High-Throughput Screening of Si−Ni Flux for SiC Solution Growth Using a High-Temperature Laser Microscope Observation and Secondary Ion Mass Spectroscopy Depth Profiling

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ABSTRACT: Screening of Si-based flux materials for solution growth of SiC single crystals was demonstrated using a thin film composition-spread technique. The reactivity and diffusion of carbon in a composition spread of the flux was investigated by secondary ion mass spectroscopy depth profiling of the annealed flux thin film spread on a graphite substrate. The composition dependence of the chemical interaction between a seed crystal and flux materials was revealed by high-temperature thermal behavior observation of the flux and the subsequent morphological study of the surface after removing the flux using atomic force microscopy. Our new screening approach is shown to be an efficient process for understanding flux materials for SiC solution growth.

KEYWORDS: high-throughput screening, SiC solution growth, pulsed laser deposition, high temperature laser microscope
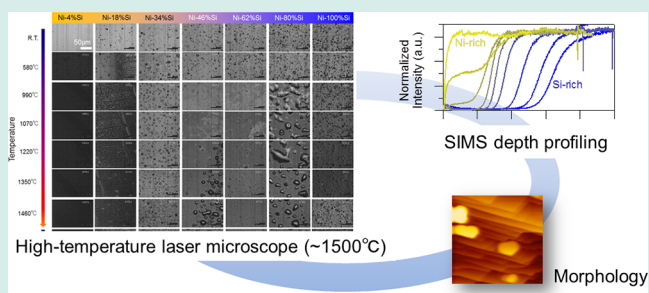
1. INTRODUCTION

Silicon carbide (SiC) has attracted much attention for applications in high temperature and high power electric devices because of its wide band gap, high electrical breakdown field, and high thermal conductivity. SiC single crystals commercially available at present are grown by the sublimation of SiC powder which requires extremely high temperatures, typically above 2000 °C, making it an expensive process. Solution growth, an alternate method to sublimation, has been tried owing to its relatively lower growth temperature than that of the sublimation method. However, its low carbon solubility in a Si melt at such low temperatures makes it difficult to obtain a SiC single crystal with a high growth rate. To overcome this problem, multi component flux systems of Si-X (X is metal such as X = Sc[1], Ti[2,3], Cr[4], Fe[5], Ge[6], etc.) have been attempted.

Typically, solution growth of SiC single crystals is carried out using a dipping method in which a SiC seed crystal is dipped into a Si-X flux melt in a graphite crucible as a carbon source. The process of crystal growth can be roughly broken down into the following steps: (1) supply of carbon into the flux melt from the graphite crucible, (2) diffusion and convective transport of the carbon in the flux melt, (3) crystallization at the SiC seed crystal. Despite the importance of understanding these processes, there are still few useful data on their thermal

behaviors and carbon solubility of flux materials, especially for multi component systems because one-by-one growth of bulk SiC single crystals is a time-consuming work to screen the composition with the resultant increase of complexity of the flux component.

In this study, we propose a new approach for high throughput screening of flux materials for SiC solution growth while obtaining the information using a thin film combinatorial method.[7] Recently, adding Ni component into Si−Ti flux was found by this method to be possibly effective for 4H-SiC growth;[8] however, it has not been fully understood how the flux works. Therefore, we chose the Si−Ni system as a target in the present study. We employed a thin film combinatorial pulsed laser deposition (PLD) technique to prepare composition spread thin films of the Si−Ni flux, not only on a SiC single crystal substrate but also on a polished graphite substrate. A secondary ion mass spectroscopy (SIMS) depth profiling technique was used to estimate carbon diffusivity in the flux thin films. High-temperature vacuum laser microscope (LM)
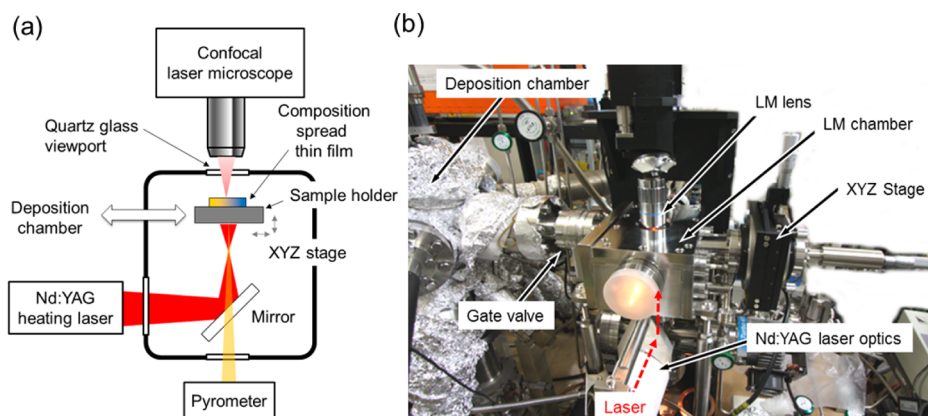
Figure 1. Schematic illustration (a) and photograph (b) of Nd:YAG laser heating high temperature laser microscope chamber.

was developed for observing the thermal behaviors of the flux materials in vacuum at high temperatures up to 1600 °C.

2. EXPERIMENTAL SECTION

Composition spread thin films of Si−Ni (~130 nm) were deposited by PLD with a moving mask in front of the Si-face 4H-SiC (0001) and hand-polished graphite substrates.[7] Pure Si and Ni targets were ablated by a KrF excimer laser (248 nm) at a repetition rate of 15 Hz and an energy density of 4.8 J/cm^2 in high vacuum (<1 × 10^{-6} Torr) at room temperature. Composition of the thin film was determined by electron probe microanalysis (EPMA) on the graphite substrate.

To observe thermal behaviors of Si−Ni flux thin films at high temperatures above 1000 °C a laser heating high-temperature vacuum LM has been developed based on our original set up of the ultrahigh vacuum LM as was reported previously.[9] A schematic illustration, along with a photograph of the chamber, is shown in Figure 1. A thin film sample mounted on a carbon sample holder (15 mm × 15 mm × 2 mm) with carbon paste was heated by a Nd:YAG laser from the back side of the sample. The temperature of the sample was estimated from the holder temperature monitored by the pyrometer, whose accuracy had been calibrated by the experiment using a thermocouple in advance. The maximum temperature of the sample is up to 1600 °C in vacuum, and rapid heating and cooling processes are realized owing to its small heat capacity. We observed the Si−Ni composition spread thin film at each position on the spread during the heating under high vacuum. After the high-temperature LM observation, the flux thin film was removed with a HF:HNO$_3$ (1:1) solution. Then, the surface morphology of the SiC crystal was observed by atomic force microscopy (AFM). Time of flight SIMS was used to characterize carbon diffusion from the graphite substrate into the Si−Ni composition spread thin film before and after annealing at 900 °C for 20 min in 300 sccm argon flow. This temperature is lower than all solidus lines of the Si−Ni bulk phase diagram.[10] Raman spectroscopy was used to investigate the graphite formation at the interface of Si−Ni flux and SiC substrate.

3. RESULTS AND DISCUSSION

Figure 2a shows a set of SIMS depth profiles of ^{12}C$^-$ intensity for different flux compositions in the Si−Ni composition spread thin film on the graphite before and after annealing at 900 °C. Each ^{12}C$^-$ intensity was normalized at the corresponding intensity that became constant where the sputtering reached
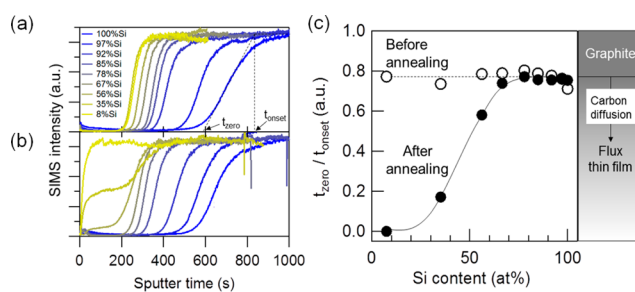

Figure 2. SIMS depth profiles of ^{12}C$^-$ intensity normalized at the corresponding intensity that became constant where the sputtering reached the substrate for Si−Ni composition spread thin film on a graphite substrate before (a) and after (b) annealing. (c) Composition dependence of t_{zero}/t_{onset} before and after annealing reduced from (a) and (b) (see detail in the text).

the substrate. To normalize the composition dependent sputtering rate, we defined a set of two specific sputtering times: t_{onset} at which the sputtering reached the interface of the graphite substrate and the flux thin film, and t_{zero} at which the carbon atoms that had diffused from the graphite substrate were first detected, as shown in the Figure 2a. Then, we take the ratio of t_{zero} to t_{onset} as a quantitative indicator of the carbon diffusivity. The smaller value of t_{zero}/t_{onset} indicates the broader interface between the flux and the graphite substrate, that is, the higher carbon diffusivity. The composition dependence of t_{zero}/t_{onset} values before and after the annealing revealed that the carbon diffusion was significantly enhanced for Ni-rich flux regions as shown in Figure 2c.

Figure 3 shows a set of high-temperature LM images of another Si−Ni composition spread thin film on a 4H-SiC substrate during elevated temperature in vacuum. First, it is noted that dark spots at Si rich compositions in the as-deposited film at room temperature were Si droplets formed by the PLD ablation process, which was confirmed by EPMA. From under 600 °C, the LM image for Ni rich flux films (<~18%Si) turned dark. Since the LM is imaging the reflection intensity of the incident laser from the sample and the brightness of images thus reflects the flatness of the sample surface, this intensity change suggests that the surface of the thin film flux became rough. The roughness increase is not due to the melting of flux thin film because the lowest bulk eutectic point is ~964 °C from the known Ni−Si binary phase diagram,[10] but can be attributed to the interfacial reaction of the flux with SiC, resulting in graphite formation, as is
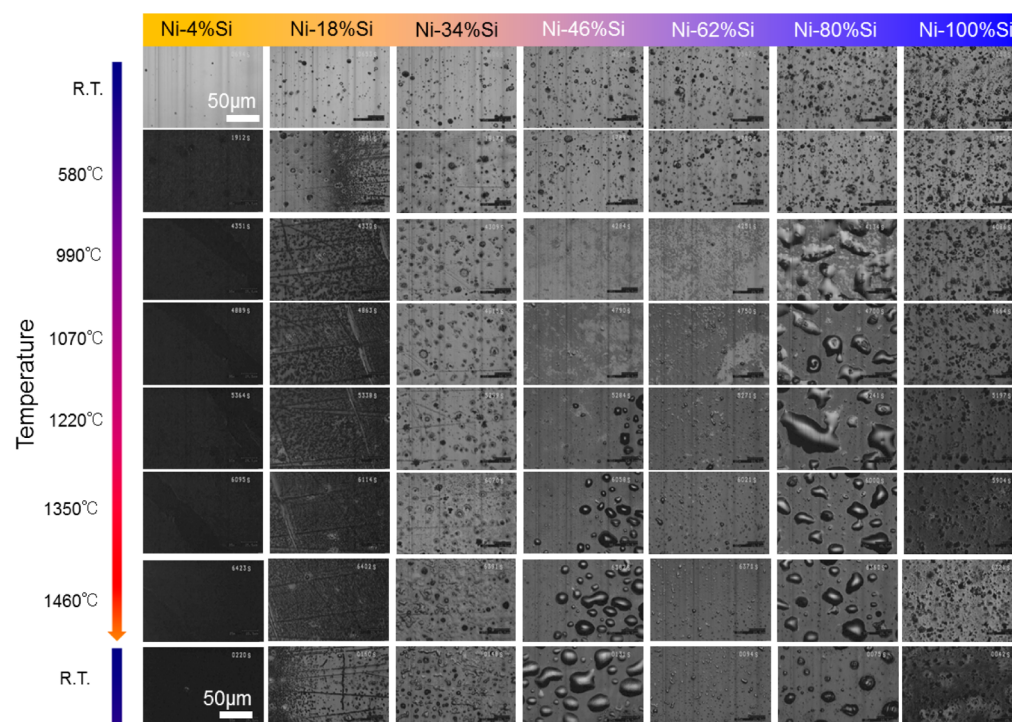
Figure 3. High-temperature LM images of the Si−Ni composition spread thin film on the 4H-SiC substrate during elevated temperature in vacuum.

suggested by the calculated Ni−Si−C ternary phase diagram.[11,12] This is supported by Raman spectra taken after removing the flux thin film, showing graphite peaks appearing at sample regions where the Ni-rich (<∼18%Si) film was contacting with the SiC substrate (Figure 4). When we heated
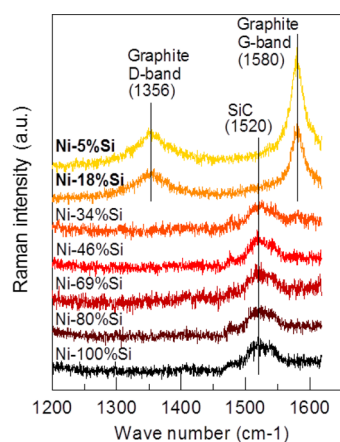

Figure 4. Raman spectra of the sample observed by high-temperature LM taken after removing the Si−Ni flux thin film by wet etching.

to around 1000 °C, the flux thin film started to melt and form liquid droplets in the composition regions of Ni-40%Si to nearly 100%Si. This temperature almost coincides with the solidus line of the Ni−Si binary phase diagram.[10] However, the droplet sizes were not uniform over the regions because of the different wettability of these liquid phases[12,13] on the sample surface. Depending on the starting composition of the melt flux, different liquids and solid precipitates will be formed with melting. Ni-34%Si and pure Si regions showed a notable change in their morphology, and the formation of droplets was

observed at ∼1350 °C and ∼1460 °C, respectively, which were both consistent with the melting point of these compositions.

Next, we turn to the AFM morphological study of the sample surface from which the flux thin film had been removed by wet etching after being observed by LM at high temperature (∼1500 °C) in Figure 3. The sample region where the Ni-4%Si flux film was deposited shows a very rough surface due to the graphite formation reaction at the interface of the flux and SiC (Figure 5a). On the other hand, a pure Si flux region (Figure
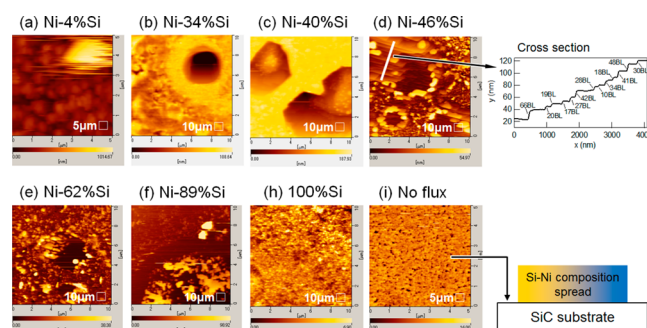

Figure 5. AFM morphologies of the sample surface observed by high-temperature LM taken after removing the Si−Ni flux thin film with different compositions (a)−(h) and the SiC surface on which the flux is not deposited for a reference in the same spread sample (i).

5h) has a smooth surface with a root-mean-square (RMS) roughness of ∼1.1 nm. The value is comparable to that of the SiC surface on which the flux is not deposited for a reference in the same spread sample (RMS = 1.9 nm, Figure 5i), indicating no significant reaction with SiC. In the middle composition of Ni-34%Si to Ni-62%Si, the anisotropic etching which reflects the hexagonal crystal structure of SiC was observed at the local places where the flux droplet probably had existed at the temperatures below the heating temperature applied to this

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sample (Figure 5b–e). Some of these places show clear step and terrace structures with several ten bilayer height of 4H-SiC (Figure 5d), which can be considered as an epitaxial ready surface for the following SiC crystal growth. These AFM morphological investigations of the interface of composition spread flux thin film and SiC substrate revealed that etching of the SiC substrate could be controlled by choosing a suitable composition of flux. This result may provide us important information not only on the process of crystallization during solution growth, in which the cycle of etching and crystallization is repeated many times almost under the thermodynamic equilibrium condition, but also on the meltback process of a seed SiC crystal surface immediately prior to the solution growth which is typically carried out to remove defects on the initial seed crystal surface and to prepare a fresh surface before a growth.

4. CONCLUSIONS

A new approach of high-throughput screening of flux materials for SiC solution growth has been proposed. A combination of composition spread thin film synthesis with SIMS depth profiling, originally developed for high temperature LM and AFM morphology observations, has been proven to be very efficient for understanding not all but some of the important parts of SiC solution growth processes as follows: (1) carbon diffusion was found to be much more enhanced in the Ni-rich flux composition even in the solid state, and (2) anisotropic etching of SiC was observed in the middle composition around Ni-34%Si to Ni-62%Si. Further studies including the comparison of our results obtained by the present approach with those of bulk SiC solution growth are needed to provide a more useful guideline for choosing the best flux materials.

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Notes
The authors declare no competing financial interest.

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