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Semi-quantitative study on the Staebler–Wronski effect of hydrogenated amorphous silicon films prepared with HW-ECR-CVD system*

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The method of numerical simulation is used to fit the relationship between the photoconductivity in films and the illumination time. The generation and process rule of kinds of different charged defect states during illumination are revealed. It is found surprisingly that the initial photoconductivity determines directly the total account of photoconductivity degradation of sample.

Keywords: hydrogenated amorphous silicon, Staebler–Wronski effect, microwave electron cyclotron resonant chemical vapour deposition, charged defects

PACC: 7000, 7155E, 7110

1. Introduction

The creation of a large number of metastable defects during illumination is a crucial fundamental property which limits the performance of solar cells, thin film transistors and other electronic devices.[1] The increase in the density of defects leads to a degradation of the photoconductivity with the illumination time.[2] Up to now, many researchers do a lot of work to reveal the micro-mechanism of the photoconductivity degradation.[3−7] It is generally accepted that light soaking results in large numbers of additional neutral dangling-bond defects inside films. However, many researchers have suggested that this is not the unique cause for the Staebler–Wronski effect (SWE); many issues still remain, such as the exact effect of hydrogen,[8,9] local bonding configurations, the presence of multiple metastable defect states and so on.[10] The experimental observations clearly indicate that the SWE is not only determined by the creation of neutral dangling-bond defects, but also arise from the presence of different types of charged defects.[11] Combining the experimental results with findings from the nuclear magnetic resonance (NMR) experiments and computer simulations performed by some researchers, some researchers draw the following conclusions: microscopic configurations introduce charged defect states; positively charged defect states are related to a complex structure composed of a hydrogen molecule and a Si dangling-bond; negatively charged defect states are attributed to the floating-bonds.[10,12] Unfortunately, there are no valid experimental techniques which can be used as a direct observation of charged defects. Electron spin resonance (ESR) has been extensively used to measure the increase of the defect density during illumination. However, ESR can only detect signals from paramagnetic centers; thereby it only appears sensitive to the silicon neutral dangling bonds.

In this paper, the method of numerical simulation is used to fit the relationship between the photocon-

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ductivity in films prepared with HW-ECR-CVD system and the illumination time, which reveal the generating and variation of kinds of different charged defect states during illumination. It is found surprisingly that the total amount of photoconductivity degradation during illumination is one-to-one correspondence with sample's initial photoconductivity. Namely, the initial photoconductivity determines directly the total account of photoconductivity degradation of sample.

2. Experiment

It is well known that in the microwave electron cyclotron resonant chemical vapour deposition (MWECR-CVD) system, the plasma with higher density can be excited in lower temperature and pressure. The energetic ions bombardment to the surface of growing film in the system is weaker than any other deposition techniques, therefore it is a very efficient film deposition technique. Moreover, for the hot wire CVD system, H content in the a-Si:H films deposited with this system is lower. And its light-induced degradation is lighter than that of others. Therefore, in the experiment, we combined these two potent deposition techniques together and developed a novel deposition system: hot wire assisted microwave electron cyclotron resonant chemical vapour deposition (HW-MWECR-CVD) system, as shown in Fig.1.[13−15] Two parallel tungsten filaments away from each other 50mm were employed in the chamber, located above the sample holder with a space between 70mm. The length of each tungsten filament is 215mm. An infrared temperature meter (Raytek Raynger 3i) was employed to correlate the tungsten temperature with the tungsten voltage, and the relationship is shown in Table 1. In the experiment, we initialize the tungsten voltage as 9V, corresponding to the temperature of 1120°C.

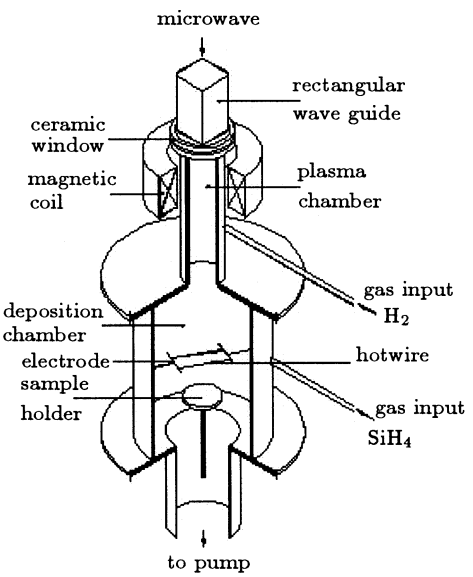


Fig.1. Schematic diagram of the HW-MWECR-CVD system.

Table 1. The relationship between the tungsten temperature and the tungsten voltage.

voltage/V	15.4	14	13	12.2	11.4	10.3	9.3	8
temperature/°C	1286	1260	1237	1218	1187	1157	1125	1079

A series of samples were deposited with the novel HW-ECR-CVD system. The samples were deposited with different conditions, and with different techniques respectively, such as atomic H annealing (AHA), layer by layer (LBL), etc. The films prepared on the quartz glass were evaporated with coplanar aluminium electrodes with a separation of 1mm. The photoconductivity and the dark conductivity are measured with Keithley 6517 High Resistance System. The photoconductivity and the light-induced degradation are measured under simulated (AM1 100mW/cm^2) illumination.

3. Experimental results and numerical simulations

Model functions about defect states evolution are founded firstly, and then model functions, in which each contains five parameters, are employed to fit the known data of degradation. The idiographic numerical values of the five parameters are determined by the data of degradation in different samples. The idiographic former of model functions is

$$\sigma_{\rm ph} = \sigma_{\rm ph}(0) + D_1 + D_2, \tag{1}$$

where

$$D_1 = A_1 \exp(-t_{ill}/t_1), \tag{2}$$

$$D_2 = A_2 \exp(-t_{ill}/t_2). \tag{3}$$

D_1 and D_2 have the same exponential functions format. The practical degradation curves fit well with theoretical simulation curves, which are supported by the photoconductivity degradation data and their theoretical simulation for two random samples as

shown in the Fig.2. The five simulation parameters of the sample A are: $\sigma_{\rm ph}(0) = 0.2323 \times 10^{-3}$s/cm, $A_1 = 0.34119 \times 10^{-3}$s/cm, t_1=55.50368s, $A_2 = 0.37787 \times 10^{-3}$s/cm, t_2=625.87828s. Those of sample B are: $\sigma_{ph}(0) = 0.06355 \times 10^{-3}$s/cm, $A_1 = 0.2469 \times 10^{-3}$s/cm, t_1=33.50856s, $A_2 = 0.21575 \times 10^{-3}$s/cm, t_2=376.97117s.

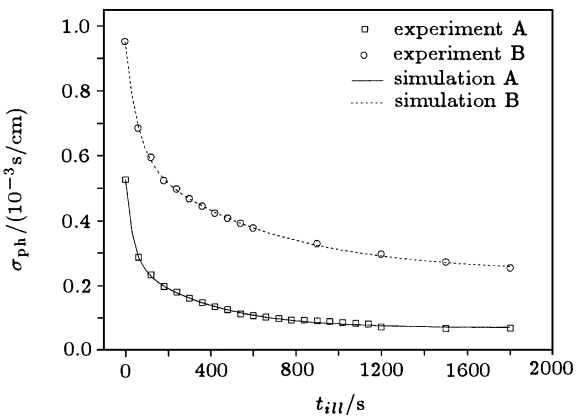


Fig.2. The photoconductivity degradation data and their theoretical simulations for arbitrary two samples.

For Eq.(1), if t_{ill}=0, then,

$$\sigma_{\rm ph} = \sigma_{\rm ph}(0) + A_1 + A_2, \qquad (4)$$

where $\sigma_{\rm ph}$ is the theoretical initial photoconductivity $\sigma_{\rm ph(0)(simul)}$. As shown in Fig.3, it is found that the initial photoconductivity and their theoretical values of most samples distribute closely to the direct proportional functions with the slope of 1. And some discontented errors occur in a bit of samples. Thus it is concluded that the errors of initial photoconductivity obtained by the model functions is small, thereby the model functions is valid.

If $t_{ill} \to +\infty$, then

$$\sigma_{\rm ph} = \sigma_{\rm ph}(0). \qquad (5)$$

This is the $\sigma_{\rm ph}(\infty)_{\rm (simul)}$ calculated by theoretical simulation data. Then the total amount of photoconductivity degradation during the process of whole photoconductivity degradation is:

$$\Delta\sigma_{\rm ph} = A_1 + A_2. \qquad (6)$$

It is found surprisingly that a simple one-to-one correspondence between $\Delta\sigma_{\rm ph}$ and $\sigma_{\rm ph}(0)_{\rm (simul)}$ exists, as shown in Fig.4. The relationship between them corresponds with the equation:

$$\Delta\sigma_{\rm ph} = -0.0144 + 0.89485 \times \sigma_{\rm ph}(0)_{\rm (simul)}. \qquad (7)$$

Namely, the total amount of photoconductivity degradation in the process of illumination is determined by the initial photoconductivity in the sample.

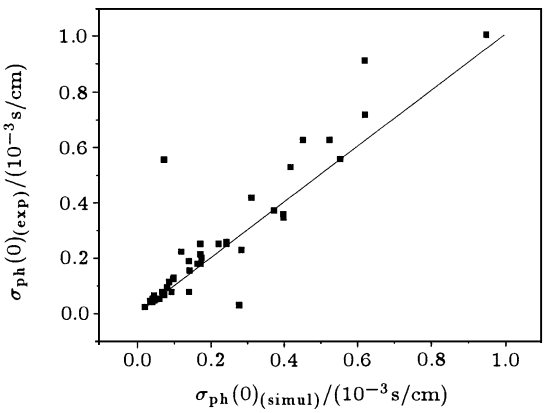


Fig.3. $\sigma_{\rm ph}(0)_{\rm (exp)}$ versus $\sigma_{\rm ph}(0)_{\rm (simul)}$ for all samples. They distribute near direct proportion functions with slope=1.

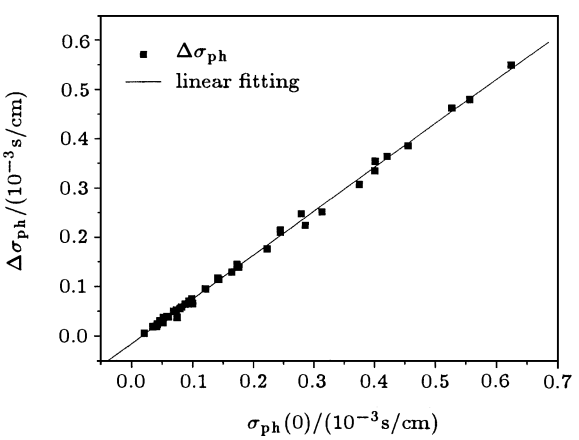


Fig.4. A simple one-to-one correspondence between $\Delta\sigma_{\rm ph}$ and $\sigma_{\rm ph}(0)_{\rm (simul)}$. The relationship between them corresponds with the equation: $\Delta\sigma_{\rm ph} = -0.0144 + 0.89485 \times \sigma_{\rm ph}(0)_{\rm (simul)}$.

It is observed that D_1 declines to 0 in a short while (within 200s), whereas the process of degradation is much slower for D_2 compared with D_1 in any samples, as shown in Fig.5 and Fig.6, which are the graph of theoretical simulation degradation for A and B respectively.

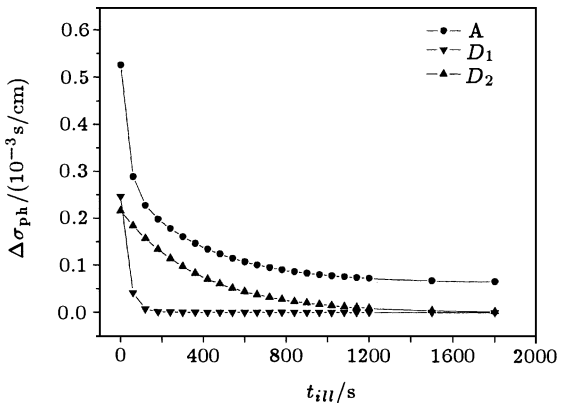


Fig.5. Theoretical simulation degradation for sample A.

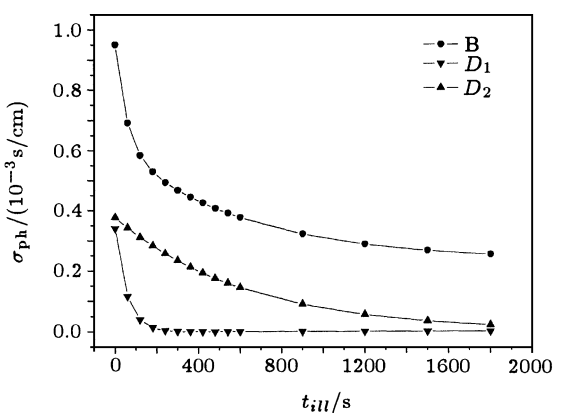


Fig.6. Theoretical simulation degradation for sample B.

4. Results and discussion

The law of photoconductivity decay predicted by the bond-breaking model is:

$$[\sigma_{\rm ph}(t_{ill})]^{-3} - [\sigma_{\rm ph}(0)]^{-3} = pt_{ill}, \qquad (8)$$

where p= (2.0±0.5) $\times 10^{10}\Omega^3{\rm cm}^3/{\rm s}$,[16] i.e., the decay of photoconductivity follows the illumination time as $\sigma_{\rm ph}(t_{ill}) \propto t_{ill}^{1/3}$. Whereas, the model functions obtained by us is $\sigma_{\rm ph} = \sigma_{\rm ph}(0) + A_1\exp(-t_{ill}/t_1) + A_2\exp(-t_{ill}/t_2)$. The photoelectric properties of semiconductor are conclusions calculated from statistics. The exponential functions play an important role in the theory of statistics. Thus, the exponential functions are prior choice to establish the model functions, rather than power-law model used in the Eq.(8). As observed in Fig.2 and Fig.3, the experimental data can be simulated validly with exponential model functions.

Schmidt *et al* have found that, as t_{ill} increases, two peaks grow in the midgap region, while the valence-band tail remains practically unchanged.[17] Sakata *et al* have also found two distinct defect states in the lower midgap of undoped a-Si:H.[18] Many experiments have shown that the density of states in the gap of a-Si:H is dominated by different charged states of silicon bond: D^+, D^0 and D^-. The positions in the gap of these three states have no consistent conclusion. Schmidt proposed that D^0, D^- centred at E_c-1.0eV and E_c-1.1eV respectively. This is consistent with Zeeman's conclusion, potential fluctuations model, and also, defect pool model etc.[18] Nevertheless, Wronski proposed that D^0, D^- centred at E_c-1.12eV and E_c-1.40eV respectively.[19] Neutral defect states and negatively charged defect states are both significantly increased during illumination in the study of photoconductivity degradation in a-Si:H using charged deep-level transient spectroscopy (Q-DLTS) spectra. Positively charged defect states hardly play a role in the degradation of films during longer illumination, compared with neutral defect states and negatively charged defect states.[10] This is the reason why Schmidt and Sakata just detect two obvious defect states, without positively charged defect states in midgap region. This is also supported by our theoretical simulation results. In the theoretical simulation model equation (1), only two exponential decay factors D_1, D_2 are included, the effect of degradation as a result of positively charged defects can not exist. D_1, D_2 characterize the effect of photoconductivity degradation due to neutral defect states and negatively charged defect states respectively.

Charged defect states are more than that of neutral defect states, which is obtained by the further research of Schmidt *et al*. This corresponds with theoretical prediction of defect pool model.[17] Our theoretical simulation of photoconductivity degradation is performed on large numbers of samples. During the degradation, curve D_1 decays rapidly and declines to 0 within 200s. The defect state density represented by curve D_1 is obviously lower than that of curve D_2. Therefore, based on the law of defect pool model, the decline of curve D_1 and D_2directly reflects the variation of neutral defect states and negatively charged defect states in the films respectively. We propose that D_1 may be introduced from Si-H bonds with lower energy. D_2 arise from Si-H bonds with higher energy or the abnormal assembly of Si and H.

It is found surprisingly that a one-to-one correspondence exists between $\Delta\sigma_{\rm ph}$ and $\sigma_{\rm ph}(0)_{\rm (simul)}$. The relationships of them meet the functions (7). Namely, for certain sample, under the condition which the ini-

tial photoconductivity is obtained, the total amount of degradation (after becoming stable during illumination) can be calculated by this function. The total amount of degradation strictly depends on initial photoconductivity. It is certain that some relationships exist between the microstructures in films and the total amount of photoconductivity degradation as well as the initial photoconductivity. The idiographic micromechanism tells us how the microstructure is in films, it determines the initial photoconductivity and there is a need to do further research on the total amount of degradation.

5. Conclusion

In this paper, the method of numerical simulation is used to fit the relationship between the photoconductivity in films and the illumination time. The photoconductivity follows the equation: $\sigma_{\rm ph} = \sigma_{\rm ph}(0)+D_1+D_2$, where $D_1 = A_1\exp(-t_{ill}/t_1)$, $D_2 = A_2\exp(-t_{ill}/t_2)$. The generation and process rule of kinds of different charged defect states during illumination are revealed. Neutral defect states and negatively charged defect states play an important role in SWE. Positively charged defect states hardly play a role in the degradation of films. It is surprising that the total amount of photoconductivity degradation during illumination is one-to-one correspondence with sample's initial photoconductivity, i.e. the initial photoconductivity determines directly the total account of photoconductivity degradation of sample. Due to the microstructure of samples, there is need to do further researches on the idiographic micromechanism.

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