

DEPOSITION OF a-SiC:H USING ORGANOSILANES IN AN ARGON/HYDROGEN PLASMA

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ABSTRACT

Selected organosilanes were examined as precursors for the deposition of amorphous hydrogenated silicon carbide in an argon/hydrogen plasma. The effect of process variables on the quality of the films was established by means of FTIR, Auger spectroscopy, XPS, XRD, chemical analysis, and weight losses upon pyrolysis. For a given power level there is a limiting feeding rate of the precursor under which operation of the system is dominated by thermodynamics and leads to high quality silicon carbide films that are nearly stoichiometric and low in hydrogen. Beyond that limit, carbosilane polymer formation and excessive hydrogen incorporation takes place. The hydrogen content of the plasma affects the deposition rate and the hydrogen content of the film. In the thermodynamically dominated regime the nature of the precursor has no effect on the quality of the film, it affects only the relative utilization efficiency.

INTRODUCTION

Amorphous hydrogenated silicon carbide is the subject of very active research because of its usefulness in a variety of optoelectronic applications such as x-ray masks, light-emitting diodes and in the manufacture of solar cells[1-3]. These developments came about after the demonstration[4] that the band gap of this semiconductor is dependent upon and can be adjusted by changes in the silicon/carbon ratio. The deposition of amorphous silicon carbide may be done by a variety of techniques, including CVD (pyrolytic, photochemical or plasma enhanced), laser ablation and sputtering, either of a preformed target or in a reactive plasma. In the CVD techniques a large variety of precursors have been used covering a wide range of structural complexity from the simplest combination of silane and methane to more complicated mixtures or single source organosilanes. Given the technological importance and the variety of synthetic approaches to amorphous silicon carbide it is not surprising that the literature on this subject is extensive and continuously expanding. Recent significant studies[5,6] explore the relationship between deposition conditions to the composition and properties of the films and seek to understand the structure of the films at a molecular level. In spite of the extensive amount of work being done there is still a need for mechanistic understanding of the effect of underlying physicochemical processes on the quality and composition of the films. Variables explored in this study to derive such information were: the composition and structure of the precursors, feeding rate and the plasma gas composition.

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ABSTRACT

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## RESULTS AND DISCUSSION

Films were deposited in a quartz tube reactor of 40 mm OD. passing through a microwave plasma source. Substrates, typically 25 mm in diameter were held at a 45 degree angle to the flow direction at the center of the cavity. No external heating was provided other than the energy input, 100 watt net power, as microwaves with a 2.45 GHz frequency. Temperatures measured immediately after extinguishing the plasma at the backside of the holder were typically about 220 C. The precursor to be examined was introduced through a micrometer needle valve upstream of the cavity into the stream of the plasma gas mixture. Organosilanes examined were: bis(trimethylsilyl) acetylene, [bTMSA, room temperature vapor pressure 6 torr]; tetramethylsilane, [TMS, R.T. v.p. > 760 torr]; triethylsilane, [TESIH, R.T. v.p. 29 torr]; tetraethylsilane, [TES, R.T. v.p. 3 torr]; and phenylsilane, [PSIH, R.T. v.p. 17 torr]. Depositions were conducted at a total pressure of 700 mtorr with a flow rate of 20 sccm of argon or an argon/hydrogen mixture containing 4, 10, 25, or 50 vol % H<sub>2</sub>. The precursor partial pressure was about 1 % of the total. Feeding rates of precursor into the reactor were 0.1 to 1.0 mmole/h. The deposition rate was established by the increase in weight of the coated substrates and assuming a density of 2.8 g/cm<sup>3</sup>. During deposition the vapor phase was sampled at the cavity and analyzed with a quadropole mass spectrometer. The total flow from the reactor was passed through a liquid nitrogen cooled trap. The condensate in the trap was examined by FTIR and GC-MS.

Most of the films deposited in the course of this study were nearly stoichiometric and relatively low in hydrogen. The influence of the variables studied (hydrogen content in the plasma gas, precursor, and feeding rate) was rather subtle, and a mechanistic insight for the deposition was derived from the pyrolytic behavior of the films, and the observation of a commonality of the volatile mixture produced by all precursors. A more detailed description of the observations and characterization follows below.

### FTIR

Infrared spectroscopy has been extensively used in the characterization of silicon carbide films. A significant contribution in this area, although indirect, was the work of Brodsky et al[7] on amorphous silicon. In their study, IR was used to assign different atomic environments for SiH bonds and most importantly to quantify the hydrogen content of their films. Additional representative work along these lines and applied to silicon carbide is that of ref. 1 and 5. Also of importance is the work of Guivarc'h et al[8], who used nuclear techniques in addition to IR analysis to establish the hydrogen content of silicon carbide films. In the present work, the hydrogen content was estimated from the IR band at about 2100 cm<sup>-1</sup> by direct comparison, using absorption coefficient values of published spectra (ref 1,5,8, and 9). The films proved to be relatively low in hydrogen, 4-8 atom %, this is readily evident by comparison of a typical IR spectrum of this study, fig 1, in which the intensity of the SiH band, expressed as absorption coefficient, is about one tenth of that of published spectra such as those given in references 1, 5, 8 and 9. The relation between density

and hydrogen content observed by Guivarc'h[8] as well as the values given by Gat et al[5] were used to estimate the density of about  $2.8 \text{ g/cm}^3$  for the films in the present study.

Features of interest in the IR spectra, among others, were the very high intensity of the SiC band at  $800 \text{ cm}^{-1}$ , equal or higher than that in films obtained by laser ablation of a SiC target[5]. Furthermore, IR proved to be useful in monitoring the effect of pyrolysis on the films. Most of the films showed asymmetry on the Si-H band, (see inset fig 1), due to the presence of SiH<sub>2</sub> moieties on the high frequency side of the band. The asymmetry disappears after heating in vacuum at  $800 \text{ C}$  with single bonded SiH remaining. The SiH band tends to disappear completely at  $900 \text{ C}$  with the onset of SiC crystallization. Also observed to disappear was a slight asymmetry on the high frequency side of the SiC band, at about  $1000 \text{ cm}^{-1}$ , due to CH wagging vibrations.

The assignment of the SiH bands above to dihydride and monohydride moieties is an oversimplification, as the frequency is influenced by the structural environment resulting from different substituents on silicon, either other silicon atoms or carbon; in addition to this, the presence of microvoids also affects the stretching frequency.

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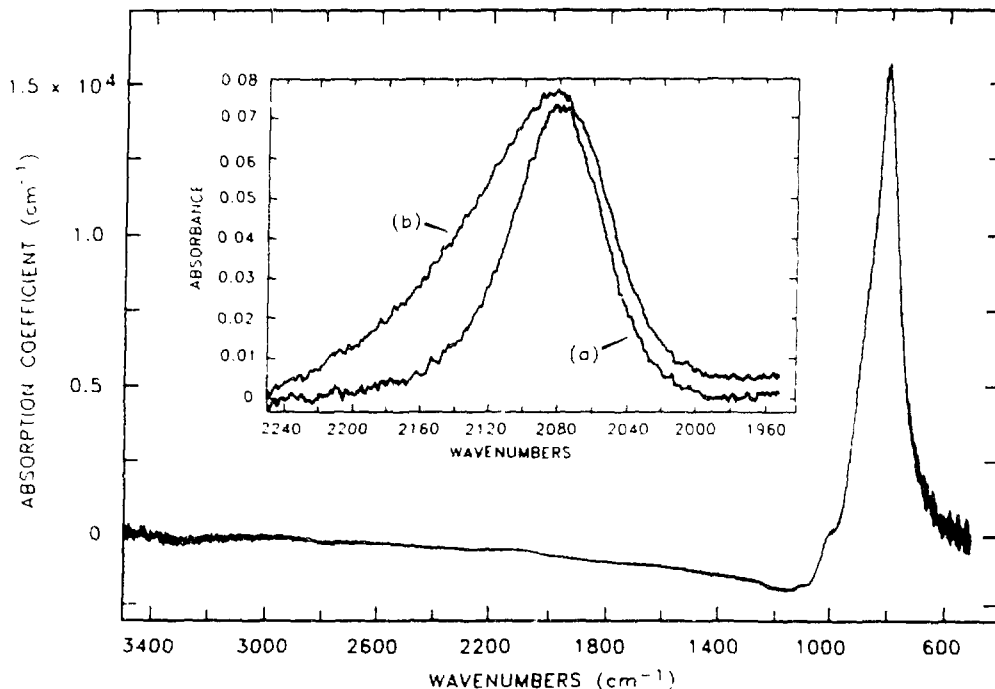


Figure 1. IR spectrum of  $a\text{-Si}_x\text{C}_{1-x}\text{:H}$  coating on silicon. Inset: SiH stretch magnified (a) before and (b) after pyrolysis.

### Film pyrolyses

Exposure of organosilicon compounds to a plasma leads to polymerization as a possible outcome and is utilized as an important technological application as described in some

representative studies[10,11]. Whether polymerization occurs as the main outcome is a complex function of power input and the pressure of the different vapor species. In the present study polymer formation was observed at relatively high feed rates,  $\geq 1$  mmole/h, and it was detected by the presence of free flowing flakes in the reactor, poor adherence of the film on the substrate and relatively high weight losses of the film upon treatment at 800 C. The flakes had IR spectra similar to those reported for the carbosilane polymers which in essence is not too different from that of amorphous hydrogenated silicon carbide films. The polymers show more intense C-H and Si-H stretching and bending vibrations. The presence of polymer in a film is also detected by relatively weaker Si-C vibration intensity at  $800\text{ cm}^{-1}$ .

A few of the coated specimens were subjected to pyrolysis to 800 C under vacuum or under a stream of high purity helium which was monitored by mass spectroscopy. Volatiles evolved were methane and hydrogen. Typical weight losses for films deposited with 25%  $\text{H}_2$  in the plasma gas were about 2-3 wt%; on the other hand, specimens generated at high feeding rates or with lower hydrogen in the plasma gas showed weight losses between 10 to 22 wt%. This would suggest a higher efficiency in converting the precursor into SiC with a higher hydrogen content in the plasma gas; however, excessive hydrogen in the plasma leads to higher hydrogen incorporation in the film and thus slightly higher weight losses.

### Volatile analyses

Volatiles produced in the deposition were detected by mass spectroscopy. Sampling was done at the substrate holder using the spectrum collected prior to ignition as background which was then subtracted from spectra collected during a run. The main signals detected under these conditions were peaks of m/e at 1,2,16,26 and 40 corresponding to hydrogen, methane, acetylene and allene. In addition to this detection mechanism volatiles were trapped and reexamined by FTIR and GC-MS. Acetylene is by far the most abundant species, about 90%. Additional minor components were detected such as ethylene, ethane, trimethyl silane, 1-butyne and benzene. The significant finding of this effort was that the volatile mixture was approximately the same for all precursors examined, including phenylsilane, which, because of the presence of a relatively more stable aromatic ring, could have produced a higher proportion of aromatic derivatives. However, that was not the case. An additional interesting observation was the lack of silicon containing species in any appreciable concentration. The commonality in volatile composition for all precursors suggests a highly energetic environment in the plasma that fragments the incoming precursor and recombines the resulting radicals or ions into a thermodynamically stable molecular mixture controlled by the interplay of a set of variables including composition, pressure and temperature. The preponderance of acetylene is in accordance with the energetics of the C/H system at elevated temperatures[12].

### Auger spectroscopy

Depth profiles were determined for films deposited on silicon and on niobium. In both cases the films were nearly

stoichiometric and free of oxygen except for the very superficial layer. Imaging of the film showed a botryoidal morphology with individual mounds of about 1 micron in diameter.

#### Photoelectron spectroscopy

Two specimens derived from the same coated silicon wafer were examined. One was the film as deposited and the other after vacuum treatment to 800°C. Survey scans of both samples revealed no significant contamination other than oxygen which decreased to a few atom percent after sputtering. Narrow window scans that encompass the C(1s) and Si(2p) binding energies showed symmetrical peaks at 283.6 and 100.4 eV respectively for both specimens, in good agreement with the XPS data base issued by the NIST (National Institute of Standards and Technology)

#### Optical band gap

The optical band gap for films prepared with each of the different precursors was derived from the optical spectra of coated quartz specimens and using Tauc plots [given by  $(\alpha h\nu)^{1/2}$  versus  $h\nu$ , where  $\alpha$  is the absorption coefficient and  $h\nu$  the photon energy in eV]. The results showed values between 2.6 and 2.8 eV in accordance with the anticipated values for nearly stoichiometric films.

#### X-ray diffraction

Diffraction patterns were obtained of materials treated at 900 C under vacuum. These included an intact film deposited on silicon as well as that of flakes peeled off from a different substrate. The patterns showed only the strongest reflections for cubic SiC, corresponding to the 111, 220, 311, and 331 indices, in the form of broad bands. The patterns indicate the onset of crystallization in accordance with earlier observations for the temperatures required to cause this transition in the system[14]. The as deposited films were amorphous.

#### Chemical analyses

Coated silicon wafers were subjected to carbon analysis in a Leco carbon analyser without stripping the films. Corrections due to the carbon content of the wafer and contamination due to sample handling were in the order of 30 micrograms for typical film weights of a few milligrams. The carbon content of the films was independent of precursor used and ranged between 35 to 52 at. %. The carbon content increased with feeding rate but it leveled off after reaching a near stoichiometric composition. Feeding rates exceeding about 0.4 mmole/h lead to polymer formation and slightly higher carbon content, up to 67 at % in one case when using a feeding rate of 1.3 mmole/h. However; such excess carbon was lost as observed in the pyrolysis experiments.

#### Precursor

Bis-trimethylsilane was examined initially because it appeared as a particularly attractive precursor to SiC since it has the  $\equiv\text{SiC}\equiv\text{CSi}\equiv$  moiety at its core. However, it was found that the other precursors were equally appropriate in producing coatings, but there were slight differences among the precursors as established by comparison of an efficiency parameter. This is an arbitrary parameter defined as the ratio of deposition to feeding rates. According to this, TMSA gives the highest

efficiency followed by TESI<sub>H</sub>, TMS, TES, and PSI<sub>H</sub>. The significant finding regarding the different precursors was the commonality of volatiles produced in the deposition. This gives an insight into the mechanism of the film deposition in the current study which confirms the notion of an energetic plasma, that fragments the incoming precursors thoroughly.

## CONCLUSIONS

Near stoichiometric amorphous silicon carbide films are deposited using a variety of single source organosilanes in a microwave generated plasma of argon/hydrogen mixtures. For a given power level, held constant in this study, there is a limiting feeding rate of precursor that assures thermodynamic control to produce silicon carbide as the solid phase and a volatile mixture dominated by acetylene, methane and hydrogen. Higher feeding rates lead to the formation of carborane polymers in addition to silicon carbide. The hydrogen content in the plasma influences the throughput of precursor that can be processed, but this is limited to an optimum level before excessive hydrogen incorporation in the film. In the thermodynamically dominated regime the nature of the precursor has no effect on the quality of the film, it affects only the relative utilization efficiency.

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