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Growth by a vapour–liquid–solid mechanism: a new approach for silicon carbide epitaxy

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Growing silicon carbide monocrystalline layers at low temperatures (<1400 °C) is a challenging problem that requires the development of less conventional epitaxial techniques. Growth from Al-based melts is an interesting alternative that can lead to a more than 300 °C temperature reduction compared to that used in the more classical chemical vapour deposition technique. Liquid phase epitaxy under a thermal gradient is often used but this approach has some drawbacks such as the difficulty in controlling the thermal gradient or the presence of the liquid on the seed at the end of the growth. A solution could come from a vapour–liquid–solid (VLS) mechanism in which a Si-based melt is fed by an alkane to form SiC on an immersed seed. The growth is then easily controlled by the alkane flux and the liquid can be eliminated *in situ* by simply sucking it up. We present in this paper a review on the use of the VLS mechanism for growing SiC at low temperatures. Results of the effect of several metal additives (Al, Ni, Fe and Co) to the melt are shown. These metals incorporate into the lattice and can give specific properties to SiC, such as heavily p-type doping with Al or semi-magnetic properties with Ni, Fe or Co. The VLS technique is shown to be very versatile as it can be applied to selective epitaxial growth of SiC. Finally, perspectives of the VLS technique for solving related problems touching SiC or for growing other semiconductor compounds are given.

Introduction

Due to its specific properties, silicon carbide is one of the best semiconductor candidates for high-power, high-temperature and high-frequency applications. Among the long list of polytypes referenced for this material, the more stable are the hexagonal (α) 4H–SiC and 6H–SiC and the cubic 3C–SiC. With the availability of α-SiC commercial substrates in the early 90′s and the success of the step-controlled epitaxy approach,[1] a lot of research has been dedicated to SiC epitaxial growth. The most used technique is chemical vapour deposition (CVD) under a mixture of H_2–SiH_4–C_3H_8. This popular chemical system has demonstrated impressive results, such as high growth rate (up to 60 μm h^{-1}), an impurity level below 10^{14} at cm^{-3} and the possibility of doping during growth, with nitrogen for n-type and aluminium or boron for p-type, over a wide range of concentrations.[2,3] However, some drawbacks arise when industrialisation of the process is to be considered. One is safety, due to the highly flammable and toxic nature of silane, which gives a potentially explosive mixture when mixed with H_2. Ideally, this source should be replaced with less hazardous alternatives such as single source precursors (organosilicon compounds) that are not inflammable in air. Promising results, in terms of high purity and smooth surface morphology, have been recently reported with hexamethyldisilane[4] and further work still needs to be done. Another drawback of CVD is the constant need to grow at elevated temperatures (> 1400 °C) to have sufficient surface mobility of the adatoms. This means higher costs due to the reduce lifetime of the susceptors or for the need of extra cooling systems. And finally, the high reactivity of H_2 at these temperatures limits the versatility of CVD. For instance, selective epitaxial growth (SEG) by surface masking, which is a well-established and useful technique for Si[5] or GaN,[6] is not simple with SiC

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due to the difficulty in finding inert materials for masking.[7] Note that promising results have been recently obtained with TaC.[8]

Growing good quality SiC epitaxial layers at low temperatures is a challenging problem that could help in reducing the costs, increasing the safety of the process or give new perspectives for SEG. Toward this aim, growth from the melt is an interesting approach due to the low supersaturation conditions promoted at the liquid–solid interface and the absence of dangerous gases like those involved in CVD. However, carbon solubility in pure liquid Si (above the melting point) is very low and is thus the limiting parameter. The use of Si-based melts with carefully selected metal additives could enable both a reduction in the growth temperature and increased C solubility. Most of the reports on SiC growth from the melt deal with liquid phase epitaxy (LPE) under a thermal gradient.[9–11] The liquid is placed in a graphite crucible that serves both as a container and as a C source (see Fig. 1). The carbon is dissolved in the hotter zone (crucible) and is transported to the cooler one (seed) where it reacts with Si to form SiC. Unfortunately, this technique has several drawbacks, such as the difficulty to evaluate and control precisely the thermal gradient between the source and the seed or the presence of liquid on the seed during the cooling.[12] In order to solve these problems, we are developing an alternative approach, called VLS for vapour–liquid–solid, where the Si-based melt is fed by an alkane in order to grow the SiC layer on the seed[13] (see Fig. 1). In this configuration, the seed is in the hotter part of the liquid but this does not prevent SiC growth as C supersaturation in the melt is achieved by cracking the alkane on top of the liquid. The dissolved C will then migrate to the seed due to the C activity gradient between the top and the bottom of the liquid. SiC will finally nucleate on the seed surface. So, the exact knowledge of the thermal gradient is not essential as the growth is mainly dependent on the alkane flux. Furthermore, the particular arrangement of the VLS configuration also allows one to remove the liquid before cooling by simply sucking it up, this step not being easy to achieve in the LPE configuration.

Since the pioneering work of Wagner and Ellis,[14] the VLS technique has been widely used for the growth of whiskers or nanofibres of various materials, mainly SiC[15,16] but also AlN,[17] Si[18] and BiSrCaCuO.[19] Application of the technique to SiC epitaxial layer formation is less frequent because difficult to carry out. Indeed, one of the main difficulties to transpose the VLS mechanism from the growth of whiskers to the growth of epilayers comes from the need to use a liquid with increased size, from several μm (whiskers) to several cm (epilayers). Some attempts in this direction were performed by feeding a Si–Sc melt with toluene[20] or more recently a Si melt with propane at high temperature ($>1400\,^{\circ}$C).[21–23] At lower temperature (950 °C) with Al–Si-based melts fed by propane, Tanaka *et al.* reported 3C–SiC heteroepitaxial growth on 6H–SiC in a special configuration.[24] Even if these primary results are promising as they demonstrate the possibility to grow SiC at low temperature by VLS, the deposit is not of good quality, perhaps due to too low a temperature or unoptimised conditions. The technique needs thus more investigation to show its true potential.

Feeding a Si-based melt only with an alkane has the advantage of avoiding the use of Si gaseous precursor. It results in safer conditions and simplifies also the growth by reducing the number of parameters to control. However, in this configuration, the amount of silicon in the reactor is fixed and not renewed during the experiment. So the consumption of Si during the growth must be taken into account to be sure that constant conditions are kept. Note that this is not the case for SiC whisker fabrication by VLS where Si-based gaseous species are introduced or created *in situ* to feed the micrometer to nanometer size melt.

For low temperature SiC growth from the melt, it is essential to choose a metal (Met)–Si alloy with low melting point, high carbon solubility and no other stable carbide phase than SiC. In practice, there is no ideal Met candidates meeting all these requirements but some are worth trying like Al, Ni, Fe or Co. This is done in this work where we present the potential of the VLS approach to growth SiC homoepitaxial layers using these Met–Si alloys. The case of Al has been extensively studied and will serve as a reference for other metals. Finally, we will show how this technique could be extended to SEG of SiC without the problem of mask material.

Experimental set-up

The experimental set-up is shown in Fig. 2. It is composed of a water-cooled, quartz vertical cold-wall reactor. The temperature of the RF heated graphite susceptor is controlled by an optical pyrometer. In order to improve the thickness uniformity, susceptor rotation up to 230 rpm can be used . High

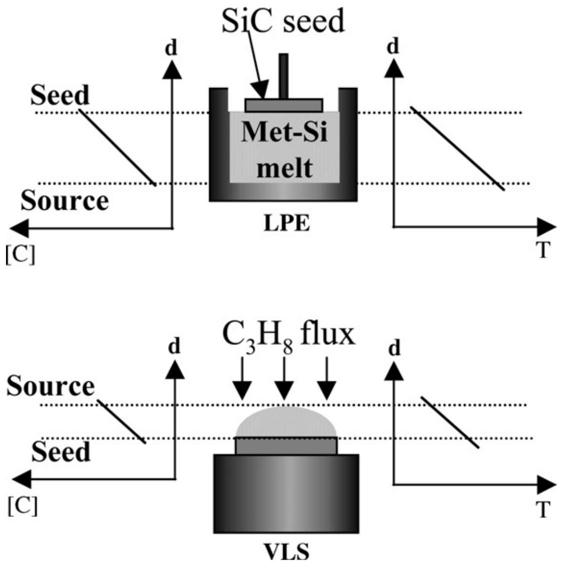

Fig. 1 Comparison between (top) LPE (upper) and (bottom) VLS configurations for SiC epitaxy. Left and right graphs represent, respectively, the C activity gradient and the temperature gradient along the vertical axis *d*.

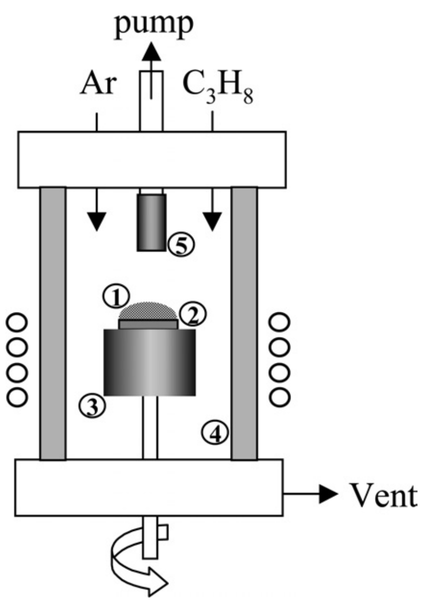

Fig. 2 Experimental set up: (1) Met-Si droplet, (2) SiC substrate, (3) graphite susceptor, (4) water-cooled quartz reactor, (5) sucking tube.

purity Ar is used as the vector gas with propane (5% diluted in H_2) as the reactant. The seeds are 4H–SiC crystals from CREE Research, ⟨0001⟩-oriented, cut 8° off toward the [11–20] direction. Maximum sample size was ~2 cm^2. The metallic (Met) sources (Al, Ni, Fe and Co) are 3N materials. Low doped pieces of Si wafers of electronic grade are used as the Si source.

A pre-growth surface preparation of the seeds was done in a CVD reactor already devoted to high purity SiC growth. After ultrasonic cleaning in methanol and deoxidisation in HF, the seeds were etched at 1600 °C under a mixture of C_3H_8 and H_2 for 10 min. Then, a 3 µm thick Si layer was deposited at 1000 °C under SiH_4 and H_2. The high temperature etching improves the seed surface while the Si layer enhances the seed wetting at the melting of the Met–Si liquid, with the additional benefit of protecting the SiC surface during the air transfer into the VLS reactor. Met and Si pieces were stacked on the Si-covered seed and the whole was placed on the susceptor and introduced into the reactor. After 30 min of pumping, Ar was flowed at 5 slm (up to atmospheric pressure and during the entire process). The temperature was increased up to its final value, at which point propane was added to start the growth. At the end of the experiments, the melt was sucked out by dipping a graphite tube, connected to a pump, into the top of the melt. This allowed the liquid to be removed from the surface of the seed before cooling, thus avoiding any additional growth during this step. In comparison, this cannot be easily done in a LPE reactor as the liquid surface is not free. Sucking up the liquid implies fixing the seed on a SiC plate with a graphite glue in order to avoid any sucking up of the sample itself.

VLS growth in Al–Si melts

The Al–Si–C ternary system has been extensively studied for composite materials.[25,26] With the view to grow SiC epitaxial layers at low temperature, this system has several advantages. First, 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.[27] Second, Al can dissolve a relatively high amount of carbon even at low temperature (for example, 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 melt content with temperature according to the graph in Fig. 3. 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.[28,29]

When Al–Si melts were used for SiC epitaxial growth by VLS, the typical surface morphology obtained is shown in Fig. 4. Large terraces are formed with a step height of several hundreds of nm. This high step bunched morphology is typical of crystal growth from the melt, similar features being found for other semiconductors grown by LPE[30,31] or for SiC grown with melts other than Al–Si.[10,32] Note the drastic improvement of the layer surface thanks to the sucking up of the liquid before cooling. This eliminates the SiC whiskers (dark spots) formed due to C supersaturation of the melt upon cooling.

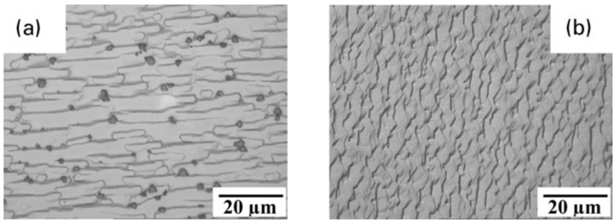

Fig. 4 Surface morphology of 4H–SiC epitaxial layers grown by VLS in an $Al_{70}Si_{30}$ melt at 1100 °C under 10 sccm propane: (a) without and (b) with sucking up of the liquid before cooling.

Growth rates were found to be linearly dependent on propane flux (see Fig. 5). As no saturation is observed at high propane flux, this means that the growth is not limited by the kinetics of dissolution of carbon from the gas phase to the melt. The growth seems to be mainly limited by the supply of carbonaceous species from the gas phase. This demonstrates the high flexibility of the VLS technique as the thickness of the SiC layer can be easily controlled by the precursor flux, as in CVD. In other liquid phase techniques, a precise control of the growth rate can only be achieved by controlling the temperature, which is more complex. The growth rate values in VLS are on the order of 1–10 µm h^{-1}, which is similar to the ones obtained in CVD but at ~400 °C higher. Recent results suggest that even higher growth rates can be achieved by lowering the Si content of the melt down to 20 at %.

In order to evaluate the average Si consumption during growth, one can make simple calculations. Assuming a 10 µm thick SiC layer homogeneously grown on a 50 mm^2 seed surface and 0.4 g of Al–Si alloy at 30 at % Si, with a SiC density of 3.21 g cm^{-3}, one can find that the melt loses only 0.3 at % Si, which is within the order of the composition error. With the same calculations, a 100 µm thick SiC layer would remove up to 1.9 at % Si from the melt, a loss that is still acceptable. So, as long as the SiC layer remains within the range of a few tens of µm, the Si loss can be assumed to be negligible.

Raman spectroscopy is a powerful non-destructive tool for SiC epitaxy characterisation as it allows polytypic identification and may also give information on the doping type and level.[33,34] Fig. 6 shows an example of Raman spectrum collected on a VLS grown SiC layer in an Al–Si melt. Firstly, the position of the peaks is characteristic of the 4H–SiC polytype. This result, together with the formation of steps on

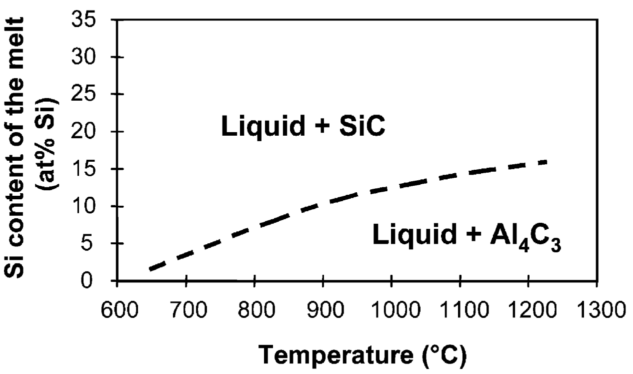

Fig. 3 Equilibrium conditions for SiC or Al_4C_3 formation in the Al–Si–C ternary system.

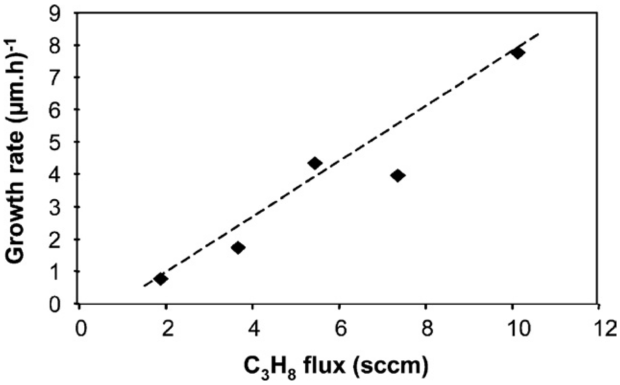

Fig. 5 Evolution of SiC growth rate as a function of propane flux at 1100 °C with $Al_{70}Si_{30}$ melt.

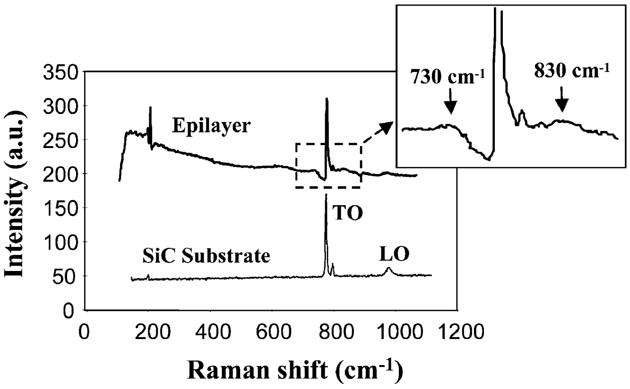

Fig. 6 Raman spectra collected on (bottom) n-type 4H–SiC substrate and on (top) VLS grown epilayer. The insert shows a close-up of the epilayer spectrum around the TO modes where the two peaks corresponding to Fano interference are visible.

the surface, shows 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 the 4H–SiC material. TEM characterisation performed on these layers confirmed the monocrystalline nature of the grown material without the presence of any inclusion.

Some doping information can be obtained from Fig. 6. Indeed, the increase of the background level at low shift values and the appearance of Fano interference around the TO mode are both typical of highly p-type doped SiC material (read refs. 34–35 for more details). This is not surprising as Al is a p dopant of SiC. This result means that Al from the melt is massively incorporated inside the SiC lattice.

SIMS measurements were performed on these layers in order to have a precise value of the Al incorporation during VLS growth from Al–Si melts. Al levels ranging from 5×10^{19} to 1×10^{21} at cm^{-3} were found on several samples. This confirms the Raman results and demonstrates the possibility to reach very high p-type doping levels of SiC layers with a low temperature technique. Similar results for Al incorporation were found in LPE grown SiC layers in Al-based melts.[9,36] On the other hand, these Al incorporation levels are very difficult to obtain by CVD.[37] Al implantation at high doses can give similar doping as in liquid phase growth techniques but it provokes amorphorisation of the SiC material.[38] High temperature treatments ($\geq$1700 °C) are then necessary to recover the crystalline quality and partially activate the dopants. However, these annealing steps are delicate as SiC starts to decompose (loss of Si) in this range of temperature. The final application of heavily p-type SiC layers is to serve as an intermediate layer between the metallic contacts and low p-type doped layers in order to reduce the contact resistance in diodes.[36] So, toward this aim VLS growth in Al–Si melt is of particular interest compared to these more traditional doping techniques. The final electrical tests on our VLS grown layers are in progress in order to evaluate the benefits of using this technique.

VLS growth in other Met–Si melts

Al–Si melts give excellent results in term of crystal growth at low temperature but high Al doping is inevitable in this way. If one wants to grow non-intentionally doped layers, metals other than Al should be chosen. Among several candidates, we selected Ni, Fe and Co for study as they are not known as active dopants of SiC. They can dissolve large amounts of carbon and their Met–Si binary phase diagrams show relatively low melting points for specific alloy compositions. Furthermore, incorporating atoms with magnetic properties inside the lattice of semiconductors is currently attracting much attention in order to fabricate devices coupling information processing and data storage.[39,40] Within this aim, III–V and II–VI semiconductors are widely studied but, to our knowledge, only one report (by Syväjärvi *et al.* for SiC material) exists.[41] A sublimation growth technique was used to incorporate Mn in SiC and the results seem encouraging, even if more work needs to be done in order to increase the amount of Mn or improve the crystalline quality of the SiC layer. The VLS technique could be an alternative solution to incorporate large amounts of magnetic atoms in the SiC lattice, as for Al. As a first step, we will study here the conditions for growing good quality epilayers with the chosen Met–Si melts.

For each metal additive, the Si content of the melt was adjusted in order to target the lowest melting points in the Met–Si binary systems: NiSi ($T_m \sim 1000$ °C), Fe_2Si (1212 °C), $FeSi_2$ (1212 °C), Co_3Si (1212 °C), $CoSi_3$ (1259 °C).[27] For comparison purposes, the growth temperature was fixed to 1300 °C for all these melts, even if some attempts were made at lower temperature in the case of Ni.

When using such metallic elements, which can dissolve a large amount of carbon, the composition of the melt was found to be a crucial parameter for the growth. Indeed, for melts with an excess of metal compared to Si (Fe_2Si and Co_3Si), significant dissolution of the seed (more than 100 μm in only 30 min) occurred instead of growth. On the other hand, by increasing the Si content to the $FeSi_2$ or to $CoSi_3$ composition, 2D growth of SiC with pronounced step bunching was evidenced without seed dissolution (see Fig. 7). These results could be easily explained if the Si–C–Fe and Si–C–Co ternary phase diagrams were well-known. As this is not the case, comparison were made with the better known Al–Si–C and Ni–Si–C ternary phase diagrams. They both show that SiC is in thermodynamic equilibrium with the Met–Si liquid (liquid + SiC domains) only for high Si contents of the melt.[42] On the other hand, for liquids with high Met content, free carbon or carbides other than SiC form. So, in order to avoid seed dissolution and favour 2D SiC growth, the experiments were performed in Si-rich melts. These conditions gave growth rates of a few μm h^{-1} for Ni–Si and Co–Si melts. Surprisingly, for Fe–Si melts, a growth rate as high as 30 μm h^{-1} was measured with the identical propane flux. Ivantsov and Dmitriev found that SiC solubility in Met–Si melts increases when the number of d electrons of the Met additive decreases.[43] In fact, higher SiC solubility means higher C solubility as this element is less soluble than Si. So we can explain the higher growth rates

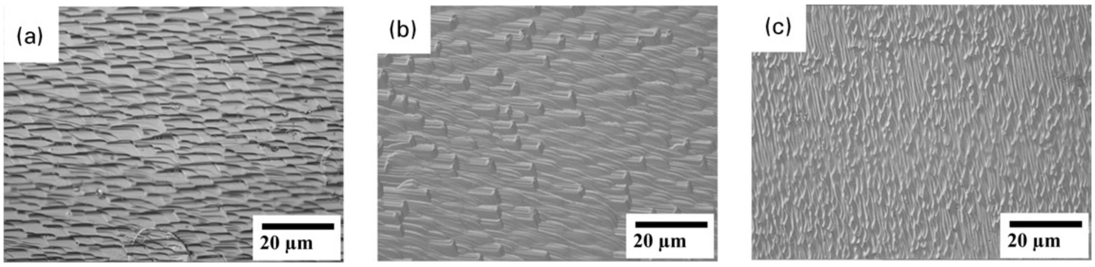

Fig. 7 Surface morphology of SiC epitaxial layers grown at 1300 °C by VLS in different melts: (a) $FeSi_2$, (b) NiSi and (c) $CoSi_3$.

observed with Fe by the higher C solubility in Fe than in Ni- or Co-based melts as Fe has fewer d electrons.

If sucking up of the liquid before cooling was important with Al–Si melts to avoid SiC whisker formation upon cooling, it was found to be even more crucial with Ni- or Fe-based melts. Indeed, with these latter melts, breaking of the samples has always been observed if the liquid was still present on the seed during cooling. This is probably due to a thermal expansion mismatch between SiC and the Ni or Fe silicides forming during solidification of the melt. In the case of Al- and Co-based melts, this problem was not evidenced, suggesting a better thermal matching of the solid alloys with SiC. Note that small droplets (in the mm diameter range) were sometimes left on the seed surface after sucking up. In the case of Ni- and Fe-based melts, this led to the appearance of local cracks upon cooling. This problem can be solved by optimising the sucking up procedure.

The experiments performed in Fe-, Ni- and Co-based melts revealed that the wetting of the liquid on both SiC and graphite is very good, or even too good. Indeed, after only a few minutes of growth, it was observed that the liquid spread over the seed toward the graphite susceptor. In extreme cases, the liquid was completely removed from the seed, thus stopping the growth. Besides the fact that this phenomenon limits the useful growth time to ~10–15 min, the evolution of the droplet shape with time should involve changes in growth rate as the liquid height diminishes. This difficulty, found for these metallic systems, was not encountered with Al–Si melts, probably due to the lower temperature used in this case, which slows down the spreading kinetics.

So, when comparing Ni, Fe or Co for SiC growth by VLS, Co seems the most promising as it does not involve breaking of the seed during cooling. If the sucking up procedure is well-optimised and does not leave any droplets on the seed, Fe would be preferable for the higher growth rates achievable. Another criterion for choosing between these metals would be to know their incorporation level inside the SiC matrix. SIMS characterisations are in progress to clarify this point.

Toward selective growth of SiC by VLS

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 subsequent high-temperature 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. The CVD technique, which is commonly used for growing thin epitaxial SiC layers, is delicate to apply for SEG of SiC, mainly due to the lack of a masking appropriate material. A SiO_2 mask does not prevent SiC deposition on it and is not stable under the growth conditions as it was shown to peel off and/or to be etched away by H_2 above 1200 °C.[44,45] Pyrolytic carbon was also used as a high temperature mask.[46] Even if better results were obtained, it was suggested that carbon from the mask may participate in 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.[8] However, this cannot solve the other difficulty of achieving high Al doping levels by CVD.[37]

It is thus interesting to develop SEG with liquid-based techniques in order to reach the high doping level targeted for devices. Toward this goal, Dmitriev *et al.* proposed to use liquid phase epitaxy (LPE) under a thermal gradient in Al–Ga–Si melts with carbon as a mask.[47] Note that the mask was not dissolved in the melt in the early stages of growth as the liquid was already C saturated by its contact with the graphite crucible in the hotter zone. This approach was successful in achieving local epitaxial growth of SiC but it is not clear if the process was truly selective, in other words if a parasitic SiC deposit was not also formed on the carbon mask. However, as discussed above, LPE has several drawbacks that limit the technique. Switching to the VLS configuration instead of LPE is of no help for SEG of SiC with a carbon mask. Indeed, because in VLS the seed is in the hotter part of the melt, the carbon mask will thus 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, in which 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 to specific zones of the seed, growth of SiC will only occur in these zones as shown schematically in Fig. 8.

In order to validate experimentally the idea, we used the following recipe. Firstly, an Al–Si bilayer stack was deposited on a SiC seed. The surface preparation of the substrate and the Si layer deposition was performed in the same way as described in standard VLS experiments. Then, Al was deposited on top by sputtering. The Si and Al layer thicknesses were 0.5 and 1 μm, respectively, leading to a melt composition of ~29 at % Si. A photolithographic step was performed 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 the masking layer. At this point, the SiC substrate was covered with patterns consisting of Si/Al bilayers as shown in Fig. 9(a). The samples were degreased but not acid etched in order to avoid loosening of the patterning material. They were then introduced into the VLS reactor and heated up to 1000 °C under 5 slm Ar so that the Al and Si layers react

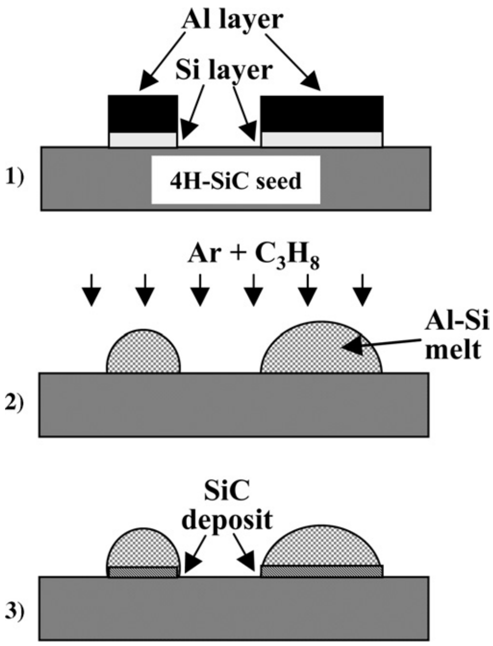

Fig. 8 Procedure for selective epitaxial growth of SiC by VLS: (1) an Al–Si bilayer stack is deposited on a SiC seed and then etched to form Al–Si patterns of various sizes and shapes, (2) the sample is heated above the melting point of the alloy and propane is flowed, (3) SiC growth occurs only under the droplets.

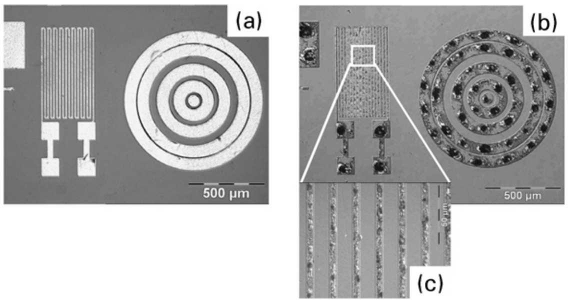

Fig. 9 Optical microscopy image of (a) as prepared Si/Al patterned substrate and (b) same area after VLS growth. (c) Enlargement of the white square in (b).

to form localised Al–Si melts. A temperature lower than 1100 °C was selected in order to limit the Al loss by evaporation. This parameter can be neglected for large amounts of liquid as 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, 4.6 sccm propane was introduced for SiC growth. After 15 min, 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.

In Fig. 9(b) is shown the same area as in Fig. 9(a) after VLS growth. Several observations can be made: (1) no SiC growth seems to occur outside of the patterns; (2) the patterns keep their original shape and size after growth; (3) the pattern dimensions have a strong effect on the efficiency of selective growth. As a general trend, when large patterns or wide lines are designed, at the melting the liquid has a tendency to form round and separated droplets of about 60–80 µm diameter with a volume roughly equal to 20×10^3 µm^3. In this case, SiC growth does not occur over the entire patterns but under the droplets, giving ~4–5 µm thick SiC hillocks. On the other hand, when narrow lines are used (6 µm wide), no evidence of round droplet formation was found and SiC growth occurred all along the lines [Fig. 9(c)]. In these places, the thickness of the SiC deposit is ~1 µm. Observations on other patterns of different sizes on the same sample suggest that the limit between droplet formation and continuous growth is around a pattern width of 20 µm.

Fig. 10 illustrates the behaviour of the liquid as a function of the pattern width d. If d is too high [as in Fig. 10(c)], upon melting the liquid forms a droplet with an initial wetting angle (θ_{ini}) lower than the equilibrium wetting angle (θ_{E}) of the Al–Si melt on SiC, which is ≈30°.[48] The liquid will then have the tendency to retract in order to reach equilibrium ($\theta_3 = \theta_{\text{E}}$). Here, dewetting is instantaneous because nothing hinders liquid movement (the 4H–SiC surface under the droplet is very smooth and clean). On the other hand, if d is too small [Fig. 10(a)], θ_{ini} will be higher than θ_{E}. As a consequence, the liquid will have a tendency to expand to get closer to its equilibrium configuration. But in this case, several factors may restrain the liquid in the pattern area, such as the possible presence of alumina particles (from Al native oxide) at the liquid edges, the formation of a step at the pattern edges due to a slight overetching of the substrate by RIE (as represented in Fig. 10) or a slight oxidation of the substrate surface in the open areas as it was not HF etched before growth. Gravity should not play a significant role in the liquid movement because of the small amount of liquid in each pattern.

When calculating the growth rates in SEG experiments, values of ~16–20 µm h^{-1} were found for the hillocks and ~4 µm h^{-1} for the continuous lines. By comparing to Fig. 5 for equivalent propane flux, one can see that the growth rate under the droplets is much higher than in standard VLS. This can be explained by the difference in liquid height: a few µm in SEG instead of a few mm in standard VLS. Assuming that transport of C in the liquid is diffusion-controlled, according to Fick's law a smaller liquid height should lead to a higher C flux reaching the seed surface, thus increasing the SiC growth rate. The case of the continuous lines is apparently in contradiction with this explanation as the growth rate is found to be equivalent to the one obtained in standard VLS conditions. In fact, we believe that the growth rate for the continuous line is underestimated since the 1 µm growth can take place in less than 15 min. Indeed, as the Si amount in the liquid is fixed by the initial Si layer thickness, growth stops when all this Si is consumed to form SiC. When comparing with the growth rate measured on the hillocks, it is very likely that this Si consumption (to form 1 µm SiC) occurs in a shorter time than 15 min. Note that in the case of the hillocks, thicker layers are locally obtained because the droplets were formed by gathering of the surrounding Al–Si material, so that the Si reserve was locally higher.

Micro-Raman characterisation performed on the grown regions gave a spectrum typical of highly Al-doped SiC material (similar as in Fig. 6) without any polytype inclusion. When the laser was focused between the patterns, only a signal from the substrate was obtained, which means that no SiC growth occurred in these areas. Instead, pyrolytic carbon was detected between the patterns, which comes from cracking of the 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 a carbon deposit between the motifs is not a major problem as it can be easily removed by a low temperature (400–500 °C) oxidation that removes carbon almost selectively from SiC.

All these results demonstrate the possibility to apply the VLS technique to SEG of SiC with the benefit of producing highly Al-doped materials at low temperature. However, optimisation is required in order to avoid droplet formation inside the patterns. This was successfully achieved by increasing the initial Al–Si bilayer thickness from 1.5 to 3 µm (1 µm Si + 2 µm Al). As shown in Fig. 11, homogeneous growth is then obtained on large area patterns. The very interesting (but intriguing) point is that the angular edges of the patterns were kept, which means that the liquid also had angular edges. This demonstrates that SEG of SiC by VLS can be done on almost all kinds of pattern sizes and shapes. Some work still remains to be done in order to reduce the roughness or to control the thickness of the deposit. Toward this goal, it is worth studying the effects of temperature and growth time.

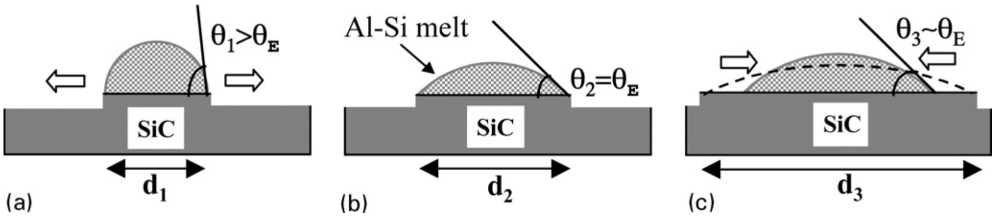

Fig. 10 Schematic drawing representing the effect of the pattern width d on the apparent wetting angle θ, assuming a constant Al–Si stack thickness: (a) narrow, (b) intermediate and (c) wide patterns. θ_{E} is the equilibrium wetting angle between the Al–Si melt and SiC (~30°).

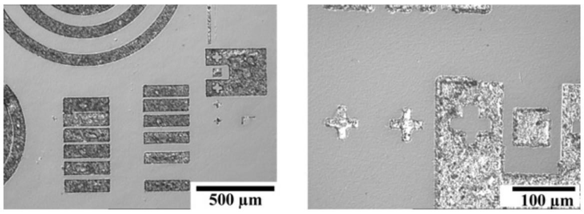

Fig. 11 SEG of SiC by VLS with 3 µm thick Al–Si bilayer stacking. Note the complex and angular shape of the patterns.

If SEG of undoped material is to be grown by VLS, one could think of using pure Si as the 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 a metal other than Al. The results presented in the previous paragraph suggest Co as an interesting alternative in order to avoid seed cracking during the cooling. The other important point when choosing the alloy is to work at sufficiently reduced temperatures to limit Si evaporation.

Perspectives

The VLS approach for SiC epitaxy is not widely used and is still a laboratory technique. The main reason is that a successful demonstration of feasibility is very recent so that the technique has not yet reached its maturity. 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 greater safety (low temperature and Ar as carrier gas) and higher Al incorporation. It can also be applied in a smart way to selective epitaxial growth with a large choice in the size and shape of the patterns. The next step is to determine the electrical characteristics of the grown layers in order to know if the VLS technique is suitable for device fabrication. This work is under way for our Al-doped layers.

From the crystal growth point of view, a milestone to reach in order to compete 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 investigate is the maximum growth rate achievable in VLS. Indeed, increasing the growth rate could find applications to grow bulk-like materials at lower temperature than in sublimation techniques. Up to now, we have no evidence of having reached the upper limit of the growth rate achievable by this technique. We believe that higher rates may be obtained with different melt compositions (in Al-based or other metal-based alloys), higher temperatures or with higher propane fluxes. However, with a aim to grow thick materials, Si-based precursors should be added during the growth in order to compensate for Si consumption and thus keep the Si content of the melt constant.

From the view point of fundamental research, it is very simple by VLS to incorporate a high amount of almost any element (dopant or not) into the 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 current SiC technology. For example, high n-type doping of SiC with nitrogen does not reduce sufficiently the resistivity of the material due to the formation of electrically inactive centres.[49] In this case, high phosphorus doping by ion implantation was shown to give better results but it still needs high temperature annealing for damage recovery.[49,50] P incorporation in high amounts by CVD is difficult because of the low incorporation level obtained and the high toxicity of PH_3, which is the common precursor used.[51] 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.

Finally, SiC is not the only semi-conducting material that can be grown by VLS. GaN growth has already been reported by reacting liquid Ga with NH_3[52,53] and there is no doubt that this approach can be extended to other nitride compounds such as $Al_xGa_{1-x}N$ or AlN. A more exploratory and challenging study would be to grow $(AlN)_x$–$(SiC)_{1-x}$ solid solutions (see ref. 54 for more details on these wide band gap compounds) by feeding an Al–Si melt simultaneously with NH_3 and C_3H_8. In this case, the VLS approach would be simpler than CVD[55] or MBE[56] for growing these quaternary compounds as the gas phase contains only two reacting species instead of four.

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