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Abstract

Vapour phase processes for the growth of both SiC ingots and epilayers have now reached the industrial point and are facing the related problems. Reducing the production costs, for example by increasing wafer size and the process yields, is an important issue for large scale development. Emerging and alternative epitaxial approaches may help either to decrease these costs or further improve the material quality. In this chapter, potentialities of the Vapour-Liquid-Solid mechanism for SiC epitaxial growth are reviewed with the aim of avoiding or solving some problems encountered in CVD growth. For instance, issues like increasing the growth rate, decreasing the temperature, reaching high p type doping ar demonstrating selective epitaxial growth are discussed from the VLS viewpoint and compared to results obtained with the CVD technique.

I. INTRODUCTION

In recent years, strong improvements have been achieved in the growth of Silicon Carbide from the vapour phase. Seeded sublimation and Chemical Vapour Deposition (CVD) processes are now commonly used for bulk crystal and epitaxial layer growth respectively. Apart from those well-established industrial processes, recently reported emerging bulk growth processes should be considered in the future to pave the way of several materials issues. Among them are the Halide-Chemical Vapour Deposition (HCVD)[1], the Modified-Physical Vapour Transport (M-PVT)[2] for the doping control during the growth and the Continuous Feed-Physical Vapour Transport (CF-PVT)[3] which enable bulk growth of the 3C-SiC polytype. Concerning the epitaxial layer growth, the successive demonstration of the "step-controlled epitaxy"[4] and the site competition epitaxy"[5] in the CVD process has driven a lot of research on the vapour phase techniques. This popular method using a mixture of H_2-SiH_4-C_3H_8 has demonstrated impressive results, such as high growth rate (up to 60 µm/h), impurity level below 10^{14} at/cm^3 or the possibility of doping during growth for a wide range of concentration levels[6,7], with nitrogen for n type and aluminium or boron for p type material. Due to these performances, alternative epitaxial growth processes have always retained less attention even if some highly interesting results have been reported, mainly by Liquid Phase Epitaxy (LPE). First, filamentary voids such as macrodefects or micropipes were observed to decompose into groups of dislocations with a

smaller Burgers vector in the course of LPE processing[8,9]. Second, the epilayers have been reported to be of higher quality than the seed[10]. Moreover, the highest structural quality ever reported so far for a 3C-SiC heteroepitaxially grown on a 6H-SiC layer has been obtained by LPE in a crucible free method[11].

As a rule, growth from the liquid phase and in particular from solutions, usually leads to lower dislocation density than with other methods[12]. In the case of SiC, growth of small crystals or epitaxial layers from the liquid phase has been achieved since a long time. Researchers were confronted with serious difficulties so that too few studies have been carried out to get convincing results. The two main problems for this liquid phase approach are first to implement the liquid at high temperature and second to control the growth front. These two key points are directly related to the very low carbon solubility in liquid silicon below 1800°C. Using a Si-Metal growth flux is a good way to increase the carbon solubility[10] but it has not proven to stabilize the growth front in a simple way.

In parallel to the research on SiC epitaxial growth, techniques for fabrication of SiC whiskers (small filamentary single crystals) have also retained much attention[13]. One of the most common techniques to grow these whiskers is the vapour–liquid–solid (VLS) mechanism. It has been widely studied for the growth of whiskers or nano-fibers of various materials, mainly binary compounds such as SiC[14,15] or AlN[16] but also multi-elemental compounds such as BiSrCaCuO[17]. The transposition of the VLS mechanism from the growth of SiC whiskers to the growth of large dimensions epilayers is difficult as additional problems occur with respect to the classical CVD method. Those technical problems which are related with the presence of a liquid interphase between the vapour and solid phases will be presented and routes to solve them will be discussed. Despite such difficulties, the VLS approach has been successfully applied to the growth of SiC epilayers. Moreover, the new possibilities offered by this technique could help solving some growth issues which could not be addressed satisfactorily by CVD. This is the case for increasing the growth rate and/or decreasing the temperature, for reaching high p type doping and for the selective epitaxial growth. In the present chapter, all these topics are reviewed and discussed with respect to CVD.

II. WHAT IS THE VLS MECHANISM

The VLS mechanism has been first proposed by Wagner and Ellis[18] to explain the appearance of SiC whiskers at certain conditions. It involves the formation of a liquid droplet on top of the crystal, which acts as a ''catalyst'' by cracking the gaseous reactants, leading to the dissolution of the carbon and silicon atoms. The growth of SiC by the VLS mechanism can be divided in four elementary steps (see Figure 1a):

1) Transport of carbon precursor to the surface of the liquid;
2) Cracking of the precursor and dissolution of carbon in the liquid at the vapour-liquid (VL) interface;
3) Transport of carbon from the VL interface to the liquid-solid (LS) interface;
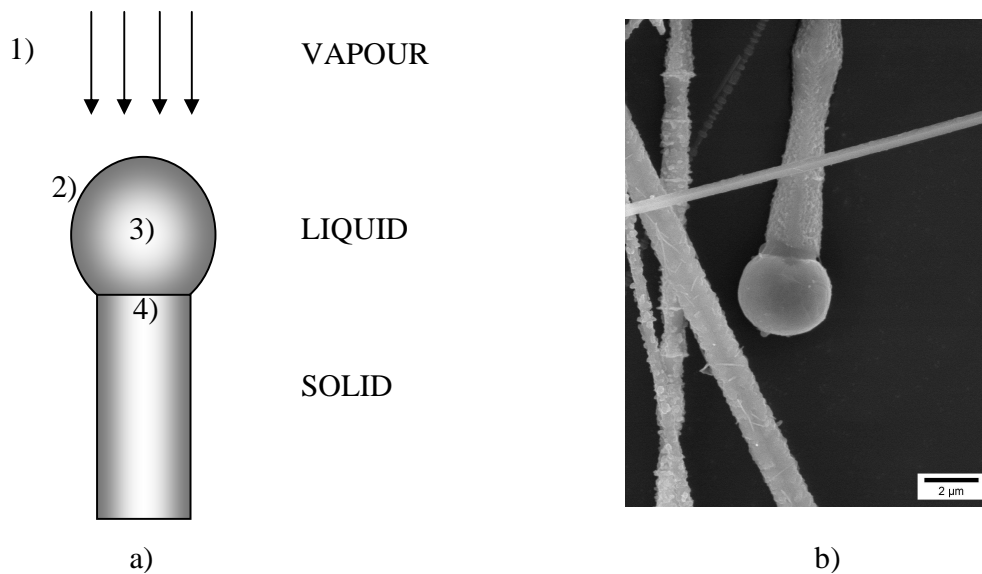4) Crystallisation of SiC at the LS interface.

Figure 1*: a) schematic representation of the Vapour-Liquid-Solid mechanism principle in the case of whiskers growth. b) SEM picture of a whisker with a solidified droplet at the end.*

Obviously, the slower step should govern the kinetics of the overall process. Such mechanism is easy to identify as a solidified droplet ends the whiskers (see Figure 1b). The droplet is usually formed by the addition of impurities, mostly transition metals, able to dissolve both silicon and carbon[19]. Several authors have demonstrated that the dissolved species are transported from the VL interface to the LS interface. The diffusion regime is provoked by an activity gradient of C and/or Si species between the two interfaces. According to its small size, the droplet is assumed to be isothermal. The necessary condition for the VLS mechanism to take place is thus to apply a carbon activity at the VL interface higher than the equilibrium carbon activity at the LS interface.

Such gradient governed mechanism also takes place in vapour phase processes like CVD. However, in VLS the conditions which govern the crystallisation are those of the liquid phase. The SiC growth is thus carried out under lower supersaturation, i.e. much closer to the equilibrium. As a consequence, the growth rate occurring at the LS interface is very high, up to 1-2 mm/h in Fe–Si liquid droplets at a temperature as low as 1500°C[19,20]. A fine control of the supersaturation degree can be achieved at the LS interface by simply tuning the gas phase composition. To summarize, the VLS mechanism combines the advantages of the CVD technique (growth control) with that of the LPE technique (low supersaturation, fast growth rate and high quality).

III. TECHNICAL ASPECTS OF VLS

Two difficulties arise when using a liquid interphase between a gas and a solid on a larger scale than for whiskers:
- Problem of wetting.

-   Problem of thermal gradient between the VL and LS interfaces.

These two problems are linked since the wetting properties of a liquid on a solid affect the droplet vertical dimension and thus the thermal gradient. Furthermore, the wetting angle usually evolves with time to reach its equilibrium value[21] so that the growth conditions may not be constant.

A. Wetting

In the case of whiskers growth, the size, shape and diameter of the whiskers are mainly related to physical parameters of the VS and LS interfaces. The whiskers diameter directly depends on the wetting angle of SiC by the liquid and the diameter of the droplet, i.e the volume of the droplet[22]. This volume is mainly dependant on the way the "solvent" is implemented before melting[15]. One of the main difficulties to transpose the VLS mechanism from the growth of whiskers (several µm to hundreds of µm) to the growth of epilayers comes from the difference of substrate size. This process would become attractive for the growth of epilayers if the diameter of the drop could reach several centimetres, i.e., the diameter of a SiC substrate. Ideally, the liquid must form a thin layer between the vapour phase and the growing crystal, that is to say the wetting angle of the liquid on SiC must be as small as possible and close to zero if possible. In practice, a droplet has always a spherical shape with a higher liquid height in the centre so that the growth conditions are different from the centre to the edges.

This phenomenon should be more pronounced when the diameter of the droplet increases. Indeed, as the wetting angle of Si on SiC can be considered as constant and equal to ~40° [23, 24], an increase of several orders of magnitude of the droplet diameter will automatically induce the same increase of the droplet height. In the case of whiskers, the lateral variation of liquid height does not affect the lateral homogeneity of the deposit since the diffusion length of the dissolved species should be much higher than the droplet dimension. But when it comes to the centimetric scale, the liquid height effect becomes visible. Fortunately, the use of several advanced implementations may help getting round Nature's laws:
    - A well chosen metal additive with lower wetting angle
    - Tensio-active elements (in the gas phase or inside the liquid)
    - Specific geometrical configurations

These points will be addressed later in this chapter.

B. Thermal gradient between VL and LS interfaces

Actually, when one wants to transpose the method from the growth of whiskers to the epitaxial growth on a substrate with larger diameter (several centimetres), the liquid should not any longer be considered as isothermal. Figure 2 presents a schematic description of the "VLS process" compared to the "LPE process" in term of growth conditions, i.e. thermal gradient and carbon activity gradient. For LPE both thermal gradient and carbon activity gradient are in the same direction while these gradients are opposite in most cases of the VLS process.
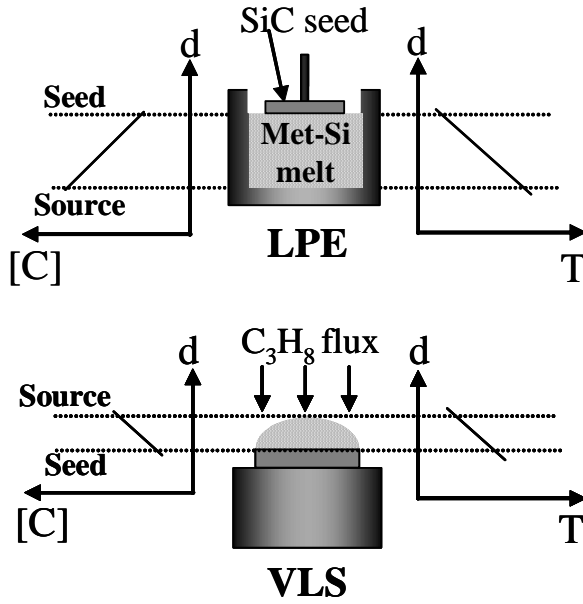
Figure 2: *Comparison between LPE (upper) and VLS configuration (lower) for SiC epitaxy. Left and right graphs represent respectively C activity gradient and temperature gradient along the vertical axis d.*

Some of our early works on this growth technique have pointed out the importance of the liquid height above the SiC seed which mainly affects the growth rate but also the morphology or even the layer crystalline quality[25]. With fixed wetting properties, i.e. in the case of pure silicon as liquid phase, evidences of the droplet size effect are given in figure 3. For the sample shown in Figure 3a), a piece of a Si wafer was placed as Si source on top of the SiC seed to form a unique and large Si droplet, and the only gaseous reactant was propane. For the sample shown in Figure 3b), CVD like conditions were used, i.e. the Si liquid phase, composed of a set of small (<200 µm) droplets, was created in situ by adding excess silane in the gas phase (Si/C ratio >>1). In our experimental conditions, the vapour phase close to the susceptor is silicon supersaturated resulting in the formation of a thin white veil floating few millimetres above the susceptor. This phenomenon has already been reported by other authors[26] and is explained by the gas phase nucleation of Si droplets or particles when Si-rich conditions are used.
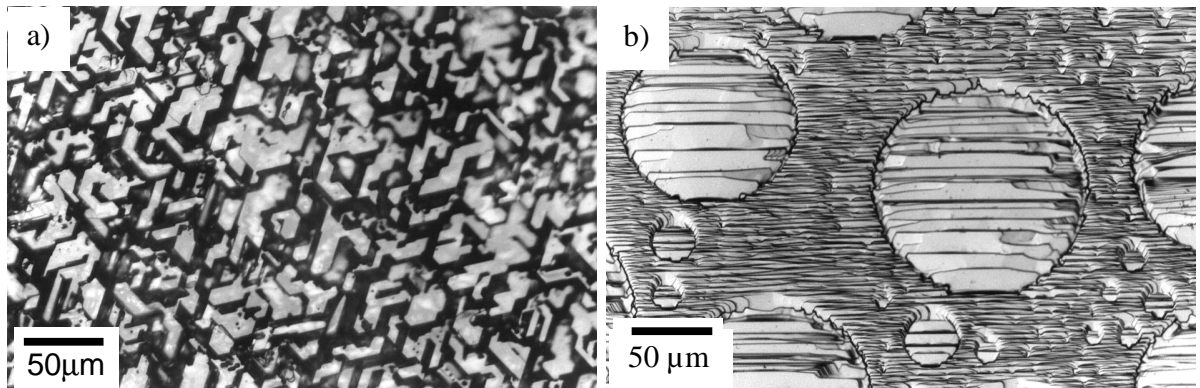

Figure 3 : morphologies of as grown 4H-SiC surfaces by a VLS mechanism a) with only one large silicon droplet (several mm) and b) with a set of small droplets (~100 µm) as "catalyst".

In the first case, white and light grey areas, for which the outlines are well-faceted, are at a higher altitude than the black areas. Thus, the growth proceeds normal to the surface and can be assumed as columnar-like. In this case of a unique large droplet, the VL and LS interfaces are separated by enough liquid so that we can consider that they are at different temperatures: cooler at the VL interface and hotter at the LS interface. Thus, the liquid can dissolve less carbon at its free surface than at the LS interface and dissolution of the seed should be favoured if no propane is injected in the gas phase. In other words, the thermal gradient inside the droplet is opposed to the natural carbon activity gradient required for crystal growth at the SiC surface. As SiC growth on the seed has been observed in this configuration, it means that the amount of carbon dissolved from the gas phase is enough to create an inverted forced regime from the VL to the LS interface. A second negative effect of having a large droplet is that the distance between the VS interface and the LS interface is important resulting in the increase of the carbon diffusion length before nucleation on the seed occurs. The combination of these two features should lead to the development of a vertical preferred growth.

To solve the problem of the thermal gradient, one can use similar approach as the one presented by A. Leycuras[27]. Indeed, the special reactor configuration used allows changing the thermal gradient between the two interfaces from positive to negative by simply adjusting two independent heating zones in the furnace. The possibility to use hot wall reactor has also been reported to avoid the problem of the thermal gradient[28]. However, those possibilities have not been further investigated.

On the other hand, it is also possible to have 2D growth even in a standard cold wall reactor if care is taken to reduce the thermal gradient inside the droplet. Firstly, Ar should be more suited as carrier gas since it is known to have a lower cooling efficiency than H_2. Secondly, it is obvious that the lower the growth temperature is, the lower the thermal gradient inside the droplet. In order to reduce significantly the growth temperature, one has to choose a metal-Si melt with low melting point. Using Al-Si melt at 1100°C under Ar gas, the growth mode of SiC by VLS was not anymore found to be columnar but 2D (see § III.C and IV.B for more details).

C. Choice of a good configuration

When the simplest VLS configuration is used with Al-Si melt, that is to say with the droplet simply put on top of the SiC seed, some problems are encountered such as the non wetting of the square edges of the substrate resulting in no growth in these areas (Figure 4). Furthermore, a thick deposition with high step bunching is often obtained at the internal periphery of the droplet due to lower liquid height. Finally, the surface is frequently covered with black SiC particles. These SiC whiskers are formed upon cooling due to the carbon supersaturation within the liquid in contact with the seed.

These problems demonstrate the need of improving the configuration used for growth by VLS. Firstly, the liquid should cover uniformly the seed surface with ideally the same liquid height everywhere. Secondly, the liquid should be removed before cooling in order to avoid SiC whiskers formation at the surface or even breaking of the seed which sometimes happens at the liquid solidification. This latter point can be solved by taking advantage of the fact that the
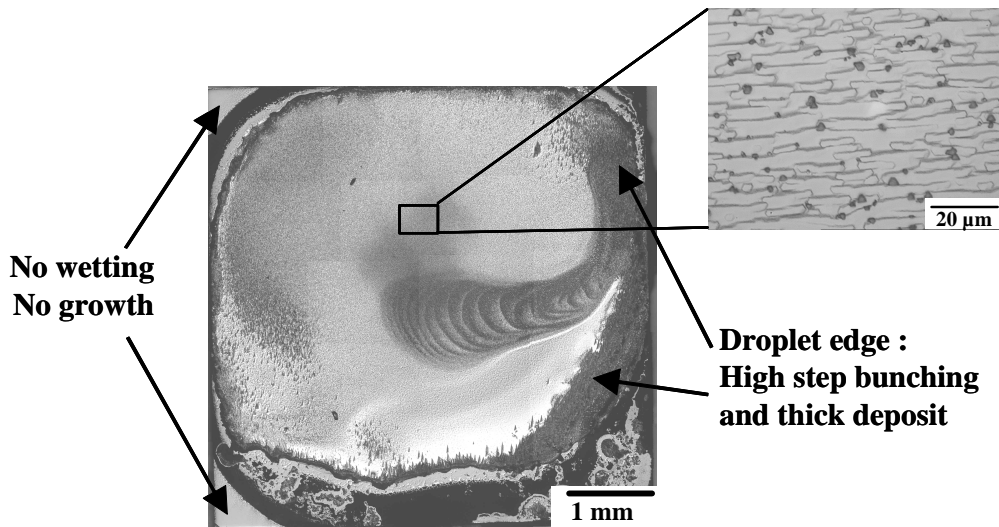
Figure 4 : *Illustration of the problems encountered using the simplest VLS configuration (drop on top af the seed) with Al$_{70}$Si$_{30}$ melt at 1100°C.*

surface of the liquid is free. It can thus be removed before cooling by approaching a steel tube equipped with a graphite tube at its bottom and a pumping system at its top (see Figure 5). The liquid can be sucked up in this way, with only small amount of alloy remaining on the surface and which does not generate any SiC whisker upon cooling. This sucking step requires gluing the seed on the susceptor (or crucible) with graphite glue in order not to suck up the whole sample.
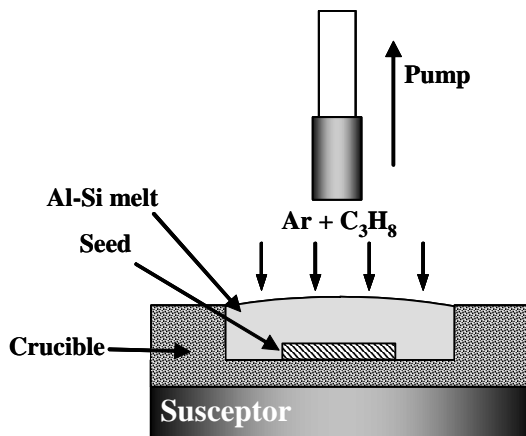

Figure 5 : Optimized configuration for VLS growth, involving a pumping system for liquid removal and a crucible of controlled depth for fixing the liquid height.

A uniform liquid height was obtained by using a crucible with controlled depth. Upon alloy melting, the crucible internal wall confines the liquid and limits its loss by wetting and spreading. By careful adjustment of the initial quantity of alloy, a constant height of liquid and a nearly flat surface can be obtained. Another advantage of this crucible configuration is that the liquid is heated laterally so that the vertical thermal gradient, which should be low at such low temperature and under Ar atmosphere, is even more reduced and its effect may be neglected.

IV. ADVANTAGES OF THE VLS MECHANISM

The presence of a liquid at the interface where crystallisation occurs drastically changes thermodynamics and kinetics. One can thus observe strong influence on of both the growth morphology and the growth rate.

A. Increasing the growth rate

Evidences on the differences between the vapour-solid and the liquid-solid interfaces in the same growth run have been given by several authors. For example, under inappropriate conditions of 4H-SiC substrates etching with hydrogen at temperatures higher than 1400°C, Neyret[29] observed silicon droplets which formed on the surface. The subsequent vapour phase epitaxy under a silane, propane and hydrogen mixture leads to a flat surface without macrostep, whereas columnar defects appear at the place where the droplets formed after etching. Most interestingly, with the same conditions of vapour phase feeding, the SiC growth rate is higher when a liquid flux acts as a "catalyst" for the crystallisation. These trends has been reported by Tairov et al[30] in the early seventies. When Scandium was used as in situ dopant during sublimation growth, Si-Sc droplets formed on the growth surface and affected the growth front. Under these droplets, the growth rate was measured to be ten times higher than in the areas between the droplets. In the CVD process, impressive growth rates have been demonstrated in the case of whiskers growth, up to several mm/h at 1100°C with a Co-Si droplet[14]. Transposition to epitaxial growth in a CVD process has also proven an effective increase of the growth rate[29].

To illustrate these trends, consider Figure 6 which shows the dependance of the growth rate as a function of the propane flow rate for two different temperatures, 1500°C and 1600°C. First, the SiC growth rate increases but does not depend linearly on the propane flow rate. Second, the growth rate is always higher at 1600°C than at 1500°C for the same propane flow rate.
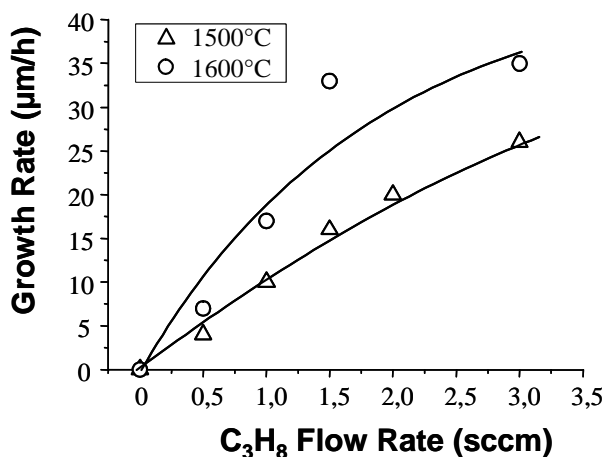

Figure 6: *Dependance of the growth rate as a function of the propane flow rate for two different temperatures, 1500°C and 1600°C.*

Figure 7 presents the dependence of the growth rate on the temperature for a propane flow rate fixed at 1.5 sccm. At low temperature, the growth rate increases with temperature, with an

assumed exponential dependence and reaching up to 35 µm/h. Slightly above 1600°C, the growth rate quickly falls to 12 µm/h at 1650°C and 9 µm/h at 1700°C. One can see that the growth rate doubles by simply increasing the temperature from 1500°C to 1600°C. It has been shown in standard CVD epitaxy that, in this temperature range, the growth rate is almost independent on the temperature[29,32]. It is clear evidence that the mechanism implied in these conditions is not a simple CVD mechanism via a VS interface. As far as a VLS mechanism is effectively achieved, it would be expected that the carbon solubility in liquid silicon plays an important role in the SiC growth rate. If we calculate this carbon solubility as a function of temperature from ref.[33], we can see that it triples from 1500°C to 1600°C (Table 1). This important increase in carbon solubility in the 1500-1600°C range is in the same order of magnitude as the increase in the growth rate measured on our samples for the same temperature range. *As a rule, as far as conditions belong to the VLS mechanism, the growth rate can be increased by increasing the temperature and/or the propane flow rate.*
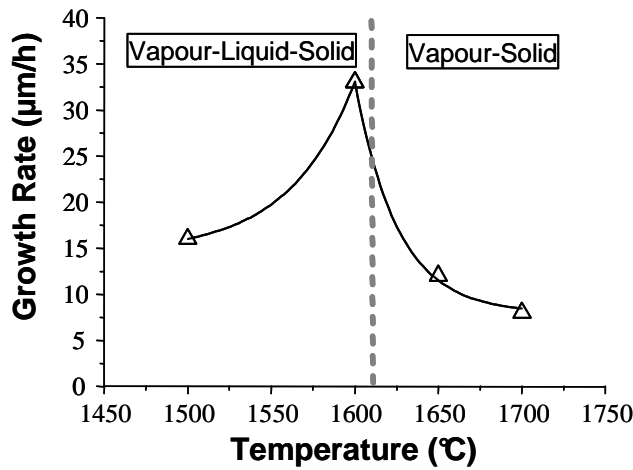

Figure 7: Influence of the temperature on the growth rate for a propane flow rate fixed at 1.5 sccm.

Table 1: Growth rates measured for two different temperatures with a 1.5 sccm propane flow rate. These values are compared to the solubility of carbon in liquid silicon at the same temperatures from the Oden and McCune formula [33].

Temperature (°C)	Growth rate (µm/h)	Carbon solubility (at%)
1500	15	$3.6.10^{-3}$
1600	35	$1.03.10^{-2}$

B. Decreasing the temperature

Growing good quality SiC epitaxial layers at lower temperature than 1400°C is a challenging problem which could help reducing the costs and increasing the safety of the process. In comparison to standard CVD, growth from solution is a more appropriated technique for decreasing the deposition temperature due to the lower supersaturation conditions. Towards this

goal, pure Si is not the best liquid phase since it requires similar temperatures (>1400°C) than in CVD. Metal-Si solutions are thus required, with low melting point, high carbon solubility and no other stable carbide phase than SiC in the metal-Si-C ternary system. In practice, there is no ideal metal candidate meeting all these requirements. The reports on SiC growth from the melt at low temperature deal mainly with Al or Ga additives for p-type layers, and Sn, Ge, Fe, Co and Ni additives for n-type[34-38]. Growth rates range from 0.1 to 6 µm/h at temperatures of 1100-1200°C. Since Al-based melts have given the best results in terms of layer quality and low temperature growth, we will focus on this element.

The Al-Si-C ternary system has been extensively studied for composite materials[33,39]. A liquid phase forms at 577 °C in the binary Al-Si system corresponding to the Al-Si eutectic transition at a composition of 12.2 at%Si[40]. Al can also dissolve a relatively high amount of carbon even at low temperature (for example, the C solubility in Al at 1100°C is equivalent to the one in Si at 1600°C). On the other hand, if inappropriate conditions are used, Al_4C_3 can form instead or together with SiC. Appearance of this aluminium carbide can be avoided by adjusting the Si content of the melt with temperature according to the graph in Figure 8. For instance, with 15 at%Si, SiC should be the only carbide forming up to 1100°C. Note that Al_4C_3 has been sometimes observed to form in out of equilibrium conditions [41]. Finally, ternary carbides such as Al_4SiC_4 or Al_8SiC_7 also exist but their formation are reported at temperatures >1400°C[39].
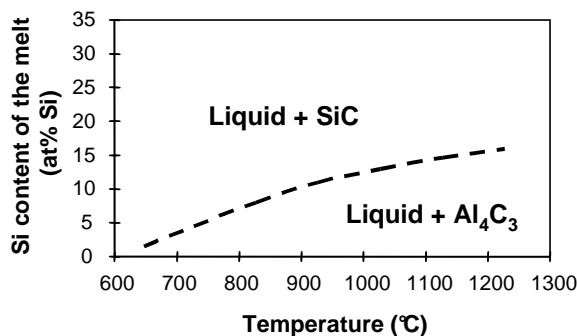

Figure 8 : Equilibrium conditions for SiC or Al_4C_3 formation in Al-Si-C ternary system.

When the simplest VLS configuration is used, that is to say with the droplet simply put on top of the SiC seed, homoepitaxial growth successfully occurs at temperatures as low as 1000°C, with better results obtained at 1100°C. The growth rate ranges within 0.5 to 10 µm/h depending on melt composition, propane flux and temperature. Examples of surface morphology obtained at 1000 and 1100°C with $Al_{70}Si_{30}$ melt are shown in Figure 9. The morphology is highly step bunched which is the sign of sufficient surface mobility of adatoms even at such low temperatures. The results shown below will always refer to a temperature of 1100°C and a melt composition of $Al_{70}Si_{30}$ except when specified.

In order to illustrate the effect of liquid height (H_L) on the growth rate, experiments have been performed with two different crucible depths. In Figure 10 the results are illsutrated as a function of propane partial pressure. Firstly, it is clear that the growth rate is linearly dependent on the propane partial pressure in the reactor for each value of H_L. *As a result, the growth rate can be simply regulated by a gas flow which gives much more flexibility and reliability than in other liquid phase techniques where one has to control both temperature and thermal gradient*.
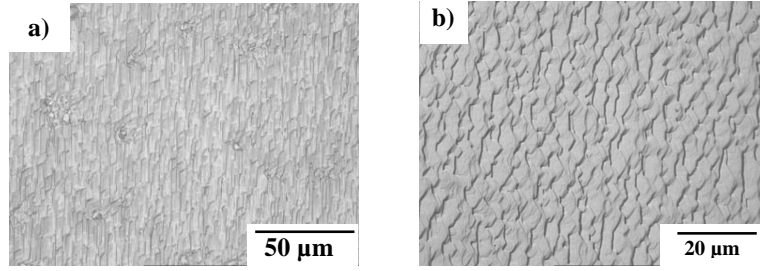
Figure 9 : *Surface morphology of 4H-SiC epitaxial layers grown in $Al_{70}Si_{30}$ melt and a liquid height of 2 mm at a) 1000°C and b) 1100°C.*
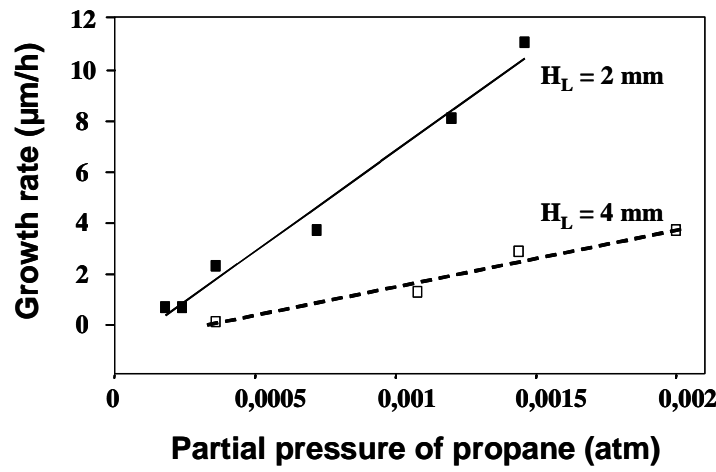

Figure 10: Dependance of growth rate as a function of propane partial pressure.

When H_L is increased from 2 to 4 mm, the growth rate decreases by a factor higher than 4. As a result, we have confirmed that with increasing liquid height, the growth rate in VLS mechanism decreases. Supposing that carbon transport is only due to diffusion through the liquid, Fick's law can be applied:

$$J_c = -D_c \frac{d\mu_c}{dx_c} \qquad \text{Eq.1}$$

where J_c the carbon flux inside the liquide, D_c the diffusion coefficient, dx_c the diffusion length of carbon and $d\mu_c$ the chemical potential gradient of carbon between the two interfaces vapour-liquid and liquid-solid. By considering the growth rate G_R as a flux of carbon impinging on the surface and the liquid height H_L as the diffusion length we can write the following equation:

$$G_R = -A.D_c \frac{d\mu_c}{H_L} \qquad \text{Eq.2}$$

where A is a conversion constant between J_c and G_R since all the impinging C atoms may not be incorporated in the SiC growing layer. From Eq.2, if diffusion is the main transport mechanism

for carbon the growth rate should be inversely proportional to the liquid height. Our results show that G_R is divided by more than 4 when H_L is only doubled. It means that a simple diffusion model cannot fit our experimental results probably because another mechanism, such as convection, slows down the process. Another evidence of this convection related slowdown effect was obtained when using 25 mm inner diameter crucible instead of 10 mm with identical H_L of 2 mm. It was found that the growth rate was 3 times smaller in the case of the larger crucible which confirms that the liquid height is not the only parameter governing the carbon transport. Note that in the case of a liquid height of 4 mm and very low partial pressure of propane, weak dissolution of the seed has been evidenced instead of growth. It was also observed that when growth occurs with H_L = 4 mm, the homogeneity of morphology is improved compared to 2 mm.

The linear dependence of growth rate with propane partial pressure gives two indications on the VLS mechanism:

1) the growth is in the carbon transport limited regime from the gas phase to the liquid surface since the more carbon is brought on the liquid, the higher the growth rate is;

2) the kinetics of propane cracking and C dissolution from the gas phase to the melt is not a limiting step of the process within the conditions studied here. If C dissolution was a limiting step, the growth rate would become independent on propane partial pressure. Furthermore, in this case one can observe formation of a SiC or graphite crust on top of the melt at high propane partial pressure. This was not the case in the discussion above. It means also that the upper limit of the growth rate, where C dissolution rate becomes smaller than the propane feeding rate, was not reached. As a result, growth rate higher than 10 µm/h can probably be reached.

The effect of melt composition was studied at 1100°C with H_L = 2 mm and propane partial pressure of $1.8.10^{-4}$ atm. As illustrated in Figure 11, the growth rate does not change significantly (~1 µm/h) for a melt composition between 25 and 40 at% Si. For 20 at% Si, a strong increase of the growth rate (up to 6.5 µm/h) is observed whereas it decreases down to nearly 2 µm/h when $Al_{85}Si_{15}$ melt is used.
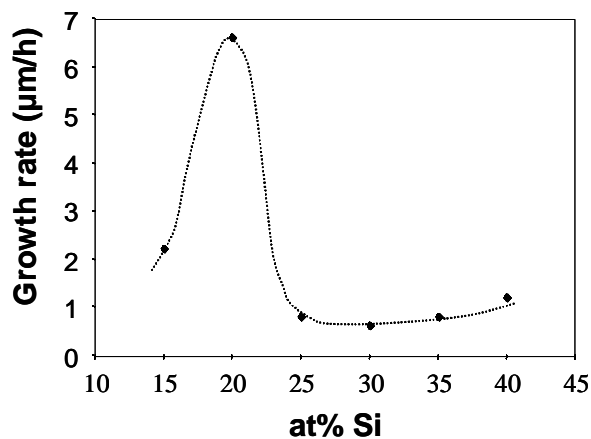

Figure 11 : Dependance of growth rate as a function of Si content in the melt for H_L = 2 mm

If we assume an increasing C solubility in the melt with decreasing Si content (hypothesis based on the higher C solubility in liquid Al than in liquid Si), we should observe an increase of

growth rate with decreasing Si content. This effect is not significant in the 25-40 at% Si region while it becomes predominant at 20 at%. However, the sharp decrease in growth rate observed at 15 at% Si does not seem to be solubility dependent. For a tentative explanation, let's consider Figure a where the conditions of SiC stability versus Al_4C_3 are shown. One can see that 1100°C and 15 at% Si is close to the limit between Al_4C_3 and SiC conditions of formation. So the abrupt decrease in growth rate at 15 at% may come from the instability of SiC in such Si poor melt. In other words, the deviation from the equilibrium is too low to ensure proper SiC growth. Note that no Al_4C_3 was detected on the seed for this low Si content.

C. Heavy p-type doping

The incorporation of high amounts of p-type doping species (in most cases Al) in a SiC matrix is difficult to achieve. Towards this goal, in situ doping during epitaxial growth has been studied either by CVD[42] or sublimation[43]. The experimental solubility limit of Al in SiC was then reported to be ~ $2x10^{20}$ at.cm^{-3} from CVD experiments at 1500°C and $7x10^{20}$ at.cm^{-3} from sublimation deposition performed at 2000°C. Altogether, these results suggest that the Al solubility limit increases with temperature. Investigation of LPE grown layers at temperature 1100-1300°C in an Al based melt gave also an Al incorporation in the range 1 to $7x10^{20}$ at.cm^{-3}, suggesting now that the solubility limit does not depend much on temperature[35,44]. Unfortunately, since the authors did not check for the possible formation of Al-based inclusions, it was not possible to conclude.

The 4H-SiC layers grown by VLS in Al-Si melt should also incorporate a high amount of Al. It was checked by means of Raman spectroscopy and secondary ion mass spectroscopy (SIMS). In Figure 12 are shown spectra collected at different depths in a typical SiC layer grown by VLS in Al-Si melt. At the surface, only the TO and TA peaks of 4H-SiC, respectively at 777 cm^{-1} and 196 & 204 cm^{-1}, are clearly visible. This result, together with the formation of steps on the surface show that epitaxial growth successfully occurred with reproduction of the substrate polytype and orientation. No evidence of any Al-based compound inclusion was found as all the peaks can be assigned to 4H-SiC material. The interesting point is the presence of Fano interference around the TO peak associated with an increase of the background intensity at low shift values. These are clear evidences of highly p-type doped SiC material[45-47]. This result means that Al from the melt is massively incorporated inside the SiC lattice. When Raman probing is focused inside the layer down to the substrate, these features gradually disappear and the LO peak at 964 cm^{-1} is then visible.

SIMS analyses were performed on such VLS grown layers. A summary of the resulting Al depth profiles is shown in Figure 13. Depending on the growth conditions, the Al concentration ranges from $5x10^{19}$ to $1x10^{21}$ at.cm^{-3}, which is by far the highest Al concentration ever reported for an as-grown, in situ doped, 4H-SiC layer. Unfortunately, while slightly different conditions (temperature, propane flux, time) were used, up to now it was not possible to isolate the growth parameter(s) which mainly determine the very high Al incorporation level in the SiC layers.
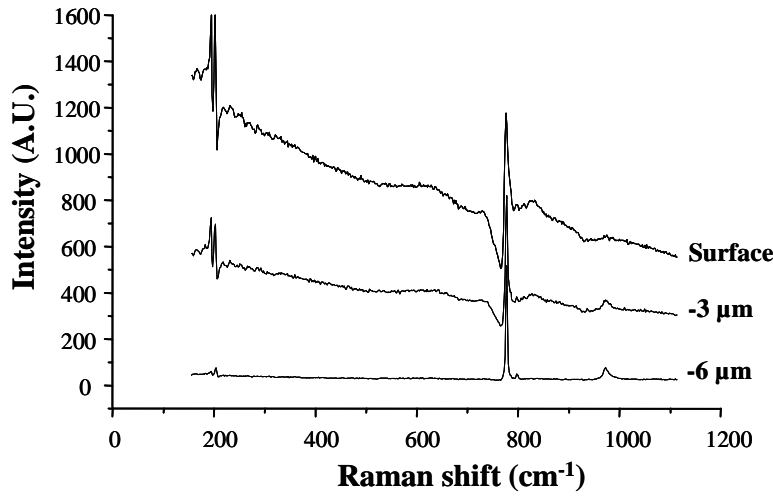
Figure 12 : *Micro-Raman spectra of a 5.5 μm thick 4H-SiC layer grown by VLS. Collection was performed at different focus depth inside the layer. [Al] = 2x10²⁰ at.cm⁻³ as measured by SIMS.*
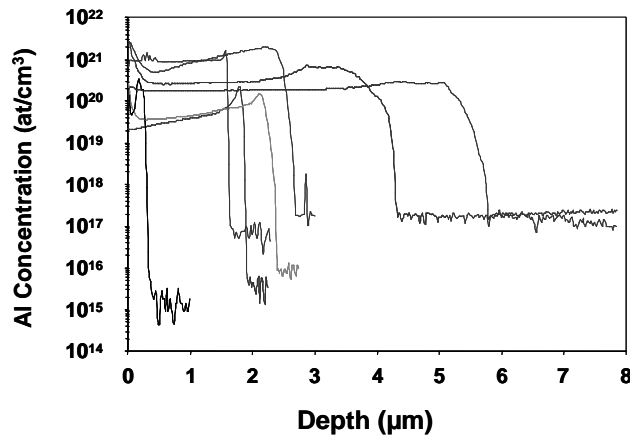

Figure 13 : *SIMS depth profiles of Al concentration in SiC layers grown by VLS at 1100°C in Al-Si melts under different conditions of melt composition and propane partial pressure.*

One can see that all Al-profiles display an overshoot at the substrate/epilayer interface. Depending on the sample, the overshoot width ranges from ~0.1 μm to more than 1 μm. On several samples an Al contamination of the near-surface region, up to ~200 nm, was observed. Such a contribution, which can be easily explained by the presence of the Al-based melt during the growth, was not taken into account in the estimation of the average concentration. Transmission electron microscopy (TEM) analyses of these VLS grown layers were performed. It was found that the grown material is single crystal, though a set of basal plane loops is formed at the substrate-epilayer interface. Surprisingly, these defects do not propagate inside the layer. They are attributed to the high Al amount which modifies the lattice parameter and thus creates a lattice mismatch with the substrate. No Al-based inclusion was detected, either in the layers or near the interface.

While it is generally believed that the solubility of a foreign element inside a solid state

matrix increases with temperature, this depends very much on the element under consideration[48]. For instance, this is well-established for boron in the silicon matrix. In this case, the solubility limit varies from 1 to 6×10^{20} at.cm^{-3} when the temperature increases from 1000 to 1350°C. This trend is much less obvious for aluminium, with a solubility limit in silicon varying from 1 to 2×10^{19} at.cm^{-3} in the temperature range 700-1350°C. The same (relative) temperature insensitivity seems to characterise Al in SiC. Indeed, all experimental results indicate that the incorporation limit for Al in SiC at low temperature (via VLS or LPE) can be equivalent (or higher) than the one obtained using a higher temperature doping technique (such as CVD at 1500°C or sublimation at 2000°C).

To better understand these results, the kinetic and thermodynamic aspects of the doping process must be taken into account. For instance, the incorporation of Al atoms during CVD decreases when the temperature increases. This comes from an increased desorption rate of Al from the growth surface[49]. The net consequence is that, due to the high vapour pressure of Al at elevated temperature, a higher Al supersaturation is required. The main limitation is then that one cannot increase too much the amount of Al introduced in the reactor, to avoid the formation of parasitic Al-based compounds, either in the gas phase or in the layer.

In the case of LPE or VLS, the conditions of supersaturation are lower as the growth occurs at a liquid-solid interface. Furthermore, the SiC surface is in contact with a very rich Al phase (even richer than Si) since the melt composition is always <40 at% Si. In such conditions it is much easier to incorporate a high amount of Al in the SiC matrix, even at low temperature. Notice also that the formation of parasitic Al-based compounds is not favoured as the conditions of growth were chosen so that the only carbide in equilibrium with the melt in the ternary Al-Si-C system is SiC. In other words, Al incorporation in the SiC matrix seems far less dependent on the temperature than it depends on the technique used for doping.

Considering ion implantation as an alternative for high level doping, in this technique care must be taken of the unavoidable defect generation and/or amorphization at high dose. An Al concentration higher than 10^{21} at.cm^{-3} could be obtained without precipitation of foreign Al phases in as implanted material[50] but a moderate temperature annealing (1400°C), necessary for dopant activation provoked the appearance of precipitates. This means that, in the case of ion implantation, Al incorporation is clearly out of equilibrium. The high defect density generated during implantation favours the migration of Al atoms and the formation of precipitates during the subsequent high temperature processing or under working device operations. In the case of VLS layers, the defects are only created at the interface and do not propagate in the layer. Their effect, if any, should be small.

D. Selective epitaxial growth (SEG)

For many electronic devices, local doping of semiconductors is very useful, for example in order to reduce the contact resistance between the metallic contact and the active layer. This is usually performed by masking followed by diffusion or ion implantation of the desired dopant. In the case of SiC, standard diffusion techniques cannot be used because of the small diffusivity of

dopants in this material. On the other hand, ion implantation is generally used even if some problems are still unsolved, especially for Al doping. For instance, the material degrades due to the high implantation dose required. Furthermore, the activation rate of the dopants is low even after high temperature subsequent annealing (>1600°C). This is critical when p+ doped zones are needed for low contact resistance. Selective epitaxial growth (SEG) of heavily Al doped SiC material would be a solution to all these problems. Applying the CVD technique, which is the most commonly used for growing thin epitaxial SiC layers, to SEG of SiC is delicat mainly due to the absence of appropriate material for masking. SiO_2 mask does not prevent SiC deposition on it and is not stable under growth conditions as it was shown to peel off and/or to be etched away by H_2 above 1200°C[51-53]. Pyrolytic carbon was also used as a high temperature mask[54]. Even if better results were obtained, it was suggested that carbon from the mask may participate to SiC growth via H_2 etching so that the local C/Si ratio in the gas phase could be altered. More recently, promising results were obtained with TaC[55]. However, this cannot solve the other difficulty of achieving high Al doping level by CVD.

It is thus interesting to develop SEG with a liquid-based technique in order to reach the high doping level targeted for devices. Toward this goal, Dmitriev et al proposed to use LPE under thermal gradient in Al-Ga-Si melts with carbon as mask[38]. It should be noted that the mask was not dissolved in the melt at the early stage of growth as the liquid was already C saturated by its contact with the graphite crucible in the hotter part. This approach was successful in achieving local epitaxial growth of SiC but it is not clear if the process was truly selective, i.e. if parasitic SiC deposit was also formed on the carbon mask. Switching to a VLS configuration instead of LPE is of no help for SEG of SiC with carbon mask. Indeed, as in VLS the seed is in the hotter part of the melt, the carbon mask will be dissolved before or during the growth.

On the other hand, it is possible to take advantage of the unique configuration of the VLS approach where only carbon is brought by the gas phase to grow SiC. Indeed, it is obvious that no SiC will be formed if no Si-based liquid is present between the seed and the gas phase. As a consequence, if the liquid can be restrained in specific areas of the seed, growth of SiC will only occur in these zones as schematised in Figure 14.
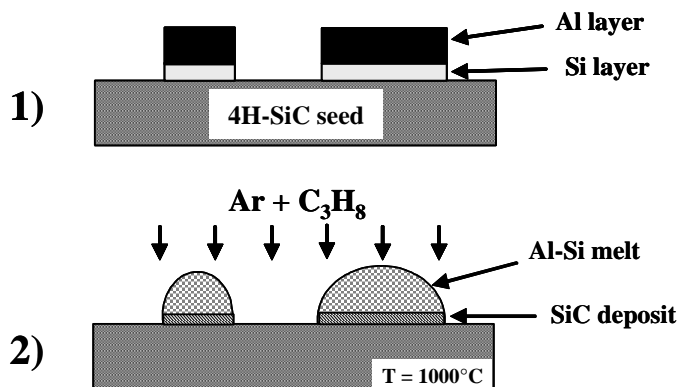

Figure 14 : Procedure for selective epitaxial growth of SiC by VLS. 1) an Al-Si bi-layer stacking is deposited on a SiC seed and then etched to form Al-Si patterns of various sizes and shapes; 2) the sample is heated above the melting point of the alloy and propane is flowed to grow SiC only under the droplets.

In order to validate experimentally the idea, the following procedure was used. Firstly, an Al-Si bi-layer stacking was deposited on a SiC seed. The Si layer deposition was performed under SiH_4 at 1000°C. Then, Al was deposited on top by sputtering. The Si and Al layers thickness was varied from 0.5-1 µm and 1-2 µm respectively but the targeted melt composition was always ~30 at% Si. A photolithographic step was done to define the test pattern prior to Al wet etching. Then, the Si layer was dry etched by Reactive Ion Etching (RIE) using the Al patterned lines as masking layer. At this point, the SiC substrate was covered with patterns consisting of Si/Al bilayers as shown. The samples were then introduced in the VLS reactor and heated up to 1000°C under Ar flux so that the Al and Si layers react to form localised Al-Si melt. A temperature lower than 1100°C was selected in order to limit Al loss by evaporation. This parameter can be neglected for high amount of liquid like in the standard VLS configuration but it could become critical in SEG as the overall amount of Al is much smaller. When 1000°C was reached, propane was introduced in the reactor to start SiC growth. After few minutes, propane was removed from the reactor and the sample was cooled down. As-grown samples were wet etched in acid to remove the excess of alloy on the surface.

The resulting morphology is shown in Figure 15. Several observations can be made:

1) as expected no SiC growth seems to occur outside of the patterns;
2) the patterns keep their original shape and size after growth;
3) the SiC deposit is rough. In some cases, formation of liquid droplets was found instead of homogeneous covering of the patterns. This was observed for non optimized conditions and/or non optimal matching between Al-Si stacking thickness and pattern width. As a general rule, the wider the patterns is, the higher the bilayer thickness must be.
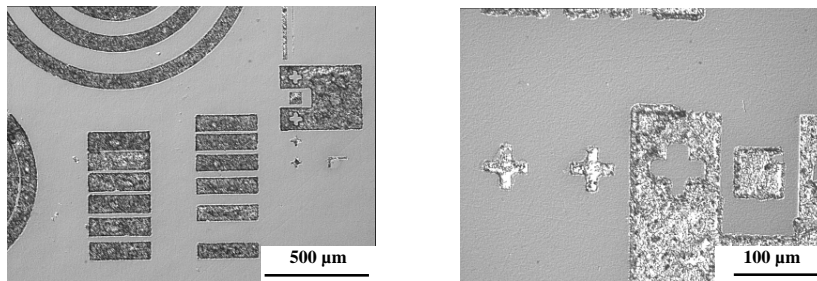

Figure 15: SEG of SiC by VLS with 3 µm thick Al-Si bi-layer stacking. Note the complexe and angular shape of the patterns. The photographs were taken after wet etching of the remaining Al-Si alloy.

Micro-Raman characterisation performed on the grown regions gave a spectrum typical of highly Al doped SiC material (similar as in Figure 12) without any polytype inclusion. When the laser was focused between the patterns, only the signal from the substrate was obtained which means that no SiC growth occurred in these areas. Instead, pyrolytic carbon was detected between the patterns. This graphite is formed by the cracking of propane on the liquid-free surface. This result suggests that the evaporation rate of Si atoms from Al-Si melt is low at 1000°C so that growth occurred only by VLS at the liquid covered places. The presence of

carbon deposit between the motives is not a major problem as it can be easily removed by a low temperature (400-500°C) oxidation which removes almost selectively carbon from SiC.

If SEG of undoped or n-type material has to be grown by VLS, one could think of using pure Si as liquid. Unfortunately, experiments performed toward this goal at 1450°C showed that SiC growth also occurred between the areas covered by the liquid due to the high vapour pressure of Si. A solution could be to use another metal additive than Al and which forms also a liquid phase with Si at low temperature to limit Si evaporation. Ge can be a good candidate even if the melting of Ge-Si is above 1000°C. It was tentatively studied in a similar manner as with Al by depositing 1 µm and 2.7 µm Si and Ge layers respectively. The targeted composition was again 30 at% Si and the growth temperature was 1220°C. As seen in Figure 16, it also works well with even a rougher surface and more homogeneous deposit. With optimal conditions, no droplets were formed even for very wide patterns.
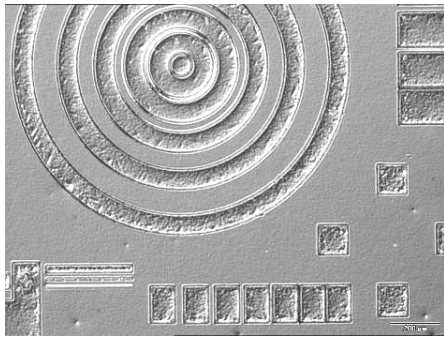

Figure 16 : *SEG of SiC by VLS with initial Ge-Si bilayer stacking. The photograph was taken after wet etching of the remaining Al-Si alloy.*

V. PERSPECTIVES

The VLS approach for SiC epitaxy is not widely used and is still a laboratory technique. The main reason is that successful demonstration of feasibility is very recent so that it has not reached its maturity yet. At present, this technique obviously cannot compete with the well established CVD in terms of surface morphology, purity, doping and thickness control. But growing SiC by VLS has several advantages such as higher safety (low temperature and Ar as carrier gas) or higher Al incorporation. It can also be applied in a smart way to selective epitaxial growth with large choice of size and shape of the patterns. Preliminary electrical measurements on the Al-Si grown layers gave promising results for long contact resistivity, for both "standard" VLS or SEG[56,57]. This has to be further investigated.

On the crystal growth point of view, a milestone to reach for competing with other techniques is the reduction of the surface roughness caused by the high step bunching of the layers. In case this cannot be done by careful control of the growth conditions, post-growth surface polishing is also possible. Another interesting point to deepen is the maximum growth rate achievable in VLS. The highest values were obtained with pure silicon at high temperature. In the case of low temperature VLS in Al-Si, we have no evidence of having reached the upper

limit of growth rate achievable by this technique. We believe that higher rates may be obtained with the combination of proper melt composition, higher propane flux and reasonable increase in temperature to 1200°C. However, in a view to grow very thick material, Si-base precursor should be added during the growth in order to compensate for Si consumption and thus to keep constant the Si content of the melt. If we now consider that it is possible first to control the wetting properties of the liquid at high temperature and second to maintain the liquid on a long time, bulk material could be obtained by a VLS mechanism.

On the view point of fundamental research, it seems very simple by VLS to incorporate high amount of almost any element (dopant or not) in SiC matrix by simply adding these elements in the liquid phase. This can give new properties, such as magnetism, to the grown material. This can also solve some technological problems encountered in SiC technology. For example, high n type doping of SiC with nitrogen does not reduce sufficiently the resistivity of the material due to electrically inactive centres formation[58]. In this case, high phosphorus doping by ion implantation has shown to give better results but still needs high temperature annealing for damage recovery[58,59]. By CVD, P incorporation in high amount is difficult because of the low incorporation level obtained and the high toxicity of PH_3 which is the common precursor used[60]. Introducing some P atoms in non Al-based melts during SiC growth by VLS could bring an alternative solution to both problems of safety and incorporation level.

The VLS mechanism could also find application for homoepitaxial growth on on-axis substrate. Indeed, the high off-axis angle required for step-controlled epitaxy introduces both economical and physical disadvantages. The high density of growth steps on the off-axis seeds increases the probability for the growing epilayer to copy the stacking faults from the substrates to the epitaxial layer. As a consequence, growing good quality homoepitaxial layers on on-axis substrate is of clear technological and economical interest. The low supersaturation conditions involved in liquid phase techniques could help reducing the temperature of homoepitaxial growth. The high step bunching observed for temperatures as low as 1000°C in Al-Si melts suggests that the surface mobility of adatoms should be sufficient for step-controlled epitaxy to occur even on on-axis substrate.

To conclude, the possibilities and potentialities of Vapour-Liquid-Solid mechanism for 4H-SiC homoepitaxial layer growth have been demonstrated. Some research directions have been given. A real development of the method from laboratory work to industrial applications would require a strong effort from the Crystal Grower's community. We believe that potentialities of this method deserve such effort.

VI. REFERENCES

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