LOW-STRESS SILICON NITRIDE DEPOSITED AT LOW SUBSTRATE TEMPERATURE USING HOT-WIRE CVD

R. Bakker[1], V.Verlaan, C.H.M. van der Werf, Z.S.Houweling, Y.Mai, J.K. Rath and R.E.I. Schropp

***Abstract*— By using Hot-wire chemical vapor deposition (HWCVD), we deposited transparent silicon nitride (SiN_x) coatings at temperatures below 250 ºC. As determined with elastic recoil detection (ERD) and Rutherford backscattering (RBS), these films show a very high mass density of 2.8 g/cm^3. The low 16BHF etch rate of 18 nm/min confirms the good compactness of the films. The deposition rate of these high-density films prepared at low temperature is just as high as when deposited at 450 ^{o}C, which is 3 nm/s. Moreover, these rapidly deposited high-density films have very low absorption in the visible wavelength region, which enables the use in optical devices. These high-density layers exhibit a total stress of only 155 MPa (tensile) at a thickness of 208 nm. The electric breakdown field of these layers was also determined and, despite the low deposition temperature, it showed values of up to 1.1 MV/cm.**

***Index Terms*— Silicon nitride, Hot-wire CVD, Low substrate temperature, Dielectric properties, low stress**

I. INTRODUCTION

Silicon nitride (SiN_x) is a well known alloy, used in many industrial applications. For instance, crystalline Si_3N_4 is widely applied as ceramic material and thermal insulator. Amorphous SiN_x is commonly used in large area electronics such as conventional thin film transistors (TFT) [1,2] and commercial (multi-)crystalline Si solar cells [3-5].

Promising new applications for SiN_x are high-quality transparent barrier coating [6-8] and implementation as dielectric medium in plastic electronics such as TFTs on flexible substrates [9-10]. These barrier coatings are important to prevent organic light-emitting devices (OLEDs) and flexible solar cells from degradation caused by oxygen and water vapor. These barrier coatings are employed as single-film coatings, although it can also be used in an organic-inorganic stack [7,8]. Amorphous SiN_x is a very promising material for these coatings since it possesses a high mass density [9,10] and is transparent for the visible wavelengths. Also for its use as dielectric medium in microelectronics, SiN_x is frequently used since conventional SiO_x is not so easily deposited at the relatively low temperatures necessary for these flexible substrates.

However, high-quality SiN_x films have thus far only been reported when deposited at high substrate temperatures of above 400 ºC [11,13,14]. For successful implementation of SiN_x in plastic electronics, these high substrate temperatures need to be lowered. This temperature decrease is not only important to enable deposition on flexible (organic) substrates, a low substrate temperature is also necessary to enable stacking with other materials, such as polymers [7,8,15], which are unstable at temperatures above 250 ºC. Therefore, research is necessary to enable depositions at low substrate temperature (<250 ºC) of high-density SiN_x.

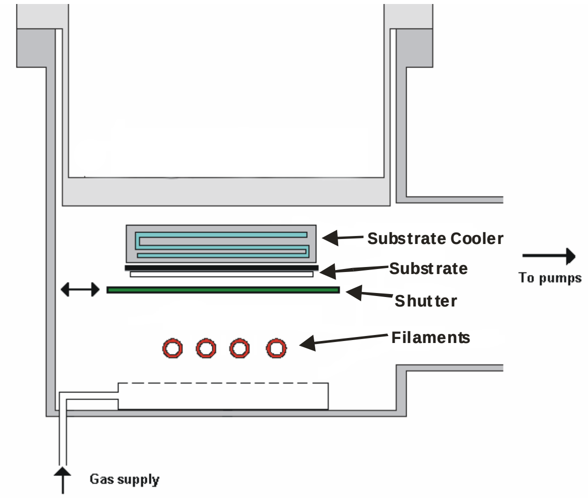

Figure 1: Schematic drawing of the cooled hot-wire CVD reactor.

One candidate for deposition of high quality SiN_x films at low substrate temperatures is hot-wire (HW) CVD. Using the HWCVD technique, the source gasses are decomposed at heated filaments to radicals only with very high efficiencies (~95%) [16,17], which enables deposition rates of up to 7 nm/s for transparent SiN_x films [14,18,19]. This deposition rate is much faster than commercial deposition systems can offer [20]. Furthermore, since no plasma is applied, HWCVD has the advantage that it prevents the substrate from possible damage by ion bombardment. The use of HWCVD for SiN_x depositions at a substrate temperature of 450 °C has resulted

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[1] Utrecht University, Faculty of Science, Department of Physics and Astronomy, SID - Physics of Devices, P.O. Box 80 000, 3508TA Utrecht, the Netherlands.
email: R.Bakker@phys.uu.nl

in films with very high mass density (3.0 g/cm^3) [12], in combination with good optical transmission, resulting in good device performance [4,17].

Lowering the substrate temperature using the HWCVD technique is not straightforward, since the substrate is irradiated by the heated filaments. One possible solution is to increase the distance between the heated filaments and the substrate, however, this also reduces the deposition rate, which is economically undesirable. Another option is to apply active cooling which enables both the low deposition temperature and high deposition rate.

In this paper we characterize high growth rate (3 nm/s) SiN_x layers deposited at substrate temperatures of 230 °C using the HWCVD process with active substrate cooling. In doing so, we will show that transparent SiN_x films can be obtained with very high density (2.8 g/cm^3) in combination with minimal light absorption. Therefore, these high-density films have great potential for application in plastic electronics.

II. EXPERIMENTAL DETAILS

All depositions were performed in a four-filament hot-wire reactor that is part of an ultra high vacuum multi chamber system (PASTA) [21]. As source gasses pure silane (SiH_4) and ammonia (NH_3) were used. In all cases the ammonia flow was kept constant and the silane flow was altered to obtain different flow ratios. The deposition pressure was set at a constant value of 200 µbar. The source gasses were catalytically decomposed at tantalum filaments held at 2100 °C. These heated wires are placed 3 cm from the substrate. In this laboratory system, a shutter is situated between the sample and the wires, to control the duration of the deposition. For thickness uniformity a square showerhead gas inlet was used, which creates a uniform deposition area of 5×5 cm^2.

Two types of substrate holders were used, one with and one without active water cooling. The cooled substrate holder is attached to a cooling body through which cooling water of 14 °C conducts the irradiated heat away from the substrate.

To investigate the influence of the substrate temperature on the composition of the deposited films, two series of depositions were performed. The first series was performed without substrate cooling, on c-Si wafer and thin (50 µm) Schott AF45 glass. These substrates were heated by the radiation from the heated wires and reached a substrate temperature of 450 °C. A second series was made using the water cooler whereby the substrate temperature was decreased to 230 °C. This temperature was directly measured by a thermocouple attached to the surface of both the c-Si substrate and the glass substrate. Other types of cooling liquids for the substrate holder would obviously also lead to different substrate temperatures, for this research only water is used. All deposited layers had a thickness of around 300 nm.

The composition of the deposited samples was investigated with elastic recoil detection (ERD) [22] using 50 MeV Cu^{8+} particles. Rutherford back-scattering (RBS) [23] with 2 MeV He^+-atoms was applied for accurate (within 5%) determination of the mass density. Fourier transform infrared spectroscopy (FTIR) was performed to investigate the bonded hydrogen, where we corrected for coherent and incoherent reflections [24,25]. The ambient H_2O and CO_2 signals were eliminated from the spectrum by intensive dry N_2 purging during the FTIR measurements. The thickness and extinction coefficient (k) of the deposited layers were measured by reflection/transmission measurements [26,27]. The etch rate of the films was determined using a 16BHF solution (5 parts 40% NH4F with 1 part 50% HF).

For the stress measurements, films were deposited on ultra flat Schott D263T glass (100 µm). The curvature, before and after the deposition, was determined over a long range of 4 cm using a DEKTAK step profiler. Due to stress in the films, the film-substrate stack curves. The stress is quantified by the approach of Glang *et al.* [28]. A more detailed discussion about the use of this method for HWCVD SiN_x films is given elsewhere [29].

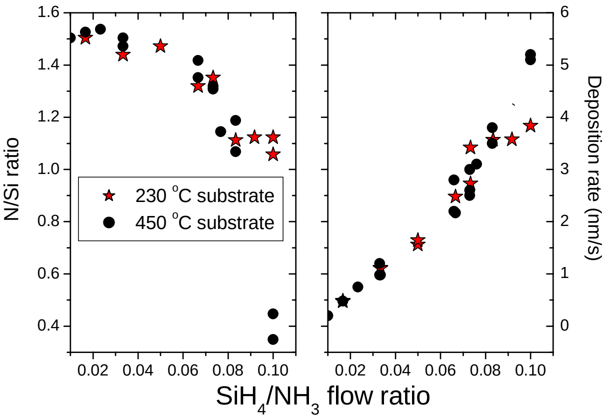

Figure 2: N/Si ratio and deposition rate dependence on the flow ratio. The trends for the different substrate temperatures are roughly the same.

III. RESULTS AND DISCUSSION

In Fig. 2, the atomic N/Si ratio of the deposited films is shown as well as the deposition rate for both the 450 °C and the 230 °C series. The flow ratio of the source gasses has a large influence on the atomic N/Si ratio (= x in SiN_x) of the deposited films. Since the NH_3 flow was constant the difference in flow ratio is created by using different SiH_4 flows. It can be seen that the deposited films have an N/Si just over stoichiometry (N/Si > 1.33) for low SiH_4 flows. When increasing the SiH_4 flow the films become more Si-rich since more SiH_4 molecules are exposed to the heated wires. Since the volume density of Si atoms in the film is independent of the composition [12-14], the deposition rate of the deposited films has a linear correlation with the SiH_4 flow, such that higher SiH_4 flows result in higher deposition rates.

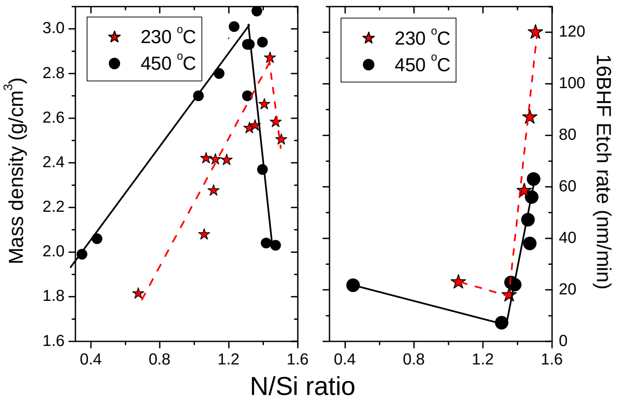

Figure 3: The mass density and 16BHF etch rate of the various SiN$_x$ samples. The etch rates confirm the high mass densities. The lines are a guide to the eye.

It is remarkable that the composition and the deposition rate reveal the same dependence on the flow ratio for the two substrate temperatures. The only difference between the two substrate temperatures is when depositing at relatively high SiH_4 flow, applying higher substrate temperature leads to lower N/Si ratios in the films compared to films deposited at 230 °C. In this paper we will use the N/Si ratio to characterize the films since this is a physically more meaningful parameter than the flow ratios during deposition.

For successful application in devices it is important to deposit compact films with a high mass density. In Fig. 3 both the mass density and the 16BHF etch rate are plotted for different compositions. For the series deposited at a substrate temperature of 450 °C the mass density increases with increasing N/Si to a very high value of 3.0 g/cm^3 for N/Si = 1.31. For higher N/Si ratios the mass density decreases. This is caused by the creation of voids in the films, which are also observed with TEM [30]. For the films deposited at a substrate temperature of 230 °C again an increase in mass density with increasing N/Si is observed. In this case however, a maximum of 2.8 g/cm^3 was achieved at a N/Si just above stoichiometry. The 16BHF etching experiments confirm these trends in mass density: a very low etch rate of 7 nm/min is reached for films deposited at 450 °C, which increases to 18 nm/min when films are deposited at a substrate temperature of 230 °C.

For applications in optical devices (OLEDs and solar cells), it is important to be transparent in the visible-wavelength range. In Fig. 4 the extinction coefficient (k) for visible wavelengths of films deposited at 230 °C with different compositions is shown. As can be observed absorption only occurs at wavelengths smaller than 600 nm and increases with decreasing N/Si ratio. This occurs since decreasing the N/Si ratio leads to more Si-rich material, which causes narrowing of the band gap.

For the application of SiN$_x$ in plastic (flexible) electronics it is obviously important for the SiN$_x$ films to have low mechanical stress. Therefore, the total stress of the films is determined. For the most N-rich samples (N/Si = 1.56) have a low value of 155 MPa tensile. Based on earlier measurements [29], it is expected that more Si-rich sample will have even less stress.

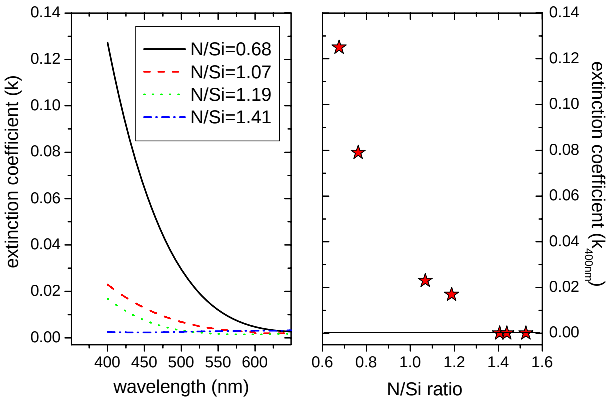

Figure 4: The extinction coefficient of the hot-wire CVD deposited SiN$_x$ deposited at 230 °C. Up to N/Si=1.20 there is negligible absorption in the coatings.

The hydrogen concentration in the SiN$_x$ films deposited at 230 °C was determined using ERD. In Fig. 5 the total hydrogen concentration in the films is shown as a function of composition. A clearly decreasing trend can be observed, in which the lowest hydrogen concentration is measured for the most N-rich samples. All samples contain a relatively high hydrogen concentration, despite their high mass density. The lowest concentration of 16.5 at.% is significantly higher than for materials deposited at 450 °C (~9 at.%) [31], however still lower than reported for SiN$_x$ films deposited at comparable substrate temperatures using PECVD [32,33].

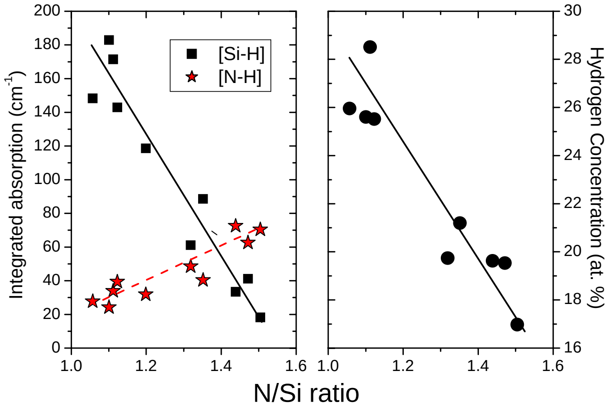

Figure 5: Total hydrogen concentration of the SiN$_x$ films deposited at 230 °C, and its relative distribution over the N–H and Si–H bond. The lines are guides to the eye.

Since cross-linking reactions at the surface are the major mechanism for hydrogen removal during the deposition process [14], these higher hydrogen concentrations are possibly caused by a lower rate of cross-linking reactions due to the lower substrate temperature. Fig. 5 also shows the integrated absorption of the Si–H and N–H stretching modes at 3340 cm^{-1} and ~2200 cm^{-1} respectively. This analysis reveals that for Si-rich material the amount of hydrogen bonded in the Si–H configuration decreases with increasing N/Si ratio. The intensity of the N–H peak shows the inverse trend with a maximum for the most N-rich samples.

To investigate if the same low substrate temperature SiN_x films also have potential for implementation as dielectric medium, I-V measurements were performed on HWCVD SiN_x films implemented in a MIS structure. Fig. 6 shows a typical I-V curve. The most N-rich samples have a breakdown field of 1.1 MV/cm.

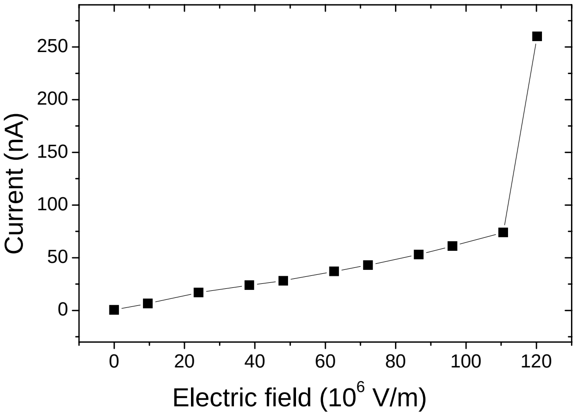

Figure 6: I-V curve of a 208 nm thick $SiN_{1.58}$ films in a MIS structure. These films have an electrical breakdown field of 1.1 MV/cm.

IV. CONCLUSIONS

For application as barrier coating in opto-electronic devices, it is important to develop transparent silicon nitride (SiN_x) coatings with a high mass density deposited at low substrate temperatures. By using hot-wire chemical vapor deposition (HWCVD) we were able to deposit dense, transparent SiN_x coatings at 230 °C. These films have a high mass density of 2.8 g/cm^3. The deposition rate of the films with the highest mass density films was kept unchanged with respect to that of films deposited at ~450 °C, at 3 nm/s. Furthermore, these high density films have very low light absorption for the visible wavelengths which enables their use in optical devices. These high-density layers exhibit a total stress of only 155 MPa (tensile) at a thickness of 208 nm. The electric breakdown field of these layers was also determined and, despite the low deposition temperature, it reaches a value of up to 1.1 MV/cm.

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REFERENCES

[1] Y. Lin, C. Chen, J. Shieh, Y. Lee, C. Pan, C. Chen, J. Peng, and C. Chao. Appl. Phys. Lett. 88 (2006) 233511.

[2] A.T. Hatzopoulos, N. Arpatzanis, D.H. Tassis, C.A. Dimitriadis, F. Templier, M. Oudwan, and G. Kamarinos. J. Appl. Phys. 100 (2006) 114311.

[3] W. Soppe, H. Rieffe, and A.W. Weeber. Prog. Photovolt: Res. Appl. 13 (2005) 551.

[4] V. Verlaan, C.H.M. van der Werf, Z.S. Houweling, I.G. Romijn, A.W. Weeber, H.F.W. Dekkers, H.D. Goldbach, and R.E.I. Schropp. Prog. Photovolt: Res. Appl. (in press) DOI:10.1002/pip.760.

[5] B. Hoex, A.J.M. van Erven, R.V.M. Bosch, W.T.M. Stals, M.D. Bijker, P.J. van den Oever, W.M.M. Kessels, and M.C.M. van de Sanden. Prog. Photovolt: Res. Appl. 13 (2005) 705.

[6] T.N. Chen, D.S. Wuu, C.C. Wu, C.C. Chiang, H.B. Lin, Y.P. Chen, and R.H. Horng. Thin Solid Films 514 (2006) 188.

[7] D. Wuu, T. Chen, C. Wu, C. Chiang, Y. Chen, R. Horng, and F. Juang. Chem. Vap. Depos. 12 (2006) 220.

[8] M.S. Weaver, L.A. Michalski, K. Rajan, M.A. Rothman, J.A. Silvernail, J.J. Brown, P.E. Burrows, G.L. Graff, M.E. Gross, P.M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennet, and M. Zumhoff. Appl. Phys. Lett. 81 (2002) 2929.

[9] K. Cherenack, A. Kattamis, K. Long, I.C. Cheng, S. Wagner, and J.C. Sturm. MRS proceedings 936 (2006) 7-12.

[10] J. Huang, M. Lee, C. Tsai, and Y. Yeh. Jpn. J. Appl. Phys. 46 (2007) 1295

[11] H.F.W. Dekkers, L. Carnel, and G. Beaucarne. Appl. Phys. Lett. (2006) 013508

[12] V. Verlaan, Z.S. Houweling, C.H.M. van der Werf, I.G. Romijn, A.W. Weeber, H.D. Goldbach, and R.E.I. Schropp. Thin Solid Films (in press). DOI:10.1016/j.tsf.2007.06.111

[13] J. Hong, W.M.M. Kessels, W.J. Soppe, A.W. Weeber, W.M. Arnoldbik, and M.C.M. Sanden. J. vac. Sci. Technol., B 21 (2003) 2123.

[14] V. Verlaan, Z.S. Houweling, C.H.M. van der Werf, H.D. Goldbach, and R.E.I. Schropp. MRS Proc. 910 (2006) 61.

[15] R. Bakker, V. Verlaan, C.H.M. van der Werf, J.K. Rath, K.K. Gleason and R.E.I. Schropp. Surface and Coatings Technology, 201 (2007) 9422.

[16] S.G. Ansari, H. Umemoto, T. Morimoto, K. Yoneyame, A. Izumi, A. Masuda, and H. Matsumura. Thin Solid films 501 (2006) 31.

[17] R.E.I. Schropp, S. Nishizaki, Z.S. Houweling, V. Verlaan, C.H.M. van der Werf, and H. Matsusmura. Solid State Electronics. Accepted for publication.

[18] C.H.M. van der Werf, H.D. Goldbach, J. Loffler, A. Scarfo, A.M.C. Kylner, B. Stannowski, W.M. ArnoldBik, A. Weeber, H.C. Rieffe, W.J. Soppe, J.K. Rath, and R.E.I. Schropp. Thin Solids Films 501 (2006) 51.

[19] J.D. Moschner, J. Schmidt, and R. Hezel. Proc. 19th Photovoltaic Solar Energy Conference, Paris, 2004.

[20] S. von Aichberger. PHOTON Int. 3 (2004) 40.

[21] R.E.I. Schropp, K.F. Feenstra, E.C. Molenbroek, H. Meiling, and J.K. Rath. Philos. Mag., B 76 (1997) 309.

[22] W.M. Arnold Bik and F.H.P.M. Habraken. Rep. Prog. Phys. 56 (1993) 859.

[23] L.C. Feldman and J.W. Mayer. Fundamentals of Surface and Thin Film Analysis, PTR Pentice-Hall, Inc. Upper Saddle River, NJ, USA, 1986.

[24] M.H. Brodsky, M. Cardona, and J.J. Cuomo. Phys. Rev., B 16 (1977) 3556.

[25] N. Maley. Phys. Rev., B 46 (1992) 2078.

[26] S.G. Tomlin. J. Phys. D 5 (1972) 847.

[27] Y. Hishikawa, N. Nakamura, and Y. Kuwano. Jpn. J. Appl. Phys. 30 (1991) 1008.

[28] R. Glang, R.A. Holmwood, and R.L. Rosenfeld. Rev. Sci, Instru. 36 (1965) 7

[29] Z.S. Houweling, V. Verlaan,. C.H.M. van der Werf, H.D. Goldbach, and R. E. I. Schropp. MRS Proceedings. 989 (2007) A4.5.

[30] B. Stannowski, J.K. Rath and R.E.I. Schropp. J. Appl. Phys. 93 (2003) 2618.

[31] V. Verlaan, C.H.M. van der Werf, W.M. Arnoldbik, H.D. Goldbach, and R.E.I. Schropp. Phys. Rev. B 73 (2006) 195333.

[32] J. Mei, H. Chen, W.Z. Shen, and H.F.W. Dekkers. J. Appl. Phys. 100 (2006) 073516.

[33] S. WinderBaum, I.G. Romijn, D. Strek, and B. van Straaten. Proc. 21th Photovoltaic Solar Energy Conference. Dresden, 2006. 9288