Analysis of Solid State Chemical Reactions in Composite Materials Raman Maps Identify and Locate Phases

SUMMARY

Composite materials are, by definition, multi-phased. Quite often these phases are not distinguishable by optical microscopy. Raman analysis provides very rapid analysis that can differentiate phases, even closely related phases such as polymorphs of a given composition, or differing stoichiometries in a solid system. Recently a SiC conversion coating on a carbon-carbon composite used in the space shuttle was analyzed and various phases were mapped. The identification of phases, in combination with maps showing the physical proximity of the phases; provide insight into the solid state chemical reactions that produce the multi-phase coating.

SiC conversion coating for the Space Shuttle

Carbon composites have been used as structural components on many high technology, engineered materials, especially in aerospace applications. Exterior surfaces of these materials have to be protected from environmental effects. In the Space Shuttle application the effects of surface exposure are considerable – the Shuttle enters the atmosphere at 18000 miles/hour. Surface protection against the highly oxidizing conditions has been provided by conversion of the carbon surface to SiC, a refractory material. The conversion is achieved by exposing the surface to silicon atoms at a high temperature, in an inert atmosphere. During engineering development of these coatings, materials were added to the silicon in order to evaluate whether they afforded improvement of the properties of the coating.
The coating tested here included boron that was added because of the refractory properties of BC.

The sample was produced by Jan Soroka at Lockheed Martin Vought in the early to mid 1980's.

Raman Microprobe characterization of the Surfaces

Initial examination of the surfaces indicated the presence of multiple phases. While SiC was indeed present in large quantities, it was not of homogeneous composition.

SiC in its simplest form is a cubic material whose structure is analogous to crystalline silicon and diamond, except that every other atom is different. However, silicon carbide can occur in many polymorphic forms related to each other by systematic stacking rotations about the 111 axis.
The first figure illustrates Raman spectra of four of the most common polymorphs. The behaviour of the spectra as a function of polytype has been rationalized by describing the phonons in the hexagonal and rhombohedral lattices in terms of folded phonons in the Brillouin zone of the cubic phase. Figure 2 (reproduced from Phonon Dispersion Curves by Raman Scattering in SiC, Polytypes 3C. 4H, 6H, 15R, and 21R - DW Feldman et.al, Phys Rev <u>173</u>, 787 (1968)) illustrates this concept.

Examination of the most bright, reflective regions indicated the presence of silicon precipitates.

However, the 1st order phonon in many of the regions examined was highly dispersive, a phenomenon known to correlate with incorporation of high levels of boron substitution in the silicon lattice. Figure 3 is reproduced from Raman Scattering by Coupled Electron-Phonon Excitations (in Heavily Doped Silicon, F. Cerdeira, 3rd International Raman Conference Brazil 1975) and shows the effect of high boron doping in silicon. The observed bandshape is a result of the "Fano Interaction" between the continuum of hole transitions in the valence band and the phonons.

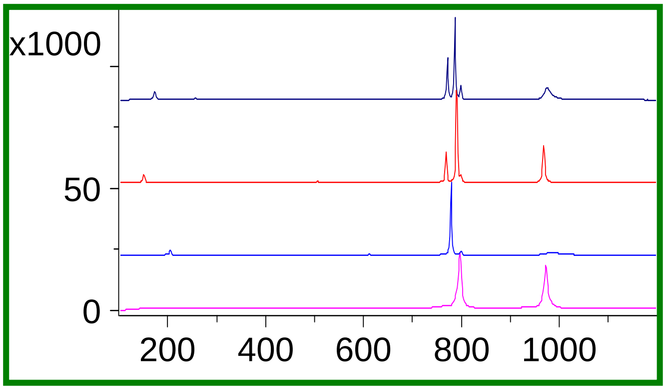

Figure 1: Raman Microprobe spectra of (from bottom to top) 3C, 4H, 6H, and 15R polymorphs of SiC. These spectra were recorded on the LabRam using the doubled YAG laser at 532nm, and an 1800 g/mm grating.

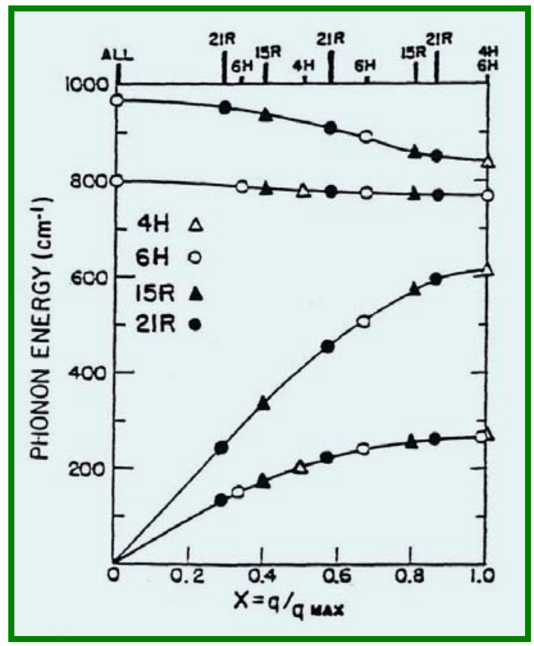

Figure 2. Phonon dispersion curve of cubic SiC, showing the positions of the zone-centered phonons of the non-cubic polytypes after the zone-folding "operation." Reproduced from Phonon Dispersion Curves by Raman Scattering in SiC, Polytypes 3C. 4H, 6H, 15R, and 21R - DW Feldman et.al, Phys Rev 173, 787 (1968).

Examination of the sample also exposed the presence of boron carbide (BC). BC is a material whose stoichiometry can vary, and the spectra are diagnostic of the stoichiometry in the probed region. The spectra shown in Figure 4, reproduced from Boron Carbide Structure by Raman Spectroscopy (Tallant, et.al., Phys Rev B 40, 5649 (1989)) document the variation of the Raman signature with composition.

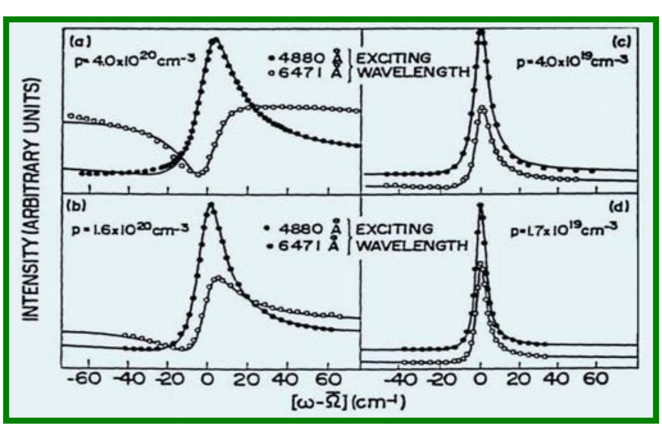

Figure 3. First order band of boron-doped Si (B:Si) as a function of doping, and excitation wavelength (488 vs, 647.1 nm). Reproduced from Raman Scattering by Coupled Electron-Phonon Excitations in Heavily Doped Silicon, F. Cerdeira, 3rd International Raman Conference Brazil (1975).

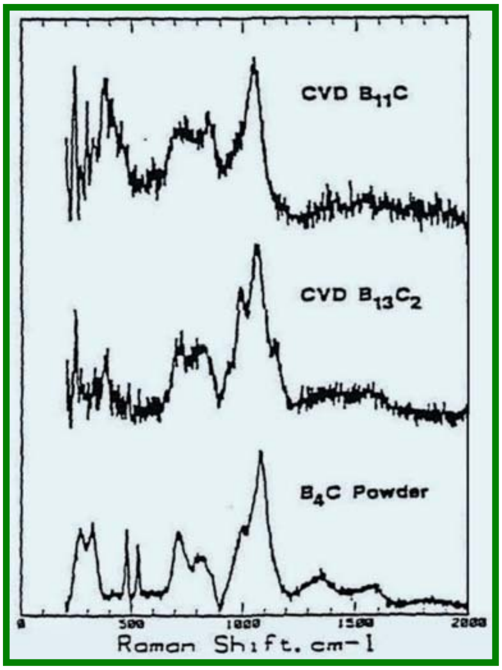

Figure 4. Raman spectra of BC, of various stoichiometries (B_4C, $B_{13}C_2$, and $B_{11}C$ from bottom to top), reproduced from Boron Carbide Structure by Raman Spectroscopy - Tallant, et al., Phys Rev B 40, 5649 (1989) .

Raman maps of SiC conversion coatings on Carbon-Carbon composites

Raman maps indicated the richness of variability of the composition of the phases in this coating. It was, of course, anticipated that there would be SiC over most of the surface, as well as some BC. We observed multiple phases of SiC as well as BC. However, the most interesting observation was that of the presence of small crystals of silicon. According to the Lockheed Martin engineer, silicon precipitates were present only when boron was added to the coating mix. It can be inferred that the presence of the B stabilised the silicon lattice enough to allow these precipitates to form at the expense of some SiC. Apparently the high solubility of boron in the silicon lattice (ca. 0.8% at room temperature which is about 4 times higher than stated dopant values of 10^{20} carriers/cc) stabilised the B:Si (boron-doped silicon) lattice, preventing some of the silicon from reacting with the carbon composite.

Figure 5 shows spectra acquired from a region that was subsequently mapped. The bottom spectrum plotted in blue shows the silicon carbide. The middle spectrum, shown in red, is that of B:Si, and the top figure is that of BC (the B_4C phase).

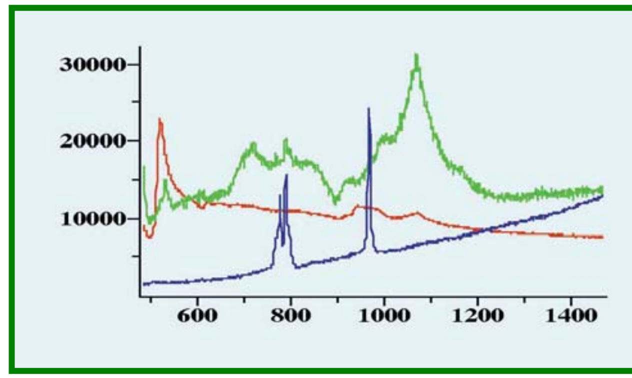

Figure 5. Raman microprobe spectra of SiC (bottom, in blue), boron-doped Si (middle, in red) and B_4C (top, in green).

The LabSpec software was used to map the various phases. The final map was colour-coded, using the colours in Figure 5, for easy correlation between phases. The most fundamental function of LabSpec was used to create the map. Cursors are set to span the wavenumber-shift region of interest, and the intensity between the cursors is used in the Raman map. Up to three phases can be mapped simultaneously using the colours red, blue and green. The results of such a map are illustrated in Figure 6, side-by-side with the TV image.

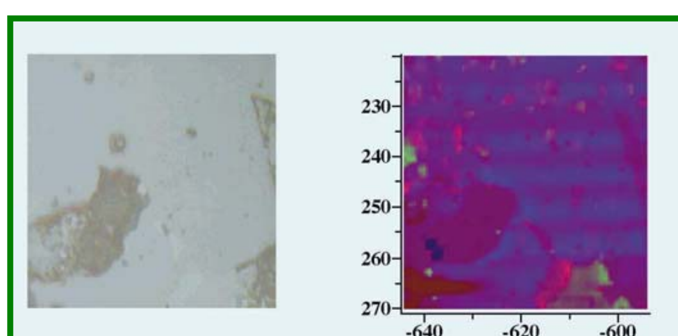

Figure 6. TV image (left) and Raman map (right) of SiC (blue), B:Si (red) and B_4C (green) in a region of the SiC conversion coating.

[A more sophisticated method of mapping, not implemented in this note, uses models in which "pure" spectra would be used to calculate amount of each species at each point in the image.] The blue part of the image shows horizontal linear texture which is most certainly a "ghost" image of the original fibers. The final figure shows a map created by bracketing lines of 2 different phases of SiC. The map shows a coherent change of phase along a horizontal line near the bottom of the figure. **This type of information can certainly by relevant to the process engineer trying to control the process, because the phase formed must be related to the physical conditions of the sample during the process.**

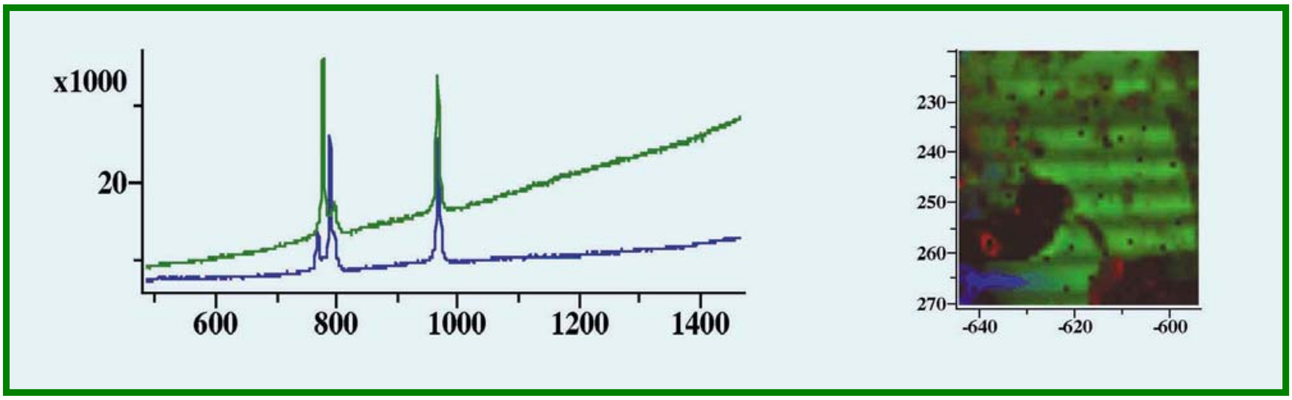

Figure 7. Color coded map (right) of same region of composite as shown in Figure 6. In this case the green and blue represent different phases of SiC, as shown in the spectra

Conclusion

The LabRam Raman Microprobe has been successfully used to determine composition and phase of areas that appear in varying shades of grey in TV-captured images. In addition, confocal maps enable correlation of spatial features with composition. Because of the subtle differences in phase, composition, and doping, that are observed in this sample, it is clear that a Raman microprobe with confocal imaging capabilities can provide information difficult to acquire with other techniques.

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