Structural and optical properties of compensated microcrystalline silicon films

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Boron-doped microcrystalline silicon films were deposited in a plasma enhanced chemical vapor deposition (PECVD) system using silane (SiH_4) diluted in hydrogen, and diborane (B_2H_6) as a dopant gas. The effects of the Boron concentration on the optical and structural properties were investigated by the constant-photocurrent method (CPM) and atomic force microscopy (AFM) measurements. The variations in the optical constants (refractive index, absorption coefficient and optical gap) as a function of wavelength were carried out from the optical transmission and CPM spectra. By increasing the doping level, a systematic increase in the absorption coefficient spectra in the low-energy region between 0.7 - 1.2 eV was observed. It was found that the increase of Boron concentration in the samples results in changes of the grain size. Correlations between optical properties and the density of states (DOS) were also studied.

Keywords: Optical properties; AFM; structural properties;thin films.

Se depositaron películas delgadas de silicio microcristalino con bajas concentraciones de Boro por latécnica de deposición química en fase de vapor asistida por plasma (PECVD) usando silano (SiH_4) diluido en hidrógeno y diborano (B_2H_6) como gas dopante. Se realizaron estudios de los efectos del Boro sobre las propiedades ópticas y estructurales a través del método de fotocorriente constante (CPM) y medidas de microscopía de fuerzaatómica (AFM). A partir de las medidas de transmisión óptica y los espectros de CPM se obtuvieron las constantes ópticas (índice de refracción, coeficiente de absorción y gap óptico) en función de la longitud de onda. Debido al aumento en el nivel de doping se observó un crecimiento sistemático en los espectros del coeficiente de absorción en la región de baja energía entre 0.7 - 1.2 eV. Se encontró que el incremento en la concentración de Boro en las muestras produce un cambio en el tamaño de grano. Se presenta también una correlación entre las propiedades ópticas y la densidad de estados (DOS) en el material.

Descriptores: Propiedades ópticas; AFM; propiedades estructurales; películas delgadas.

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1. Introduction

In recent years, hydrogenated microcrystalline silicon (μc-Si:H) has been increasingly used in the production of thin film based solar cells due to its higher stability compared to hydrogenated amorphous silicon (a-Si:H) [1, 2]. μc-Si:H is usually deposited by plasma enhanced chemical vapor deposition (PECVD) from silane-hydrogen mixtures, at a frequency of 13.57 MHz [3, 4]. The successful usage of thin μc-Si:H films for photovoltaic applications requires reliable techniques to characterize its properties. In this work we present results from the characterization of thin μc-Si:H films doped with boron. We measured optical properties from spectral transmittance and the constant photocurrent method (CPM), structural properties from atomic force microscope (AFM) observations, and electrical transport properties from the modulated photoconductivity (MPC) technique [5]. These last measurements were used to estimate the effect of boron incorporation on the density of states (DOS) within the forbidden gap of the material. Structural properties were obtained from X-ray diffraction measurements.

2. Experimental

Samples were prepared in a capacitively coupled PECVD reactor described in a previous work, [6] operated at a frequency of 50 MHz. The substrate was Corning 7059 glass and the substrate temperature was set at 160°C. We used a mixture of 94% hydrogen - 6% silane as source gas, with a total flux of 20 sscm. Diborane was used as a dopant gas, with a concentration in the gas phase varying between 0 and 100 ppm relative to silane. The base pressure in the reactor previous to the deposition was lower than 10^{-6} Torr, while during the sample deposition, it was fixed at 4.5×10^{-1} Torr. The power density was 50 mW/cm^2. The films' thickness, calculated from the interference of the transmittance spectra in the near infrared region, ranged from 0.6 to 1 μm. The absorption coefficient for energies lower than 2 eV was determined from constant photocurrent measurements (CPM [7]). The MPC measurements were performed on samples provided with interdigitated aluminum contacts, separated 0.01 cm and with a total length of 25 cm, deposited by photolithography. Samples were mounted in a cryostat provided with an optical window, connected to a vacuum system. A 10 mW He-Ne laser was used as a light source. The incident light intensity was partially modulated (12.5%) by using an electro-optical modulator driven by a function generator (HP 3325A). We applied to the samples a voltage of 100 V, provided by a stabilized power source. For dc photoconductivity measurements we used a Keithley 617 electrometer, while for the MPC mea-

surements, we used a lock-in amplifier (Stanford 830) to detect the modulus and phase shift of the ac photocurrent. To evaluate the DOS from the MPC measurements we assumed a DOS at the conduction band edge of 1×10^{21} $cm^{-3}eV^{-1}$ and a mobility gap of 1.8 eV. To study the morphological properties, we used an atomic force microscope (Park Scientific Instruments). X rays diffractio was used to confirm the microcrystalline nature of the samples.

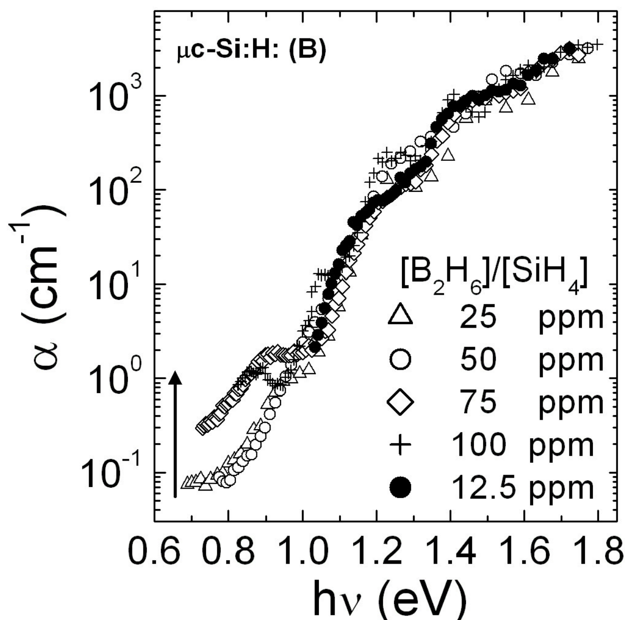

FIGURE 1. α(hν) spectra obtained by CPM for the set of μc-Si:H simples deposited varying the doping concentration $[B_2H_6]/[SiH_4]$ between 12.5 and 100 ppm.

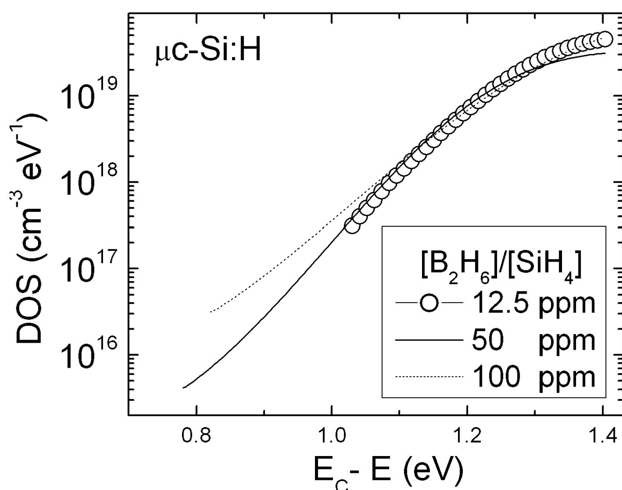

FIGURE 2. Density of occupied states extracted from the CPM measurements by using the de-convolution procedure proposed by Jensen [9], for the samples with diborane concentrations of 12.5, 50 and 100 ppm.

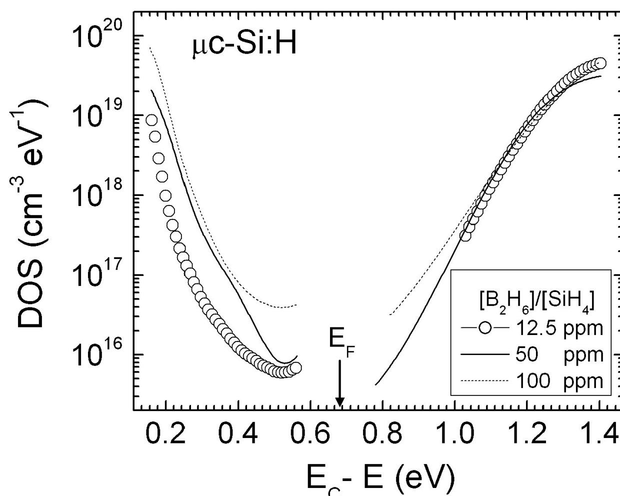

FIGURE 3. Effect of boron compensation on the DOS of μc-Si:H samples. The DOS in the upper gap region was obtained from MPC measurements, while in the lower bandgap region, it was obtained from CPM measurements. The Fermi level position for the compensated sample (25 ppm diborane) is marked with an arrow.

3. Results and discussion

In Fig. 1 we present the α(hν) spectra obtained by CPM for the whole set of μc-Si:H samples. In this figure, a clear increase of the absorption coefficient in the region of energies lower than 0.9 eV can be seen when the diborane concentration increases from 12.5 to 100 ppm. The absorption coefficient in this subgap region is known to be related to the presence of defects in the material [8]. In Table I we report the refractive index, optical bandgap and thickness of the different samples, as obtained from the analysis of the spectral transmittance data, and the grain size and roughness obtained from the AFM observations.

In Fig. 2 one can observe that the DOS of the samples increases with the increase of the doping concentration in the region of energies lower than from the conduction band edge. This fact is consistent with the observations of Fig. 1, where the absorption coefficient gradually increases in the subgap region with the increase of the diborane concentration. For the sample doped with 12.5 ppm of diborane, the α(hν) spectrum could only be obtained for photon energies larger than 1.05 eV. The DOS changes are closely related to the level of doping of the material, and can be attributed to the boron incorporation during the sample deposition. The increase of the boron concentration leads to an increase of the number of B-H-Si sites, and consequently, to the creation of dangling bonds. These type of sites are known as B-H complexes [10]. It has been shown [11] that the incorporation of small amounts of boron to compensate the sample close to the unset of microcrystallinity leads to the creation of defects. Thus, the DOS in the subgap region changes.

In Fig. 3 we show the effect of doping on the DOS of the μc-Si:H samples, detected through MPC (DOS in the upper

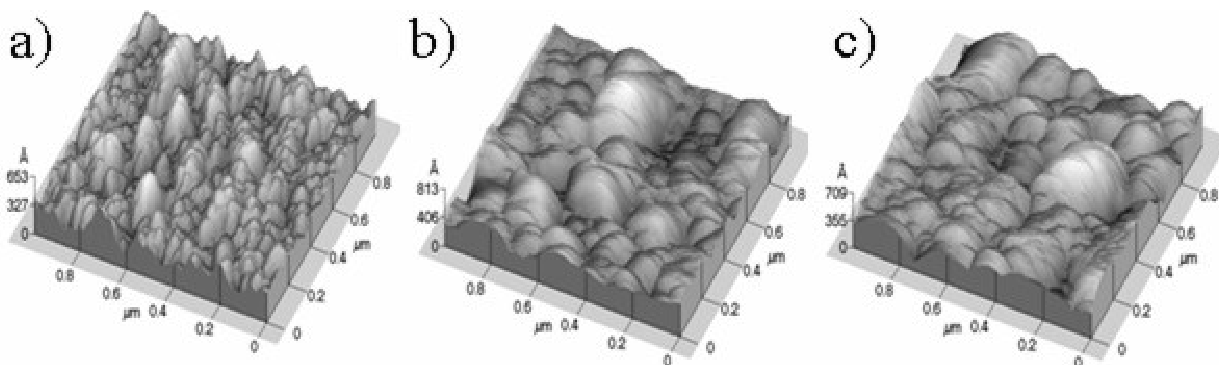

FIGURE 4. AFM images of hydrogenated microcrystalline silicon with different diborane concentrations. a)12.5 ppm, b) 50 ppm and d) 100 ppm.

TABLE I. Optical constants and morphological parameters of the thin c-Si:H samples obtained varying the $[B_2H_6]/[SiH_4]$ concentration between 12.5 and 100 ppm. n stands for the refractive index, d for the thickness, Eg for the optical bandgap, Z for the mean grain size, and R for the root mean square roughness of the surface.

$[B_2H_6]/[SiH_4]$ (ppm)	n	d (nm)	E_g (eV)	Z (Å)	R (Å)
12.5	3.17	500	1.28	562	90
25	3.19	618	1.30	564	92.1
50	3.17	619	1.29	986	105
75	3.15	649	1.30	1040	84.7
100	3.17	916	1.13	1510	93.6

half of the bandgap) and CPM (DOS in the lower half of the bandgap) measurements. This figure clearly shows that boron incorporation leads to an increase in the DOS of the samples. The Fermi level position for the compensated sample (25 ppm of diborane) is indicated by an arrow ($E_F = 0.68$ eV, midgap).

Through AFM observations we gained information about the morphological properties of the thin boron-doped μc-Si:H samples. In Fig. 4 we present AFM images of some of the samples.

Figure 4 shows an increase in the grain size of the samples with the increase of the diborane concentration. We notice that when the Boron concentration is increased from 12.5 ppm to 50 ppm (Figs. 4a and 4b), the grain size changes from 562 Åto 564 Å, whereas we observed that when the Boron concentration is 100 ppm, the grain size was 986 Å(Fig. 4c)) (see Table I). On the other hand, it can be seen that the roughness of the samples is not strongly affected by the boron incorporation at concentrations higher than 12.5 ppm (see Table I). The mean grain size values and the rms roughness have already been reported in Table I.

4. Conclusion

In this work we have presented a study of the optical and structural properties of thin hydrogenated microcrystalline silicon samples with different boron concentrations. We found that the absorption coefficient in the subgap region is strongly influenced by the boron incorporation. From the study of the morphological properties, we found that the mean grain size increases when the diborane concentration in the gas phase is increased from 0 to 100 ppm; however, the roughness of the samples is not strongly affected. We observed that the DOS changes are directly related to the incorporation of boron to the samples.

Acknowledgements

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1. Haijun Jia, Jhantu K. Saha, Naoyuki Ohse, and Hajime Shirai, *J. Non-Cryst. Solids* **352** (2006) 896.
2. P. Delli Veneri, L.V. Mercaldo, C. Minarini, and C. Privato, *Thin Solid Films* **451** (2004) 269.
3. G. Ambrosone *et al.*, *Solar Energy Materials and Solar Cells* **87** (2005) 375.
4. Michio Kondo, Hiroyuki Fujiwara, and Akihisa Matsuda, *Thin Solid Films* **430** (2003) 130.
5. R. Bruggermann, C. Main, J. Berkin, and S. Reynolds, *Philos. Mag. B* **62** (1990) 29.
6. R.H. Buitrago *et al.*, *Avan. Energ. Renv.* **2** (1998).
7. M. Vanecek *et al.*, *Solar Energy Materials* **8** (1983) 411.
8. M. Vanecek, A. Poruba, Z. Remes, N. Beck, and M. Nesladek, *J. Non-Cryst Solids* **227-230** (1998) 967.
9. P. Jensen, *Solid State Commun.* **76** (1990) 1301.
10. P. Stahel, P. Roca I Cabarrocas, P. Sladek, and M.L. Theye, *Mat. Res. Soc. Symp. Proc.* **507** (1998) 649.
11. S. Sheng, X. Liao, and G. Kong, *Appl. Phys. Lett.* **78** (17) (2001) 2509.