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Study of the Nucleation of p-doped SiC in Selective Epitaxial Growth using VLS Transport

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Abstract

This work deals with the study of the Selective Epitaxial Growth (SEG) of SiC using the Vapour-Liquid-Solid (VLS) transport at temperature $\leq 1100^\circ\text{C}$. Focus was made on the nucleation step by observing the evolution of the growth mainly as a function of time and Si content of the Al-Si liquid phase. It appeared that addition of propane during the initial heating ramp up not only avoids liquid dewetting but also allows good starting of the epitaxial growth. Also, it was observed that the higher the silicon content, the better the SiC morphology, without aluminum carbide inclusions. Limiting the growth rate is found to be essential for better control of the growth processes.

Introduction

Most of the semiconductor devices require localized doping in order to realize junctions or functional layers. But for SiC, the standard solution for p-type doping, which is Al ion implantation, is obviously still an issue. An alternative and promising solution is the selective epitaxial growth (SEG) of p-doped 4H-SiC by Vapour-Liquid-Solid (VLS) transport. This technique has been demonstrated by some of the present authors since several years using an Al-Si liquid phase [1-2] and electrical results are promising for fabricating high quality p-n junctions [3]. In this approach, a stacking of silicon and aluminum layers is deposited on the substrate and patterns are created by photolithography. Upon melting, the Al-Si liquid droplets are fed by propane to obtain the SEG of p-doped SiC (see figure 1). Previous work showed that the introduction of propane during the heating ramp is crucial to avoid liquid dewetting [2]. However, the exact effect of the early propane introduction on liquid wetting, SiC nucleation and more generally on the whole growth process, is not well understood. That is why, in this work, the focus is made on the early stage of growth.

Experimental Details

SEG by VLS transport was performed on commercial 4H-SiC(0001), 8° off substrate. The Si+Al stacking (total thickness $< 3 \mu\text{m}$) was chosen so that to target a Si content in the melt of 15, 30 and 40 at%. Patterns of various lateral sizes (from 10 to 800 μm) and shapes were prepared. VLS growth was performed in a vertical cold wall reactor working at atmospheric pressure. The samples were heated under Ar (10 slm) + propane (1 sccm) from room temperature up to 1100°C , then the plateau at this temperature was maintained for 5 min. The initial heating ramp rate was $\sim 5^\circ\text{C/s}$. To study the first steps of the growth, some experiments were stopped just after reaching the desired temperature (without plateau). After

the growth the samples were wet etched to remove the remaining alloy using HCl+HNO₃+HF followed by hot NaOH. Measurement of the deposit thickness was performed using mechanical profilometer. Information of deposit polytype was obtained from μ -Raman spectroscopy which also gives information on the doping level. These latter characterizations were done using a HeNe laser beam ($\lambda=633\text{nm}$) focused down to a spot of a few μm^2 in the co-focal mode configuration. SEM images were done on a FEI Quanta 250 FEG microscope.

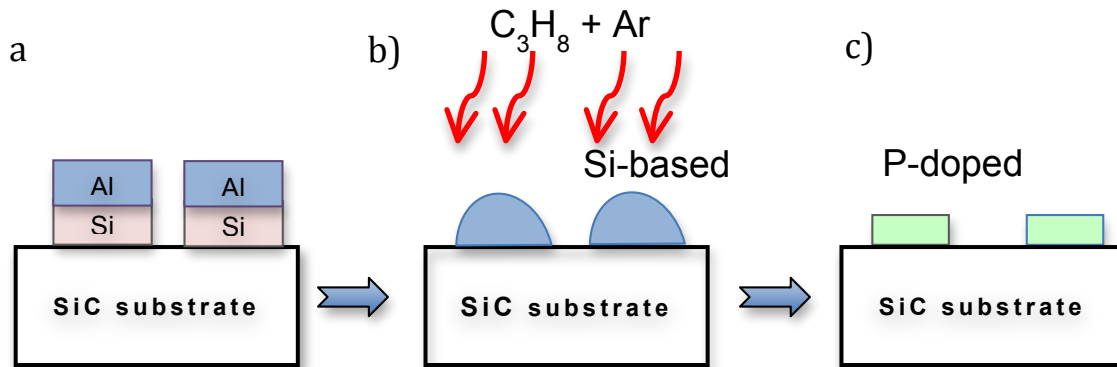


Figure 1 - Schematic description of the SEG-VLS process investigated in this work: a) deposition of Al-Si stack, b) addition of propane and melting of Al-Si to start the VLS growth, c) formation of SEG of p⁺ doped SiC. Since only the carbon source is supplied by the gas phase, SiC deposition only occurs by VLS mechanism at the places where the liquid is present.

Results and discussion

The first steps of the growth were studied with the Si content of the liquid set to 30 at%. For the two first samples, experiments were stopped during the initial ramp up when reaching 900°C (figure 2a) and 1100°C (figure 2b). The third sample corresponds to a standard SEG-VLS growth with 5 min plateau at 1100°C (figure 2c). One can see that all these samples present a SiC layer but with different morphologies. After stopping at 900°C, one can see a beginning of step bunching with rather regular and small terraces, the thickness is 60 nm. Upon increasing the temperature to 1100°C, the thickness increases to 100 nm and the step bunching gets more pronounced with less regular steps. Finally after 5 min plateau at 1100°C, the surface is very rough with the formation of a $\sim 650 \pm 50$ nm thick porous layer.

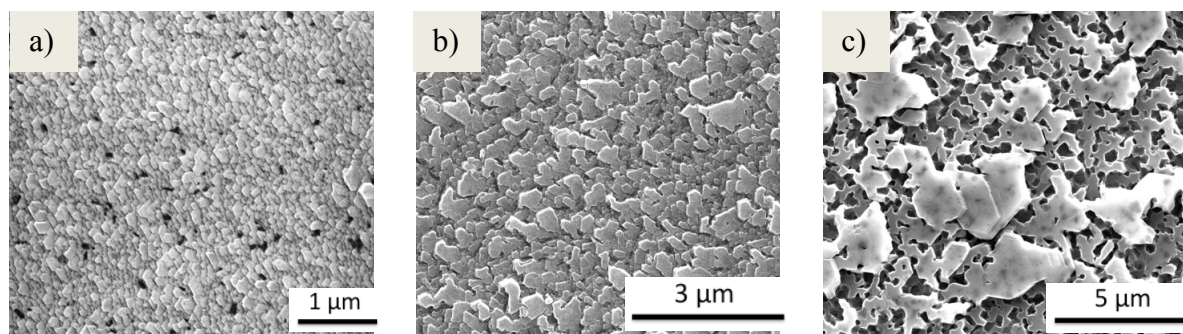


Figure 2: SEM observation of samples surface after stopping the SEG-VLS experiments a) at 900°C during the ramp up, b) at 1100°C without plateau and c) after 5 min plateau at 1100°C.

The most interesting point is that a complete SiC layer is already formed during the temperature ramp at a temperature as low as 900°C, without the formation of islands. It means

that the addition of propane during the heating ramp not only avoids dewetting of the droplets but also begins the VLS growth in rather good conditions. Probably, these two results are linked if one considers that starting the growth roughens the solid-liquid interface and thus limits liquid movement at the triple point. One cannot exclude also some surface-active effect of propane on Al-Si liquid.

Understanding the reason of the morphology roughening during growth is more difficult. Let us first consider the growth rate. Though it is difficult to calculate any values for experiments stopped during the ramp up, the one extrapolated for the 5 min plateau is $6.6 \mu\text{m/h}$ which is very high. When comparing to our previous results of VLS growth in standard (non-SEG) configuration and with identical propane partial pressure, the growth rate obtained in SEG-VLS is one order of magnitude higher (figure 3). This is most probably due to the difference of liquid height which is only of few μm in the present work while of few mm in ref.[1]. Reduction of the growth rate should be an essential parameter to improve the surface morphology of the SiC layer. It could be obtained via the reduction of growth temperature or C_3H_8 partial pressure, or via the increase of the liquid height (thickness to the initial Al-Si stack). However, one has also to consider that the Si content of the liquid (and thus the liquid height) is constantly diminishing during SiC growth so that the growth parameters are not constant during SEG-VLS growth. For instance, after 5 min plateau at 1100°C , the liquid should roughly contain only 15 at% Si. This could lead to an uncontrolled acceleration of the growth after a while. Also, if the Si content becomes too low, SiC growth can be in competition with Al_4C_3 , according to figure 4. This can also affect the growth mode of the layer.

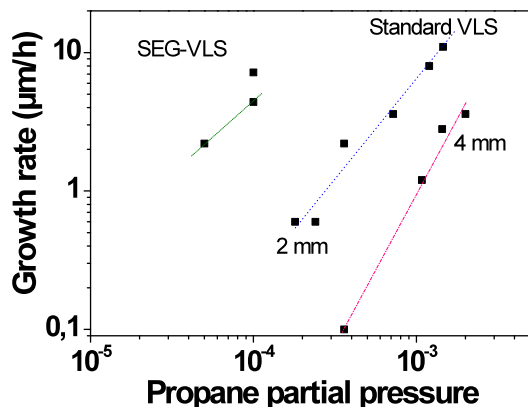


Figure 3: Comparison of growth rates obtained in the present work (SEG-VLS) and in a previous work (standard VLS) where two liquid heights (2 and 4 mm) were studied [1]

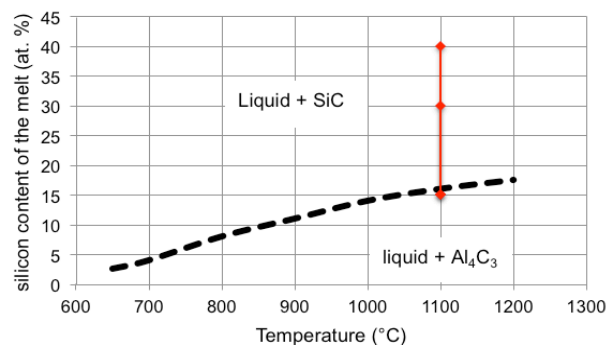


Figure 4: Equilibrium conditions for SiC or Al_4C_3 formation in the Al-Si-C ternary system. The three different liquid compositions studied here are marked by diamond-shaped patterns.

In order to check if SiC growth could be in competition with Al_4C_3 formation, we prepared a set of samples with different Si content of the liquid from 40 down to 15 at%. After 5 min of VLS experiments at 1100°C , all liquid compositions led to SiC growth (as seen from μ -Raman analyses), even for 15 at% Si (figure 5). However, on this particular sample, some additional peaks attributed to Al_4C_3 were sometimes seen in the Raman spectra before wet etching. After wet etching, which is supposed to remove also Al_4C_3 compound, one can observe large (several μm) and faceted holes in the SiC layer (figure 5a), the facets being parallel from one hole to another. These holes are attributed to this unwanted carbide which seems to appear already from the nucleation and to grow epitaxially with the substrate. For 30 at% Si, rare and less faceted micrometric holes were observed and the SiC deposit display

irregular step front (figure 5b). Finally, for 40 at% Si, no micrometric holes can be seen and the SiC layer exhibits a regular step bunching morphology, though with some nanometric disturbances of the step front (figure 5c). Obviously, Al_4C_3 seems to nucleate and form even for 30 at% Si but it disappears at 40 at% Si. This trend follows well the one of figure 4 but with some shift toward higher Si content.

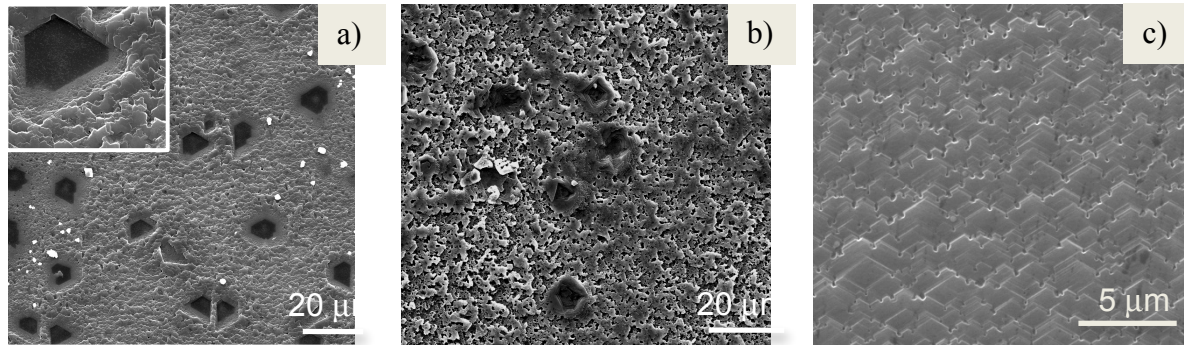


Figure 5: SEM images taken after wet etching of layers grown with initial liquid Si content of a) 15 at% (170 nm thick), b) 30 at% (700 nm thick) and c) 40 at% (300 nm thick). Inset in a) shows a close-up on a faceted hole.

Evolution of the deposit thickness as a function of Si content of the liquid does not follow an obvious trend but one needs to consider also the fact the initial Al-Si stack was not constant in thickness for this set of samples. Indeed, the Si content of the liquid was changed by only changing the Si layer thickness deposit. Further study is thus required with identical initial liquid height in order to comment this point.

Conclusion

The study of the initial step of SiC growth during SEG-VLS epitaxy shows that the introduction of propane during the heating ramp is not detrimental to the nucleation. However, one needs to start with a rather high Si content of the liquid in order to avoid Al_4C_3 nucleation and to obtain a more regular growth front. Reduction of the growth rate is also one essential parameter to better control the layer quality.

Acknowledgments

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