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Plasma Treatment of 3C-SiC Surfaces

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Abstract. Surfaces of cubic silicon carbide (3C-SiC), grown by vapour phase epitaxy with silane and propane as precursors, were treated with plasma to remove residual species deposited during the growth procedure and the sample cooling down, or due to atmospherical contamination. The impurity traces were investigated with optical absorption spectroscopy. No morphology changes due to the plasma exposure were observed.

Introduction

The interface of a biological system with tailored made detectors at the molecular scale opens the possibility to develop an entirely new class of devices and personal monitoring systems. The materials selected for these devices must be biocompatible, to ensure not to be toxic or invasive for the organism, and must be capable to work in a very harsh environment such as blood and humany body.

Silicon carbide (SiC) is mechanically robust, chemically inert, non-toxic and biocompatible, thus representing a good material for biomedical purpose [1].

Covalent bonding between specific molecules and stable interfaces are required for the realisation of biosensors based on molecular recognition. Since it was also demonstrated that SiC surfaces can be functionalized to be reactive to specific biomolecules, this material is an optimal candidate for biosensor and bioelectronic applications. Nevertheless, in view of its real use for biomedical devices, high quality and extreme purity are fundamental.

As a matter of fact, some residues, e.g. CH groups, graphitic carbon, or -CH_3 groups, can be present due to carbon excess or to thermal decomposition of propane. Residual silicon compounds or mixed-type Si-CH may also be present due to the interaction with the substrate. Moreover, the state and history of the growth chamber can also influence the presence of residues, especially during the cooling down step. The exposure of the surface to the atmosphere can result in the incorporation of other contaminants. The aim of this work is to check the presence of SiC surface residues and verify the efficiency of plasma assisted treatments in their removal.

Experimental

The SiC layer is epitaxially grown at atmospheric pressure on silicon substrates using Vapor Phase Epitaxy (VPE) technique, propane and silane (diluted 3% in H_2) as precursors and palladium purified H_2 as carrier gas [1]. The growth temperature was 1200 ° C, the C/S ratio about 1.6, and the growth time 10 minutes. Silicon was subjected to chemical etching with HF before being placed in the growth chamber, where it was thermally annealed at 1000 °C for 10 minutes and then carbonized by inserting propane during a thermal ramp from 400 °C to 1100 °C [2]. The SiC samples are grown immediately after the carbonization with an average thickness of about 0.5 μm.

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They were thus treated with plasma (Low Pressure Plasma Enhanced, LPPE), more specifically with Radio Frequency Inductively Coupled Plasma (RF-ICP), operating at different experimental conditions in O_2, Ar, H_2, and Ar + O_2 mixture, with a flow of 30 SCCM, at the power of 200 and 400 W, for 1.5 and 5 minutes. Plasma treatmens have been frequently used in industry as surface preparation technique instead of wet-etch approaches.
A treatment in hydrogen was carried out at a temperature of 1200 °C on SiC samples exposed to the atmosphere, at a pressure of 100 mbar for 10 minutes to check the efficiency of the heat treatment to remove the residues.
The presence of residual impurities was investigated by means of absorption spectra taken at room temperature with a Fourier Transform spectrophotometer (FTIR Bomem DA8) operating in the 500-6000 cm^{-1} range. The absorption spectra were measured with a resolution of 1 cm^{-1} both before and after plasma treatments.
The morphology of sample surfaces was analyzed with Atomic Force Microscopy (AFM) using a Digital Instruments Nanoscope IIIa before and after treatments.

Results and discussion

Fig. 1 shows the room temperature absorption spectra measured on the SiC layers before and after the plasma treatments. All spectra exhibit an intense peak at about 800 cm^{-1}, associated to the Si-C bond. The full width at half maximum varies between 32 and 45 cm^{-1}, in agreement with those observed in single crystalline thick films of SiC [2], [4]. The as-grown samples are characterized by a non-homogeneous distribution of unwanted impurities, as seen in curves a and b referring to spectra measured on different portions of the same sample. In fact, while curve a is practically flat apart from the band at 800 cm^{-1}, curve b shows a variety of structured bands, some of them in positions typical of Si-O asymmetrical stretching (1100 cm^{-1}), CH_3 bending (1372-1450 cm^{-1}), stretching of single and double CO bonds (1250 and 1739 cm^{-1}, respectively), and H-O-H vibrations of adsorbed water (1649 cm^{-1}) [3-5]
All these complexes disappear when the samples are treated with plasma (independently on nature of the gas flow), see, as an example, curve c, representing a spectrum measured on a large portion of the sample, including the inlet and outlet zones, of a treated SiC layer. The only feature surviving to the plasma treatment is a shoulder at about 900 cm^{-1}, still not attributed to a specific group, whose amplitude exhibits a non-reproducible variation with the type of gas flow, its power or the exposure time (see, as an example, figure 2).
The Si-C peak is rather intense in all samples (beyond the regime of non-linearity of the detector), therefore it is not possible to make a quantitative estimate of its amplitude or to determine the dependence on the type of flow used for the treatment.

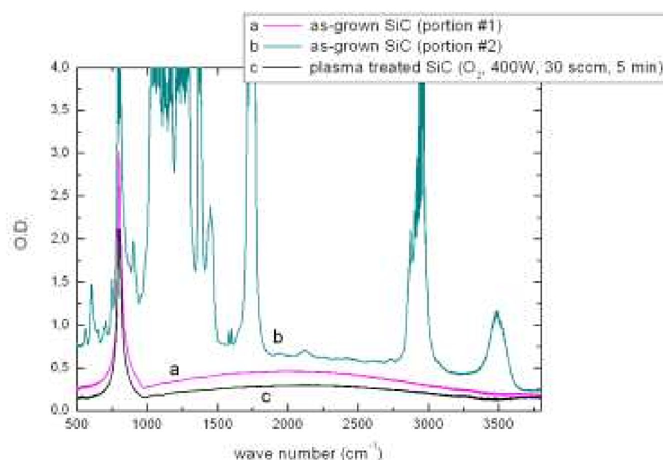

Figure 1: Absorption spectra of the SiC sample. Curve (a): example of spectrum taken in a section of the as-grown sample without residues. Curve (b): example of a spectrum measured on a zone of the as-grown sample with residues. Curve (c): spectrum measured on a large portion of a plasma-treated sample.

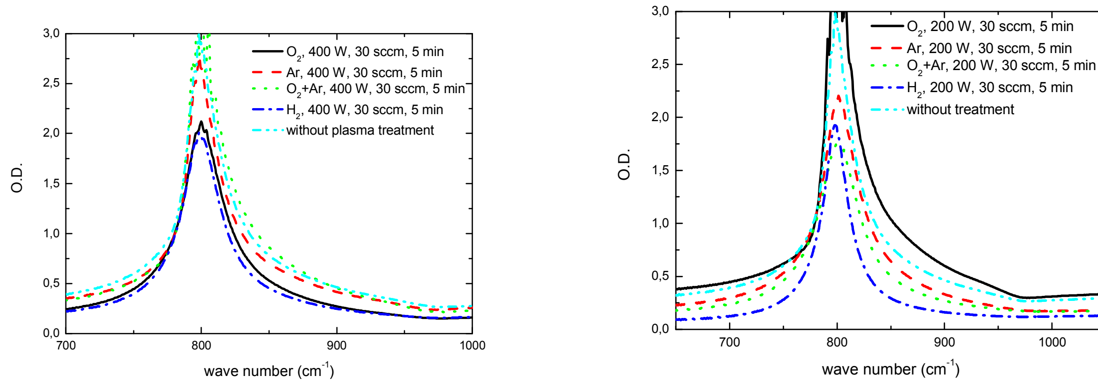

Figure 2: Absorption spectra of the SiC sample after plasma treatment in different conditions.

In order to remove the residues observed by FTIR, we tried an high temperature H_2 treatment on the as-grown samples in the same growth chamber we used for the depositing the 3C-SiC films. The main idea is that the residues could be removed by both the high temperature, if there is sufficient energy to break the bonds, and by the reduction of the complexes promoted by the H_2. If successful, the advantages of such a treatment would be the possibility to perform it with the same apparatus used by the growth, avoiding the necessity of ancillary equipment. Nevertheless, we must observe that if some residues are due to the grow chamber or grow atmosphere, this process could be largely ineffective, or can even increase the amount of residues. After the treatment in hydrogen at 1200 °C for a time of 10 minutes we observe only a slight decreasing of the signal intensity of a few lines; the absorptions related to the Si-O bond and CH_3 are the only ones exhibiting a measurable reduction, see figure 3.
No significant change in morphology after plasma treatment appears, as shown in by AFM analysis in figure 4, surface root mean square roughness, as calculated using Gwyddion software (www.gwyddion.net), was about 5 nm both before and after the process.

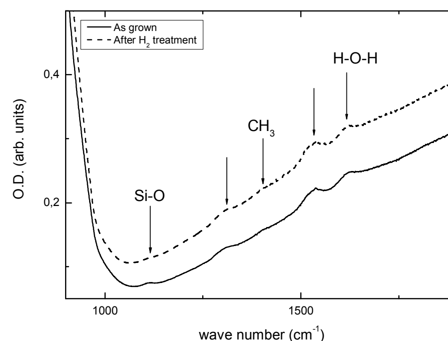

Fig.3: Absorption spectra of SiC samples as grown and after H_2 treatment in the growth chamber.

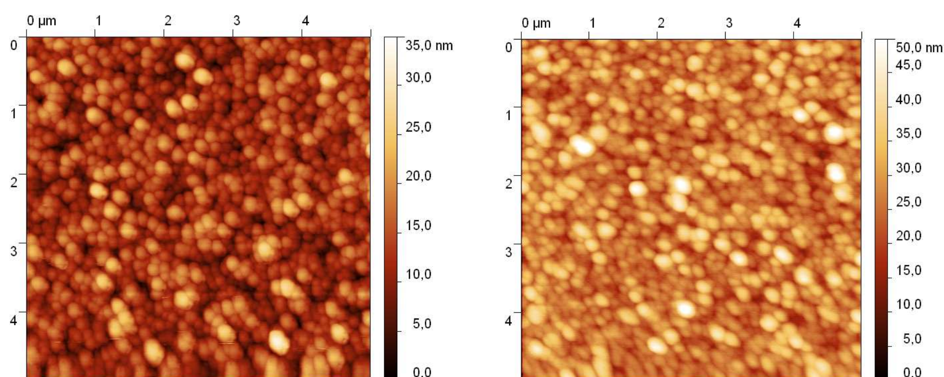

Figure 4: AFM image of the surface before (left) and after (right) plasma treatment

Conclusions

SiC samples analyzed by FTIR after growth process show the presence of structured bands, in positions typical of Si-O, CH_3, CO and H-O-H, particularly in the inlet and outlet zones of the wafer. The samples surface were treated with plasma and the process was found effective in removing residues, therefore can be exploited for cleaning purpose without any change in the morphology. In comparison, a treatment in H_2 at 1200 ° C does not introduce substantial modifications in the spectra.

Acknoledegements: AFM measurements were obtained at the “Centro Interfacoltà Misure” of Parma University.

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