

Characterization of thin-film amorphous semiconductors using spectroscopic ellipsometry

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Abstract

Spectroscopic ellipsometry (SE) has been used to routinely characterize amorphous silicon nitride and diamond thin films. Since SE measurements do not yield quantities of interest directly, the SE data must first be fit to a model to obtain useful parameters such as film thickness and optical functions. Recently, we have developed the Tauc-Lorentz (TL) model for the optical functions of amorphous materials [*Appl. Phys. Lett.* **69**, 371-373, 2137 (1996).], which has been very useful in interpreting these SE results. A 4-parameter model is usually sufficient to describe the optical functions of the thin film to the accuracy of the ellipsometer. One of these parameters, the band gap E_g , correlates with other mechanical and chemical properties of the film, such as the silicon-to-nitrogen ratio in silicon nitride films, and to the sp^3 -bonded carbon fraction and the hardness of amorphous carbon films.

I. Introduction

Spectroscopic ellipsometry (SE) has been used for several years as a premier tool for the analysis of thin films.¹ The technique is sensitive to many quantities of interest to the film grower, such as film thickness, surface roughness, interface roughness, and the optical properties of the thin films and the substrate. However, the data from an SE measurement is not useful by itself, but must be compared with an appropriate model in order to extract the useful information.² In the process of this modeling, the number of layers must be selected and the optical functions of each layer must be determined. If the optical functions of the layer or the substrate are well known, then tabulated data can be used for the optical functions of materials, but for materials with unknown optical functions, a parameterizable model must be employed.

Many materials examined by spectroscopic ellipsometry are amorphous. If the band gap of the amorphous material is significantly higher than the highest energy sampled by the ellipsometer, the Sellmeier model is usually sufficient to parameterize the optical functions of the thin film. However, if the band gap of the amorphous thin film is within the spectral range of the ellipsometer, the Sellmeier model is inadequate.

There have been several attempts to model the optical functions of amorphous materials.³⁻⁷ In all cases, the model uses 5 or more parameters to calculate the real and imaginary parts of the complex dielectric function as a function of wavelength. If the wavelength of interest is restricted to a range of wavelengths, then the requirements are somewhat less stringent than are the requirements for a more general model. For example, the Sellmeier model, mentioned above, can often be used in the transparent region of the material. Many of the models of refs. 3-7 claim to be Kramers-Kronig

consistent; which implies that the models must approach reasonable limits as the photon energy goes to 0 and to infinity. Of course, any model used to interpret experimental results must fit real data; for spectroscopic ellipsometry measurements, this is a particularly stringent requirement, since SE measurements are generally very accurate.

Recently, we have developed the Tauc-Lorentz (TL) model to parameterize the optical functions of amorphous materials.⁸ This model has reasonable values at the limits of the spectrum, is Kramers-Kronig consistent, and fits real data within the experimental error of the data. Furthermore, as we will show in this paper, many of the fitted parameters of the TL model can be correlated with other measured quantities of the material. We have studied tetrahedrally coordinated amorphous carbon^{9,10} (ta-C) and hydrogenated silicon nitride^{11,12} ($\text{Si}_x\text{N}_y\text{:H}$) extensively, and have been able to correlate some of the parameters associated with the Tauc-Lorentz model with parameters such as the ratio of sp^2 -bonded carbon to sp^3 -bonded carbon, the hardness of the films, and the silicon to nitrogen ratio in the $\text{Si}_x\text{N}_y\text{:H}$ films.

II. Tauc-Lorentz Model

The Tauc-Lorentz model uses the Tauc expression for the imaginary part of the dielectric function near the band edge:^{13,14}

$$\epsilon_2(E) = A_T \frac{(E - E_g)^2}{E^2} \Theta(E - E_g) \quad (1)$$

where E_g is the band gap of the material and Θ is the Heaviside Theta function, where $\Theta(E < 0) = 0$ and $\Theta(E \geq 0) = 1$. The traditional application of this expression has been to fit optical transmission data near the band gap, where the real part of the dielectric function

is assumed to be constant. Eq. 1 has been used very successfully for decades and on many different amorphous semiconductors. However, Eq. 1 is only an empirical relation, since there is no generally acceptable theoretical explanation.¹⁵

The Tauc-Lorentz (TL) expression⁸ for the imaginary part of the complex dielectric function is obtained by multiplying Eq. 1 by the complex dielectric function for a Lorentz oscillator. In this case, we get

$$\varepsilon_2(E) = \frac{AE_o\Gamma(E - E_g)^2}{E[(E^2 - E_o^2)^2 + \Gamma^2 E^2]} \Theta(E - E_g). \quad (2)$$

This expression has 4 parameters: the band gap E_g , the peak in the joint density of states E_o , the broadening parameter Γ , and the prefactor A , which includes the optical transition matrix elements. Implicit within this model is that the TL expression is only valid for interband transitions. The dielectric response from infrared transitions, Urbach tail effects and core transitions are not included in Eq. 2. Obviously, the TL expression is also an empirical model. Not only is the Tauc expression (Eq. 1) empirical, but also the Lorentz oscillator expression is used here to approximate a joint density of states multiplied by an average transition probability matrix element.

The real part of the TL dielectric function is obtained by performing a Kramers-Kronig integration of $\varepsilon_2(E)$:

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi, \quad (3)$$

where the P stands for the Cauchy principal part of the integral and an additional parameter $\varepsilon_1(\infty)$ has been included. Normally, $\varepsilon_1(\infty) = 1$, but it can be greater than 1 if

there is a significant optical transition at an energy greater than is sampled by the ellipsometer. This integral can be evaluated exactly, but the expression is long (see ref. 8).

Although the TL expression (Eqs. 2 and 3) is empirical, it does satisfy the major criteria for models of dielectric functions;

- 1) The TL expression is consistent with known physical phenomena, within the limitations of the model. At large E , the $\epsilon_2(E)$ of the TL model $\rightarrow 0$ as $1/E^3$. This is consistent with observed behavior in the x-ray and γ -ray regime, where it is known that the absorption coefficient is very small. Furthermore, $\epsilon_2(E) = 0$ below E_g . The only mechanisms that give a non-zero value of $\epsilon_2(E)$ below the band gap are the mechanisms that are explicitly ignored in the TL model, such as Urbach tail absorption and vibrational absorption in the infrared.
- 2) The TL expression is Kramers-Kronig consistent, in that $\epsilon_1(E)$ is determined by Kramers-Kronig integration. This implies that the integration of Eq. 3 must converge, which requires that $\epsilon_2(E)$ must approach 0 at least as fast as $1/E^2$. As mentioned above, $\epsilon_2(E) \rightarrow 0$ as $1/E^3$.
- 3) Finally, the TL expression has been successfully used to fit hundreds of SE measurements of amorphous films in our laboratory. A sampling of these will be discussed below.

III. An example: a-Si_xN_y:H

Figure 1 shows a plot of the real and imaginary parts of ρ determined by 2-modulator generalized ellipsometry (2-MGE)¹⁶ for a silicon nitride film grown on oxidized silicon using PE-CVD. The SE data is expressed in the ρ representation, which is defined by

$$\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta} = \frac{C + iS}{1 + N}, \quad (4)$$

where r_p (r_s) is the complex reflection coefficient for light polarized parallel (perpendicular) to the plane of incidence. The angle ψ and Δ are the standard ellipsometric angles, and $N = \cos(2\psi)$, $S = \sin(2\psi)\sin(\Delta)$, and $C = \sin(2\psi)\cos(\Delta)$ are the associated ellipsometry parameters.

The solid lines in Figs. 1a and 1b are the best fit to the data using a 9-parameter model consisting of four layers. The top layer is roughness where the optical functions are determined using the Bruggeman effective medium approximation¹⁷ consisting of 50% voids and 50% silicon nitride. The second layer (a-Si_xN_y:H) is approximated using the 4-parameter TL expression given above, where $\epsilon_1(\infty)$ is set to 1. The third layer (a-SiO₂) is parameterized using the Sellmeier expression

$$\epsilon_1(\lambda) = 1 + \frac{A_S \lambda^2}{\lambda^2 - \lambda_o^2}, \quad \epsilon_2(\lambda) = 0 \quad (5)$$

where A_S and λ_o are treated as fitting parameters. The substrate is silicon where the optical functions of ref. 18 are used. Nine parameters (see Table I) are varied to obtain the best fit as measured by the χ^2 “goodness of fit” criterion. The fitting procedure resulted in a $\chi^2 = 0.64$, indicating that the model fits the data. The errors shown in Table I are the correlated errors as determined by the Levenberg-Marquardt algorithm. The

only perceptible parts of the spectrum where the fit appears to be poor are near peaks in $\text{Re}(\rho)$ and discontinuities in $\text{Im}(\rho)$. Actually, the error at these points is quite large, due to very small errors in the wavelength being sampled by the monochromator. Since the errors of these few points is quite large, the fitting algorithm will weigh them very little.

With a nine-parameter fit, one must be concerned about correlations between the fitted parameters. This is monitored by calculating the cross-correlation coefficients, and by calculating the correlated errors of the fitted parameters. As can be seen from Table I, none of the correlated errors is very large, indicating that this procedure determines these nine parameters very well. The parameters from the TL fit can then be used to calculate the refractive index and extinction coefficient, as discussed below.

In some cases, the parameters A , E_o , and Γ can be highly correlated, particularly if the band gap of the material is greater than the highest energy measured using the SE. However, it is possible to determine the spectroscopic refractive indices reasonably accurately, even when the correlations between A , E_o , and Γ are large, but the calculation of the error limits must use the cross correlation coefficients. In this case, the refractive indices of the two layers are determined to ± 0.001 - 0.002 .

IV. Correlations with other measured parameters

The fitting procedure described above gives very accurate values of film thicknesses as well as accurate spectroscopic values of the refractive index and extinction coefficient. Furthermore, the band gap obtained from the fitting procedure is often correlated with other parameters of the film that relate directly to the quality of the film. In this section, we will discuss these correlations for two types of thin films: tetrahedrally coordinated

amorphous diamond (ta-C) and amorphous silicon nitride (SiN). Both families of amorphous materials result in a wide variety of chemical, mechanical, and optical film properties that depend on deposition conditions.

A. Tetrahedrally coordinated amorphous diamond

The tetrahedrally coordinated amorphous diamond (ta-C) films were made by laser ablation and therefore will not contain a significant amount of hydrogen. Although carbon is the only major atomic species present in the films, each carbon atom can be either sp^2 -bonded (graphitic-like) or sp^3 -bonded (diamond-like). The fraction of sp^3 -bonded carbon atoms will have a dramatic affect on many of the mechanical, electrical, and optical properties of the film. A wide range of ta-C film properties can be obtained using pulsed laser ablation, and these properties will depend primarily on parameters such as the average kinetic energy of the plume, the direction of the ablated species, and the background gas.

Figure 2 shows the spectroscopic refractive index and extinction coefficient for a ta-C film grown on silicon at several different points on the sample. Since the films are made using laser ablation, the film will have a non-uniform thickness. Furthermore, the properties of the film may be a function of the position of the film, since the impingement direction and kinetic energy of the deposited species will depend upon the angle from the plume centerline. The thickest part of the film corresponds to the normal to the plume, which also corresponds to the highest band gap. As one goes away from this part of the film, the thickness, as well as the band gap, gets smaller.

Hardness and bulk modulus measurements were also made on this film at the same places where spectroscopic ellipsometry measurements were made. These results are shown in Fig. 3. Clearly, the parts of the film where the band gap was the highest corresponds to the parts of the film where the hardness and modulus were the highest.

Figure 4 shows the sp^3 fraction, plasmon peak energy (both determined from EELS measurements), and TL band gap determined by SE plotted versus the average kinetic energy of the plume. The highest percentage of sp^3 bonds (~75%) occur near 90 eV kinetic energy. Similarly, ta-C films made at this energy also have the highest band gap.

B. Silicon nitride

The SiN films were grown using plasma-enhanced chemical vapor deposition (PE CVD), where silicon is supplied by silane (SiH_4 or Si_2H_6) gas. Nitrogen is introduced either as atomic nitrogen (N_2 must first be disassociated before it can be incorporated into the film in any significant quantities). These films can contain significant amounts of hydrogen and the Si to N ratio can vary significantly. In some cases, the films can contain oxygen, which also dramatically affects the optical functions.

Figure 5 shows the refractive index and extinction coefficient of a series of SiN films labeled by the TL energy gap determined from fits to the SE data. The nitrogen gas flow was varied to obtain the films with various properties. Three of the films were grown on silicon substrates, and three other films were grown on oxidized silicon (indicated by the "Ox" in Fig. 5), where the oxide thickness was ~300 nm.

Rutherford backscattering (RBS) and Hydrogen forward scattering (HFS) experiments were also performed on these samples by Charles Evans and Associates to determine film

thicknesses, and the concentrations of the elements Si, N, O, and H. From this data, the Si/N ratio could be determined to $\sim\pm 3\%$. Figure 6 shows the Si/N ratio for these films plotted versus the TL band gap determined from fits to the SE data, as well as the refractive indices of the films at 600 nm. The films grown on oxidized silicon (bare silicon) are indicated by the open (filled) data points in Fig. 6. The RBS measurements indicated that there was less than 4% oxygen in these films, but that there was $\sim 8\%$ hydrogen in all the films.

V. Discussion and Conclusions

In this paper, spectroscopic ellipsometry data from a variety of silicon nitride and amorphous carbon thin films have been fit using the Tauc-Lorentz model. The reduced χ^2 obtained from the fitting procedure were all in the range of 0.5 to 1.5, stating that the models do fit the data within the error limits of the data. The models used were the simplest possible given the structures and the parameterizations used. That is, no thickness-dependent refractive indices or effective medium approximation interface layers were needed to obtain good fits to the data. In most cases, only 4 parameters in the Tauc-Lorentz model were needed (E_g , A , E_o , and Γ), and $\epsilon(\infty)$ could be set to 1. Since spectroscopic ellipsometry generally produces very accurate data, this is a very good indication that the Tauc-Lorentz model does work very well in parameterizing the refractive index and extinction coefficient of these films.

The band gap parameter from the Tauc-Lorentz model E_g is particularly useful, in that it can be correlated with chemical and mechanical properties of the films. For the case of ta-C films, E_g correlates with the bulk modulus and the hardness of the films, with higher

values of E_g corresponding to harder films. The quantity E_g also correlates with the fraction of sp^3 -bonded carbon atoms, with higher values of E_g corresponding to higher values of the sp^3 fraction. These two observations are consistent, since the higher the sp^3 fraction, the more diamond-like the film, and the harder it will be.

Similar observations can be made about the silicon nitride films. It has been shown that E_g correlates with the silicon to nitrogen ratio, where stoichiometric silicon nitride corresponds to an $E_g \sim 4.4$ eV. Silicon-rich films have lower values of E_g , but higher values of the refractive index; this has also been observed in other work,^{11,12} where the silicon nitride films were optimized for antireflection coating applications. Oxygen contamination plays an important role in silicon nitride films, where the addition of oxygen increases the value of E_g and lowers the value of n .

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Table I

Results of the fitting procedure to the data shown in Fig. 1. The χ^2 of the fit is 0.64.

Parameter	Value
Roughness thickness (nm)	2.8±0.5
SiN thickness (nm)	232.5±0.8
SiO ₂ thickness (nm)	295.7±1.9
SiN band gap (E_g eV)	3.76±0.05
SiN E_o (eV)	9.2±0.1
SiN Γ (eV)	3.7±0.5
SiN A	100.4±4.1
SiO ₂ A_s	1.104±0.016
SiO ₂ λ_o (nm)	91.9±4.1

Figure Captions

1. The real and imaginary parts of the spectroscopic ellipsometry data expressed in the ρ representation. The straight line is the best fit to the data, with a $\chi^2 = 0.64$. The model for the sample surface is shown in the upper left hand corner.
2. Refractive index and extinction coefficients of a tetrahedrally coordinated amorphous carbon film grown by pulsed laser ablation. The 4 spectra shown correspond to different points on the sample surface, where the highest band gap energy (E_g) corresponds to both the center and the thickest part of the film.
3. The hardness and modulus of the film plotted in Fig. 2 plotted versus the band gap of the film at that position.
4. The sp^3 fraction, the plasma energy position (determined from EELS measurements), and the band gap determined using spectroscopic ellipsometry measurements plotted versus the average kinetic energy of the plume.
5. Refractive index and extinction coefficient plotted versus photon energy for 6 SiN films. Three of the films (labeled Ox) were grown on ~ 300 nm SiO_2 , while the remaining films were grown on a silicon substrate. The curves are labeled according to the band gap E_g as determined by the TL fit to the SE data. The data and fit for the 3.76 Ox film is shown in Fig. 1.
6. Silicon to Nitrogen ratio for the 6 SiN films plotted versus photon energy (top), and the refractive index at 600 nm plotted versus photon energy (bottom). The open data points represent films grown on ~ 300 nm SiO_2 , while the filled data points represent films grown on a silicon substrate.

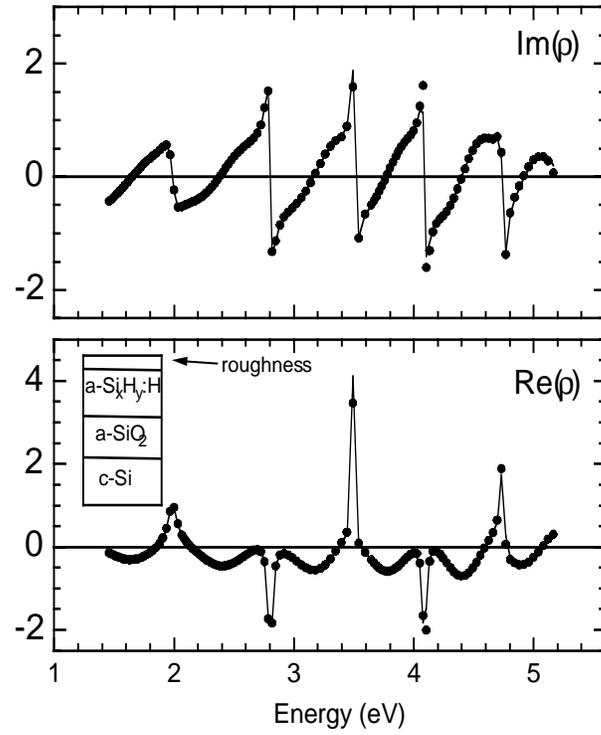


Figure 1 Jellison et. al.

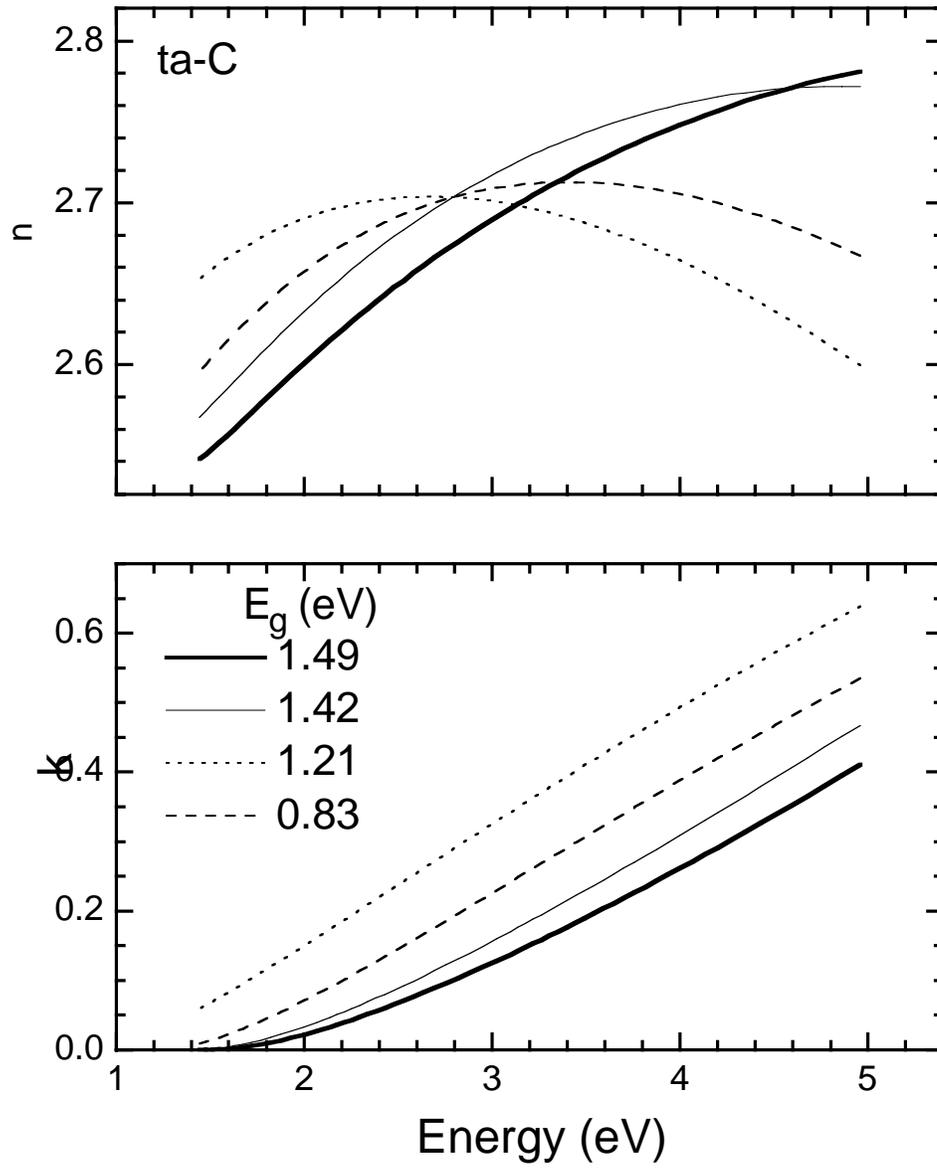


Figure 2 Jellison et. al.

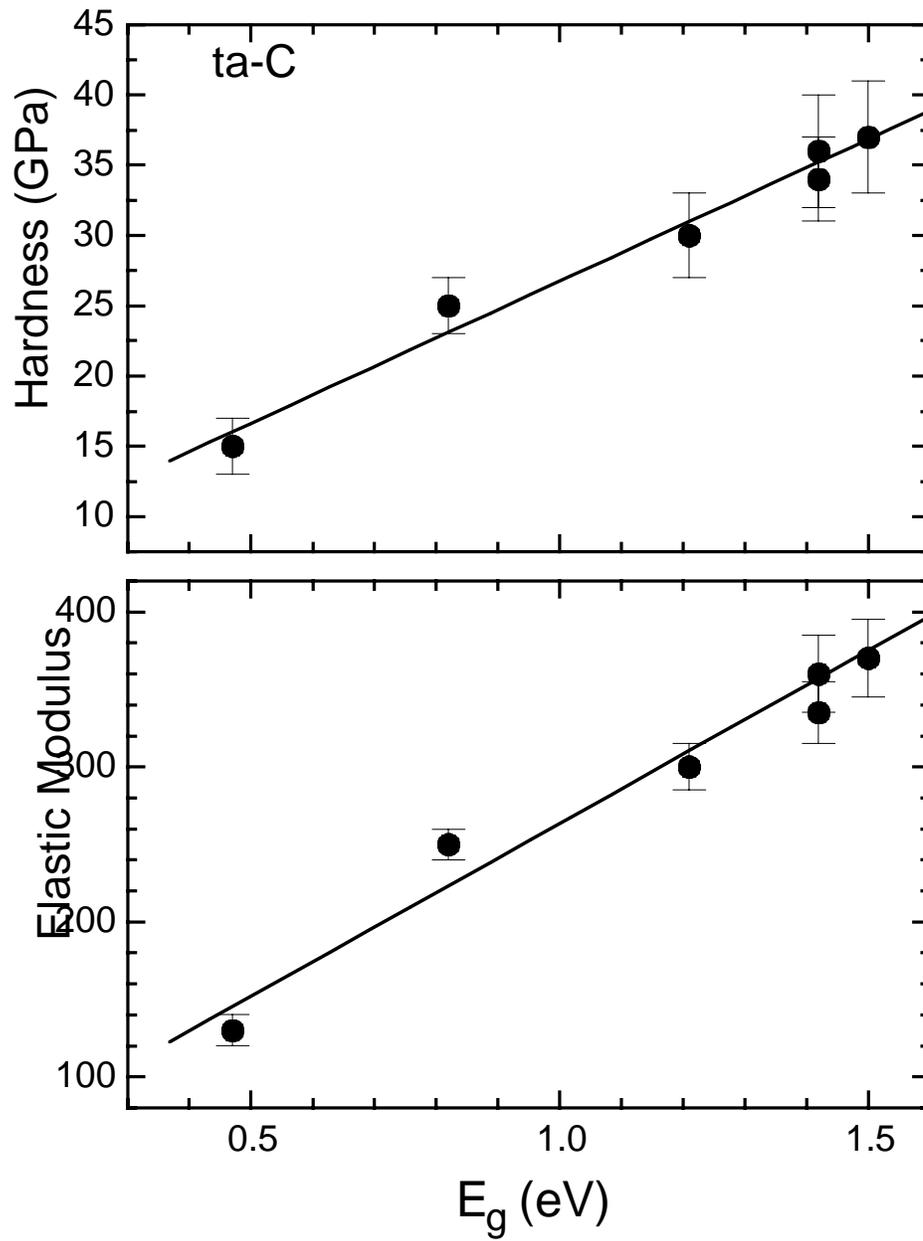


Figure 3 Jellison et. al.

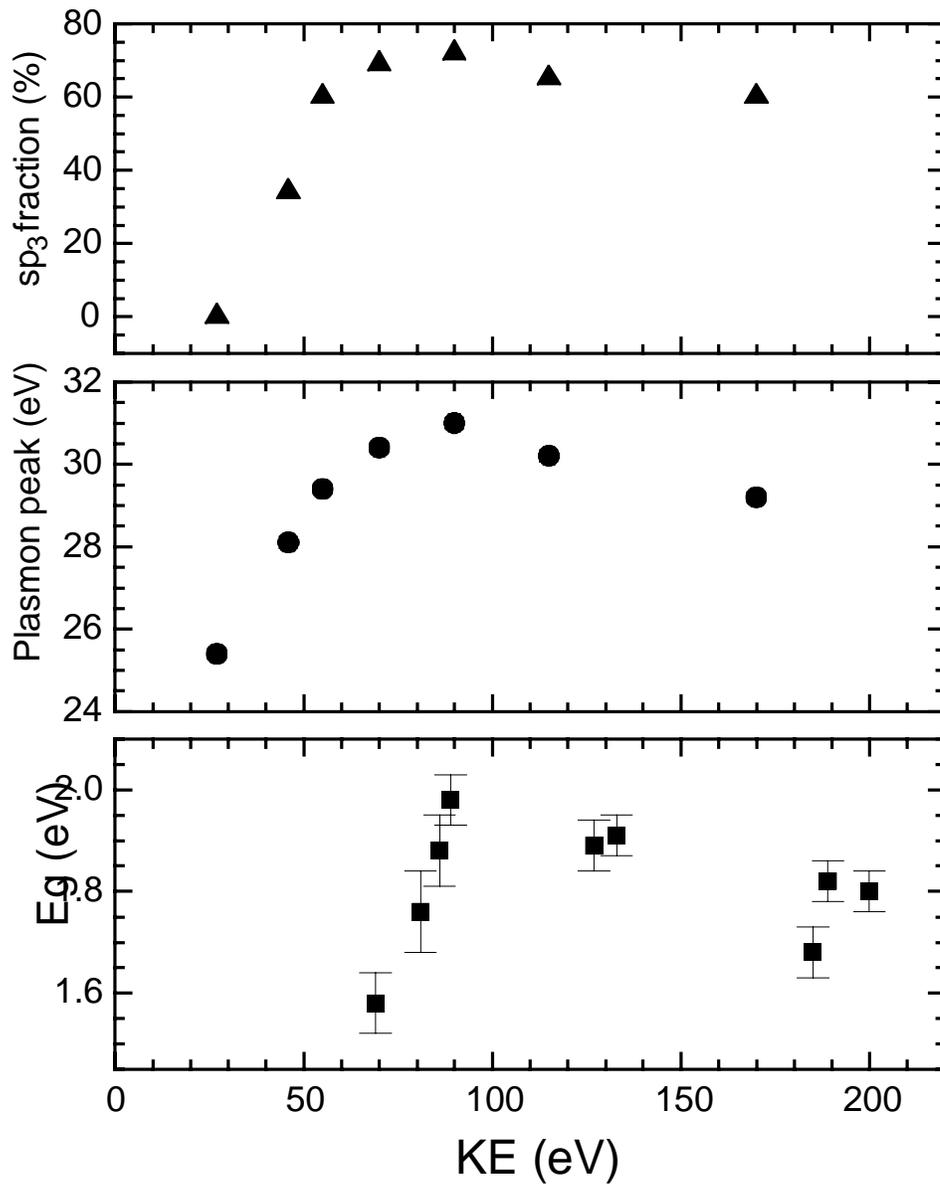


Figure 4 Jellison et. al.

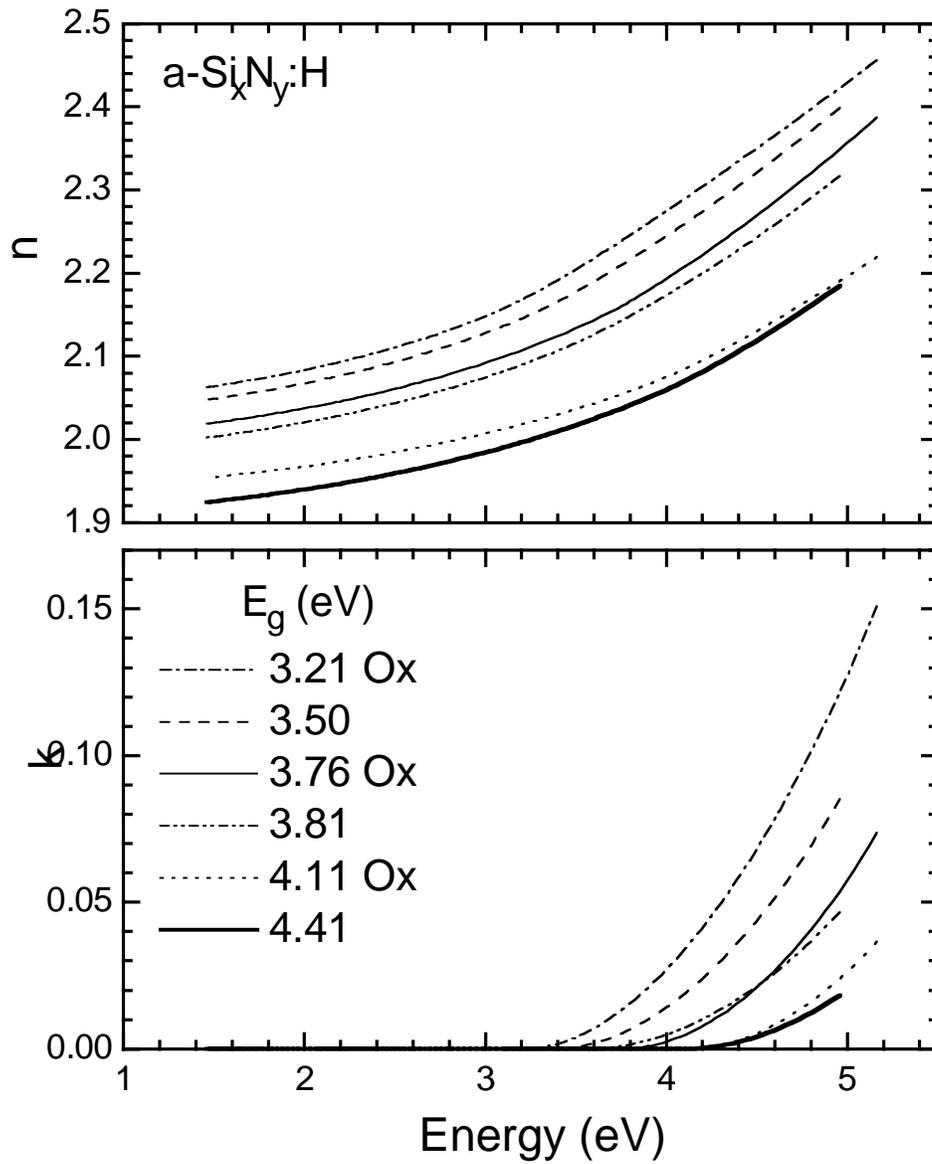


Figure 5 Jellison et. al.

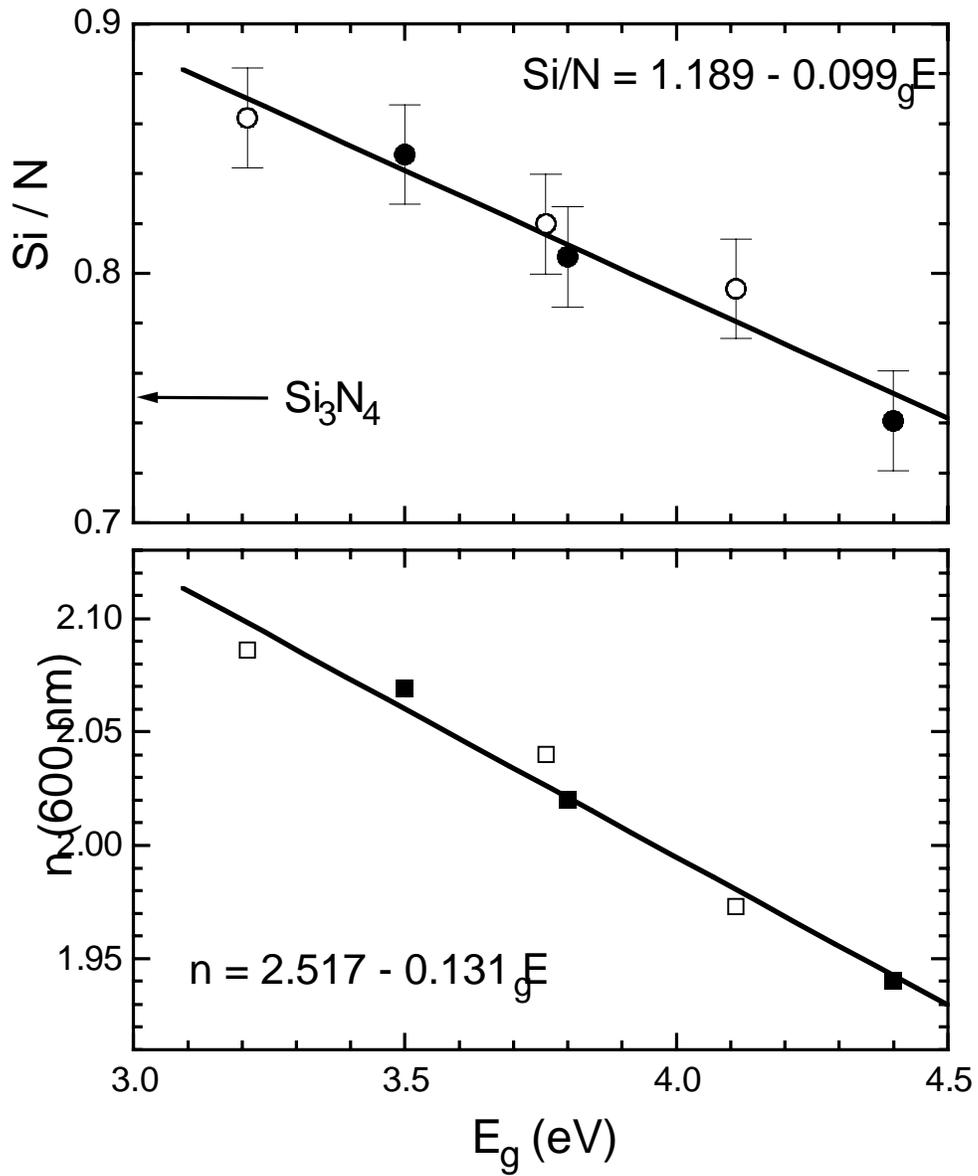


Figure 6 Jellison et. al.