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Growth of a 3C-SiC layer by carburization of silicon nanopillars

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ABSTRACT

An original process to grow cm-squared stress-free 3C-SiC layer is described here. Based on the carburization of silicon nanopillars at relatively low temperature (1150 °C) with methane, the process uses the outdiffusion mechanism of silicon atoms through silicon carbide. After the growth at high pressure of a very thin silicon carbide layer (3 nm), the pressure is decreased to enhance the outdiffusion of silicon through the SiC layer, and thus grow a stress free, 450 nm-thick SiC layer on top of silicon nanopillars. The crystalline quality of the as-grown 3C-SiC layer is good (FWHM of 3C-SiC TO-mode = 10 cm^{-1}), despite the presence of stacking faults. This original process could be used to grow by epitaxy a free-standing 3C-SiC layer of high crystalline quality.

Among various semiconductor materials, cubic silicon carbide (3C-SiC) has shown significant promise for a wide range of applications in micro–nano-electronics [1–4], micro– nano-systems [5–8], and biotechnologies [9]. This interest is mainly due to its physical properties such as its biocompatibility, a high breakdown field (1.5×10^5 V cm^{-1}) and a high electronic mobility (1000 cm^2 V^{-1} s^{-1}), or a high chemical inertness and a high hardness [10]. Despite these very interesting properties, 3C-SiC substrates are still too expensive to see an emerging mature market. This is mainly due to the difficulties to grow 3C-SiC in bulk [11] or by epitaxy. The heteroepitaxy of 3C-SiC on silicon is particularly challenging because of the high lattice mismatch between 3C-SiC and Si (19.7%) and because of the difference between the coefficient of thermal expansion of silicon (2.6×10^{-6} K^{-1}) and SiC (2.77×10^{-6} K^{-1}). Thus, the direct epitaxy of SiC on Si leads to very poor crystalline quality of SiC. A lot of studies have already been published in this subject, and a key-solution have been given by Nishino et al. in the 80s [12]. This consists in adding a carburization step of the Si substrate before the heteroepitaxy of SiC. As main crystalline defects in epi-SiC nucleates at the interface Si/SiC, the carburization crucial step has been widely studied these past years [13,14]. In parallel, the preparation of silicon substrate before the carburization step has also been explored. Besides *in-situ* H_2-based cleaning process, or off-axis growth [15–18], patterned Si-substrates have been studied [19–22] with interesting results.

In this context, this paper suggests an original way to grow directly a SiC layer on a patterned Si substrate only by carburization thanks to the control of total pressure during the process.

Firstly a Si(100) substrate is patterned on a 1 cm-squared zone with Si nanopillars (Si-NPs) thanks to a plasma etching process described elswhere [23]. Si-NPs have a diameter of 200 nm and a height of 1 μm, with a pitch of 200 nm, as it is shown in Fig. 1a. This substrate is then used as template to grow the SiC layer by a carburization process described as follows.

In the first step, the sample of Si nanopillars is heated up at a high pressure $P_1 = 4 \times 10^4$ Pa and carbon precursor is introduced in the furnace at 800 °C to grow a 3 nm-thick SiC layer surrounding the Si-NPs. The second step is a dwell at 1150 °C during 45 min when the total pressure ($P_2 = 3.5 \times 10^2$ Pa) is decreased in order to enhance the outdiffusion of Si atoms through SiC. Finally the system is cooled-down naturally at a higher pressure ($P_3 = 4 \times 10^4$ Pa) to prevent any deterioration of the SiC layer. This experimental process used to grow a 3C-SiC layer is presented in Fig. 1b.

Raman spectroscopy (Horiba/Jobin-Yvon LabRam spectrometer, $\lambda_0 = 514.5$ nm, laser power = 0.1 mW on sample), scanning electron microscopy (SEM, Zeiss Ultra plus) and transmission electron microscopy (TEM, FEI Tecnaï, 200 keV) have been used to characterize morphologically and structurally the as-grown SiC layer.

SEM observation of the Si substrate after the carburization process confirms that a layer has been grown on the whole 1 cm-squared patterned surface. This layer is rough, crystalline, and seals entirely the surface (cf. Fig. 2a). Using a dual FIB/SEM microscope equipped with a STEM detector, it has been possible to mill a transversal cross-section of the layer. Fig. 2b shows a STEM image of the as-grown layer on top of the NPs network: the thin film has a thickness of ≈450 nm and large voids can be observed under the surface.

The growth of 3C-SiC has been demonstrated using Raman spectroscopy (cf. Fig. 3). To understand this spectrum, it is important to notice that all the Si substrate does not react with

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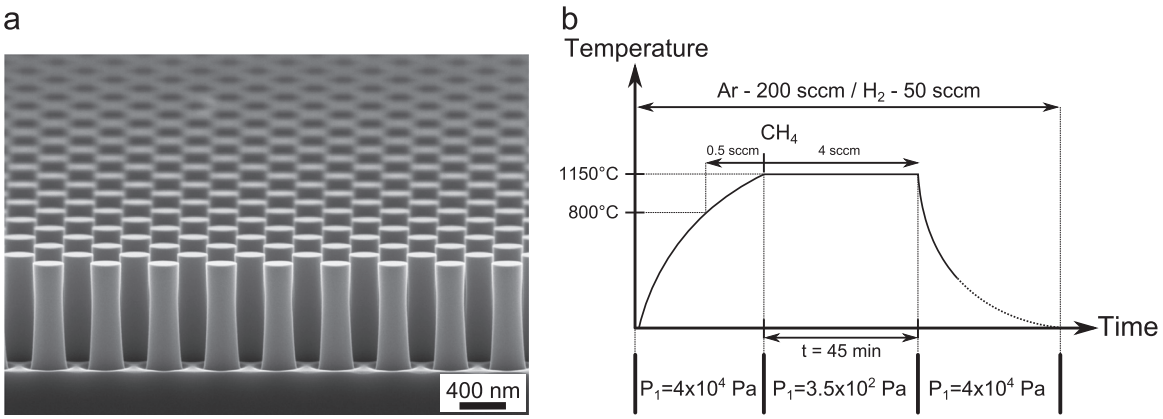

Fig. 1. (a) SEM image of Si-NPs obtained with a SF_6/O_2 plasma etching on Si(100). The diameter of Si-NPs is 200 nm and their height is 1 μm. (b) Schematic showing the three-step processing schedule.

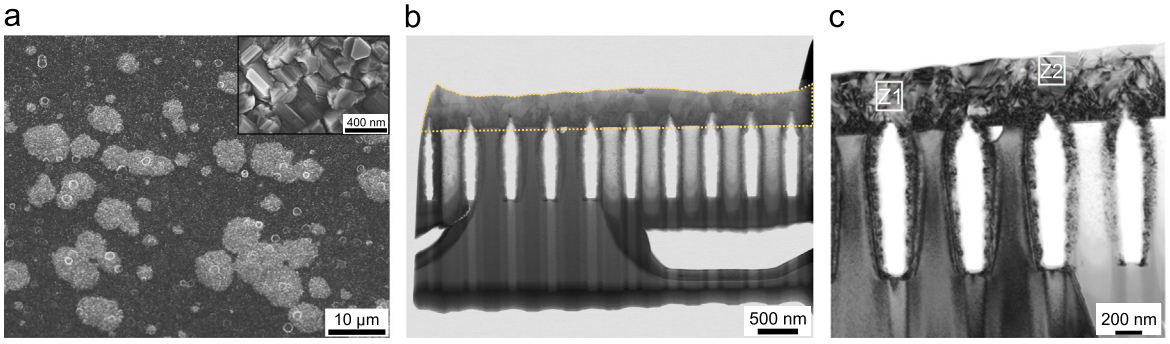

Fig. 2. Images of the SiC layer. (a) SEM image in top view of the surface showing the important roughness. Higher magnification in inset. (b) STEM image after FIB milling showing the SiC layer on top of NPs (broken lines). The SiC layer is 450 nm thick. (c) TEM image in bright field at 200 keV of the thin lamella, showing two zones Z1 and Z2, observed at high resolution in Fig. 5.

the carbonaceous species, thus the band at 940–990 cm^{-1} is attributed to the second order of the Si TO-mode related to the Si substrate. This band partially hides the 3C-SiC LO-mode at 972 cm^{-1} and it is rather difficult to deconvolve these two signals. Moreover the TO-mode of 3C-SiC is revealed at 796 cm^{-1}, and C-band and G-band of carbon can also be assigned, respectively at 1350 cm^{-1} and 1600 cm^{-1}. Finally, the shoulder at 1600 cm^{-1} is related to the second order of the 3C-SiC TO-mode.

With a FWHM of 10 cm^{-1}, the TO-mode of 3C-SiC has to be highlighted. This value is close to best results found in the literature, both for 3C-SiC heteroepitaxially grown on Si [24–26] (≈ 7 cm^{-1}), and bulk-grown 3C-SiC [27] (≈ 4 cm^{-1}). The 3C-SiC layer obtained here is however grown at – relatively – low temperature, and only by carburization. As the Raman peak position is very sensitive to the residual strain, it is also possible to evaluate the residual stress in the 3C-SiC layer, taking into consideration the lattice mismatch $\Delta a/a$ [28]:

$$\omega_{TO} = 796.5 - (3734 \pm 30) \times \Delta a/a \quad (1)$$

Considering the TO-mode peak position at 792.9 cm^{-1} we can estimate a tensile lattice strain $\Delta a/a$ in the buffer of about 0.1%, estimation in accordance with the work of Bosi et al. [25].

The interface Si/SiC as well as the 3C-SiC layer have been characterized thanks to TEM observations (see Figs. 4 and 5). Stacking faults (SF), the most common defects in SiC have been identified, but no inversion domains have been observed. The density of defects is very high from the Si/SiC interface, on the first 100 nm, then the SF density is lower (but variable). Indeed it is well known that the quality of the 3C-SiC layer grown on Si substrate is increasing while the thickness of the film is increasing by annihilation of structural defects [29,30]. However the SF density – which

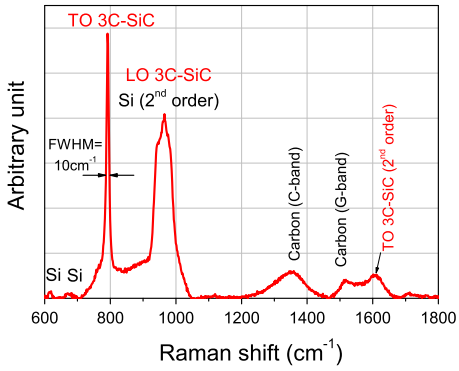

Fig. 3. Raman spectra of SiC layer on top of Si-NPs. Excitation wavelength: 514.5 nm, laser power on the sample: 0.1 mW. The peak at 796 cm^{-1} is assigned to the 3C-SiC TO-mode. The band at 940–990 cm^{-1} is attributed to the superposition of the second order of the Si TO-mode related to the Si substrate and the 3C-SiC LO-mode at 972 cm^{-1}. G-band and C-band of carbon are also easily assigned. The last peak at 1600 cm^{-1} is attributed to the second order of the 3C-SiC TO-mode.

are oriented along {111} planes – depends on the individual 3C-SiC grain. Moreover grains coming from different Si-NPs met during the 3C-SiC growth, leading to new grain boundaries as shown in Fig. 4d.

With high resolution TEM images, the 3C-SiC layer reveals a good crystalline quality (see Fig. 5a) despite the presence of SF. The density of these latter can be either high (see Fig. 5c) or very low (see Fig 5a), depending on the grain observed. For example, the difference between two grains is shown in Fig. 5b: the left side grain is highly faulted while the right one has a low density of SF. The growth direction of 3C-SiC grains has been identified as ⟨200⟩