

# Photoconductivity of Selenium and Sulphur Doped a-Si:H thin Films

Sanjeev Kumar SHARMA<sup>1</sup>, Himanshu GUPTA<sup>2</sup>,  
Rajendra KUMAR<sup>2</sup> and Ram Mohan MEHRA<sup>1</sup>

<sup>1</sup>*Department of Electronic Science, University of Delhi South Campus,  
New Delhi-110021, INDIA*

<sup>2</sup>*Department of Physics, Gurukula Kangri Vishwavidyalya,  
Haridwar-249404, INDIA  
e-mail: rammehra@netscape.net*

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## Abstract

This paper presents a study of photoconductivity of S- and Se-doped a-Si:H as a function of composition and temperature. Temperature dependence of photoconductivity of the films was measured under the illumination of white light at 100 mW/cm<sup>2</sup>. The room temperature photoconductivity for the same doping concentration of 10<sup>-4</sup> (to develop H<sub>2</sub>Se/SiH<sub>4</sub> and H<sub>2</sub>S/SiH<sub>4</sub>) is found to be higher in Se-doped – than S-doped – a-Si:H film due to a low defect density. From the measurement of intensity dependence of photoconductivity, it is found that the addition of Se and S changes the recombination mechanism from monomolecular, for low-doped films, to bimolecular at higher levels of doping of Se and S.

**Key Words:** Se, S, a-Si:H, Photoconductivity, recombination mechanism.

## 1. Introduction

Photoconductivity (PC) plays a central role in the study of hydrogenated amorphous silicon (a-Si:H). It is associated not only with carrier excitation, trapping and radiative and non-radiative recombination, but is also associated with various transport mechanisms of extended state conduction and hopping through the distribution of localized band tail states. The presence of metastable defects in a-Si:H was discovered by Beyer, Fritzsche et al. [1, 2] from photoconductivity measurements. It was shown that photoinduced metastable defects are created within the material upon recombination of excess carriers. This photoinduced degradation, which is known as the Staebler Wronski Effect (SWE), is reversible and the initial properties can be recovered by annealing the films at a temperature of 200 °C in dark. It is an intrinsic effect and is observed in the device quality of amorphous silicon alloys. It is not associated with impurities and can be considerably reduced by pursuing preparation conditions which promote a dense, void free structure with quasi-crystalline regions and low hydrogen concentration such that recombination takes place without structural changes [3]. Advances in amorphous hydrogenated silicon technology have been hindered by limited understanding of the microstructure. In particular, shortly after the realization of effective doping of a-Si:H [4], it was found the material suffers from light-induced metastable changes [5]. Light incident on a-Si:H causes metastable Si dangling bond (DB) defects to form with the result of increased carrier trapping and

decreased photoconductivity. Much theoretical and experimental effort has been put into understanding the SWE, but a comprehensive explanation has yet to be achieved [6]. The electrical transport in hydrogenated amorphous silicon (a-Si:H) is sensitive to doping concentration. Doping can also have an effect on the temperature dependence of dc dark and photoconductivity. A metastable excess conductance, which can be enhanced by several orders of magnitude above the initial dark conductivity by brief light exposure, has been observed in compensated a-Si:H films [7–12] as well as in doping modulated multilayers [8, 11, 13–18] of a-Si:H. This metastable excess conductance, called persistent photoconductivity (PPC), decays slowly over several days at room temperature and disappears by annealing near 100 °C in multilayered films and 200 °C in compensated films [19, 20].

We report on the photoconductivity of a-Si,Se:H and a-Si,S:H films as a function of temperature and intensity. The results of temperature and intensity dependence of photoconductivity of a-Si,Se:H and a-Si,S:H films are reported. The temperature variation photoconductivity was studied in the range 27 °C to 200 °C. An estimate of the photosensitivity of the two materials has also been made.

## 2. Experimental

Dark and photoconductivity measurements have been performed on a-Si,Se:H and a-Si,S:H films prepared by the technique of plasma enhanced chemical vapour deposition (PECVD). H<sub>2</sub>Se and H<sub>2</sub>S vapour were mixed with silane gas (SiH<sub>4</sub>) in order to achieve Se and S doping, respectively [21]. For conductivity measurements, the aluminum contacts in a coplanar configuration were evaporated. Thickness of the films was measured using Surface Profiler (DekTak3). The absence of sharp peaks in X-ray diffraction (XRD) pattern confirmed the amorphous nature of the films. The initial state of the films were reached by 200 °C annealing in a specially designated vacuum cryostat, to remove surface absorption and metastable defects in the Se and S-doped a-Si:H films. The measurements were then carried out under a vacuum higher than 10<sup>-3</sup> torr. The dark conductivity was measured once again upon warming. The photoconductivity was measured by illuminating the light of a tungsten halogen lamp (intensity of ~100 mW/cm<sup>2</sup>) that was calibrated using a standard detector (Hamamatsu S. 2281, Photodiode), under vacuum in temperature range of 27 to 200 °C.

## 3. Results and Discussion

The room temperature photoconductivity was assumed to follow the relation

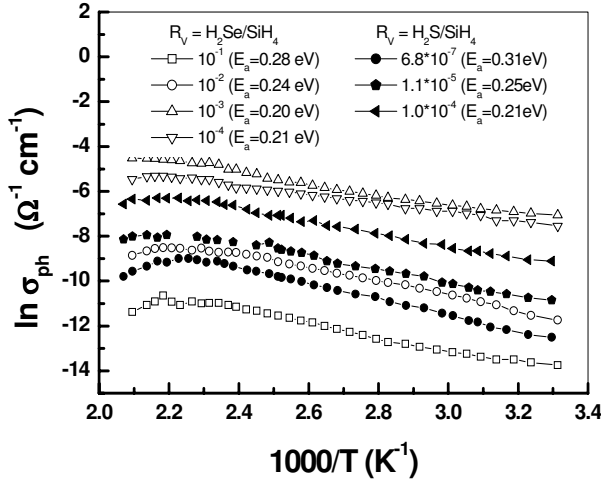
$$\sigma_{ph} = \sigma_{ill} - \sigma_{dc},$$

where  $\sigma_{ill}$  is the conductivity of illumination and  $\sigma_{dc}$  is the dark conductivity. Temperature dependence of dark conductivity of a-Si,Se:H and a-Si,S:H for conduction is assumed to follow the relation

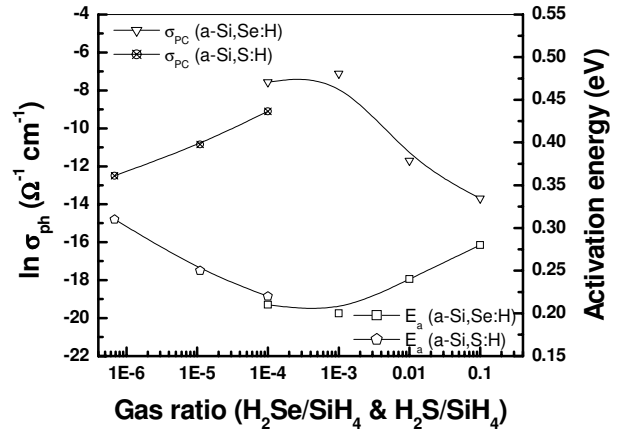
$$\sigma = \sigma_o \exp\left(-\frac{E_a}{kT}\right),$$

where  $E_a$  ( $= E_C - E_F$ ) is the temperature independent activation energy,  $E_C$  is the mobility edge,  $E_F$  is the Fermi energy and  $\sigma_o$  is the pre-exponential factor. The photoconductivity (PC) versus inverse temperature with different Se and S dopant concentrations is shown in Figure 1. At low temperature the photoconductivity is much larger than the dark conductivity. This is due to the fact that absorption of light introduces effective recombination centers other than normal dangling bond (DB) with relatively low concentrations. The recombination-induced weak bond breaking with successive hydrogen mediated separation of the DB.

It is clear that the DB separation process becomes less effective at lower temperatures. The temperature dependence of photoconductivity for the Se and S-doped a-Si:H films is also similar to that observed for P-doped films [22, 23]. At temperatures above room temperature the concentration of  $D_o$  (neutral dangling bonds, which is equal to  $N_o \approx n_t + N_o^o$ , where  $N_o^o$  is the concentration of  $D_o$  in the dark and  $n_t$  is the concentration of electrons trapped by the conduction band tail states) seems to be determined by  $N_o^o$ . As the Fermi-level in n-type a-Si:H is located above the position of  $D_o$  states [12], according to the occupation functions for charged states of defects with positive correlation energy [13],  $N_o^o$  has to increase with temperature and correspondingly photoconductivity has to reduce. It is worth noting that according to the defect equilibrium model [14] the whole concentration of dangling bonds has to increase with temperature above the equilibrium temperature in Se and S-doped a-Si:H [21]. The values of activation energy and room temperature photoconductivity (300 K) as a function of doping gas ratios for Se and S-doped a-Si:H films is shown in Figure 2. The photoconductivity increases from  $5.31 \times 10^{-4}$  to  $8.85 \times 10^{-4} (\Omega\text{cm})^{-1}$  as the doping gas ratio increases from  $\text{H}_2\text{Se}/\text{SiH}_4 = 10^{-4}$  to  $10^{-3}$  and then decreases to  $1.07 \times 10^{-6} (\Omega\text{cm})^{-1}$  as the gas ratio increases to  $\text{H}_2\text{Se}/\text{SiH}_4 = 10^{-1}$ . The activation energy decreases from 0.21 to 0.20 eV as the gas ratio increases from  $\text{H}_2\text{Se}/\text{SiH}_4 = 10^{-4}$  to  $10^{-3}$  and then activation energy increases to 0.28 eV as the gas ratio increases to  $\text{H}_2\text{Se}/\text{SiH}_4 = 10^{-1}$ . That is the photoconductivity found to be activated in the temperature range of about 27 °C to 200 °C. At high temperature the photoconductivity is found to saturate and above 170 °C and the photoconductivity decreases. For higher doping levels,  $\text{H}_2\text{Se}/\text{SiH}_4 = 10^{-2}$  and  $10^{-1}$ , photoconductivity becomes less than the dark conductivity for temperature greater than 170 °C. The photoconductivity of S-doped a-Si:H increases from  $3.73 \times 10^{-6}$  to  $1.105 \times 10^{-4} (\Omega\text{cm})^{-1}$  as the gas ratio increases from  $\text{H}_2\text{S}/\text{SiH}_4 = 6.8 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  and the activation energy decreases from 0.31 to 0.21 eV.



**Figure 1.** Variation of photoconductivity versus inverse temperature for a-Si,Se:H and a-Si,S:H films.



**Figure 2.** Photoconductivity at room temperature and activation energy versus doping gas ratio ( $\text{H}_2\text{Se}/\text{SiH}_4$  and  $\text{H}_2\text{S}/\text{SiH}_4$ ) for a-Si,Se:H and a-Si,S:H films.

Photoconductive sensitivity is often used as a rough criterion for the quality of amorphous semiconductor and its usefulness in optoelectronic devices. The photosensitivity ( $\sigma_{ph}/\sigma_d$ ) versus Se/Si and S/Si concentration is shown in Figures 3 and 4, respectively. The photosensitivity of a-Si,Se:H films decreases with Se/Si concentration from  $1.6 \times 10^{-4}$  to  $2.5 \times 10^{-1}$ . The photosensitivity of a-Si,S:H films increases with S/Si concentration from  $1.6 \times 10^{-6}$  to  $1.1 \times 10^{-3}$ . It is observed that at same doping concentration  $\text{H}_2\text{Se}/\text{SiH}_4 = 1.0 \times 10^{-4}$ , the photosensitivity of a-Si,Se:H films is much higher than that of a-Si,S:H films.

Intensity dependence of photoconductivity is shown in Figure 5. The photoconductivity as a function of the intensity of the exciting light is very similar to that commonly observed in a-Si:H [5] and is found to

obey the power-law dependence

$$\sigma_{ph} = F^\gamma, \tag{3}$$

where  $\gamma$  is an empirical exponent and  $F$  is the intensity. The value of  $\gamma$  is found to be  $\approx 0.75$  for the gas ratio  $H_2Se/SiH_4 = 10^{-4}$  to  $10^{-3}$ , indicating a mixture of monomolecular and bimolecular recombination mechanism; and from the gas ratio  $H_2Se/SiH_4 = 10^{-3}$  to  $10^{-1}$  decreases to 0.51, indicating the bimolecular mechanism. This is consistent with the results that heavily doped samples are more resistive and so bimolecular recombination is predominant in these samples. For the S-doped samples from the gas ratio  $H_2S/SiH_4 = 6.8 \times 10^{-7}$  to  $1.0 \times 10^{-4}$ ,  $\gamma$  has been found to be  $\approx 0.73$ , indicating a mixture of monomolecular and bimolecular recombination mechanism.

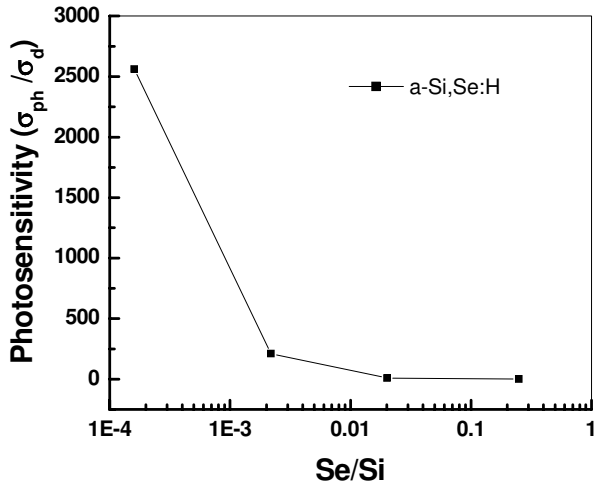


Figure 3. Variation of photosensitivity versus Se/Si concentration for a-Si,Se:H films.

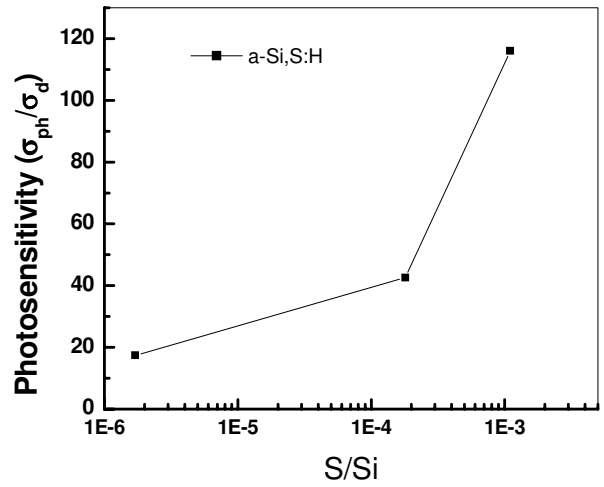


Figure 4. Variation of photosensitivity versus S/Si concentration for a-Si,S:H films.

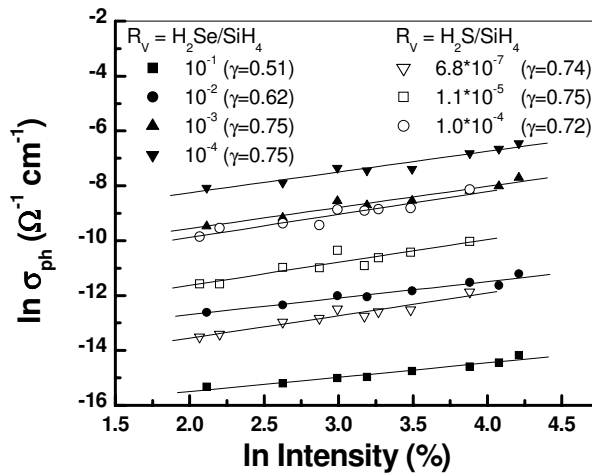


Figure 5. Intensity dependence of photoconductivity of Se and S doping gas ratio ( $H_2Se/SiH_4$  and  $H_2S/SiH_4$ ) for a-Si,Se:H and a-Si,S:H films.

## 4. Conclusion

Photoconductivity and the activation energy of Se and S-doped a-Si:H films are found to be strongly dependent on the gas ratio. Comparing the results for the same gas ratio,  $\text{H}_2\text{Se}/\text{SiH}_4$  and  $\text{H}_2\text{S}/\text{SiH}_4 = 10^{-4}$ , the photoconductivity in the Se-doped sample is found to be more than that for in the case of S-doped films. This would mean that a lower defect density in the Se-doped films. At low temperature the photoconductivity is much larger than the dark conductivity. This is due to the fact that absorption of light introduces effective recombination centers other than normal dangling bond with relatively low concentrations and becoming less effective at lower temperature. The photosensitivity of a-Si, Se:H films is much higher than that of a-Si, S:H films.

Intensity variation of photoconductivity of the films suggests that the recombination process is mixture of monomolecular and bimolecular in the films with low resistivity. However, in high resistivity films it bimolecular only, as expected.

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