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M. Sarikaya, J.A. Reimer, and
M. Petrich

April 1986

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ABSTRACT

The utility of various electron optical methods to characterize the microstructure and composition of thin films of amorphous silicon-carbon films formed by plasma-activated CVD of SiH_4 and CH_4 has been investigated. The techniques employed include conventional and high resolution transmission electron microscopy and diffraction, non-dispersive x-ray spectroscopy and electron energy loss spectroscopy.

INTRODUCTION

The unique properties of amorphous hydrogenated silicon-carbon alloys make them candidates for a wide variety of applications for advanced materials. They have been studied for possible use as a wide band-gap semiconductor for multilayer solar cells [1], as a visible-light emmitting device [2], and for very hard, thin-film coatings [3]. The large number of new publications on this subject promises that other applications for these materials will surely be discovered in the future (e.g. MRS 1986 Spring Meeting, Palo Alto).

To understand their properties and to explain the effects of the many processing variables it is necessary to gain deeper knowledge of the complex relationships among microstructure, atomic structure, deposition conditions, and mechanical and electronic properties. As a first step toward this goal, we have evaluated the applicability of some of the electron optical tools that are available to characterize microstructures and chemical composition with reference to the influence of deposition conditions on plasma-activated CVD films of amorphous hydrogenated silicon-carbon alloys.

EXPERIMENTAL METHODS

The following conditions for plasma-activated CVD of α-SiC:H films were employed. The pressure in the reaction chamber was maintained at 300 mtorr with a total gas flow rate of 100 sccm. The $SiH_4 + CH_4$ content of the gas stream totalled 5% and He was used as a dilutent at 95% concentration. The power density of the plasma was maintained at 0.08 Watts/cm^2. The CVD films, from 50nm to 1100nm in thickness, were formed on either Al foil (or Al evaporated on glass), glass, quartz or evaporated carbon films mounted on electron microscope grids. The usual substrate temperature was 275 ^{o}C although in some cases the substrates were not heated and remained close to room temperature.

CVD films of SiC:H on carbon films were examined directly in the electron microscope. Films deposited on Al foil were stripped from the substrate by dissolving the Al in HCl and capturing small pieces on 200 mesh electron microscope Cu grids. Mounted specimens were rinsed in a methyl alchohol-water solution. SiC:H specimens were examined in a JEOL 200CX transmission electron microscope (TEM) or in a Philips 400 equipped with a Kevex energy dispersive x-ray spectrometer ((EDS) system and a Gatan Inc. electron energy loss spectrometer (EELS).

ELECTRON MICROSCOPY

The microstructure of a CVD film of Si:H, i.e. contains no carbon, deposited on Al foil to a thickness of about 1 micrometer is illustrated in Fig. 1. The columnar structure with hemispherical tops is quite apparent. The darker lines that appear in the micrograph are roll markings on the surface of the Al and it may be noted that the columnar structure is not influenced by this or other structures on this scale. The films are surprisingly clean except for occasional aluminum oxide particles that adhere to the film.

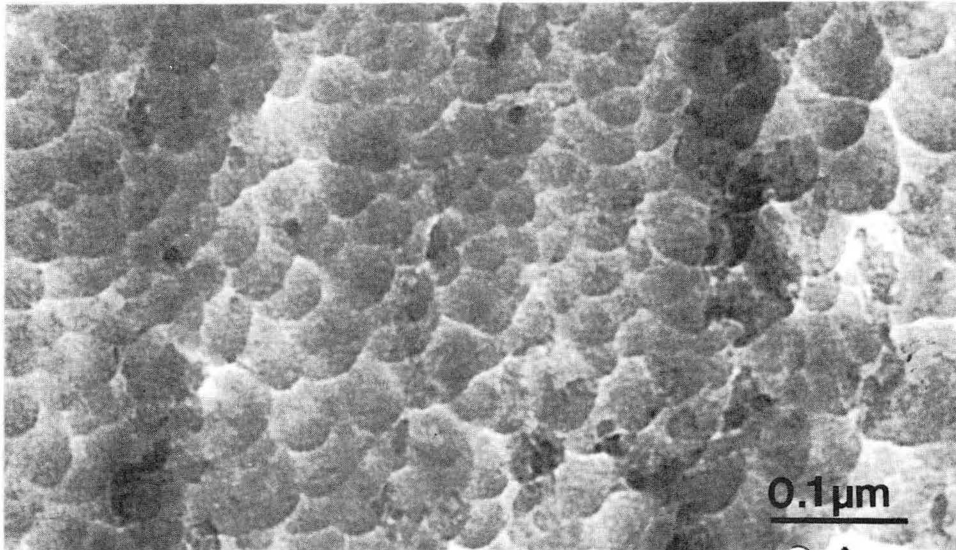


Fig. 1) TEM of a thick (1um) CVD film of Si:H deposited on Al foil.

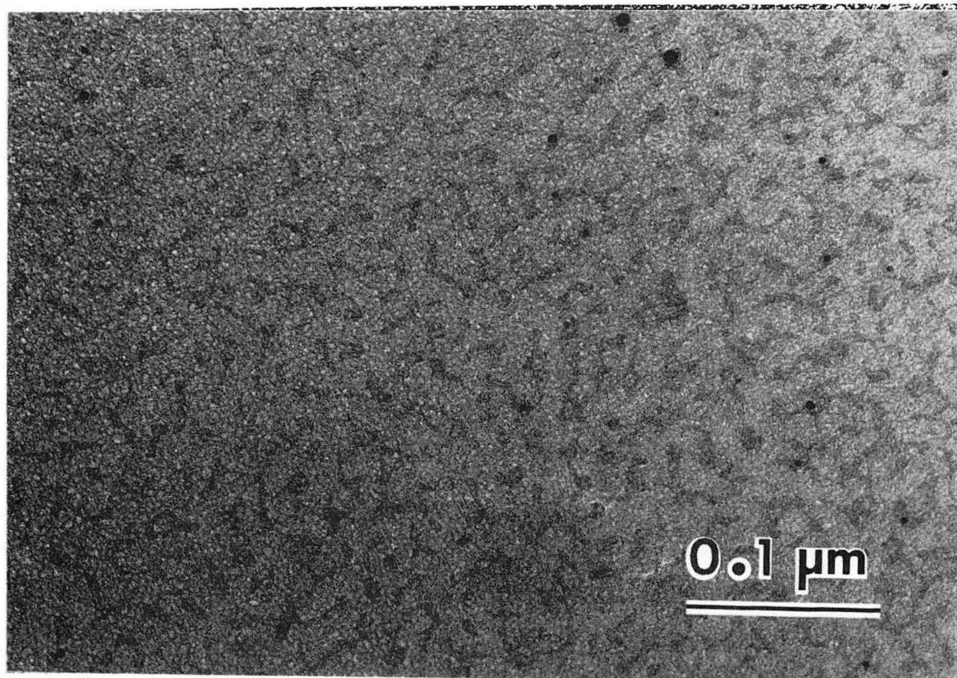


Fig. 2) TEM of a thin film (100 nm) of $Si_{0.65}C_{0.35}$:H CVD on carbon.

The apparent tendancy for CVD films with Si/C around 1.5 and deposited on evaporated carbon to separate into 2 "phases", as illustrated in Figure 2, is under further study. High resolution TEM revealed the presence of small particles from 5 to 50 nm in diameter. Electron diffraction analysis of the larger particles showed that they were crystalline graphite. Lattice images and optical diffraction of the very small particles suggested that the small particles are also graphite although the identification was not definitive.

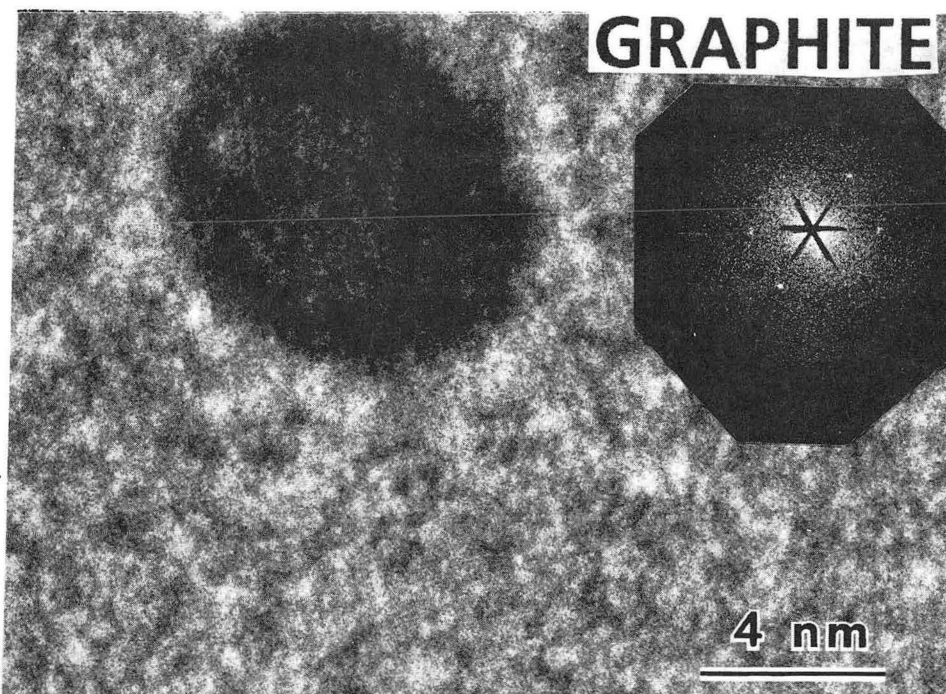


Figure 3. TEM of SiC:H film CVD on an evaporated carbon substrate.

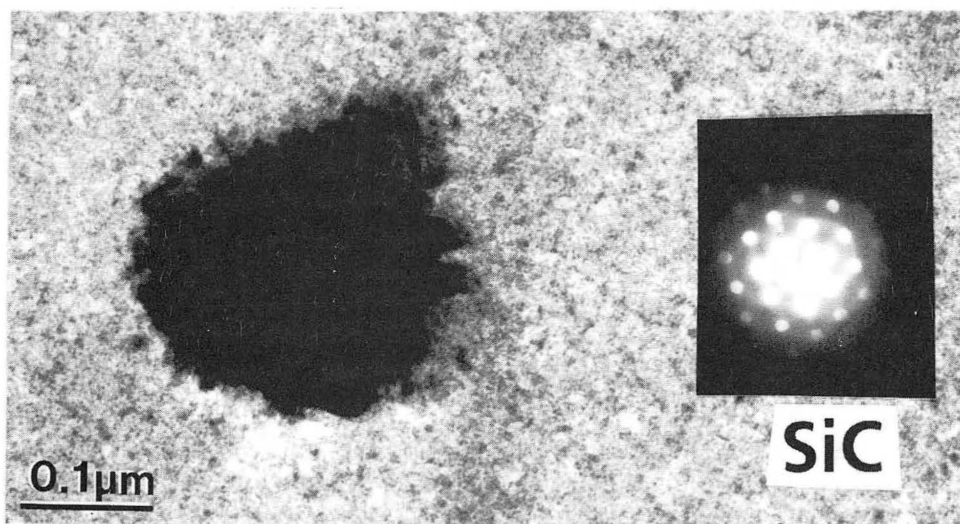


Fig. 4) CVD $Si_{0.65}C_{0.35}$:H showing beam-induced SiC crystallization.

The higher beam intensity used in the TEM-STEM mode for EDS and EELS analyes resulted in the crystallization of CVD films with Si/C near 1.

ENERGY DISPERSIVE X-RAY SPECTROSCOPY

EDS was used to confirm that the films stripped clean from the Al substrate. The occasional particles found on the films were readily identified as Al oxide. The carbon content is measurable with a thin window detector and such measurements will be carried out for comparison with EELS analysis.

ELECTRON ENERGY LOSS SPECTROSCOPY

During transmission through a thin foil specimen some or all of the electrons in the beam undergo inelastic scattering and transfer energy to the sample by exciting atomic and lattice transitions [4]. These energy losses can be detected with a magnetic prism spectrometer and can be used to identify the atomic species present in the sample and their concentration by the location and magnitude of K, L and M edges. Information about specimen thickness and other parameters can be derived from observations and measurements of the low-loss (5-100 ev) portion of the spectrum. The results of such measurements are illustrated in this section.

Fig. 5a shows the EELS for a CVD sample with a Si/C of about 1.4. The spectrum covers the range from 0 to about 500 ev. The scale is changed by a factor of 400 at 50 ev to reveal the C K edge. The Si K edge of this sample is shown in Fig. 5b.

The 0 and low loss region is shown with an expanded scale in Fig. 5c. The occurance of 1 strong plasmon peak indicates that the specimen is about 160 nm in thickness. Plasmon peaks are quite sensitive to electron density and related factors. Changes due to H content of the samples were noted and will be reported separately.

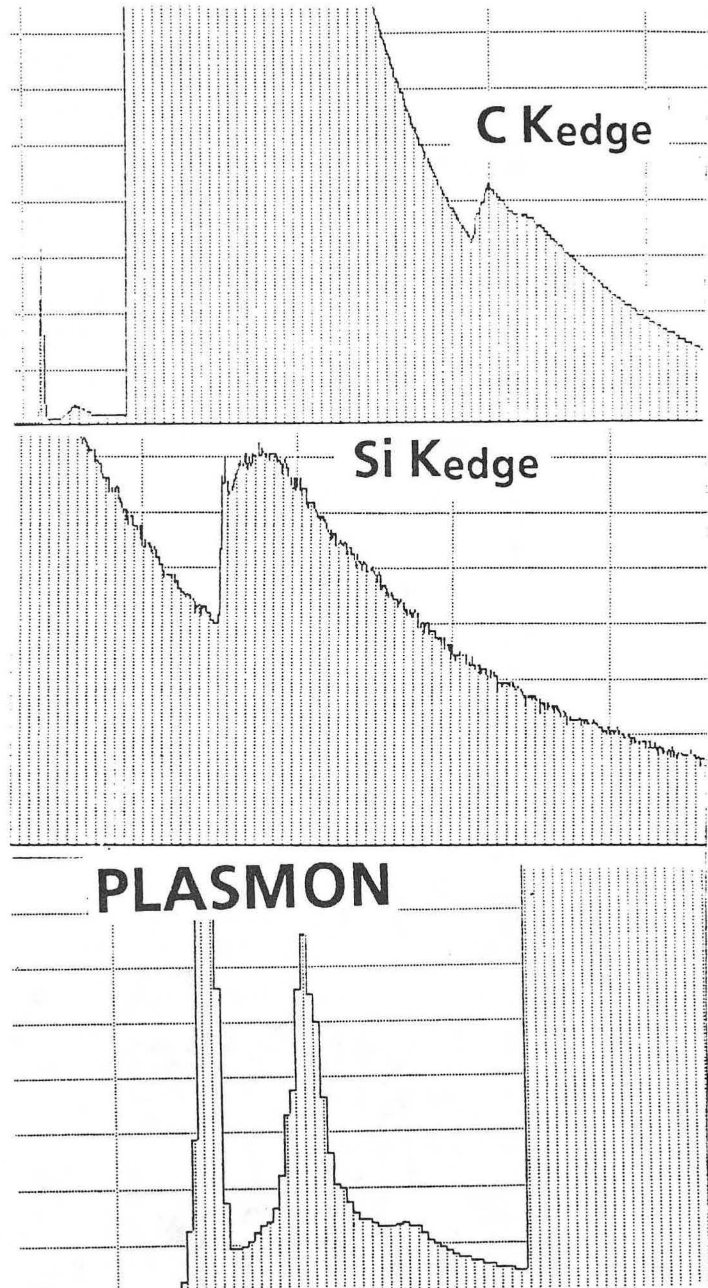


Fig. 5) EELS spectra of CVD SiC.

The total amount of inelastic scattering, I_{in}, (integrated from 0 to max. loss, usually taken to 1000 ev as contribution beyond this level is very small) depends on the scattering cross (atomic number and density) and the sample thickness. Apparent scattering cross sections depend on instrument parameters so that it is preferable to run a sample of known thickness to check the calibration. Results of measurements of total inelastic scattering are shown in Fig. 6.

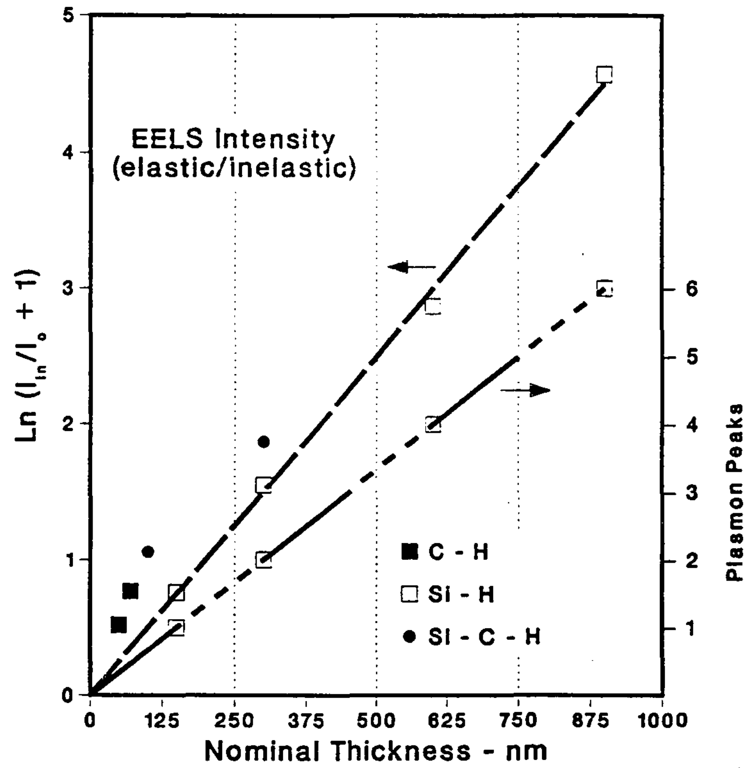


Fig. 6) Effect of thickness on plasmon spectra and inelastic scattering.

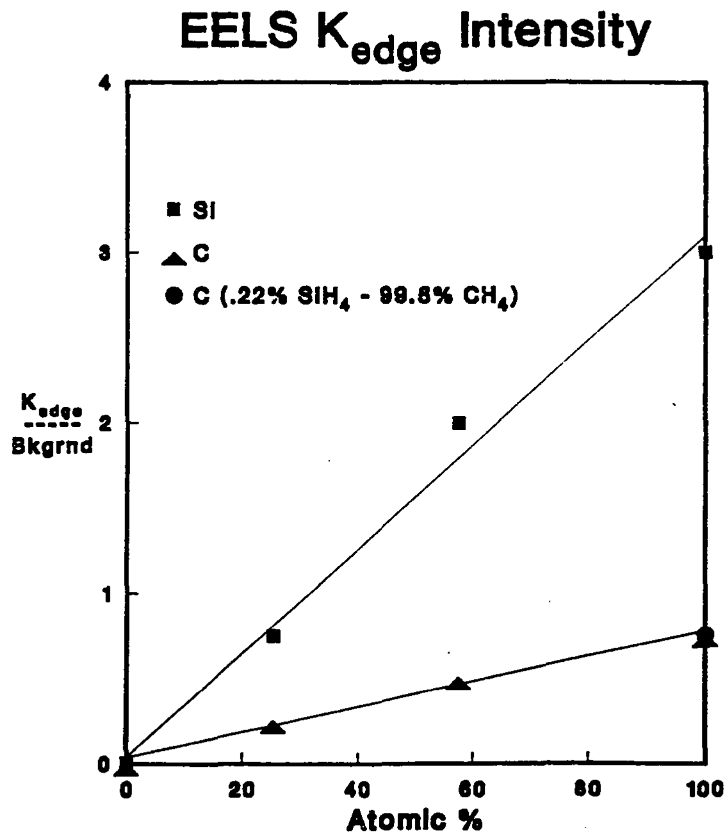
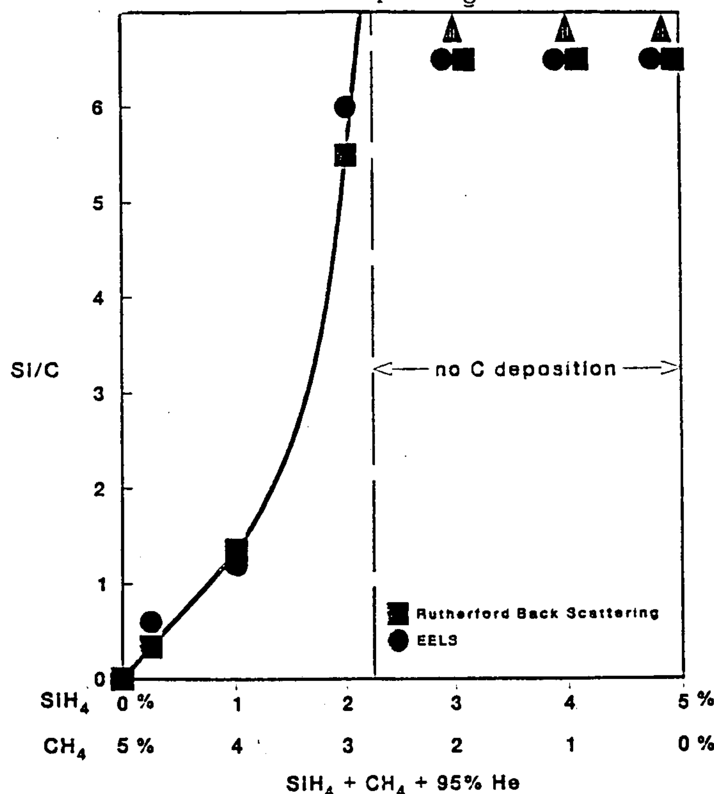


Fig. 7) Effect of composition on Si and C k edge intensity.

As illustrated in Fig. 7, EELS can be used to obtain a qualitative measure of the composition of thin films. A comparison of Rutherford Back Scattering measurements and EELS data on companion samples is shown in Fig. 8. The agreement between the two methods is quite good.



DISCUSSION

This preliminary study of CVD films of SiC:H has demonstrated that analytical electron microscopy can provide a great deal of information about their thickness and composition and their stability under the beam. TEM and electron diffraction indicate that the samples are amorphous but atomic-level microscopy and image simulation will be necessary to establish a more specific structural model for these materials. As for chemical analysis the EELS technique has the advantage that it can be used in the course of electron microscope and electron diffraction studies of the microstructure of CVD thin films without recourse to other instruments. The relationships between microstructure as determined in this study and electronic properties will be reported separately.

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