Optical and structural evaluation of SiC nanocrystallites

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Abstract. This paper presents results of the non-contact and non-destructive characterization of porous SiC layers using Raman scattering spectroscopy, scanning electron microscopy as well as atomic force microscopy methods. The comparative study of the Raman spectroscopy on the bulk SiC and porous SiC layers has shown a number of new features specific for nanocrystallite materials, which have been analyzed and discussed.

1. Introduction.
In recent days, silicon carbide (SiC) has attracted increased attention as material for future high-temperature electronic devices and high power microwave devices due to its wide bang gap and high breakdown field, therefore, porous SiC (PSiC) has been around for many times as an object of interest for developing new technologies. Blue emission had been investigated in porous SiC layers [1, 2]. Latter it was shown that porous SiC is a promising medium for diffusion, which allows one to control electrical properties of bulk SiC material using diffusion doping [3]. Some perspective applications of SiC-based homoepitaxial device structures formed on PSiC substrates with improved quality were reported [4]. Due to lattice mismatch between GaN and c-SiC, some surface roughness of SiC substrates improves quality of the grown GaN layers [5,6]. Despite of the technological progress achieved the fundamental properties of porous SiC and methods of its non destructive characterization are not studied in so many. Thus, the porous SiC investigation and development of the characterization techniques are strongly motivated. In this work we present results of non-contact and non-destructive characterization of porous SiC layers.

2. Sample and experiment.
At the first the porous SiC layers were prepared by electrochemical etching on (0001) oriented n-type 6H-SiC wafers with resistivity of 0.052  Ω cm using HF-ethanol solutions (HF: H₂O:C₂H₅OH = 1:1:2).

The dc anodization regimes are presented in the Table 1. Each sample contained porous layer and non porous part (bulk SiC), which served as a reference.
Raman spectra was measured in the backscattering configuration using a Labram Dilor micro-
raman spectrometer at room temperature with He-Ne laser excitation. The surface morphology was
analyzed using AFM Nanoscope IIIa system, SEM spectra was measured with FEG 35-SIRION
model.

3. Experimental results.

After the samples were grown by electrochemical etching, the porous layers of SiC present an
increment in their thickness in function of the etching current or time. This was confirmed from the
scanning electron microscopy study, where the profile pictures have been taking for measuring the
porous layer thickness.

Typical SEM image of the porous SiC sample anodized at 6 min and 80 mA/cm² is presented in
figure 1. We estimated the average nano crystallite size in the direction parallel to the surface of 50 nm
and the roughness of the surface morphology of 40 nm with the pore cross section diameter 100-150
nm. The estimated thicknesses of the porous SiC layers are presented in Table 1. The AFM image
shown in figure 2 is confirmed mentioned above nano crystallite size estimation.

![Figure 1. SEM image of studied porous SiC layer anodized at 6 min. after RIE treatment.](image1)

![Figure 2. AFM image of studied porous SiC layer after RIE treatment.](image2)

| Table 1. Electrochemical etching regimes and porous SiC layer thicknesses. |
| Sample | Etching time (min) | Etching current density (mA/cm²) | Porous SiC layer thickness (μm) |
|--------|--------------------|---------------------------------|-------------------------------|
| 1      | 1                  | 80                              | 2.50                          |
| 2      | 3                  | 80                              | 6.00                          |
| 3      | 6                  | 80                              | 12.00                         |
| 4      | 3                  | 4                               | 0.07                          |
| 5      | 3                  | 8                               | 1.20                          |
| 6      | 3                  | 16                              | 2.80                          |
| 7      | 10                 | 8                               | 2.20                          |
| 8      | 10                 | 16                              | 6.80                          |
| 9      | 10                 | 30                              | 7.50                          |

A Raman spectrum of the porous and non porous parts of the sample anodized at 6 min. and 80
mA/cm² is presented in figure 3. The dispersion Raman has been studied for several polytypes of the
SiC [7], and is possible the identification of these polytypes using Raman technique. In the table 2 the
main modes of different polytypes of the bulk and porous SiC are shown. According to the table 2 the
bulk SiC wafer is comprised of 6H-SiC with inclusions of 4H-SiC and 15R-SiC polytypes.
Figure 3. Raman spectra of (1) bulk SiC and (2) sample anodized at 6 min and 80mA/cm².

Table 2. Show the main Raman modes of different polytypes of the bulk and porous SiC. Only shown FTA and FTO modes with symmetry E(E₁, E₂) and modes FLA y FLO with symmetry A₁ [7].

| Material  | Polytype | FTA (cm⁻¹) | FLA (cm⁻¹) | FTO (cm⁻¹) | FLO (cm⁻¹) |
|-----------|----------|------------|------------|------------|------------|
| Bulk      | 6H-SiC   | 144.9      | 502.3      | 765.5      | 965.3      |
|           |          | 262.7      | 511.0      | 786.4      |            |
| Bulk      | 4H-SiC   | 197.9      |            |            |            |
|           |          | 262.4      |            |            |            |
| Bulk      | 15R-SiC  | 177.0, 180.5 |          | 786.4      | 964.3      |
| Porous    | 6H-SiC   | 144.9      | 502.3      | 765.5      | 967.3      |
|           |          | 231.8, 236.4 | 511.0      | 786.4      | 968.3      |
|           |          | 262.7      |            | 795.7      |            |
| Porous    | 4H-SiC   | 197.6      |            |            |            |
|           |          | 262.4      |            |            |            |
| Porous    | 15R-SiC  | 177.0, 180.5 |          | 786.4      | 965.3      |
|           |          |            |            | 794.7      |            |

4. Discussion and Conclusions.
A comparison of the Raman spectra in PSiC versus reference SiC region shows that the full width at half maximum (FWHM) of Raman lines increased, the background of entire Raman spectrum raised, additional FTA lines (231.8, 236.4 cm⁻¹) and FTO lines (794 cm⁻¹) are observed and a new phonon mode at 942.0 cm⁻¹ appears.

The effect of Raman line broadening and the enhancement of diffused scattering were observed and interpreted previously in heavily disordered SiC [8]. This effect was attributed to the existence in disordered crystals of short-range 6H-SiC nano (or micro) crystallites. We suggest that this is a case in studied PSiC layers. The electronic confinement of an elementary excitation in the nano-crystalline SiC particles can be an origin of new electronic effects not observed in the bulk material such as: appearance of a new localized states in the band gap, band gap broadening, phonon confinement, surface polariton creation and so on. Raman scattering by the surface phonon (SP) can be observed when the size of crystals is about an order of magnitude smaller than the wavelength of the incident light [9]. This condition is realized in our Raman study with the He-Ne laser as an excitation source. Its excitation wavelength (632.8 nm) is larger by an order of magnitude than SiC nanocrystal sizes.
(40-50 nm) estimated from AFM. Therefore, a new phonon mode at 942.0 cm\(^{-1}\) in PSiC Raman spectra can be attributed to the surface phonon (SP) mode.

As follows from figure 3, the intensities of FTA modes (231.8, 236.4 cm\(^{-1}\)) and FTO modes (764.5, 785, 794 cm\(^{-1}\)) increase in porous SiC layer. Some changes in the bond Raman polarizabilities can take place at the creation of porous SiC, due to the change of the porous materials dielectric constant, which stimulate the FTA and FTO mode Raman intensity increase.

It is known that when the frequency of the free-carrier plasma oscillations in a polar semiconductor is close to that of the LO phonon, the two excitations interact via their macroscopic electric fields and as result LO phonon-plasmon coupling appears [10]. The high frequency shift of the FLO mode and its asymmetric broadening in porous SiC can be attributed to the effect of LO-phonon-plasmon coupling in SiC nano crystallites.

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