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Effects of hydrogen partial pressure on boron-doped hydrogenated amorphous silicon (a-Si:H(B)) properties

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Abstract. Boron-doped hydrogenated amorphous silicon (a-Si:H(B)) thin films have been prepared by DC magnetron sputtering technique under argon and hydrogen mixture. The films were deposited at various hydrogen pressures between 0 and 9 10^{-5} mbar. The boron concentration estimated from Secondary Ion Mass Spectrometry (SIMS) analysis was found to be around 1.5 10^{21} cm^{-3} for all samples. Their physico-chemical, optical and electrical properties are investigated. The physico-chemical properties were studied by infrared absorption measurements. The bonded hydrogen content in the films is then determined using the absorption band of stretching mode. The optical transmission measurements show an increase of the static refractive index and a decrease of optical gap value when hydrogen pressure increases. The dark-conductivity and the photo-conductivity measurements according to the temperature are also reported. We have observed the decreasing of dark-conductivity when hydrogen pressure increases. A slight sensitivity of light was observed for the film deposited at the highest hydrogen pressure. The dark-conductivity was affected by annealing temperature for the whole of the films through its increase in the annealing temperature region 200-350°C.

Introduction

Hydrogenated amorphous silicon (a-Si:H) for low power applications appeared on the scene in 1975. Spear and Le Comber [1] produced, for the first time, a-Si:H doped with boron and phosphorus, and Carlson and Wronski [2] obtained the first a-Si:H junction. Moreover, this material attracted a great deal of interest because it can be deposited on large areas of flexible substrates at very low costs as compared with crystalline silicon. Therefore, a-Si:H is a promising material in technological and commercial useful. Thin film transistors (TFT), image sensors, light emitting diodes, random access memories, radiation detectors but most of all large area photovoltaic use this material.

The preparation of this type of material in thin films can be made frequently by two methods of deposition: (i) CVD (Chemical Vapor Deposition) and (ii) sputtering. The sputtering technique is not extensively used, but it has the advantages of simplicity and possibility of separating material radicals (Si, H and B). Then, it facilitates the control of the chemical composition of material. Furthermore, this technique doesn't use dangerous gases (toxics and explosives) like SiH_4 and B_2H_6 largely used in CVD techniques.

In this paper, we present characterization results of boron-doped a-Si:H thin films deposited by DC magnetron sputtering technique. All the films are deposited in the same deposition conditions except the hydrogen pressure which is varied. The characterization techniques used here to investigate a-Si:H(B) films are the micro-analysis SIMS, the Raman spectroscopy, the infrared absorption, the optical transmission, the conductivity and the photoconductivity measurements. The obtained results are discussed as function of hydrogen partial pressure.

Experimental details

The samples were prepared in DC magnetron sputtering system by co-sputtering of silicon target with small boron platelets in argon and hydrogen plasma mixture. The deposition parameters were kept as follows: substrate temperature of 260°C, argon pressure of 10^{-4}mbar and deposition time of 10min. The hydrogen pressure was the only varied parameter between 0 and 9 10^{-5}mbar. The a-Si:H(B) films were deposited on crystalline silicon substrates for SIMS and infrared analysis, and on 9075 corning glass substrates for Raman scattering, optical transmission and electrical conductivity measurements. The boron concentration measured by SIMS technique, remains constant around 1.5 10^{21}cm^{-3} for all samples. The Raman scattering measurements were performed at room temperature using a *JOBIN YVON T64000* Raman spectrometer equipped with an argon laser. The excitation wavelength was 514.5nm. The infrared absorption measurements were made using a *Perkin Elmer (FTIR)* spectrometer. The amount of hydrogen bonded to silicon was determined from the intensity of silicon-hydrogen stretching band situated around 2000cm^{-1}. The values of absorption coefficient, optical gap and static refractive index were determined from the transmission spectra measured in 400-2500nm range. Electrical conductivity measurements were performed in a coplanar configuration (gap of 0.1cm) under 3 10^{-5}mbar pressure using a d.c. electric field of 10^{2}V.cm^{-1} which were made by evaporating aluminium under secondary vacuum. The photoconductivity measurements are carried out with white light source of 100mW/cm^2 power. These measurements were made according to the temperature from room temperature to 150°C, and the data were collected during the heating cycle. The temperature was raised at the rate of 5°C/min.Annealing of samples was performed at different T_{anneal} in the range 40-450°C for 20min.

Results and discussion

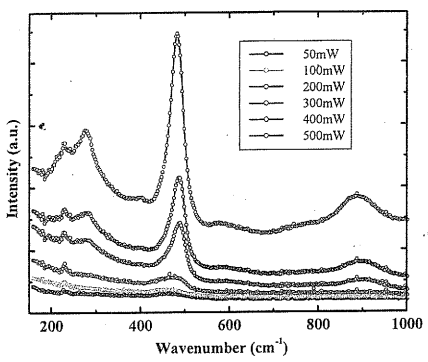

Fig. 1: Raman scattering spectra of unhydrogenated sample (prepared at hydrogen pressure P_{H2} = 0 mbar) for different laser power.

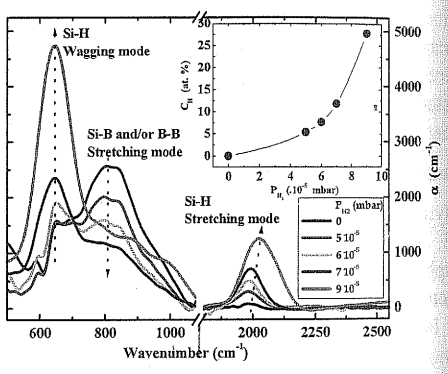

Fig. 2: Infrared absorption spectra of a-Si:H(B) films deposited at different hydrogen pressure. In inset, variation of hydrogen content C_H as function of hydrogen pressure P_{H2} is presented.

To analyse the structure of a-Si:H(B) material, Raman scattering experiment were performed. Fig. 1 shows an example of Raman spectra of a-Si:H(B) film those obtained for different laser power (50, 100, 200, 300, 400 and 500 mW). The spectra are characteristic of amorphous silicon with particularly the wide transverse-optical-like peak at 480 cm^{-1}.

The infrared spectra are studied to gain some information about the structure and the ways hydrogen is incorporated as well as to estimate the bonded hydrogen content. Fig. 2 illustrates the evolution of infrared absorption spectra of our films as a function of hydrogen pressure P_{H2}. Three principal absorption bands are clearly observed. The bands situated at 640 and 2000cm^{-1} are well known in literature and can be attributed to wagging and stretching mode of Si-H bond [3-5],

respectively. Whereas the absorption region observed between 700 and 900cm^{-1}, is certainly related to Si-B and/or B-B vibrations bonds in stretching mode [6-8]. Note here the absence of any absorption around 2500cm^{-1}, due to B-H vibration bonds in stretching mode [6, 7, 9]. Therefore this result indicates that there is preferential attachment of hydrogen to Si atoms rather than B atoms. The hydrogen pressure P_{H2} effect on infrared spectra can be observed through the increase of 2000 and 640cm^{-1} band area and the decrease of absorption in 700-900cm^{-1} region. These results may be explained by the progressive creation of Si-H and Si-H-B bonds. The last kind of bonds, created through the presence of boron atoms in the vicinity of Si-H bonds, is probably responsible of absorption reduction in 700-900 cm^{-1} region.

The quantitative investigation of infrared absorption spectra was made in 2000cm^{-1} stretching band. This band can be fitted by two Gaussian peaks centred at 1995 and 2100cm^{-1} corresponding, respectively, to the vibration of Si-H bonds in mono-hydride (SiH) and di-hydride (SiH_2) units. Using this fitting, the amount of hydrogen bonded to silicon (C_H) has been determined by the following equation:

$$C_H = A \int \frac{\alpha}{\omega} d\omega \qquad (1)$$

where α is the absorption coefficient and ω is the wavenumber. The constant A value is taken from the Refs. [10, 11].

The variation of C_H as a function of P_{H2} is presented in the inset of Fig. 2. It is clearly shown that C_H increases markedly from 0 to 27.7% with the increase of P_{H2} from 0 to 9 10^{-5}mbar. This increasing of C_H the films affects strongly their optical and electrical properties, as will be presented in the following part.

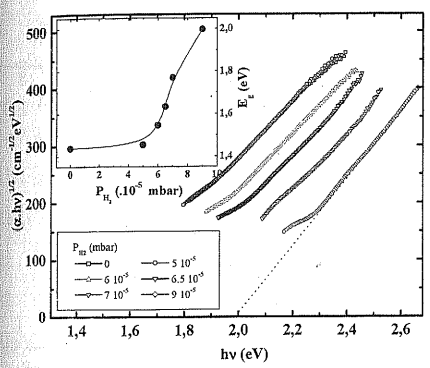

Fig. 3: The $(\alpha h\nu)^{1/2}$ versus photon energy hν plot of the a-Si:H(B) films deposited at different hydrogen pressure P_{H2}. In inset the variation of optical gap E_g with the hydrogen pressure P_{H2} is presented.

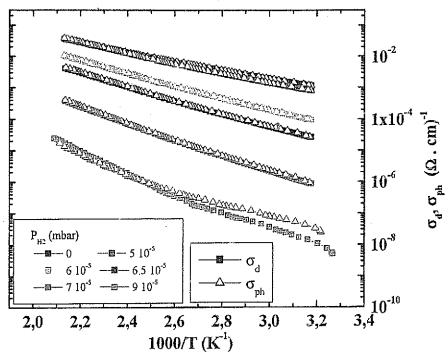

Fig. 4: Evolution of dark conductivity σ_d and photoconductivity σ_{ph} versus temperature in Arrhenius representation for different hydrogen pressure P_{H2}.

The optical absorption coefficient α and the static refractive index n_s of our films were obtained, respectively, from the treatment of transmission spectra in high absorption and low absorption region. Fig. 3 shows the evolution of $(\alpha.h\nu)^{1/2}$ versus hν, where hν represents the photon energy. It seems clearly that the increase of P_{H2} incite the shift of frontal absorption to the high photon energy with the same slope. The values of optical gap E_g were extracted according to the empirical formula derived by Tauc [12]:

$$(\alpha . h\nu)^{1/2} = B_0 (h\nu - E_g) \qquad (2)$$

where B_0 is the Tauc's factor.

Therefore, the value of E_g is obtained by extrapolation of the linear fit of frontal absorption to photon energy axis (α=0). The variation of E_g versus P_{H2} is illustrated in Fig. 3 inset. When P_{H2}

varies from 0 to 5 10^{-5}mbar, the gap value remains practically constant around 1.45eV. Beyond P_{H2}=5 10^{-5} mbar, it increases uniformly to reach its maximum value (2 eV) for P_{H2}=9 10^{-5} mbar. This behavior is observed as well in undoped material as in doped a-Si:H [13-16], and can be explained by the influence of hydrogen bonding on the valence band edge through the transforming of Si-Si weak bonds to Si-H bonds those correspond to the deep energetic levels in valence band.

The values of B_0 and refractive index n_s are given in Table 1. The decrease of n_s with the increase of P_{H2} is well known either in the case of doped or non-doped materials [13, 14], and it is often correlated to the decrease of the compactness of material [17].

P_{H2} (. 10^{-5} mbar)	B_0 (cm . eV)$^{-1/2}$	n_s
0	494	3.4
5	505	3.7
6	490	3
6.5	496	3.2
7	504	2.9
9	600	3.1

Table 1: Deposition hydrogen pressure P_{H2}, Tauc's factor B_0 and static refractive index n_s.

Fig. 4 presents the variation of the dark conductivity σ_d and photoconductivity σ_{ph} versus temperature in the Arrhenius plot representation. The dark conductivity σ_d shows a linear variation. This linearity indicates that the conduction in our films is thermally activated. Excepted for of the sample prepared at P_{H2}=9.10^{-5}mbar which shows a slight sensitivity to light at room temperature, no light sensitivity is observed for other samples.

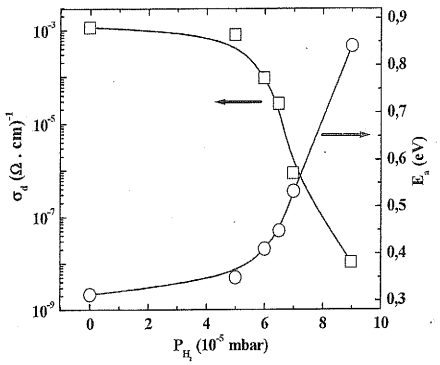

Fig. 5: Variation of the dark conductivity σ_d and its activation energy E_g versus hydrogen pressure P_{H2}.

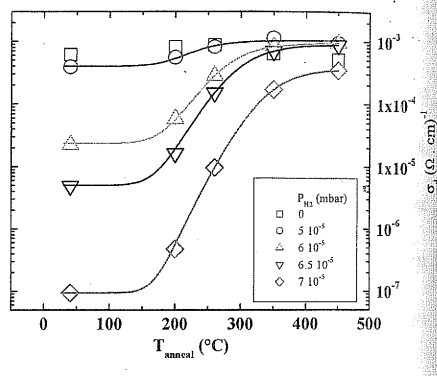

Fig. 6: Evolution of the dark conductivity σ_d versus the annealing temperature for various hydrogen pressure P_{H2}.

The variation of the dark conductivity σ_d, measured at T=40°C, and its activation energy E_a as a function of P_{H2} are illustrated in Fig. 5. We observe an important decrease of σ_d by 5 orders of magnitude when P_{H2} varies between 5 10^{-5} and 9 10^{-5}mbar. This degradation of σ_d is certainly the consequence of the increase of its activation energy from ~0.3eV to 0.85eV, and can be correlated to the passivation of boron atoms by hydrogen through the creation of Si-H---B bonds [18, 19].

The annealing temperature (T_{anneal}) effect on the dark conductivity σ_d of the films is shown in Fig. 6. The present σ_d data for various T_{anneal} can be broadly divided into three distinct temperature regions. In 40-200°C region the value of σ_d increases slightly. Thereafter, it increases significantly in 200-350°C region, where the order of magnitude of this increase seems more important for the films prepared at high hydrogen pressures. In 350-450°C region, the values of σ_d are found to tend to be constant. The increase of σ_d between 200°C and 350°C can be explained by the boron activation through the dissociation of Si-H-B bridging bonds [18, 20, 21].

Conclusion

The effect of hydrogen partial pressure on the properties of a-Si:H(B) thin films deposited by DC magnetron sputtering has been systematically reported. We have studied the physico-chemical properties of the films by the infrared absorption measurements then we have observed a preferential attachment of hydrogen to Si atoms rather than B atoms. We have also shown that the optical gap increases and the static refractive index decreases as the hydrogen pressure increases. The conductivity measurements show that hydrogen plays a handicap role for the electrical properties through its boron passivation. The annealing effect on conductivity confirms the possibility of boron activation for the annealing temperature between 200 and 350°C.

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