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The Temperature Dependence of Dark Conductivity in Hydrogenated Amorphous SiN_x Films

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Abstract

Thin film samples of hydrogenated amorphous silicon nitride with varying nitrogen content were prepared by conventional plasma deposition from a mixture of SiH_4 and NH_3. The dark conductivity (σ_d) of the films have been measured in the temperature range 420 K - 100 K. The conductivity is thermally activated with a single activation energy down to 250 K and conduction is dominated by electrons in extended states. A strong decrease is observed in σ_d when the nitrogen content is increased.

Key Words: A. Dark Conductivity; B. Activation energy; C. Pre-exponential factor D. Hydrogenated amorphous silicon nitride

1. Introduction

Hydrogenated amorphous silicon based alloys, such as a-$Si_{1-x}C_x{:}H$ and a-$SiN_x{:}H$, are important materials in electronic devices. The hydrogenated silicon-nitrogen alloys (a-$SiN_x{:}H$) can be prepared by sputtering silicon in an ammonia containing atmosphere by chemical vapour deposition (CVD) of SiH_4 - NH_3 gas mixtures at high temperatures or by plasma deposition (PD) from SiH_4 - NH_3 or $SiH_4 - N_2$ gas mixtures at lower temperatures. PD silicon nitride is used as the gate dielectric in a-$Si{:}H$ based thin film transistors (TFT) while CVD silicon nitride is used as a storage medium in metal-nitride-oxide-semiconductor (MNOS) devices [1].

The temperature dependence of the dark conductivity of amorphous silicon and its alloys can be written by a general expression of the form

$$\sigma_d = \sigma_{01}\exp\left(-\frac{E_1}{kT}\right) + \sigma_{02}\exp\left(-\frac{E_2}{kT}\right) + \sigma_{03}\exp\left(-\left(\frac{T_0}{T}\right)^{1/4}\right) \tag{1}$$

where the first term is due to conduction in extended states at the high temperatures. The activation energy,E_a(=E_1) is given by

$$E_a = E_C - E_F \tag{2}$$

where E_C defines the mobility edge in the conduction band of the amorphous semiconductor films and E_F is the energy of the fermi level in darkness. The second term dominant in the intermediate temperature region, represents electron transport in the band tails below E_C. The third term is the variable-range hopping conductivity at low temperatures derived by Mott [2].

In this study, the dark conductivity of the a-$SiN_x{:}H$ films, which are prepared by plasma deposition of SiH_4 and NH_3 gas mixtures in a capacitively coupled RFplasma reactor, have been investigated as a function of temperature. The influence of nitrogen ratio on the dark conductivity (σ_d), the activation energy (E_a) and the conductivity pre-exponential factor (σ_0) have also been studied.

2. Experimental Method

Films of $a\text{-}SiN_x{:}H$ used in this study were prepared at Hacettepe University by glow-discharge decomposition of SiH_4 - NH_3 gas mixtures in a capacitively coupled RF plasma reactor [3]. The films were deposited on Corning 7059 glass substrates which were kept at ~ 300°C and their thickness was ~ 1μm. The thickness of the film was determined from the optical transmission measurements using the method described by Swanepoel [3,4]. The other deposition parameters, the RF power and the gas pressure were 5 W and 200 mTorr, respectively. The flow rate of SiH_4 and NH_3 gases was controlled by a flowmeter and a needle valve. Evaporated Al electrodes separated by 100 μm were used for conductivity measurements. The current in all experiments was measured with a Keithley 619 electrometer under the electric field 10^3 V/cm in the temperature ranges of 420 K - 100 K.

In this study, the nitrogen concentration in the a-$SiN_x{:}H$ films has been given as the ratio of NH_3 in the SiH_4 - NH_3 gas mixture, and it is denoted by r. Therefore, the r ratio, which is defined as

$$r = \frac{[P_{NH_3}]}{[P_{NH_3}] + [P_{SiH_4}]} \tag{3}$$

has been taken as a deposition parameter and kept constant during a film preparation process.

3. Experimental Results and Discussion

Figure 1 illustrates temperature dependence of the dark conductivity of a-$SiN_x{:}H$ films corresponding to the r values shown. σ_d of the samples prepared with $r \leq 0.25$ was linear for temperatures in the range from 420 K to 250 K, indicating a well-defined activation energy for each sample.

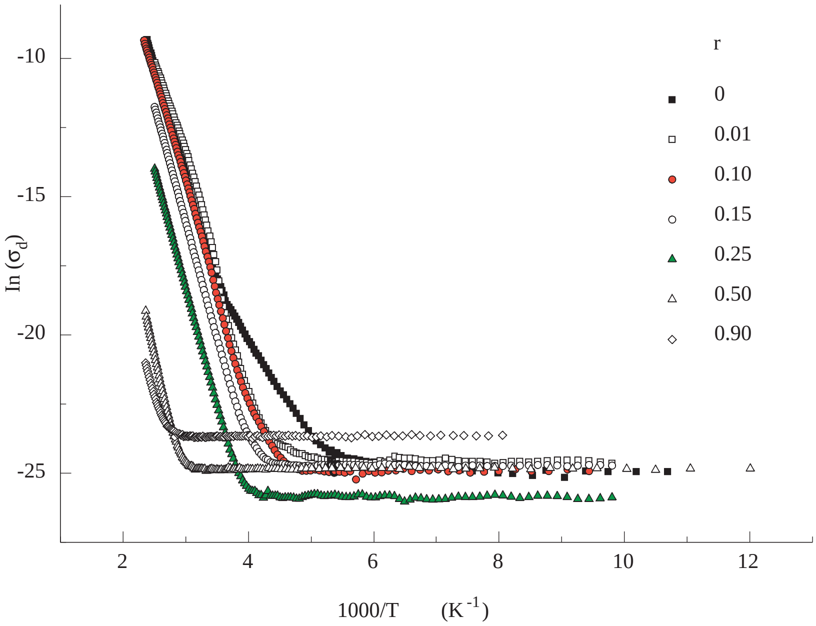

Figure 1. Temperature dependence of the dark conductivity for various nitrogen content.

The variation of the room-temperature conductivity with gas ratio r is given in Figure 2. As r is increased from zero the conductivity rises by nearly one order of magnitude and a maximum of $\sim 3.10^{-7}(\Omega.\mathrm{cm})^{-1}$ is reached at r=0.05. With a further increase in r, conductivity falls rapidly to $6.10^{-10}(\Omega.\mathrm{cm})^{-1}$ at r=0.25. The samples prepared with $r \geq$ 0.5 conductivity was independent on temperature and these samples became insulator.

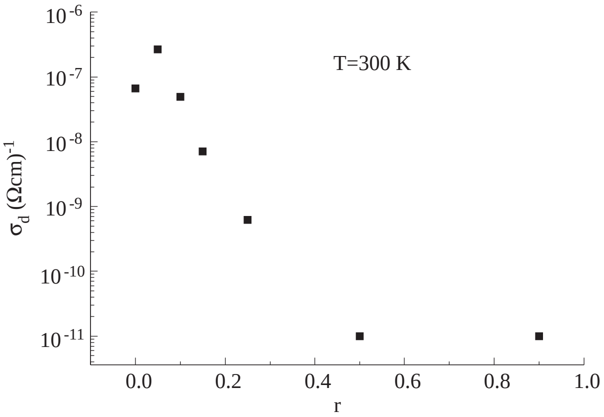

Figure 2. Room temperature dark conductivity as a function of the nitrogen ratio.

Figure 3 shows the dependence of the conductivity activation energy on gas ratio. E_a remains constant for values of r between 0 and 0.10. Above $r = 0.10$ the activation energy increases slowly.

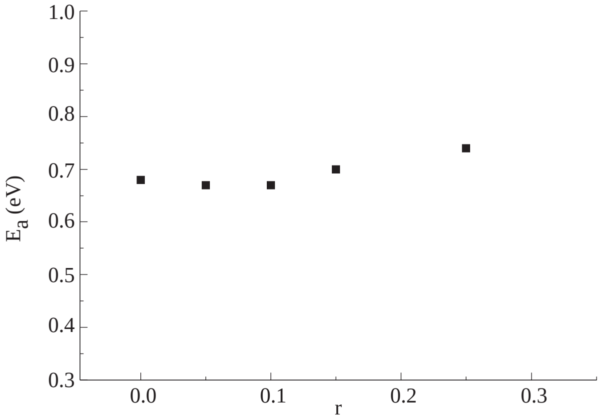

Figure 3. Activation energy for conduction as a function of the nitrogen ratio.

As shown in Table 1 the conductivity pre-exponential factor σ_0 ($=\sigma_{01}$) is roughly independent of gas ratio for $r \leq 0.10$ with $\sigma_0 \quad \sim 10^4$ $(\Omega\text{cm})^{-1}$. Above $r = 0.10$ the σ_0 decreases to $\sim 10^3$ $(\Omega\text{cm})^{-1}$. For all samples σ_d(T=300K), E_a and σ_0 values are given in Table 1.

Table 1. For all samples nitrogen ratios (r), pre-exponential factors (σ_0), activation energies (E_a) and room temperature conductivities (σ_d).

Sample	***r***	σ_0 **(Ωcm)$^{-1}$**	E_a **(eV)**	σ_d**(Ωcm)$^{-1}$ T=300K**
S112	0.00	1.63×10^4	0.68	6.62×10^{-8}
NH111	0.05	1.72×10^4	0.67	2.67×10^{-7}
NH122	0.10	1.38×10^4	0.67	4.90×10^{-8}
NH151	0.15	5.60×10^3	0.70	7.10×10^{-9}
NH131	0.25	1.64×10^3	0.74	6.22×10^{-10}
NH141	0.50	-	-	$\sim 10^{-11}$
NH83	0.90	-	-	$\sim 10^{-11}$

From these experimental results, we see that for the samples prepared with $r \leq 0.25$ except r=0 the conductivity is thermally activated with a single activation energy down to 250 K. We have found that E_a = 0.67- 0.74 eV in the high and intermediate temperature range. These results indicate that the conduction is dominated by electrons in extended states. Below 250 K, the dark conductivity is independent on temperature. Therefore, for a-SiN_x:H samples, only the first term in equation (1) is significant. This observation is consistent with the dark conductivity measured by Dunnett et al. [5], Herak et al. [6] and Pietruszko et al. [7].

Tolunay et al. [8] reported that the temperature dependence of dark conductivity in a-$Si_{1-x}C_x:H$ films shows two different conduction regimes. In the case of a-$SiN_x:H$ films only one activation energy region is observed in the same temperature range. In a-$Si_{1-x}C_x$:H the conductivity data breaks approximately at 350 K showing two different activation energy regions.

4. Conclusions

PD a-SiN_x:H films were prepared at 300°C from SiH_4 - NH_3 gas mixtures, and the dark conductivity of the films have been measured in the temperature range 420 K - 100 K. The experimental results obtained in this investigation are summarized as follows:

1) As nitrogen content r increases, a gradual increase in dark conductivity is observed for a very small nitrogen content (r=0.05). σ_d rapidly decreases with further increase in r.

2) Activation energy E_a is roughly independent of nitrogen content for $r \leq 0.10$

3) The conductivity pre-exponential factor σ_0 is independent of gas ratio for $r \leq 0.10$

4) Extended-state conduction predominates in the temperature range 250 K < T < 420 K with a single activation energy.

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