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Electrochemical etching of silicon carbide thin films for energetic application

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***Abstract*—The Porous layers of hydrogenated Amorphous Silicon Carbide thin films (PASiC) was formed by anodization of a-$Si_{0.72}C_{0.28}$:H in HF/ethylene glycol (ETG) solution at current density of 50 mA/cm^2 for 45 s. The optical and structural properties of a-$Si_{0.72}C_{0.28}$:H thin films deposited by DC magnetron co-sputtering using single silicon crystal, 6H-SiC targets. The PASiC films were investigated by scanning electron microscopy (SEM), infrared spectroscopy (FTIR), spectrophotometer UV, Raman spectroscopy, Secondary ion mass spectroscopy (SIMS) and photoluminescence. Then, we demonstrated the interest and the application of a-SiC in Schottky photodiode based onto a-$Si_{0.72}C_{0.28}$:H and PASiC thin films. A spectral response value (SR) of 36 mA/W at λ = 900 nm has been obtained for Pd/PASiC/pSi/Al Schottky photodiode with porous amorphous SiC (PASiC). Finally, it was found that the surface porous structure have strong effect on sensitivity.**

***Keywords*— thin films; electrochemical etching; porous amorphous SiC; spectral response;**

I. INTRODUCTION

Silicon carbide (SiC) is an important semiconductor which can be operated at high powers, high temperatures, and high frequencies. Micrometer-sized whiskers of SiC have been widely used to strengthen ceramic composites which had brought dramatic revolution in mechanical and optoelectronic industries **[1]**. Furthermore, nanostructures of SiC **[2]** are of great interest because of their broad range of potential applications such as field electron emitter, light emitter other than their reinforcing use **[3–7]**. In particular, hydrogen amorphous silicon carbide (a-SiC:H) films have attar cted much interest for their potential applications in many kinds of opto-electronic devices **[8, 9]**. By controlling the carbon content in a-SiC:H films, the optical band gap could be readily adjusted between 1.8 and 3.2 eV, which makes them become suitable candidates in application in full-color light emitting diodes (LED). In our previous work, we have studied the microstructures and optical properties of PASiC films prepared by DC magnetron co-sputtering using 6H-SiC polycristal chips which are deposited onto single silicon crystal and anodized in HF/ethylene glycol (ETG) solution. The PASiC films elaborated are used to investigate spectral response of Schottky photodiode under experimental conditions.

II. EXPERIMENTAL PROCEDURE

The PASiC samples are prepared by electrochemical etching of p-type a-$Si_{0.72}C_{0.28}$:H that deposited on p-type Si single crystals, which are grown by DC magnetron co-sputtering of p-type 6H-SiC polycrystalline and p-type Si single crystal **[10]**. The porous a-$Si_{0.72}C_{0.28}$:H films are formed in a mixture of hydrofluoric acid (HF), water and ethylene glycol (ETG) (1:1 by volume) solution at a constant current density of 50 mA/cm2 **[11, 12]**, for 45 s etching time. The surface morphologies of PASiC were characterized by scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), Raman spectroscopy, Secondary ion mass spectroscopy (SIMS) and photoluminescence (PL). After formation of the ohmic contact as Aluminum, the samples were placed into a deposition chamber in order to evaporate a thin layer of palladium (99.9% purity) on the PASiC to form Schottky contact (Pd/PASiC/pSi/Al) with 250 nm of palladium layer, the later serves as a catalytic metal.

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The current– tension (I(V)) characterization of the sample a-$Si_{0.72}C_{0.28}$:H in a 50%HF(5%)/50%ETG solution, allows us to reach various information, concerning a-$Si_{0.72}C_{0.28}$:H/HF-ETG interface, to know the chemical processes, which have occurred on-surface (states of oxidations, reductions, corrosions). The first peak corresponds to the porosification of the silicon carbide (formation of SiO_x) and the second peak is attributed to the state of oxidation (x=1.4–2) of SiC (formation of the SiO_2, x=4). Also, the I(V) allows to determine the value of the flat band potential (V_{fb}) and the coefficient of carrier transfer (α) (Eq.1) **[13]**.

$$I = I_0 e^{\alpha(ZqV/(kT))} \qquad \text{Eq.1}$$

where I_0 is the transfer current, α is the coefficient of carrier transfer, q is the electron charge ($1.6\text{x}10^{-19}$ C), Z is the number of charge, T is the absolute temperature (K), V is the bias voltage and k is the Boltzmann constant=$1.38\text{x}10^{-23}$ J/K. **Fig. 1** illustrates the I(V) characteristic of a-$Si_{0.72}C_{0.28}$:H amorphous film in a 50%HF(5%)/50%ETG solution. We can observe that the flat band was around 1.4 V and the value of the coefficient of transfer carrier α was 0.27 in the region of porosification (state of oxidation 2).

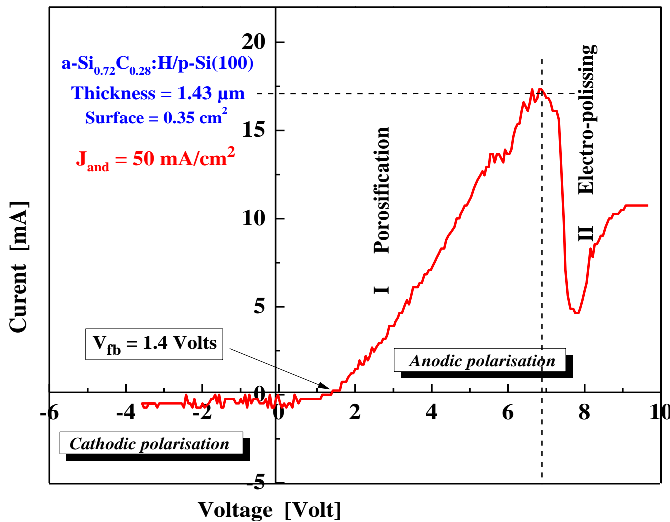

Fig. 1. I(V) characteristics of a-$Si_{0.72}C_{0.28}$:H films in 50% HF(5%)/50% ETG solution.

III. RESULTS AND DISCUSSION

A. *Capacitance–voltage of a-$Si_{0.72}C_{0.28}$:H /p-Si*

Capacitance–voltage (C(V)) characteristic of a-$Si_{0.72}C_{0.28}$:H/HF allows to determine the value of the flat band potential (V_{fb}) and N_A is the doping concentration. The capacitance can be expressed as (Eq.2) **[14]**:

$$C = \frac{Q}{V} = \frac{\varepsilon_0 \varepsilon_{SiC} \alpha}{W} \qquad \text{Eq.2}$$

where, ε_0 is the vacuum permittivity = $8.854\text{x}10^{-14}$ F/cm, ε_{SiC} is the material permittivity of the material (SiC) = 9.7, a is the surface junction = 0.20 cm^2 and W is the width of the space charge region.

The equation of $1/C^2$ according to the bias voltage is given by the following relation:

$$\frac{1}{C^2} = \frac{\varepsilon_0 \varepsilon_{SiC} \alpha}{\varepsilon_0 \varepsilon_{SiC} a^2 q N_A}\left(V + V_{fb}\right) \qquad \text{Eq.3}$$

Based on the equation (Eq.3), the value of flats bands (V_{fb}) and the concentration of the impurities (N_A) are calculated by the assumption and the slope of the plot $1/C_2$ versus reverse bias voltage (V), respectively **Fig. 2**.

Experimentally, the acceptor concentration (N_A) was found in order of 1.47 $\text{x}10^{11}$ at/cm^3 for the SiC amorphous (Eq.4). These values are in agreement with those calculated from the electric resistivity of the material (MΩcm for a-$Si_{0.72}C_{0.28}$:H), this by using the equation below:

$$N_A = \frac{1}{q \mu_p \rho_p} \qquad \text{Eq.4}$$

where, ρ_p is the electrical resistivity of the material and μ_p is the hole mobility (6H-SiC) = 90 cm^2/V s.

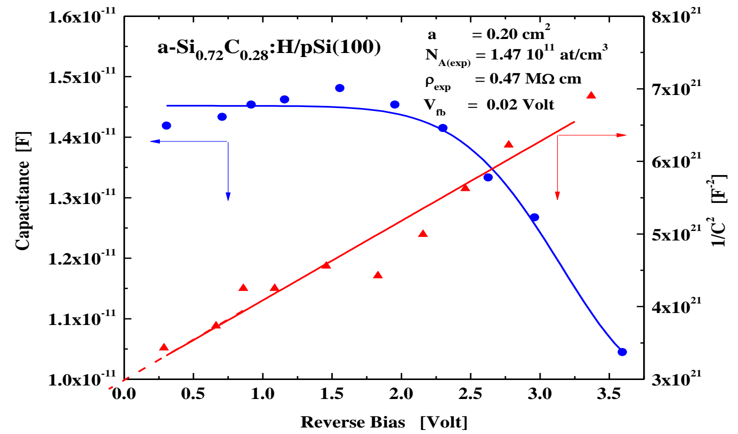

Fig. 2. C(V) and $1/C^2$ (V) of a-$Si_{0.72}C_{0.28}$ films.

B. *Morphologies of a-$Si_{0.72}C_{0.28}$:H films*

Fig. 3.a illustrates plan view SEM image of a-$Si_{0.72}C_{0.28}$:H surface film. We notice that the surface is very homogeneous and exempt from structure defects. Fig. 3.b shows that the anodization process influences the morphology of a-$Si_{0.72}C_{0.28}$: H surface films. For 45 s anodization time, we noticed the formation of a macroporous layer with a diameter pore varies between 50 and 150 nm (**Fig. 3.b**).

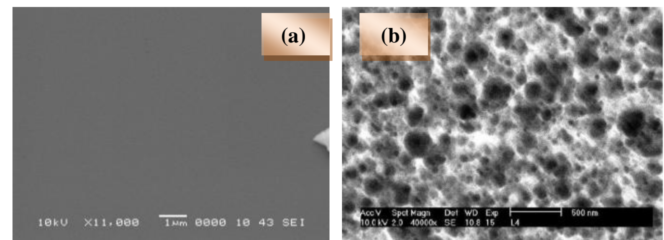

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Fig. 3 illustrates plan view SEM image surface film of: a)- Unetched a-$Si_{0.72}C_{0.28}$:H, b)- PASiC

C. Infrared spectroscopy (FT-IR)

The study of the surface of the amorphous thin a-$Si_{0.72}C_{0.28}$:H films before and after anodization (PASiC), shows several bands of vibrations. Infrared spectroscopy (FT-IR) revealed that the intensity of the peak located at 765 cm^{-1} corresponds to Si–C **[15]**, its intensity decreases, and the band becomes less large after the chemical treatment, as well as to indicate that the Si–C bond is broken to form the oxide of silicon (SiO_2) on the surface film at 1106 cm^{-1}, indicated by the presence of siloxane group Si–O–Si at 466 cm^{-1}. The absorption bands located at 570 cm^{-1} and 680 cm^{-1} correspond to Si–H bond and SiH_2, respectively. The band centered at 2286 cm^{-1} and 2396 cm^{-1} corresponds to CO_2 **[16]**. It shows that the area under the band is more important after anodization. It reflects that the density of CO_2 increases, and indicates a high level of degassing gas (**Fig. 4**).

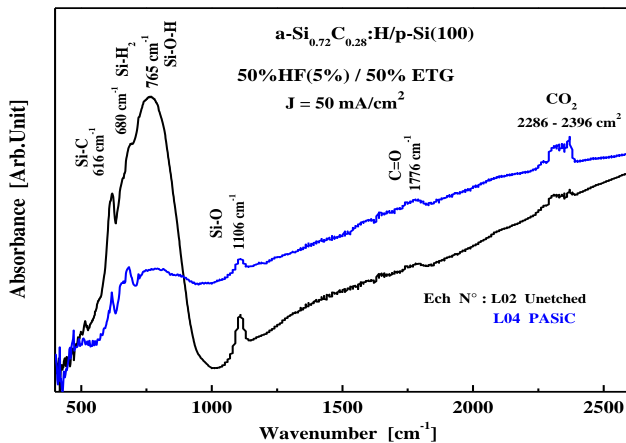

Fig. 4. Infrared spectra of unetched a-$Si_{0.72}C_{0.28}$:H and PASiC films

D. Raman Spectroscopy analysis

Fig. 5 shows Raman spectra of polycrystalline bulk 6H-SiC (Target), unetched thin a-$Si_{0.72}C_{0.28}$:H/pSi and PASiC films, respectively. The primary peaks in 6H-SiC (spectra (a)) are two planar or transverse optical modes of E2 symmetry at 768 cm^{-1} and 789 cm^{-1}, and a longitudinal optical phonon at 970 cm^{-1}. The spectral features presented in spectra (b) and (c) are evident: a band at 462 cm^{-1} which arises from amorphous silicon (Si); a relatively strong and broad band located at around 800 cm^{-1} is typical for amorphous SiC configuration **[17]**. One can note that the etching of amorphous SiC films increases the amorphous character of the films. The corresponding shapes are typical of disordered or amorphous compounds, with in place of the sharp lines of 6H-SiC, some broad band's characteristic of phonon density of states due to the release of the zone-center Raman selection rules. Nevertheless, the shapes displayed in Fig. 5 do not look similar to amorphous SiC, obtained for instance by ion implantation **[18–21]**. The amorphous bands seen here look more analogous to amorphous Si **[22]** consistent with a carbon-deficient a-$Si_{1-x}C_x$ ($x < 0.5$) composition.

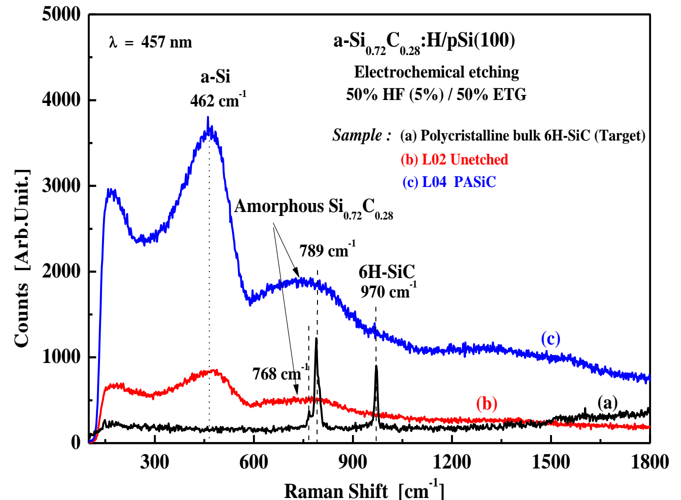

Fig. 5. Raman spectra of of unetched, 6H-SIC (Target), a-$Si_{0.72}C_{0.28}$: H and PASiC films

E. Secondary ion mass spectroscopy (SIMS) analysis

A Cameca *IMS 4FE7* from CRTSE *Algiers* instrument was used for trace element analysis, which was carried out by dynamic SIMS using a Cesium source (Cs^+) with an energy +10 kV with a negative sample polarization of −5 kV to analyse H, C, O, F, Si elements. The analysis was carried out in dynamic mode, in which the intensity versus the sputtering time gives the atomic ratio composition of SiC sample, which is close to 2.02 [^{28}Si(signal)/^{12}C(signal) = 2.19] (Fig. 6.a). After electrochemical etching in HF/ETG solution, SIMS analysis reveals that the etched films are mainly composed of Si, O, H and F (Fig. 6.b), The formation of an insoluble white layer on the a-$Si_{0.72}C_{0.28}$:H surface was noticed, hexafluorosilicate (H_2SiF_6) has always been considered as a final reaction product in the dissolution mechanisms as generally observed by several authors in the case of silicon **[23, 24]**.

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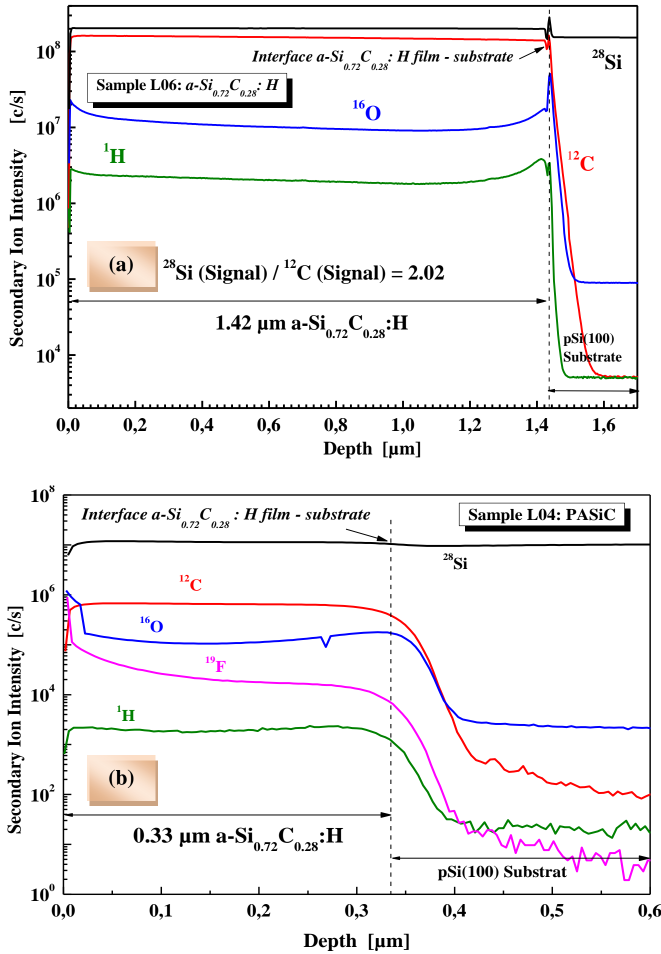

Fig. 6. SIMS Profile of of: : a)- Unetched *a-Si*$_{0.72}$*C*$_{0.28}$:H, b)- *PASiC* samples

F. Photoluminescence measurements

The luminescence measurements were carried out at room temperature with a Perkin–Elmer LS-50B spectrometer and a Xenon lamp (150 W) with an excitation wavelength of 325 nm was used. Figure 7 shows the PL spectra of amorphous thin a-Si$_{0.72}$C$_{0.28}$:H films before and after before and after anodization (PASiC). The PL spectra exhibit two bands: a blue one with two peaks 415 nm (2.99 eV) and 460 nm (2.69 eV) and a green band centered at 542 nm (2.28 eV), the sample etched exhibits a high PL intensity compared to the unetched sample. Wang et al. found that the PL intensities are enhanced by UV irradiation 325 nm at room temperature and the luminescence center with peak energy 2.20 eV is induced by the UV light for the anodized porous-like SiC samples, they suggested that UV irradiation may induce metastable states as luminescence centers in the sample **[25, 26]**.

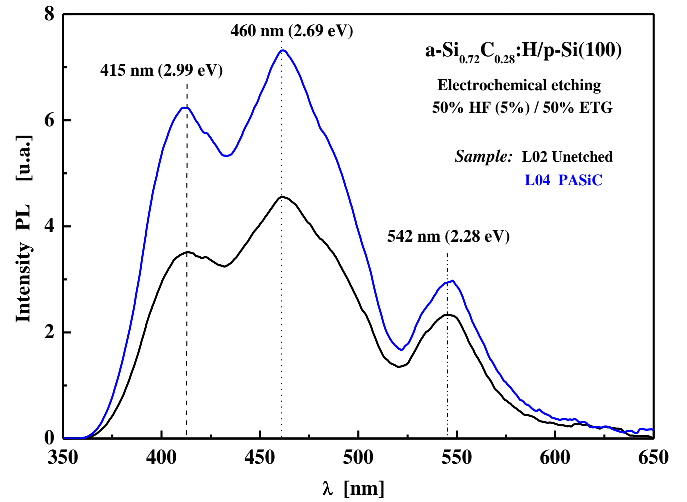

Fig. 7. Photoluminescence spectra of unetched a-Si$_{0.72}$C$_{0.28}$:H and PASiC films

G. Energetic application: Spectral response properties

The photodiode spectral responsivity was in direct relation with the depletion width (*W*) and then silicon carbide layer resistivity. The spectral response (*SR*) is given by the formula (Eq.4):

$$SR[A/W] = \frac{I_{ph}}{q} \cdot \frac{P_{inc}}{h\nu} \qquad \text{Eq.4}$$

where P_{inc} is the incident power and $h\upsilon$ is the photo energy.

The results presented in this work show the role of the surface structure on the spectral response (SR) of the Pd/a-Si$_{0.72}$C$_{0.28}$:H/pSi/Al Schottky photodiodes. A relative high spectral response value of 0.36 mA/W in the read region at a wavelength of 900 nm (Fig. 8) was obtained from porous a-SiC structure (Pd/PASiC/pSi/Al Schottky photodiodes); this is due to the increase of the specific area of the porous thin a-SiC film, it is four to five times higher compared to the photodiode of non-porous thin SiC film Pd/a-Si$_{0.72}$C$_{0.28}$:H/pSi/Al Schottky photodiodes. In the latter case a low spectral value around 0.08 mA/W is obtained in the read region (Fig. 8). In addition, the low value of the spectral response can be due to the sensitive layer (palladium). Finally, in order to increase the spectral response, we propose to use a semitransparent palladium (Pd) layer metal with a thickness 7.5 nm instead of palladium, operating under ideal conditions of minimum reflectance, high quality crystal structure and a nanoporous surface preparation allows to approaching a high spectral value, which will be our next preoccupation.

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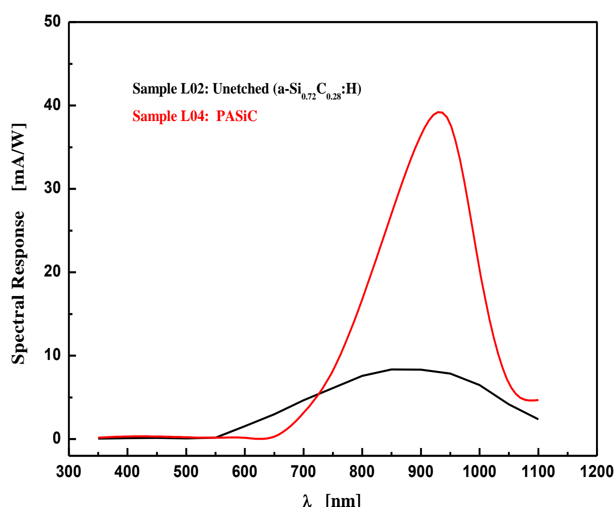

Fig. 8. Spectral response versus wavelength of unetched a-$Si_{0.72}C_{0.28}$:H and PASiC films

IV. CONCLUSION

In this work the results show that the anodization of an amorphous thin SiC film grown on p-Si (a-$Si_{0.72}C_{0.28}$:H/pSi) in HF/ETG solution with 50 mA/cm^2 during 45 s influences the morphology of the surface of these films, and produces spongy and macroporous structure, with pore diameters varies between 50 to 150 nm. This structure we encourage to elaborate devices structures based on this substrate as Pd/a-SiC:H/pSi Schottky photodiode. The results obtained indicate clearly the role of the porous structure on the optical properties of the Pd/a-SiC:H/pSi Schottky photodiode. Finally, Schottky photodiodes realized from a macroporous thin SiC films (Pd/PASiC/pSi/Al) show a good rectifying behavior from the fabricated diodes and a high spectral sensitivity compared to a Schottky photodiodes realized from a-$Si_{0.72}C_{0.28}$:H/pSi.

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