Simple and quick enhancement of SiC bulk crystal growth using a newly developed crucible material

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Newly developed highly reliable low-cost TaC-coated graphite materials prepared by a wet ceramic process were applied to SiC sublimation growth. We demonstrated an increased long-duration growth rate and a resultant increase in crystal size by a factor of ~1.2 (experimental value) after 24 h of growth [and ~1.5 (extrapolated value) after the optimum duration of 53.1 h] by simply and quickly replacing graphite crucibles with TaC-coated graphite crucibles. Growth with the TaC-coated graphite crucibles reduced source gas leakage and increased the material yield for single crystals because the TaC layers were gas-tight and had a low emissivity.

Graphite is the most commonly used material for ultrahigh-temperature processes such as the sublimation growth of silicon carbide (SiC). The major issue with graphite as a crucible material in SiC growth is chemical corrosion by the sublimed gases (e.g., Si and Si2C), which results in the incorporation of carbon inclusions into the grown crystals and the unintentional drift of growth conditions through dimensional changes of the crucibles. Since the incorporation of carbon inclusions is recognized as the main cause of crystalline defects, such as micropipes and dislocations, it is crucial to enhance the corrosion resistance of crucible materials in order to realize high-crystal-quality SiC wafers and highly reliable high-performance SiC power devices.

Although tantalum carbide (TaC) ceramics (or surface-carbonized Ta metal) are highly stable under SiC sublimation growth conditions, their particularly high material cost and low degree of freedom in shape forming have hampered their adoption in actual manufacturing processes. CVD-TaC-coated graphite materials have demonstrated excellent stability in the growth process along with a decreased carbon inclusion incorporation, however, their high cost has restricted their use.

We previously proposed highly reliable low-cost TaC-coated graphite materials prepared via a wet ceramic process, which we call “SinTaC” (Sintered Tantalum carbide Coatings on graphite). Furthermore, we have already demonstrated their excellent reliability and durability under extremely corrosive AlN sublimation growth conditions.

Here, we demonstrate the use of SinTaC crucibles in SiC sublimation growth to evaluate their effectiveness. Promising results were obtained, especially in terms of the increases in the growth rate and size of the crystals. The results suggest that considerable improvements in actual production processes involving SiC wafers can be obtained by a simple and quick change of the crucible material.

Figures 1(a) and 1(b) show growth setups for SinTaC and graphite crucibles, respectively. Both setups consist of top-lid seed holders, separators (corresponding to the radiation shield in Ref. 13, which can separate a single-crystalline ingot from the surrounding polycrystals), and SiC source powder containers. They were employed as growth setups by simple stacking, as shown in Figs. 1(a) and 1(b), without any sealing of the crucible joints. The shapes and dimensions of the SinTaC and graphite crucibles were exactly the same, except for the thickness of the TaC coating layer (SinTaC layer). Figures 1(c)–1(e) show photos of SinTaC crucibles (after sintering, with a seed attached and the SiC source powder charged). Furthermore, Figs. 1(f)–1(h) show photographs of semiprocessed SinTaC crucibles before sintering (just after the TaC slurry application). A comparison of Figs. 1(c)–1(e) with Figs. 1(f)–1(h) reveals that the matte-brown powder compact films transformed into lustrous-gold dense films via sintering. The SinTaC top-lid seed holder and SinTaC separator were fully coated with the SinTaC layer, whereas the SinTaC source container was only partly coated on the inner wall and top-edge surfaces (and bare on the outer-wall surface). The thickness of the SinTaC layers after sintering was controlled within the range of 100–200 μm.

Seed crystals of 4H-SiC(0001) on-axis substrates (carbon-face seeds) were placed in the seed holders. The back sides of the seeds were adhered to a 1-mm-thick graphite sheet to allow direct monitoring by a pyrometer, which controlled the growth. We demonstrated an increased long-duration growth rate and a resultant increase in crystal size by a factor of ~1.2 (experimental value) after 24 h of growth [and ~1.5 (extrapolated value) after the optimum duration of 53.1 h] by simply and quickly replacing graphite crucibles with TaC-coated graphite crucibles. Growth with the TaC-coated graphite crucibles reduced source gas leakage and increased the material yield for single crystals because the TaC layers were gas-tight and had a low emissivity.
seed temperature during bulk crystal growth. The source powder was a high-purity (99.9%) SiC powder with a median diameter ($D_{50}$) of 500 μm, 378.5 g of which was charged into the source containers. The spacing between the seed surface and the source powder top edge was 43 mm. The crucibles containing the seed and source powder were covered with carbon-fiber-molded thermal insulators, which were installed in a radio-frequency induction furnace. The sublimation growth of the SiC bulk crystal was performed under the growth conditions of a reduced-pressure Ar + N$_2$ atmosphere ($P_{\text{Ar}} = 191$ Pa, $P_{\text{N}_2} = 9$ Pa), a seed temperature of 2200 °C, a source temperature (monitored at the bottom of the source container) of 2330 °C, a nominal axial temperature gradient of 16 °C/cm, and a growth duration of 24 h. We introduced nitrogen delta-doping markers$^{14-16}$ into the grown crystals to precisely measure the time-dependent growth height and growth rate. The procedures were performed with 1 min of high-concentration nitrogen delta doping ($P_{\text{Ar}} = 100$ Pa, $P_{\text{N}_2} = 100$ Pa) every 3 h.

The grown crystals and crucibles were visually inspected after growth, and each part of the crucibles (including the grown single crystals and polycrystals) was weighed to determine the crucible weight deficit and material yield. The grown crystals were sliced parallel to the growth direction and the sliced substrates were polished as cross-sectional specimens. We directly read the time-dependent growth heights from the specimens and observed the distribution of foreign particles such as carbon inclusions in the grown crystals.

Figures 2(a) and 2(b) show photos of SiC single-crystal ingots and SiC source powder after 24 h of growth in SinTaC crucibles, and Figs. 2(c) and 2(d) show those grown in graphite crucibles. As shown in Figs. 2(a) and 2(b), there was no peeling-off of the SinTaC layers and no damage to the underlying graphite substrates due to chemical corrosion by sublimed gases, although there were some cracks generated during the cooling process due to the thermal expansion mismatch between the crucibles (graphite material) and the grown SiC crystals (SiC single-crystal ingots or polycrystals adhered to the inner crucible wall). The weight deficit fractions [defined as (crucible weight deficit after growth)/ (crucible weight before growth)] with a SinTaC source container and a separator were nearly 0% (0.03 ± 0.03% and 0.0 ± 0.1%, respectively), while those with a graphite container and a separator were 0.2 ± 0.03% and 5.6 ± 0.1%, respectively. These results indicate that there was no weight deficit of the SinTaC crucibles after the growth process. On the basis of visual inspection and weight deficit results, the SinTaC crucibles had excellent reliability and durability under conventional SiC sublimation growth conditions. Although cracks due to thermal expansion mismatch hampered the repetitive use of these crucibles for multiple growth runs, this is avoidable by preventing the deposition of polycrystals on the inner wall through better control of the temperature distribution in the process. Moreover, SinTaC is potentially low-cost, and even single-use SinTaC crucibles might not significantly affect the production cost of SiC wafers.

A comparison of the colors of after-growth source powders in Figs. 2(b) and 2(d) reveals that the SinTaC source powder in the SinTaC container [Fig. 2(b)] had a blue-green surface, indicating suppressed carbonization of the powder, whereas the powder in the graphite container [Fig. 2(c)] was carbonized$^{17,18}$ As described in the supplementary data and later in this paper, the suppression of SiC source powder carbonization in the SinTaC crucibles can be attributed to a relatively Si-rich gas content in the SinTaC crucibles.

A comparison of the appearance of the grown crystals shown in Figs. 2(a) and 2(c) reveals that the SiC single-crystal ingot grown in a SinTaC crucible separated perfectly from the surrounding polycrystals, whereas the ingot grown in the graphite crucible adhered to them. Moreover, polycrystals were not observed on the SinTaC seed holder [Fig. 2(a)] owing to the peeling-off of the SiC polycrystals (which are thinner than those grown in graphite) during the after-growth cooling. This thinner polycrystal formation in the SinTaC crucibles can be attributed to the lower material yield for polycrystals, as discussed in the following sections, which enhanced single/poly crystal separation. Enhanced single/poly crystal separation is an advantage of using SinTaC crucibles for SiC wafer production, both in terms of crystal quality and production cost.

Figures 3(a) and 3(b) show photographs of cross-sectional specimens sliced out from the grown crystals shown in Figs. 2(a) and 2(c), respectively. The dark striations nearly parallel to the seed surface were nitrogen markers, used to indicate the shape of the growth front at 3 h growth intervals. Figure 3(c) shows plots of the time-dependent growth heights measured from the nitrogen markers. The dependence of the growth height $h$ on the growth duration $t$ can be precisely fit using the following equation, similar to Michaelis–Menten kinetics:\n
$$h = \frac{h_{\text{max}} t}{t_{\text{opt}} + t},$$

where $h_{\text{max}}$ is the maximum growth height after indefinitely prolonged growth and $t_{\text{opt}}$ is the optimum growth duration when the growth height reaches $h_{\text{max}}/2$ (here, we call this the optimum growth height). Equation (1) indicates that the growth height saturates after sufficient growth duration and approaches $h_{\text{max}}$, which is consistent with the well-known phenomenon of growth height saturation in SiC sublimation growth due to source exhaustion and thermal gradient decay with increasing growth duration.$^{14,20}$ Regression functions and their determination factors $R^2$ of the time-dependent growth heights fitted by Eq. (1) are shown alongside the legends in Fig. 3(c). The $R^2$ values are greater than 0.99,
Table I. Summary and comparison of maximum growth height, optimum growth duration, 24 h growth height (experimental value), 53.1 h growth height (extrapolated value), initial growth rate (growth duration of 0 h), and terminal growth rate (growth duration of 53.1 h, extrapolated value) between SinTaC and graphite crucibles. The errors represent one standard deviation.

| Crucible material | Maximum growth height $h_{\text{max}}$ (mm) | Optimum growth duration $t_{\text{opt}}$ (h) | Growth height after 24 h of growth (mm) | Growth height after 53.1 h of growth (mm) | Growth rate at 0 h of growth ($\text{mm/h}$) | Growth rate at 53.1 h of growth ($\text{mm/h}$) |
|-------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| SinTaC            | 56.8 ± 1.3                     | 53.1 ± 1.6                     | 18.1                           | 28.4 ± 1.1                     | 1.07 ± 0.06                     | 0.27 ± 0.01                     |
| Graphite          | 24.1 ± 1.5                     | 16.7 ± 2.0                     | 15.1                           | 18.4 ± 2.1                     | 1.45 ± 0.23                     | 0.08 ± 0.01                     |

indicating that the regression functions almost perfectly explain the time-dependent growth height. Table I shows the regression parameters $h_{\text{max}}$ and $t_{\text{opt}}$ for the growth height with SinTaC and graphite crucibles, the growth height after 24 h of growth, and the extrapolated growth height after 53.1 h (the optimum growth duration for the SinTaC crucibles) of growth. Next, we calculate the time-dependent growth rate $R_g$ using the following equation obtained by the differentiation of Eq. (1):

$$R_g = \frac{h_{\text{max}} t_{\text{opt}}}{(t_{\text{opt}} + t)^2}.$$  

The curves of the time-dependent growth rate calculated using Eq. (2) were added to Fig. 3(c) as bold lines. The initial growth rate at a growth duration of 0 h and the terminal growth rate at the optimum growth duration of 53.1 h were calculated using Eq. (2), and the resulting values are shown in Table I.

A comparison of the time-dependent growth heights with SinTaC and graphite crucibles in Fig. 3(c) reveals that the growth height with graphite crucibles is larger than that with SinTaC crucibles during the early stage of growth (0–12 h). After this early stage, the growth height with SinTaC crucibles overtakes that with graphite crucibles, and the difference in growth height increases with increasing growth duration. The growth heights tabulated in Table I show that the growth height after 24 h with SinTaC crucibles was larger than that with graphite crucibles by a factor of ~1.2, and after 53.1 h, the SinTaC growth height is estimated to be larger by a factor of ~1.5 (extrapolated value) than the graphite growth height. Furthermore, after infinitely prolonged growth, this factor is estimated to reach ~2.4. These differences directly result from the time-dependent growth rate [bold lines in Fig. 3(c)]. As shown in Fig. 3(c), the growth rates with SinTaC and graphite crucibles both decrease exponentially with increasing growth duration, plausibly owing to both the decay of the source gas supply with source carbonization and decreased supersaturation because of the thermal gradient decay as mentioned above. The differences are that the growth rate in the very early stages of growth with SinTaC crucibles is lower by a factor of ~0.7, but this factor increases over time to ~3 at a growth duration of 53.1 h. In other words, the decay of the growth rate is more gentle with SinTaC crucibles than with graphite crucibles.

There are three plausible causes for the differences in time-dependent growth rates between SinTaC and graphite crucibles, as follows.

1) Additional carbon supply from the bare graphite crucibles [due to reactions such as $2\text{Si(g)} + \text{C(s)} \rightarrow \text{Si}_2\text{C(g)}$ temporarily increases the growth rate.

2) Gas-tight SinTaC layers (without open porosity) suppress the leakage of sublimed SiC gas.

3) The lower thermal radiation emissivity of SinTaC surfaces modifies the temperature distribution around the growth zone. These mechanisms are schematically drawn in Figs. 1(a) and 1(b). To investigate these possible causes, we observed cross-sectional specimens by optical microscopy, as shown in Figs. 3(d) and 3(e), and also evaluated the material leakage fraction, the amount of sublimed SiC, the single-crystal material yield, and the poly-crystal yield from the crucible weight changes before and after growth, as summarized in Table II.

As evidence for cause (1), differences in the foreign particle distribution were clearly evident during the early stages of growth (3–6 h), as shown in Figs. 3(d) and 3(e). Figure 3(d) shows that the early-stage crystal grown with SinTaC contained a high density of droplet-like inclusions, which are most likely Si because their shape is almost identical to that of the Si droplets reported in Ref. 4. This indicates excessively Si-rich growth conditions during the early stages of growth owing to the absence of any carbon supply from the SinTaC crucibles themselves. To prevent the incorporation of Si droplets when using SinTaC crucibles, the intentional addition of a solid carbon source might be beneficial. On the other hand, Fig. 3(e) shows that the early-stage crystal grown with graphite crucibles contained no Si droplets, but a small number of carbon inclusions were...
present in the region grown at the very initial stage. This absence of Si droplets indicates that excessive Si vapor sublimated from the fresh SiC source powder and reacted with the graphite crucible, resulting in relatively C-rich growth conditions and temporarily enhancing the initial-stage growth rate due to the additional carbon supply from the graphite crucibles. Thus, the difference in initial-stage growth rate can be attributed to the absence or addition of a secondary carbon supply from the crucibles themselves.

As for cause (2), the data describing the material leakage out of the crucibles corresponds well to direct evidence. As summarized in Table II, the material leakage with SinTaC crucibles is smaller by a factor of ∼0.7 than that with graphite crucibles. In other words, material leakage via the open porosity of the graphite crucibles accounts for ∼30% of the total material leakage. In growth with gas-tight SinTaC crucibles, this material instead contributes to crystal growth. Therefore, the gas tightness of the SinTaC layers partly contributed to the higher growth rate with SinTaC crucibles after the initial stage of growth.

Regarding the proposed cause (3), the material yield data also corresponds to the available evidence. As summarized in Table II, because the amounts of sublimed gas supplied from the SiC source powder with both growth setups were almost equal, the true source temperatures and overall degrees of supersaturation for both setups were almost the same, as intended. Nevertheless, there are non-negligible differences in the material yields shown in Table II. The material yield for single-crystal growth with SinTaC crucibles was higher than that with graphite crucibles, while the material yield for polycrystal growth with SinTaC crucibles was lower than that with graphite crucibles. Therefore, we can realize a more efficient single-crystal growth by the simple and quick procedure of replacing conventional graphite crucibles with SinTaC crucibles, made using novel wet ceramic processes, were applied to bulk SiC sublimation growth. The advantages of using SinTaC crucibles in the growth process are as follows: (a) suppression of carbon inclusion incorporation and increased process robustness because they do not corrode under the employed growth conditions, (b) enhanced single- polycrystal separation and an accompanying improved crystal quality, and (c) higher growth rate and resultant larger crystal size along with lower material leakage and higher material yield. One disadvantage of using SinTaC in the growth processes is that the sublimed gas tends to be excessively Si-rich, resulting in the formation of Si droplets. To avoid Si droplets, the intentional reduction in the degree of supersaturation in the early-stage growth or the use of additional solid carbon sources might be beneficial. It was also confirmed that there was no significant contamination from the SinTaC crucibles to the grown crystals (see the online supplementary data at http://stacks.iop.org/APX/9/ 055507/mmedia). Finally, the application of SinTaC technology to SiC sublimation growth will help provide larger crystals and higher-quality wafers at a lower cost.

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In conclusion, low-cost and high-reliability SinTaC crucibles, made using novel wet ceramic processes, were applied to bulk SiC sublimation growth. The advantages of using SinTaC crucibles in the growth process are as follows: (a) suppression of carbon inclusion incorporation and increased process robustness because they do not corrode under the employed growth conditions, (b) enhanced single-poly crystal separation and an accompanying improved crystal quality, and (c) higher growth rate and resultant larger crystal size along with lower material leakage and higher material yield. One disadvantage of using SinTaC in the growth processes is that the sublimed gas tends to be excessively Si-rich, resulting in the formation of Si droplets. To avoid Si droplets, the intentional reduction in the degree of supersaturation in the early-stage growth or the use of additional solid carbon sources might be beneficial. It was also confirmed that there was no significant contamination from the SinTaC crucibles to the grown crystals (see the online supplementary data at http://stacks.iop.org/APX/9/055507/mmedia). Finally, the application of SinTaC technology to SiC sublimation growth will help provide larger crystals and higher-quality wafers at a lower cost.

Table II. Summary and comparison of the amount of sublimed SiC source [= (weight deficit of the SiC source powder and source container)], material leakage fraction [= (weight deficit of the entire growth setup)/(amount of sublimed SiC source)], material yield for single-crystal growth [= (weight of single crystal)/(amount of sublimed SiC source)], and material yield for polycrystal growth [= (weight of polycrystals)/(amount of sublimed SiC source)] in the sublimation growth of SiC with SinTaC and graphite crucibles.

| Crucible material | Amount of sublimed SiC (g) | Material leakage fraction (%) | Material yield for single crystal (%) | Material yield for polycrystals (%) |
|-------------------|---------------------------|------------------------------|--------------------------------------|----------------------------------|
| SinTaC            | 164.6                     | 23.5                         | 53.6                                 | 22.5                             |
| Graphite          | 168.5                     | 32                           | 43.8                                 | 27.3                             |

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