

Substrate type effect on boron doped polysilicon films properties

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Abstract- In this work, we studied the effect of substrate type on structural and electrical properties of heavily in situ Boron doped polycrystalline silicon. The films have been elaborated by LPCVD technique, on monocrystalline silicon substrate oriented <111>, oxidized or bare, at deposition temperature 585°C and pressure of 700 mtorr. From the XRD spectra, it can be seen that the polycrystallized films B-LPCVD/SiO₂ possess (111) textured columnar grains, meanwhile the film deposited on bare monosilicon (B-LPCVD/c-Si) is randomly oriented, although weakly, (111), (222) and (511) textures. The FTIR spectroscopy analysis reveals changes in chemical bonding structure which is constituted of different bonds as: Si-Si, Si-O-Si, Si-O, Si-H, Si-OH and Si₂O₃. Overall, the associated intensity and wave number depend on the substrate type. The characterization by Hall effect shows that the resistivity is two times more weakly for B-LPCVD/SiO₂ films than for B-LPCVD/c-Si ones. In the other hand, the results pointed out a typical electrical behavior of the layers linked to intermediate oxide layer. The resistivity decreases greatly at low temperatures in c-Si substrate case, however this occurs at high temperatures in SiO₂ substrate case.

Keywords: Si-LPCVD, monosilicon substrate, oxide, boron doping, resistivity, Hall effect, structure, XRD, FTIR.

I. INTRODUCTION

Polycrystalline silicon has widely been used in the last few decades for different electronic applications in microelectronics and photovoltaic fields, like in microsystems and flat-faced screens [1,2]. The properties of this material depend strongly on the elaboration conditions and heat treatment. One obtains polysilicon in the form of films deposited on substrates of various natures. It is generally obtained by crystallization of an amorphous precursor. Indeed, although it is possible to obtain polycrystalline material directly by chemical deposition in vapor phase (CVD) around 600° C, it has in general a rough surface quality which gives rise to bad electronic transport on surface [3].

II. EXPERIMENTAL PROCEDURE

In this study, we used polysilicon thin layers of 2000 Å thickness, square-shaped (15mm×15mm), elaborated by thermal decomposition of silane (SiH₄) at low partial pressure of 700mtorr, and temperature 585°C. The films have been highly in situ boron doped (about 10²² cm⁻³) by means of boron trichloride (BCl₃). Within the framework of this work we used two deposits series:

- The first deposits was carried out on oxidized single crystal silicon substrate (B-LPCVD/SiO₂);
 - The second deposit was carried out on bare single crystal silicon substrate (B-LPCVD/c-Si).
- Both substrates are of type p, and oriented <111>.

The electrical parameters values were raised by Hall Effect technique, by means of HMS-300 Ver. 3.51.3 apparatus type. The structural characterization was performed by X-Rays Diffraction thanks to an X'Pert PRO PAN diffractometer type. Otherwise, the nature identification of the chemical bonds between films atoms has been achieved by Fourier Transform Infra-Red spectroscopy (FTIR) on an "IR Affinity-1 Shimadzu" spectrometer type. The recording was made in adsorption mode, for wave numbers ranging from 500 to 4000 cm⁻¹. Before any handling, the samples were passed into hydrofluoric acid HF bath (40%) during some seconds, to etch the oxide coating on surface, and then rinsed and dried.

III. THEORETICAL ASPECT

The electrical properties of polycrystalline silicon depend strongly on the temperature. The presence of the grain boundaries in the polysilicon makes the properties for this material basically different from that of single crystal silicon. The electrical characteristics are principally the resistivity, the carriers' concentration and the carriers' mobility. The resistivity is described by the following relation (1):

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

Where E_a is the activation energy which takes into account the potential barrier height, and K_B is the Boltzmann constant.

The electrical conduction of the polycrystalline silicon layers is founded on the segregation of the doping agents and the carriers trapping [4]. It takes account of the two mechanisms of transport, by thermionic emission and tunnel effect.

At low temperature, the conductivity of the grain boundaries is expressed by the following relation of mott [5]:

$$\sigma_{gb} = \frac{A}{\sqrt{T}} \exp\left(\frac{3}{4} \sqrt{\frac{T_0}{T}}\right) \quad (2)$$

A is a constant and T₀ is a quantity expressed by :

$$T_0 = 18\alpha^3 / K_B N(E_F) \quad (3)$$

Where $N(E_F)$ is the localized states density at Fermi level, and α is the exponential weakening coefficient of the localized states, equal to $1,24 \text{ nm}^{-1}$ [5].

IV. RESULTS AND DISCUSSION

A. Structural characterization by XRD

The structure of polysilicon deposits and the crystalline orientation of their grains have been studied by x-rays diffraction.

It appears on fig.1, that B-LPCVD/c-Si film crystallizes according to five crystallographic directions : [111], [511], [110], [222] and [332]. On the other hand, the film deposited directly on oxidized monoSi substrate, crystallizes according to two crystallographic directions, namely [111] and [110]. One can notice the same preferential orientation [111] in the case of the two deposits. Indeed, the most intense peak (111) corresponds to the cumulated reflexions on polysilicon layer and substrate, as it has been shown elsewhere [6,7]. Compared to film directly deposited on single-crystal silicon substrate (fig.2), it is noticeable that the peaks (222), (332) and (511) do not appear on the diffraction diagram of the B-LPCVD/SiO₂ films. This is explained by the role played by the oxide layer which prevents the appearance of grains of weak probability orientation in the films structure.

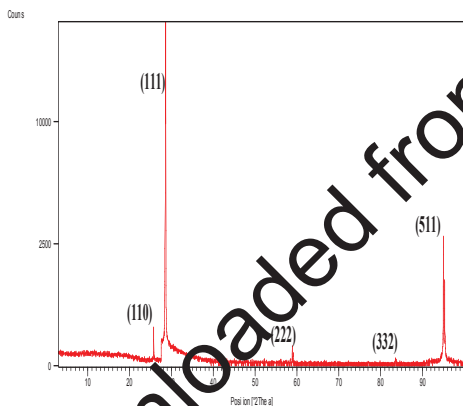


Figure 1. XRD spectrum of B-LPCVD films deposited on monosilicon substrate

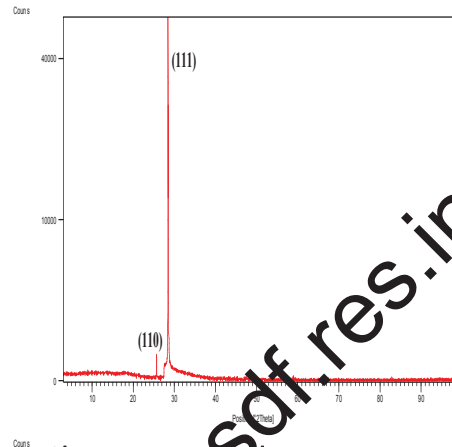


Figure 2. XRD spectrum of B-LPCVD films deposited on oxidized monosilicon substrate

B. Physicochemical characterization by FTIR spectroscopy

The analysis of Si-LPCVD films by Fourier Transform Infra-red spectroscopy (FTIR) enables us to identify the chemical bonds existing between the various atoms of these films. Fig.3 and 4 represent the infrared absorption spectra obtained for boron doped Si-LPCVD films and undoped ones, before heat treatment. We observed that the principal atoms being able to make bonds are: Si, O, H and B. It is known that the vibration mode of the bond Si-Si [8] is around $609\text{-}617 \text{ cm}^{-1}$.

The bending mode of the bond Si-O [9] is localized around 743 cm^{-1} . This vibration mode is not detectable in the case of B-LPCVD/c-Si films spectrum. This can be explained by a small quantity of oxygen associated with this vibration mode, or that oxygen bind by other configurations (Si-O-Si). The vibration of the Si-O-Si bond in stretching mode [8,10,11] is located around $1095\text{-}1114 \text{ cm}^{-1}$, in this case oxygen is inserted between two silicon atoms (interstitial site). The peak of this mode moves towards a higher wavenumber for the B-LPCVD/c-Si deposit. We think this is due to the oxygen proportion which can bind with silicon, i.e. a great oxygen concentration contained within polysilicon film. The two peaks around $2309\text{-}2338 \text{ cm}^{-1}$, of low intensity can correspond to the vibration mode of Si-H bond [12], and other peaks around 2362 cm^{-1} represent the vibration mode of Si-H_x bonds [8]. The formation of these bonds is associated to hydrogen incorporation at the source of deposition. Two bonds characterized by low intensity appearing on these spectra, are localized around $2852\text{-}2929 \text{ cm}^{-1}$, and can correspond to OH grouping, according to the vibration mode of Si-OH [13]. The formation of this Si-OH connection is explained by water absorption which leads to films properties degradation [13]. We noticed that the vibration mode of the Si-O and Si₂O₃ bonds do not appear on the diffraction diagram of B-LPCVD/c-Si film. We think that the absence of the oxide doesn't allow the

formation of these bonds, when the oxygen diffusion is thermally activated.

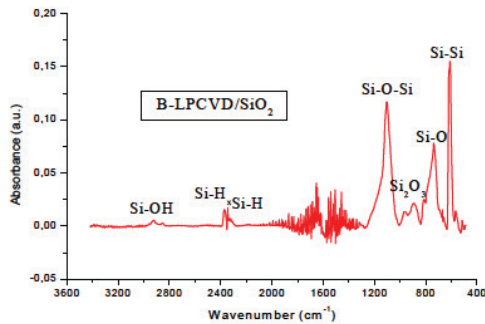


Figure 3. B-LPCVD/SiO₂ films FTIR Spectrum

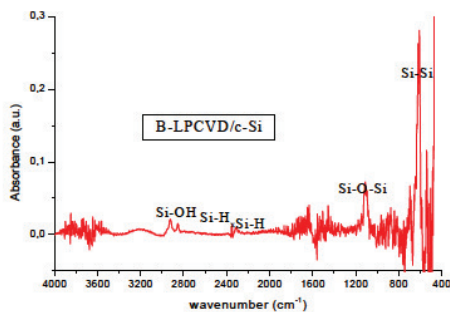


Figure 4. B-LPCVD/c-Si films FTIR Spectrum

C. Electrical characterizations

On table I, one can notice that the characteristics of two deposits deduced by Hall Effect at ambient temperature are rather not very different, taking into account the identical orders of magnitude. One raises for the B-LPCVD/SiO₂ film, a resistivity of approximately $6.31 \times 10^{-3} \Omega \text{cm}$, a value slightly higher than that of B-LPCVD/c-Si one deposited on monosilicon substrate ($\rho = 5.88 \times 10^{-3} \Omega \text{cm}$). These values correspond to a carrier concentration superior to 10^{19}at/cm^3 , confirming the heavy doping of the films.

On figures 5 and 6 we plot the measurements results of resistivity and conductivity according to the temperature of boron doped Si-LPCVD films, for both substrate types: single-crystal nated (c-Si) and oxidized (SiO₂), respectively. On figure 5, it results that the resistivity values lie all between 1.1×10^{-3} and $2.0 \times 10^{-3} \Omega \text{cm}$. The variation of this resistivity lets appear two domains of distinct evolution: a diminishing in the first, followed by a remarkably and obvious increasing in the second, when the temperature decreases, with a minimum around 190°K. On the other hand, concerning films carried out on oxidized substrate, one observes different behavior from those deposited on monosilicon (see fig.6). Indeed, it can be seen that the resistivity decreases all the time when the sample temperature increases, and moreover this decreasing is

slower. This fact was reported elsewhere [14], where it is noted that the reduction is largely influenced by the choice of the deposit temperature and the substrate type. Moreover, values of the resistivity in the case of not oxidized substrate (c-Si) remain lower than those of film deposited on silicon oxide (SiO₂). These resistivity results indicate that the polycrystalline silicon films have a conducting behavior.

TABLE I. FILMS' CHARACTERIZATION BY HALL EFFECT, AT AMBIENT TEMPERATURE.

Sample	B-LPCVD /SiO ₂	B-LPCVD c-Si
$\rho (\Omega \text{ cm})$	6.31×10^{-3}	5.88×10^{-3}
$\sigma (\Omega^{-1} \text{ cm}^{-1})$	$1.58 \times 10^{+2}$	$1.70 \times 10^{+2}$
$\mu (\text{cm}^2/\text{Vs})$	6.97	7.87
$p \text{ ou } n (\text{cm}^{-3})$	1.1×10^{19}	1.8×10^{19}

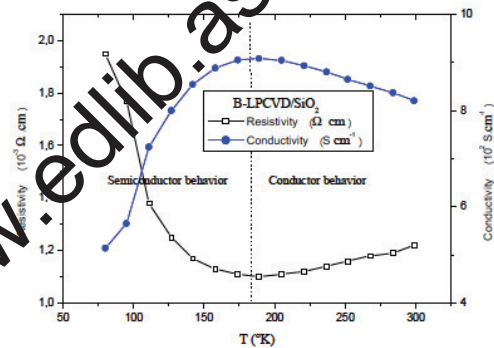


Figure 5. Variation of ρ and σ of B-LPCVD/c-Si film according to the temperature

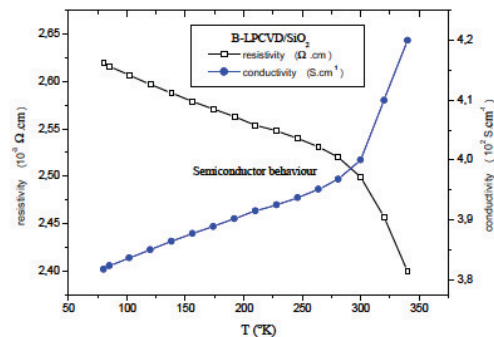


Figure 6. Variation of ρ and σ of B-LPCVD/SiO₂ film according to the temperature

In order to express by a relation the evolution of the films conductivity, we represent the variations of electrical conductivity logarithm according to the reverse of the temperature.

Figures 7 and 8 show that the evolution of the electrical conductivity logarithm as function of $1/T$, clearly highlight

the existence of two distinct areas: low temperatures (1), high temperatures (2), with a different behavior of the material according to the substrate used. In the first temperature range, the material behaves as semiconductor and the conduction process would be associated to thermal action of the impurities, while in the second, the resistance effect on the carriers' movement acts dominantly and in this case the material behavior is conductive.

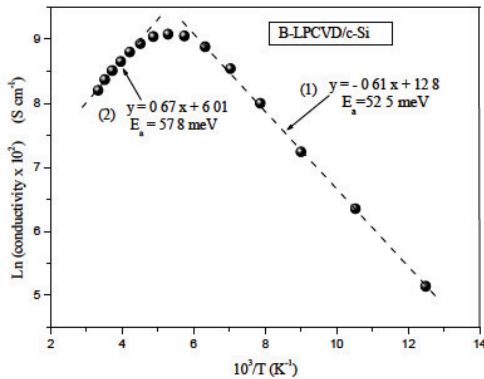


Figure 7. Variation of $\ln(\sigma)=f(1/T)$ for B-LPCVD/c-Si film

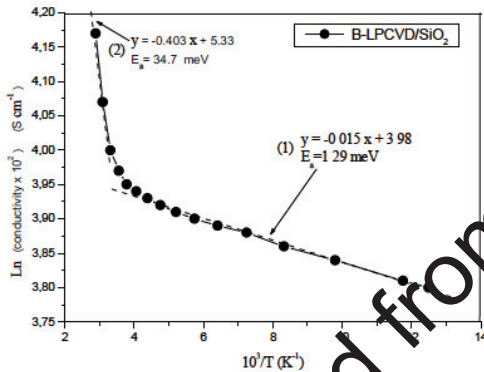


Figure 8. Variation of $\ln(\sigma)=f(1/T)$ for B-LPCVD/SiO₂ film

Figures 9 and 10 show the representative curves, relating to boron doped Si₃N₄ LPCVD films, of the function $\ln(\sigma T^{1/2})=f(T^{-1/4})$. One can notice that they are made up of linear parts on intervals which are practically the same ones in both cases. The application of the Mott relation, enables us to determine the density of localized states $N(E_F)$ around the Fermi level.

The values of the localized states density at Fermi level and the conduction activation energy, determined from curves of figures 9 and 10, are given at table 2. For B-LPCVD/c-Si deposit these constants are higher compared to that of the deposit carried out on oxidized substrate (B-LPCVD/SiO₂).

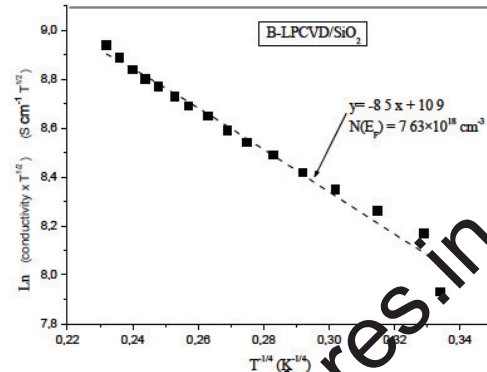


Figure 9. Evolution of $\ln(\sigma T^{1/2})=f(T^{-1/4})$ for B-LPCVD/SiO₂ film, according to Mott theory

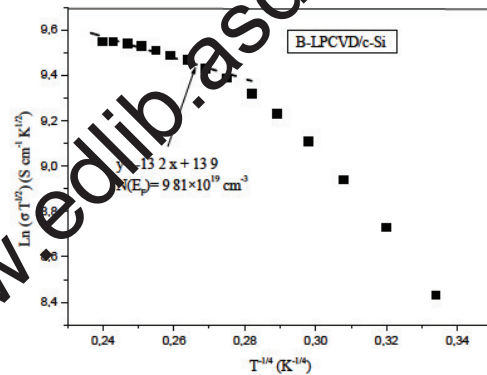


Figure 10. Evolution of $\ln(\sigma)=f(T^{-1/4})$ for B-LPCVD/c-Si film, According to Mott theory

TABLE II. CONDUCTION ACTIVATION ENERGIES ACCORDING TO MOTT AND THE STATES DENSITY IN THE GRAIN BOUNDARIES

	B-LPCVD/c-Si		B-LPCVD/SiO ₂	
E_a (meV)	52,5	57,8	1,29	34,7
$N(E_F)$ (cm ⁻³)	9,81×10 ¹⁹		7,63×10 ¹⁸	

CONCLUSION

The structural characterization enabled us to identify the crystallinity of B-LPCVD/c-Si and B-LPCVD/SiO₂ deposits. The spectrum of the former presents various crystallographic peaks, namely: (111), (110), (222), (332) and (511). In addition, the FTIR spectroscopy enabled us to identify the chemical bonds present within our deposits. One raised thus the presence of Si-OH bond in films. Globally, the intensity and the bonds wavenumber depend on substrate type. The characterization by Hall Effect technique at low temperature shows that the growth of the temperature induces a different behavior for the two deposits. The resistivity evolution undergoes a direction modification, at 190°K for film deposited on c-Si, and at 300°K for the other. Moreover, one notes that the effect of intermediate oxide is pronounced much more for the high values of the resistivity.

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