Low temperature deposition of silicon nitride thin films by hot-wire CVD

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Abstract. Amorphous silicon nitride (a-SiN$_x$:H) is known for its superior transmission in the visible range and its tuneable optical band gap, which makes it a suitable candidate for anti-reflective coatings in photovoltaic applications. Plasma-enhanced chemical vapour deposition (PECVD) is currently the industrial workhorse for a-SiN$_x$:H thin films. However, hot-wire CVD (HWCVD) provides an alternative to PECVD in that it allows for high deposition rates, no ion damage, reduction in cost and ease of up scaling. This contribution reports on the effect of the ammonia gas (NH$_3$) flow rate on the structural and optical properties of a-SiN$_x$:H thin films deposited by HWCVD at low temperatures. Fourier transform infrared spectroscopy confirms that the Si-N bond density peaks at a flow ratio of 0.6. Changes in the growth rate, refractive index and optical band gap are attributed to the variation in the Si-N bond density, illustrating a clear relation between the structural and optical properties.

1. Introduction

Amorphous silicon nitride (a-SiN$_x$:H) grown by hot wire chemical vapour deposition (HWCVD) has attracted the attention of researchers far and wide, mainly as a result of the superior film quality deposited at low temperatures [1-2]. Plasma enhanced chemical vapour deposition (PECVD) is the industrial technique of choice for device quality a-SiN$_x$:H films; due to its reproducibility. However, PECVD has its drawbacks in terms of film quality caused by ion bombardment, which results in void formation and undesirable oxidation [2-3]. HWCVD provides a means of reducing these voids by production of radicals as compared to ions in PECVD.

The study of oxidation and passivation is among the major motivating factors for extensive research being done on bond quantification and structural properties of a-SiN$_x$:H thin films [4-6]. In this work the dependence of the optical and structural properties of a-SiN$_x$:H thin films on ammonia (NH$_3$) flow rate was investigated by Fourier transform infrared spectroscopy (FTIR) and ultraviolet visible (UV-VIS) spectroscopy. Bond quantification was determined using FTIR, whereas optical constants and film thickness was determined by UV-VIS.

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2. Experimental Details

Amorphous silicon nitride films were deposited by HWCVD using a heated tantalum filament at 1460 °C at a fixed pressure of 100 μbar and a gas flow ratio varying from $R = \Phi_{NH3}/\Phi_{SiH4} = 0.2 - 1.4$, where Φ refers to the flow rate. All thin films were deposited using a constant H_2 flow rate of 20 sccm and a substrate heater temperature of 240 °C.

FTIR was performed using a Perkin Elmer Spectrum 100 spectrophotometer from $400 - 4000$ cm^{-1} with a resolution of 4 cm^{-1}. The spectra were corrected for coherent and incoherent reflections using the methods proposed by Brodsky [7] and Maley [8], respectively. Bond quantification was performed using proportionality constants determined by Hasegawa et al [9] and the integrated absorbance of the stretching modes of Si-N and Si-H. UV-VIS was performed using a Semiconsoft thin film analyser in reflection geometry in the range $200 - 900$ nm with a resolution of 1 nm. The optical spectra were modelled using Scout® software and a model developed by O'Leary et al [10] to determine the complex refractive index, thin film thickness and the absorption coefficient. The optical band gap was extrapolated using the procedures proposed by Tauc [11].

3. Results and Discussion

3.1. Structural Properties

The FTIR spectra shown in figure 1 shows three distinctive vibrational peaks: (a) Si-H wagging mode centred around ~ 640 cm^{-1}, (b) Si-H stretching mode centred around ~ 2080 cm^{-1} [12] and (c) Si-N stretching mode centred around ~ 840 cm^{-1} [13]. Also present are the less pronounced N-H bending peak centred around 1170 cm^{-1} and the Si-O-Si peak centred around 1100 cm^{-1}. The latter peaks are due to the penetration of H_2O into the thin film [14], resulting in Si-N bonds being broken and replaced by more thermodynamically stable Si-O-Si bonds. This peak however was not present in the film prepared at R = 0.6, indicating this film to be dense in Si-N bonds.
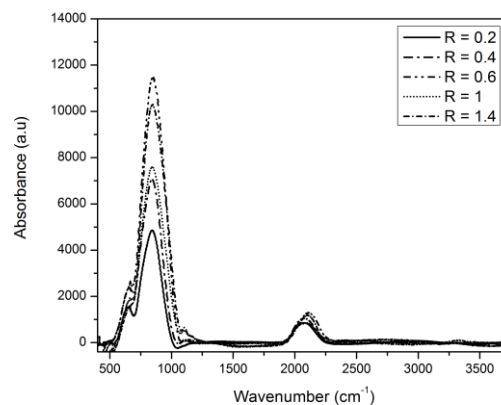
Figure 1: FTIR spectra for different gas flow ratios

Figure 2(a) shows that the Si-N and Si-H bond densities increase as a function of R, both peaking at R = 0.6. A reduction in the bond densities is observed for R > 0.6. This behaviour is in contradiction to that observed by Mahan et al [15], where the Si-N bond density increases as NH_3 is added for R > 2. This maximum at R = 0.6 can be explained by considering the chamber reaction mechanisms

described by Stannowski et al [16]. The NH_3 gas is dissociated by secondary gas phase reactions of radicals desorbed from the filament. In this flow regime these radicals are believed to have the optimum mean free path for NH_3 dissociation at R = 0.6, which thus results in the increased nitrogen incorporation.
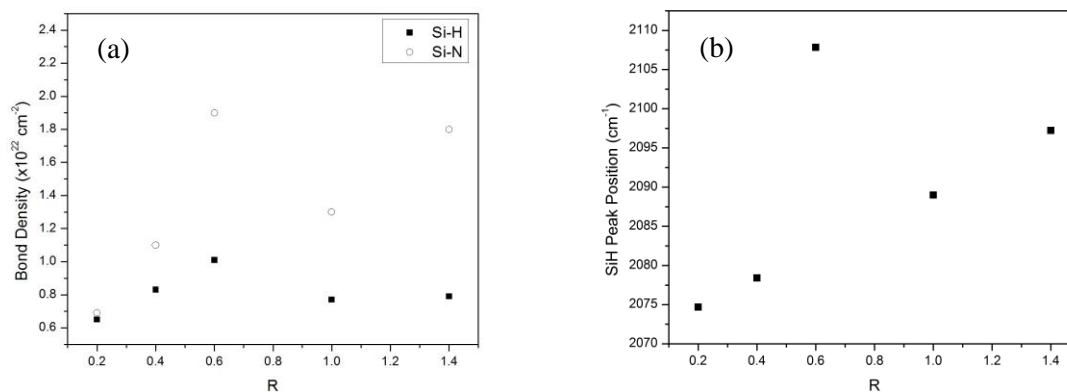

Figure 2: (a) Bond densities and **(b)** Si-H peak position as a function of gas flow ratio

The increased nitrogen incorporation has an effect on the position of the Si-H stretching peak, as seen in figure 2(b), which is analogous to that found by Alpium et al [17]. The shift to higher wavenumbers is attributed to the increase in electronegativity resulting from the incorporation of nitrogen into the film, since nitrogen has a higher electronegativity than silicon. The sample prepared at R = 0.6 shows the highest wavenumber shift, which confirms the result shown in figure 2(a).

3.2. Optical Properties

Figure 3 shows a decrease in the growth rate as a function of flow ratio for R ≤ 1, which is consistent with that observed by Stannowski et al [18]. This behaviour is ascribed to the reduction in the concentration of Si-H radicals available for growth, caused by the increased supply of NH_3 over the heated filament. For R > 1 an unexpected increase in the deposition rate is observed, which can be attributed to the complex reactions at the filament surface at elevated NH_3 flow rates.
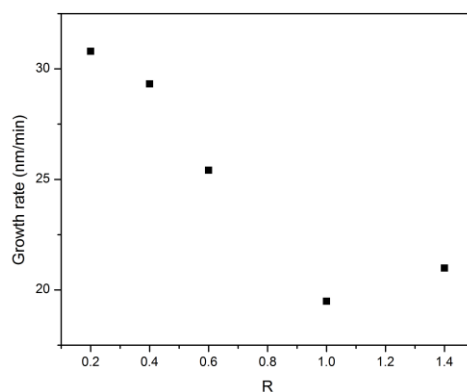
Figure 3: Growth rate as a function of gas flow ratio

The refractive index (at zero energy) shows a decreasing trend with an increase NH_3 flow rate, as shown in Figure 4(a). This is in agreement with literature [18-19]. The reduction in the refractive index is attributed to the increase in the Si-N bond density, as seen in see Fig. 2(a), indicative of a N-rich a-SiN$_x$:H layer.
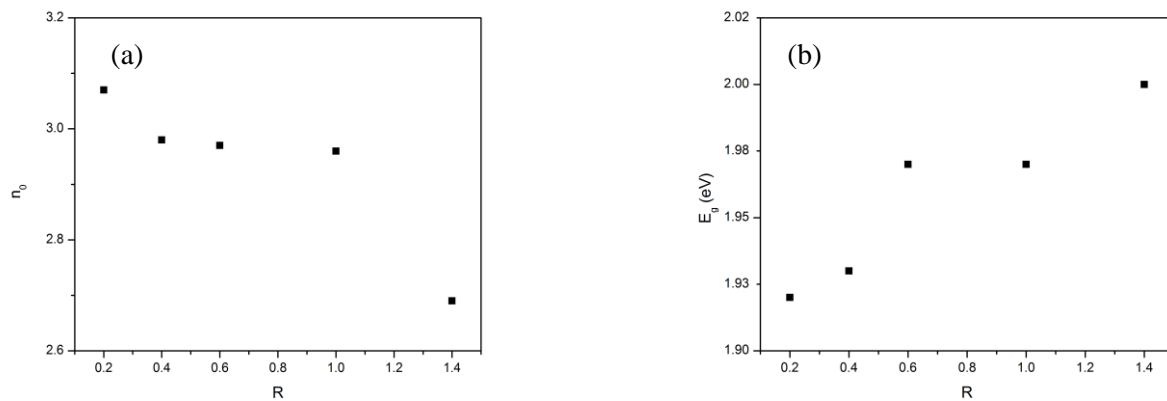
Figure 4: (a) Refractive index and **(b)** Tauc band gap as a function of the flow ratio

The band gap rises as the flow of NH_3 increases as shown in figure 4(b). This is an indication that the nitrogen incorporation in the film causes the band gap to increase. The widening of the band gap can be explained as result of the Si-Si bonds being replaced by Si-N bonds. In Si-N bonds the valance electrons are more tightly bound thus, resulting in more energy required for electron excitation [20].

4. Conclusion

The optimum ratio for the presented flow regime for structurally stable films was observed at R = 0.6, as an oxidation peak was not observed in this film and the Si-N bond density is at a maximum. The reduction in the growth rate with increasing NH_3 flow rate is attributed to the reduction in the supply of SiH radicals during the growth. The widening of the band gap and the decrease in the refractive index are associated with the growth in the Si-N bond density. Therefore, we have shown that the optical properties of the film can be tuned by means of varying NH_3 flow rate.

5. References

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