CHAPTER 4

DEPOSITION PARAMETERS AND OPTICAL TRANSMISSION SPECTROSCOPY: DISCUSSION AND ANALYSIS OF RESULTS

4.1 Introduction

The optical spectroscopy results obtained in this work are presented in this chapter. In this work, two groups of samples were prepared under various deposition conditions, at room temperature. For all the samples, silane(SiH₄) gas and argon(Ar) gas were introduced into the deposition chamber at different flow rates. In the first group, samples were prepared from the discharge of pure silane gas at a flow rate of 20 sccm and three samples prepared from the discharge of a mixture of silane at this flow rate with argon at flow rates of 5, 10 and 15 sccm. The second group consists of samples prepared from the discharge of silane gas at the flow rate of 5 sccm and three other samples from the discharge of a mixture of silane and argon the same flow rate mentioned previously. The deposition conditions of the samples prepared are presented in chapter 3. The optical spectroscopy was done using the Jasco UV-VIS-NIR 3102-PC double beam spectrophotometer in the range of 200 to 2500 nm.

Section 4.2 of this chapter will discuss on the deposition pressure of argon and silane gases. The optical transmission spectra of the samples prepared will be presented and discussed in section 4.3. The deposition rate of the a-Si:H films prepared in this work and its dependence on the ratio of argon flow rate to silane flow rate will be discussed in section 4.4.
CHAPTER 4

DEPOSITION PARAMETERS AND OPTICAL TRANSMISSION

SPECTROSCOPY: DISCUSSION AND ANALYSIS OF RESULTS

4.1 Introduction

The optical spectroscopy results obtained in this work are presented in this chapter. In this work, two groups of samples were prepared under various deposition conditions, at room temperature. For all the samples, silane(SiH₄) gas and argon(Ar) gas were introduced into the deposition chamber at different flow rates. In the first group, samples were prepared from the discharge of pure silane gas at a flow rate of 20 sccm and three samples prepared from the discharge of a mixture of silane at this flow rate with argon at flow rates of 5, 10 and 15 sccm. The second group consists of samples prepared from the discharge of silane gas at the flow rate of 5 sccm and three other samples from the discharge of a mixture of silane and argon the same flow rate mentioned previously. The deposition conditions of the samples prepared are presented in chapter 3. The optical spectroscopy was done using the Jasco UV-VIS-NIR 3102-PC double beam spectrophotometer in the range of 200 to 2500 nm.

Section 4.2 of this chapter will discuss on the deposition pressure of argon and silane gases. The optical transmission spectra of the samples prepared will be presented and discussed in section 4.3. The deposition rate of the a-Si:H films prepared in this work and its dependence on the ratio of argon flow rate to silane flow rate will be discussed in section 4.4.
The variation of the refractive index with different argon to silane flow rate ratios is discussed in section 4.5. Since the film thickness too plays a role in determining the refractive index value, the variation of deposition rate with refractive index will also be discussed in this section.

In section 4.6, the variation of the optical energy gap, $E_g$ with various deposition conditions is discussed. Discussion in this section includes the effects of argon to silane flow rate ratios and deposition rate on the optical energy gap values are discussed. Discussion on the Urbach tail bandwidth, $E_e$ will be reported in section 4.7. Similar to the other two constants, the Urbach tail bandwidth is being discussed based on the effects of argon to silane flow rate ratio and deposition rate.

### 4.2 Deposition Pressure of Argon and Silane Gases.

The electronic properties and quality of a-Si:H film is well known to be very sensitive to deposition conditions. One of the parameters which are capable of affecting the properties is the deposition pressure.

In this work, a-Si:H films were prepared by DC glow discharge technique and the preparation procedures were carried out in deposition conditions as mentioned in chapter 3. Once the deposition chamber was ready for deposition, argon gas and silane gas were flown into the deposition chamber at different flow rate ratios. For argon diluted samples, argon gas was first allowed to flow into the deposition chamber at a required flow rate. The pressure in the deposition chamber was measured and noted as the pressure of argon. Then silane gas was released into the deposition chamber. At this point,
<table>
<thead>
<tr>
<th>sample</th>
<th>flowrate (sccm):</th>
<th>pressure (mbar):</th>
<th>ref index</th>
<th>(eV)</th>
<th>(eV)</th>
<th>(Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar</td>
<td>SiH4</td>
<td>Ar/ SiH4</td>
<td>Ar</td>
<td>SiH4</td>
<td>Ar/ SiH4</td>
</tr>
<tr>
<td>A1</td>
<td>0</td>
<td>20</td>
<td>0.00</td>
<td>0.00</td>
<td>0.46</td>
<td>0.00</td>
</tr>
<tr>
<td>A2</td>
<td>5</td>
<td>20</td>
<td>0.25</td>
<td>0.18</td>
<td>0.32</td>
<td>0.56</td>
</tr>
<tr>
<td>A3</td>
<td>10</td>
<td>20</td>
<td>0.50</td>
<td>0.26</td>
<td>0.24</td>
<td>1.1</td>
</tr>
<tr>
<td>A4</td>
<td>15</td>
<td>20</td>
<td>0.75</td>
<td>0.37</td>
<td>0.23</td>
<td>1.6</td>
</tr>
<tr>
<td>A5</td>
<td>0</td>
<td>5</td>
<td>0.00</td>
<td>0.00</td>
<td>0.10</td>
<td>0.0</td>
</tr>
<tr>
<td>A6</td>
<td>5</td>
<td>5</td>
<td>1.00</td>
<td>0.19</td>
<td>0.07</td>
<td>2.7</td>
</tr>
<tr>
<td>A7</td>
<td>10</td>
<td>5</td>
<td>2.00</td>
<td>0.30</td>
<td>0.07</td>
<td>4.3</td>
</tr>
<tr>
<td>A8</td>
<td>15</td>
<td>5</td>
<td>3.00</td>
<td>0.40</td>
<td>0.06</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 4.1: Refractive index (n), optical energy gap (Eg), Urbach tail bandwidth (Ee), thickness (d) and deposition rate of argon diluted a-Si:H films prepared by DC glow discharge technique at different silane and argon flowrate.
Figure 4.1: Variation of ratio of argon deposition pressure to silane deposition pressure with ratio of argon flow rate to silane flow rate.
silane gas and argon gas will mix in the deposition chamber thus resulting in an increase of the chamber pressure. The chamber pressure was again measured and noted as the total pressure of argon and silane gas. Table 4.1 shows the values of the pressures for every prepared sample.

In order to study the behavior of the optical constants toward the deposition condition, the relation between the flow rate and the pressure of silane and argon gases is first reviewed. It was learned that linearity occurs in relation between the flow rate ratio of argon to silane and the pressure ratio of argon to silane. Hence, these two parameters are chosen to be used in studying the behavior of refractive index (n), optical energy gap (E_g) and Urbach tail bandwidth (E_e) of the films produced. Figure 4.1 shows the variation of the ratio of argon pressure to silane pressure with the ratio of argon flow rate to silane flow rate.

4.3 Optical Transmission Spectra of a-Si:H Films

In this work, samples prepared were divided into two groups, one group with high silane flow rate (20 sccm) and the other group is with low silane flow rate (5 sccm).

The optical transmission spectra of the films obtained in this work by using silane gas at the flow rate of 20 sccm with and without argon dilution are shown in figure 4.2. Referring to these spectra, it is observed that the transmission spectrum for sample A1, the sample without argon dilution, has 9 sharp interference fringes with a large difference between the maximum and the minimum intensities of consecutive interference pattern. In the second
transmission spectrum (A2) of a-Si:H film prepared using a mixture of 20 sccm silane and 5 sccm argon, the number of interference fringes has increased quite significantly to a total of 12. It is also observed that the difference between the extrema has decreased. For the sample where the argon flow rate was increased to 10 sccm, the total number of fringes reduced to 7 but the difference between the extrema has increased again, almost equal in magnitude as the sample without argon dilution. However, for the sample with argon flow rate of 15 sccm, a transmission spectrum with only 2 broad peaks were observed and the difference between the extrema has shrunk as shown in the fourth spectrum of figure 4.2 (A4). It was also noted that the absorption edge of sample A4 was shifted towards a shorter wavelength of about 300 nm as compared to the other spectra where the absorption edge were consistent at 500 nm wavelength.

Generally, in a transmission spectrum, interference fringes are observed in a particular wavelength region due to multiple reflections at the film-substrate interface. As the absorption is strong in the short wavelength region, no interference was observed here. Interference fringes were observed when the film thickness is of the same order as the wavelength scanned. Therefore, if the film is thinner or thicker, no interference fringes will be observed.

Generally, in a transmission spectrum, interference fringes are observed in a particular wavelength region due to multiple reflections at the film-substrate interface. As the absorption is strong in the short wavelength region, no interference was observed here. Interference fringes were observed when the film thickness is of the same order as the wavelength scanned. Therefore, if the film is thinner or thicker, no interference fringes will be observed.
Thus the optical transmission spectra of a-Si:H samples produced from the discharge of silane at flow rate of 20 sccm with and without argon dilution suggest that argon dilution did affect the film thickness and deposition rate of the film. The sharpness of the interference fringes with large difference between the extrema usually indicates larger refractive index. Thus argon dilution on these samples does affect the refractive index of the film especially the sample produced from the highest argon dilution (15 sccm) where the difference between the extrema is significant. The significant shift of the absorption edge towards lower wavelength suggests that high argon dilution significantly increased the optical energy gap.

The optical transmission spectrum of the films obtained in this experiment by using silane gas at the flow rate of 5 sccm with and without argon dilution are shown in figure 4.3. Except for the sample without any argon dilution, the rest of the spectra showed almost no interference fringes. In fact, sample A7 and A8 which have the argon flow rate of 10 sccm and 15 sccm respectively failed to show any fringes thus making the calculation of refractive index and thickness using the method proposed by J. C. Manifacier and Davies combined impossible. Hence, for these two samples, the calculation for deducing refractive index and film thickness was obtained by utilizing a stimulation method proposed by Khedr M. Hassan. The detail of Khedr's method was earlier discussed in chapter 3.
Figure 4.2: Optical transmission spectra of a-Si:H films prepared by d.c. plasma glow discharge technique using 20 sccm silane and different argon flow rate.
Figure 4.3: Optical transmission spectra of a-Si:H films prepared by d.c. plasma glow discharge technique using 5 sccm silane and different argon flow rate.
From the optical transmission spectrum shown in figure 4.3, samples A5, A6, A7 and A8 show absorption edges at different wavelengths. Generally, the absorption edges shifted to shorter wavelengths with increasing argon flow rate. This is an indication of an increase in energy gap when argon was introduced at higher flow rates. This result is similar to the results obtained for the samples prepared using silane gas at the flow rate of 20 sccm. Comparing the samples without argon dilution, sample A1 (20 sccm SiH₄) and sample A5 (5 sccm SiH₄), sample A5 seems to have an absorption edge at a longer wavelength. This indicates that a-Si:H films prepared by plasma glow discharge with 5 sccm silane flow rate has smaller value of energy gap compared to the films prepared with 20 sccm silane flow rate and is proven by the calculated values of $E_g$ for both samples as shown in table 4.1.

In this work also, it was observed that the introduction of argon being diluted into the silane plasma had somehow increased the value of optical energy gap in the film. This was shown by the shifted absorption edge in the optical transmission spectrum to shorter wavelength region. Sample A6, with 5 sccm argon flow rate showed an absorption edge at 350 nm while sample A7, with 10 sccm argon flow rate showed an absorption edge at 300 nm. Sample A8, which was prepared with 15 sccm argon flow rate did not show total absorption but has a minimum value of transmission at 300 nm. The shifted absorption edges together with the increased energy gap values was observed when the ratio of argon flow rate to silane flow rate is between 0.75 and 2.00.

The values of the deposition rate, refractive index and the optical energy gap of a-Si:H samples prepared using silane flow rates of 20 sccm and 5 sccm
with and without argon dilution are presented in table 4.1. The effects of these parameters on the argon to silane flow rate ratios will be discussed later in this chapter. The effects of deposition rate on the refractive index and the optical energy gap will also be discussed.

4.4 Deposition Rate of a-Si:H

Deposition rate is one of the important parameters that is usually being discussed in experimental works involving amorphous silicon (a-Si). Previous researchers have shown that high quality a-Si films have to be prepared in the silane glow discharge at deposition rates of less than about 3 Ås⁻¹ along with the minimum radio frequency power. Under these conditions, ion and electron energies in the plasma remain sufficiently low to reduce defect formation at the growing surface to an acceptable level. On the other hand, from electronic point of view, J. C. Knights suggested that the ‘optimal’ material has to be prepared from plasmas of pure silane at low discharge power densities because these conditions are associated with very low deposition rates of about 1 Ås⁻¹.

From the tabulated values of table 4.1, deposition rate of the samples prepared in this work were plotted versus the ratio of argon flow rate to silane flow rate and is shown is figure 4.4. Figure 4.4 showed that introduction of argon at a very low flow rate compared to silane flow rate had decreased the deposition rate but as the flow rate approaches unity, he deposition rate increased with increase of the ratio. However, when the argon flow rate was higher than the silane flow rate, the deposition rate began to decrease slowly. This trend suggested that low argon dilution of silane plasma had enhanced the
Figure 4.4: The dependence of deposition rate to the ratio of argon flow rate to silane flow rate.
growth of a-Si:H film as argon dilution was increased. In contrast, the high argon diluted silane plasma, high deposition could slow down the deposition process. The reduced mean free path due to the large number of argon atoms in the plasma could reduce the sticking probability of the film.

4.5 Reative Index (n) of a-Si:H Film in Variation of Flow Rate and Deposition Rate.

The refractive index is usually referred to the bulk density of a film. High bulk density films have high values of refractive index due to microstructure arrangement.

Figure 4.5 shows the dependence of refractive index to the ratio of argon flow rate to silane flow rate for the a-Si:H samples prepared in this work. The trend shows that the refractive index decreases as the flow rate ratio increases. When the argon flow rate is twice the silane flow rate, the refractive index is at its lowest value but as the ratio increases further, the refractive index begins to increase. This result suggests that the introduction of argon into the silane plasma produced a less dense a-Si:H film if the ratio of argon flow rate to silane flow rate is about 2.0. Since low bulk density could be due to columnar structures the results of this work suggest that when prepared using high flow rate of argon, the a-Si:H films produced have columnar structures.

The dependence of refractive index to the deposition rate is presented in figure 4.6. The figure showed that in variation of deposition rate, the refractive index of the films obtained in this work showed a decrease as the deposition rate increases.
Although figure 4.4 did not show a clear relation between the ratio of argon flow rate to silane flow rate with deposition rate, the decrease in refractive index on increasing both parameters suggest that these parameters could be utilized together in order to obtain a required density of a-Si:H film. The result which showed that low density film could be produced with high ratio of argon flow rate to silane flow rate as well as high deposition rate indicated that increasing the ratio of argon flow rate to silane flow rate actually result in higher deposition rate thus combining the two factors will result in low density a-Si:H film.

The refractive index (n), of the films in this work were deduced from the Cauchy equation and is actually the refractive index value at infinite wavelength. Thus, the dispersion curve of n at different wavelengths will show the saturated n value that corresponds to the calculated n.

The dispersion of the refractive index for all samples is shown in figure 4.7. In figure 4.7(a), the dispersion curve for the sample without argon dilution (A1) and the sample diluted in argon at the flow rate of 10 sccm (A3) are overlapped. The sample prepared with 5 sccm argon (A2) has a smaller value of saturated n and the sample prepared with the highest argon flow rate (A4) saturates at the lowest value.

The samples prepared at the lower silane flow rate (5 sccm) presents a different pattern of dispersion and is shown in figure 4.7(b). Except for the sample without argon dilution (A5), the other samples (A6, A7, A8) have the same saturation value for n which is smaller than the n of the non-argon sample. Comparing the two undiluted samples with silane flow rate of 20 sccm
Figure 4.5: Refractive index (n) in variation of the ratio of argon flow rate to silane flow rate.
Figure 4.6: The dependence of refractive index (n) to deposition rate.
Figure 4.7: Dispersion curve of refractive index for argon diluted a-Si:H films in variation of argon flow rate. (a) with 20 sccm silane flow rate. (b) with 5 sccm silane flow rate.
and 5 sccm (A1 and A5), the sample prepared with the higher silane flow rate (A1) saturates at a lower n value. This result suggested that the a-Si:H films prepared with high silane flow rate is less dense compared to the films prepared with low silane flow rate.

4.6 Optical Energy Gap (E_g) of a-Si:H Film in Variation of Flow Rate and Deposition rate.

According to Freeman and Paul⁶, the band gap in pure amorphous silicon (a-Si:H) is about 1.3 eV and typically lies between 1.7 to 2.0 eV in hydrogenated films. The variability of the results is due to high sensitivity to the details of film deposition especially ion bombardment and impurity incorporation.

Ross and Messier⁷ report that sputtered a-Si:H films with band gaps as low as 0.55 eV is attainable if a low pressure, hydrogen deficient (H₂/Ar) plasma is used. Such films were extremely stable and had a very homogenous microstructure, which is attributed to the beneficial effects of argon ion bombardment on the film growth surface. Tardy and Meaudre⁸ applied a negative DC substrate bias, obtained argon ion bombardment during film growth and a reduction of band gap from 1.91 to 1.81 eV. They explained the decrease in band gap as correlated with a decrease in oxygen contamination in the film.

Optical energy gap (E_g) values obtained in this work are deduced from the Tauc’s plot. In figure 4.8, the values of E_g are plotted versus the ratio of argon flow rate to silane flow rate. The figure shows an increase of energy gap
Figure 4.8: Optical energy gap ($E_g$) in variation of the ratio of argon flow rate to silane flow rate.
Figure 4.9: The optical energy gap (Eg) does not show a clear trend towards deposition rate.
as the flow rate ratio increases and reached a maximum value when the flow rate ratio is around 1.5 before it decreased as the flow rate ratio increases further. Comparing figure 4.5 with figure 4.8 which shows the relation between refractive index and optical energy gap reveals that at low ratio of argon flow rate to silane flow rate, the value of energy gap increases as the refractive index decreases. This observation indicates that reduction in bulk density of the film resulted in expansion of energy gap.

As shown in figure 4.9 in which optical energy gap is plotted in variation of deposition rate, the optical energy gap did not show any dependence on deposition rate. At any deposition rate, the films produced in this work maintained a value of energy gap in the range of 1.8 to 2.8 eV.

4.7 Variation of Urbach Tail Bandwidth ($E_x$) of a-Si:H Film with Flow Rate and Deposition Rate.

In this work, the Urbach tail bandwidth ($E_x$) is deduced from the slope of plot Ln($\alpha$) versus photon energy where $\alpha$ is the absorption coefficient. The values of $E_x$ are plotted versus the flow rate ratio of argon flow rate to silane flow rate and is shown in figure 4.10

It was observed from figure 4.10 that the Urbach tail bandwidth decreases as the ratio of Ar flow rate to SiH$_4$ flow rate increases. The reduction is very similar to the refractive index trend. The similarity indicates that a-Si:H films that have higher values of refractive index also have high values of Urbach tail bandwidth. As high value of $E_x$ is always correlated to highly disordered structures, the result obtained in this work suggests that highly
Figure 4.10: Urbach tail bandwidth (E e) in variation of the ratio of argon flow rate to silane flow
Figure 4.11: The dependence of Urbach tail bandwidth ($E_e$) to deposition rate.
disordered structures had increased the density of the film and thus causing it to have high refractive index.

The behavior of $E_g$ as shown in in figure 4.8 is also supportive to this latter discussion. As discussed earlier, the optical energy gap increased as the ratio of argon flow rate to silane flow rate increased for values lower than 2. When compared to the reduction of $E_g$ in the same range, the result suggests that the reduction of tail states at the band edges has increased the values of optical energy gap.

The dependence of Urbach tail bandwidth to deposition rate is shown in figure 4.11 in which an increase in deposition rate practically decrease the Urbach tail bandwidth. This observation suggests that beside the ratio of argon flow rate to silane flow rate, deposition rate could also be utilized to obtain a-Si:H film with less disordered structure.

4.8 References


