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Microstructural analysis of single crystal SiC prepared by novel liquid phase epitaxy

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Abstract

Single crystal SiC has been synthesized by a novel liquid phase epitaxy using mixture of (Sm:Co) as unique solvent. The synthesized high quality crystals have been characterized by field emission gun scanning electron microscopy and field emission gun transmission electron microscopy. The above analysis shows the epitaxial growth of single crystal SiC along [1 1 1] direction parallel to the Si wafer, followed by polycrystalline 3C–SiC and 6H–SiC whiskers. The formation mechanisms of single crystal SiC and SiC whiskers have been proposed.

Keywords: Microstructure; Liquid phase epitaxy; Solvents; Semiconducting materials

1. Introduction

Silicon carbide (SiC) is a wide band gap semiconductor which has received a great interest for many potential high-technology applications [1,2]. It has drawn attention as a potential hopeful material to replace Si. Sublimation method [3] and chemical vapor deposition (CVD) [4–8] method are the most common techniques for growing 3C–SiC. The growth of 3C–SiC on Si substrates using CVD has great economic advantages over sublimation method due to its large-area formation and high productivity. To prepare SiC single crystal semiconductor devices, liquid phase epitaxial (LPE) growth is more preferable than the conventional CVD method because of the low operating temperature, high growth rate and low impurity level. The first choice of solvent for liquid phase epitaxy would be Si, since this is a component of SiC and high purity Si is commercially available. However, Si exhibits high melting point (1411 °C), low solubility in C and use of this solvent inhibits high growth temperature (1600–1800 °C) and low growth rate. Kumagawa et al. [9] used Cr as solvent for LPE growth of SiC. Although the growth rate was very high (210 μm/h) but it is not convenient due to high operating temperature (1650 °C). The growth of 4H–SiC by low-temperature liquid phase epitaxy was studied by Jacquier et al. [10] in Al rich Al–Si melts. They observed low growth rate and high reactivity of the melt with graphite at temperature above 1200 °C. Sc–Si was used as solvent by Syväjärvi et al. [11] in a sandwich configuration. They found that the growth rate was exceeding 300 μm/h but the growth temperature was very high (1700–1850 °C). Mauk et al. [12] reported an experimental survey of metal solvents for low-temperature liquid-phase epitaxy (LPE) of SiC on 6H–SiC substrates. According to them, the most promising solvents for low-temperature (900–1200 °C) LPE include Ga, Sn, Ga/Sn, Ni, Cu, and Zn–Al. The purpose of the metal solvent is to increase the solubility of the carbon, thereby facilitating faster growth rates, thicker SiC layers and lower growth temperatures. Several growth mechanisms have been proposed by several authors for growth of SiC crystal. Among them, vapor–liquid–solid (VLS) is the well known mechanism for SiC growth reported by [13–15].

The alloy consisting of rare earth element Sm and transition element Co, i.e. (Sm:Co = 64:36) at % exhibits eutectic point

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(<600 °C) from the phase diagram of Sm–Co [16]. The choice of this solvent has the following advantages, which can be described as:

(1) Both Sm and Co can dissolve in C and Si.
(2) Sm, Co, C and Si are hard to react with one another.
(3) C has high solubility in Sm.

In the present study, Sm–Co powder mixture and thin film of Sm–Co with composition (Sm:Co = 64:36) at % prepared by co-sputtering process have been used as solvent for liquid phase epitaxial growth of SiC. High quality SiC single crystals have been prepared on Si wafer using this low temperature liquid phase epitaxy. The SiC prepared using (Sm–Co) thin film as a solvent has been submitted elsewhere for publication [17]. The experimental procedure, microstructure and possible growth mechanism of SiC prepared using Sm–Co powder as solvent have been presented here.

2. Experimental

Mixture of Sm and Co powder with composition (Sm:Co = 64:36) at % was put in a graphite mold. Si (1 1 1) wafer was placed on this solvent. Before placing, the Si (1 1 1) wafer was subjected to standard cleaning procedures using trichloroethylene, acetone, isopropanol, hydrofluoric acid and de-ionized water. Then the whole assembly was heated up to 1300 °C in vacuum furnace to melt the Sm:Co. Annealing was carried out with a heating rate of 5 °C/m with holding time of 2 h. Ar gas was flowing with a rate of 40 sccm and the pressure of the chamber was maintained at 1 atm. The temperature gradient between the lower and upper surface of the solvent was maintained in the range of 10–15 °C. After furnace cooling, the as formed SiC wafer was subjected to etching by hydrofluoric acid (HF) and nitric acid (HNO_3) to remove the contamination of solvent. The as-formed SiC wafer was characterized by field emission gun scanning electron microscopy (FEG-SEM, XL-40 FEG) and field emission gun transmission electron microscopy (FEI, Tecnai G2, F20, Netherlands).

3. Results and discussion

The schematic view of surface topography of the as-formed SiC film deposited on Si wafer at 1300 °C is shown in Fig. 1(a). It is observed that the schematic view consists of 4 regimes with different morphology. In regime 1, SiC grows densely in the center of the sample. From TEM microstructure observation of SiC in regime-1, the grain size is found to be around 200 nm (Fig. 1(b)). The electron diffraction pattern (Fig. 1(c)) recorded on regime 1 along [0 1 1] zone axis and high resolution (HR)

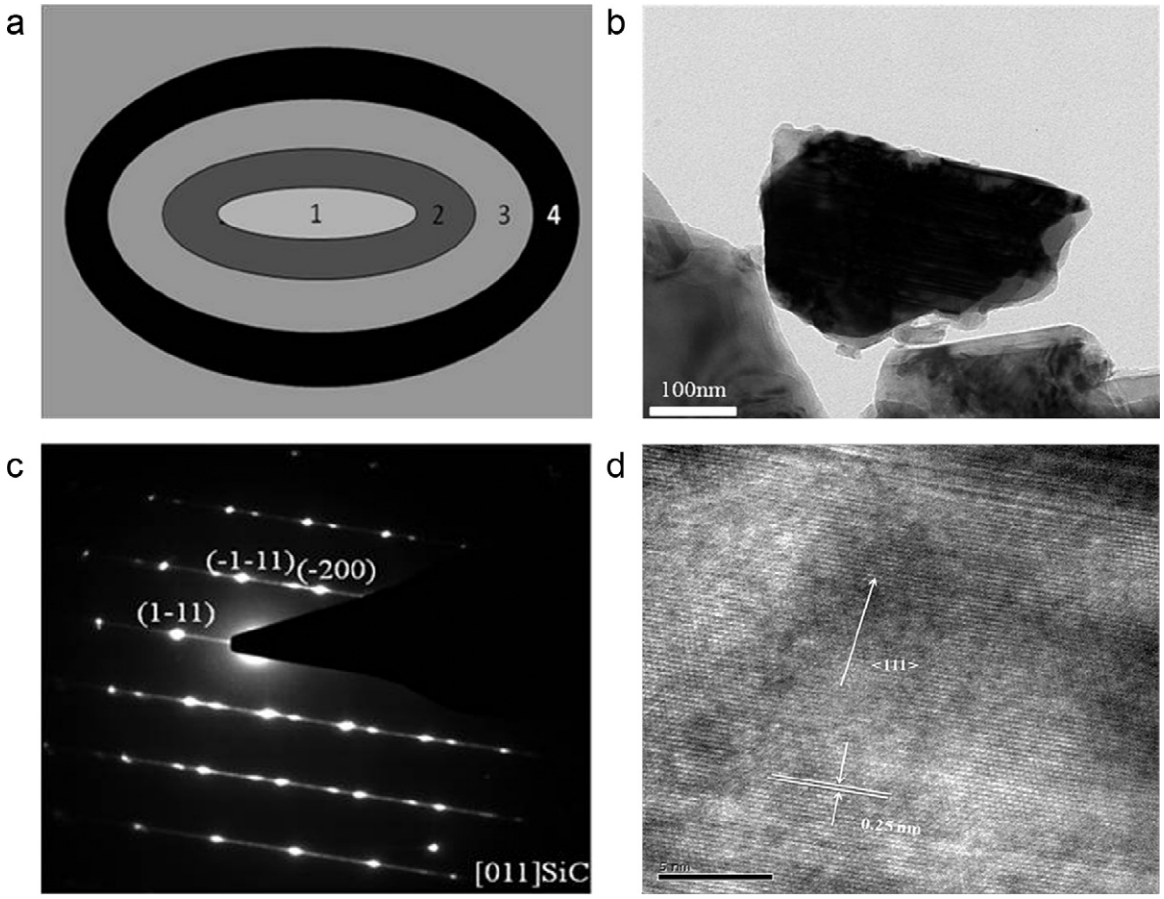

Fig. 1. Surface topography of the SiC film deposited on Si wafer at 1300 °C. (a) Schematic diagram of the SiC, (b) TEM image, (c) diffraction pattern and (d) HR image of the SiC grain grown in regime 1.

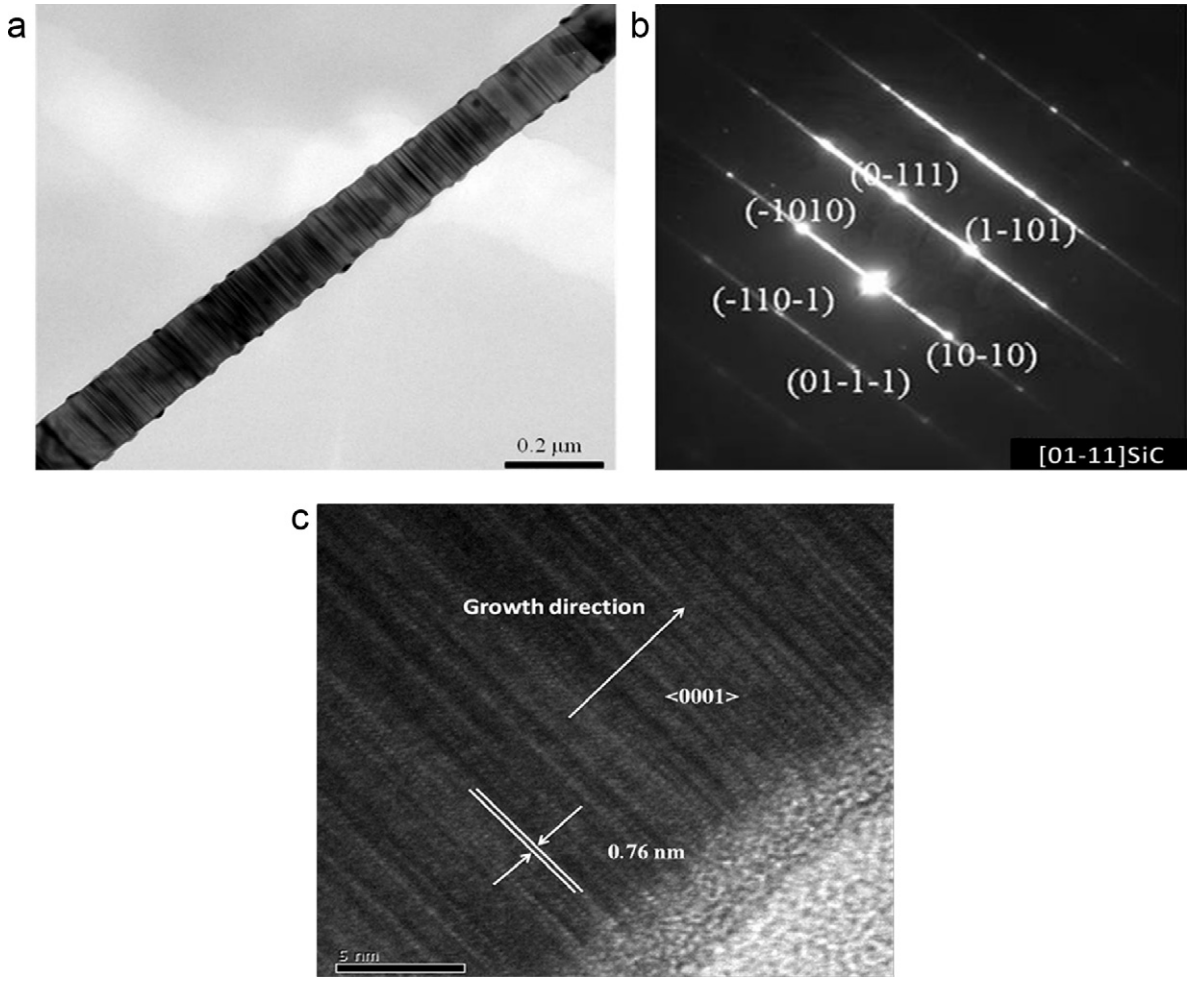

Fig. 2. TEM morphologies and diffraction pattern of SiC rod grown in regime-4 (a) TEM image, (b) diffraction pattern and (c) HRTEM image.

electron microscope (HRTEM) image shown in Fig. 1(d) confirm that the SiC is single crystalline in nature i.e. 3C–SiC with a growth along <1 1 1> direction accompanied with lattice spacing of 0.25 nm. Regimes 2 and 3 consist of SiC grains with some porous structures, which are not shown here.

The outermost part of the sample (regime 4) contains the ensemble of SiC rod like structures. Fig. 2(a) shows the typical TEM microstructure observation a SiC rod grown in regime 4. A clear elongated structure of SiC rod with length exceeds 800 nm is observed. The electron diffraction pattern (Fig. 2(b)) recorded on regime-4 along [0 1 −1 1] zone axis and its corresponding HRTEM image (Fig. 2(c)) also further confirm the SiC to be rod/whisker like structure i.e. 6H–SiC with growth direction along <0 0 0 1>. The closest packing direction for 6H–SiC is in <0 0 0 1> and its energy is lowest along this direction, which has been reported by several studies [18,19].

Fig. 3(a) shows the TEM cross sectional image of SiC film deposited on Si wafer. Epitaxial growth of single crystal 3C–SiC is clearly observed over the Si wafer. There is formation of silicon oxide (SiO_2) shown as white pattern followed by polycrystalline 3C–SiC. Interfacial image between Si and SiC, and between single crystal 3C–SiC and polycrystalline 3C–SiC are shown in Fig. 3(b) and (c) respectively. The diffraction patterns of Si, single crystal 3C–SiC and polycrystalline 3C–SiC are shown in Fig. 3(d)–(f) respectively. Such type of transformation from single crystal to polycrystalline SiC is in accordance to the ratio of C/Si. The gradual change in the ratio of C/Si leads to Si wafer to become single crystal SiC. If the C/Si ratio changes violently, epitaxial film of SiC becomes polycrystalline SiC [20]. The high magnification SEM image showing the plane view of the SiC film is given in Fig. 4. It is observed that the SiC whiskers and SiO_2 are formed over polycrystalline 3C–SiC. The low magnification SEM image is not shown here as it does not any clear information about the morphology of the sample.

The metal solvent (Sm:Co) melts during the sintering process and convert to liquid phase. The silicon wafer floats on this liquid as the density of silicon is less than a quarter of the molten alloy. With the silicon wafer floating on molten liquid, both silicon and graphite dissolve into the liquid. As the Si wafer base temperature is low, the C atoms from graphite diffuse to Si surface, and then substitute for the Si sites and grow to solid SiC films. During the sintering process, the temperature gradient across the solvent was maintained transversely caused by cooling Ar gas, which results different surface morphology between middle and outside the sample.

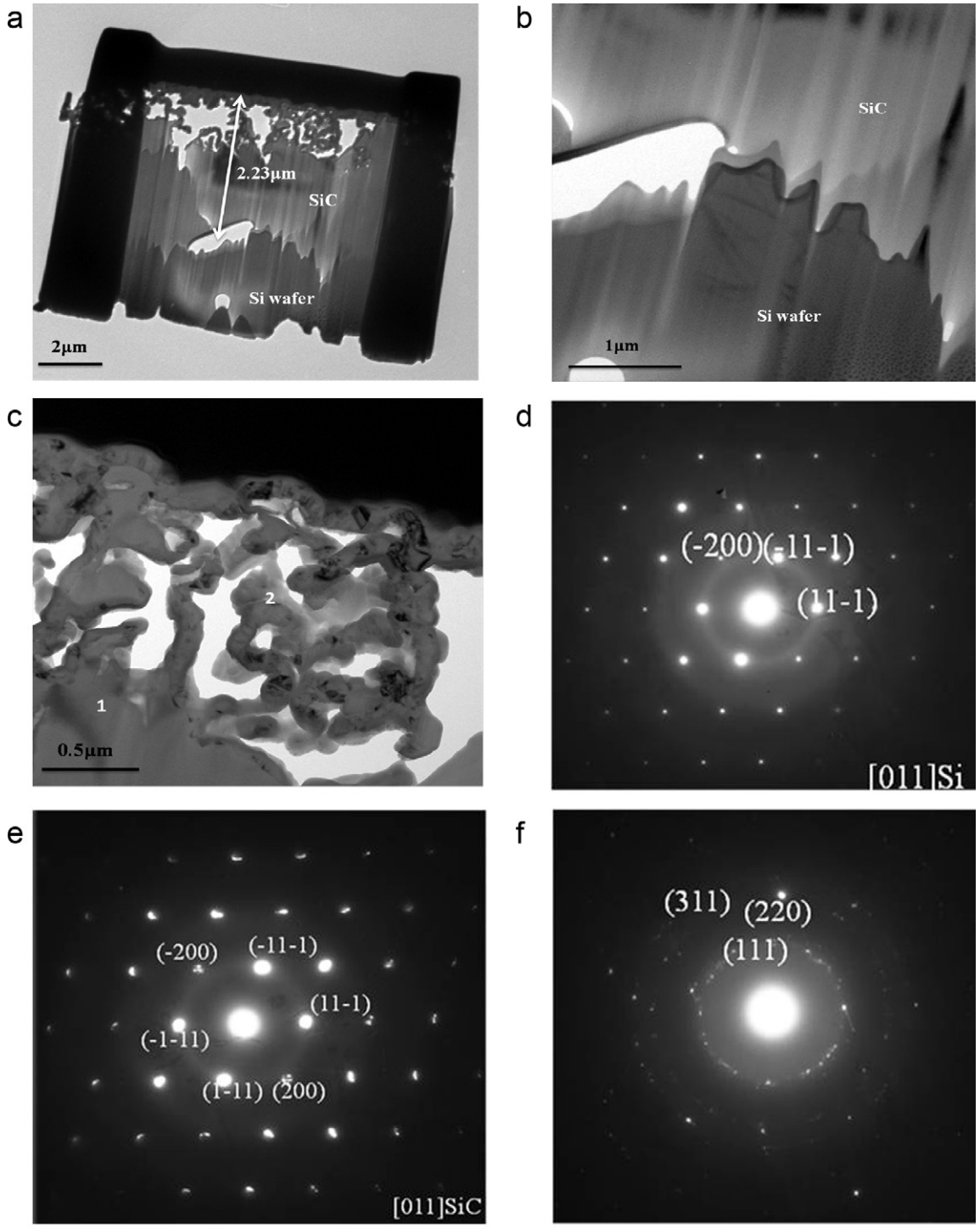

Fig. 3. The TEM cross section image of (a) SiC film on Si wafer; interfacial image between (b) Si and SiC, (c) single and polycrystalline SiC; diffraction pattern of (d) Si, (e) single crystal 3C–SiC and (f) polycrystalline 3C–SiC.

Some regime of the sample grows from liquid phase and some regime grows from vapor phase. The single crystal SiC is supposed to form from liquid phase and SiC whiskers are from vapor–solid (VS) process.

In VS process, the Si turns to vapor phase at 1300 °C, which is close to the melting pointing of Si and mix with the oxygen present there to form gaseous silicon oxide (SiO). Solid carbon from graphite crucible reacts with silicon oxide gas and form solid SiC whiskers by the following equation [21]:

$$2SiO(g) + 2C(s) \rightarrow 2SiC(s) + O_2(g) \quad (1)$$

In another way, the SiO_2 present on SiC observed in Fig. 3 also produces SiC whiskers by the following multi step process [22].

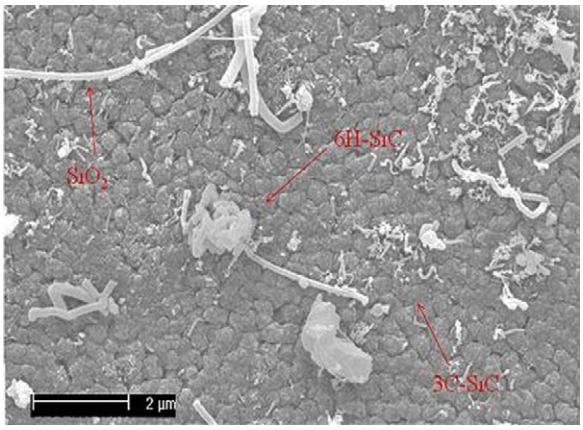

Fig. 4. High magnification SEM Image of the SiC film (plane view).

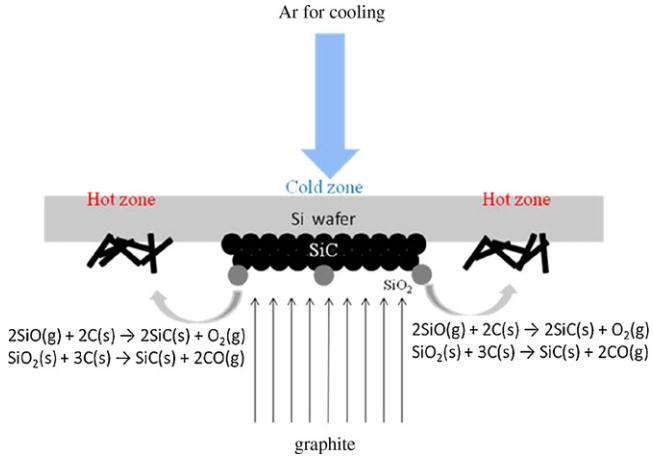

Fig. 5. Schematic diagram showing the growth mechanism of 3C–SiC and 6H–SiC whiskers.

At 1300 °C, SiO_2 decomposed to SiO and oxygen gas according to the reaction,

$$SiO_2(s) \rightarrow SiO(g) + \frac{1}{2}O_2(g) \quad (2)$$

In the presence of carbon, the chemical potential of oxygen (O_2) gas produced is reduced by the formation of a stable gas, carbon monoxide (CO)

$$C(s) + \frac{1}{2}O_2 \rightarrow CO(g) \quad (3)$$

Adding Eqs. (2) and (3) yields

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \quad (4)$$

The SiO gas is subsequently reduced by carbon to produce SiC(s) and CO gas as follows

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \quad (5)$$

Combining Eqs. (4) and (5) yields

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g) \quad (6)$$

The schematic diagram showing the growth mechanism of 3C–SiC and 6H–SiC whiskers are shown in Fig. 5.

4. Conclusions

We have demonstrated a novel liquid phase epitaxy method by using mixture of Sm and Co (Sm:Co) as unique solvent for growth of SiC at low temperature. From microstructural analysis, the main structure of SiC is found to be 3C–SiC and other is 6H–SiC. This novel liquid phase epitaxy method can grow single crystal SiC film on the Si wafer, and then it change to polycrystalline gradually. The single crystal SiC is grown from liquid phase and the SiC whiskers is from vapor–solid (VS) process.

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