Screening of metal flux for SiC solution growth by a thin-film combinatorial method

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Abstract

4H-SiC is a wide-bandgap semiconductor with potential applications in power devices. The lack of a liquid phase in SiC hinders conventional crystal growth from the melt; consequently, SiC wafers still have low quality and are nearly 100 times more expensive than Si wafers. To take advantage of the solution growth for improving the quality and reducing the cost of SiC, Ni addition to Si–Ti flux has been investigated. A combinatorial approach was employed to accelerate the screening of metal flux for the SiC solution growth.

Keywords: SiC, solution growth, flux materials, combinatorial

1. Introduction

The 4H polytype of silicon carbide (4H-SiC) is an attractive wide-bandgap semiconductor material for high-power devices owing to its high breakdown electric field and stability at high temperatures. However, SiC wafers are still low in quality and nearly 100 times more expensive than Si wafers. Since there is no liquid phase in the Si–C phase diagram, a sublimation method (temperatures ∼2400 °C) has been mainly employed for fabricating SiC wafers [1]. Although extensive efforts have been made to reduce crystal defects in SiC, it contains many more dislocations than Si and GaAs, typically ∼10⁴ cm⁻². Moreover, the so-called ‘device killer defects’, which result in a large leakage current and/or low breakdown voltage, need to be eliminated from the SiC device fabrication process.

The growth of SiC from binary Si-rich Si–C solutions has been investigated to take advantage of its thermal equilibrium conditions [2]. Although the reduction of dislocation density has been reported in the solution-grown SiC, the growth rate was low owing to the low carbon solubility, and high temperatures were required when using a binary Si–C solution. Recently, the addition of Ti and/or Sc metals to Si–C solution has been found to help increase the rate and decrease the temperature of 6H-SiC growth [3, 4]. However, in 4H-SiC growth with ternary Si–Ti–C solution, 6H-SiC would be included if growth rate is not kept low enough.

In this study, we propose adding Ni to the Si–Ti alloy for growing 4H-SiC. To find the optimum flux composition, we applied the thin-film combinatorial screening method aiming at both high growth rate and polytype control in the SiC solution growth. The combinatorial technique is an efficient method to create large composition libraries of materials and systematically test these compositions for specific properties of interest, as opposed to the time-consuming one-composition-at-a-time approach [5–7].

2. Experimental details

To realize the solution growth of a single 4H-SiC phase at low temperature and high rate, the flux metal material was selected from the phase diagrams by comparing the formation Gibbs energies of metal carbides. We considered the following criteria: (i) the Si-metal solution exists below 1600 °C, (ii) the carbon concentration in flux solution is higher than that in the Si–Ti solution, and (iii) the formation Gibbs energy is higher for metal carbide than for SiC. From this screening, Fe, Mn and Ni were selected, with Ni being the first candidate owing to its resistance to oxidation.
Figure 1. (a) Schematic of triangle mask movements for depositing Si–Ti–Ni flux composition spread. (b) Typical optical microscopy image of the spread (15 mm²).

Figure 2. Schematic of composition spread with measured areas marked by letters a to o.

Figure 3. SEM image of precipitates in area-a.

Figure 1(a) shows a schematic of the triangle mask movements for preparing a ternary combinatorial composition spread on a 4H-SiC substrate by pulsed laser deposition (PLD). A thickness gradient was achieved by moving the masks continuously during the deposition. Commercial 4H-SiC, 8° off-axis, silicon-face substrates were used in these experiments. Firstly, a gradient poly-Si layer (200–300 nm) was deposited by PLD using the triangle line masks, either directly on SiC or on a uniform poly-Si layer formed on the SiC substrate by liquid-phase chemical vapor deposition. Then, Ti and Ni thickness-gradient films (0–120 nm) were deposited on the Si layer using the triangle mask. Finally, a uniform poly-SiC capping layer (100–300 nm) was formed. All the gradient layers were deposited using a KrF excimer laser (248 nm) at a repetition rate of 10–100 Hz and an energy density of 5 J/cm², under ambient pressure of 1 × 10⁻⁵ Pa at room temperature. After the deposition, the sample was annealed at 1200°C for 20 min in Ar flow to induce either a traveling solvent reaction and/or solid-state reaction. Then, the flux layer was removed from the SiC substrate by etching with a mixture of HF and HNO₃ acids. The deposited SiC layer was examined by optical microscopy, scanning electron microscopy (SEM) and micro-Raman microscopy in backscattering configuration.

3. Results and discussion

Figure 1(b) shows a typical optical image of the Si–Ti–Ni composition-spread sample. The top of the triangle was set to be pure Si and the baseline corresponded to a total metal content of 40%. The vertical or slanted lines represent typical ternary flux metal contents and the horizontal lines indicate the total metal content in the flux material. Figure 2 shows a schematic of the composition spread with the measurement areas labeled from a to o. Figure 3 shows a typical SEM image (20 000×) of area a revealing a surface covered with hexagonal precipitates.
Figure 4. (a) Typical Raman spectrum of 4H-SiC precipitates at area-c, together with reference 4H-SiC and 6H-SiC spectra. (b) Map of FTO(0):(Ib) to FTO(2/4):(Ia) Raman intensity ratio at area-h.

Figure 5. (a) Coverage of 4H-SiC precipitates, and (b) spatially averaged Ib/Ia Raman intensity ratio plotted versus Ni/(Ni + Ti) fraction, for different ratios of metal flux to total Ni + Ti + Si content.

An example of the Raman spectrum of precipitates at area-c is shown in figure 4(a), together with reference 4H and 6H-SiC spectra. The precipitates are made of 4H-SiC and exhibit the characteristic transverse optical (FTO) peaks: FTO(2/4):(Ia) peak at 776 cm$^{-1}$ and FTO(0):(Ib) peak at 796 cm$^{-1}$ [8]. Similar Raman spectra were observed at all the measured points, revealing that pure 4H-SiC was precipitated at any flux composition.

Figure 4(b) is an example of micro-Raman spectral mapping of the FTO(0):(Ib) to FTO(2/4):(Ia) peak intensity ratio at area-h. The higher value of this ratio corresponds to a lower crystallinity of SiC, e.g. due to stacking faults [9]. By spatially averaging this intensity ratio, the crystallinity of SiC was evaluated for each area from a to o.

In figure 5, (a) the coverage ratio of the 4H-SiC precipitates, and (b) the averaged Ib/Ia Raman intensity...
ratio are plotted as functions of Ni content represented as a Ni/(Ni + Ti) fraction, for different ratios of the metal flux to the total Ni + Ti + Si content. The precipitates coverage ratio tends to increase with Ni content, irrespective of the metal flux ratio to the total, although a slight decrease is observed at a Ni content of 0.5. This increase in the precipitates coverage ratio might correspond to an increase in the growth rate. Therefore, as shown in figure 5(a), the 4H-SiC growth rate is expected to increase with the Ni content in the metal flux. In figure 5(b), the Ib/Ia ratio remains constant reflecting no dependence of the SiC crystallinity on the Ni content. The large scatter at the Ni content of 0.5 for various total metal contents might be due to the existence of a refractory phase such as Ni₄Si₇Ti₆ around the Ni : Ti = 50 : 50 composition, making the liquid phase unstable at this process temperature [10]. This is an advantage of the thin-film combinatorial method, where these phenomena can be detected continuously throughout vastly varying compositions, compared with the conventional bulk growth. Further evaluation might yield a phase-diagram-like map.

On the other hand, etched areas are observed at a high Ni content (figure 6(a)). SEM and Raman spectroscopy revealed that the surface was partially bunched, and other precipitate types were found. The Raman spectra of two precipitates are shown in figure 6(b), one is the usual 4H-SiC and the other is graphite identified via characteristic peaks called D-band and G-band. The appearance of graphite in the etched area suggests different elution mechanisms for the solution growth of 4H-SiC with and without Ni addition. The elution in the Si–Ti solution proceeds through TiC, which is a possible origin of the 6H-SiC inclusions. The different elution mechanisms in the Si–Ti–Ni solution may suppress the formation of 6H-SiC, resulting in the better crystallinity of the precipitated 4H-SiC. According to our preliminary bulk growth results, the 6H-SiC inclusions were observed upon addition of pure Ti, but not for Ti with Ni, suggesting that high-quality pure 4H-SiC single crystals can be grown using a Si-Ti-Ni flux. The details will be reported elsewhere.

4. Conclusions

We have demonstrated a new method of high-throughput screening of metal flux for SiC solution growth using a thin-film combinatorial method, and the reported results suggest a flux candidate for the solution growth of 4H-SiC. We investigated the ternary Si–Ti–Ni system at 1200 °C and found that the amount and crystalline quality of 4H-SiC precipitates increase with Ni content. A different elution mechanism of SiC upon Ni addition was suggested, which may affect the polytype control in the SiC growth. The combination of Ni and Ti as a flux material might also be suitable for the bulk 4H-SiC growth from the melt.

References

[1] Avrov D D, Bulatov A V, Dorozhkin S I, Lebedev A O and Tairov Y M 2008 Semiconductors 42 1450
[2] Rendakova S V, Nikitina I P, Tregubova A S and Dmitriev V A 1998 J. Electron. Mater. 27 292
[3] Yashiro N, Kamei K, Kusunoki K and Yauchi A 2007 Mater. Sci. Forum 556 303
[4] Kusunoki K, Kamei K, Okada N, Yashiro N, Yauchi A, Ujihara T and Nakajima K 2006 Mater. Sci. Forum 527 119
[5] Koinuma H and Takeuchi I 2004 Nat. Mater. 3 429
[6] Matsumoto Y, Takahashi R and Koinuma H 2005 J. Cryst. Growth 275 325
[7] Takahashi R, Kubota H, Murakami M, Yamamoto Y, Matsumoto Y and Koinuma H 2004 J. Comb. Chem. 6 50
[8] Nakashima S and Harima H 1997 Phys. Status Solidi a 162 39
[9] Nakashima S, Nakatake Y, Ishida Y, Takahashi T and Okumura H 2001 Physica B 308–310 684
[10] Hu X, Chen G, Ion C and Ni K 1999 J. Phase Equilib. 20 508