

Al-Assisted Photochemical Etching of a-SiC Thin Films for NH₃ Sensor

A. BOUKEZZATA*, H. MENARI AND S. KACI

Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE),
Division Couches Minces Surfaces et Interfaces (CMSI), Algiers, Algeria

In this work, we present the formation of porous amorphous silicon carbide (PASiC) fabricated on a thin amorphous silicon carbide (a-SiC) film. The film was deposited on *p*-type silicon substrate (a-SiC/Si(*p*)) by co-sputtering DC magnetron using a single crystal Si target and deposited onto 86 sprigs of hot pressed polycrystalline 6H-SiC. The thickness of the elaborated a-SiC films was 0.2 μm . Due to its high electrical resistivity of a-SiC:H thin film (higher than 2 M Ω cm), and in order to facilitate the chemical etching, a thin metallic film of high purity aluminum (Al), was deposited under vacuum. The PASiC films were made by Al-assisted photochemical etching using HF/AgNO₃ solution under UV illumination at $\lambda = 254$ nm with different etching times. The results show that the sample surface is uniformly covered with pores. The diameter of pores varied between 150 and 700 nm. The optimum etching time corresponded to 30 s that exhibited a high PL intensity. The NH₃ sensors were fabricated by evaporating coplanar interdigital gold (Au) electrodes on PASiC and the vapor sensing properties were tested. Finally, the sensing performances are attributed to the unique surface structure, morphology of the pore and its size, which provide an effective pathway for vapor adsorption and enlarge the sensing area of Au-PASiC.

DOI: [10.12693/APhysPolA.137.454](https://doi.org/10.12693/APhysPolA.137.454)

PACS/topics: amorphous silicon carbide, porous SiC, metal-assisted, photochemical etching

1. Introduction

Silicon carbide, a wide band gap semiconductor, is believed to be the ideal material for the fabrication of electronic devices that can operate at higher power levels and operating temperatures than devices produced from Si. Not only does silicon carbide display superior electrical and mechanical properties but processing technologies using silicon carbide are compatible to silicon microfabrication technology. Also, silicon carbide has many advantages compared with silicon for micro-electro-mechanical systems (MEMS) [1–3], such as its high toughness, and its capability to work at high temperature and harsh environment. However, porous silicon carbide (PSC) has been found to be an interesting object for developing new technologies and applications for a number of years now. It is a potentially attractive material for fabricating ultraviolet light emitting diodes, efficient ultraviolet photodetectors, and chemical or physical sensors [4–7]. Also, it is a novel substrate for epitaxial film growth [8, 9]. One major reason for some of these interests is that PSC has higher photoluminescence emission efficiency than bulk SiC. There have been a large number of reports on PSC, which exhibits a variety of porous structures produced under various chemical etching conditions. Detection of ammonia (NH₃) is required in many applications including leak-detection in air-conditioning systems [10], sensing of trace amounts ambient NH₃ in air for environmental analysis [11], breath analysis for medical diagnoses [12], animal housing [11], etc. Generally, because

it is toxic, it is required to be able to sense low levels (\approx ppm) of NH₃, but it should also be sensitive to much higher levels. NH₃ gas is very corrosive, often causing existing NH₃ sensors to suffer from drift and have short lifetimes. SiC with its well-known ability to withstand harsh chemical environments, should in principle be a better material for sensors in such environments. Membrane or thin film structures have also been demonstrated, which is a big advantage regarding ease of integration with standard processing due to greater flexibility in choice of doping type and concentration. We found porous SiC, when used as the dielectric in a capacitive sensing arrangement, to be extremely sensitive to the presence of NH₃ gas. Compared to existing FET NH₃ sensors [13], our devices are a lot simpler to fabricate and achieve similar sensitivities.

In this work, we have investigated the effect of metal-assisted electroless etching parameters in chemical solutions containing HF/AgNO₃. Scanning electron microscopy shows that the porous a-SiC (PASiC) is formed at Al-assisted photochemical etching method. In addition, we have made sensors of NH₃ using porous PASiC. NH₃ sensors were fabricated by evaporating coplanar interdigital gold electrodes on PASiC and these sensors were tested for adsorption and desorption of NH₃ vapor.

2. Experimental details

Porous amorphous silicon carbide (PASiC) was fabricated using the thin amorphous a-SiC films. They were deposited on *p*-type silicon substrate (a-SiC/*p*-Si(100)) by co-sputtering DC magnetron using a single crystal Si target deposited onto 86 hot pressed polycrystalline 6H-SiC slices of 10 mm \times 5 mm. The thickness of the

*corresponding author; e-mail: boukezzataassia@crtse.dz

films was ≈ 2000 Å. Two types of samples were prepared. In the first set, because of the high electrical resistivity of the thin a-SiC:H film around $2 \text{ M}\Omega \text{ cm}$, and in order to facilitate the chemical etching, a thin metallic film of high purity aluminum (Al) was deposited under vacuum onto the thin a-SiC:H layer for reinforced solution etching. In the second set, samples were subjected to the one-step Al-assisted electroless chemical etching in 1HF(25%)/1AgNO₃ (0.05 M) solution under UV illumination at 254 nm wavelength for different etching times varying from 5 to 90 min. After the etching, the samples were found to be covered with a thick Ag layer, which was removed by immersion into aqueous HNO₃ solution for 3 min. Samples were rinsed with deionized water H₂O and dried with nitrogen N₂ gas. The properties of a-SiC:H layer etched were investigated by scanning electronic microscopy (SEM), the Fourier transform infrared spectroscopy (FTIR), and photoluminescence spectrometry (PL). The NH₃ sensors were fabricated by evaporating coplanar interdigital gold electrodes on PASiC and the vapor sensing properties were tested and carried out at atmospheric pressure and room temperature. The sensing principle of a NH₃ sensor is based on the variation of current density of a sensor's surface caused by the NH₃ vapor adsorption and desorption.

3. Results and discussions

3.1. Macrostructure of PASiC

The first stages of the etching were investigated by SEM. Plan view of the PASiC surface at different etching times are shown in Fig. 1. The sample surface is uniformly covered with pores. The diameter of pores, which is close to the surface of the sample, varies between 150 and 700 nm.

3.2. Infrared spectroscopy (FTIR)

The study of the surface of the amorphous thin a-Si_{0.70}C_{0.30}:H films, which were treated in a solution 1HF(25%)/1AgNO₃ (0.05 M) for different etching times by infrared spectroscopy, revealed that the intensity of the peak located at 766 cm^{-1} [14] corresponds to Si-C vibration band decreases when the chemical etching time increases (Fig. 2). The growth is less after the chemical treatment, which indicates that the Si-C bond is broken to form the oxide of silicon on the surface. The absorption band which is observed at 619 and 2088 cm^{-1} [15] is attributed to Si-H₂ and Si-Hn peaks. The band centered at 97 cm^{-1} is assigned to the absorption pattern that marks the stretching vibration of the Si-O₂ bond [16, 17], as well as to the interstitial oxygen which dissolves itself in the substrate Si. Consequently, it shows that the SiC dissolution goes to the formation of an oxide on the surface. This study revealed also the presence of a band at $2343\text{--}2373 \text{ cm}^{-1}$ which can be assigned to CO₂ stretching band (Fig. 2).

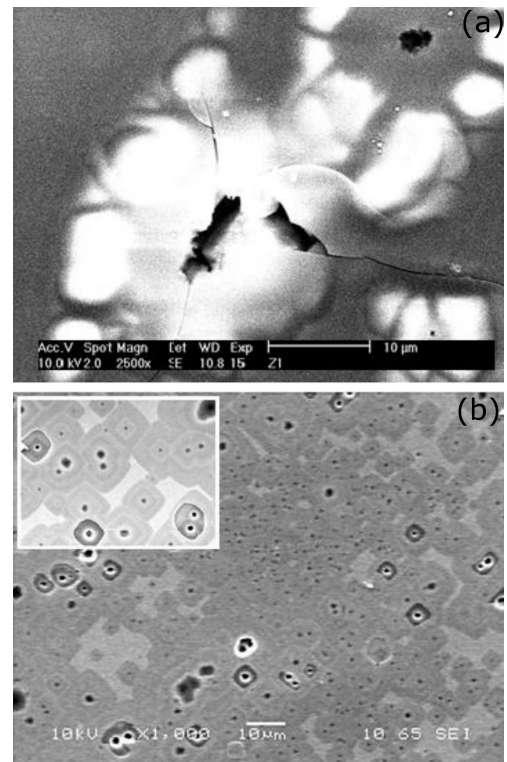


Fig. 1. Plan view SEM images of Al/a-SiC:H/Si thin films etched in 1HF(25%)/1AgNO₃ (0.05 M) solution for $t = 30$ min (a), and $t = 60$ min (b).

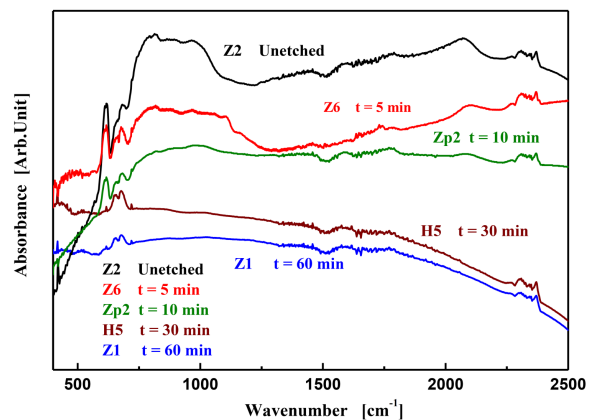


Fig. 2. FTIR spectrum of Al/a-SiC:H/Si thin films etched in 1HF(25%)/1AgNO₃ (0.05 M) solution for different etching time.

3.3. Photoluminescence measurements

Figure 3 shows PL spectra of amorphous thin a-SiC:H films before and after photochemical treatment in a solution of 1HF(25%)/1AgNO₃ (0.05 M) for different etching times ranging from 5 to 60 min. The PL spectra exhibit two bands, a blue one with two peaks at 385 nm (3.22 eV) and 450 nm (2.75 eV) and a green band centered at 520 nm (2.38 eV). The sample etched for 30 min

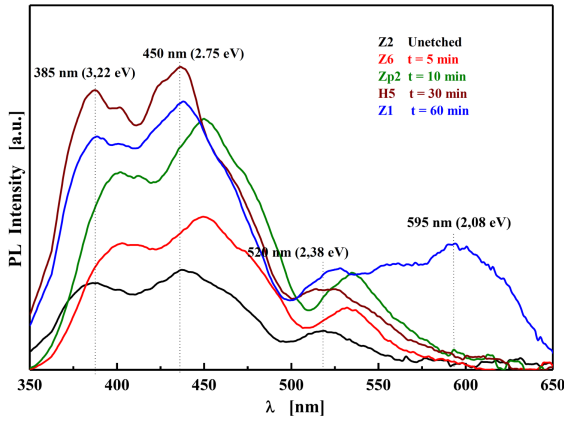


Fig. 3. Photoluminescence spectra of a-SiC:H films before and after etching in 1HF(25%)/1AgNO₃ (0.05 M) solution at different etching times.

exhibits a high PL intensity compared to the unetched sample. After increasing the etching time above 60 min, where the luminescence measurement exhibited both previous band and a red band centred at 595 nm (2.08 eV), this later band was due to etched silicon and the optimum etching time corresponds to 30 min (Fig. 3). This time indicates that the PL intensity of the blue band is more important and decreases when the etching time increases. 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 2.3 eV is induced by the UV light for the porous-like SiC samples. They suggested that UV irradiation may induce metastable states as luminescence centers in the sample [18, 19]. We observe that the photoluminescence (PL) spectrum of the etched thin SiC layer exhibits much more intense visible luminescence at room temperature than that of the non-etched sample. There are several reports in the literature that report an increase in photoluminescence intensity in the 2.47–3.3 eV region of the spectrum upon the formation of PSC [20]. Note that the luminescence intensity varies inversely with the pore diameter and the time of porosification corresponding to macroporous structure has been found to be 5 min.

3.4. Au-PASiC/p-Si(100) NH₃ sensors

The NH₃ vapor sensor was constructed by evaporating coplanar interdigital gold electrodes onto surface of PASiC under a vacuum thermal evaporation method. The schematic diagram of electrode arrangement on the surface of PASiC sensor is shown in Fig. 4.

3.5. Device responses of sensors

Figure 5 indicates clearly the role of porous structure SiC on the electrical properties of the sensor in presence of hydrogen nitride vapor NH₃. The values of electrical parameters determined in different ambient (air ambient and NH₃ vapor) are found to be dependent on the SiC

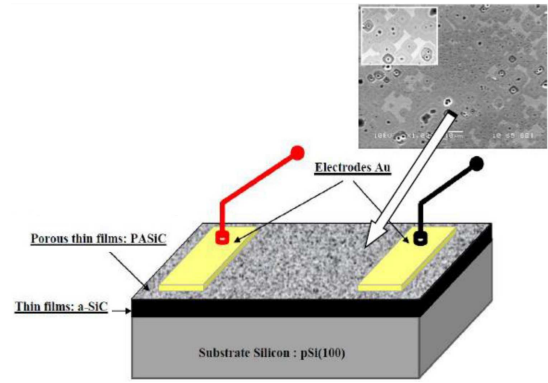


Fig. 4. A schematic of the devices used in this work. The sensing mechanism with porous SiC as sensing di-electric.

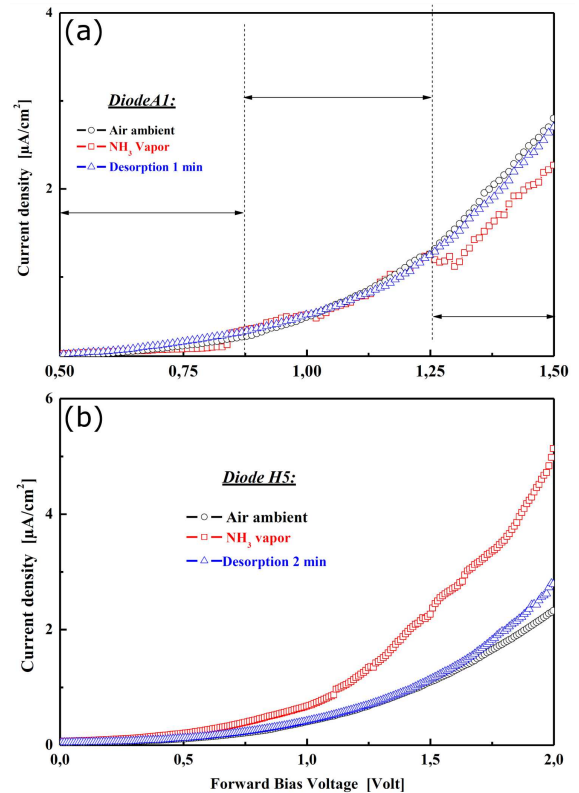


Fig. 5. Current–voltage characteristics of NH₃ vapor sensor: (a) Au/a-SiC/Si sensor, (b) Au/PASiC/Si sensor.

structures and the nature of ambient vapor, shown in Fig. 5ab. Finally, the maximum sensitivity of the structure Au/PASiC is reached at low bias voltage (0.5 V) in presence of vapors (Fig. 5b).

However, we noted that the performance of the sensor depends strongly on the quality of the metal–semiconductor interface which is significantly influenced by the sample morphology, sponginess, and macroporosity of the semiconductor.

3.6. Response and recovery time

Figure 6 depicts the response/recovery curves of Au-PASiC/*p*-Si(100) structure for adsorption and desorption of NH₃ vapor. As it can be seen, the calculated response and recovery times are found to be about 76 s and 84 s, respectively. Moreover, the response and recovery time are relatively equal and longer than those of sensors based on traditional porous silicon (PSi) [21].

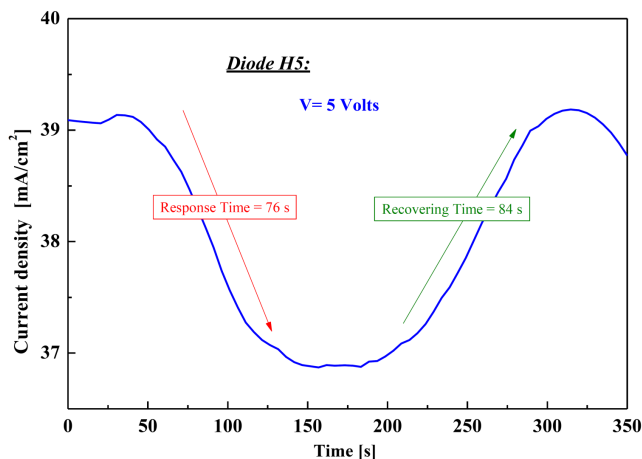


Fig. 6. Response/recovery time characteristics of NH₃ vapor sensor.

4. Conclusion

Macrocomposite PASiC films were prepared by growing a-Si_{0.70}C_{0.30}:H on *p*-Si(100) using co-sputtering DC magnetron process. These thin films were treated by photochemical etching and the average diameters of the pores were evaluated to be 150 nm. The PL intensity indicates that the optimum etching time corresponds to 30 min. On the sample surface, by evaporating coplanar interdigital gold electrodes, the room-temperature NH₃ vapor sensing properties of PASiC were studied. We noticed that the resistance of Au-PASiC highly increases compared to unetched Au-a-SiC:H films. Moreover, it has been shown that the measured resistance of the structure highly depends on the applied bias voltage. Finally, our results indicate that PASiC might be a promising NH₃ vapor sensing material for practical application.

Acknowledgments

This work was supported by Funds National Research (DG-RSDT/MESRS, Algeria).

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