

Investigation of isochronal annealing on the optical properties of HWCVD amorphous silicon nitride deposited at low temperatures and low gas flow rates

T F G Muller¹, S Jacobs¹, F R Cummings¹, C J Oliphant², G F Malgas¹ and C J Arendse¹

¹Department of Physics, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

²National Metrology Institute of South Africa, Private Bag X34, Lynwood Ridge, Pretoria 0040, South Africa

E-mail: tmuller@uwc.ac.za

Abstract. Hydrogenated amorphous silicon nitride (a-SiN_x:H) is used as anti-reflection coatings in commercial solar cells. A final firing step in the production of micro-crystalline silicon solar cells allows hydrogen effusion from the a-SiN_x:H into the solar cell, and contributes to bulk passivation of the grain boundaries. In this study a-SiN_x:H deposited in a hot-wire chemical vapour deposition (HWCVD) chamber with reduced gas flow rates and filament temperature compared to traditional deposition regimes, were annealed isochronally. The UV-visible reflection spectra of the annealed material were subjected to the Bruggeman Effective Medium Approximation (BEMA) treatment, in which a theoretical amorphous semiconductor was combined with particle inclusions due to the structural complexities of the material. The extraction of the optical functions and ensuing Wemple-DeDomenici analysis of the wavelength-dependent refractive index allowed for the correlation of the macroscopic optical properties with the changes in the local atomic bonding configuration, involving silicon, nitrogen and hydrogen.

1. Introduction

The dielectric function, and therefore refractive index of hydrogenated amorphous silicon nitride (a-SiN_x:H) can be tailored according to the requirements for its intended application. This is achieved by varying the deposition conditions, thus ultimately altering the structural properties, and hence the optical properties of the material. In this study thin films were deposited using HWCVD from SiH₄/NH₃/H₂ gas mixtures with gas flow rates and wire temperature deliberately chosen lower than typically seen in literature [1-2] to reduce gas, thermal and power budgets. Changes in structural and optical properties in the annealed state were investigated and related to bonding configurations in a-SiN_x:H. It was found that successful modelling of UV-vis reflectance spectra of a-SiN_x:H necessitates the application of complex virtual models for both as-deposited and annealed films.



2. Experimental Procedure

Silicon rich a-SiN_x:H thin films of 710 nm nominal thickness and N/Si = x = 0.26 were simultaneously deposited in 10⁻⁷ mbar vacuum on 7 cm × 4 cm Corning® 7059 glass and crystalline silicon (100) substrates in a MVSystems® HWCVD chamber as described elsewhere [3]. The low Ta filament temperature of 1490°C and substrate heater temperature of 240°C were combined with low gas flow rates of 5 sccm, 7 sccm and 20 sccm respectively for SiH₄, NH₃ and H₂. The overall gas pressure in the deposition chamber was maintained at 100 μbar for 30 minutes. After deposition the glass and Si substrates were sectioned into 1 cm × 1 cm squares and isochronally annealed for 30 minutes in 1.3×10⁻⁶ mbar vacuum. At maximum annealing temperature of 1000°C only the Si substrate sample was annealed due to choice of temperature resistant transparent substrate. Fourier transform infrared (FTIR) spectra were collected in transmission mode on the c-Si substrate samples and thereafter corrected for coherent and incoherent reflections [4-5]. The Si-N stretching and the Si-H stretching mode centred around 850 cm⁻¹ and 2100 cm⁻¹ [6] were investigated for bonding configurations as N-H bending and stretching modes at 1200 cm⁻¹ and 3330 cm⁻¹ respectively were absent from the as-deposited samples. Elastic Recoil Detection (ERD) data from a 3 MeV ⁴He⁺ ion beam experiment was used to probe the total hydrogen content. UV-Vis spectroscopy was performed in reflection mode on a spectral range of 200-1000 nm. The spectra were analysed with SCOUT® simulation software [7], employing an iterative function with fitting parameters according to the O'Leary, Johnson and Lim (OJL model) for an amorphous semiconducting material [8], combined with Bruggeman Effective Media Approximations (BEMA) [7]. X-ray diffraction (XRD) and Raman spectroscopy probed the long range order information of the network. Atomic Force Microscopy (AFM) and High Resolution Scanning Microscopy (HRSEM) were used to study the surface features of the films.

3. Results and Discussion

XRD and Raman spectroscopy results (not shown) confirmed the absence of long range bonding order in the silicon matrix due to the absence of crystalline peaks, for annealing temperatures up to 700°C. HRSEM and AFM surface studies on the as-deposited films revealed distinct areas on the surface of the film rich in columnar structures, while some areas appear smooth due to the growth process. The low-temperature anneals (300°C - 500°C) exhibited smooth features with average rms roughness of 2.36 ± 0.53 nm. At annealing temperatures ≥ 600°C two regions of roughness were discerned: (i) blistered regions where we postulate that trapped gas escaped and broke the surface of the film and (ii) a relatively smooth surface where a decrease in rms roughness is detected. As shown in figure 1, at 1000°C the blistered region (4.99 ± 0.45) showed a pitted surface with holes extending into the film in this region. The smoother region still retained a small rms roughness.

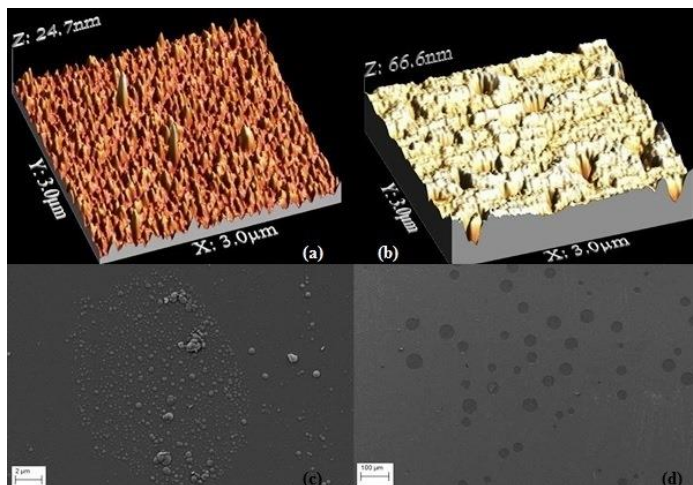


Figure 1. Topographical AFM graphs of (a) smooth region (b) pitted region at 1000°C, and HRSEM viewgraphs of (c) smooth region (2μm scale) (d) pitted region (100 μm scale) at 1000°C.

Overall, a decrease in roughness is observed for the annealing series, as the columnar growth sizes decreased with an increase in annealing temperature. The total hydrogen content in the films is seen to decrease as the annealing temperature is increased, as shown in figure 2. This signifies effusion of hydrogen from the material as the annealing temperature is increased. At 1000°C only surface hydrogen is detected. Complimentary information is given by FTIR difference spectra for the main nitrogen and hydrogen containing modes, calculated as the difference between each sample in its annealed and as-deposited state, as shown in figures 3 and 4. A positive result implies an increase in vibrational intensities for a specific bonding configuration, and a negative result indicates a loss in intensity. The difference spectra can also detect increase of another bonding type due to scavenging of hydrogen or nitrogen atoms from another vibrational mode. There is good agreement between the decrease in the total hydrogen content in the films at high annealing temperatures from ERD analysis and the 2100 cm^{-1} mode in the FTIR difference spectra. Figure 4 further suggests that after an initial decrease in the Si-N bond density no clear pattern for this mode can be discerned. However, at 1000°C anneal temperature a large increase in Si-N mode density is observed. A nitrogen-rich interface between the SiN_x and the underlying c-Si substrate act as possible source of the extra nitrogen available for bonding was discussed in previous work [2]. Increasingly complicated optical models were implemented and discarded to improve the optical fitting result, since the basic OJL construction proved ineffectual, as did a BEMA consisting of an OJL semiconductor containing voids (particles of air). A film-surface interface, refractive index variation along the depth of the thin film, and a substrate-interface [2] in a generic heterogeneous optical model was then developed which successfully modelled all as-deposited and annealed states. It consisted of three virtual layers constituting one thin film. Each virtual layer contained a BEMA matrix which was built up from (OJL amorphous semiconductor + small amounts of Si crystallites for ordering of the network + dielectric functions of generic Si_3N_4 from the database to steer the fitting parameters). Air was inserted as particle material in the overall matrix. The OJL parameters accounted for variations of disorder from near-stoichiometric material types. A BEMA of SiONO-SiO_2 was inserted on top of the stack and a software defined formula to account for scattering effects was implemented. It was found that the high temperature anneal produce material with silicon characteristics from the silicon-rich as-deposited state, which determined the starting value refractive index. We also postulate that effusion of hydrogen and nitrogen bonding type rearrangements also contribute to the optical properties at the respective annealing temperatures. This was concluded from single oscillator Wemple-DiDomenico (WD) analysis [9] performed on the wavelength dispersed refractive index data, and absorption coefficient curves (not shown). The WD results are displayed in figure 5. The single oscillator energy E_0 , suggestive of an ‘average band gap’ of the material provides quantitative information on the total band structure whereas the so-called Tauc gap probes the optical properties near the fundamental band gap of the material.

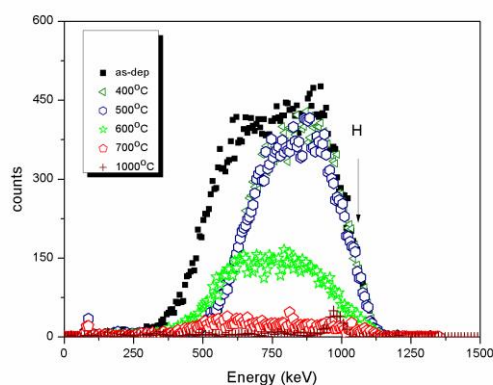


Figure 2. ERD spectra for the annealing series.

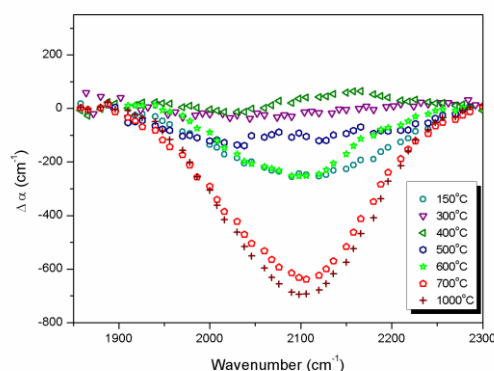


Figure 3. FTIR difference spectra of modes centred around 2100 cm^{-1} .

The oscillator energy E_0 can be empirically related to the optical gap. The dispersion energy E_d , which is a measure of the strength of the interband optical transitions, and the static refractive index n_0 , are displayed for the anneal series together with E_0 . It is observed for the series that both n_0 and E_d start to increase at 600°C, while E_0 decreases; this is also the first anneal temperature where the greatest loss in hydrogen bonded in Si-H mode occurs, which would influence the density of the thin film.

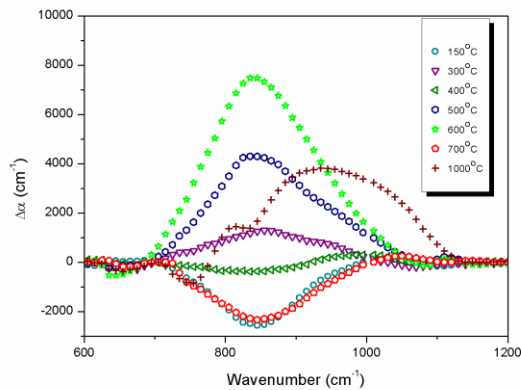


Figure 4. FTIR difference spectra of modes centred around 850 cm^{-1} .

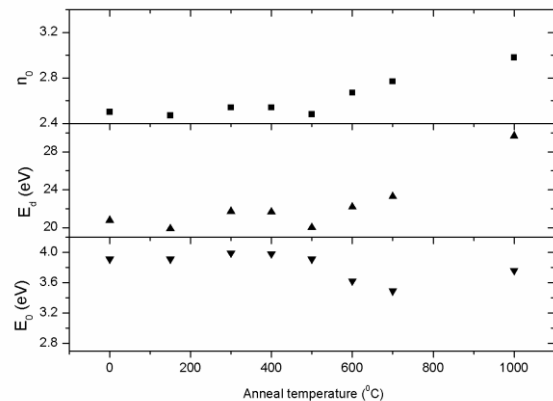


Figure 5. Optical data generated from WD analysis for anneal series.

The variation in the values of the optical parameters would therefore depend on x for the starting material, which determines the microstructure of the material and the manner in which the local bonding environments change at the different annealing temperatures. The analysis therefore makes it possible to undertake an in-depth study of annealing experiments on films with different x values in our deposition series' on low temperatures and gas rates.

4. Conclusion

It was established that hydrogen effuses from the thin films as the annealing temperature increased, with bond rearrangements occurring at the different annealing temperatures. A complex model normally reserved for spectroscopic ellipsometry (SE), was based on the physical and structural characteristics of the film-substrate system and then applied on UV-vis reflectance data, which is a more readily available measurement technique. Wemple-DeDominici analysis proved a valuable tool to relate the microstructure of the material to the optical properties.

Acknowledgements

The authors thank the National Research Foundation of South Africa for financial support.

References

- [1] Liu F, Ward S, Gedvilas L, Keyes B, To B, Wang Q, Sanchez E and Wang S 2004 *J. Appl. Phys.* **96**(5) 2973
- [2] Oliphant C J, Arendse C J, Muller T F G and Knoesen D 2013 *Appl. Surf. Sci.* **285**P 440
- [3] Adams A 2013 *Hot-Wire Chemical Vapour Deposition of Silicon-Nitride Thin Films* (MSc. Thesis, University of the Western Cape, Bellville, South Africa)
- [4] Brodsky M H, Cardona M and Cuomo J 1977 *Physical Review B* **16** 16
- [5] Maley N 1992 *Phys. Rev. B* **46** 46
- [6] Verlaan V, van der Werf C H M, Arnoldbik W M, Goldbach H D and Schropp R E I 2006 *Phys. Rev. B* **73** 195333
- [7] Theiss W 2006, Hard and Software for optical spectroscopy, <http://www.wtheiss.com>
- [8] O'Leary S K, Johnson S R and Lim P K 1997 *J. Appl. Phys.* **82** 3334
- [9] Wemple S H and DiDomenico M 1971 *Phys. Rev. B* **3** 1338