Thin films with a higher refractive experience lower losses in reflection, but at the same time the thin films become more absorbent [3.49], which can be observed for both as-deposited series as annealing temperature increases.

Similar trends are observed with the WD parameters, E_0 and E_d, compared to the $E_{g\ (Tauc)}$ as the annealing temperature increases. As the annealing temperature increases a decrease is observed in both E_0 and E_d as seen in figures 3.25 and 3.26 respectively. For MW 303 this trend is not obvious at first glance, as there are not as many data points as in MW 304.

A deeper understanding of the a-SiN_x microstructure is offered by E_d, which was obtained from the refractive index dispersion for the single oscillator model. The WD model was extensiv[illegible]e empirical relationship of the coordination number of [illegible]hbour to the anion; this was conducted on a variety of [illegible]d samples. E_d can be expressed as [3.36]:

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$$E_d = \beta N_c Z_a N_e, \tag{3.7}$$

where β, Z_a, and N_e are constants specific to the material, and N_c the coordination number. The WD model was extended to describe amorphous materials such that

$$\frac{{E_d}^a}{{E_d}^b} = (\frac{\rho^a}{\rho^b})(\frac{{N_c}^a}{{N_c}^b}), \tag{3.8}$$

where a and b refers to the amorphous and crystalline form respectively. In an amorphous material E_d provides information and insight on the density and coordination number of the material.

Analysis performed on the TO peak belonging to a-Si in Raman spectroscopy indicates an increase in the FWHM was observed after annealing MW 303 and MW 304 at 700°C, thus signifying an escalation in the disorder of the thin film.

The reduction in band gap, for both $E_{g\ (Tauc)}$ and E_d observed indicates structural rearrangement of the material, and a reduction in E_d indicates that the density of the thin films increases as the annealing temperatures increase. The reduction in Tauc band gap is not due to a decrease in the conduction edge, but instead may be due to further tailing of the valence and conduction bands into the forbidden region as an increase in disorder occurs as indicated by the increase in Γ values observed in Raman Spectroscopy. The increase in disorder in the thin films due to the heat treatment, which causes structural rearrangement to take place at high temperatures. During the effusion of hydrogen and nitrogen, trap states may have been formed within the forbidden region, thus giving the illusion of a decreasing band gap, while increasing the absorption coefficient of the film.

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Conclusion

XRD was performed to determine the bonding structure of the SiN_x molecules in the thin film, and was characterised as amorphous in its as-deposited state. No change in the structure was observed after high temperature annealing and the structure retained its amorphous nature.

Raman spectroscopy was used to determine if any changes in the short range bonding order occurred after being exposed to high temperatures. This was done by analysing TO peaks of the a-Si contributions in the as-deposited and annealed spectra and comparing the FWHM and $\Delta\vartheta_b$ values. No change in the short-range order for the silicon matrix was observed for the as deposited and the annealed

thin film samples in both series, confirming the amorphous nature of the thin films.

The measured values of Γ from the FWHM of the TO peak of a-Si:H allowed for the calculation of the RMS bond angle values of the same peak, the as-deposited samples correlated well with those for amorphous structures. After annealing an increase in the Γ values was observed and this was associated to an increase in disorder in the thin films.

Fourie Transform Infrared Spectroscopy and Elastic Recoil Detection Analysis was conducted on the as-deposited and annealed thin film samples to probe both the bonded and total hydrogen contained in the thin films, as well as the overall bonded structure of the thin films.

FTIR revealed that changes in the bonding structure occurs as the annealing temperature increased, causing a decrease in specific bonding configuration and an increase in others. At lower annealing temperatures rearrangement of the bonds are detected, after annealing at 600°C a huge loss in bonded hydrogen is observed in the MW 304 sample, with an increase in the bonded modes at lower wavenumbers.. Unfortunately the thin films belonging to the MW 303 annealing set were not stable at templeratures higher than 500°C and a similar trend could not be investigated.

ERDA was conducted to reaffirm the trends observed in the FTIR as well as to track the changes in the total hydrogen content of the thin film. At lower annealing temperatures no significant change in the hydrogen content is observed, with slight changes in the bulk of the thin film. It is only once the thin films were

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exposed to temperatures exceeding 500°C that a loss in the bulk of the thin films is observed. After annealing at 1000°C only surface hydrogen is observed.

AFM and HRSEM were used to characterise the surface features present on the as-deposited and the annealed thin films for MW 303 and MW 304. An overall decrease in roughness was observed with increasing annealing temperature, as the protrusions seen in the as-deposited thin films were observed to decrease in height and width for each increase in annealing temperature.

At high annealing temperatures (1000°C) two types of surfaces were detected by AFM, a blistered surface as well as a uniformly smooth surface, and this was corroborated with the use of HRSEM. The HRSEM detected little clusters of protrusions; this was not seen by the AFM due to the area selected on the surface of the thin film, whereas with the HRSEM, the chosen magnification and operating voltage allowed for a broader overview.

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The optical properties of a-SiN_x both as-deposited and annealed were investigated. The thin films described here were deposited under varying conditions such as low flow rates and the low temperature of the wire, in contrast to the usually used conditions in literature. The results however are no different to those observed in the thin films deposited under high gas flow rates conditions and using deposition techniques such as the industrially favoured PECVD, with many of the same trends being observed.

The OJL model used to describe the dielectric functions of semiconducting material was used to analyse the optical reflection spectra. A single layer OJL model on its own was not powerful enough to calculate the optical constants of the material, as the material is highly complex and riddled with inhomogeneities

due to the deposition effects. EMA theory was used to create more complex, and together an (EMA + OJL) optical model was used to calculate the optical parameters.

The single oscillator WD model was used to calculate the optical constants from the results obtained from the optical model. A comparison is drawn between the Tauc band gap and the "centre of gravity" average gap. The latter band gap is calculated to be higher compared to that of the Tauc band gap, but follows the same decreasing trend as annealing temperature increases.

The increase in disorder which was calculated in Raman Spectroscopy was correlated to the decrease in band gap as an increase in the number of trap states introduced into the forbidden region, and not the decrease of the conduction band. The refractive index was observed to increase as the annealing temperature increases, the refractive index values tended towards those of a-Si:H. As the annealing experiment progressed, and the annealing temperatures increased, hydrogen and nitrogen effused out of the thin films. The final product ultimately being like a pure semiconducting material such as a-Si:H, with the $\Delta\vartheta_b$ values calculated corroborating these results.

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References

[3.1] A. Adams, MSc Thesis, University of the Western Cape, Bellville, South Africa (2013).

[3.2] L. Giacomazzi, P. Umari, *Phys. Rev. B.*, **80** (2009) 144201.

[3.3] R. Nietubyć, E. Sobczak, O. Šipr, J. Vackář, A. Šimůnek, *Journal of Alloys And Compound*, **286** (1999) 148.

[3.4] F. Giorgis, C. F. Pirri, E. Tresso, *Thin Solid Films*, **307** (1997) 298.

[3.5] Y. Lai, S. W. Yung, J. Wang, *Thin Solid Films*, **519** (2011) 2235.

[3.6] W. C. Tan, S. Kobayashi, T. Aoki, R. E. Johnson, S. O. Kasap, *J Mater Sci: Mater Electron*, **20**, (2009) S15.

[3.7] V. Verlaan, A. D. Verkerk, W. M. Arnoldbik, C. H. M. van der Werf, R. Bakker, Z. S. Houweling, I. G. Romijn, D. M. Borsa, A. W. Weeber, S. L. Luxembourg, M. Zeeman, H. F. W. Kekkers, R. E. I. Schropp, *Thin Solid Films*, **517** (2009) 3499.

[3.8] 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.

[3.9] W. Xu, B. Li, T. Fujimoto, I. Kojima, *Surface and Coatings Technology*,**135** (2001) 274.

[3.10] J. K. Holt, D. G. Goodwin, A. M. Gabor, F. Jiang, M. Stavola, H. A. Atwater, *Thin Solid Films*, **430** (2003) 37.

[3.11] A.K. Panchal, C.S. Solanki, *Thin Solid Films* **517** (2009) 3488.

[3.12] J. Xu, Y. Rui, D. Chen, J. Mei, L. Zhou, Z. Cen, W. Li, K. Chen, *Materials Letters*, **61** (2007) 5010.

[3.13] D. Beeman, R. Tsu, M. F. Thorpe, *Phys. Rev*, **B 32** (1985) 184.

UNIVERSITY of the
WESTERN CAPE

[3.14] A.J.M. Berntsen, '*Structural Disorder in Pure and Hydrogenated Amorphous Silicon*',PhD thesis, Utrecht University, Utrecht, The Netherlands, (1993).

[3.15] B. P. Swain, B. S. Swain, and N. M. Hwang, *Applied Surface Science*, **225** (2008) 2557.

[3.16] J.M. Owens, D. Han, B. Yan, J. Yang, K. Lord, S. Guha, *Mat. Res. Soc. Symp. Proc.* **762** (2003) A4.5.2.

[3.17] E.M. Esposito, L.V. Mercaldo, P.D. Veneri, L. Lancellotti, C. Privato, *Energy Procedia*, **2** (2010) 159.

[3.18] C.S. Cook, T. Daly, R. Liu, M. Canonico, M. Erikson, Q. Xie, R. Gregory, S. Zollner, *International Conf. on Compound Semiconductors* (2003).

[3.19] V. Verlaan, '*Silicon Nitride at High Growth Rates Using Hot Wire Chemical Vapor Deposition*', PhD Thesis, Utrecht University, Netherlands, (2008).

[3.20] G. Scardera, T. Puzzer, I. Perez-Wurfl, G. Conibeer, *Journal of Crystal Growth*, **310** (2008) 3680.

[3.21] G. Beshkov, D. B. Dimitrov, N. Velchev, P. Petrov, B. Ivanov, L. Zambov, T. Dimitrova, *Vacuum* **58** (2000) 509.

[3.22] F. Liu, S. Ward, L. Gedvilas, B. Keyes, B. To, Q. Wang, *J. Appl. Phys*., **96** (2005) 29730.

[3.23] F. L. Martínez, and I. Mártil, G. González-Díaz, B. Selle, I. Sieber, *J. Appl. Phys*. **86** (1999) 2055.

[3.24] Y. Mai, V. Verlaan. C.H.M. van der Werf, Z.S. Houweling, R. Bakker, J.K. Rath, R.E.I. Schropp, *Journal of Non-Crystalline Solids* **354**

UNIVERSITY of the
WESTERN CAPE

(2008) 2372.

[3.25] M. Ionescu, B. Richards, L. McIntosh, R. Siegele, E. Stelcer, O. Hawas, D. Cohen, T. Chandra, *Material Science Forum Vols*. **539-543** (2007) 3551.

[3.26] M. Mayer, SIMNRA User's Guide.

[3.27] C. Savall, J.C Bruyère, *Thin Solid Films* **258** (1995) 1.

[3.28] C. Boehme, G. Lucovsky, *J. Appl. Phys*., **88** (2000) 6055.

[3.29] R. R. L. De Oliveira, D. A. C. Albuquerque, T.G.S. Cruz, F. M. Yamaji and F. L. Leite, '*Measurement of the Nanoscale Roughness by Atomic Force Microscopy:Basic Principles and Applications*', InTech (2012).

[3.30] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez Herrero, A. M. Baro, Rev. Sci. Instrum., **78** (2007) 013705.

[3.31] W. Xu, B. Li, T. Fujimoto, I. Kojima, *Surface and Coatings Technology* **135** (2001) 274.

[3.32] C. J. Oliphant, C. J. Arendse, T. F. G. Muller, D. Knoesen, *Appl. Surf. Sci*. (2013), http://dx.doi.org/10.1016/j.apsusc.2013.08.075 (Article in press).

[3.33] C.H.M. van der Werf, H.D. Goldbach , J. Löffler , A. Scarfó, A.M.C. Kylner ,B. Stannowski , W.M. ArnoldBik , A. Weeber , H. Rieffe , W.J. Soppe , J. K. Rath , R.E.I. Schropp, *Thin Solid Films* **501**, (2006) 51.

[3.34] S. H. Wemple, M. DiDomenico, *Phys. Rev.* ***B*** **3** (1971) 1338.

[3.35] R. Swanepoel, J. Phps. *E: Sci. Instrum.*, 16 (1983) 1214.

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

[3.37] S. K. O'Leary, S. R. Johnson, P. K. Lim, *J. Appl. Phys*., **82** (1997) 3334.

UNIVERSITY of the
WESTERN CAPE

[3.38] W.Theiss Hard- and Software, Accessed on April 2012, from: http://www.mtheiss.com.

[3.39] A. Gordijn, J. K. Rath, and R. E. I. Schropp, *Appl. Phys. Lett*. **85**, (2004) 5096.

[3.40] D.A.G. Bruggermann, *Ann. Physik (Leipzig)*, **24** (1935) 636.

[3.41] T. F. G. Muller, C. J. Arendse, S. Halindintwali, D. Knoesen, R.E.I. Schropp, *Thin Solid Films*, **519** (2011).

[3.42] A.-S. Keita, A. En Naciri, F. Delachat, M. Carrada, G. Ferblantier, A. Slouli, M. Stchakovsky, *Thin Solid Films*, **519** (2011) 2870.

[3.43] K. J. Laildler, J. H. Meiser, '*Physicsal Chemistry'*, 2nd Edition', Houghton Mifflin Company, Boston (1995).

[3.44] K.N. Anderson, W.E. Svendsen, T. Stimpel-Linfner, T Sulima, and H. Baumgärrtner, *Applied Surface Science* **243** (2005) 401.

[3.45] M. Fox, '*Optical Properties of Solids'*, Oxford University Press (2001).

[3.46] N. Piggins, S. C. Baylisst, E. A. Davis and T. Shen, *J. Phys.: Condens. Matter*, **1** (1989) 8111.

[3.47] J. Yoo, S.K. Dhungel, J. Yi, *Thin Solid Films*, **515** (2007) 7611.

[3.48] F. L. Martínez, and I. Mártil, G. González-Díaz, B. Selle, I. Sieber, *Journal of Non-Crystalline Solids*, **227** (1998) 523.

[3.49] B. Karunagaran, S.J. Chung, S. Velumani, E.-K. Suh, *Materials Chemistry and Physics* **106** (2007) 130.

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Summary

Chapter one highlights the need for sources of cheap alternative energy such as photovoltaic solar cells, which is a viable clean energy source to replace the depleting stocks of harmful fossil fuels. The conversion efficiency of a photovoltaic solar cell (bulk or thin film) can be increased by incorporating an anti-reflective coating, ensuring that the majority of the radiation is transferred to the active bulk layer deep within the solar cell. SiN_x is put forward as a practical choice as an anti-reflective coating, as the optical parameters may be tailored by varying the deposition conditions.

Chapter two undertakes a description of the deposition and post deposition conditions in the preparation of the two sample sets used in the current study, with details of the analytical techniques used in the characterisation of the thin films. The techniques include XRD and Raman spectroscopy for the determination of the structural changes which may have occurred during the heat treatment, FTIR and ERDA for the determination of the bonding structure and the total hydrogen content of the thin films respectively. AFM and HRSEM were used to study the evolution of the surface of the material, with increasing annealing temperature. The optical parameters such as refractive index and Tauc band gap were determined with the use of optical reflection measurements. EMA theory was required to successfully extract the optical parameters from the simulations.

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In chapter three a comparison of the two types of thin films were conducted, describing how a difference in nitrogen content affects the overall structural and optical properties of the thin film during the annealing experiment. It was found that the thin films remained amorphous after annealing at 1000°C. FTIR analysis showed an increase in Si-N bonds, and a shift to higher wavenumbers in both sets of samples. The total hydrogen content was found to decrease with an increase in annealing temperatures. AFM as well as HRSEM analysis revealed protruding structures on the surface of the thin film, which affected the as-deposited roughness in both series. The protrusions formed as a consequence of the growth process, and the size of the structures were observed to decreased as the films were exposed to high temperatures, reducing the overall roughness of the thin film. The major difference between the two series described is the difference in nitrogen over silicon ratio contained in the in the silicon matrix. During annealing the thin film with the higher N/Si ratio withstood a higher annealing temperature compared to the thin film containing the lower N/Si ratio, with refractive index for the higher N/Si ration containing thin film calculated to be lower when compared to the lower containing N/Si counterpart. This was attributed to the deposition conditions, as NH_3 catalyses more readily on the hot wire compared to SiH_4. A reduction in thickness is observed after films were exposed to high temperatures, as the residual gas diffuses outwards.

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An overall decrease in band gap ($E_{g\ (Tauc)}$ and E_0) was observed as the refractive index increased with annealing temperature. A decrease in thin film density was observed as the annealing experiment progressed, and the optical parameters tended towards those of a pure semiconducting material, with the loss of

hydrogen, and the formation of absorbing Si-Si bonds. The changes in optical properties were linked to changes observed in structural techniques such as FTIR, Raman spectroscopy, and ERDA.

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