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Microelectronics Journal 39 (2008) 1292–1295

Microelectronics Journal

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Microcrystalline silicon thin films: A review of physical properties

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Available online 17 March 2008

Abstract

In this work we present a study of the optical, electrical, electronic and structural properties of Boron doped hydrogenated microcrystalline silicon thin films (μc-Si:H). The films were deposited in an RF plasma reactor using as reactive gas a mixture of silane and diborane, both highly diluted in hydrogen. The Boron concentration in the reactive gas was modified from 0 to 100 ppm. The addition of Boron to the silicon films not only moves the Fermi energy level to the center of the gap, but also induces changes in all the physical properties. The Boron effect on structural and morphological properties was studied by X-ray diffraction and atomic force microscopy (AFM); the rugosity and grain size increased with the Boron concentration. The absorption coefficient measured by the constant photocurrent method (CPM) at low photon energies also showed an increase, which can be explained and correlated with an increase in the density of state (DOS) in the gap, due to Boron's bonding. At high temperatures ($T > 300$ K) the controlling transport mechanism is thermally activated; the curves conductivity log versus the inverse of temperature gives straight lines. The activation energy, measured from the valence band, decreases with Boron concentration, as expected, passing through a maximum, corresponding this point to the position of Fermi energy of an intrinsic film. At low temperatures ($T < 300$ K) the predominant transport mechanism was variable range hopping (VRH). The behavior of the charge hopping under different electrical fields was followed. Results showed that conductivity remained constant in a VRH regime only for a narrow range of electrical field.

PACS: 68.60.Wm; 68.55.Ln; 73.20.At

Keywords: Microcrystalline silicon; Optoelectronic properties; Density of state (DOS)

1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) has been studied over the past years as a potentially important material in the development of photovoltaic devices based on thin film [1,2]. μc-Si:H is commonly deposited by the plasma enhanced chemical vapor deposition (PECVD) method from a gas mixture of silane and hydrogen (SiH_4–H_2), using a radio frequency ranging from 13.56 to 70 MHz. It has been proved that a high dilution of silane in hydrogen is vital for film growth since it interacts with the surface favoring the formation of crystals in the material [3]. The properties of the material deposited with this technique are strongly influenced by the conditions of the deposition. μc-Si:H is type n by nature; however, through the incorporation of small quantities of doping impurities (micro-doping) it is possible to obtain samples of compensated (intrinsec) μc-Si:H or else, extend its character from a type n material (not doped or slightly doped samples) to a type p material (highly doped or over-compensated samples).

This work presents a study on the optical, electrical, structural, morphological properties and density of state (DOS) in thin μc-Si:H films doped with Boron. It was observed that the incorporation of small quantities of Boron induces changes in all the physical properties of the material.

The effect of the microstructure on the optical and transport properties was studied by the measurement of transmittance in the range UV–Vis, constant photocurrent method (CPM), atomic force microscopy (AFM) and conductivity measurements, respectively. It was found that the absorption in the region of the subgap and the increase

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doi:10.1016/j.mejo.2008.01.019

in the DOS in the gap of the material are closely related with the quantity of Boron present in the samples. It was established that the mechanism governing the electric transport in the region of low temperatures is variable range hopping (VRH).

2. Experimental details

Samples were prepared in a PECVD reactor operated at a frequency of 50 MHz, the characteristics of which were described in a previous work [4]. Corning Glass 7059 was used as a substrate at a temperature of 160 °C. A mixture of 94% hydrogen and 6% silane with a total flow of 20 sccm was used. The B_2H_6 concentration in the gaseous phase varied from 0 to 100 ppm relative to silane flow. Base pressure prior to deposition was 1×10^{-6} Torr. During deposition, pressure remained constant at 4.5×10^{-1} Torr. RF power density was 50 mW/cm^2.

Film thickness was calculated from the interference pattern of the transmittance spectrum in the visible and near infrared regions, resulting in ~1 μm for all samples. The absorption coefficient for energy values lower than 2 eV was obtained applying the CPM method.

Conductivity was measured using aluminum interdigited contacts deposited by photolithographic techniques and separated by 0.01 cm with a total length of 25 cm. Current was measured with a Keithley 617 electrometer connected to a computer. MPC measurements were used to evaluate DOS, assuming a state density on the conductivity band edge of 1×10^{21}/cm^3/eV and a mobility gap of 1.8 eV.

Raman measurements were taken with a Micro-Raman spectrometer belonging to the Ecole Polytecnique Laboratory, France. Laser power was 20 mW, using a 10× objective and a 3 min exposure time. All Raman spectra were obtained at room temperature. The crystalline volume fraction was estimated from the deconvolution of crystalline (520 cm^{-1}) and amorphous (480 cm^{-1}) peaks from Raman spectra, together with a third peak around 510 cm^{-1}, associated to grain size dispersion [6]. To study the morphological properties, a Park Scientific Instrument (PSI) Company atomic force microscope was used. The microcrystallinity of the samples was confirmed by X-ray diffraction. Diffraction spectra were obtained with a glazing angle Phillips diffractometer.

3. Results and discussion

Fig. 1 shows absorption coefficient—α—as a function of photon energy, for the set of samples of μc-Si:H doped with Boron, obtained by the CPM method [5]. Fig. 1 clearly shows an increase of absorption coefficient in the subgap region, as Boron concentration increases from 12.5 to 100 ppm [7]. This evidenced an increase of density of the defect status with the increase of doping [8]. Likewise, a change in the optical absorption coefficient was seen in the same region, when samples were subjected to successive annealings in search of an electrical conductivity saturation level [9].

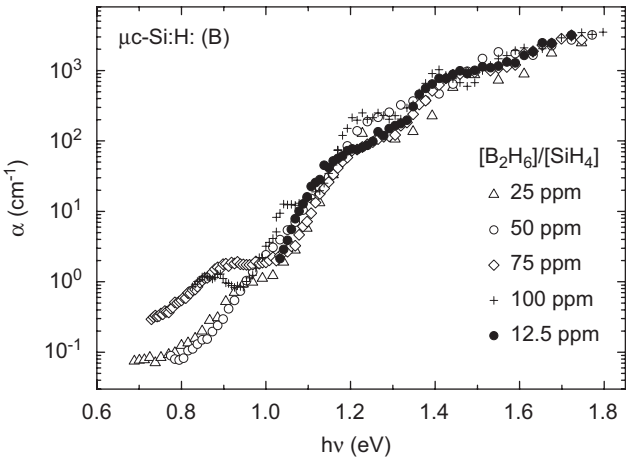

Fig. 1. α(*hν*) measured by CPM for μc-Si:H samples, varying the doping ratio of $[B_2H_6]/[SiH_4]$ between 12.5 and 100 ppm.

Table 1
Properties of thin films of μc-Si:H doped with Boron, varying the ratio $[B_2H_6]/[SiH_4]$ between 12.5 and 100 ppm, d being thickness, E_g the gap energy, X_c the crystal volume fraction, Z the grain size and RMS the sample rugosity

$[B_2H_6]/[SiH_4]$	d (nm)	E_g (eV)	Z (Å)	X_c (%)	RMS (Å)
12.5	500	1.28	562	54.7	90
25	618	1.30	564	55.8	92.1
50	619	1.29	986	61.2	105
75	649	1.30	1040	60.8	84.7
100	916	1.13	1510	52.3	93.6

The crystal volume fraction (X_c) was obtained from deconvolution of Raman spectra, using the ratio reported in previous works [10]. The values corresponding to this parameter together with the optical constants are shown in Table 1. It can be observed that the increase in the concentration of Boron induces a change in the amorphous-crystalline transition, showing an increase in Xc in the samples with concentrations of 0–75 ppm, whereas there is a decrease of this parameter for the Boron concentration of 100 ppm. This fact is related to an amorphization of the material for higher doping concentrations [10].

Fig. 2 shows the curves obtained for dark conductivity (σ_{dk}) as a function of $1/T^{1/4}$. A good adjustment of date through the linear relationship proposed by Mott can be clearly observed for the region of low temperatures [11].

It was found that, for all samples, the dominant transport mechanism for the region above room temperature (300–420 K) is that of thermally activated carriers, whereas for the region of low temperatures, the dominant transport mechanism is VRH among defect states near the Fermi level. In a previous work [12], we developed a model called "diffusional model" from which hopping parameters

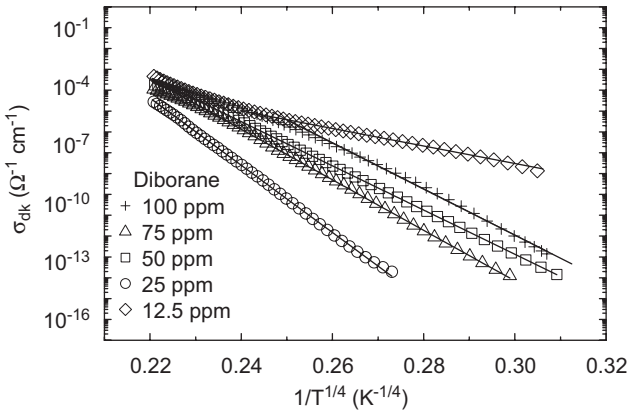

Fig. 2. Dark conductivity as a function of $T^{-1/4}$ in samples of μc-Si:H slightly doped with Boron.

were obtained and correlated with those obtained by the percolation theory.

Fig. 3(a) shows XRD spectra obtained for μc-Si:H (B) samples. In comparison with c-Si, a microcrystalline structure in all samples, with a preferential orientation in a (2 2 0) plane can be clearly seen [13].

The peak associated with growth plane $2\theta \simeq 47^{\circ}$ is shown in detail in Fig. 3. This figure exhibits a systematic increase in the ratio intensity-width of the diffraction peak when Boron concentration increases from 0 to 75 ppm, whereas for a concentration of 100 ppm its intensity decreases dramatically [14].

Information was obtained on the morphological properties of c-Si:H thin films doped with Boron by AFM measures. Fig. 4 presents AFM images of μc-Si:H samples.

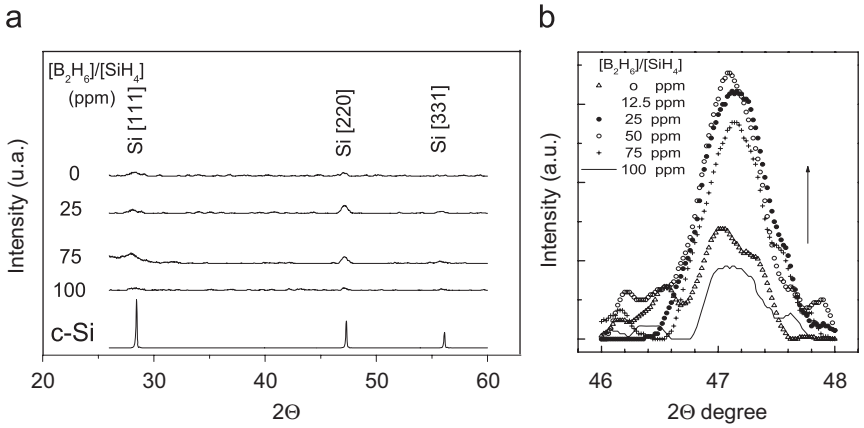

Fig. 3. X-ray diffraction spectra in μc-Si:H samples, varying Boron concentrations between 0 and 100 ppm.

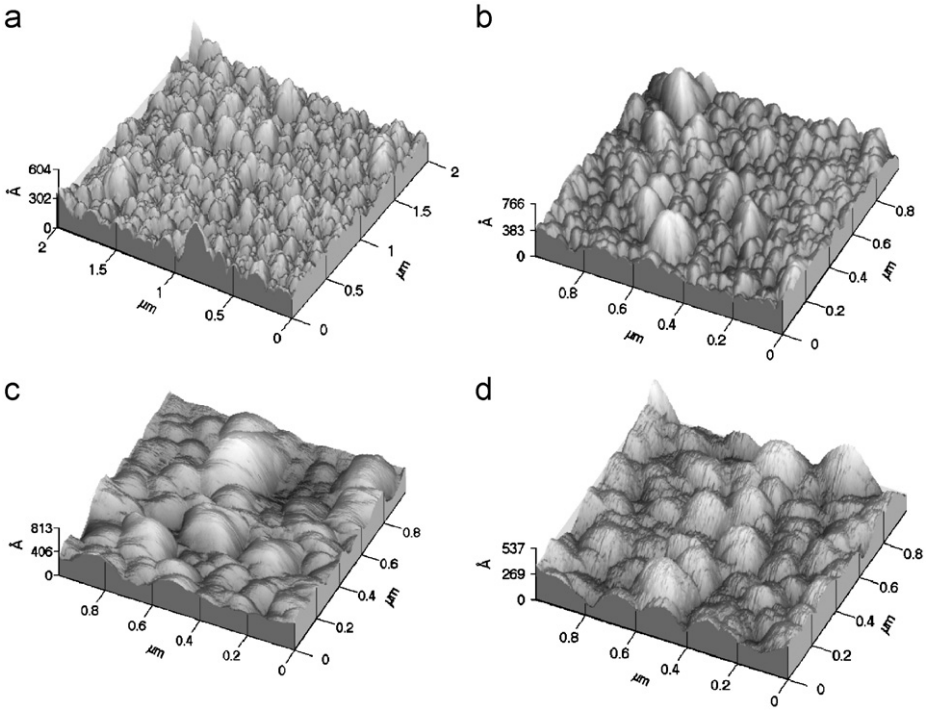

Fig. 4. AFM images of μc-Si:H samples with Boron concentrations: (a) 0 ppm, (b) 25 ppm, (c) 50 ppm and (b) 75 ppm.

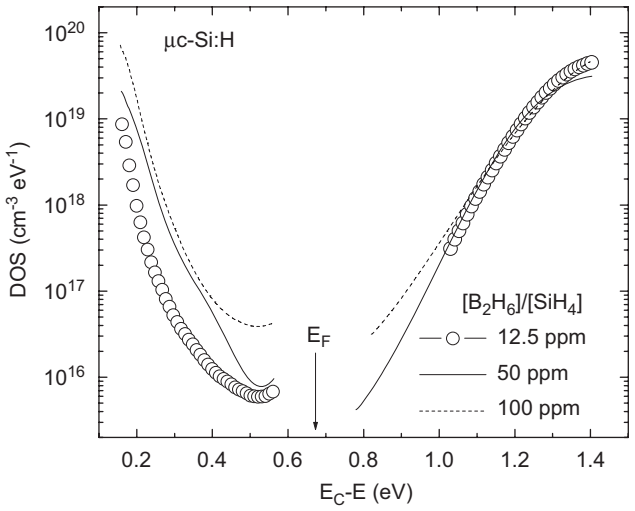

Fig. 5. Effect of Boron compensation on the DOS of μc-Si:H samples. DOS in the upper region of the gap was obtained from MPC measurements, whereas DOS in the lower region of the gap was obtained by CPM measurement. The Fermi level for the compensated sample is indicated by an arrow.

An increase in grain size in the μc-Si:H samples is observed as Boron concentration increases in the material. On the other hand, it is observed that the rugosity of the samples is not strongly affected by the incorporation of Boron for concentrations of over 0 ppm. The values corresponding to the size of average grain and rugosity (RMS), from AFM measurements are reported in Table 1.

The presence of substructures in μc-Si:H samples with much smaller grains located among grains protruding from the surface has been previously reported.

Fig. 5 shows the doping effect on the DOS of the μc-Si:H samples obtained by MPC measurements (DOS above the center of the gap) and CPM (DOS below the center of the gap). It can be clearly seen that the incorporation of Boron increases the DOS of the samples. The position of Fermi level of the sample compensated around 25 ppm is indicated by an arrow ($E_F = 0.68$ eV, center of the gap).

4. Conclusions

This work presents a study of the optical, electrical, structural, morphological and DOSs in μc-Si:H thin films doped with Boron. It was found that the increase of Boron content in the material causes significant changes in all its physical properties, making it an attractive material for use in photovoltaic devices. The increase in grain size together with a progressive increase in the crystal volume fraction is closely related to the DOS of defects in the material gap as Boron concentration rises from 0 to 100 ppm. It was also found that Boron induces a change in the behavior of samples, starting from a material characterized as type n, for low Boron concentrations, going through a compensated state and obtaining a behavior type p for concentrations higher than 25 ppm. It was established that the mechanism governing electrical transport in the region of low temperatures is VRH.

Acknowledgments

This work was partially financed with funds from the ANPCyT (PICT 12-06950).

References

[1] G. Ambrosone, U. Coscia, S. Lettieri, P. Maddalena, M. Ambrico, G. Perna, C. Minarini, Thin Solid Films 511–512 (2006) 280.
[2] C. Brabec, A. Jager-Waldau, J. Poortmans, A. Slaoui (Eds.), Proceedings of E-MRS-2003, Thin Solid Films, vol. 451, 2004.
[3] A. Matsuda, Thin Solid Films 337 (1999) 1.
[4] R.H. Buitrago, et al., Avan. Energ. Renv. 2 (1998).
[5] M. Vanecek, J. Kocka, J. Stuchlik, Z. Kozisek, O. Stika, A. Triska, Solar Energy Mater. 8 (1983) 411.
[6] Ch. Ossadnik, S. Veprek, I. Gregora, Thin Solid Films 337 (1999) 148.
[7] A. Dussan, R. Arce, J.A. Schmidt, R.R. Koropecki, Rev. Col. Física 39 (1) (2007) 281.
[8] J.A. Schmidt, R.R. Koropecki, R. Arce, A. Dussan, R.H. Buitrago, J. Non-Cryst. Solids 338–340 (2004) 322.
[9] A. Dussan, R.R. Koropecki, R. Arce, J.A. Schmidt, R. Buitrago, J. Non-Cryst. Solids 338–340 (2004) 430.
[10] R. Saleh, N.H. Nickel, Thin Solid Films 427 (2003) 266.
[11] N.F. Mott, Philos. Mag. 19 (1969) 333.
[12] A. Dussan, R.H. Buitrago, J. Appl. Phys. 97 (2005) 043711.
[13] L. Li, Y.-M. Li, J.A. Anna Selvan, A.E. Delahoy, R.A. Levy, J. Non-Cryst. Solids 347 (2004) 106.
[14] A. Dussan, R.R. Koropecki, Phys. Status Solidi (c) 4 (11) (2007) 4134.