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Effects of Substrate Temperature on Properties of a-SiN_x:H Films

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Abstract

Hydrogenated amorphous silicon nitride films were prepared in an rf glow-discharge system by the decomposition of silane + nitrogen gas mixture at various substrate temperatures. The effects of substrate temperature on the electrical and optical properties of the films have been studied.

Key Words: A. Hydrogenated amorphous silicon nitride; B. Substrate temperature; C. Dark conductivity; D. Photoconductivity; E. Optical gap.

1. Introduction

The use of hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon nitride (a-SiN_x:H) thin films in semiconductor technology has prompted a number of investigations concerning their electrical and optical characteristics. Amorphous silicon nitride films prepared by plasma deposition (PD) are increasingly being used in the fabrication of solid-state devices. Owing to low processing temperatures and good dielectric properties, PD silicon nitride films have been used as a gate insulator of amorphous silicon field-effect transistors (a-Si FET's)[1]. The electrical and optical properties of a-SiN_x:H films are strongly dependent on the preparation conditions such as substrate temperature, rf power density, gas ratio and gas flow rate etc.

In this study, dark conductivity (σ_d), photoconductivity (σ_{ph}), optical absorption coefficient (α) and refractive index (n) of a set of a-SiN_x:H films, which were prepared by glow-discharge deposition of SiH₄+N₂ gas mixture in a capacitively coupled rf plasma reactor, have been investigated as a function of substrate temperature, T_s. The effects of the substrate temperature on the electrical and optical properties have been studied.

Optical absorption coefficient can be determined by Constant Photocurrent Method (CPM) for energies lower than the optical gap [2]. In this method, the absorption coefficient $\alpha(h\nu)$ is inversely proportional to the incident photon flux $F(h\nu)$ via

$$\alpha_{CPM}(h\nu) \approx \frac{\text{constant}}{F(h\nu)}. \quad (1)$$

This is obtained based on the assumptions of one dominating recombination center and the existence of only one type of carrier when keeping the photocurrent constant by adjusting the incident photon flux. The film thickness d , refractive index $n(\lambda)$, and absorption coefficient $\alpha(h\nu)$ for the energies higher than the optical gap can be determined by using the optical transmission spectra with a method proposed by Swanepoel [3, 4].

2. Swanepoel Method

A thin film on a transparent substrate is shown in Figure 1. In the figure d , n , α and T denote the film thickness, refractive index, the absorption coefficient and the transmission, respectively. The transparent substrate has a thickness several orders of magnitude larger than d and has index s and absorption coefficient $\alpha_s=0$.

The index of refraction for air is taken to be $n_0=1$. The transmission spectrum can be roughly be divided into four regions. In the transparent region ($\alpha=0$) the transmission is determined by n and s through multiple reflections. In the region of weak absorption α is small and the transmission begins to decrease. In the medium absorption region α is large and transmission decrease mainly due to the effect of α . In the region of strong absorption the transmission decreases drastically due almost exclusively to the influence of α .

If the thickness d is uniform, interference effects give rise to the spectrum, shown by the full curve in Figure 2. These interference fringes can be used to calculate the optical constants of the film. The basic equation for interference fringes is

$$2nd = m\lambda, \quad (2)$$

where m is an integer for maxima and half integer for minima.

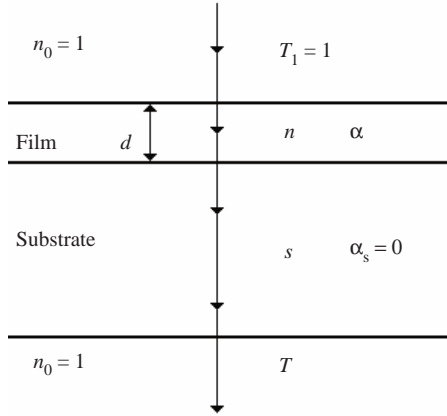


Figure 1. System of an absorbing thin film on thick finite transparent substrate.

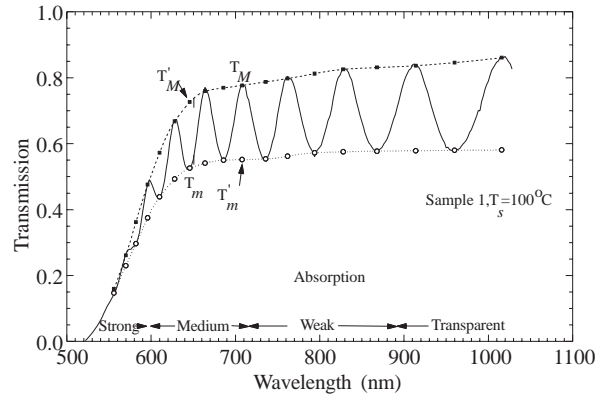


Figure 2. Measured optical transmission spectrum for the Sample 1 ($T_s=100^{\circ}\text{C}$).

The transmission T , for the case of Figure 2, is given as

$$T = T(n, x) = \frac{Ax}{B - Cx \cos \phi + Dx^2}, \quad (3)$$

Where

$$A = 16n^2s \quad (4a)$$

$$B = (n + 1)^3(n + s^2) \quad (4b)$$

$$C = 2(n^2 - 1)(n^2 - s^2) \quad (4c)$$

$$D = (n - 1)^3(n - s^2) \quad (4d)$$

$$\phi = \frac{4\pi nd}{\lambda} \quad (4e)$$

$$x = \exp(-\alpha d). \quad (4f)$$

If T_M and T_m are maximum and minimum values of the transmission and T_s is the maximum value of the transmission in the absence of the film, then substrate refractive index s , T_M and T_m are given by the following equations:

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2} \quad (5)$$

$$T_M = \frac{Ax}{B - Cx + Dx^2} \quad (6)$$

$$T_m = \frac{Ax}{B + Cx + Dx^2}. \quad (7)$$

The absorption coefficient α for the regions of medium absorption will be non-zero. From the Equations (6) and (7) we obtain an equation that is independent of x :

$$\frac{1}{T_M} - \frac{1}{T_m} = \frac{2C}{A}. \quad (8)$$

The method to determine the envelopes is based on the parabolic interpolation between three nearest adjacent maximum (T_M) or minimum (T_m) [3, 5]. For any λ , T_M has corresponding value T'_M and T_m has corresponding value T'_m . Substituting Equation (4) into (8) and solving for n yields

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \quad (9)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}.$$

If n_1 and n_2 are the refractive indices for two adjacent maxima (or minima) at λ_1 and λ_2 then the film thickness is given by

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}. \quad (10)$$

Once $n(\lambda)$ is known, all the constants in Equation (4) are known and x can be calculated. Both Equation (6) and (7) are quadratic equation in x that can be solved for x and the results simplified using Equation (5). Solving equation (6) gives

$$x = \frac{E_M - [E_M^2 - (n^2 - 1)^3(n^2 - s^4)]^{1/2}}{(n^2 - 1)(n - s^2)} \quad (11)$$

where

$$E_M = \frac{8n^2 s}{T_M} + (n^2 - 1)(n^2 - s^2).$$

$\alpha(h\nu)$ can be calculated from x and d using equation (4f).

3. Experimental Details

The hydrogenated amorphous silicon nitride films were prepared on Corning 7059 glass substrates by rf glow-discharge decomposition of $\text{SiH}_4 + \text{N}_2$ gas mixture. The nitrogen content in the samples were determined from the partial pressure of the constituent gases

$$r = \frac{[PN_2]}{[PN_2] + [PSiH_4]}. \quad (12)$$

The substrates temperature was kept at 100°C , 200°C , 300°C and 400°C for four samples. The nitrogen content was fixed at 0.1. Total pressure of the plasma chamber was held at 200 mTorr. Aluminium electrodes were evaporated onto the surface of the film to provide $0.1 \times 9.0 \text{ mm}^2$ gap cell for dark conductivity and photoconductivity measurements. Before the measurements of the dark conductivity and the photoconductivity, the samples were annealed in vacuum at 430 K for 1 hour to avoid the surface effects. The current in all experiments was measured with a Keithley 619 electrometer under the electric field 10^3 V/cm .

For the photoconductivity measurements a LED having emission band centered at 630 nm is placed above the gap cell. Measurements were carried out under the photon flux, $1.0 \times 10^{17} \text{ photons/cm}^2 \text{ s}$ and 430K-100K temperature range.

Optical transmission measurements were recorded in the spectral range 500-1000 nm using conventional spectrophotometer (Cary-5) and a home-made spectrophotometer with CVI-DK240 monochromator [6]. Figure 2 shows measured optical transmission spectrum for the Sample 1 ($T_s=100^\circ\text{C}$).

4. Experimental Results and Discussion

Figure 3 shows temperature dependence of the dark conductivity of a-SiN_x:H samples deposited at four different substrate temperatures. As seen in Figure 3, the temperature-dependent dark conductivity curves of all the samples was singly activated over the temperature range under investigation. It is well expressed by [6]

$$\sigma_d = \sigma_0 \exp(-E_a/kT), \quad (13)$$

where σ_0 , E_a , k and T were conductivity pre-exponential factor, activation energy, the Boltzmann constant and absolute temperature, respectively. The variation of the $\sigma_d(340\text{K})$ with substrate temperature T_s is given Table 1. The highest dark conductivity [$\sigma_d(340\text{K})$] occurs with Sample 3, prepared at 300°C T_s . Sample 2, which is prepared at 200°C , has the lowest dark conductivity [$\sigma_d(340\text{K})$]. The highest dark conductivity is about two orders of magnitude greater than the lowest dark conductivity.

For all samples, activation energy (E_a) with corresponding substrate temperature are given Table 1. While samples with substrate temperature of 100°C , 200°C and 400°C , have approximately the same activation energy ($\sim 1.0 \text{ eV}$), Sample 3 has a lower activation energy ($\sim 0.8 \text{ eV}$) with substrate temperature of 300°C .

The temperature dependence of the photoconductivity of the samples as a function of substrate temperature is shown in Figure 4. These samples can be classified into two groups: The first group is composed of Sample 1 and Sample 2 which are deposited lower substrate temperature (100°C and 200°C , respectively); the second group is composed of Samples 3 and 4, which are deposited with higher T_s (300°C and 400°C , respectively). At temperature above $\sim 200 \text{ K}$, it was observed that, for both group samples, the photoconductivity curves overlap. The photoconductivity of the second group samples is nearly two orders of magnitude higher than the first group samples. The photoconductivities of the samples significantly deviate from each other, as the temperature decreases. The magnitude of photoconductivities follow the same order as we observed for dark conductivities, as shown in Figure 3 and Figure 4.

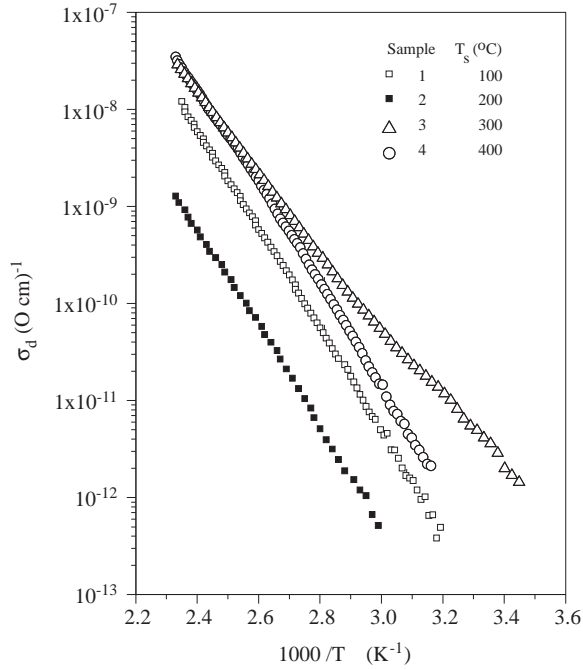


Figure 3. Temperature dependence of the dark conductivity as a function of substrate temperature.

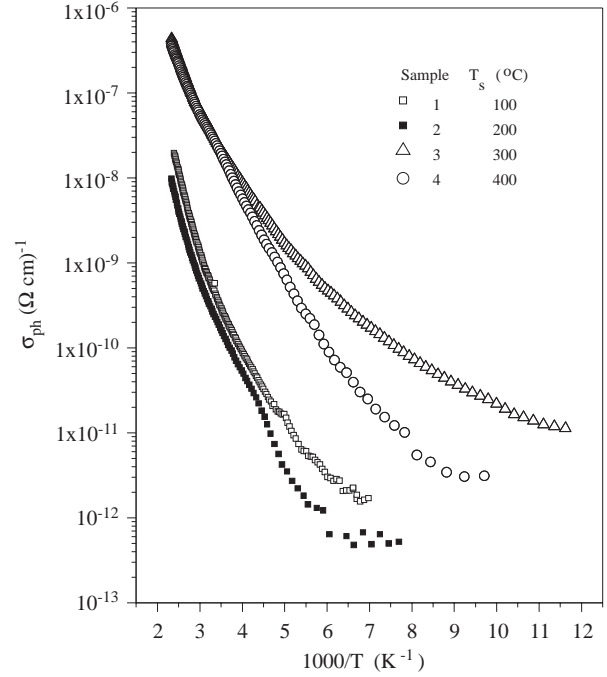


Figure 4. Temperature dependence of the photoconductivity as a function of substrate temperature.

In general, both the dark current and photoconductivities for samples of the second group prepared at high substrate temperature are observed to be greater than those for the first group samples prepared at low substrate temperature. However, σ_d and σ_{ph} are not systematically ordered as a function of temperature. Watanabe et al. [7] reported that both σ_d and σ_{ph} increase with increasing substrate temperature for the samples prepared under of $\text{SiH}_4 + \text{N}_2$, atmosphere.

The film thickness d , deposition rate dr , refractive index n and optical absorption coefficients α were determined from the optical transmission measurements using the method described by Swanepoel [3]. The Tauc gap E_g and Tauc slope B were also deduced by fitting the optical absorption coefficients to the relation [8, 9]

$$\sqrt{\alpha h\nu} = B(h\nu - E_g). \quad (14)$$

d , dr , n ($\lambda = 700$ nm), E_g and B of the samples are given in Table 1. Figure 5 shows the wavelength dependence of the refractive index of the samples. The value of n ($\lambda = 700$ nm) is nearly the same for the Sample 1, Sample 2 and Sample 3. Sample 4 has higher refractive index value than the other samples. The Tauc gap and the deposition rate of the samples are nearly independent of the substrate temperature, as seen in Table 1.

Table 1. Selected sample parameters for the a-SiN_x:H samples used in the experiment*

| Sample | r | T_s (°C) | d (μm) | dr ($\mu\text{m}/\text{h}$) | n (700 nm) | E_g (eV) | B ($\text{cm eV}^{-1/2}$) | E_a (eV) | $\sigma_d(340\text{K})$ (Ωcm) ⁻¹ |
|--------|-----|---------------|--------------------------|------------------------------------|--------------|---------------|----------------------------------|---------------|----------------------------------------------------------------|
| 1 | 0.1 | 100 | 2.03 | 0.41 | 2.32 | 1.87 | 397 | 1.07 | $1.01 \cdot 10^{-11}$ |
| 2 | 0.1 | 200 | 2.16 | 0.43 | 2.22 | 1.76 | 348 | 0.99 | $1.05 \cdot 10^{-12}$ |
| 3 | 0.1 | 300 | 2.05 | 0.41 | 2.30 | 1.84 | 263 | 0.79 | $8.58 \cdot 10^{-11}$ |
| 4 | 0.1 | 400 | 1.75 | 0.35 | 2.66 | 1.82 | 335 | 1.02 | $3.07 \cdot 10^{-11}$ |

* T_s , d , dr , n , E_g , B and $\sigma_d(340\text{K})$, are respectively, substrate temperature, film thickness, deposition rate, refractive index, Tauc gap, Tauc slope, activation energy and dark conductivity at 340K.

The variation of optical absorption coefficient α as a function of the photon energy, $h\nu$ is shown in Figure 6. It was observed that α is nearly independent of substrate temperature in the high energy range ($h\nu > 1.8\text{eV}$). The highest absorption coefficient occurs with Sample 1 which is prepared a substrate temperature of 100°C in the low energy range ($h\nu = 1.4\text{eV}$).

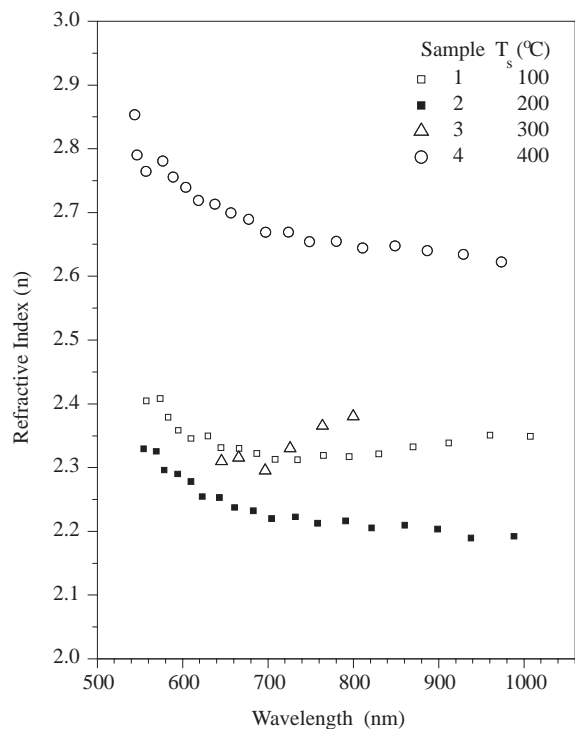


Figure 5. The refractive index as a function of the wavelength for various substrate temperature.

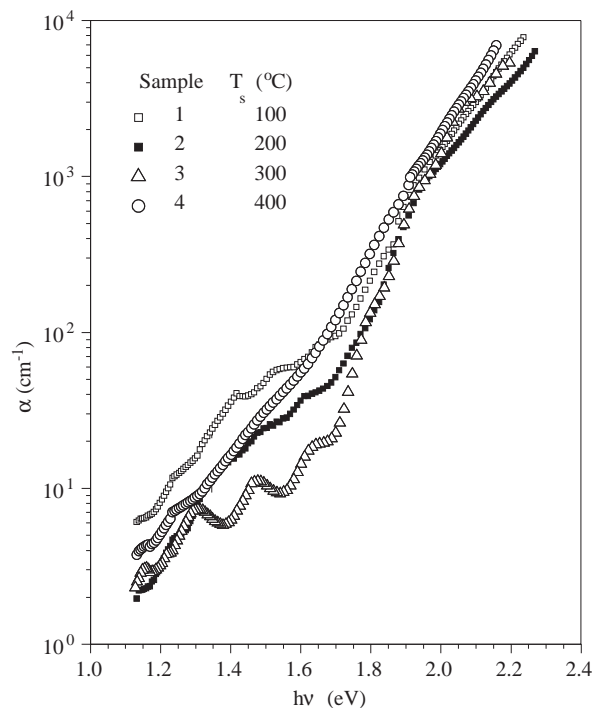


Figure 6. Optical absorption coefficient as obtained from CPM and optical transmission for four samples.

In summary, we have reported the effects of substrate temperature on the electrical and optical properties of the $a\text{-SiN}_x\text{:H}$ films deposited in an rf glow-discharge system. In conclusion:

- 1) Observations show that there is no systematic dependency of dark currents and photoconductivities on substrate temperature,
- 2) The deposition rate, the activation energy and optical gap are approximately independent of substrate temperature,
- 3) The highest refractive index occurs with the sample which is deposited at the highest substrate temperature and highest absorption coefficient occurs with the sample which is deposited at the lowest substrate temperature.

Acknowledgments

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