at an N/Si ratio of 1.0 [12]. Thus using HW CVD SiN_x, films can be obtained that are closer to stoichiometry with high mass density. The decrease in mass density for samples with an N/Si higher than 1.20 is caused by the formation of voids in the films, which are observed in TEM pictures [9]. The hydrogen concentration shows an inverse trend with respect to mass density with a minimum of hydrogen for those films with the maximum in mass density. Because all structural parameters shown in Fig. 2 reveal clear trends as a function of N/Si ratio, we conclude that the structure of the deposited films depends only on the N/Si ratio of the samples, and are independent of the deposition parameters (pressure and flow ratio) used to reach that N/Si ratio.

Table 1
Solar cell parameters for HWCVD SiN_x ARC applied on mc-Si cells

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Efficiency (%)
HW CVD best	604	34.6	0.750	15.7
MW RPE CVD best	606	34.3	0.774	16.1

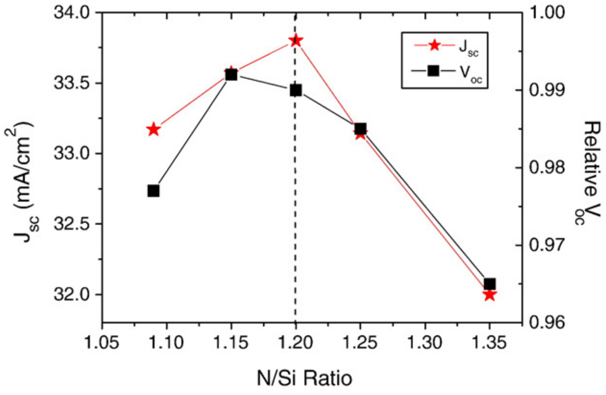

Fig. 3. The V_{oc} and J_{sc} averages for mc-Si solar cells with HW SiN_x for different N/Si ratios. At an N/Si ratio of 1.2 the generated power in the solar cell is optimal.

4. HWCVD SiN_x on mc-Si solar cells

To investigate the passivating properties of the deposited layers, series of mc-Si solar cells from ECN Solar Energy were made containing HW deposited SiN_x ARC. Each series of solar cells contained a different composition of HW SiN_x. The best solar cell (6.5 × 6.5 cm^2) reached a high efficiency of 15.7%, close to the 16.1% reached by the reference cells containing optimized MW PECVD SiN_x. The J_{sc} and the V_{oc} values of solar cells with HW deposited SiN_x were similar to those of the reference cells, as can be observed in Table 1. The main difference in cell efficiencies was caused by a lower fill factor, caused by unoptimized cell processing such as firing conditions. By analyzing the effect of structure on the cell performance, a clear trend can be observed whereby the maximum in V_{oc} is

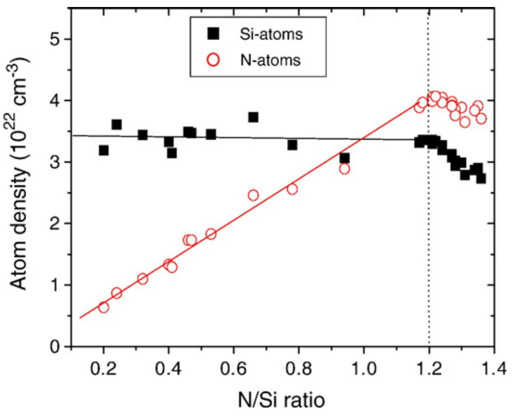

Fig. 4. The atomic volume concentration of Si and N for a wide range of N/Si ratios. The Si density appeared to be constant for all compositions. The lines are a guide to the eye.

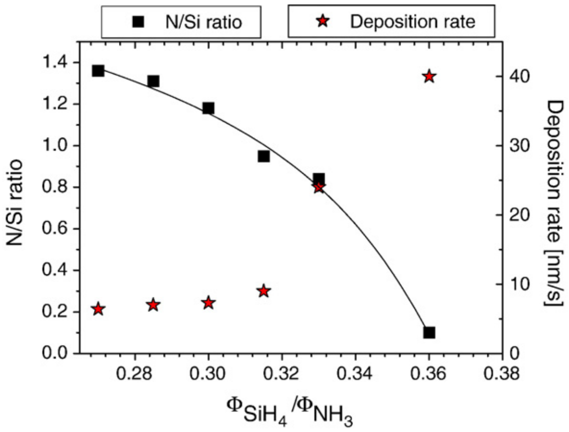

Fig. 5. The effect of flow ratio on the composition of the layers at high pressure. It also shows that high quality films with an N/Si ratio of 1.20 can be obtained at a very high 7 nm/s.

reached for N/Si values between 1.15 and 1.2. From Fig. 3, it can also be deduced that the average J_{sc} value also discloses a clear trend, whereby the optimal result was obtained at N/Si = 1.20. Therefore, the $V_{oc} * J_{sc}$ product (a good indicator of the SiN_x layer quality) is optimal for the layers with an N/Si ratio of 1.20 [13].

5. High deposition rate

ERD analysis (Fig. 4) shows that the Si volume concentration in the deposited layers is roughly constant, and thus the N/Si ratio of the films is a consequence of the amount of nitrogen incorporated in the film. Consequently, the deposition rate is mainly determined by the rate at which the Si depositions occur, whereby higher silane flows lead to an increase in silane decomposition and higher deposition rates. However, by only increasing the silane flow the films become too Si-rich and therefore unsuitable for device application. To avoid this, it is necessary to increase the ammonia decomposition at the same time. This can be realized by simultaneously increasing the deposition pressure which leads to a higher nitrogen incorporation.

Fig. 5 shows that various N/Si ratios can be obtained at 800 μbar using different flow ratios. It also shows that high-density transparent films with the optimal N/Si ratio of 1.20 can be obtained at very high deposition rates of 7 nm/s. These films have no absorption and a refractive index of $n_{632\ \mathrm{nm}} = 1.95$. This deposition rate of 7 nm/s is 2–70 times higher than commercial deposition techniques at present can offer for device quality SiN_x [1]. One additional benefit is the enhancement of gas utilization. To increase the deposition rate from 3 to 7 nm/s, the total gas flow was increased by only 20%. This means that the total gas utilization has been doubled.

6. Conclusions

In hot wire CVD deposition process of SiN_x, the gas flow ratio and the deposition pressure have a large influence on the N/Si ratio of the deposited films. High silane flows increase the rate of Si deposition, while with a higher deposition pressure the ammonia decomposition is greatly enhanced. Since the N/Si ratio of the films determines the structure and the volume concentration of Si-atoms is roughly constant for all compositions, the layer properties are determined by the nitrogen incorporation. By combining a high SiH_4 flow with high deposition pressures we have been able to increase the deposition rate of device-quality SiN_x to 7 nm/s. mc-Si Solar cells with HW SiN_x as ARC, deposited at a high deposition rate of 3 nm/s reach very good efficiencies of 15.7%, comparable to reference cells with optimized PECVD SiN_x.

References

[1] S. von Aichberger, Photon Int. 3 (2004) 40.
[2] R.E.I. Schropp, K.F. Feenstra, E.C. Molenbroek, H. Meiling, J.K. Rath, Philos. Mag., B 76 (1997) 309.
[3] W.M. Arnold Bik, F.H.P.M. Habraken, Rep. Prog. Phys. 56 (1993) 859.
[4] N. Maley, Phys. Rev., B 46 (1992) 2078.
[5] S.G. Tomlin, J. Phys., D, Appl. Phys. 5 (1972) 847.
[6] Y. Hishikawa, N. Nakamura, Y. Kuwano, Jpn. J. Appl. Phys. 30 (1991) 1008.
[7] A.W. Weeber, A.R. Burgers, M.J.A.A. Goris, M. Koppers, E.J. Kossen, H.C Rieffe, W.J. Soppe, C.J.J. Tool, J.H. Bultman, Proc. 19th Photovoltaic Solar Energy Conference Paris, WIP-Munich, Munchen, Germany, 2004, p. 532.
[8] A.H. Mahan, A.C. Dillon, L.M. Gedvillas, J.D. Perkins, J. Appl. Phys. 94 (2003) 2360.
[9] B. Stannowski, J.K. Rath, R.E.I. Schropp, J. Appl. Phys. 93 (5) (2003) 2618.
[10] J.D. Moschner, J. Schmidt, R. Hezel, Proc. 19th Photovoltaic Solar Energy Conference Paris, WIP-Munich, Munchen, Germany, 2004, p. 1082.
[11] E. Bustarret, M. Bensouda, M.C. Habrard, J.C. Bruyere, S. Poulin, S.C. Gujrathi, Phys. Rev., B 36 (12) (1998) 12.
[12] S. Hasegawa, L. He, Y. Amano, T. Inokuma, Phys. Rev., B 48 (1993) 5315.
[13] V. Verlaan, C.H.M. van der Werf, Z.S. Houweling, I.G. Romijn, A.W. Weeber, H.F.W. Dekkers, H.D. Goldbach, R.E.I. Schropp. Prog. Photovolt. (in press) doi:10.1002/pip.760.