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Correlation between physicochemical and electrical properties of hydrogenated amorphous silicon doped with boron: effect of thermal annealing

H.Y. Seba [a], R. Cherfi [b], F.Hamadache [c] et M. Aoucher

Laboratoire de Physique des Matériaux équipe « Couches Minces et Semi-conducteurs », Faculté de physique USTHB, BP. 32 EL ALIA 16111 Bab Ezzouar, Algiers, ALGERIA

[a] seba_yahia@ yahoo.com, [b] r.cherfi@yahoo.fr, [c] hamadache_farida@hotmail.com,

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Abstract. This communication reports on the effect of thermal annealing on the physicochemical and electrical properties of boron doped amorphous silicon thin films deposited by reactive magnetron sputtering in a mixture of argon and hydrogen atmosphere. The IR absorption spectra of as prepared samples exhibit the peaks characteristic of Si-H, Si-B and B-H bonding vibrations. After annealing, our analyses revealed some modifications in the peak characteristic of B-H bonding, while no significant increase in Si-B peak intensity was observed. In other respects, electrical measurements showed an increase in the conductivity from 10^{-8} to 10^{-5} Ω^{-1} cm^{-1} and a decrease in its activation energy from 0.57 eV to 0.33 eV after a successive annealing at temperatures varied between 150°C and 450°C. These results showed that boron doping becomes increasingly efficient after annealing, which could be assigned to the reduction in the content of hydrogen playing an important role in the passivation of boron atoms.

Introduction

After the original work of Spear and LeComber [1] that showed the possibility of doping hydrogenated amorphous silicon (a-Si:H), many efforts was made to understand the effectiveness of doping in this material [2,3] in order to develop electronic components such as PIN junctions intended for solar cells and X-ray detectors applications [4].

It is obvious that the variation of the deposition parameters like the partial pressure of hydrogen, the doping concentration [5], or the temperature of the substrate [6], affects the physicochemical and electrical properties of this material. In particular, the effect of hydrogen was shown, it plays a significant role in the structure and the properties of a-Si:H [7]. In this work, physicochemical and electrical characteristics of boron doped amorphous silicon (a-Si:H(B)) was investigated. We studied the effect of thermal annealing which can modify its hydrogen content and alter the doping effectiveness. In this purpose, a-Si:H(B) was prepared by co-sputtering of silicon and boron using DC magnetron sputtering technique and was characterized before and after annealing by means of Fourier Transform Infrared (FTIR) spectroscopy and electrical conductivity measurements .

Experimental

The samples studied in this work consist of thin layers of amorphous silicon doped with boron deposited on both corning glass and two polished faces silicon wafer substrates. The a-Si:H(B) was deposited by DC magnetron sputtering of a target of silicon in a plasma consisted of a mixture of argon and hydrogen. The doping element was introduced in-situ by sputtering grains of boron placed on the target of silicon. We varied the partial pressure of hydrogen from 1.8 10^{-4} mbar to 3.8 10^{-4} mbar, while boron content and all other deposition parameters were maintained constant.

The samples were annealed in vacuum following successive stages of twenty minutes at temperatures between 150°C and 640°C. The Physicochemical characteristics of the samples were investigated by FTIR analyses using a Perkin-Elmer FTIR spectrometer. The IR spectra were recorder on as deposited samples and after each annealing step. Note that the samples were taken out of the annealing chamber for analysis and that it was possible to anneal them until a temperature of 640°C. The electrical properties study consists on the conductivity measurements that were performed at different temperature in order to determine its activation energy. In this case, the samples were annealed in-situ in the cryostat used for the measurements and the annealing temperature was limited to 450°C. For the electrical measurements, aluminum electrodes were deposited on the surface of a-Si:H layers by thermal evaporation and then the electrical contact was ensured by silver paste.

Results and Discussion

IR measurements

The infrared absorption spectra of as prepared samples are presented on the Fig.1 for various partial pressures of hydrogen. Absorption peaks corresponding to the characteristic vibrations in a-Si :H (B) are observed. The principal absorption bands that characterize the layer of a-Si:H are (640 cm^{-1}, 880 cm^{-1}, 2000 cm^{-1} and 2090 cm^{-1}). The bands at 640 cm^{-1} are attributed to the wagging modes of all Si-H vibrations, the peak at 880 cm^{-1} is assigned to bending mode of the $Si\text{-}H_2$ bonds and the bands at 2000 and 2090 cm^{-1} are attributed to the stretching mode of the mono-hydrides Si-H and poly-hydrides $Si\text{-}H_x$ x=2,3 respectively. In addition, we observe other peaks at approximately 720 cm^{-1}, 800cm^{-1} and 2360 cm^{-1}. These peaks can be attributed to the wagging mode of B-H bond, to the stretching mode of Si-B and to the stretching mode B-H bonds respectively [8].

On the Fig.1, we can see that the absorption at both 640 and 880 cm^{-1} increases with the increase of the partial pressure of hydrogen. We can also notice that the band (2000-2090) cm^{-1} broadens out towards the high frequencies. These two features attest that the hydrogen content in the deposited layers increases with the increase of the hydrogen partial pressure [9]. At high hydrogen pressure, the absorption at 880 cm^{-1} is so high that these bands mask the presence of Si-B bonds vibrating at 800 cm^{-1}.

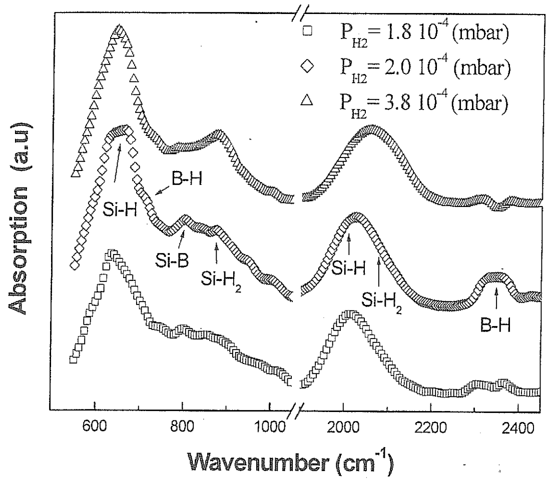

Fig.1. FTIR analysis showing the peaks of absorption in a-Si:H doped with boron for samples prepared at different partial pressures of hydrogen.

We represent on the Fig.2 the infrared absorption spectrum of a-Si:H layer annealed at successive stages of temperature from 200 to 640 °C, compared to that recorded on as deposited layer with partial pressure of hydrogen equal to 2.0 10^{-4} mbar. Annealing at 640 °C is carried out to confirm the presence of the peak characteristic of the Si-B vibration at 800 cm^{-1}.

We observe on the Fig.2 the presence of the principal absorption bands given previously, which characterize the layer of a-Si:H(B). We notice on these spectra that the (2000-2090 cm^{-1}) band doesn't practically vary when the material is annealed at temperatures smaller than 450°C. An important variation is shown after annealing at 640°C, at which hydrogen content decreases considerably. At this temperature, the peak corresponding to the vibration of Si-B bonds is clearly shown as the Si-H_2 bands absorption at 880 cm^{-1} is reduced. But it is difficult to analyse its evolution with annealing temperature because of its low intensity and its almost overlapping with Si-H_2 bands absorption. In return, some modifications of the peak characteristic of the B-H vibration (2360 cm^{-1}) can be seen when the sample is annealed from 200°C to 640°C at which this peak disappears. The decrease of the absorption due to the B-H vibration attests that the effect of boron passivation with hydrogen is reduced after annealing.

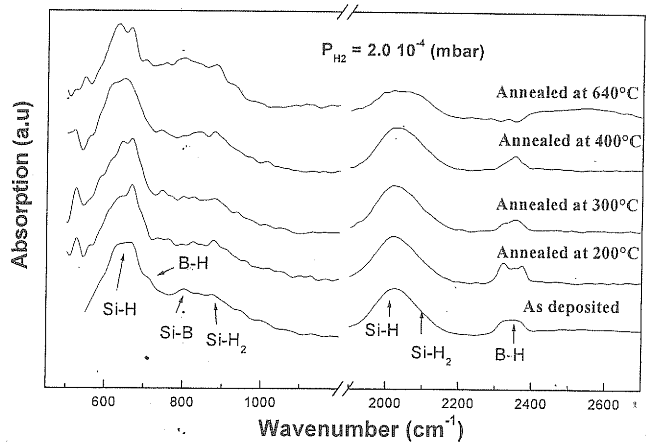

Fig. 2: Evolution of FTIR absorption with successive annealing steps of 20 minutes in vacuum for the sample deposited at P_{H2}=2.0 10^{-4} mbar.

Electrical measurement

The Fig.3 shows the behavior of conductivity sample and its activation energy as a function of annealing temperature, for different hydrogen partial pressure. We observe on Fig.3 that the general tendency of the electric parameters evolution, after successive annealing of all the layers deposited with various pressures of hydrogen, is an increase in conductivity and a reduction in its activation energy. The increase becomes more important when the hydrogen content increases. For the layers deposited with P_{H2} = 3.8 10^{-4} mbar, the conductivity increases by four decades when the material is annealed from 150 °C to 450°C, while it increases only by two decades for the layers deposited with P_{H2} = 1.8 10^{-4} mbar. Accordingly to the FTIR analysis, the increase of the conductivity and the decrease of its activation energy after annealing can be attributed to the diffusion of hydrogen and its exo-difffusion from the layer. Hydrogen actually plays an important role in the passivation of the doping agent [10,11].

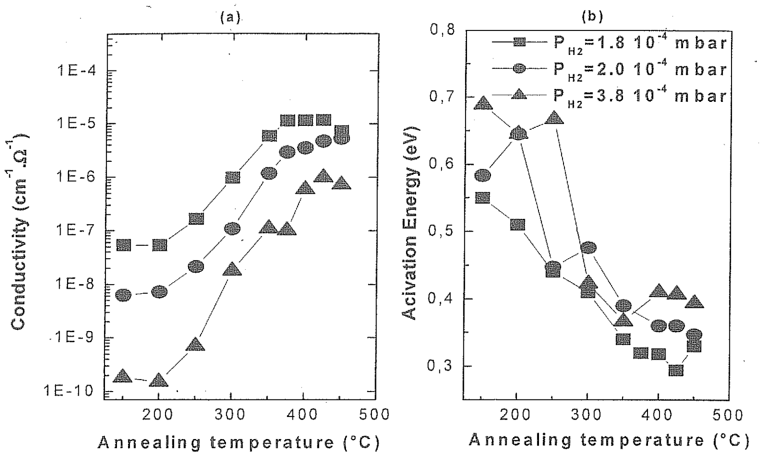

Fig.3: Evolution of conductivity measured at 300 °K (a) and of its activation energy (b) with the annealing temperature for samples deposited with various pressures of hydrogen.

Conclusion

This study enables us to show that the conductivity of a-Si:H doped with boron increases when the material is annealed. This increase is related to the modifications in the B-H bonds attesting the hydrogen diffusion and exo-diffusion from the annealed samples.

Acknowledgments

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