Optical properties of Si_xN_y, SiO_x, and SiO_xN_y thin films deposited by PECVD and measured by scanning electron microscopy, ellipsometry, and spectroscopy

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Abstract
Investigation of silicon-based thin films is of growing interest in modern physics. This experiment in particular explored properties of Si_xN_y, SiO_x, and SiO_xN_y films in the thickness range 300-2400nm deposited by plasma enhanced chemical vapor deposition (PECVD) at 300°C. Thickness and gas flow ratio were varied and the resulting effects on deposition rate and refractive index were observed. Measurements were taken using a Perkin-Elmer spectrophotometer (PE), RAITH150 scanning electron microscope (SEM), and WVASE32 ellipsometer. Maximum deposition rates were found for gas flow ratios of Si_xN_y and SiO_x films, while trends for SiO_xN_y films were inconsistent. Trends for refractive index versus gas flow ratio in Si_xN_y and SiO_x films were also observed, whereas measurements for SiO_xN_y films remained inconclusive.

Introduction

Si_xN_y, SiO_x, and SiO_xN_y thin films have many practical uses in modern technology, specifically in video cameras and semiconductors. They are used as passivation films, diffusion masks, and anti-reflective coatings. These films have high resistance to migrating ions, moisture, and surface oxidation [1], and they adhere well to most surfaces. They may minimize unwanted reflection while maintaining desired transmission in some devices. For example, a film may be used on a semiconductor in an active pixel sensor (APS). APS's have low resolution when used as image sensors, and increasing the number of pixels while reducing their size tends to increase noise. The thin film helps solve this problem by enhancing transmittance and reducing noise on the device [2].

It is important to have the refractive index (n) of the film match that of the semiconductor for optimal performance. The refractive index is the ratio of the speed

(phase velocity) of light, c, in vacuum to the phase velocity of light, v, passing through a medium:

$$n = \frac{c}{v} \tag{1}$$

Thus a higher refractive index indicates a greater decrease in speed of light. An important property of films related to refractive index is extinction coefficient k:

$$\mathrm{k} = \alpha \frac{\lambda}{4\pi} \tag{2}$$

where λ is the wavelength of the light in vacuum and α is the absorption coefficient derived from the change in intensity of the light through the medium. The extinction coefficient is a measure of the amount of light absorbed by the medium. A higher value of k indicates greater absorption. Both n and k are dependent on the frequency of the light passing through the medium. Together they give the complex index of refraction:

$$\tilde{\mathrm{n}} = \mathrm{n} + \mathrm{ik} \tag{3}$$

By measuring the transmittance T, we may obtain the complex index of refraction, and thus the index of refraction, from the following equation:

$$T = \frac{t_1^2 t_2^2 x}{1 + 2r_1 r_2 \cos(\frac{4\pi\, \tilde{\mathrm{n}} d}{\lambda}) x + r_1^2 r_2^2 x^2} \tag{4}$$

where ñ = complex index of refraction, r_1 and t_1 = reflection and transmission coefficients of the air-film interface, r_2 and t_2 = reflection and transmission coefficients of the film-substrate interface, d= film thickness, λ=wavelength, and x is absorption given by [3]

$$x = e^{(\frac{4\pi kd}{\lambda})} \tag{5}$$

Our experiment was designed to find optimal gas flow ratios and thicknesses of the films to obtain predictable refractive indices and consistent film composition. We achieved this goal by varying the gas flow ratios and thicknesses of the films during the deposition process and measuring their optical properties afterward. The films were deposited by Plasma enhanced chemical vapor deposition (PECVD). This system was designed so that deposition could be achieved at lower temperatures than typical thermal oxidation deposition, which requires temperatures as high as 800°C. Deposition at lower temperatures reduces the possibility of damaging the devices onto which the films are deposited. Plasma enhancement also accelerates the deposition process, reducing the time it takes to deposit the films.

The PECVD system has a base pressure of 2mTorr and chamber process pressure between 500 and 800mTorr with a constant temperature of 300°C. It works as follows: the gases flow into a chamber that contains plasma, which either breaks the bonds or excites the molecules so that they may bind with other atoms. The gas flow ratio expresses the rate of one gas flowing into the chamber versus the rate of another gas flowing into the chamber. These gas flow rates are measured in standard cubic centimeters per minute (sccm). We varied the gas flow rates used to make the films in order to change the ratio of the gases. The molecules formed (Si_xN_y, SiO_x, or SiO_xN_y) deposit onto substrates. A substrate may be any device or material that is to be coated with the film. Si_xN_y films were deposited onto quartz and silicon wafers while the SiO_x and SiO_xN_y films were deposited onto BK7 glass and silicon wafers.

Transparent substrates were used so that the films could be measured by spectroscopy, while opaque substrates were used for measurements by ellipsometry.

Spectroscopy requires a Perkin-Elmer spectrophotometer to deflect infrared and visible light through our sample. A detector measures the transmittance, yielding a plot of transmission versus frequency from which we may determine n and k. Conversely, the JA Woollam Company WVASE32 ellipsometer gives n and k values by deflecting light off our sample. The ellipsometer shines a beam of light onto a sample (such as our film on its substrate) through a polarizer that converts any light beam to linearly polarized light. The beam deflects off the sample and passes through a second polarizer that measures the output polarization state. A detector measures the light passing through the second polarizer. Then, the refractive index is determined by the propagation speed and direction of the wave through the sample, and the extinction coefficient relates how much energy of the wave is absorbed in the material.

The opaque substrates were also required for measurements of film thickness using a scanning electron microscope (SEM). The SEM utilizes a focused electron beam that strikes the sample, and the scattering of electrons gives an image of the sample on the computer screen. Each material scatters the electrons differently, so the film can be distinguished from the substrate and its thickness may be determined. Finally, plots of thickness/deposition time versus the ratio of the gas flow show a curve with a maximum where the deposition rate is fastest. The maximum deposition rate gives a film where the amount of nitride, oxide, or oxynitride balances the amount of silicon such that the film properties, such as density consistency, are optimal.

Optical Properties Measurements and Results for Si_xN_y films

The first Si_xN_y films we made maintained a gas flow ratio of 800sccm 5%NH_3/N_2

to 2000sccm 2%SiH_4/N_2 = 0.4. Knowing the deposition rate for Si_xN_y films in the PECVD, we created a number of films with different thicknesses. Theoretically, for materially consistent films, measurements performed on the spectrophotometer should not be effected by variations in thickness. However, if crystalline clusters of silicon are present in the films, then increasing thickness heightens the probability of forming such clusters. Thus our results would show the quality and consistency of the films.

Refractive indices of the films were measured using the Perkin-Elmer spectrophotometer as well as the ellipsometer. The first films we made were deposited solely onto quartz since we did not anticipate the need for opaque substrates for the ellipsometer. Since the films were deposited onto transparent quartz substrates, we had to place the samples on top of another substrate as a background for ellipsometric measurements. The background used was a sample of SiO_x film on Si substrate left over from Dr. Kravchenko's previous experiments. Measuring the films this way had a number of disadvantages. For one, it required fitting models to a sample with four layers (Si_xN_y, quartz, SiO_x, and Si). The WVASE32 software has a limited number of fit models to choose from, and there was no model for quartz. We assumed the quartz was sufficiently transparent that it would not significantly affect the light beam, so we fit models to the three remaining layers. However, the model for Si_xN_y is set to fit films in the form of Si_3N_4 and the model for SiO_x is set for SiO_2. Our films may not have those exact ratios of silicon to nitrogen and silicon to oxygen. As an example, Figures 1 and 2 show the fit obtained for 1300nm Si_xN_y film on quartz with Si wafer coated with SiO_x film as background.

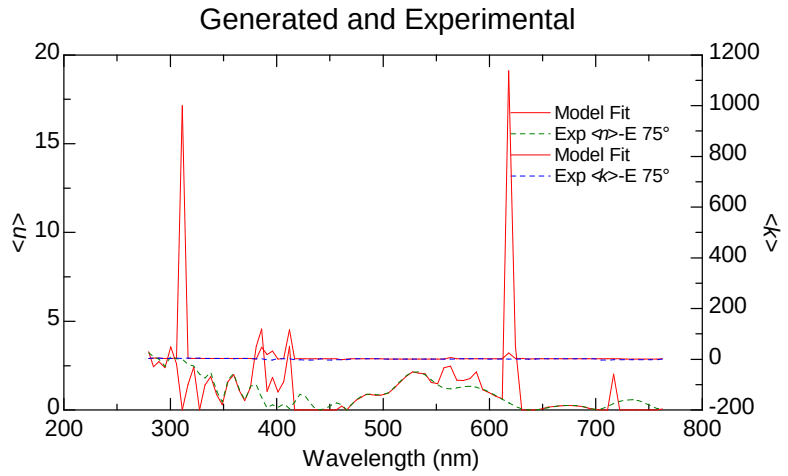

Fig. 1

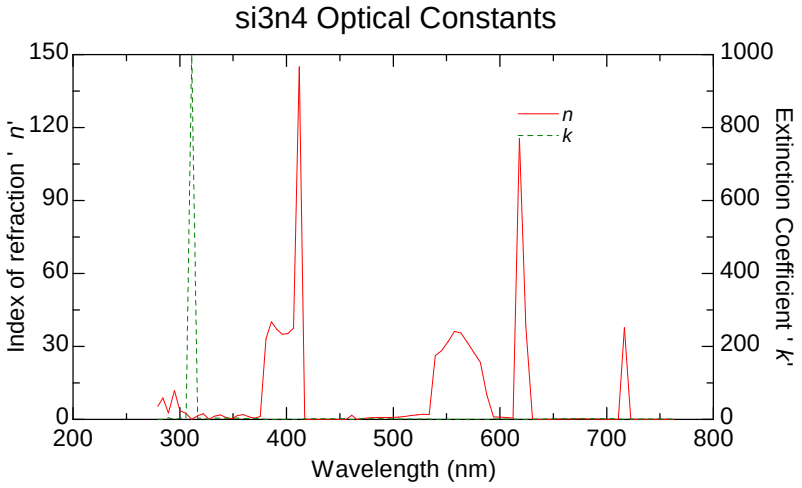

Fig. 2

Figure 1 shows a fit to measured n and k for the sample obtained using three models, one for each layer except quartz. Figure 2 shows the optical constants for the Si_xN_y layer obtained from the fit in Figure 1. We would expect values of n and k for our Si_xN_y films to be between 1 and 3 around a wavelength of 600nm; thus the fit seems to be dramatically incorrect. We chose to neglect these values on the grounds of the disadvantages stated previously and proceeded to measure n by spectroscopy.

Measurements of n using the Perkin-Elmer spectrophotometer (PE) were much more successful. Analysis of the data obtained from the PE was an extensive process. The PE measures transmission versus frequency in a number of steps, obtaining data for a

narrow frequency range in each step. These steps must be merged together using QW software to obtain a complete plot. Once merged, the spectrum must be patched so that a model may be fit to it. A patch uses the general curve of the spectrum and a power fit to smooth out regions of excessive noise. I patched each film at frequencies of approximately 5400 and 7200 cm^{-1} where a great amount of noise existed due to water vapor in the air. To obtain smooth curves, I also patched other noisy regions that may have resulted from light pollution from the surroundings or dust particles on the sample. Once each spectrum was merged and patched, I used the software to fit a model curve for each film, and the fits were used to calculate the refractive indices. Each model required a number of parameters to fit the film and the substrate. Those parameters are the components of the formula for calculating n:

$$n^2 = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - \omega_o \gamma} \qquad (6)$$

For both the substrate and the film, the program needed to know the values of ω_p, ω_o, and γ, which are the oscillator strength, central frequency, and line width respectively for each material. These values are known for the quartz substrate, but they vary for each film. By plugging in the values known for quartz, I obtained a reasonable fit using a guess-and-check method to adjust the remaining parameters for each Si_xN_y film. Finally, I used DLcalc software, which takes the parameters and calculates the value of n over a range of frequencies. We chose to compare the n values at a single frequency, namely 1600cm^{-1}, equivalent to a wavelength of 625nm. A plot of refractive index versus thickness is shown in Figure 3.

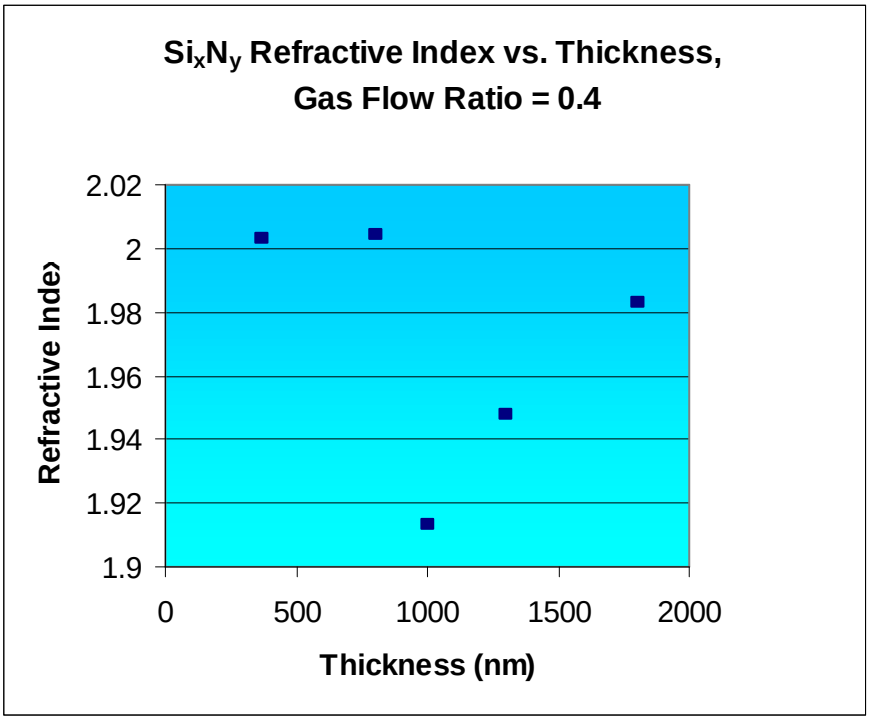

Fig. 3.

Our results do not show a direct relationship between thickness and refractive index for these films. However, they do indicate that there is some effect on refractive index due to thickness variations. Further investigation of this effect would require measuring luminescence in the films. Instead, due to equipment availability and time constraints, we chose to move on to our investigation of gas ratio variations.

The ratio of the gas flow was varied from 0.0127 to 1. This time, each film was deposited for 40 minutes onto both quartz and silicon substrates. Their thicknesses were measured using the SEM afterward. For each film, the measured thickness over deposition time gave the rate of deposition. I plotted the deposition rates versus the gas flow ratios to see what ratio would give the fastest deposition. The results are shown in Figure 4. The maximum deposition rate was found to be 11.1nm/min when the gas flow ratio was 0.0554.

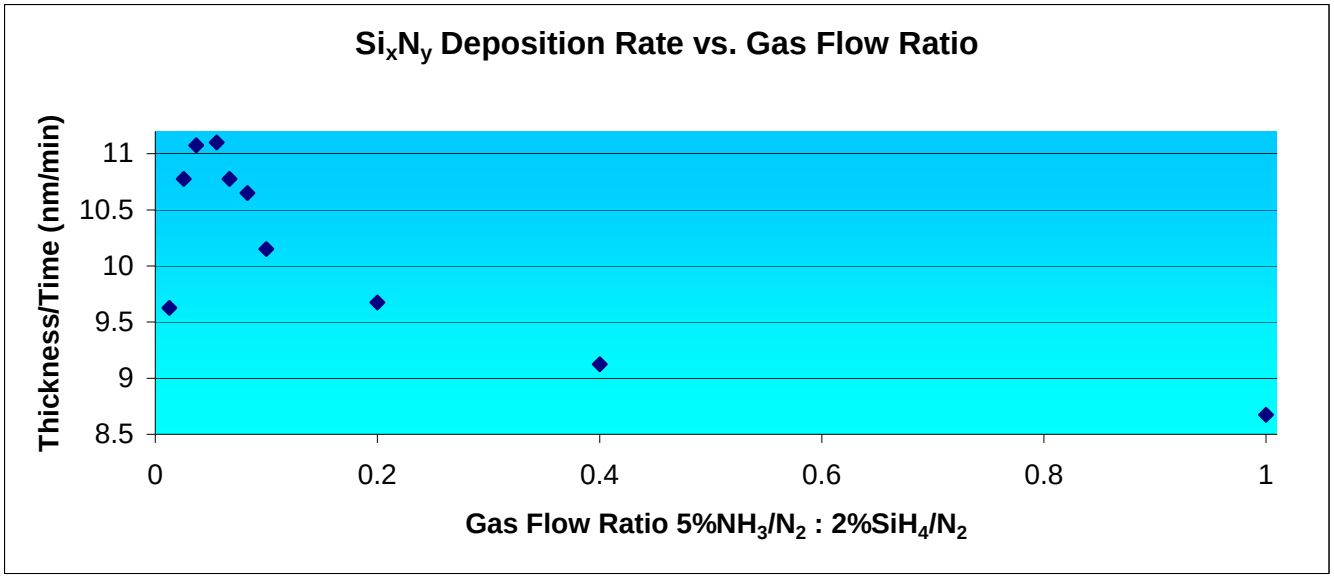

Fig. 4.

After plotting deposition rate versus gas flow ratio, I investigated the relationship between gas flow ratio and refractive index. Once again I used the ellipsometer and the PE to measure the refractive indices. We had deposited these films onto both quartz and silicon wafers- the quartz to be used for measurements with the PE and the silicon to be used with the ellipsometer. As before, the models for Si_3N_4 on Si in the WVASE software with the ellipsometer did not give a fit accurate enough to yield reliable measurements of n. Thus we relied on the measurements from the PE for our n values. The results are shown in Figure 5. The plot indicates an increasing refractive index with decreasing gas ratio.

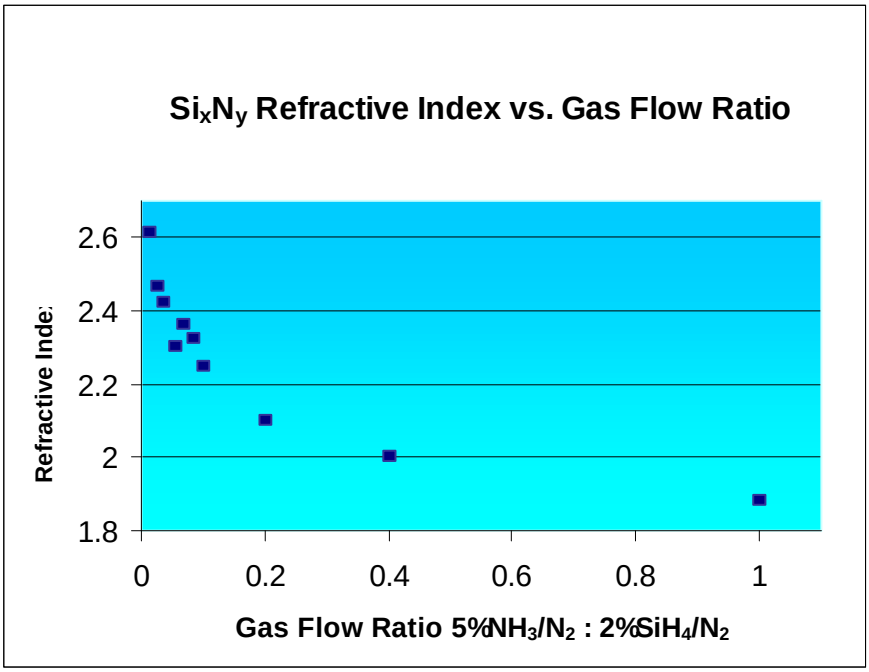

Fig. 5.

Optical Properties Measurements and Results for SiO_x and SiO_xN_y films

Our SiO_x films were deposited onto BK7 glass and silicon substrates to be measured in a similar manner as Si_xN_y films were. The films were deposited for 50 minutes, varying the gas flow ratio of N_2O to 2%SiH_4/N_2 from 0.25 to 10. We first measured the thicknesses of the films using the SEM to obtain a plot of deposition rate versus gas flow ratio similar to that for Si_xN_y. The results are shown in Figure 6. The gas flow ratio of 1 gave a maximum deposition rate of 48.1nm/min.

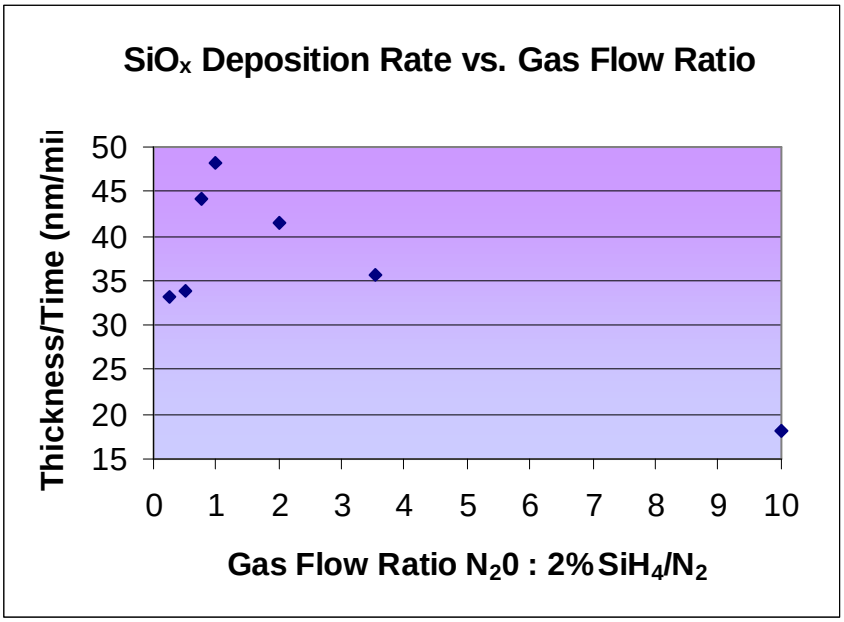

Fig 6.

For SiO_x, we had the opposite problem to that which we encountered with Si_xN_y films; the measurements for refractive index using the ellipsometer were trustworthy, while the data analysis using the PE and its software would not give an accurate fit. Hence we relied on the ellipsometric data for our values of n in this case. I formed a plot of refractive index versus gas ratio, shown in Figure 7. A maximum refractive index of 1.472 was observed when the gas ratio was 2.

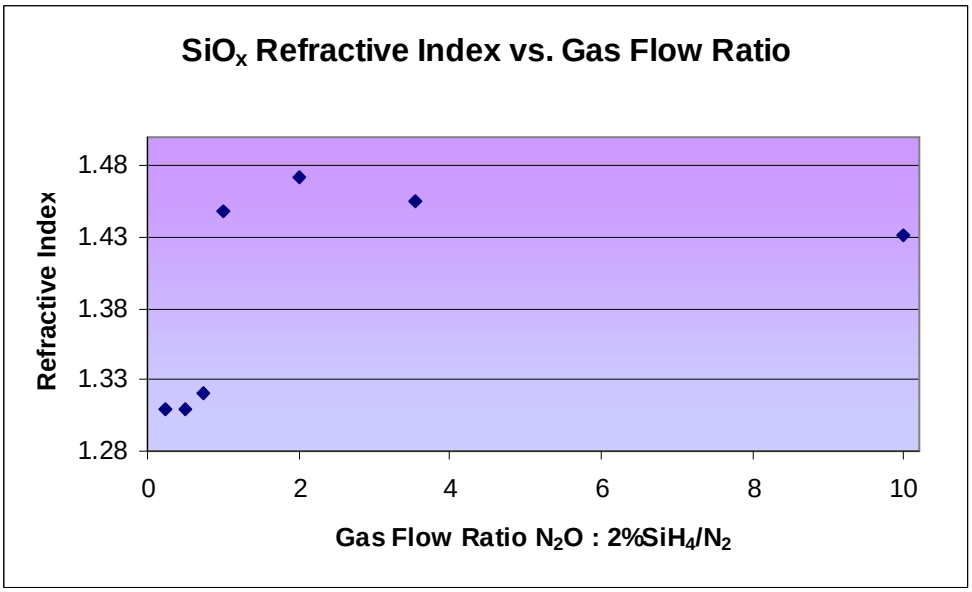

Fig. 7

Finally we sought to investigate properties of SiO_xN_y films, the original goal of our project. SiO_xN_y films require three gases in plasma for deposition: N_2O, 5% NH_3/N_2, and 2%SiH_4/N_2. We chose to hold constant the original values for gas flow rates of N_2O and SiH_4/N_2 at 800 and 1420sccm respectively, while varying the flow rate of NH_3/N_2 from 20 to 80sccm. The thicknesses were measured on the SEM and a plot of deposition rate versus gas flow ratio was obtained as shown in Figure 8. There is not much of a trend between deposition rate and gas flow ratio for these SiO_xN_y films. Due to time constraints, only four films were measured and their ratios only differed by about 2%; perhaps more films would show a direct relationship between these two parameters. Our measurements of the refractive index on both the ellipsometer and the PE were not very successful as well. Neither software could obtain a fit that matched the spectrum with substantial accuracy.

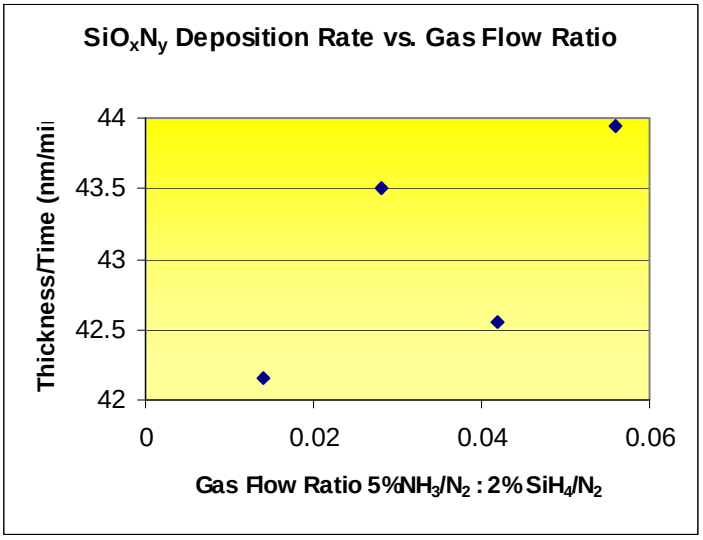

Fig. 8

Conclusion

Our investigation of Si_xN_y, SiO_x, and SiO_xN_y films finished with most of our

experimental goals accomplished. We found the gas ratios for Si_xN_y and SiO_x films that would yield maximum deposition rates. These maximums construct films with optimal density consistency; thus we have found the rates for the best quality films. We also found direct relationships between refractive index and gas ratio for Si_xN_y and SiO_x films. The relationship is useful for making predictions of a gas ratio to use in order to obtain a desired refractive index. While refractive index and gas ratio optimums for SiO_xN_y films remain to be discovered, we created the films and opened doors for further investigation in other laboratories.

In addition to achieving our personal goals, the experiment also provided useful information for other scientists working on real-world applications of the films. Video camera manufacturers, for example, may find our data useful when constructing anti-reflective coatings; we have already found thicknesses, gas ratios, and refractive indexes of films that may match the necessities of their devices.

Given more time, I would have further explored the properties of these films and searched for explanations to our problems with SiO_x and SiO_xN_y spectra. This would require measurements of luminescence in all three types of films in order to see whether regions of high density formed due to silicon clustering. Additionally, I would have liked to observe the chemical structure of the films to determine the molecular bonding and other subatomic phenomena that may have caused our SiO_x and SiO_xN_y spectra to be so noisy. Perhaps REU students could pursue these accomplishments in years to come.

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