

DEPOSITION AND CHARACTERIZATION OF A-SI:H FILMS DOPED (N-TYPE OR P-TYPE)

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ABSTRACT

Hydrogenated amorphous silicon (a-Si:H) is a promising material in the photovoltaic industry due to its high absorption coefficient and low manufacturing cost. The optical and electrical properties of a-Si:H doped p-type or n-type films were studied: transmittance, absorption coefficient, conductivity, activation energy, and thickness. The films were fabricated through plasma enhanced chemical vapor deposition (PECVD) at low frequency with a substrate temperature of 300°C by varying the flow of hydrogen and dopant gases. The characterization of the films was completed using electrical characterization techniques, optical transmission, and UV-visible ellipsometry. The results show that hydrogenated amorphous silicon is a good alternative for the manufacture of photovoltaic devices.

KEYWORDS: Amorphous silicon, hydrogenated silicon, doped amorphous silicon, amorphous silicon films, doped semiconductor films, hydrogenated silicon films.

DEPÓSITO Y CARACTERIZACIÓN DE PELÍCULAS DOPADAS DE A-SI:H (TIPO N O TIPO P)

RESUMEN:

El silicio amorfo hidrogenado (a-Si:H) surge como un material prometedor en la industria fotovoltaica gracias a su alto coeficiente de absorción y a su bajo costo de producción. En este trabajo se estudiaron las propiedades ópticas y eléctricas de películas de a-Si:H dopadas tipo p y tipo n tales como: transmitancia, coeficiente de absorción, conductividad, energía de activación y espesor. Dichas películas se fabricaron mediante la técnica Depósito Químico en fase Vapor Asistido por Plasma (PECVD, por su sigla en inglés) a baja frecuencia con una temperatura de sustrato de 300 °C, variando el flujo de hidrógeno y de los gases dopantes. La caracterización de las películas se hizo mediante las técnicas de caracterización eléctrica, transmisión óptica y elipsometría UV - Visible. Los resultados muestran que el silicio amorfo hidrogenado es una buena alternativa para la fabricación de dispositivos fotovoltaicos.

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PALABRAS CLAVE: Silício amorfo, silício hidrogenado, silício amorfo dopado, películas de silício amorfo, películas semiconductoras dopadas, películas de silício hidrogenado.

DEPOSITO E CARACTERIZAÇÃO DE FILMES DOPADOS DE A-SI:H (TIPO N OU TIPO P)

RESUMO

O silício amorfo hidrogenado (a-Si:H) surge como um material promissor na indústria fotovoltaica devido ao seu alto coeficiente de absorção e baixo custo de produção. Neste trabalho, foram estudadas propriedades ópticas e elétricas de filmes de a-Si:H dotados tipo p y tipo n tais como: transmitância, coeficiente de absorção, condutividade, energia de ativação e espessura. Tais filmes foram fabricados usando a técnica de Deposição Química em fase Vapor assistida por plasma (PECVD) a baixa frequência com uma temperatura do substrato de 300 °C, variando o fluxo do hidrogênio e dos gases dopantes. A caracterização dos filmes foi feita por meio de técnicas de caracterização elétrica, transmissão óptica e elipsometria e UV-Visível. Os resultados mostram que o silício amorfo hidrogenado é uma boa alternativa para a fabricação de dispositivos fotovoltaicos.

PALAVRAS-CHAVE: Silício amorfo, silício hidrogenado, silício amorfo dopado, filmes de silício amorfo, filmes dopado de semicondutores, filmes de silício hidrogenado.

1. INTRODUCTION

A material that has had a great reception in the microelectronic industry due to its low cost compared to monocrystalline silicon (c-Si), is amorphous silicon (a-Si). Amorphous silicon, a-Si, presents great randomization in its atomic ordering to the extent that its atoms are not localized at defined distances and angles. It was Chittick *et al.* (1969) who added hydrogen to the amorphous silicon to beneficial effect because the hydrogen saturates the defects of the network. This discovery was fundamental at a time when amorphous semiconductors were being developed because it demonstrated that a-Si:H could be doped with phosphorous or boron (Spear *et al.* 1975). Obtaining a-Si requires techniques in the deposit of thin film, the most utilized of which is plasma-enhanced chemical vapor deposition (PECVD), which is a variant of CVD in that a plasma is applied to a mix of gases with the aim of dissociating the molecules contained in the gas at low temperatures. In the event that it is necessary to dope the film, the injection of the dopant atom into the chamber as an essential gas component is suggested (Poortmans J. *et al.* 2006; Roca iCabarrocas P. J. 2000; Roca iCabarrocas, FontcubertaiMorrall, Lebib & Poissant 2002).

In this study thin a-Si:H films doped with PH_3 (n-type) and B_2H_6 (p-type) were deposited through the PECVD technique at low frequency, varying the flow of PH_3 , B_2H_6 , and H_2 gases to observe how the concentration of the gases in the chamber influences the optic and electric properties of the films (Butte R. *et al.* 2000). These films were manufactured and characterized at the National Institute of Astrophysics, Optics and Electronics' (INAOE) Microelectronics Laboratory in Puebla, Mexico.

2. METHODS AND MATERIALS

To obtain the doped n-type and p-type a-Si:H films three types of samples must be deposited into the PECVD system thusly: first, a thin film of intrinsic a-Si:H which will serve as a benchmark, and afterwards two series of thin films of doped a-Si:H. In the first series the n-type samples are doped. For this a mix of SiH_4 , H_2 , and PH_3 gases is used. In the second series the p-type samples are doped, and in this case a mix of SiH_4 , H_2 , and B_2H_6 is used. The substrates utilized in both series were samples of Corning Glass 2974 and 1737 (Benmenssaoud A., 2001).

In **Tables 1** and **2** the values of the flows employed in each series are shown.

The absorption coefficients of the films were determined by the results of the transmission measurements taken with the Perkin Elmer Lambda spectrometer between a range of 300 nm and 900 nm, as well as PUMA software (Pointwise Unconstrained Minimization Approach) [3].

Activation energy (E_a) and conductivity were obtained through current-voltage measurements, which in turn were obtained within a wide range of temperatures, between 300 K and 400 K.

Through the UV-visible spectroscopic ellipsometry technique the imaginary part of the pseudo-dielectric ($\text{Im}[\epsilon]$) of the doped a-Si:H films was measured to obtain the thickness of the films.

Table 1. Series 1: Parameters of the dopedn-typea-Si:H film deposits. This series was produced with a 600 mTorr pressure chamber under 300 W of power, a power density corresponding to 90 mW/cm², and a flow of SiH₄ equal to 50 sccm. It was produced at a temperature of 300 K during 30 minutes.

Gas	Unit	Series 1 – Process No.					
		1	2	3	4	5	6
H ₂	sccm	1000	200	1000	1000	1000	1000
PH ₃	sccm	0	4	4	6	8	8

Table 2. Series 2: Parameters of the dopedp-typea-Si:H film deposits. This series was produced with a 600 mTorr pressure chamber at 300 W of power, a power density corresponding to 90 mW/cm², and a flow of SiH₄ equal to 50 sccm. It was produced at a temperature of 300 K during 30 minutes.

Gas	Unit	Series 2 – Process No.					
		1	7	8	9	10	11
H ₂	sccm	1000	200	1000	1000	1000	1000
B ₂ H ₆	sccm	0	4	5	6	8	10

3. RESULTS

The transmittance spectrums of the doped films behave differently in their transmittance for the intrinsic film. That is how both types of film produce a major

transmittance between 600 nm and 700 nm, although between 400 nm and 550 nm their transmittance is low enough, lower than the intrinsic film. In the graphs in **Figure 1** the transmittance's dependence on the flow of dopant gas can be observed; the features encountered in them include:

- In the 300 nm to 550 nm range the intrinsic sample showed a higher transmittance; however, in the 550 nm to 900 nm range, for both series, a transmittance of almost double for the intrinsic sample can be observed.

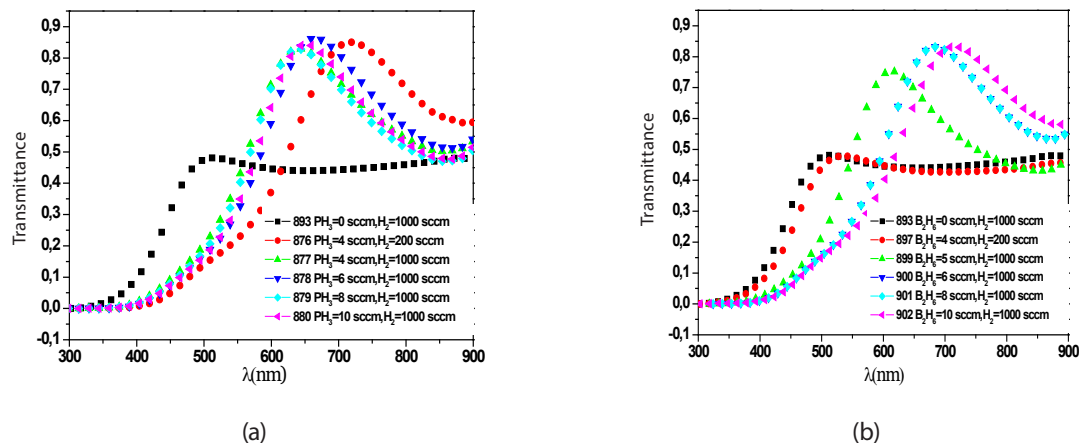
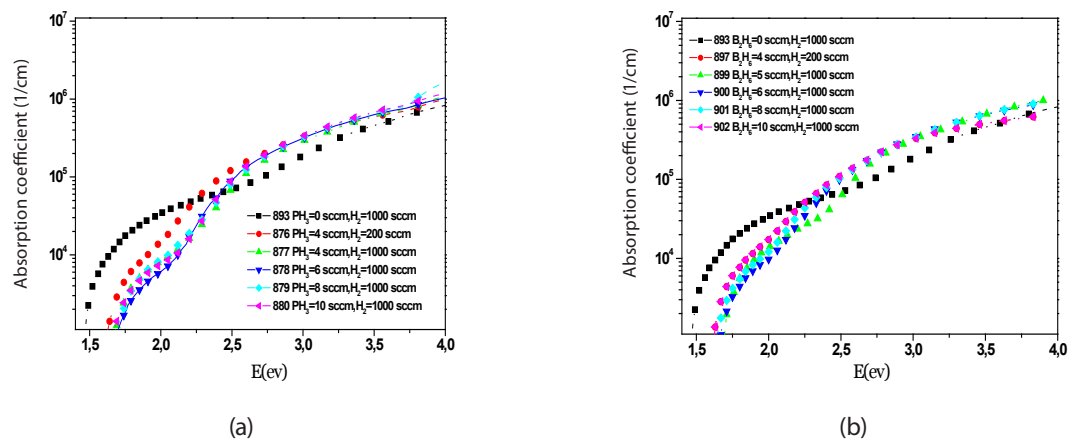
- The samples deposited with less H₂ flow for both series, Process 2 (dopedn-type) and Process 7 (dopedp-type), display the opposite behavior for each type, while the n-type film displays a higher transmittance at a higher wavelength and the p-type sample behaves in a similar manner to the intrinsic sample, meaning there is less transmittance at a higher wavelength.

The absorption coefficients are determined by entering the data from the transmittance into the PUMA software according to the wavelength (T Vs. λ) The results are shown in the graphs in **Figure 2**.

In the graphs in **Figure 2** a similar behavior for all of the samples can be observed; the only different sample is the intrinsic one, which has a higher absorption coefficient in the 1.5 eV to 2.2 eV range. In the 2.2 eV to 4.0 eV range, however, the doped samples display a higher absorption coefficient than the intrinsic one.

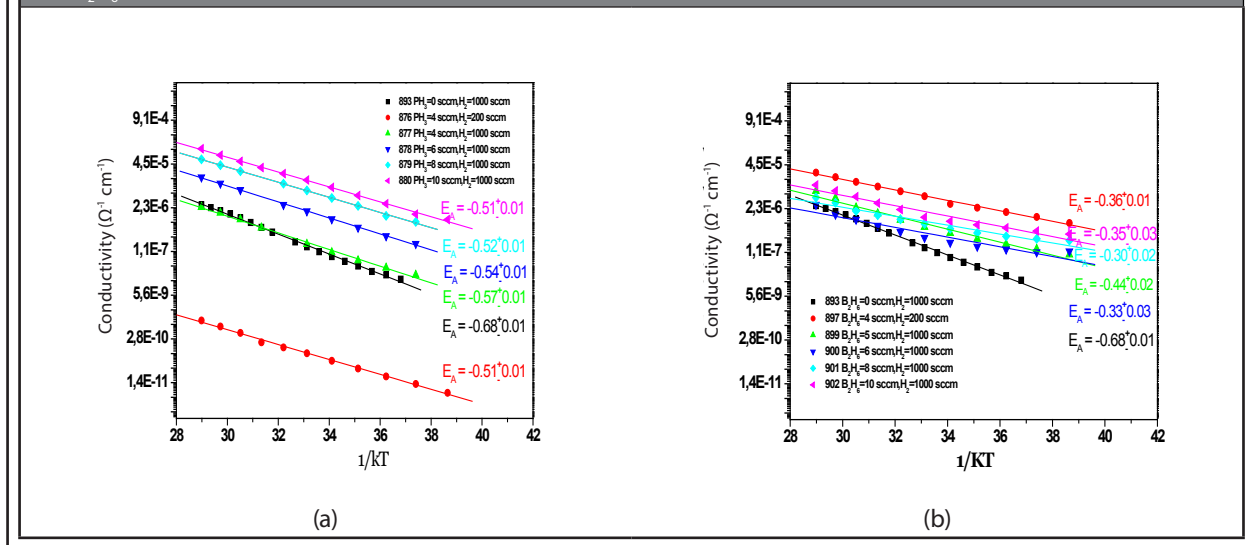
The results of the conductivity measurements are shown in **Figure 3**, with the respective Arrhenius graphs displaying the energy activation values for each film. It can also be observed in the graphs that there is a higher conductivity with a higher dopant flow. If we analyze the results of the fabricated samples with a lower flow of H₂ one can see that the sample from Process 2 (n-type) shows less conductivity, while the sample from Process 7 (p-type) shows more.

With the measurements from the UV-Visible ellipsometry the thickness of the films can be obtained, as can be observed in **Table 3**. Here it can also be noted that none of the films surpasses 110 nm in thickness.

Figure 1. Transmittance spectrum for both series of films. a) With SiH_4 , H_2 and PH_3 flows. b) With SiH_4 , H_2 and B_2H_6 flows.

Figure 2. Graphs of the absorption coefficients for both series. a) Films deposited with SiH_4 , H_2 and PH_3 flows. b) Films deposited with SiH_4 , H_2 and B_2H_6 flows.

Table 3. Results of the thickness and width measurements of the gap of each sample from the processes of series 1 and 2.

Series 1			Series 2		
Process	Thickness (Å)	Gap (eV)	Process	Thickness (Å)	Gap (eV)
1	583	1,97	1	583	1,97
2	1066	1,71	7	601	1,83
3	942	1,71	8	860	1,74
4	995	1,82	9	986	1,70
5	911	1,79	10	1030	1,69
6	956	1,78	11	1079	1,67

Figure 3. The conductivity measurement in the dark, based on the display temperature which increases with the dopants for both types. a) Series of films deposited with SiH_4 , H_2 and PH_3 flows. b) Series of films deposited with SiH_4 , H_2 and B_2H_6 flows



4. DISCUSSION

The doped p -type and n -type a-Si:H films were successfully deposited utilizing the PECVD technique at low frequency. In each series specific conditions for the flows of each of the gases were evaluated: silane, hydrogen, diborane, and phosphine.

Upon comparing the intrinsic sample with the doped samples one finds that the doped samples display better properties than the intrinsic sample. This is made apparent by the conductivity and gap measurement graphs: the doped samples display better conductivity, and their gap decreases in values that range from 7% to 15%.

It can be concluded from the doped p -type and n -type a-Si:H samples that the best conditions occur with higher dopant flows, that is to say with phosphine or diborane gas, as they reach a conductivity superior to the minimum required in a-Si:H materials for quality solar cells.

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