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Uniform growth of SiC single crystal thin films via metal-Si alloy flux by vapour-liquid-solid pulsed laser deposition: a possible existence of the precursor liquid flux film

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For the use as a next generation power semiconductor, new vapor growth processes for SiC single crystal films have been highly demanded, among which is the VLS growth with metal-Si flux. If the metal-Si flux liquid were well wettable on the SiC, a thinner flux liquid layer would be favored for a higher growth rate in the VLS process. We demonstrated that a thin NiSi₂ layer, even as small as 150nm in thickness to form liquid droplets, could work effectively as a flux in the pulsed laser deposition (PLD)-based vapor-liquid-solid (VLS) process for the uniform growth of high-quality 3C-SiC (111) films on 4H-SiC(0001). In situ direct observation of the interface between the flux and single crystal SiC by laser microscope strongly implied the existence of a precursor liquid flux film spreading between the NiSi₂ droplets that can have a similar role in the flux growth process, resulting in significant improvements in the surface morphology, crystallinity as well as stoichiometry of SiC films.

1. Introduction

Silicon carbide (SiC), which has a variety of polytypes including 3C, 4H and 6H, etc. is a promising material to overcome the existing limitations of Si-based devices, especially in the field of high power applications. SiC has various superior properties to those of Si, such as of wide band gaps, high electrical breakdown fields, high electron saturation drift velocities and high thermal conductivity. SiC-based devices are thus expected to exhibit higher performance in power density and efficiency than Si-based ones, operatable at high temperature and frequency regions. Among the challenges to be tackled for commercial uses of such SiC devices are reducing the production costs, lowering defect densities and controlling polytypes of SiC films as well as bulk wafers. However, the sublimation method, the only industrial production process for SiC bulk wafers, requires operating-temperatures of over 2000 °C, resulting in huge production costs of running equipment with high heating energy consumption. It follows that a further cost cutting would be difficult in principle as long as the sublimation method is employed. Moreover, the essentially non-equilibrium nature of this process may not be favored for further decrease in defect density and enlargement of the wafer size of SiC bulk crystals, which are key to acceleration in the development of SiC electronics technology.

Recently, the flux growth method, one of the solution growth processes, has attracted much attention as an alternative process that can solve the problems discussed above. The growth of SiC bulk single crystals with higher quality is, in principle, possible by crystallization from a flux

melt even at a temperature lower than those in the sublimation method. It is because the growth condition is very close to the equilibrium state through the solid-liquid interface. However, the remaining problem in this process is its relatively slow growth rate as compared in the sublimation process, the reason for which is the low solubility limit of carbon in Si melt at any temperature. In order to increase the carbon solubility and thereby to achieve a high growth rate even at low growth temperature, multi component Si-based metal flux¹ containing, for example Ni², Cr^{3,4}, Al⁴, Ge^{5,6}, Ti⁷, and Fe⁸ have been tried to use. In addition, the use of such metal elements as a flux component is potentially effective in controlling the SiC polytypes. For example, according to our previous study, 6H-SiC inclusions are found in the flux growth of 4H-SiC upon addition of pure Ti, but not of Ti with Ni².

On the other hand, there has been also a challenge to apply the flux growth method to vapor growth of SiC films. It was in 2002 that Ferro et al first reported a successful growth of epitaxial SiC layers in chemical vapor deposition (CVD) by vapor-liquid-solid (VLS) mechanism with Si melt⁹; since then followed by those with multi component Si-based metal flux such as Si-Ge⁶ and Si-Al¹⁰. It should be noted that in their growth of uniform SiC films Si is supplied from Si-based melt flux, and only C is from the gas phase by continuously feeding a hydrocarbon gas source such as propane⁹ as shown in Fig. 1a. In this case, the amount of Si in the flux will gradually decrease as the SiC film grows, and thus the pre-mounted Si flux must be bulky, sufficient enough to stabilize the process in a long-term run. However, such an excess Si flux in this CVD-based VLS process may cause a serious reduction in the crystal

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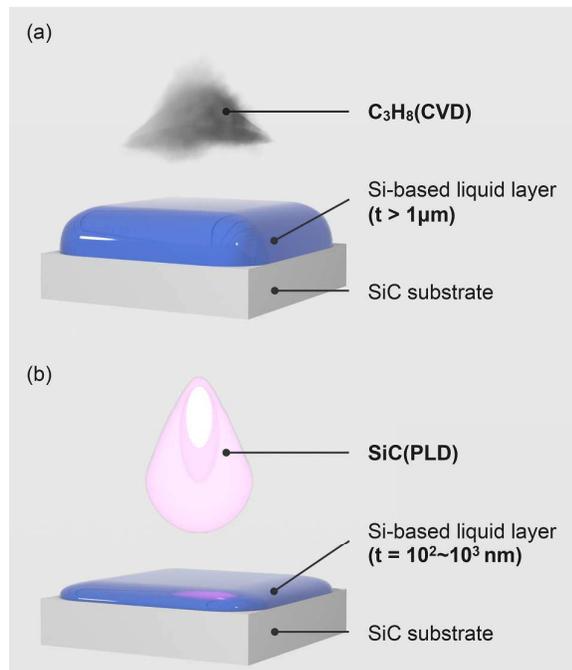


Fig. 1 Comparison of (a) CVD-based and (b) PLD-based VLS processes of SiC thin film growth.

growth rate because the slow carbon diffusion process in the bulk flux will become a rate-limiting step.

In contrast, we also have proposed, independently of the group by Ferro et al, a similar VLS process in pulsed laser deposition (PLD) since 2002¹¹, and named the process “flux-mediated epitaxy (FME)” in 2005¹², to emphasize the roles of flux in the vapor process. In this process, as shown in Fig. 1b, one distinct difference from the CVD-based VLS process by Ferro et al is that a flux material is first deposited in a thin layer form of several tens to hundreds nm in thickness, followed by continuous deposition of the growing film by PLD at a high temperature to melt the flux layer. Even through such a thin flux layer, we have succeeded in the fabrication of uniform single crystal oxide films such as superconducting $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}$ grown with Ba-Cu-O self-flux¹¹ and ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with Cu-stabilized BiO_x flux available in vacuum¹³. More recently, the FME concept has been extended to the growth of organic crystals/films of pentacene¹⁴ and fullerene (C_{60})¹⁵ with ionic liquids, which are a new class of organic solvents stable in liquid even in vacuum.

In the growth of SiC films the advantages of the use of a flux layer as thin as possible are not only being able to avoid the slow carbon diffusion limit to the total growth rate, but also, no matter of their solubility limit, i.e. the wide availability of the flux composition. It is because the material sources from the gas phase can reach the substrate to precipitate upon their dissolving into the liquid flux if the liquid flux layer is very thin even though the solubility is small. However, one possible problem is the thickness limitation. Unfortunately, Si-based fluxes generally will not spread homogeneously over the SiC

surface so that the uniform growth of SiC films seems not expected. In fact, the minimum thickness of liquid flux layer is, at most, 2-3 μm for high quality and uniform SiC thin films in the CVD-based VLS process¹⁶.

In this study, we demonstrate that a thin Si-Ni alloy layer, can work effectively as a flux to produce a uniform SiC film. The key point is a simultaneous supply of pure Si and C sources from the gas phase by PLD using a SiC stoichiometric target, stabilizing the flux during the process. The high-temperature laser microscope observation revealed that the Si-Ni alloy took a droplet form with several micrometers in diameter on SiC, apparently inconsistent with the uniform flux growth of SiC films. To explain this inconsistency the possible existence of “precursor film”, a nm-thick liquid film spreading between liquid droplets that can have a similar role in the flux process will be discussed.

2. Experimental

2.1 Thin film fabrication

As a flux, a 1:2 composition ratio of Ni to Si (NiSi_2) was selected in this study on the basis of the data of its lower melting point, and better wettability on and more reactivity with SiC, investigated in our previous laser microscope study¹⁷. At first, a 150 nm-thick flux layer was deposited on 4H-SiC (0001) on-axis by PLD using a NiSi_2 target with KrF excimer laser (248 nm) at a repetition rate of 10 Hz and energy density of 1.9 J/cm^2 at room temperature. The sample was then mounted on a carbon plate ($15 \times 15 \times 2 \text{ mm}^3$) with carbon paste and heated from the backside of the carbon plate by a Nd:YAG laser; the sample temperature was measured with a radiation thermometer. After the sample temperature reached 1160 $^\circ\text{C}$ at which NiSi_2 had melted, a 200 nm-thick SiC was deposited using a SiC target at a repetition rate of 2 Hz and energy density of 3.8 J/cm^2 . During the depositions of NiSi_2 and SiC, the backpressure was kept in high vacuum below 1×10^{-6} Torr. After the deposition, the remaining flux was removed from the film surface by etching with a $\text{HF} : \text{HNO}_3$ (1 : 1) solution.

2.2 Thin Film and flux characterizations

The surface morphology of films and remaining flux after deposition was observed by scanning electron microscopy (SEM, S-4000, Hitachi High-Technologies Co., Ltd.) and atomic force microscopy (AFM, SPA-400, Seiko Instruments Inc.). Energy dispersive X-ray spectrometry (EDX) with which the SEM was equipped was used to examine the composition of the flux. The polytypes of SiC in the film were identified, including their epitaxial relationships to the 4H-SiC (0001) substrate, by transmission electron microscopy (TEM) with electron diffraction (ED). The degree of excess carbon inclusion in the SiC film was also examined by TEM-EDX as well as Raman spectroscopy (RAMANOR T64000, HORIBA, Ltd.).

2.3 High-temperature laser microscope observation in vacuum

During the heating of a NiSi₂-deposited 4H-SiC (0001) sample, the solid-liquid interface was directly observed by using a confocal laser microscope (LM, VK-X130/120, KEYENCE CORPORATION). In our system, the sample was heated by a Nd:YAG laser from the front side of the sample up to 1710 °C with a heating rate of 30 °C/min in high vacuum, while the laser probe was introduced from the backside of the substrate using an objective lens with a focal length of 20.5 mm.

3. Results and Discussion

3.1 Flux effects on the surface morphology, crystallinity and composition of SiC thin films

Fig. 2 is a set of SEM images for samples just after depositing SiC without flux (a) and with flux (b). The former sample, grown without flux, shows granular structures all over the surface. The grain sizes are less than 1 μm, as is more clearly seen in the inset AFM image of Fig 2a, which was taken for the surface after removing the remaining flux. In contrast, for the latter sample, grown with flux, the surface becomes very flat with some hemispherical droplets segregated on the surface. The composition analysis of these droplets by EPMA confirmed that they were the remaining flux. The droplet shape suggests that the NiSi₂ flux film was once melted to form liquid droplets, inhomogeneously covering the growing SiC film surface during the deposition of SiC. Nevertheless, the obtained SiC film surface is more uniform for the flux droplet size of several micrometers, the mechanism of which will be discussed later in section 3.2. Furthermore it exhibits a step-and-terrace structure with “triangle step” edges, as seen in the inset AFM image of Fig. 2b for the SiC surface after removing the remaining flux. The dominant “triangle edge” angle of 60 degrees, i.e. the three-fold symmetry of the surface step pattern suggests that the polytype of the growing SiC film is 3C-SiC with the (111) face exposed.

Fig. 3a and 3b show a set of bright field cross-sectional TEM images for SiC films grown without and with flux, respectively after removing the remaining flux. The SiC thin film without flux shows granular structures not only on the surface, as is observed in the SEM, but also in the bulk including many voids therein. In contrast, the SiC thin film with Si-Ni flux was extremely uniform and almost no dislocations and grain

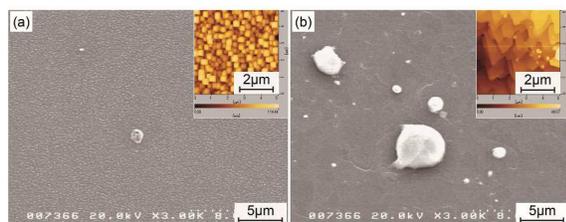


Fig. 2 SEM images of SiC thin films grown (a) without and (b) with flux before removing the remaining flux. The insets are AFM images of the thin film surfaces after removing the remaining flux.

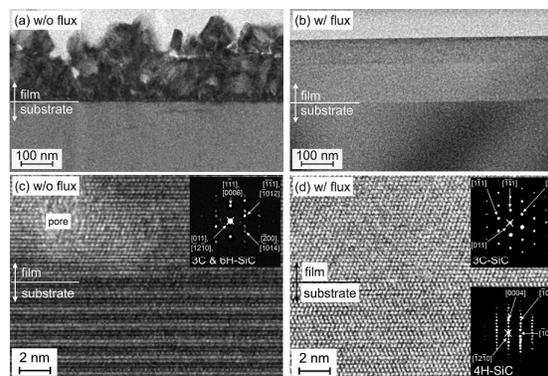


Fig. 3 Bright field cross-sectional TEM images of SiC films grown (a) without and (b) with flux after removing the remaining flux. (c, d) The expanded HRTEM images, together with their selected area diffraction pattern, for the corresponding SiC films of (a) and (b), respectively, comparison of (a) CVD-based and (b) PLD-based VLS processes of SiC thin film growth.

boundaries can be found within an observable range. Fig. 3c and 3d show the expanded high resolution TEM (HRTEM) images, together with their selected area diffraction pattern, for the SiC films of Fig. 3a and 3b, respectively. As is clearly identified in the HRTEM image and diffraction pattern of Fig. 3d, the SiC thin film grown with Si-Ni flux has a single phase of 3C-SiC, as is expected from the three-fold symmetry of the surface step pattern, growing along the <111> direction on 4H-SiC (0001). On the other hand, the diffraction pattern of Fig. 3c shows that the granular film consists of a mixture of 3C and 6H-SiC polytypes. In addition, near the interface are often found some pore-like features with 10 nm or less in diameter in the HRTEM image. The TEM-EDX analysis in Fig. 4a revealed that the pore was the result of carbon-aggregation with a higher C/Si intensity ratio of 3.91, after calibrated so as to be unity in the SiC substrate. In fact, the granular SiC film grown without flux has a carbon-rich composition with a C/Si intensity ratio of 1.24 in average, while the flux grown SiC film has a C/Si intensity ratio of 1.01, almost stoichiometric composition in average. These results are in good agreement with the macroscopic analysis by Raman spectroscopy as shown in Fig. 4b. Besides the peak around ~1520 cm⁻¹, an overtone of TO (X) phonon modes of 4H-SiC¹⁸ and 3C-SiC^{18,19}, there are observed two carbon-associated broad peaks at 1350 cm⁻¹ and ~1600 cm⁻¹ in the granular SiC film, but not in the 3C-SiC single crystal film. These peaks are assigned to D-band^{20,21} and G-band, respectively. The G-band peak is typically located at 1580 cm⁻¹ for bulk carbon, while it is likely to shift to around 1600 cm⁻¹ for nano graphite flakes^{20,21}. The G-band peak at ~1600 cm⁻¹ observed in the granular SiC film, therefore, should be originated from nanometer sized carbon clusters such as carbon nano-pores found in the HRTEM image for the granular SiC thin film. The excess carbon inclusion in the SiC film grown without flux suggests that non-negligible amount of Si in the total supplied from the SiC target by PLD is ready to evaporate again even at the optimal growth temperature of 1160 °C. Hence, the Si-Ni flux may have an additional role to compensate for the Si deficiency in the growth of SiC films at such a high growth temperature.

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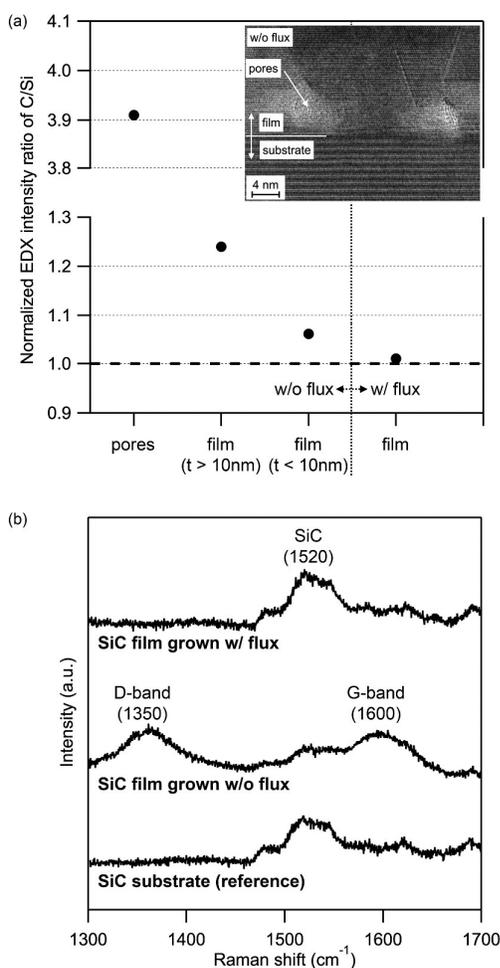


Fig. 4 (a) Comparison of C/Si intensity ratios, analyzed by TEM-EDX, depending on the positions in the TEM image (inset). (b) Raman spectra of SiC films grown with and without flux, along with that for the 4H-SiC (0001) substrate as a reference.

3.2 Mechanism of the uniform flux growth of SiC films via NiSi₂ liquid droplets

As already pointed out in section 3.1, we have succeeded in the uniform growth of SiC films with even a sub-micron thin alloy NiSi₂ layer, however the remaining flux droplets suggests that the NiSi₂ flux was once melted to form liquid droplets inhomogeneously dispersed over the SiC surface during the deposition of SiC. In fact, according to our previous in situ laser microscope study on the melting behavior of Ni-Si alloy films on a 4H-SiC substrate, many liquid droplets of NiSi₂ are dispersed over the surface¹⁷. Most of them will not move around, but just stay near their original position around at the growth temperature. Here one question may arise: why is the flux effect so uniform over the sizes of flux droplets? One possible hypothesis is that there is a nm-thick liquid flux film spreading between liquid droplets that can have a similar role in the flux growth as shown in Fig. 5, as is pointed also by Ferro and co-workers²². The nm-thick film is historically well-known as a precursor film^{23,24}, for example in liquid-on-solid systems^{25,26}, and metal-on-metal systems^{27,28}, though the precursor film

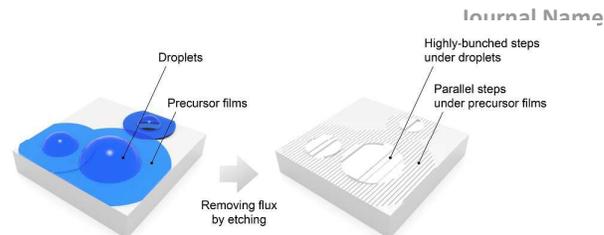


Fig. 5 Schematic of possible precursor liquid flux film spreading around and between the flux droplets on the SiC surface.

is generally hard to detect because of its inherent nature of nm-thinness²⁵⁻³⁰. The existence of such a precursor liquid flux film was also suggested by the step-bunching behaviour directly observed at the interface between the 4H-SiC (0001) on-axis substrate and NiSi₂ flux thin film (150 nm) in the following LM experiment.

In the LM observation during the temperature increase, the NiSi₂ flux thin film started to melt above 1100 °C, which is very close to the melting temperature of NiSi₂, and completely became liquid droplets at 1160 °C, the details of which mechanism will be discussed elsewhere. We confirmed that once the droplets were formed, they were likely to stay almost at their original position even after further temperature increase, as is pointed out above, as pointed out above. Fig. 6a-c are sequential LM images just focused on the interface of the substrate with keeping the temperature at 1710 °C. The circular regions imaged in white, indicating a higher reflection intensity of the incident probe laser on the gray scale, are those underneath the droplets, and thus the circular shape is just a silhouette of the droplet. In contrast, the regions around and between the droplets are imaged in gray, indicating a lower reflection intensity due to the transparent nature of SiC to the probe laser light.

In Fig. 6c, we can clearly see some meandering steps, imaged as dark lines, gradually appear underneath the droplets, indicative of the formation of step-bunched structures, and such a distinct morphological change was observed after reaching the top temperature. On the other hand, the parallel steps also can be found to run around and between the droplets, whose step-heights were estimated to be 20 to 30 nm by AFM as shown in Fig. 6d after removing the flux. In contrast, as shown in Fig. 6e-g, no formation of step-bunching structures is observed for a bare SiC surface as a reference, in which other experimental conditions were exactly the same as when heating with the flux. In order to rule out a possible detection limit by the LM, the etched sample surface was also observed by AFM, as shown in Fig. 6h, to confirm no step-bunching structures. It is therefore concluded that the step-bunching is definitely resulted from the etching by the liquid flux. The observation that the step-bunching also occurred even around and between the NiSi₂ droplets on SiC also strongly suggests the precursor liquid flux film of NiSi₂ covering almost whole the surface of SiC as is illustrated in Fig. 5. The thickness should be very thin, at the nm scale, because of almost no reflection intensity of the probe laser light in areas around and between the droplets. The similar situation is expected in the growing process by PLD and the possible precursor film may have an important role in the uniform

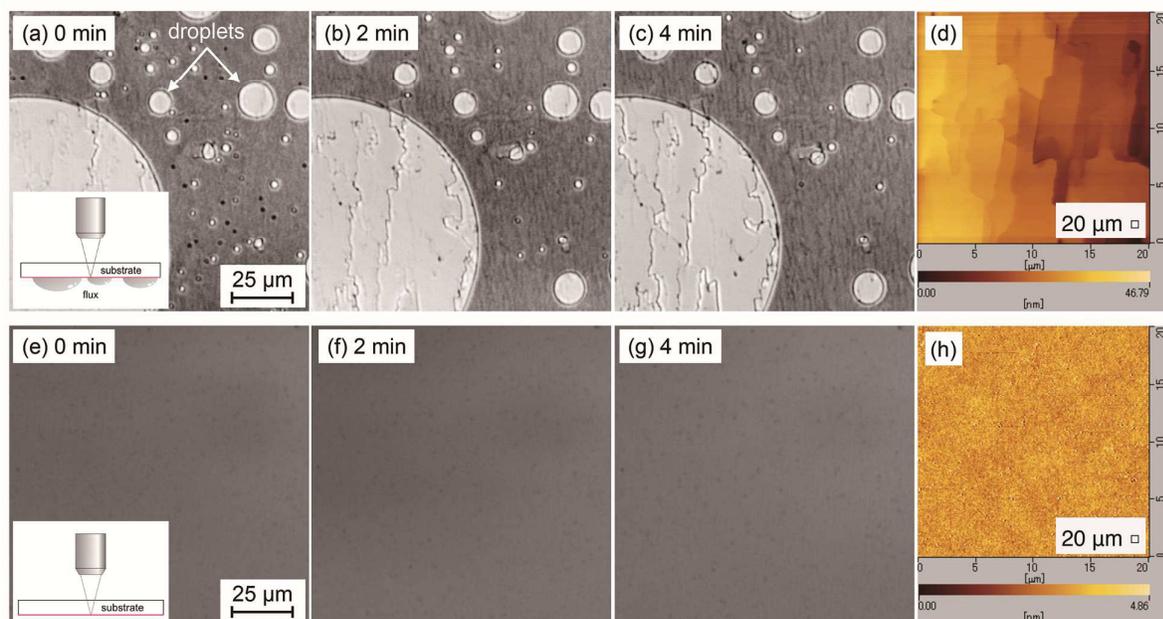


Fig. 6 (a-c) Laser microscope images of the interface between the SiC substrate and flux at 1710 °C. Step-bunching behavior of the SiC substrate contacted with the flux was clearly observed. (d) AFM image of the surface after removing the flux for the sample observed in (a-c). (e-h) Laser microscope and AFM images of the SiC substrate without flux observed at the same condition with (a-d) as reference.

growth of SiC films even though such a sub-micron alloy NiSi₂ layer (~150 nm) was used as flux.

Here, it should be pointed out that the possibility of a bunch of very small mobile flux droplets even invisible by LM between micro-droplets, having the similar flux effect, cannot be completely ruled out at moment. However, if there were such very small mobile droplets between micro-Ni-silicide droplets, the growth of SiC nanowires or islands, though it may depend on the laser fluence, would be dominant rather than uniform SiC films in our PLD process as well^{31, 32, 33}.

4. Conclusions

We successfully grew the high-quality 3C-SiC single crystal film by the PLD-based VLS process with a thin NiSi₂ layer flux, even as small as 150 nm in thickness to form liquid droplets. The existence of a precursor liquid flux film spreading around and between the droplets was proposed to explain the uniformity of the obtained SiC film. Such a possible precursor film also could explain the step-bunching behaviour even around and between the NiSi₂ droplets on SiC, as was directly visualized by high-temperature LM in vacuum. Although there has not yet been any direct evidence for such a precursor film, it would be a useful hypothesis for further development of the PLD-based VLS process for fabricating high-quality SiC films with a higher growth rate.

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