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Hydrogen Etching Process of 4H-SiC (0001) in Limited Regions

A.Mancuso[1-4,a*], S. Boninelli[1,b], M. Camarda[1-2,c], P.Fiorenza[1,d], A. Mio[1,e], V. Scuderi[1,f], P.Godignon[3,g], S. Aslanidou[3,h], L. Calcagno[4,i], F. La Via[1,j]

[1]CNR Institute for Microelectronics and Microsystem, 95121 Catania, Italy

[2]STLab, Catania, Italy

[3]Institute of Microelectronics of Barcelona (IMB-CNM), 08001 Barcelona, Spain

[4]Physics Department, Catania University, Catania, Italy

[a*]alfio.mancuso@phd.unict.it, [b]simona.boninelli@ct.infn.it, [c]massimo.camarda@stlab.eu, [d]patrick.fiorenza@imm.cnr.it, [e]antonio.mio@imm.cnr.it, [f]viviana.scuderi@imm.cnr.it, [g]philippe.godignon@cnm.es, [h]sofia.aslanidou@imb-cnm.csic.es, [i]lucia.calcagno@unict.it, [j]francesco.lavia@imm.cn

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Abstract. In this work we have studied hydrogen etching of Silicon Carbide (SiC) chips at high temperatures and in confined limited regions, to elucidate and control the formation and propagation of terraces on the surface of SiC (0001) 4° off-axis samples. This process is very important for the development of high-power transistors. The effects of process parameters on the etching of 4H-SiC (0001) have been extensively investigated using several types of surface analysis (Atomic Force Microscopies (AFM), Scanning Electron Microscope (SEM) and High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). We correlated the growth of terraces with etching temperature and time. Moreover, we found the average width of terraces increases decreasing the dimension of the structure from 20 μm to 1 μm using the same process parameters. The nanofacet formation of typical hill-and-valley structure has been observed in localized region on SiC (0001) basal plane.

Introduction

The epitaxial process in SiC is extremely different with respect to the process for Si devices. The two main differences are related to the high temperatures needed for the diffusion of Si and C on the SiC surface to obtain an epitaxial layer (about 1600 °C vs. 1000 °C for Si), and the fact that, to avoid the formation of different polytypes during the epitaxial growth process, the substrate is cut off-axis with respect to the (0001) axis [1,2]. Several studies reported that these off-axis substrates produce a rough surface that can generate several effects on the device realization [3,4]. A possible solution to avoid such roughness can be an etching that remove this roughness without introducing defects.
Between the different etching processes, we have selected a simple etching in hydrogen at high temperature that is generally used in the first steps of the epitaxial growth process.
Systematic studies of hydrogen etching on the surface morphology of on-axis 4H-SiC (0001) wafers reveal that etching temperature and time are considered as two controlling parameters which determine the terrace features [5,6]. Until now there is not a precise study of off-axis 4H-SiC etching in delimited regions. Such a study and the understanding of the physical and chemistry mechanisms is extremely important for improving the shape and smoothness of the trench, for the purpose of manufacturing high mobility trench MOSFET [7]. In this work, we have investigated the surface morphology of 4H-SiC substrate off-oriented 4° off-axis with respect to the (0001) axis, after hydrogen etching at high temperatures in delimited regions using SEM, AFM and HAADF-STEM. We have observed a clear evolution of terraces and nano-faceting of the step-and-terrace morphology, as nano undulations of the surface. This is the so-called step bunching, defined as the formation of multiple-height steps.

Experimental Setup

Samples cut from 4H-SiC 4° off-axis with respect to the (0001) axis wafers were employed. On these samples different regions with different line width have been opened in the resist on the SiC surface (fig.1,a). Subsequently the samples were then annealed at 900-1000 °C to transform the resist into a graphite mask. Then the SiC surface was exposed to a hydrogen flow of 250 sccm at different temperatures in the range 1300-1450 °C for 30 and 60 minutes. The parameters of the etching processes developed in this study are summarized in table 1.

Table 1. The etching temperature and time used in this study.

Samples	1	2	3	4	5
Temperature [°C]	1300	1360	1400	1400	1450
Time [min]	30	30	30	60	30

A Zeiss FEG-SEM Supra 25 Microscope (Oberkochen, Germany) was used to perform a plan SEM image using an acceleration voltage of 2 kV. Atomic Force Microscopy (AFM) analyses were performed using a PSIA XE 150 microscope operating in non-contact mode (NCM). A FEI Helios Nanolab 650 was used to get thin film (lamella) containing a cross- section of the sample. A Transmission electron microscopy carried out with JEOL ARM200F Cold FEG STEM/TEM working at 200 kV was used to employ HR micrographs of the sample. A resolution of around 0.68 Å was established to achieve HRSTEM images. To reduce local contamination during the acquisition of HR images, the sample was exposed to a beam shower. Possible artifacts due to sample drift or noise have been avoided by using SmartAlign which captures multiple scans acquiring multiple scans every 90° in each area. SmartAlign reconstruction was performed by means of non-rigid alignment (pixel level alignment) of each image

Results and Discussion

Yishida et al. proposed the chemical reaction model for SiC etching by H_2 at the mass transfer limit [8]. At high temperatures, SiC decomposes on the surfaces, leading to the generation of Si and C atoms. The Si atoms desorb due to high vapor pressure, while C atoms irreversibly regroup in clusters. At same time H_2 molecules diffuse through stagnant layers and decompose into hydrogen atoms on SiC surfaces. The SiC surface acts as a catalyst for this dissociation. When C atoms or clusters encounter atomic hydrogen on surfaces, they react immediately, forming hydrocarbons that are then released.

After the etching process at 1300 for 30 minutes, we observed a certain roughness which was generated by some oriented terraces towards [1-100] crystallography direction within 1 μm line (fig.1,b). This behavior has been also observed by AFM image in the work of M. Horita et al. [9]. In our work, the average width of terrace was calculated (111 ± 35 nm) on 10 data points. If the etching temperature was increased to 1450 °C we were able to identify a clear widening of terrace. Within 1 μm line the average width of terrace was (391 ± 95 nm) on 5 data points (fig.1, c). With the same process parameters, the average width increased (570 ± 120 nm) on 20 data points as the size of the line increases from 1 to 20 μm (fig.1,d).

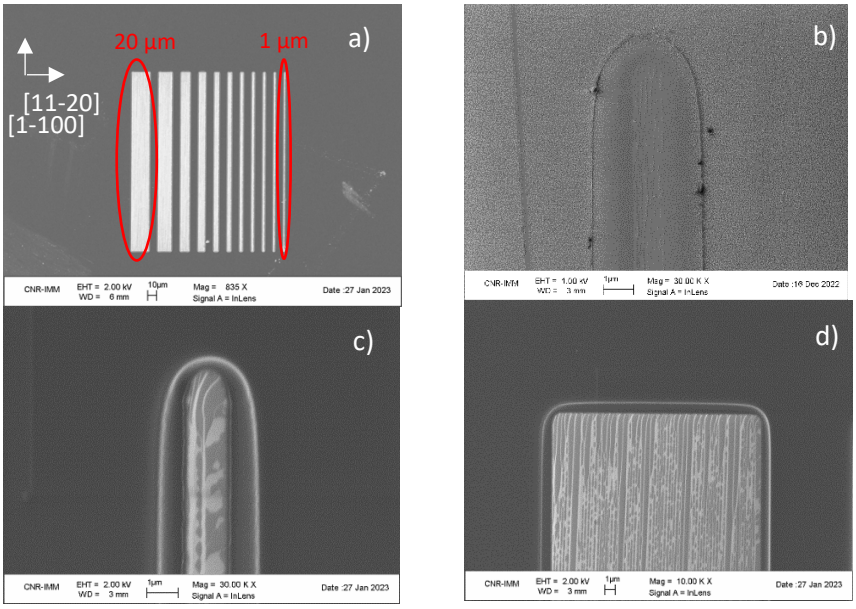

Fig.1 SEM images of surface 4H-SiC (0001). a) limited regions with width from 1 to 20 µm b) line width of 1 µm line after H_2 etching at 1300 °C for 30 minutes c) line width of 1 µm and d) line width of 20 µm after H_2 etching at 1450 °C for 30 minutes.

The morphology of the 4H-SiC surface after H_2 etching at 1450 °C for 30 minutes appeared to show a carbon contamination on the terraces (fig.1a,b). This was confirmed through Raman spectrum within 20 µm lines (fig.2). According to the group-theoretical analysis and Raman selection rules for 4H-SiC polytypes the A_{1L} (LO: longitudinal optical) band peaks located at 972 cm^{-1}, while the E_{2T} (TO: transverse optical) at 776.2 cm^{-1}. Instead, it can be seen clearly the G band peaks at 1580 cm^{-1} of a form polycrystalline graphite which is mixed with amorphous carbon [10]. In addition, a quasi-tic D peak was found to emerge at 1400 cm^{-1}, but the D peak in the Raman spectrum of graphite should be actually at 1350 cm^{-1}. The shift of D peak was induced by a weakly disordered structure, indicating that the samples contain defective graphite. This again reveals that the coexistence of defective graphitic structure and SiC crystal occurred on SiC surface.

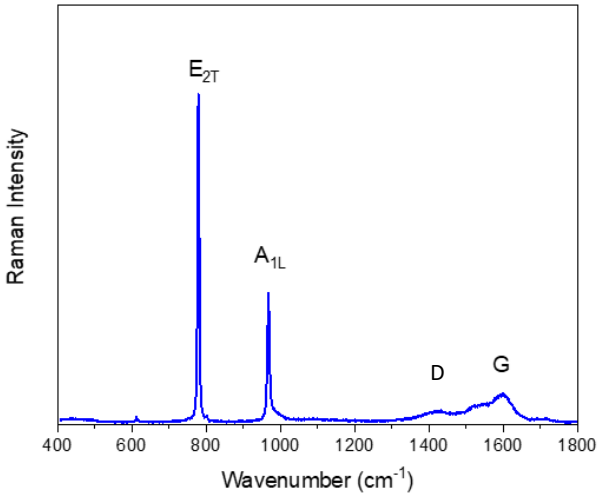

Fig.2 Raman spectrum after H_2 etching at 1450°C for 30 minutes.

The graphite mask could interfere on the chemical mechanism proposed by Yishida et al. High etching temperatures allowed to increase the C atoms clusters on SiC surface. The graphite material consisted in unsaturated sp^2 carbon atoms were highly susceptible to adsorbing hydrogen atoms, resulting in cleavage of C─C bonds and generation of CH compounds on the surface of the substrate. As a result, the number of dissociated H_2 molecules in reactive hydrogen become smaller. In the etching process,

SiC was carried out away into the gaseous state of silicon and hydrocarbons. If the silicon vaporization reaction was more predominant than the formation of hydrocarbons, the etch rate of the SiC surface will be controlled by the rate of hydrocarbon formation [10]. Under these experimental conditions, the saturated vapor pressure of hydrocarbons was lower than that of the gaseous state of silicon. As a result, the terraces were covered with C clusters.

From AFM analysis, we can also observe the terraces with many crossovers between terraces, indicating their anisotropy along [1-100] crystallography direction. Similar morphologies were also observed from AFM image in the work of L. Dong et al. [11]. However, in our case, Root Mean Square (RMS) roughness of substrate was 0.277 nm after etching at 1400 °C for 30 minutes along the lines scan in the orthogonal direction to terrace (fig.3,a). The terraces exhibit a higher roughness (RMS = 1.73 nm) at 1450 °C (fig.3,b). This roughness difference could be due to the fact that during the etching process at higher temperatures, the surface atoms which acquired sufficient energy and mobility to move into energetically favorable positions at the edges of the terrace. Thus, terraces with a steep edge could determine a rougher surface. On the other hand, the effect of anisotropic etching is suppressed due to more Si-C compounds reacted with hydrogen [12].

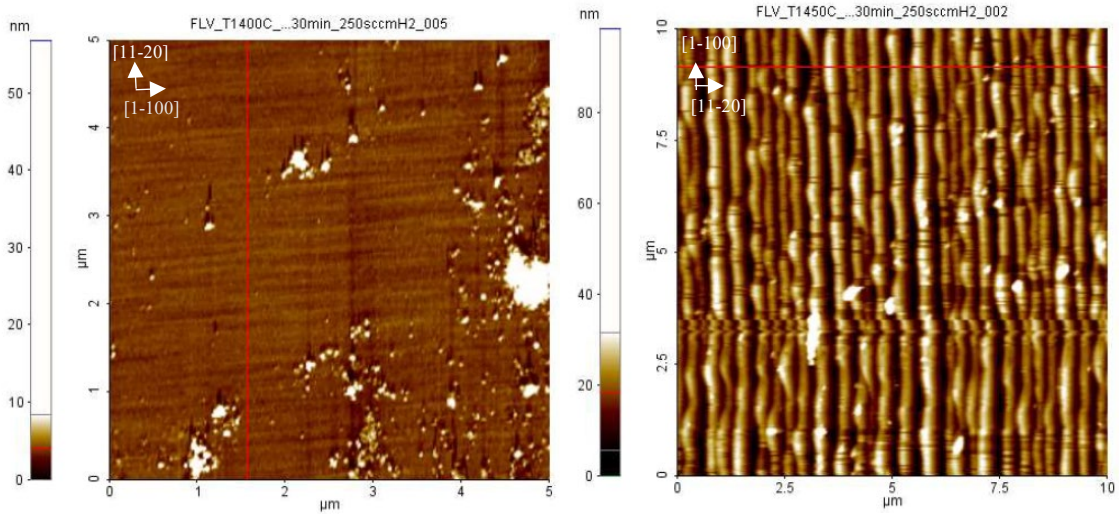

Fig.3 AFM analysis of surface 4H-SiC (0001). a) 10 µm x 10 µm AFM image of terraces inside 20 µm line after hydrogen etching at 1400 °C for 30 minutes. b) 10 µm x 10 µm AFM image of terraces inside 20 µm line after hydrogen etching at 1450 °C for 30 minutes.

We also observed a linear proportionality between average width of terrace and the etching time (fig.4,a). This proportionality may be due to the fact that this etching process was limited by the diffusion of atoms on the surface. In addition, the slope and the error bars increased from 1300 to 1450 °C for the same amount of time and size of the line. The results revealed that the widening rate of the terrace increased at higher temperature, but at the same time the terrace width distribution became less uniform that can be reflected by the error bars which stands the variation scope of measured values. It indicates that higher temperature needs less time for terrace formation. An Arrhenius plot of the etching rate extrapolated (from fig.4a) has been reported in fig.4,b. The activation energy was determined by the linear regression of the data in the temperature range between 1300 and 1450 °C and was found to equal 1.481 ± 0.281 and 1.538 ± 0.309 eV for terraces in lines of 1 µm and 20 µm respectively.

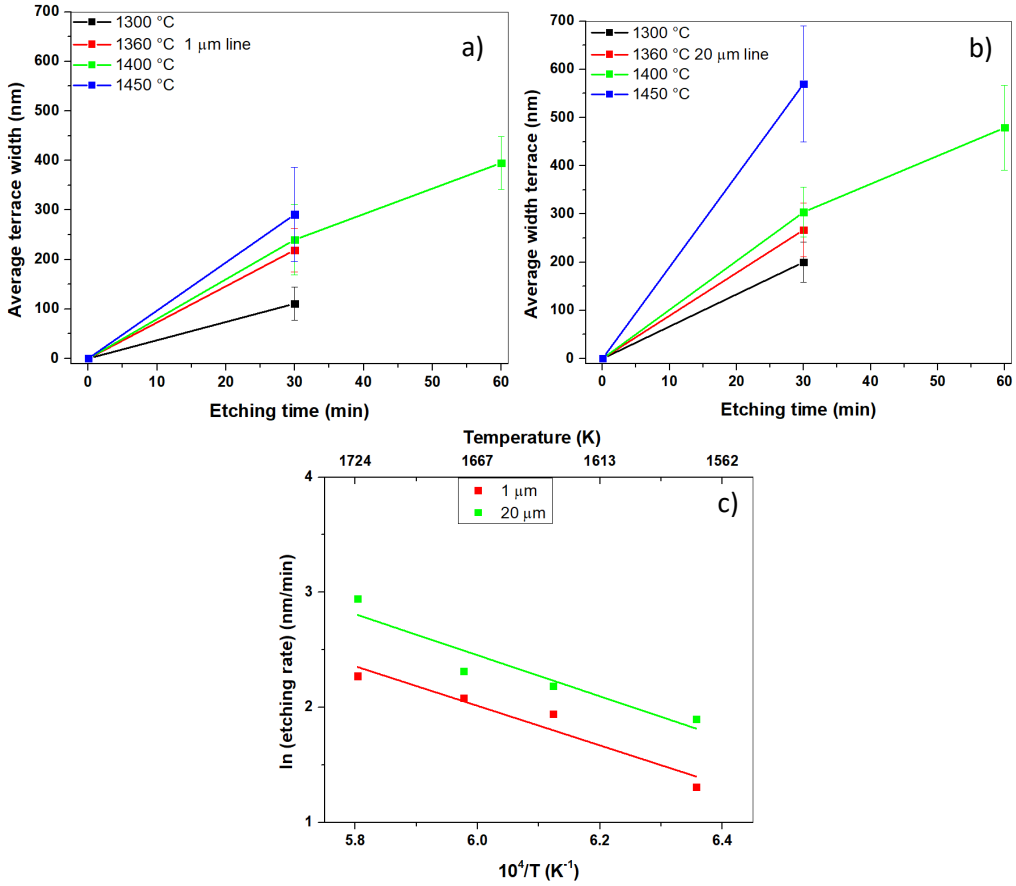

Fig.4. Correlation between average terrace width and time etching. a) In black, red, green (linear fit), and blue lines the correlations have been reported for 1300 °C to 1450 °C and for line width of 1 µm respectively. b) linear correlations at different temperatures for line of 20 µm**. c) Arrhenius plot.** The red and green lines are for line width of 1 and 20 µm respectively.

The study by P. Sukkaew et al. focused on investigating a surface kinetic model of hydrogen etching on a silicon carbide (SiC) surface using a $Si_{24}C_{24}$ cluster model [13]. In their model, hydrogen atoms terminated all the edges of the cluster to maintain the bulk geometry of SiC. They observed that the etching of CH_3(ads) by H_2 occurs via a transition state. Despite being thermodynamically favourable at 1600 °C, the calculated transition barrier height was relatively high at 5.514 eV, resulting in an extremely low etching rate constant at this temperature. In contrast, we observed that the etching of C clusters was not kinetic favourable at 1450 °C. On the other hand, the graphite mask increased the adsorption rate of CH_X compounds. As a result, unless the gas phase concentration of H a significantly exceeds that of CH_x compounds, the etching rates will be much lower than the adsorption rates, potentially resulting in a significant amount of CH_x (ads) surviving the etching process.

Some double hill-and-valley structures were distributed on the (0001) basal plane after etching process at 1450 °C for 30 minutes within 1 µm line (fig 5,a). These double hill-and-valley structures consisted in alternating step edges and facets. The “Facet 1” is 106.8 nm in length with a characteristic angle of inclination at 17.2 ° from (0001) basal plane, while the “Facet 2” is 244.9 nm in length with inclination at 11.3°. Although the “Step 1” and “Step 2” exhibits an atomically flat surface, the morphology of facets showed several stairs on the interface by HAADF-STEM images (fig.5, b and c).

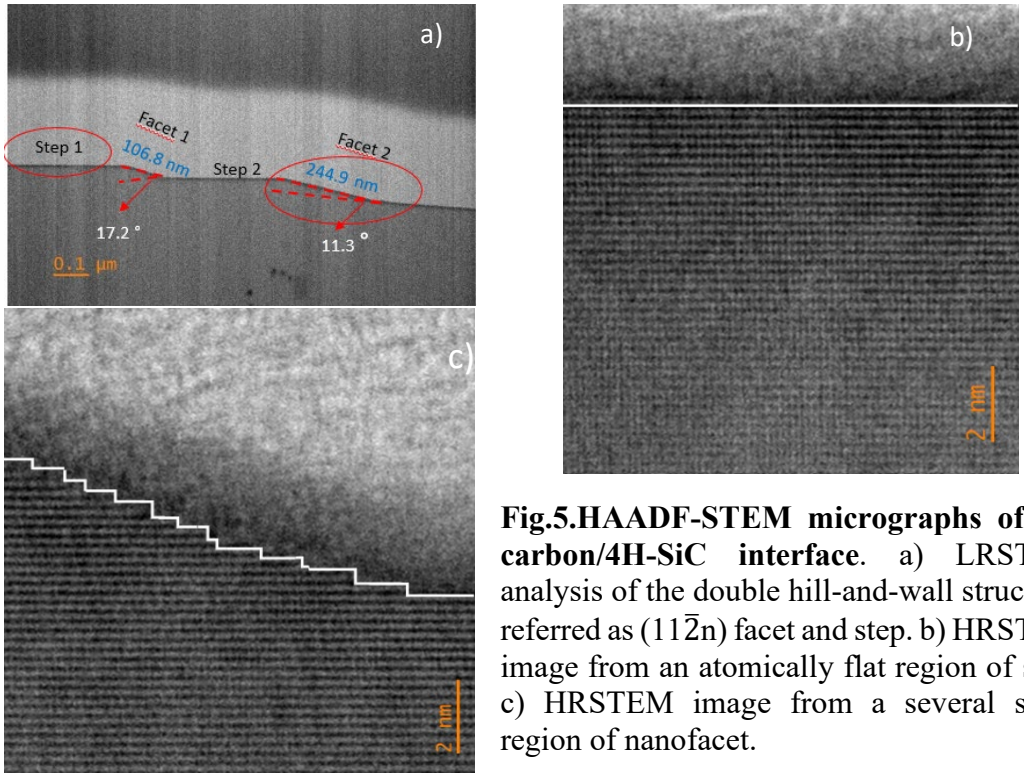

Fig.5.HAADF-STEM micrographs of the carbon/4H-SiC interface. a) LRSTEM analysis of the double hill-and-wall structure, referred as $(11\bar{2}n)$ facet and step. b) HRSTEM image from an atomically flat region of step. c) HRSTEM image from a several stairs region of nanofacet.

The nanofacet formation comprising two alternate facet planes (0001) and $(11\bar{2}n)$ (with high Miller index n = 11-12). Also, Nakagawa et al. reported similar double hill-and valley structure after etching process by HCl (0%-0.1%)/ H_2 mixture flow at 1430 °C at 760 Torr for 15-30 minutes [14]. Several authors argued that the origin of the nanofacets was attributed to minimization of surface free in (0001) steps, but it increases monotonically with the vicinal angle. However, the existence of $(11\bar{2}n)$ facets indicates that there would be an energy minimum at the vicinal angle of 13°-14° which is assumed to be induced by the presence of attractive step-step interactions between closely spaced bilayer steps [14,15, 16].

Summary

The experimental results reveal that increased etching temperature can effectively establish the broadening of terraces. After the etching process at 1450°C for 30 minutes we have observed a certain roughness by AFM analysis, which was generated by some oriented terraces in $1\bar{1}00$ crystallography direction. The decrease of the line width from 20 to 1 µm also will accelerate the growth rate of the terraces, because this process is a more kinetically favorable process. Therefore, it is possible to suggest that by maintaining at higher temperature or longer etching time, the formation of only one terrace in a 1 µm line can be possible, to obtain ideal surface with large macrostep atomically flat. HAADF-STEM studies revealed that the surface investigated shows double hill- and- valley structure through $(11\bar{2}n)$ nanofacets and (0001) steps, which are induced by equilibrium surface phase separation.

Acknowledgments

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