

Effect of Hydrogen on Silicon Carbide Deposition from Tetramethylsilane – Raman Scattering Studies

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1. Introduction

Silicon carbide has long been recognized as an ideal material for applications where superior attributes such as stiffness and hardness, strength at elevated temperatures, high thermal conductivity, low coefficient of thermal expansion and resistance to corrosion, oxidation, wear and abrasion are of primary value. Silicon carbide or its composites for structural applications are usually fabricated using hot pressing (HP), sintering, reaction sintering, pressureless sintering, or hot isostatic pressing (HIPing). All these belong to powder metallurgy approach. To reduce processing temperature and/or processing time, the second phase is almost widely strategically used in above techniques. In other words, the "impurity" materials, at least two phases, act to compromise the true performance of the silicon carbide. For example, some reaction bonded SiC contains as much as 40% second phase. This, of course, is not a case in the electronic applications of SiC where high purity SiC is required. It is also obvious that using powder metallurgy is difficult to produce SiC parts with a complex shape because of its high hardness and low toughness.

Selective area laser deposition (SALD) is a unique technique for fabricating complex ceramic shapes, tailoring functionally graded structures and embedding in-situ sensors into ceramic parts. In general, high deposition rate is desired. For the case of fabricating in-situ sensors, the chemical composition must also be controlled. Proper shapes and deposition rate using tetramethylsilane (TMS) precursor to deposit SiC has been demonstrated in previous studies¹⁻³. However, carbon contamination has been found to be a potential obstacle for the further application of this precursor in sensor-related fabrication. It has been suggested using the thermodynamic calculation that hydrogen has significant effect on the composition of SiC deposits⁴. In this study, therefore, the effect of hydrogen on the SALD SiC will be experimentally evaluated.

2. Experimental procedures

The SALD system used for this study has been described elsewhere in detail⁵. To avoid the carbon tail phenomenon⁶, a stationary beam was used to grow the SiC dots. TMS precursor was chosen for deposition of SiC. Its pressure varied from 2 torr to 75 torr. Hydrogen pressure varied from 0 to 500 torr. The target temperature varied from 800 to 1200°C.

In this study, Renishaw Raman Imaging Microscope system (2000) was used to characterize the SALD SiC products. This system is a compact laser Raman microprobe/microscope that can collect both Raman spectra and global images. An argon ion laser (514.5nm) provides the light for illuminating the sample and exciting Raman scattering. The sample was measured in the as-deposited state and at a near backscattering geometry. The wave number range was set to 100 - 2000 cm^{-1} , within which all the first-order Raman scattering

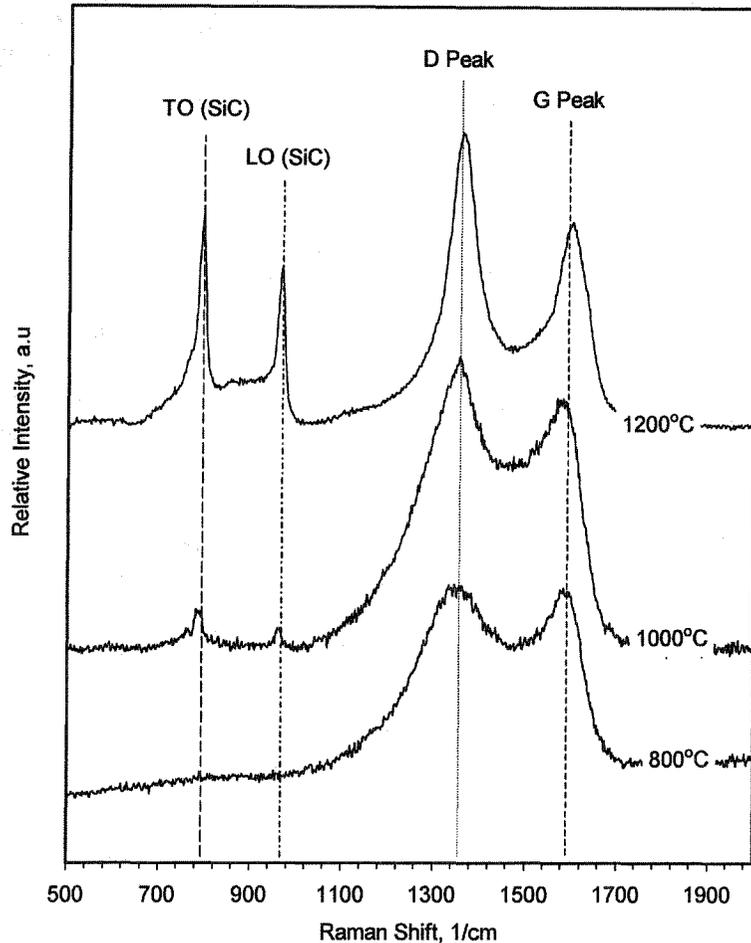
can be recorded for SiC and graphite. For 3C-SiC, there are a longitudinal optical (LO) mode and a doubly degenerate transverse optical (TO) mode in optical branches. The Raman shift corresponding to LO active mode appears at 972 cm^{-1} while that of TO mode appears at 796 cm^{-1} in spectra.⁷

3 Results

3.1 Temperature Effect

The typical Raman spectra from SiC deposited at different target temperatures using 20 torr TMS were shown in Figure 1. There are four Raman peaks. Two peaks labeled as G and D are ascribed to graphite and the other two peaks labeled as LO and TO are contributed by SiC. Presence of the graphite peaks clearly indicates the existence of excess carbon in the deposited SiC samples. It is also found that graphite peaks appear in other samples when only TMS precursor is used.

Figure 1. Effects of target temperatures (800, 900 and 1200°C) on the Raman spectra of SiC deposits (preparation conditions: 20 torr TMS, stationary beam, 100 seconds of growth time; measured at the spot center)



3.2 Raman Mapping

It is important to know the structure information from point to point for a laser deposited materials because the structure and/or composition at any specific location could be related to the local growth temperature. At the spot center, the temperature is highest due to the non-linear Gaussian distribution. Thus, it is supposed that microstructure distribution along the radial position of a spot has a similar result to the target temperature effect. This study was performed using a 20 torr TMS at different target temperatures. Because there is no attempt to perform quantitative analysis, only spectra plots are given here for qualitative purpose. Figure 2 to Figure 4 give the information of radial Raman measurements corresponding to 800, 1000 and 1200°C target temperature, respectively.

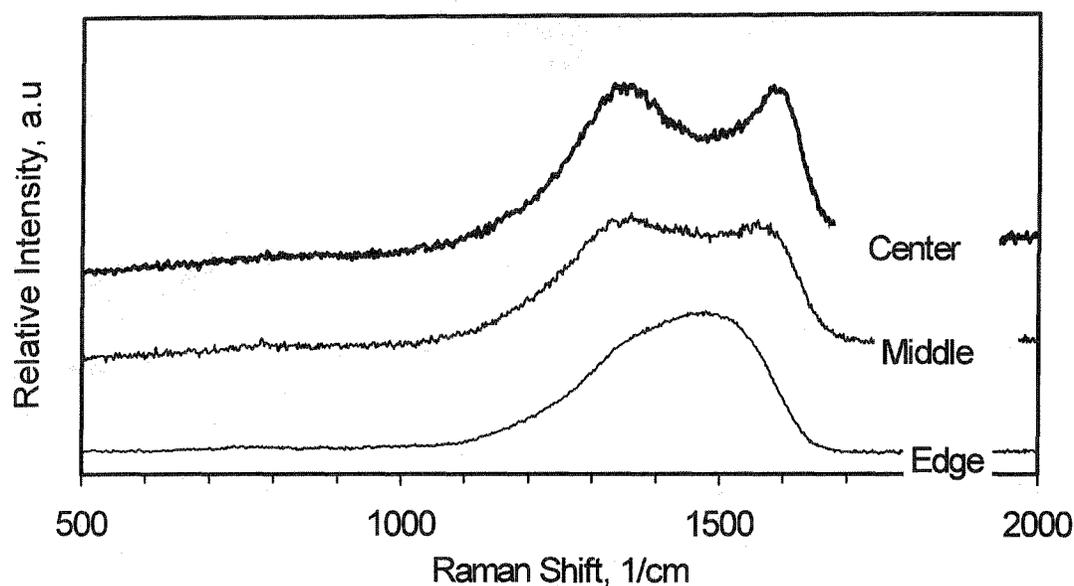


Figure 2. Raman mapping on the sample deposited at a target temperature of 800°C using 20 torr TMS.

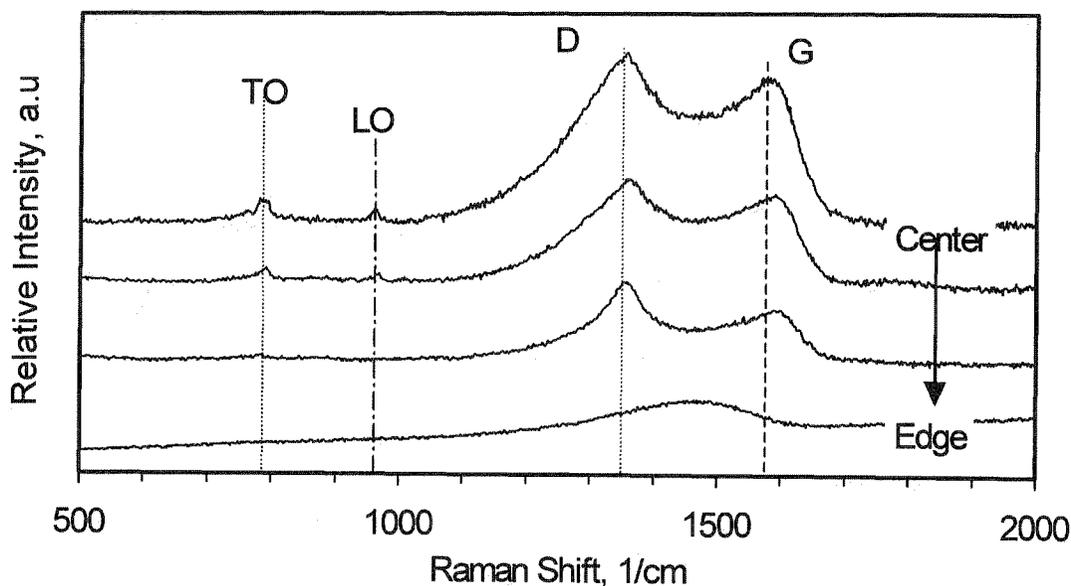


Figure 3. Raman mapping on the sample deposited at a target temperature of 1000°C using 20 torr TMS.

Based on the Raman mapping results from Figure 2-4, it can be concluded that carbon always codeposits with SiC over a wide temperature range (from spot center to its edge) when only pure TMS is used. The crystallinity of deposits increases with the local temperature as

reflected in the increasing peak sharpness seen in Figure 2-4. The co-deposited carbon within SiC has very small crystallite size.

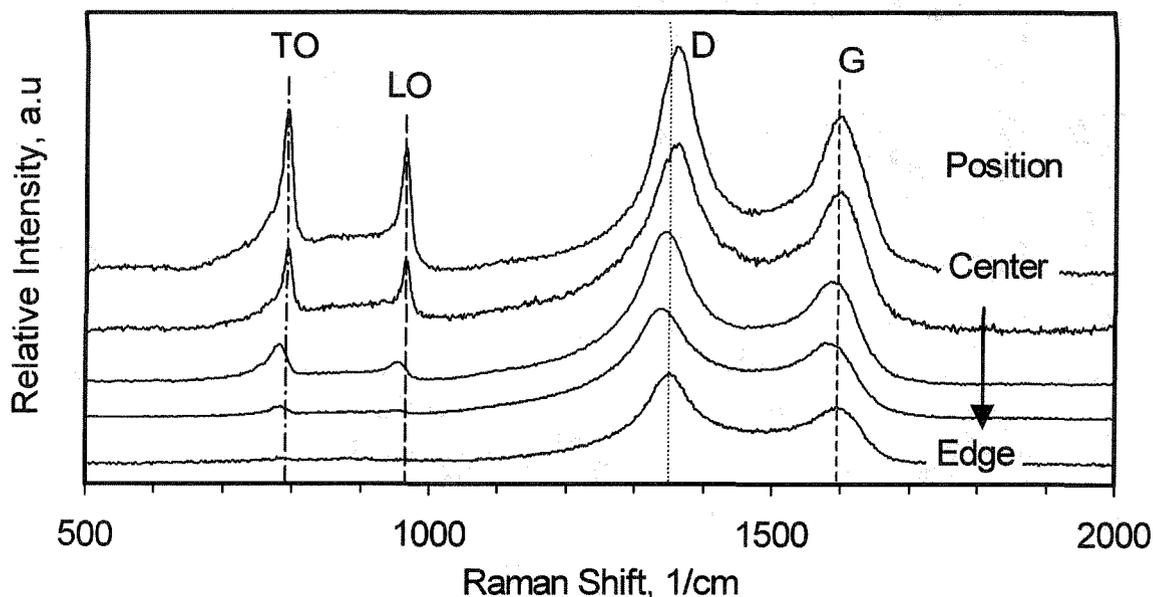


Figure 4. Raman mapping on the sample deposited at a target temperature of 1200°C using 20 torr TMS.

3.3 Hydrogen Effect

Raman mapping on a sample prepared using 2 torr TMS and 500 torr H₂ at a target temperature of 1200°C is shown in Figure 5. It can be seen that graphite still exists at the spot center under current experimental conditions. In the middle region of the spot, however, crystalline SiC was identified without the graphite contamination. At the outer region of the deposited spot, pure SiC exists in amorphous state. In Figure 5b, a small peak around 1500cm⁻¹ was observed and denoted as DO shift. The same peak has been observed from the commercial SiC samples. Some investigators have also reported this peak and ascribed to disordered SiC^{7,8}. Since this peak is located between G and D peak, it is not visible when there exists a certain amount of carbon in the SiC sample.

This result clearly indicates that it is possible to achieve pure SiC deposition as long as the target temperature can be controlled below a certain level. Additional experimental studies on the systems containing 20 torr TMS and up to 500 torr H₂ indicate that small amount of carbon still coexists with SiC and thus it is believed that in addition to temperature there is an upper limit for TMS pressure to achieve pure SiC deposition.

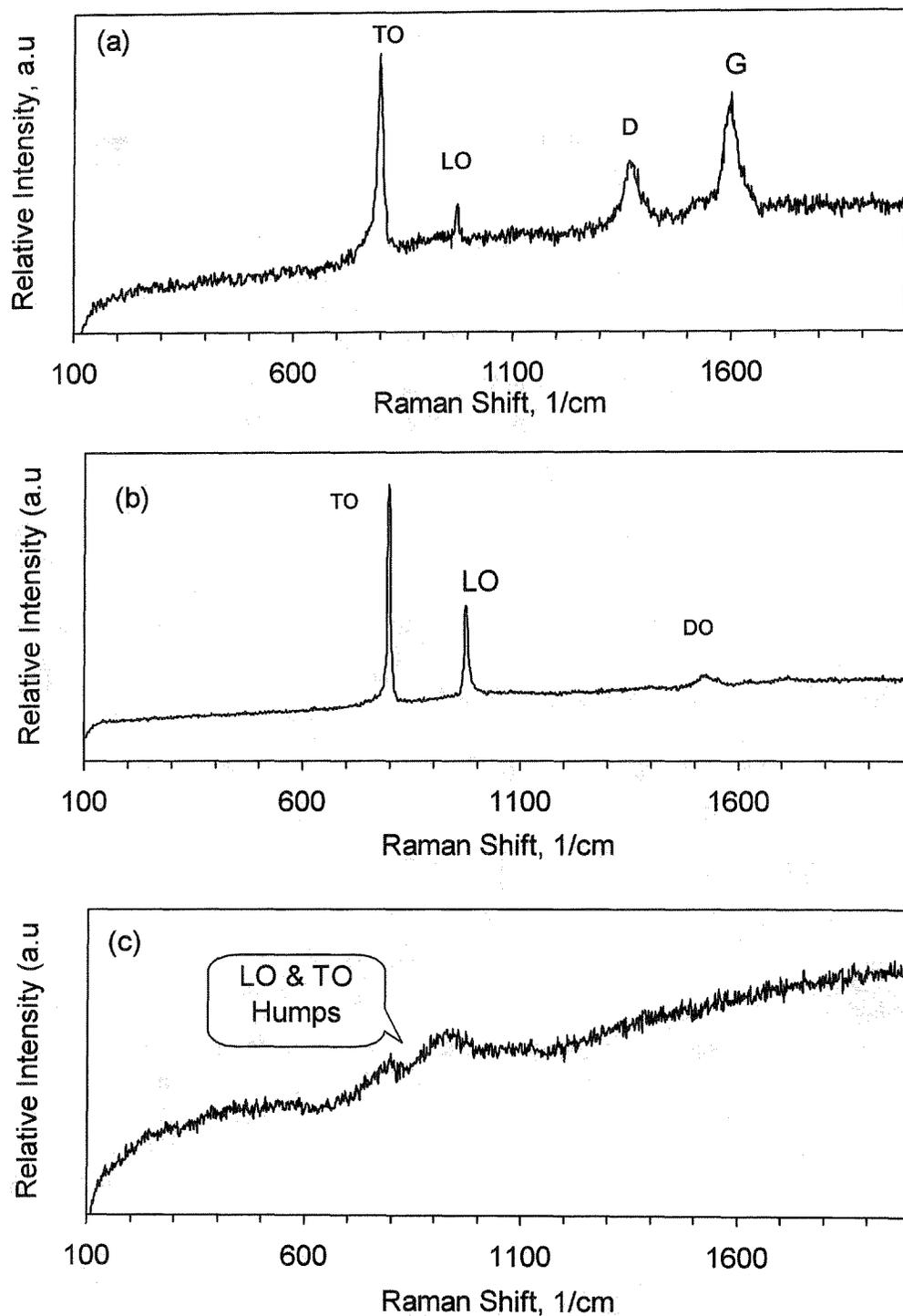


Figure 5. Raman spectra from the sample deposited using 2 torr TMS and 500 torr hydrogen at 1200°C. They were collected from (a) spot center, (b) middle (between center and edge of the spot), and (c) edge.

4. Discussions

No carbon co-deposition has been reported by many researchers^{9,10}. For example, using the same precursor TMS and a ratio of about 6 P_{H_2}/P_{TMS} between 1100°C - 1500°C, Figueras et al claimed that no excess C was detected. Although it is possible that no carbon co-deposition takes place due to the use of high partial pressure of hydrogen, it can not be completely eliminated at high temperatures. It is expected that graphite should be co-deposited based on thermodynamic modeling and present experimental results under the same experimental conditions as those used by the above researchers. The conclusion made by these researchers was based on the X-ray diffraction. It is well known that carbon has a very low mass absorption coefficient at a wavelength of 1.5 Å. It is also believed that the very small crystallite size (nano-size) itself makes diffraction very weak or not sensitive. For example, the previous study by the authors showed that carbon is not detectable in the as deposited samples. However, it could be revealed after heat treatment⁵.

Within the visible light range, the situation would be totally different. The absorption coefficients of carbon and β -SiC crystals have been experimentally determined¹¹. The relevant data are given in Table 1. It can be seen that carbon has a much higher absorption coefficient than SiC. The penetration depth is thus much smaller than that of SiC. The small penetration depth, only 50 nm for carbon, indicates that relatively strong Raman scattering intensity can be obtained for even a very small amount of carbon coexisted with SiC. For example, if there exists a 50 nm thick carbon tail on the surface, SiC signal may not be detectable.

Table 1. Absorption data for C, Si and SiC at 514.4nm

$\lambda=514.5$ nm	C	Si	SiC
Absorption coefficient (α), μm^{-1}	20	1.47	25×10^{-4}
Extinction coefficient (κ)	0.82	0.06	1.024×10^{-4}
Depth of the exciting radiation (δ), μm	0.05	0.68	400

Thus, the Raman scattering technique is an effective tool for detecting excess carbon. By using this technique, it has been clearly confirmed that hydrogen could significantly reduce the amount of carbon co-deposited with SiC or even completely eliminate carbon co-deposition. It is believed that the observed phenomena such as decrease in growth rate and increase in electrical resistivity after adding hydrogen are related to the hydrogen's role in reducing the carbon amount⁶.

The hydrogen's role observed in this study could be discussed based on the thermodynamic calculations. Using the CET89 code (calculation method has been described elsewhere⁴), effect of hydrogen on the decomposition of TMS precursor has been calculated and it is found that hydrogen's role lies in its inhibition to the hydrocarbon's further decomposition. A 3D solid phase diagram from thermodynamic calculation showing the stable zone of pure SiC is given in Figure 6

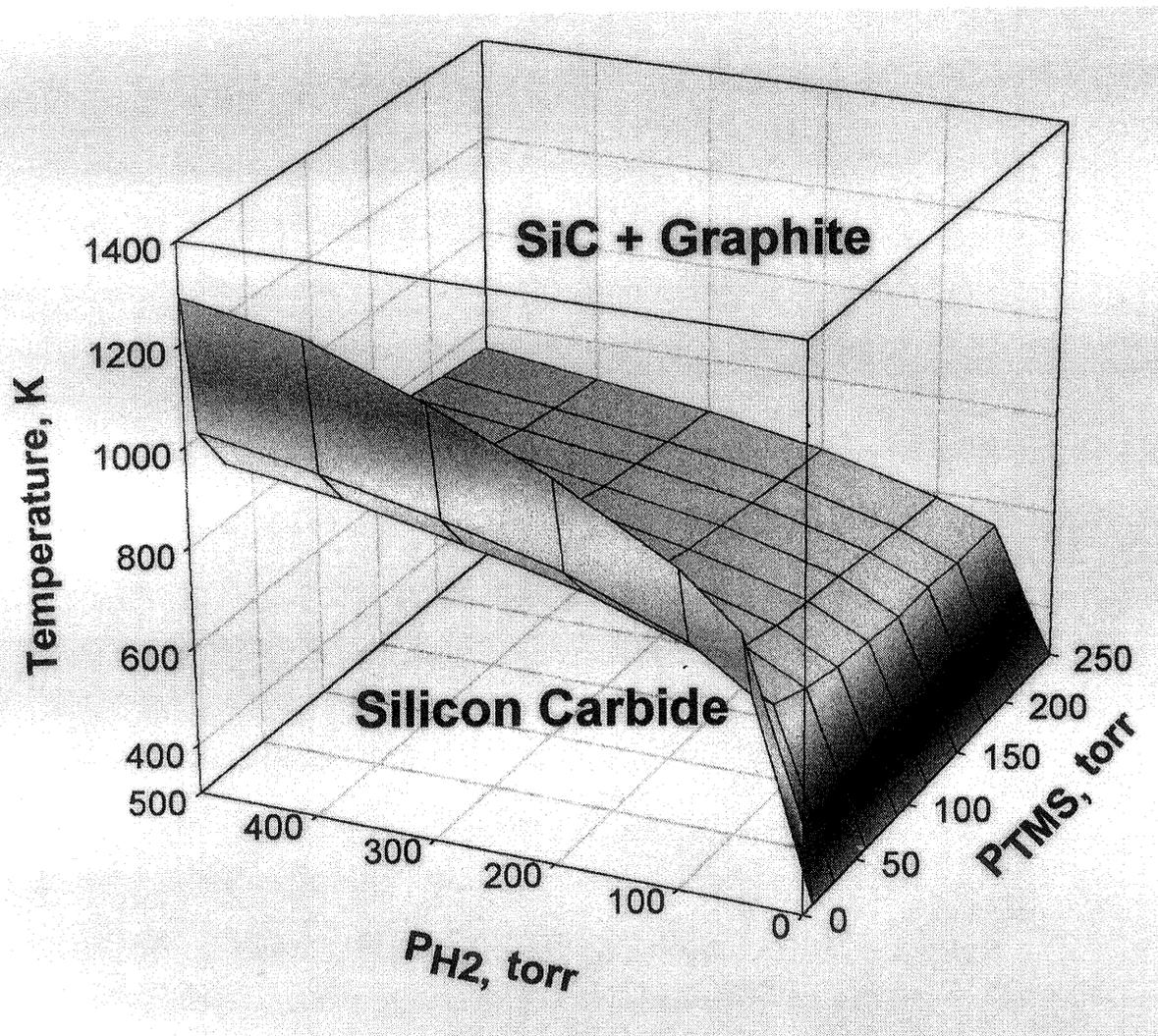


Figure 6. 3D diagram – effect of hydrogen on TMS decomposition

From Figure 6, it can be seen that pure SiC can only be deposited through adding hydrogen. The phenomenon that carbon still codeposits at the spot center even with the addition of 500 torr H_2 to 2 torr TMS can be explained as follows. It has been calculated that the temperature rise at the beam center is higher than the target temperature¹². For example, at a target temperature of 1200°C, the estimated center temperature at the beam center is about 1800°C. Examining Figure 6, the co-deposition will take place because the local temperature at the beam center has exceeded the threshold temperature for carbon codeposition. At the middle position of the spot, the temperature there may have dropped to the pure SiC deposition region, but the temperature is still fairly high and therefore the pure crystalline SiC can be obtained. At the outer region of the spot, temperature is low, and therefore deposited SiC has very short-range order or is amorphous due to low diffusivity or mobility of species.

5. Summary and Conclusions

Selective area laser deposition of silicon carbide from the tetramethylsilane precursor has been studied using the Raman scattering technique. It is found that carbon always codeposits with SiC when pure TMS gas is used. Hydrogen significantly reduces the amount of excess carbon under low TMS pressures. Pure SiC without carbon contamination can be achieved at low temperatures and low TMS pressures with addition of hydrogen. Raman mapping of the deposited SiC revealed that the composition of the deposit varies with the local deposition temperature. The finding is consistent with the thermodynamic prediction and confirms that temperature is one of the most important factors in depositing pure SiC using TMS precursor. Thermodynamic analysis also indicates that reduction or elimination of carbon codeposition through addition of hydrogen is due to the inhibition of H₂ to the hydrocarbon decomposition.

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