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Influence of Thermal Conductive Material on the Activation Energy of Amorphous Silicon Thin Films

Sevilay UĞUR
TUBITAK, Ulusal Metroloji Enstitşsş (UME),
P.O. Box 21, 41470 Gebze, Kocaeli - TURKEY
Merih SERİN
Y.T.U., Faculty of Arts and Sciences,
Department of Physics, 80270 Şişli,
İstanbul - TURKEY

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Abstract

The activation energy of amorphous silicon thin films are usually measured by placing the thin film sample on a heating surface and monitoring the change in the dark conductivity as a function of temperature. The most widely used devices for temperature measurements are surface thermometers and thermocouples.

Sensors such as surface thermometers or thermocouples simply measure temperature by reaching an equilibrium state with the measured environment. If the heat conduction to the sensor somehow is obscured by several reasons (sensors having a much larger dimensions than the thin film or not having proper vacuum) different thermal conduction to the sensor than that to the sample, resulting an improper reading of the actual sample temperature, results. By placing a thermally conductive material between sample, sensor and heating surface the heat exchange could be improved resulting in better thermal equilibrium between these surfaces.

This present study will report dark conductivity of carbonated hydrogenated amorphous silicon samples (a-Si_{1-x}:C_x:H) obtained with various Silane (SiH_4), Methane (CH_4) ratios, and p-type a-Si_{1-x}:C_x:H obtained with various Silane (SiH_4), Methane (CH_4) and Diborane (B_2H_6) ratios. The measurements, which were performed before and after using thermally conductive material, will be compared and the influence of this conductive material to the activation energy will be discussed.

1. Introduction

After Ovsinsky [1] presented the first amorphous switching device, amorphous semiconductors attracted a wide range of attention as a new electronic device. After it was shown

that the Fermi level of glow discharge grown amorphous silicon could be controlled by doping [2], it was understood that the characteristics of this material strongly depended on the structure.

Aside from being p-type or n-type dopeable, characteristics such as having excellent photoconductivity, high absorption coefficient in the visible region [3] and being able to be deposited on wide areas as a thin film, made amorphous silicon a very suitable material for photovoltaic applications.

It was demonstrated by Anderson and Spear that when hydrocarbons are added to silane during deposition, a-Si:C:H alloy could be obtained. The importance of this alloy lies in the fact that by varying the carbon content the material band gap could be controlled over a wide range. Combined with very good conductivity, a-Si_{1-x}:C_x:H alloy is a suitable window material for a-Si:H solar cells [4].

With the motivation of determining the most efficient Si/C composition for solar cell window layers, series of samples were deposited in the TÜBİTAK, UME Thin Film Laboratory. Dark conductivity of each sample was measured several times in order to verify true, reliable and repeatable results and the experimental conditions were determined in order to obtain such measurements.

2. Experimental

In this study, a-Si_{1-x}:C_x:H samples were produced in a capacitively coupled Ultra High Vacuum-Plasma Enhanced Chemical Vapor Deposition System (UHV-PECVD) [5]. These films were grown on Corning-7059 glass substrates. Substrates were placed on a grounded electrode and no external bias was applied. Typical growth conditions are summarized in Table 1.

Table 1. Typical deposition parameters for hydrogenated amorphous silicon.

Deposition Parameters	a-Si_{1-x}:C_x:H	p-type a-Si_{1-x}:C_x:H
UHV	$4 \cdot 10^{-8}$ Torr	$4 \cdot 10^{-8}$ Torr
Deposition Temperature	$190 - 227$°C	195°C
RF Power Forward	5 mW/cm^2	4.2mW/cm^2
Reverse	0.4mW/cm^2	0.3mW/cm^2
DC Bias	-3 V	-3 V
Deposition Pressure	700-800m Torr	630m Torr

By changing the silane and methane flow rates, variable Si/C ratios for the samples were obtained. Variable incorporation of carbon into samples influenced the growth rates and resulted in a decrease in film thickness as the carbon content increased. The film thickness were in the range of 0.4-1.4 μm and were determined by measuring the interference amplitude and fringe spacing [5]. The characterization of amorphous thin films were made by measuring temperature dependent dc dark conductivities. Dark conductivity of amorphous silicon is expressed as [6]

$$\sigma_D = \sigma_0 \exp(-\Delta E/kT),$$

where σ_D is the dark conductivity, $\Delta E = (E_C - E_F)$ is activation energy, and σ_0 the preexponential factor. Optimal quality films exhibit a straight line over many orders of magnitude on $\ln \sigma_D$ vs 1000/T arrhenius plot and hence its slope exhibits a well defined activation energy.

The measurements were taken in a home made vacuum chamber. Since water vapor and surface conditions affect the sample features all the measurements were made under vacuum and samples were heated after vacuum chamber pressure dropped to a pressure of 2.10^{-6} torr or below. Samples were placed on top of a copper plate that is heated by a bolt heater embedded within. A second sample was symmetrically placed with respect to first one on top of a copper plate. A thermocouple was placed on the second one and attached to the surface of the sample with silver paint.

Two 5mm $\times$ 5mm aluminum contacts separated by 2mm were evaporated on the samples. 100 Volts was applied to the samples and under this condition the contacts exhibited ohmic behavior [5]. The current was measured by spring loaded pogo contacts and was read via a Keithley 617 electrometer. During annealing the samples were held at 170°C more than two hours under the $2 \cdot 10^{-6}$torr. Activation energy was determined from the slope of the cooling curve.

Initially, measurements were performed without using thermally conductive material. Results of these measurements can be seen in the "before" column of Table 2. Later, In-Ga alloy as a thermally conductive material was placed between the copper plate and the sample and between the second sample on which the sensor was placed. Under these conditions, dark conductivity measurements were repeated. The activation energy values are listed in the "after" columns of Table 2.

The main concern with these measurements were keeping the actual sample temperature and sensor temperature the same. Keeping in mind that the thickness of the samples are on the order of 1 μm and the typical thermocouple junctions are on the order of 1 mm, maintaining the above condition is quite a difficult task. In order to obtain reliable and repeatable results, measurements were repeated until we were sure that the temperature read was correct.

One quick way to check whether the measurements are correct is to compare the heating and the cooling curves of a well annealed sample. If the temperature of the sample is measured correctly both curves will be the same. If temperature readings have problems, heating and cooling curves will be different, yielding a hysterisis type effect.

In Table 2, in Part I carbonated hydrogenated silicon samples prepared with different carbon ratios (R_C) are listed. Gas ratio represents the ratio of methane flow rate of the total flow rate of the individual gases, namely CH_4/SiH_4+CH_4. In Part II p-type samples produced using 0.600, 0.948, and 0.785 carbon ratios are listed. Gas ratios represent diborane flow rate to the total gas mixture flow rate, $B_2H_6/B_2H_6+SiH_4+CH_4$.

For the p-type samples, diborane rate to total gas mixture changes between 0.047 and 0.231 and activation energy in the "before" column stays nearly constant, which could possibly be interpreted as the diborane concentration has no effect at all on the activation energy. But in the "after" column it is clearly shown that as the diborane rate increases, and activation energy decreases as expected.

Table 2. Activation energies of the amorphous silicon thin films with and without using thermally conductive material.

Sample	Gas Ratios R_C	Activation Energy eV		Sample	Gas Ratios	Activation Energy eV	
		Before	After	R_C=0.600		Before	After
2I008	0	0.84	0.88	2P022	0.047	0.47	0.43
2C019	0.200	0.99	0.98	2P024	0.090	0.49	0.41
2C011	0.429	1.01	0.98	2P026	0.130	0.46	0.40
2C012	0.529	1.08	1.04	2P028	0.167	0.48	0.36
2C013	0.600	1.17	1.17	2P030	0.231	0.47	0.35
2C014	0.646	1.19	1.20	R_C=0.948			
2C016	0.785	1.31	1.25	2P023	0.061	0.93	0.92
2C017	0.879	1.35	1.26	2P025	0.115	0.87	0.80
2C020	0.948	1.38	1.29	2P027	0.163	0.76	0.69
				2P029	0.206	0.68	0.59
				R_C=0.785			
				2P040	0.051	0.51	0.51
				2P039	0.139	0.50	0.48
				2P038	0.244	0.53	0.44

The activation energies between before and after using thermal contact are plotted with respect to gas rate in Figure 1.

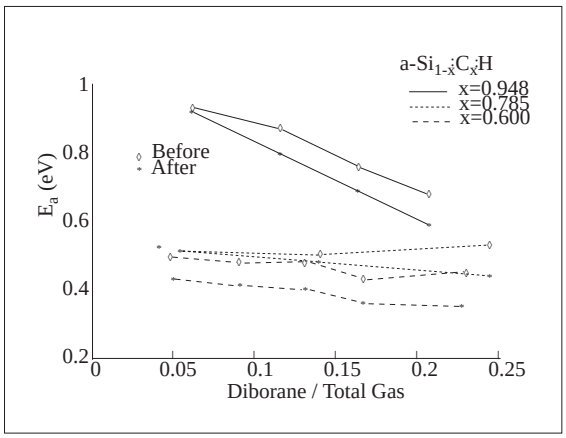

Figure 1. Activation Energies obtained before and after using In-Ga alloy

It is clearly indicated in Table 2 that using thermally conductive material may change the activation energy as much as 30% (Figure 2).

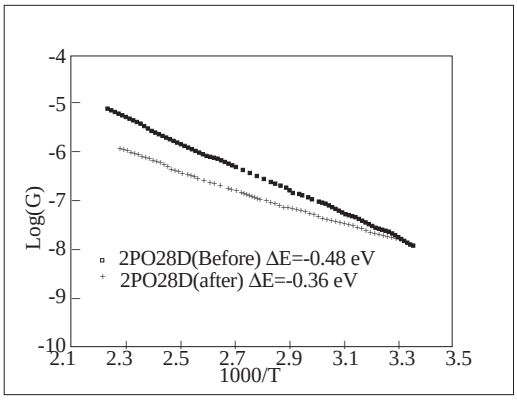

Figure 2. Plot of cooling curves

Possible reasons for such a discrepancy between using a thermal conduction material or not, may have the following explanations:

- Heating medium copper does not have a smooth surface as required, surface roughness prevents the sample from touching the copper block at every point resulting different thermal conduction and horizontal heat flow at the bottom surface.
- We suspect that Corning-7059 glass bends during deposition contributing to the uneven thermal conduction between sample and the copper block due to internal stress and the different thermal expansion properties of the film on it.
- Dimensions of the thermocouple junction is much larger than the sample thickness resulting heat losses. Here, the vacuum level is very important. If the desired vacuum is not maintained, contribution of this factor will be large.
- Other than the geometrical factors, there is one more thing which affects the results: Amorphous silicon responds to temperature changes much faster than the thermocouple. That is, the copper temperature changes current through a-Si:H before the thermocouple reading.

Owing to the above listed reasons, measurements taken without a thermally conductive material results in totally unpredictable slope of dark conductivity curve whose outcome depends on the measurement conditions. When In-Ga is prepared as a nearly euthetic alloy (21.4% In, 78.6% Ga) it is in solid form below 15.3°C and liquefies above 15.3°C [7]. While the sample was heated above room temperature In-Ga alloy fills the space between the sample and the copper block providing a perfect heat conduction.

For this work repeated measurements were taken in order to asses the effect of In-Ga alloy and the following observations were made:

- Using the In-Ga alloy reduced the power requirement to heat the sample and the heating time to reach 170°C.

- Without changing the vacuum conditions, if the sample was reheated the same arrhenius curve was obtained (Fig 3). Also keeping the temperature constant at several points did not influence the current measured. Heating rate and cooling rate did not influence the slope.

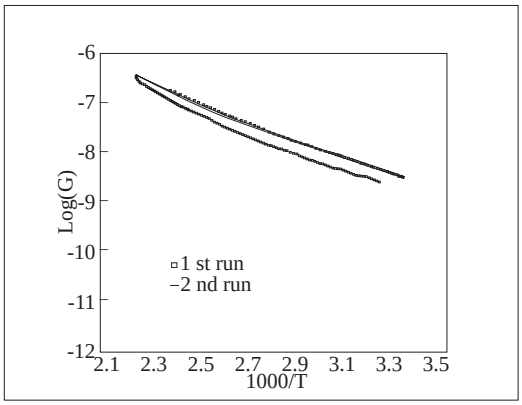

Figure 3. Repeated heating and cooling processes using the In-Ga alloy.

Figure 2 indicates the dark conductivity values at room temperature are the same in both cases, namely with and without In-Ga. But at higher temperatures, as the temperature rises, the difference grows. This behavior is consistent with the fact that at room temperature in both cases the sample and thermocouple are in thermal equilibrium; but as the copper block heats up if thermally conductive material is absent the thermocouple indicates lower temperature than the actual sample temperature for the reasons we stated earlier.

3. Results

While measuring the temperature of thin films utmost care should be taken. Many circumstances may contribute to faulty surface temperature information. In order to avoid faulty readings various conducting media should be tested many times for various characteristics:

- Conduction from heating medium to sample,
- Conduction from sample to sensor,
- Possible heat losses in the system should also be examined.

  Additionally, the junction tip of thermocouple must be kept as small as possible so does the mass of the paste material since this mass will increase the heat losses.

For a-Si:H samples measurement should be made under vacuum better than 10^{-6} torr, and thermally conductive material should always be used to improve the thermal conduction. This work has shown that In-Ga euthetic alloy is a suitable thermally conductive material for dark conductivity measurements of a-Si:H.

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