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Light-Induced Degradation of Hydrogenated Amorphous Silicon

(光照射에 따른 非晶質 실리콘의 劣化)

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(Jin Seok Park, Min Koo Han and Chung Han Lee)

要 約

수소화된 진성, N 및 P형 비정질 실리콘의 장시간 빛의 조사에 의한 특성의 열화현상을 정량적으로 규명하였다. 비정질 실리콘의 암 전도도, 광 전도도 및 활성화 에너지의 빛의 조사시간에 따른 열화를 도우핑의 정도에 따라서 비교 분석하였다. 진성 비정질 실리콘의 암 전도도 및 광 전도도가 빛의 조사에 의하여 급격히 감소되었다. 그러나, 도우핑의 농도가 증가되면, 광 조사에 의한 암 전도도의 열화 효과는 급격히 감소되는 결과를 확인하였다. 전도도와 활성화 에너지와의 상관 관계가 실험적으로 규명되었으며, 적외선 스펙트럼 해석에 의하여 실리콘과 수소와의 결합량의 변화가 동시에 고찰되었다. 광 흡수 계수 및 광학적 밴드갭은 빛의 조사가 진행되어도 변화가 거의 없는 것으로 측정되었다. 비정질 실리콘의 광 조사 효과에 의한 전기적 특성의 열화 정도는 도우핑의 농도에 따라서 매우 민감하게 변화하였다.

Abstract

This paper presents the light-induced effects on the electrical and optical properties of undoped and doped hydrogenated amorphous silicon films. The changes in the conductivities and the activation energies of various types of a-Si:H films due to the prolonged exposure to light have been characterized as a function of deposition conditions and illumination periods. The dark conductivity changes may be quenched for heavier doped a-Si:H films. We have also analyzed the variations of micro-structure of a-Si:H film such as silicon-hydrogen bondings in the rocking and stretching modes utilizing infrared spectroscopy. From the experimental results, it is elucidated that doping effects must be crucial to the degradations of the fundamental properties of a-Si:H due to light-induced effects.

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I. Introduction

Hydrogenated amorphous silicon (a-Si:H) has attracted a considerable interest due to an excellent photoconductivity and high optical absorption coefficients[1,2]. A fairly uniform a-Si:H with a large area can be deposited by various methods such as sputtering, ion-cluster beam, CVD, rf and dc glow discharges, and photo-CVD. It is well known fact that rf glow discharge and photo-CVD produce high quality a-Si:H films[3-6]. Doping of either n- or p-type can be also realized in-situ by controlling doping gas flow. Our paper deals with a-Si:H films deposited by rf glow discharge which is most widely used.

The electrical and optical properties of a-Si:H may be controlled by deposition methods and conditions. The properties of a-Si:H films may be potentially affected more readily by the interactions with induced photons because of its inherent bonds,voids, internal surfaces and stresses. Specially the application of a-Si:H to terrestrial photovoltaic power generation renders the effects of prolonged exposure to light extremely important. Light-induced effects on a-Si:H films and the stability of thin film devices have been investigated intensively. However, most of previous researches have been centered on the degradation of undoped a-Si:H films, probably due to the fact that undoped a-Si:H layer plays a dominant role to determine the performances of widely used a-Si:H P-I-N solar cell. It has been reported[7-12] that prolonged illumination causes a considerable drop in the conductivities, whereas the conductivities have been restored closely to the initial value by the thermal annealing at 150 – 200°C. However, light-induced effects on doped a-Si:H films have been scare in the literature. The built-in potential of P-N device depends on the Fermi level of doped layers and the characteristics of solar cells may be controlled by doped as well as undoped layers[13].

In this paper, we have investigated the photo-induced effects on the electrical and the optical properties of doped (n- and p-type) and undoped a-Si:H deposited by rf glow discharge. The degradation of dark and photoconductivities of undoped and doped a-Si:H due to prolonged exposure to light were characterized as a function of deposition conditions and illumination periods. We also examined the activation energies of light-soaked a-Si:H films by I-V-T measurements. The photo-induced effects on the bonding structure[14] of a-Si:H films were also analyzed with illumination time from infrared spectra of those films. It has been attempted to correlate various experimental results for the purpose of interpreting the light-induced effects.

II. Deposition Details of Undoped and Doped Hydrogenated Amorphous Silicon

Undoped and doped hydrogenated amorphous silicon films have been deposited by PECVD (plasma-enhanced chemical vapor deposition) technique employing rf (13.56 MHz) glow discharge. As has been well known, the discharge-produced films have a low density of dangling bonds and correspondingly good photoconductivity and carrier lifetimes because the rf glow discharge of silane forms an amorphous solid still rich in hydrogen[15]

PECVD system was capacitively coupled one and a-Si:H films were deposited on various substrates such as silicon wafer, stainless steel, indium tin oxide (ITO), corning glass. The substrates were loaded on the upper electrode which was grounded in order to reduce ion bombardment caused by self-bias. The upper electrode was rotated with a low speed of 5 rpm. in order to enhance the lateral uniformity of deposited a-Si:H. The applied rf power density was varied from 0.02 to 0.06 W/cm^2. The distance between the electrodes was about 2 inches. Phosphorus and boron doped a-Si:H with the doping ratios of 0.05 - 1% defined by the volumetric ratio of PH_3 or B_2H_6 to SiH_4 input gases were deposited and accurately controlled using mass flow controller.

III Experimental Results and Discussion

1. Conductivity changes due to prolonged illumnation

The conductivity as a function of time before, during, and after optical exposure of sample has been measured. The conductivities were obtained from I-V characteristics of sandwich type a-Si:H films deposited with the structure of Al/a-SiH/ITO. Aluminum electrode with 0.5μm of thickness was deposited on a-SiH film of which was about 0.25 μm and ohmic behaviors were observed up to 5 volts. Optical exposure was done with light from a tunsten lamp (ELH) focused onto ITO coated glass. The Light was filtered to pass the wavelength range of 550-560 nm where the radiation was fully absorbed through this sample. The incident power density was about 100 mW/cm^2.

It was found that the degradations of conductivities due to prolonged illumination depended on the types of a-SiH. Fig. 1. shows the conductivity variations of undoped a-Si:H as a function of illu-

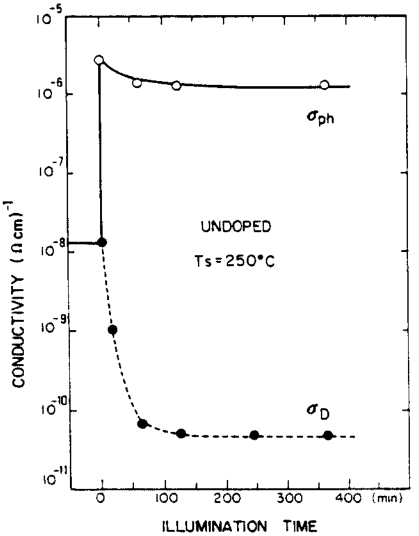
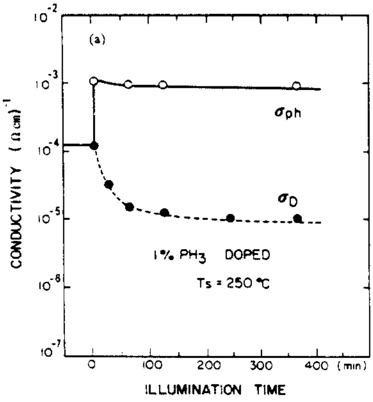
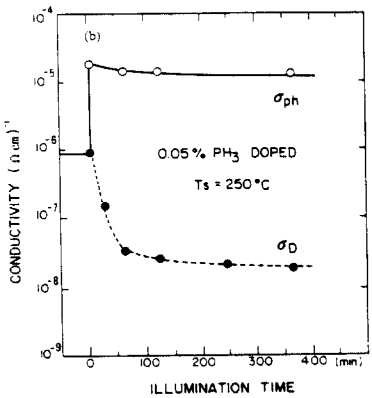


Fig.1. The degradations in dark and photoconductivity of undoped a-Si:H film due to prolonged illumination.



(a)



(b)

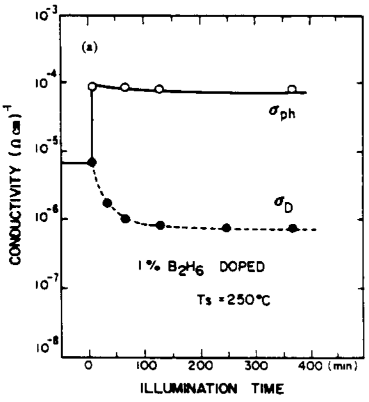
Fig.2. The light-induced changes of dark and photoconductivity of phosphorus dopd a-Si:H films as a function of illumination time: (a) 1% PH_3 doped; (b) 0.05% PH_3 doped a-Si:H films respectively.

mination time. The dark conductivity (σ_D) decreased rapidly at first and was saturated after 100 minutes of illumination. The ratio of dark conductivity in stable initial state before light exposure to that in metastable state after 60 minutes of continuous illumination were about 200 - 220. At the same time, the photoconductivity (σ_{ph}) also decreased by about half of initial value with elapsed illumination time. The degradation of photoconductivity may be caused by the reduction of diffusion length and thus deteriorate the performances of a-Si:H solar cells [16,17].

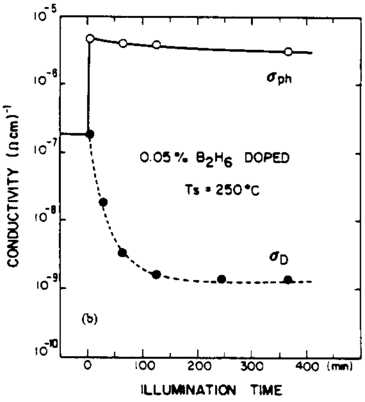
The light-induced changes in the conductivities of either phosphorus or bornon doped a-SiH films deposited at the identical substrate temperature of 250°C were shown in Fig. 2 (a, b) and Fig. 3 (a, b). The decay rates of dark conductivities due to prolonged illumination were about 50 - 55, 6 - 7 for 0.05 and 1% PH_3 doped a-Si:H and about 90 - 95, 7 - 8 for 0.05 and 1% B_2H_6 doped a-Si:H respectively. However, the changes in photoconductivities of doped samples were negligible enought not to be detected. These experimental evidences give such a consideration that induced effects on the conductivity changes may be quenched for heavier doped a-Si:H films. That is the reason why the densities of light-induced defects in heavier doped films are too small to overcome the pinning of Fermi levels by the significantly larger amounts of donors and acceptors. Consequently, it may be concluded that the rate of transition from thermally stable state to metastable state depends strongly on the types of a-Si:H films.

2. Temperature dependence of the dark conductivity of a-Si:H in the light-soaked state

As shown in section III-A, the decrease in the conductivity due to prolonged illumination may be



(a)



(b)

Fig.3. The light-induced changes of dark and photoconductivity of boron dopd a-Si:H films as a function of illumination time: (a) 1% B_2H_6 doped; (b) 0.05% B_2H_6 doped a-Si:H films respectively.

caused by the fact that the creation of metastable defects decreases the density of free carriers. Decay of free carriers results in the shift of Fermi level of a-Si:H, that is, the decrease of conductivity causes the increase of activation energy which can be described as following form[18,19]:

$$\sigma_D = \sigma_0 \exp(-E_a/kT)$$

The conductivity prefactor σ_0 depends on the carrier mobility and on the density of states at some energy. E_a is the activation energy which depends on the temperature and indicates the position of Fermi level with respect to the bottom of the conduction band for n-type and with the respect to the top of valence band for p-type respectively.

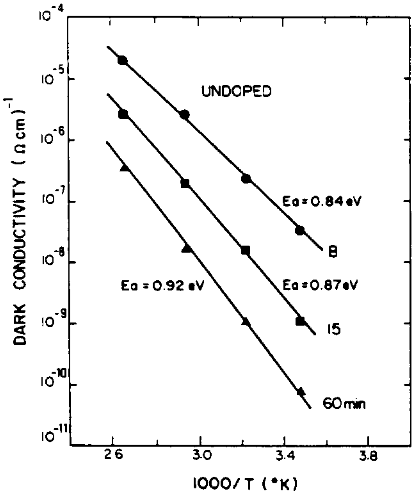


Fig.4. The activation energies of undoped a-Si:H film before and after illumination from the temperature dependence of dark conductivity. E_a and B represents the activation energy and before illumination respectively. Numbers indicate illumination time.

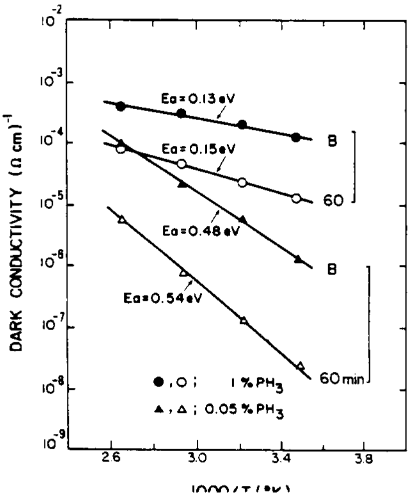


Fig.5. The changes of activation energies due to prolonged illumination for 1% (●,○) and 0.05% (▲,△) PH_3 doped a-Si:H films. E_a and B represents the activation energy and before illumination respectively. Numbers indicate illumination time.

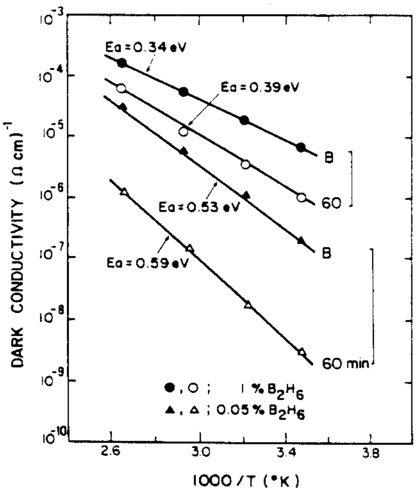


Fig.6. The changes of activation energies due to prolonged illumination for 1% (●,○) and 0.05% (▲,△) B_2H_6 doped a-Si:H. E_a and B represents the activation energy and before illumination respectively. Numbers indicate illumination time.

Fig. 4,5 and 6 show that the temperature dependences of the dark conductivities of undoped and doped a-Si:H films depend on light exposure. The dark conductivities were measured at temperature range from room temperature to about 100°C. The durations of temperature during the measurements were too low to cause any change in metastable state. As seen by the increase of the slopes in Fig. 4,5 and 6, the activation energy increased by about 0.08 eV for undoped and 0.02-0.06 eV for PH_3 and B_2H_6 doped a-Si:H films respectively, which indicates the displacement of the Fermi level away from the electron (or hole) mobility edge. The fact that the rate of activation energy increase is larger in undoped a-Si:H than in doped a-Si:H film may give an experimental evidence to the light-induced effects on the conductivity changes of different types of a-Si:H films as discussed in section III-1.

From this experiment, it was also found that prolonged illumination has affected the values of conductivity prefactor σ_0 as well as E_a, which was evidenced in Fig. 7 (a) and (b). These results were obtained from the exponential dependence of σ_0 on E_a, known as the Meyer-Neldel rule. A similar exponential dependence of σ_0 on E_a has been

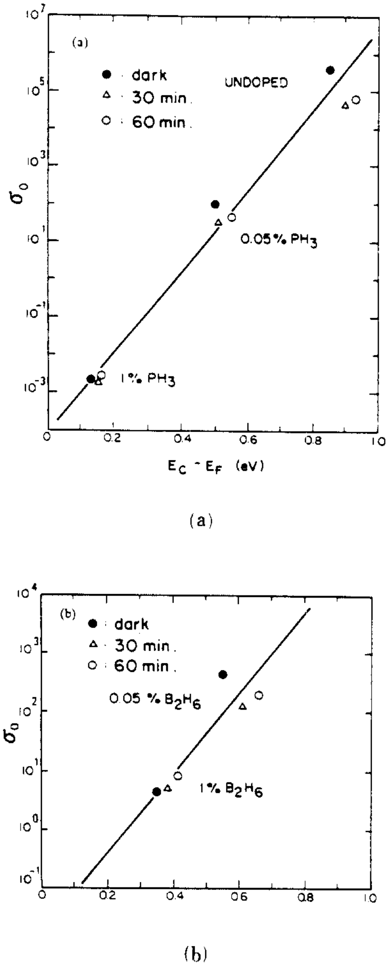


Fig.7. The variations of conductivity prefactors σ_0 and activation energies E_a due to light-induced effects for various types of a-Si:H films: (a) undoped and phosphorus doped a-Si:H; (b) boron doped a-Si:H films respectively: Numbers (30min. and 60min.) indicate the illumination time.

observed for both undoped and doped a-Si:H. However, the simultaneous increase in both σ_0 and E_a was observed with illumination elapsed. Such opposing effect of σ_0 and E_a on the conductivity change indicates that the dynamics of the conductivity decreases are not simply related to the photo-induced defects but related to complex mechanism of various types of defects. The reasons for the changes in σ_0 and E_a caused by light exposure have not been clear yet. However, it can be concluded from above experimental results that the danging bond centers are created by prolonged bandgap illumination even though it is not clear whether the same metastable defects are reponsible for these all results.

3. Reversible changes in SiH absorption

In order to investigate the micro-structural changes of a-Si:H films due to the prolonged exposure to light, we have measured infrared spectra in the wavenumber of 2500 - 400 cm^{-1} (corresponding to the wavelength range of 4 - 26 μm) of those films before and after illumination. Infrared spectroscopy has been used to determine the density of molecular species in a-Si:H by measuring the characteristic frequency which depends on both the mass of the oscillating dipole and the strength of the bond between the atoms comprising the dipole. The types of vibrational modes for a-Si:H and their frequencies have been reported as follows[14,20] : the absorption near 2000 and 630 cm^{-1} due to SiH stretching and rocking modes respectively, the weaker bands between 800 and 900cm^{-1} due to SiH_2 or SiH_3 vibrational modes, and absorbing SiO_x mode in the 1100-1000 cm^{-1} region. Among these modes, the silicon-hydrogen bondings have been considered to be important in that the role of hydrogen must be crucial in determining the properties of a-Si:H.
1000 cm^{-1} region. Among these modes, the silicon-hydrogen bondings have been considered to be important in that the role of hydrogen must be crucial in determining the properties of a-Si:H.

In our experiment, the variations of relative SiH absorption at both stretching and rocking mode due to prolonged illumination have been measured for undoped and doped a-Si:H films as shown in Fig. 8, 9, and 10. After 4 hours of illumination, SiH absorptions of undoped a-Si:H film decreased substantially at both two modes as seen in Fig. 8. However, by annealing the light-soaked films at 180°C for 30 minutes, it was restored nearly to its initial value before illumination. As also seen in Fig. 9 and 10, the similar effects of light exposure on SiH absorption were observed in either phosphorus or boron doped samples, whereas the decay rates of SiH absorption were larger for undoped a-Si:H than those of doped a-Si:H. It was noticeable that the light-induced changes in SiH absorptions exhibited the similar trends with the conductivity changes due to prolonged illumination as examined in section III-1. However, neither of changes in optical absorption coefficients nor in optical bandgaps of those films were detected from the visible absorption measurements.

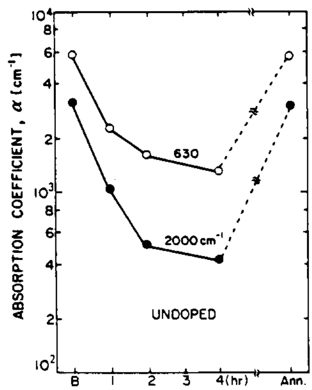


Fig.8. The changes in SiH absorptions of undoped a-Si:H film due to the light-induced effects: 630 and 2000 cm^{-1} refer to the wavenumbers of rocking and stretching mode respectively. B represents before illumination and Ann. indicates the thermal-annealing at 180°C for 30 minutes respectively.

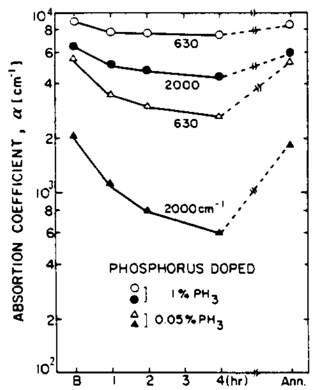


Fig.9. The light-induced changes in SiH absorption at rocking (630 cm^{-1}) and stretching (2000 cm^{-1}) modes of n-type (1% and 0.05 PH_3 doped) a-Si:H films: B represents before illumination and Ann. indicates the thermal-annealing at 180°C for 30 minutes respectively.

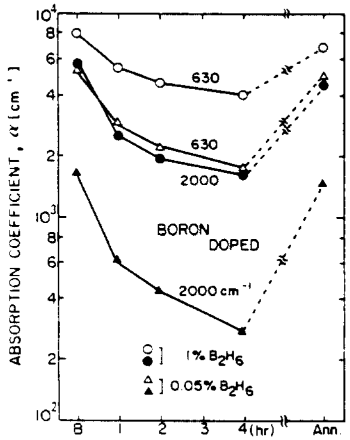


Fig.10. The light-induced changes in SiH absorptions at rocking (630 cm^{-1}) and stretching (2000 cm^{-1}) modes of p-type (1% and 0.05% B_2H_6 doped) a-Si:H films: B represents before illumination and Ann. indicates the thermal-annealing at 180°C for 30 minutes respectively.

Table 1. Experimental results regarding to the effects of prolonged illumination on the conductivities, the activation energies, and the relative SiH absorptions of different a-Si:H films.

types of a-Si:H (T_s=250℃)		$\sigma_{D,i}/\sigma_{D,f}$ [a]	$\sigma_{Ph,i}/\sigma_{Ph,f}$ [a]	ΔE_a (eV) [b] ($E_{a,f}-E_{a,i}$)	$\alpha_i(2000)/\alpha_f(2000)$ [c]	$\alpha_i(630)/\alpha_f(630)$ [c]
PH_3-doped	1%	6-7	1.02	0.021	1.5	1.2
	0.05%	50-55	1.15	0.062	3.5	2.1
B_2H_6-doped	1%	7-8	1.08	0.049	3.3	2.0
	0.05%	90-95	1.24	0.056	6.0	3.0
undoped		200-220	2.47	0.084	7.7	4.5

[a] $\sigma_{D,i}/\sigma_{D,f}$ and $\sigma_{Ph,i}/\sigma_{Ph,f}$ refer to the decay rate of dark and photoconductivity due to prolonged illumination repectively.

[b] $\Delta E_a(E_{a,f}-E_{a,i})$ indicates the increment of activation energy due to prolonged illumination.

[c] $\alpha_i(2000)/\alpha_f(2000)$ and $\alpha_i(630)/\alpha_f(630)$ refer to the ratio of SiH absorption before illumination to that after 60min. of illumination at the stretrching(2000 cm^{-1}) and the rocking(630 cm^{-1}) mode respectively.

[d] The subscripts i and f refer to the paraments measured before illumination and after 60min. of illumination respectively.

IV. Conclusions

We have investigated the light-induced effects on the electrical properties such as conductivities and activation energies of doped and undoped a-Si:H films. At the same time, the changes in SiH absorptions at stretching and rocking modes due to light exposure have been characterized. The experimental results are summarized in table 1.

As seen in table 1, the dark and photoconductivities of undoped a-Si:H film decreased substantially after prolonged illumination. However, photoconductivities of heavily doped (1% of either n- or p-type) a-Si:H films did not decrease much, whereas dark conductivities of those films degraded significantly. We also found that the changes of activation energies were closely related with the degradations of conductivities. The degradation of conductivity with light exposure may be accounted by the reduced carrier lifetime and mobility. However, we confirm that light-induced effects on the conductivities and the activation energies may also be due to the decreases of SiH absorptions at stretching and rockiong modes as evidenced by infrared spectra results, whereas the optical absorption coefficients and the optical bandgaps of a-Si:H films have not changed after illumination. Light-induced effects on the electrical and the optical properties have been reduced with increasing doping levels. It is concluded that the doping levels of a-Si:H films may be crucial to the rates of variations in conductivities, activation energies, and SiH absorptions due to prolonged illumination.

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