

Electronic Conduction in Annealed Sulfur-Doped a-Si:H Films

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In present work, the effect of annealing on dark and photo conductivity as well as the various causes of conduction mechanics in S doped amorphous hydrogenated silicon films (a-Si:H) is discussed. The variation of the dark conductivity as a function of temperature has been carried out on unannealed and annealed (annealed at an optimized temperature of 300 °C) thin film samples and the activation energy of dark conductivity of respective samples was also calculated at different temperatures. The Study concludes that at high temperatures, an activated type mechanism is responsible for conduction in the a-Si:H films.

Keywords: a-Si:H, Dark and Photoconductivity, Annealing effect, S doped a-Si:H.

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1. INTRODUCTION

An a-Si:H film has advantage over a crystalline silicon (c-Si) based film because of its property of absorbing more energy by a less quantity. Therefore, allowing materials to be deposited inexpensively at large areas. Hence, a-Si:H films is a promising material to use in variety of fields as photo sensors [1] photovoltaic solar cells [2], gas sensors[3], photo detectors [4], optical imaging[5], pixel detectors for high energy particles [6] and micro-electro-mechanical systems [7] to deposition for gate metal in thin film transistors [8] and so forth. However, at prolonged illumination there occurs a light induced degradation, known as Staebler Wronski Effect (SWE) [9]. This problem has been reported to overcome by applying a polymer coating on the film [10]. The SWE results in reduction of dark and photoconductivity. The phenomena of light induced metastable Si dangling bond defects (DB) confined its use in optoelectronic. Therefore, it is required to drive off the introduced gap states raised due to structural disorder and defects which either can be reduced by variation of hydrogen contents during preparation, or with post preparation treatment as thermal annealing and light soaking. The hydrogen incorporation is known to reduce the number of deep lying localized states due to dangling bonds but light soaking is also known to introduce dangling bond defect states. Many researchers have shown that reducing the dangling bond density reduces the recombination rate. However, there are two ways to decrease the dangling bond density; as discussed either by annealing or by doping/alloying with halogen or with a tetrahedrally coordinated element such as carbon and germanium or with a group III element. Annealing is an important tool to tailor the disorder and defect level when annealed out below 250 °C but are created above that temperature. Generally, annealing above the deposition temperature tends to drive off hydrogen leaving behind unsaturated dangling bonds. Heat treatment signifi-

cantly influence the structure and the electrical properties of a-Si:H films. The conductivity of doped a-Si:H is very sensitive to the rate at which the sample is cooled following a high temperature anneal hence, much emphasis has been paid to the preparation conditions to improve photo conductivity.

In a work by Sharma et. al. [11], we presented a study on conduction mechanism in S and Se doped a-Si:H films in low temperature range (less than 370 K). Now, in present work the effect of annealing on the dark and photoconductivity at high temperature of S doped a-Si:H (a-Si:H,S:H) films is investigated which were annealed at an optimized temperature of 300 °C.

2. EXPERIMENTAL

The a-Si:H,S:H thin film samples were prepared by RF plasma-enhanced chemical vapor deposition (PECVD) technique using a standard reactor configuration by decomposition of H₂S vapour mixed with silane gas (SiH₄) on 7059 corning glass at 230 °C. The thicknesses of the films were found in the range 2.21-5.44 μm (using a surface profiler (Dek TeK3)). The X-ray diffraction patterns of the films confirmed the films

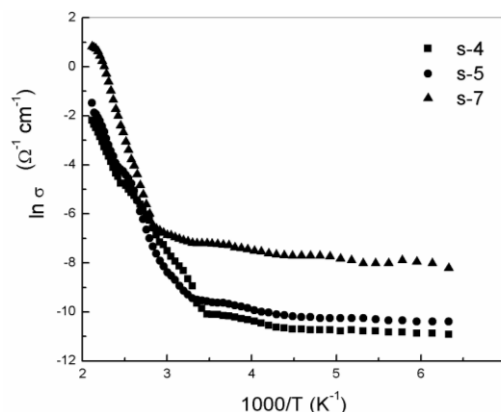


Fig. 1 – Variation of conductivity with inverse temperature for S-doped a-Si:H films annealed at 300 °C
Table 1 – Activation energy of unannealed and annealed a-Si,S:H films prepared at different gas ratio by PECVD technique

Sample code	R_V (H ₂ S/SiH ₄)	Activation Energy (un-annealed)		Activation Energy (annealed at 300 °C)	
		E_a (eV) Low Temp. range	E_a (eV) High Temp. range	E_a (eV) Low Temp. range	E_a (eV) High Temp. range
S-7	6.8×10^{-7}	0.086	0.76	0.019	0.91
S-5	1.1×10^{-5}	0.040	0.74	0.016	0.66
S-4	1.0×10^{-4}	0.060	0.69	0.014	0.48

as amorphous. The aluminum contacts were made in coplanar configuration. The dark conductivity of samples was observed in vacuum (10^{-3} torr) from room temperature to 200 °C at the rate of 2-3 °C/min using a Keithley source meter. After that the samples were annealed at the different temperature from 100 °C to 500 °C in a microprocessor controlled vacuum furnace ($\sim 10^{-6}$ torr) for an hour and again observed the photo conductivity under the illumination of white light at 100 mW/cm².

3. RESULTS AND DISCUSSION

Temperature dependent dark conductivity is affected by doping concentration. Temperature dependence of dark conductivity of a-Si,S:H thin films for conduction is assumed to follow Arrhenius equation

$$\sigma = \sigma_0 \exp\left(\frac{E_a}{kT}\right), \quad (1)$$

where, E_a is the temperature dependent activation.

The activation energy is determined from the linear fit of Arrhenius plot between $\ln \sigma$ versus $1000/T$. The conductivity prefactor σ_0 in equation 1 can be determined either by linear shift coefficients of Arrhenius plot between $\ln \sigma$ versus $1000/T$ or by Meyer-Neldel (MN) rule proposed as

$$\sigma_0 = \sigma_{00} \exp\left(\frac{E_a}{E_{MN}}\right).$$

In a work with Sanjeev et. al. [14, 16, 19], a correlation between MN prefactor and activation has been observed and for low temperature range conductivity and conductivity is attributed to hopping of electrons between localized states [11].

In present work, we measured the conductivity upon heating the samples from lower temperature to higher temperature (160 K to 473 K). The activation energy of the samples was found to decrease with doping concentration after annealing (Fig. 4). The net decrease in the number of dangling bonds after each anneal is possibly due to some of the double donor impurity introduced by S which have been effectively passivated by hydrogen in annealed state [12]. Thereby, less number of localized states due to unsaturated hydrogen bonds (dangling bonds) after each anneals is possible. The observation concludes that optical activation seems to be more efficient; as a result, there occur a metastable photo-induced increase in both the dark and photo conductivities and the Fermi level moves towards the

conduction band edge. This metastable increase is similar in some multilayer heterostructures of a-Si:H and other amorphous alloys [9].

The effect of doping concentration can also be realized by determining the intensity dependence of photoconductivity σ_{ph} . The photo intensity dependence of photoconductivity of a-Si:H thin films obey the power-law dependence

$$\sigma_{ph} = F^\gamma$$

where F is the intensity and γ is an empirical exponent. Comparing our published work [13] For Se doped a-Si:H, the γ was found to be 0.75 to 0.51 for gas ratio of 10^{-4} to 10^{-1} respectively. As For a-Si,H,S:H film, the γ lies between 0.72 to 0.74 for gas ratio of 6.8×10^{-7} to 1.0×10^{-4} . This observation in S doped a-Si:H films also indicates that there occurs both the monomolecular and bimolecular recombination process [14].

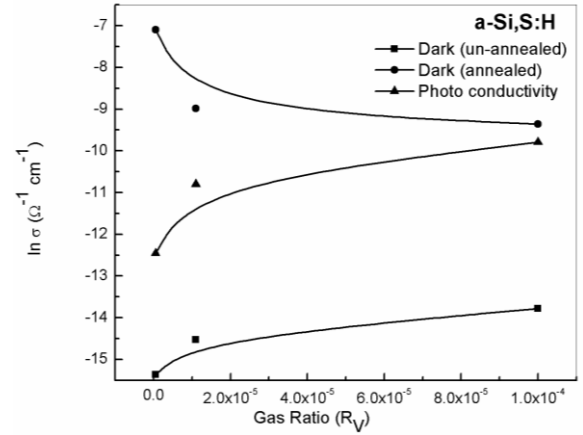


Fig. 2 – Variation of dark and photo conductivity with doping ratio for unannealed and annealed a-Si,H,S:H samples

The Fig. 2 shows the comparison of dark conductivity of annealed and unannealed films as well as of photoconductivity with doping gas ratio for a-Si,H,S:H films respectively. The reason for decrease in photoconductivity than dark conductivity of annealed films is due to the fact that absorption of light introduces effective recombination centers other than normal number of dangling bonds in dark at room temperature in annealed films. At temperature above room temperature, the concentration (N_0) of neutral dangling bond is given by

$$N_0 = n_i + N_0^0,$$

where n_i is the number of trapped electron at conduc-

tion band tail and N_0^0 number of dangling bonds in dark. As the N_0^0 increases due to occupation function for charged states of defects with positive correlation energy [15], the net number of dangling bonds (N_0) increases at above the room temperature. Moreover, defect model also [16] explains that the number of dangling bonds increases from their normal number at above the equilibrium temperature.

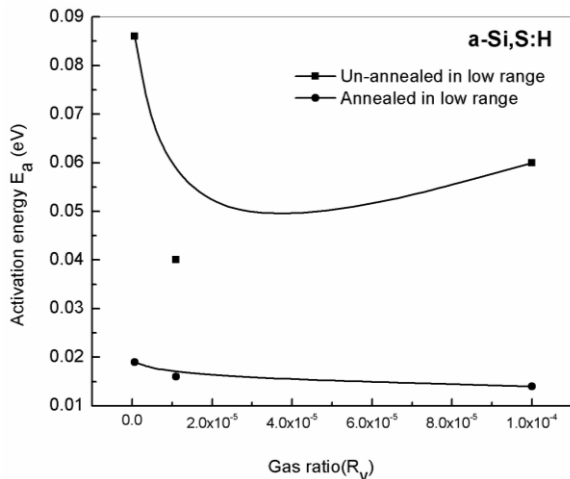


Fig. 3 – Variation of activation energy with gas ratio H_2S/SiH_4 for unannealed and annealed a-Si:H, S:H films samples in the low temperature range

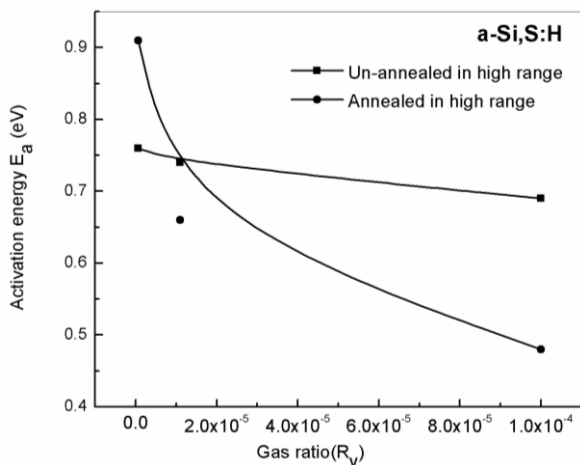


Fig. 4 – Variation of activation energy with gas ratio for unannealed and annealed S-doped a-Si:H films in high tempera-

ture range

Fig. 3 shows the variation of activation energy with gas ratio for unannealed and annealed S doped films in the low temperature range. At low temperature range the increased metastable defects level affects hopping of electrons through localized states in the band gap from valence band to conduction level. Consequently, the photo conductivity is found less than the dark conductivity.

In Fig. 4, the variation of activation energy with gas ratio for unannealed and annealed a-Si:H, S:H films in high temperature range are shown respectively. The activation energy is quite high than the activation energy observed at low temperatures. At high temperatures the localized states positioned in mid gap probably are shifted towards the valence band. Hence, at high temperatures, there occurs an activated type mechanism of conduction.

4. CONCLUSION

The effect of annealing on dc dark and photoconductivity of a-Si:H, S:H films is studied. The concentration of dangling bonds in S doped a-Si:H films are effectively reduced by annealing process, hence reduce the non-radiative centers and defects states lying near midgap. It is because hydrogen breaks the weak bonds, hence passivate dangling bonds [17]. Hereby, it is to mention that some other worker, using Car-Parrinello molecular dynamics has shown the hydrogen bonds with two silicon atoms only in Si_2H , Si_3H and Si_5H clusters, while in other clusters (i.e. Si_4H , Si_6H , Si_7H , Si_8H , Si_9H and $Si_{10}H$) hydrogen is bonded to only one silicon atom and the calculation of the lowest energy fragmentation products of Si_nH clusters shows that hydrogen is easily removed from Si_nH clusters [18]. Our observation concludes that in the low temperature range the conductivity is attributed to hopping of electrons through localized states between valence band to conduction band; and at high temperatures, an activated type mechanism takes place.

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