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of Sublimed Fullerenes and Silicon**

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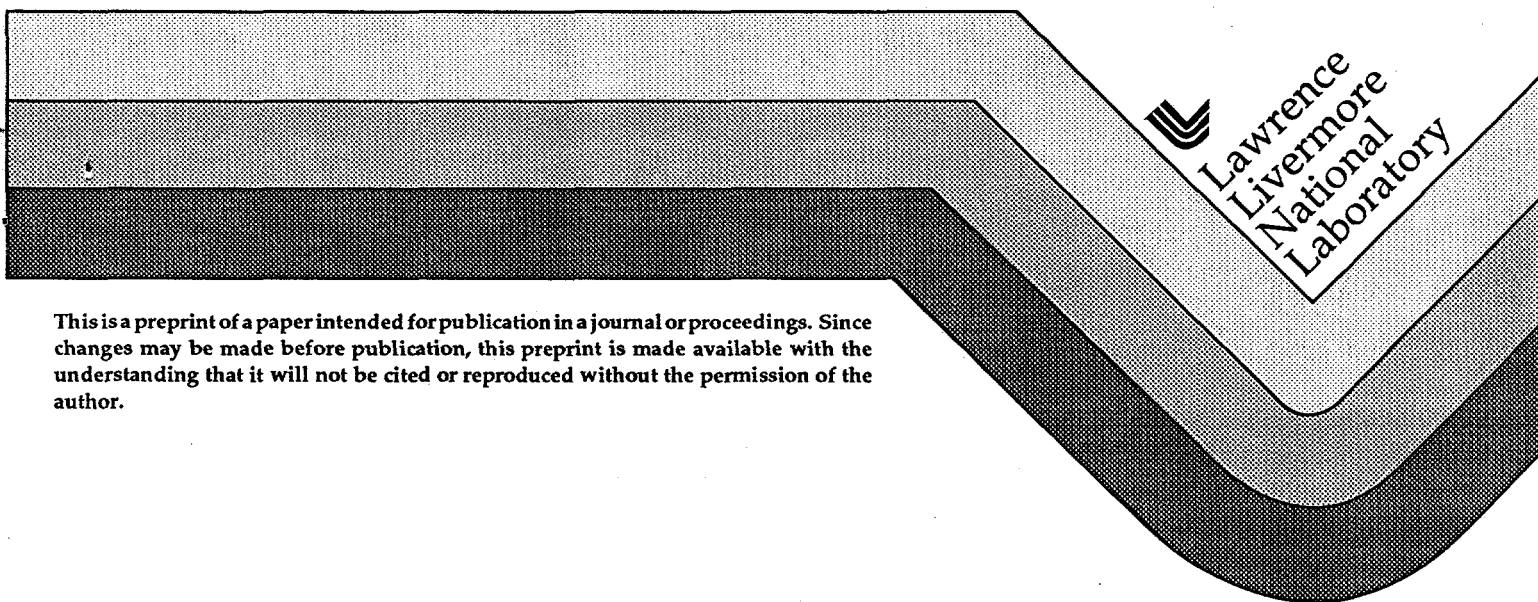
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GROWTH OF SILICON CARBIDE ON SILICON VIA REACTION OF SUBLIMED  
FULLERENES AND SILICON

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# GROWTH OF SILICON CARBIDE ON SILICON VIA REACTION OF SUBLIMED FULLERENES AND SILICON

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## ABSTRACT

Epitaxial silicon carbide films are grown on Si(100) substrates at a surface temperature of 1200 K via fullerene precursors. Films have been grown up to a thickness of 2500 Å. The growth rate of the SiC film is not limited by the surface reaction rate of fullerene with silicon at these temperatures, rather by the arrival rate of the reactants Si (by diffusion from substrate or from gas phase) or fullerene. This results in rapid film growth. Films have been characterized by low energy electron diffraction, ultraviolet photoelectron spectroscopy and Auger electron spectroscopy. Stoichiometric, epitaxial SiC films are grown. Supply of silicon to the growing SiC surface via sublimation greatly reduces the tendency for silicon diffusion to form voids at the Si/SiC interface.

## INTRODUCTION

The growth of SiC films on silicon substrates by conventional chemical vapor deposition techniques is expensive because of the high temperatures required in deposition reactors (~1700 K or higher). In addition SiC is extremely inert, and thus, forming device structures on blanket deposited films is also time consuming. By taking advantage of the reactive properties of fullerenes on silicon substrates and silicon oxide substrates epitaxial SiC films can be selectively grown at relatively low substrate and gas temperatures of 900 to 1250 K (1).

Moalem et al. (2) have demonstrated that while C<sub>60</sub> accommodates thermally with an silicon dioxide surface, C<sub>60</sub> is unreactive at surface temperatures below 1250 K with silicon dioxide. In addition, the surface mobility of C<sub>60</sub> on silicon dioxide is quite high, i.e. C<sub>60</sub> behaves like a two-dimensional gas. Many groups (3-5) have shown that fullerenes react at temperatures above 900 K with silicon substrates to form SiC. Making use of the different interactions of fullerenes with silicon and silicon dioxide leads to a straightforward process to selectively grow SiC on silicon substrates. A silicon wafer patterned with silicon dioxide by semiconductor industry standard lithographic techniques is exposed to a fullerene vapor stream at substrate temperatures between 950 and 1250 K. SiC grows on the bare silicon areas. After reaction the silicon dioxide is stripped from the wafer by rinsing in hydrofluoric acid, leaving a wafer patterned with SiC.

Unfortunately, the silicon necessary to grow the SiC film is supplied from the wafer substrate by diffusion (1,6). For small structures on the order of 1-5 micron feature size, interface and surface diffusion is fast enough to supply silicon to the SiC growth area. This leads to undercut of the feature for thick (~1 micron) SiC films (6). For larger

features diffusion of Si through the growing SiC film is the mechanism by which the surface is supplied with silicon. This leads to void formation at the Si/SiC interface, which are nucleated at defects (6).

In this paper we show that void formation can be strongly reduced by supplying silicon to the growing SiC film from the gas phase. The silicon carbide films were grown on a silicon substrate by first depositing sufficient Si to cover the substrate, and subsequently, depositing a monolayer of fullerene at room temperature. Heating the substrate to 1200 K converts the silicon-fullerene sandwich to SiC.

## EXPERIMENTAL

Experiments were performed in an ultra-high vacuum (UHV) apparatus. The low energy electron diffraction (LEED) apparatus is equipped with reverse view LEED optics and a cylindrical mirror analyzer for Auger electron spectroscopy (AES). Silicon (100) substrates were resistively heated and the temperature monitored either by a K type thermocouple or by optical pyrometer. A fullerene doser supplied fullerene vapor to the sample substrate by sublimation. A silicon doser supplied silicon by sublimation as well.

## RESULTS AND DISCUSSION

SiC films have been grown on a Si(100) substrate by first nucleating SiC by depositing a multilayer of C<sub>60</sub> on the wafer at room temperature and then heating the wafer to 1200 K. On the nucleated SiC layer at room temperature enough Si is sublimed such that the carbon 272 eV AES peak is at the detection limit. Then a multilayer of C<sub>60</sub> is deposited on the silicon layer also at room temperature. The sample is then heated to 1200 K. This is considered a single deposition cycle. Between cycles the surface composition and structure are monitored by AES and LEED. Stoichiometric SiC is grown epitaxially by this technique. Even (2x1) and (3x1)-(100) SiC surface reconstructions were observed in the LEED patterns. After 60 cycles, ~2500 Å of SiC had been grown as determined by cross section scanning electron microscopy. Voids at the Si/SiC interface were observed at ~250/cm<sup>2</sup>. This is approximately a five order of magnitude reduction in the void formation as compared to the case where no silicon is supplied from the gas phase.

Unfortunately, different growth parameters are required. A smooth surface is not grown everywhere by this technique. Roughly spherical mounds of SiC embedded in the SiC film are observed at a highest density of 107/cm<sup>2</sup> and with sizes from 0.6 to 0.3 microns in diameter by atomic force microscopy. The mounds are confirmed to be SiC by scanning Auger microscopy. The size of the mounds and the density correlated with the sublimed silicon. In areas where the sublimed silicon flux was smallest the density and size of mounds was also smallest (~106/cm<sup>2</sup> and 0.2 micron diameter).

Sublimed silicon deposited on graphite surfaces clusters upon heating of the substrate (7). If clustering were to occur on SiC during the heating of the wafer, this could be the mechanism of mound formation. The clustered silicon atoms may nucleate a new SiC

domain. Simultaneous deposition of fullerene and silicon at appropriate SiC growth temperatures may eliminate the mound formation.

Ultraviolet photoelectron spectroscopy was used to probe the electronic properties of the SiC films grown via fullerene precursors. The work function of the sample is measured to be  $4.8 \pm 0.1$  eV, which is similar to that for bulk SiC. The work function increases slightly (0.13 eV) with exposure (2 Langmuir) to dioxygen at room temperature as measured by a Kelvin probe (resolution  $\pm 0.01$  eV). The increase is likely due to physisorption of dioxygen on the surface, since the effect (0.05 eV increase at 2 Langmuir at 443 K) decreases with surface temperature. At high temperature (810 K) exposure to dioxygen has no effect on the work function, which is in surprising contrast to silicon surfaces where the work function decreases by 0.3 eV with exposure to dioxygen. The decrease for silicon is attributed to oxidation of the surface. The resistance of the SiC surface to oxidation is evidenced by the lack of change in the work function during exposure of the surface to dioxygen at 810 K.

### SUMMARY

Stoichiometric, epitaxial SiC films can be grown via reaction of fullerenes with sublimed silicon on silicon substrates. Sublimed silicon greatly reduces the void formation at the Si/SiC interface by 5 orders of magnitude. The electronic properties of the silicon carbide surface film indicate that the surface is not easily oxidized in the presence of dioxygen at high temperature, 810 K.

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