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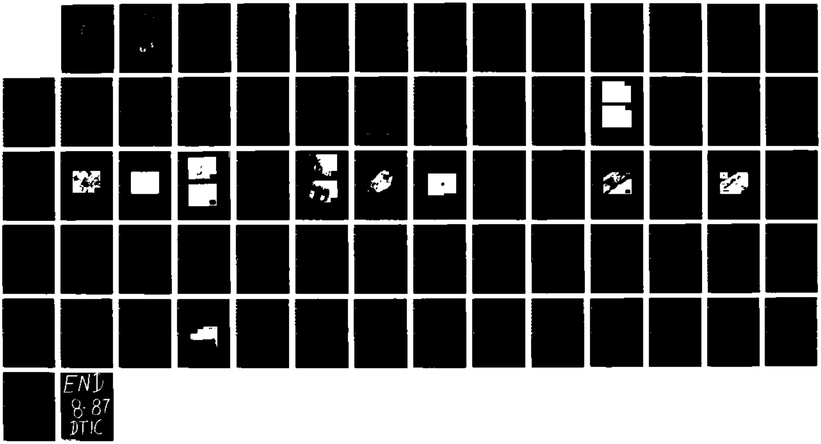

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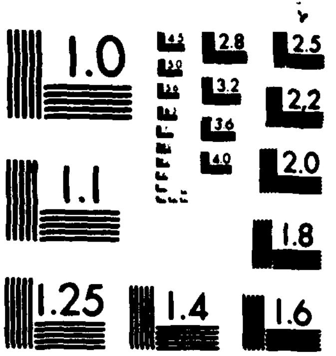
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Annual Report

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Growth, Characterization and Device Development in Monocrystalline Diamond Films

Supported under Contract #N00014-86-K-0666
for the period June 1, 1986 - May 31, 1987

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An apparatus for the growth of diamond films by remote or immersed microwave plasma chemical vapor deposition (CVD) has been designed. This system will also be capable of testing the effect of ultraviolet photon bombardment and a heated tungsten filament on diamond growth. Analytical instruments have been purchased to conduct Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XDS) and Reverse View Low Energy Electron Diffraction (RVLEED). A chamber to be attached to the CVD apparatus to house these analytical techniques is being designed. Copper single crystal boules have been grown for use as substrates during diamond CVD and a system for the deposition of dielectrics onto diamond has been constructed. Finally, several diamond films from outside sources have been examined by various analytical techniques including AES, XPS, as well as scanning and transmission electron microscopy.

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I. Introduction

Diamond is an excellent candidate material for various electronic microwave devices as well as devices for use in high temperature and/or high flux radiation environments and for high current density or high power applications. This very diverse applicability is due to its superior thermal conductivity, saturated drift velocities, resistance to chemical attack and thermal stability. However, to realize this potential of diamond, high quality monocrystalline films must be grown and thoroughly characterized. The latter research is necessary as an iterative procedure for the improvement of the growth process and to guide future device design and fabrication. To achieve these goals, the NCSU diamond program couples investigators from four departments to obtain a unique combination of expertise and experience.

More specifically, the principal objectives of this collaborative research are to (1) grow monocrystalline diamond films on suitable substrates such as Ni and SiC using both past and newly generated knowledge regarding gas species generation, deposition and reaction, and energy and momentum transfer at the growing surface, (2) characterize these films in terms of bonding, structural and electrical character, (3) model and fabricate device structures from these films and (4) work in a collaborative manner with personnel at the Research Triangle Institute in their diamond fabrication research.

Although this document is technically an annual report, it should be noted that Fiscal Year 1987 funding was not received until April, 1987. Therefore, certain equipment purchases and personnel commitments were not possible until very recently. Regardless of this drawback, it is felt that substantial progress has been made regarding the diamond program at North Carolina State University during the past year as is discussed in this report.

II. Film Growth Systems (Davis/Glass)

A. Long Range UHV System

The design of the chemical vapor deposition (CVD) system with ultra-high vacuum (UHV) capabilities is nearing its final stages. Schematics of the system are shown in Fig. 1. The major components will be:

- **Pumping System** - in order to achieve high film purity, UHV pumping ($< 10^{-9}$ Torr) will be obtained with a turbomolecular system prior to growth. During the growth process, in order to obtain the high throughput necessary, a roots blower/mechanical pumping system will be employed.
- **Specimen Preparation Chamber** - a load locked preparation chamber with argon sputter cleaning and heating (1000°C) capabilities will be utilized to obtain reproducible substrate surfaces.
- **Plasma/Remote Plasma Deposition** - a unique design for the deposition chamber will allow both remote and immersed plasma deposition. This will enable direct comparison of these two techniques.
- **Analysis chamber** - an analysis chamber will be connected to the sample preparation chamber via a transfer tube. This will allow surface analysis to be performed prior to exposing samples to the atmosphere.
- **In Situ Gas Species Analysis** - at various points in the system a Residual Gas Analyzer will be employed to determine reactant and product gas species. This is essential for the evaluation of reaction mechanisms of the diamond film growth.

The substrate preparation chamber and the deposition chamber will contain load lock stations for the introduction of samples into the system. Pumping will be accomplished by turbomolecular pumps backed by dual stage rotary vane mechanical pumps to obtain ultra-high vacuum (UHV) base pressures and a roots blower package for high gas throughput during low pressure growth. Purchase Orders are currently

Figure 1a. Top View - Overall System

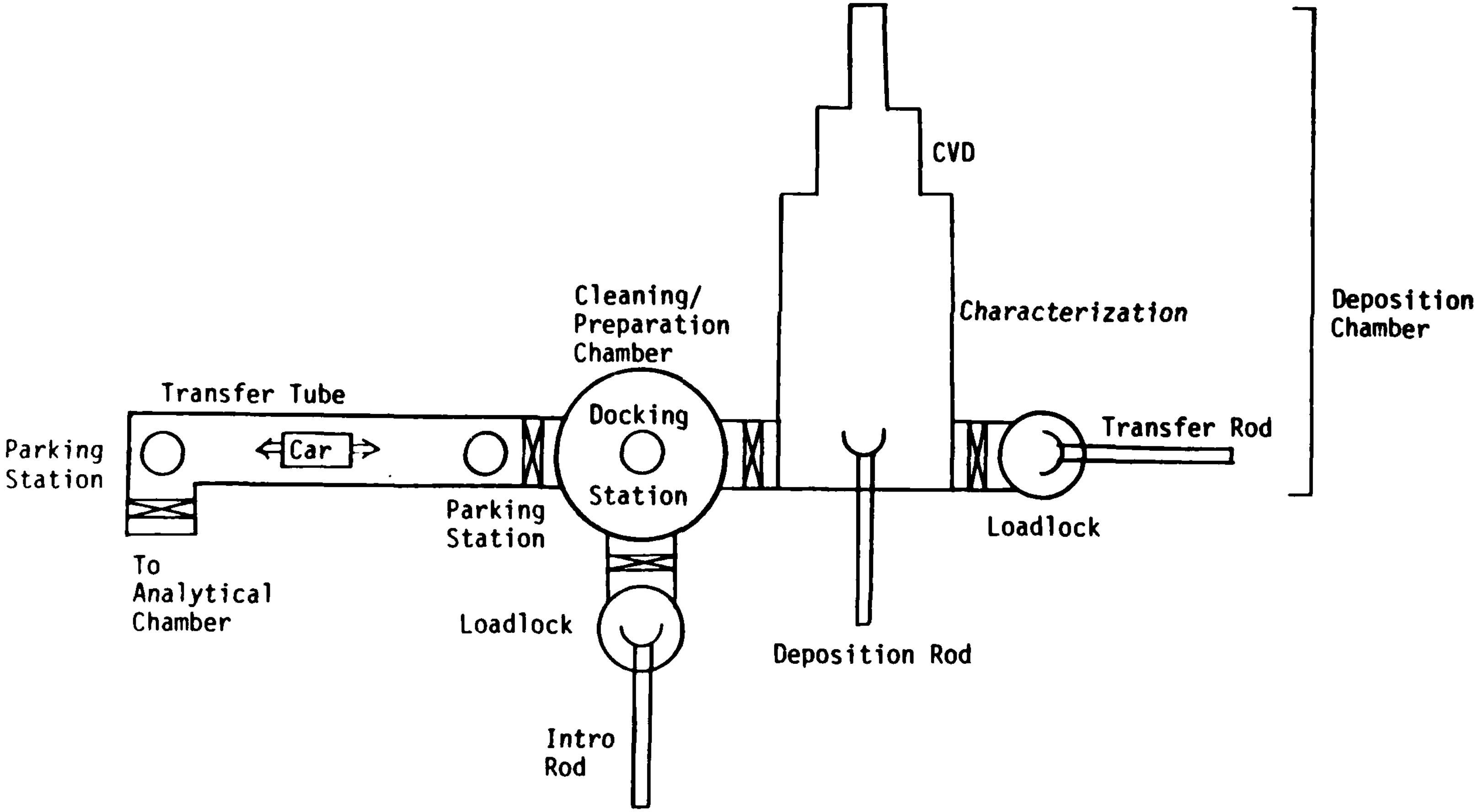


Figure 1. Schematics of CVD apparatus for growth of diamond films.

Figure 1b. Top View - Deposition Chamber

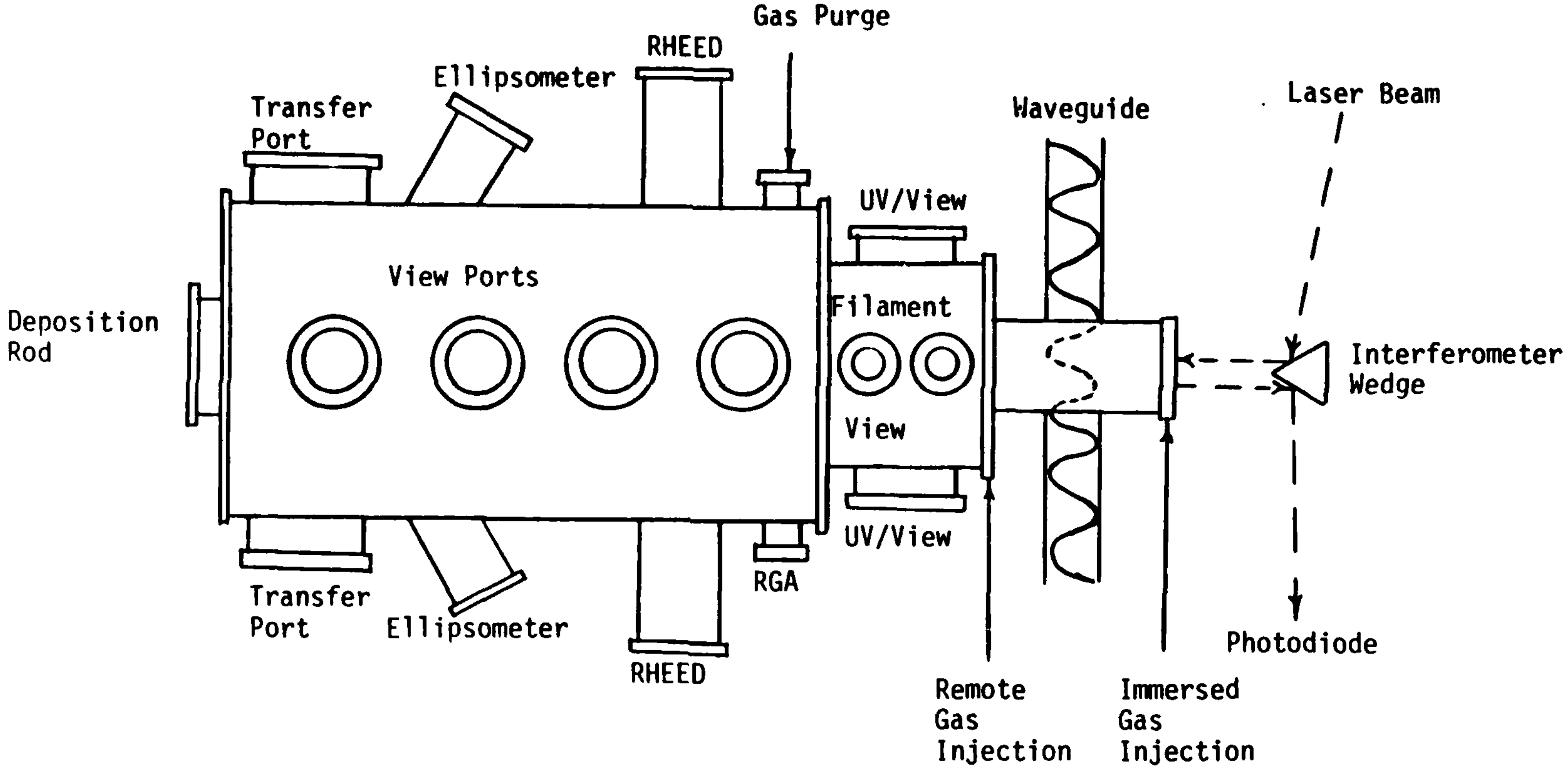


Figure 1c. Side View - Deposition Chamber

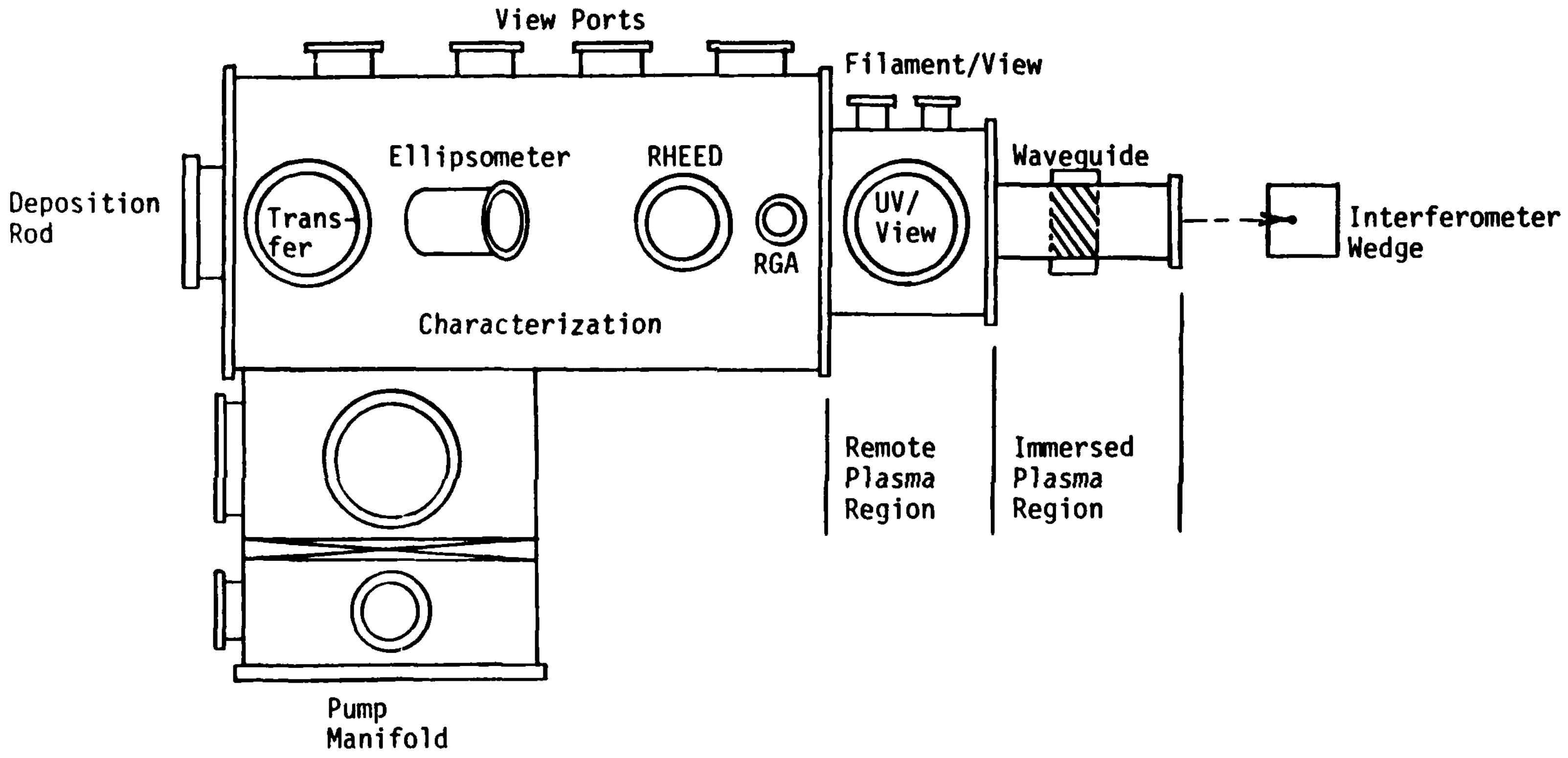


Figure 1d. Back View - Deposition Chamber with Pumping Manifold.

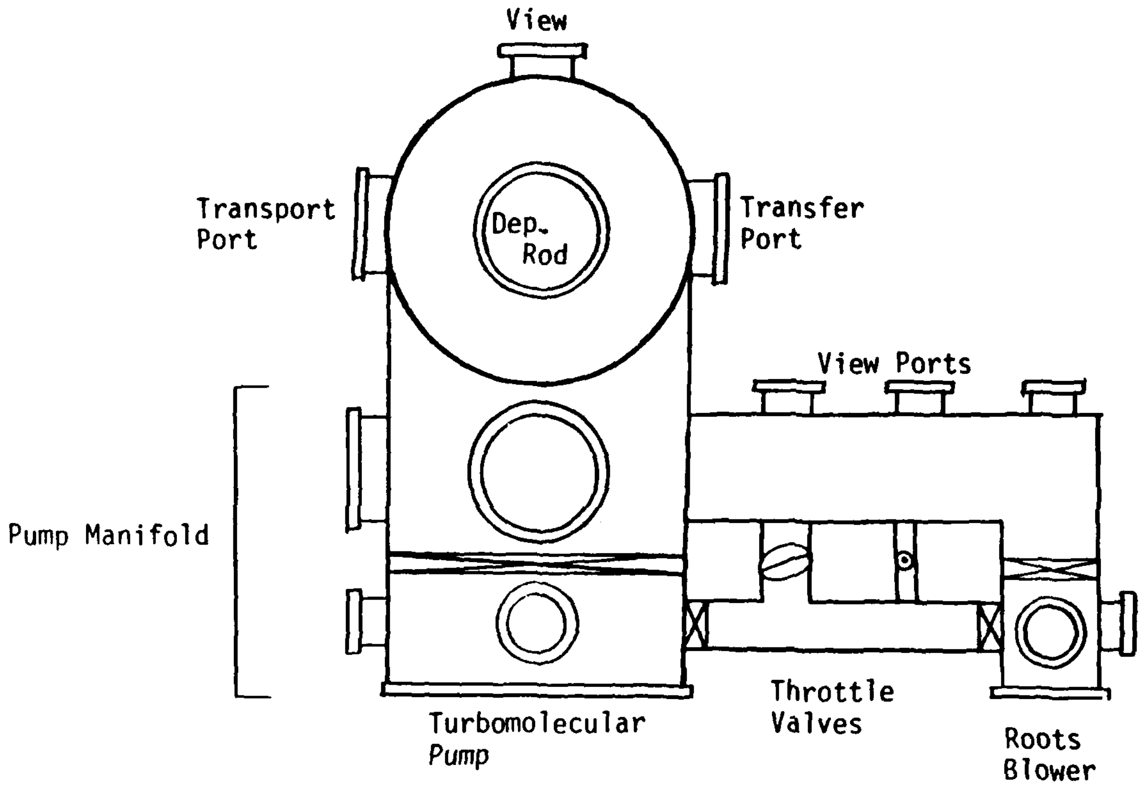


Figure 1e. Side View - Cleaning/Preparation Chamber

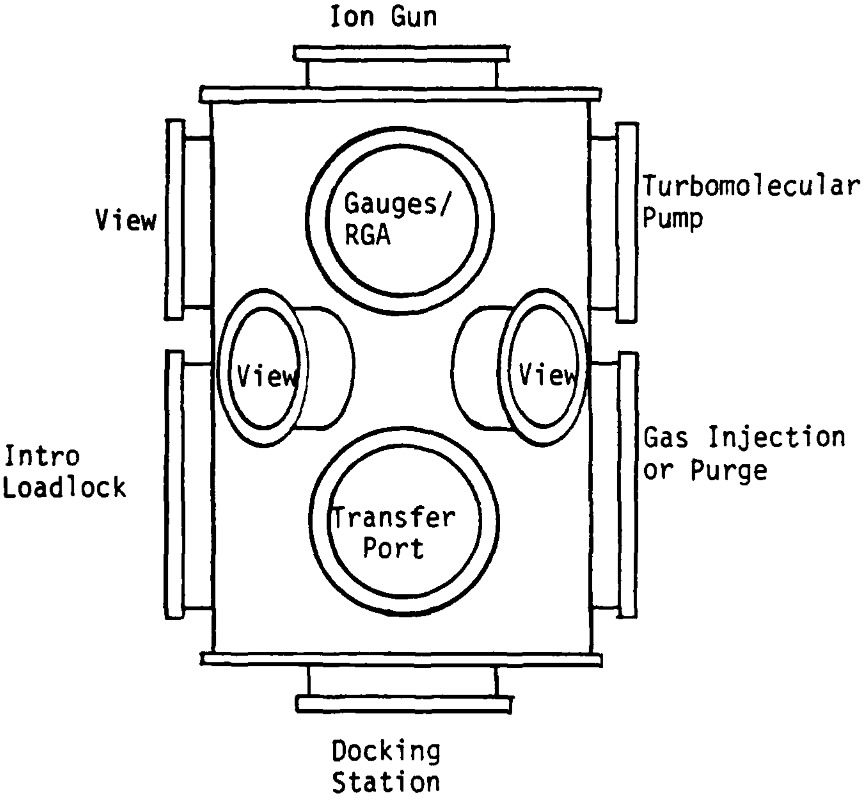
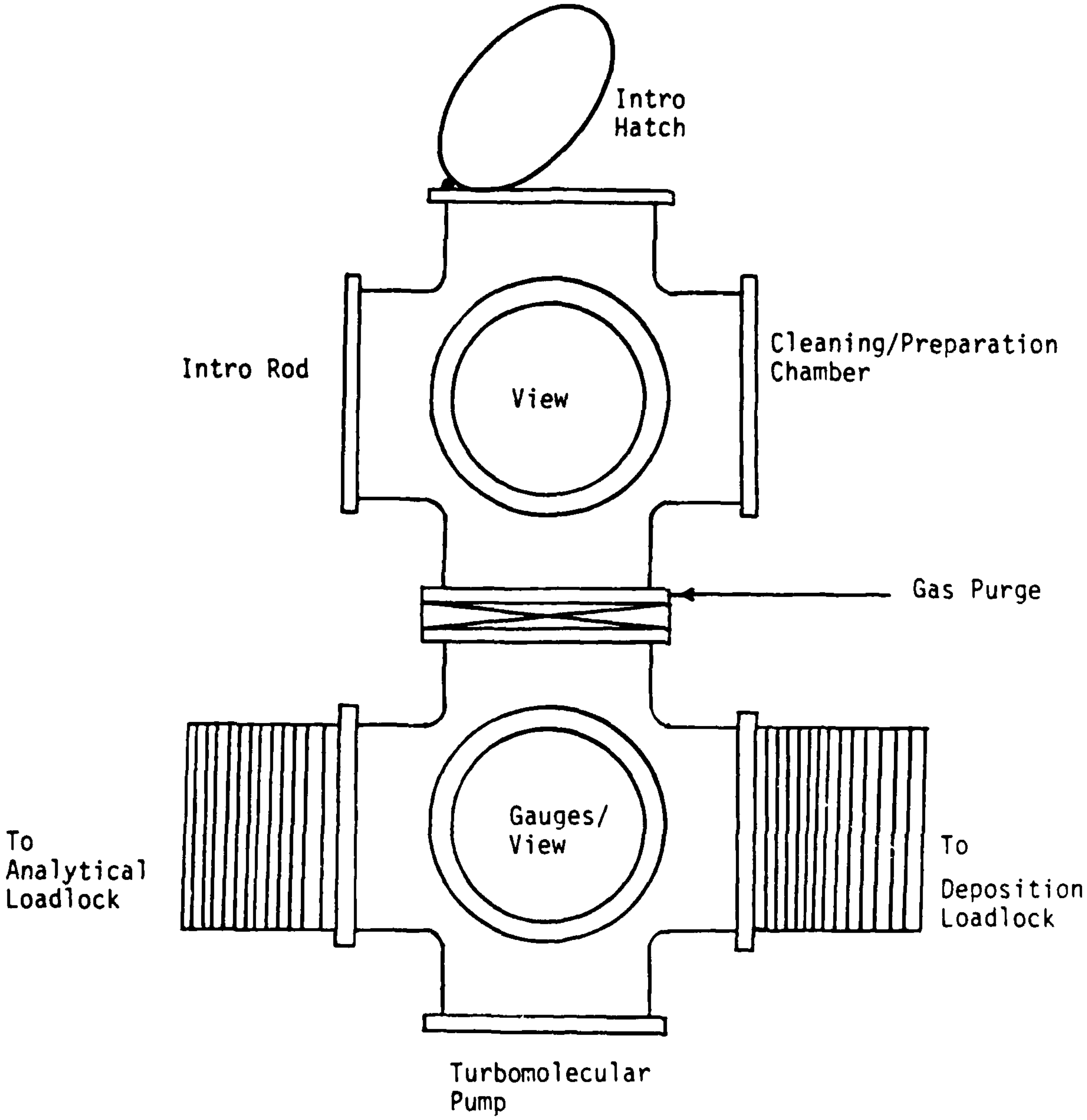


Figure 1f. Side View - Intro Loadlock



Manipulator Table

(1), (3) Parking Station(s)

Functions: 2" Z

Description: These platforms move up and down to move sample from transfer rod to transfer "car."

(2) Internal Transfer Mechanism

Functions: 60" Z

Description: This transfer tube should be large enough to transport 1" dia. wafers from one parking station to the other by means of some transfer "car."

(4) Docking Station

Functions: 2" Z
Resistance heating to 1000°C (optional)

Description: This station will be used to heat up and sputter clean 1" wafer sample before deposition. It also serves the purpose of interfacing the intro rod to the transfer rod.

(5) Intro Rod

Functions: 18" Z
Allignment necessary
Loadlock (optional)

Description: This rod introduces 1" dia. wafer to preparation chamber, dropping sample off at the docking station. Pivotal or x-y allignment will be necessary, initially, to match up with docking station, but will remain stationary afterward.

(6) Deposition Rod

Functions: 40" Z (may be able to decrease this distance if necessary)
1" X
1" Y
Z-axis rotation
Motorized Z rotation (optional)
Motorized Z translation (optional)
Resistance heating to 1200°C (optional)
Water or LN cooled (optional)

Description: This high tech manipulator will be the heart of the system. It needs to interface directly with transfer rod to receive the 1" dia. sample for deposition. CVD conditions require resistance heating to 1200°C and the potential for cooling when sample is immersed in plasma.

Manipulator Table (continued)

(7)	Transfer Rod
Functions:	36" Z Allignment necessary Loadlock (optional)
Description:	The transfer rod will be an alternate way of introducing 1" dia. wafer to system. It will provide transfer function between deposition rod, docking station, and parking station. Again, pivotal or x-y adjustment may be necessary, but will not be changed frequently.

being written for these pumps. All sample transfers will be obtained using the UHV manipulators listed in Table 1.

The deposition chamber will consist of a CVD "head" and a characterization section. The CVD head will contain a microwave plasma source, an ultra-violet light source and a feedthrough for the addition of a tungsten filament at a later date. Deposition may be accomplished via immersed microwave plasma (as the Japanese have shown to be successful) or any combination of remote microwave plasma excitation, UV excitation of the gas and/or substrate and tungsten filament enhancement. This will be possible due to the unique chamber design coupled with the long travel manipulator with an integral substrate heater (1200°C). The characterization section of the deposition chamber will contain a RHEED system for electron diffraction identification of the as grown films, an ellipsometer station for their optical characterization and a residual gas analyzer for the identification of gaseous species present during successful film growth. An interferometric thickness monitor will also be included in the system simply to identify when growth has taken place. It will enter and exit through a window in the CVD head of the system.

The substrate preparation chamber will be utilized to obtain the purity and structure necessary on substrate surfaces prior to the growth of epitaxial films. Cleaning methods have been investigated for this purpose. Si substrates will be chemically cleaned and oxidized outside of the chamber and then heated in UHV to remove the oxide. The heater assembly in this chamber will be housed in the docking station and will be capable of heating to 1000°C. Diamond substrates will be chemically cleaned and heated in atomic hydrogen to insure that no graphitic bonding occurs at the surface. Therefore a gas injection port and a feedthrough for a tungsten filament will also be incorporated into the substrate preparation chamber. Finally, for certain metallic substrates such as Ni which easily allow impurity segregation to the surface, an ion bombardment/anneal sequence is desirable. Therefore an ion gun will also be housed in this chamber. RGA will be attached to this chamber in order to conduct thermal desorption studies to identify surface species on both the substrates and the films.

A transfer chamber will be incorporated into the system (Fig. 1) to allow samples to be transported to the analytical chamber in UHV. This is essential for the proper characterization of both film and substrate surfaces since exposure to the atmosphere will generally cause oxidation and hydrocarbon contamination. Therefore, if accurate surface information is needed, as in the determination of proper conditions for epitaxial growth, samples must not be exposed to atmosphere. The lack of true surface characterization in current diamond deposition systems is believed to be a major contribution to the failure of the achievement of epitaxial growth to date. Although the in-situ analysis of samples causes many design complications, it is believed to be worthwhile. The specifics of the analysis chamber will be discussed in the next section.

B. Short Range Low Vacuum System

As can be seen from the discussion above, this diamond growth apparatus is quite complex and thus its design and construction is very time consuming. Therefore, in order to achieve diamond growth in a reasonable time period, a second system, much smaller and less expensive, is also being designed and constructed in the Materials Science and Engineering Department at NCSU. It will not be UHV and will only contain a tungsten filament for diamond deposition with the option of adding a UV light source in the future. It will be similar to Japanese systems already shown to yield diamond. A resistive graphite heater will be utilized to achieve the proper substrate temperatures. The mass flow control system is already in hand and purchase orders are currently being written for the pump and chamber for this system. It should be noted that this second system will also allow the immediate comparison to tungsten filament growth with the Plasma or UV enhanced growth in the larger more complex system. It is expected to be operational by the next quarterly report.

III. Analytical System (Davis/Glass)

The design of the analytical chamber has proven to be more difficult than first envisioned due to the numerous techniques being incorporated into a single apparatus. Therefore, discussions have been held with Professor Gar Hoflund of The University of Florida to aid in the design of this system. Professor Hoflund has recently started a company called Custom Surface Technologies, Inc. (CST) for precisely this purpose. His vast experience in analytical techniques and UHV design has already been very helpful. Two of Professor Hoflund's systems at the University of Florida are capable of 30 different analytical techniques. Initial meetings have caused us to increase the number and change some emphasis on the techniques to be incorporated in the system. The most significant immediate design change is the addition of a slit in front of the electron analyzer to accommodate angle resolved AES and ESCA. Furthermore, ports for the future addition of UPS, ISS, SIMS, STM (Scanning Tunneling Microscopy), ESD (Electron Stimulated Desorption) and IPS (Inverse Photoemission spectroscopy) will be part of the new design. To obtain some of these techniques, additional funding will be sought in the future. The system will initially be capable of conducting AES (conventional, high resolution and angle resolved), ESCA (conventional and angle resolved), ELS and RVLEED. The RVLEED system, electron analyzer, and x-ray source have already been delivered.

IV. Centennial Campus Facility (Davis/Glass)

Ground has been broken for the new Centennial Campus Research Facility which will house the Diamond CVD and Analytical System as well as the GaN MBE Unit also funded by ONR under a different contract. A floor plan of the laboratory with schematics of the instruments within is shown in Fig. 2. This laboratory will be a class 100,000 clean room isolated from the rest of the building by air locks. Local areas of class 100 will be obtained near specimen introduction chambers by utilizing portable HEPA filters, laminar flow hoods and, in some cases, soft walled regions. Windows will be included to allow visitors to view the laboratories without having to enter the clean room space.

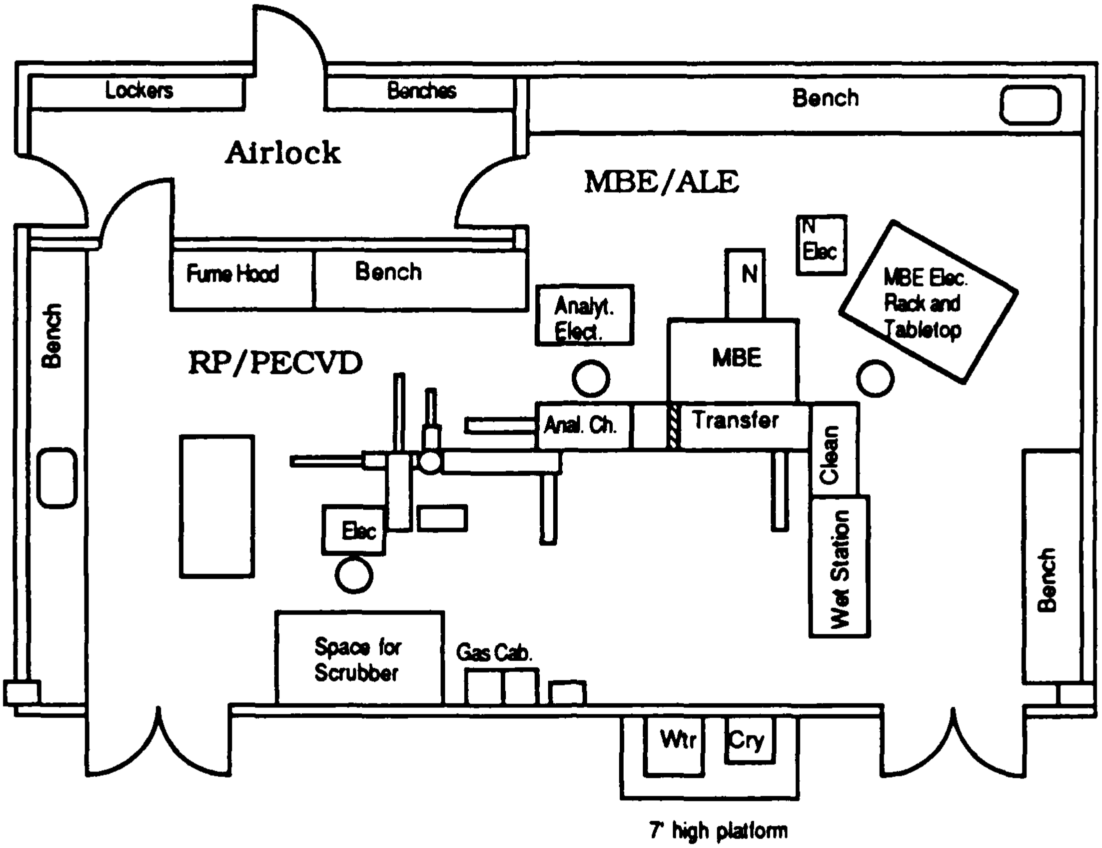


Figure 2. Floor plan of new laboratory in NCSU Research Facility currently under construction. Diamond CVD apparatus, analytical system and GaN MBE Unit are also shown.

V. Diamond Film Analysis (Davis/Glass)

In conjunction with the design and construction of an NCSU diamond growth system, diamond films from other sources are being examined. This is felt to be extremely advantageous to enable NCSU and other U. S. investigators to quickly reach the state-of-the-art in the area of diamond research. Furthermore, the proper analysis and characterization of diamond films is essential for the improvement of growth processes.

The main source of films has thus far been Kobe Steel, Ltd., of Kobe, Japan. These films were grown by immersed microwave plasma enhanced chemical vapor deposition. Kobe has also given NCSU a small research grant to analyze the films they have supplied. Although it is understood that no proprietary information will be given to, or is desired by, NCSU, Kobe has been very open and very helpful to the diamond research efforts here. Similarly, the National labs which investigators here at NCSU have had contact with have also been quite open as shown in a later section of this report discussing recent developments in Japan. In general, an excellent relationship is developing between Kobe and NCSU, which is very beneficial for the diamond program. A diamond film was also supplied by the Research Triangle Institute (RTI) grown early in their program and has been analyzed as thoroughly as possible. However, the small size and very thin nature of this sample prevented a thorough analysis.

Initial analyses of the films were presented in a poster at the February 6, 1987 Diamond Workshop held at MIT, Lincoln Laboratory. This data, as well as many interesting new results are given in the following sections.

A. Secondary Ion Mass Spectrometry (SIMS)

SIMS analysis was conducted both on the Kobe and RTI films with a Cameca IMS-3f direct imaging microprobe in order to determine the impurity elements present.

Scans of Ion Counts/sec. vs. Atomic Weight (usually referred to as Bar Graphs), depth profiles and chemical maps were conducted using an O^- primary ion beam. Unfortunately, accurate quantification of SIMS data (i.e., atomic concentrations) is not possible unless implanted standards are utilized. This requires that each impurity whose concentration is desired be implanted into "standard" films at known ion doses and used for comparison with the unknown concentration of that impurity in the films of interest. This is well suited for the analysis of specific dopant level concentrations but is not feasible for a large number of impurities, as is needed in an overview analysis , due to the time and expense of implanting and analyzing the standards. Another disadvantage of SIMS analysis is its high cost. Nonetheless, if utilized properly, SIMS can discern various important facts about impurities in a material as discussed below.

1. Bar Graphs

Ionic counts per second were recorded for molecular weights from 1 to 200. During this sweep, molecular filtering was utilized to avoid interference from molecular, as opposed to elemental, species generated during the analysis. However, interference is still possible, thus relative isotope abundance patterns were utilized to identify elements. As previously discussed, quantification is not possible due to the absence of standards for diamond SIMS analysis. However, a very rough order of magnitude approximation of impurity concentrations can be obtained if matrix effects are ignored and published relative ion yield data* is utilized to determine concentrations relative to C ion yield. The results of such an analysis are shown in Table 2. The identification of the elements present is believed to be accurate but caution should be exercised in the use of the concentration values. They are only useful to bracket one to two orders of magnitude.

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* From H. A. Storms, et. al., Anal. Chem 49, No. 13 Nov. (1977).

SIMS COMPOSITIONAL ANALYSIS (~ $^{a}/_{o}$)

Kobe Film #	Kobe Film#	RTI Film
H(.2)	H(.2)	H(2)
0(.7)	0(.9)	0(.8)
Al(.03)	Al(.05)	N(.4)
Si(.03)		Si(.01)
		H(?)$^{+}$

Trace Impurities (< .005 $^{a}/_{o}$)

Mg, Ca, Na Cl	Si, Ca, K, Fe,	Na, Mg, Al, K
Fe, C, Ti	Cu, Z, Cr	Ca, Ti, Cr, Fe,
		Cu, Ge

Table 2. - Concentrations are rough order of magnitude approximations. Implanted standards were not utilized and impurity segregation may affect results significantly (see chemical mapping section)

Besides the lack of standards, inaccuracies arise due to impurity segregation which causes much higher local concentrations since the image field for these bar graphs (~ 150µm) is iarger than the segregated regions (see chemical mapping section). When different scans yielded different concentrations due to this

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+ Detected only during Cs^{+} bombardment segregation, the maximum concentration observed is given. Furthermore, a high hydrogen background and the use of O^- as the primary beam imply that data for these elements are approximations of the upper bounds on the concentrations and in actuality they may be much lower. Nonetheless, the impurity elements have been identified and rough approximations of upper bounds on their concentrations have been determined.

2. Chemical Maps

Since the Cameca instrument is a direct imaging probe, chemical mapping of impurities is possible with a spatial resolution of ~ 5 to 10µm and an image field of 400µm. Although this data cannot be quantified, it indicates that impurities are segregated as shown in Figure 3 for Si and Al in Kobe Sample #1. Similar results were observed for O and H impurities. Furthermore, in certain maps these elements appeared to come from the same regions of segregation, whereas in others the segregated regions of different elements were unrelated. RTI films were also observed to contain regions of segregated impurities, especially Si and Al. However, due to the very thin nature of the RTI film, these results may be attributed to pinholes in the film thus allowing a contribution from the substrate.

3. Depth Profiles

Depth profiles of C, Si, O and H were also obtained and are shown in Figure 4 for Kobe Film #1, which is very similar to Kobe Film #2. The hydrogen ion yield is similar in both the film and the substrate indicating that it is possibly due to the background level. Although the O appears to be greater in the substrate than in the film, this is probably due to the change in matrix (i.e., diamond to Si) interacting with the primary O^- beam. Thus, no conclusions should be drawn about the O concentrations except the rough approximation of the upper limits as discussed in the

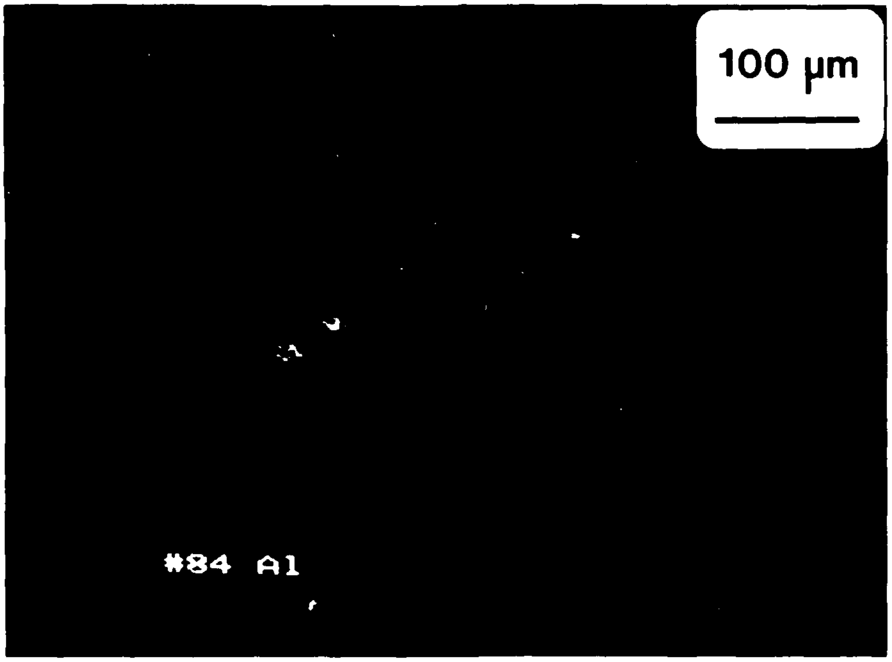


Figure 3. Chemical Maps of silicon and aluminum for Kobe sample #1.

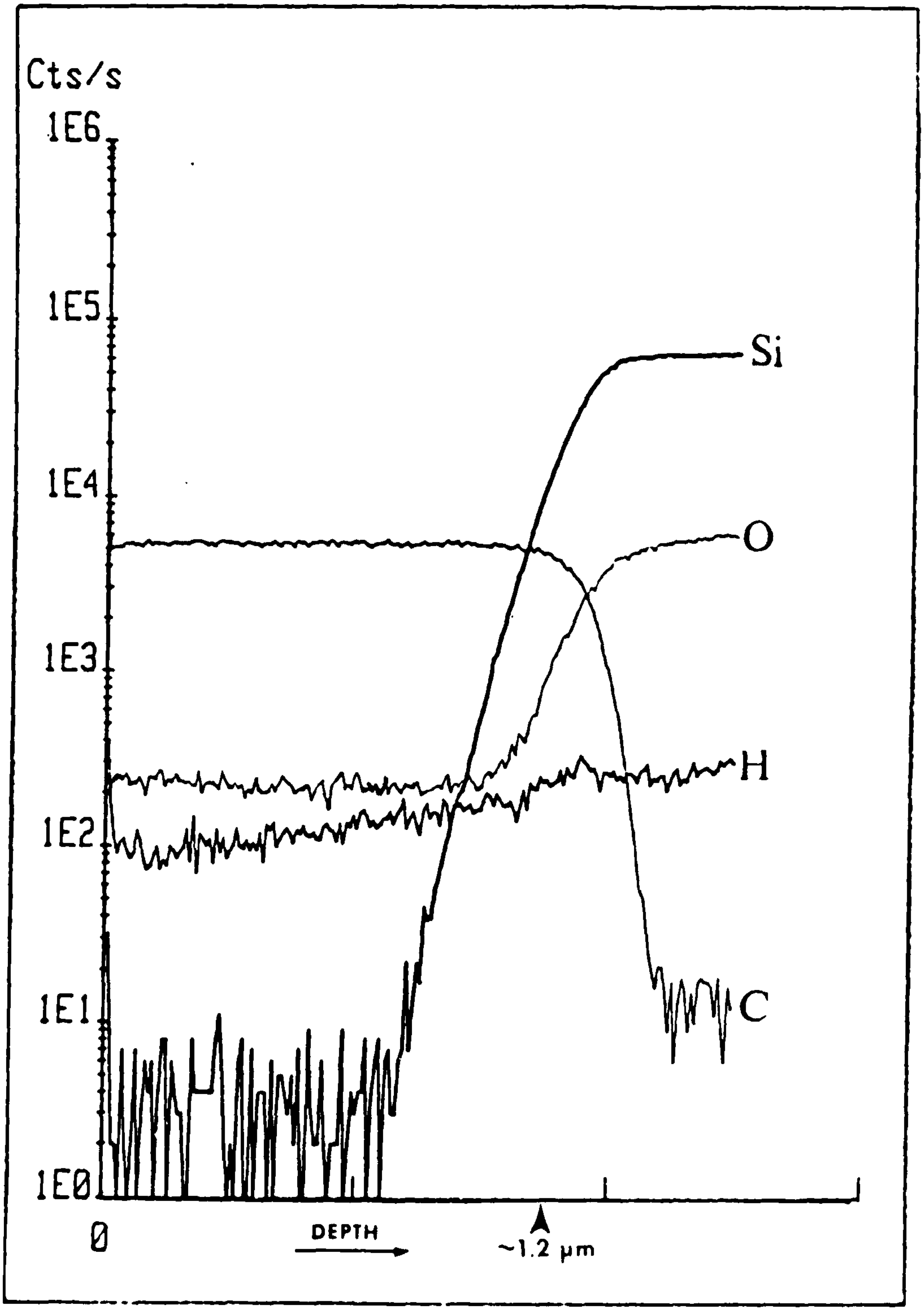


Figure 4. SIMS depth profile of Kobe sample #1.

section on SIMS Bar Graphs. One of the most interesting features of the depth profiles of Kobe films are the very smooth concentration changes across the interface. This is contrary to observations of the films from the Research Triangle Institute (Fig. 5) which clearly shows an ion yield change for C at interface, suggesting the presence of a buffer layer such as SiC. If such a buffer layer exists in the Kobe films, it must be less than 500 Å to be undetected in the SIMS Analysis.

From the depth profiles of the Kobe films it also appears that the change in C concentration across the interface is more rapid than the change in Si. This may indicate more Si diffusion into the film than C diffusion into the Si, possibly due to the numerous grain boundaries in the films. The opposite appears to be true for the RTI film. However, this is a very tentative conclusion and has not been verified by repeated depth profiling. A final conclusion from the depth profiling is that the thickness of the Kobe Samples #1 and #2 are ~ 1.1 and ~1.2μms, respectively. This was determined by depth profiling until the interface was reached and then measuring the resultant crater depth with a profilometer.

B. Scanning Electron Microscopy (SEM)

In order to examine the surface morphology of the diamond films, an Hitachi S530 scanning electron microscope (SEM) was used. Film surface morphology is very important because it gives an indication of the predominant growth mechanism. An understanding of the mechanism is very beneficial for improving film quality. The SEM which was utilized also contains a Tracor energy dispersive x-ray spectrometer which was used to obtain semi-quantitative compositional analysis of the diamond films.

All of the Kobe diamond films examined thus far consist of multi-faceted diamond grains ranging from less than one micron up to approximately one micron in size (as measured across a single facet). Although the orientation of the individual diamond grains appears to be random relative to the film, numerous facets have

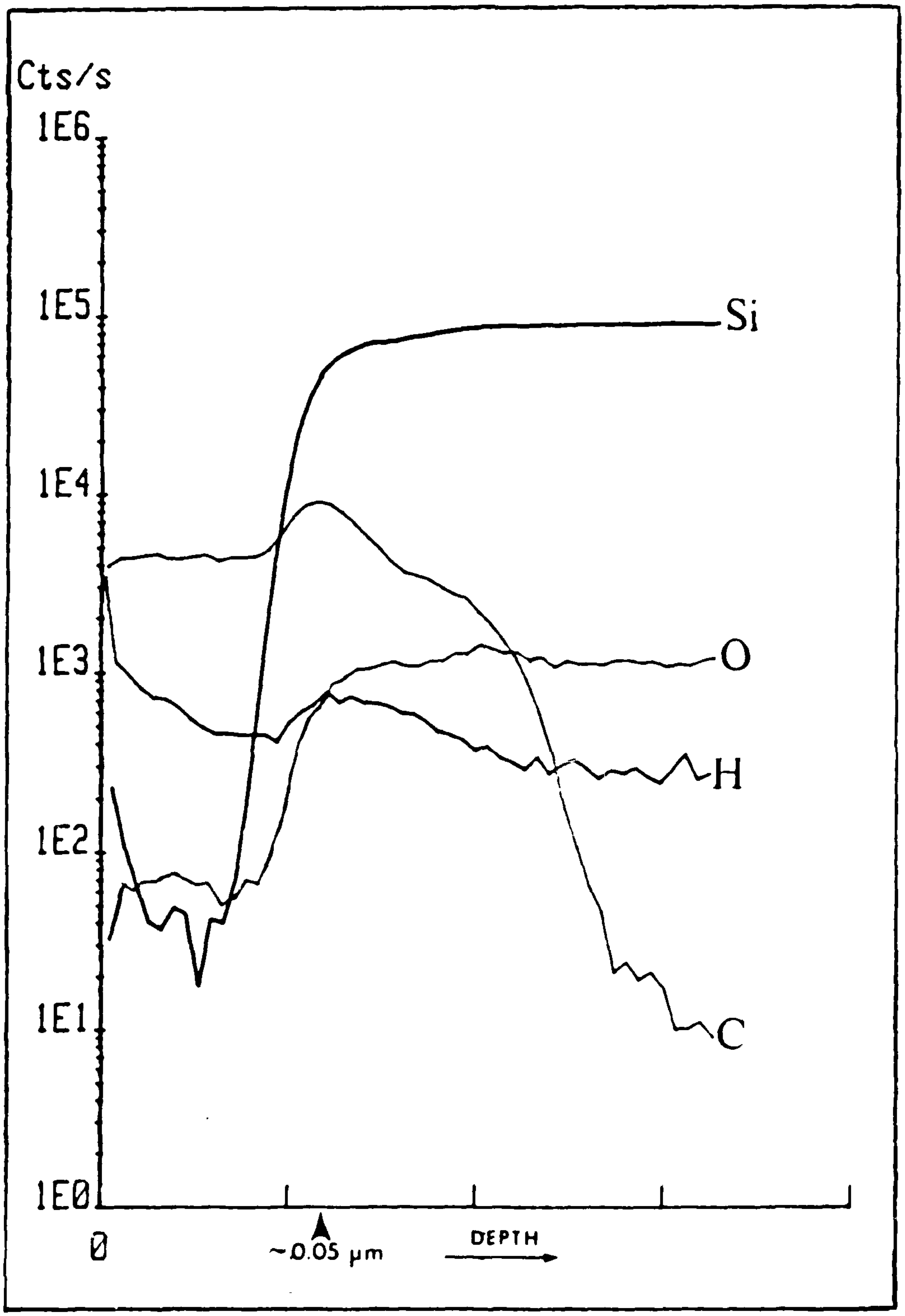


Figure 5. SIMS depth profile of RTI sample.

symmetry characteristic of crystallographic planes. For example, SEM micrographs of sample #2 show that four-fold symmetry cube faces are present on several of the grains as shown by the arrow in Fig. 6. This symmetry indicates that these faces are (100) planes. Other high symmetry planes such as three-fold (111) facets have also been observed as shown in the micrograph of Sample #1 (Fig. 7). A network of apparent growth ledges on the primary grain is also observed, causing the surface of the facet to appear rough.

Another interesting feature observed in Fig. 7 is the secondary nucleation which occurred on the large facet of the predominant grain. This secondary growth appears to have formed another grain with three-fold symmetry which has a distinct relationship to the primary face. Energy dispersive x-ray analysis (EDX) of the diamond film has also been attempted to determine its elemental composition. Although this EDX cannot detect elements lighter than sodium, it is useful for qualitative analysis of heavier impurities. The results indicated that, other than Si, all impurity concentrations were below the limits of detectability (~ 1%). The silicon which was detected may have been caused by spurious signals due to the presence of the silicon substrate.

SEM of the RTI films showed an entirely different morphology as seen in Fig. 8. As opposed to faceted grains, the surface consisted of small rounded features best described as "hillocks". The hillocks were approximately .25 µms in diameter and were also observed during transmission electron microscopy. As with the Kobe films, no impurities other than Si (probably from the substrate) were observed during EDX in the SEM.

C. Transmission Electron Microscopy

An Hitachi H-800 STEM at 200 keV was utilized to observe the diamond film via plan-view transmission electron microscopy (TEM), cross-sectional transmission electron microscopy (XTEM), and selected area diffraction (SAD).

For plan-view TEM, the silicon substrate was first thinned to 65 microns using

Figure 6. Scanning electron micrograph of Kobe sample #2. Note the four-fold, (100) type symmetry of the facets.

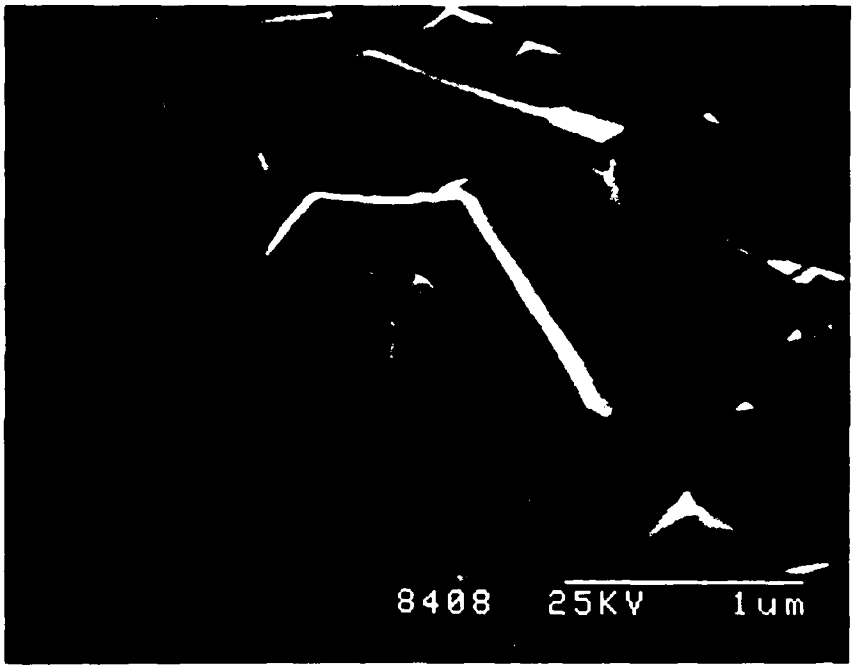


Figure 7. Scanning electron micrograph of Kobe sample #1. Note the three-fold, (111) type symmetry of the facets.

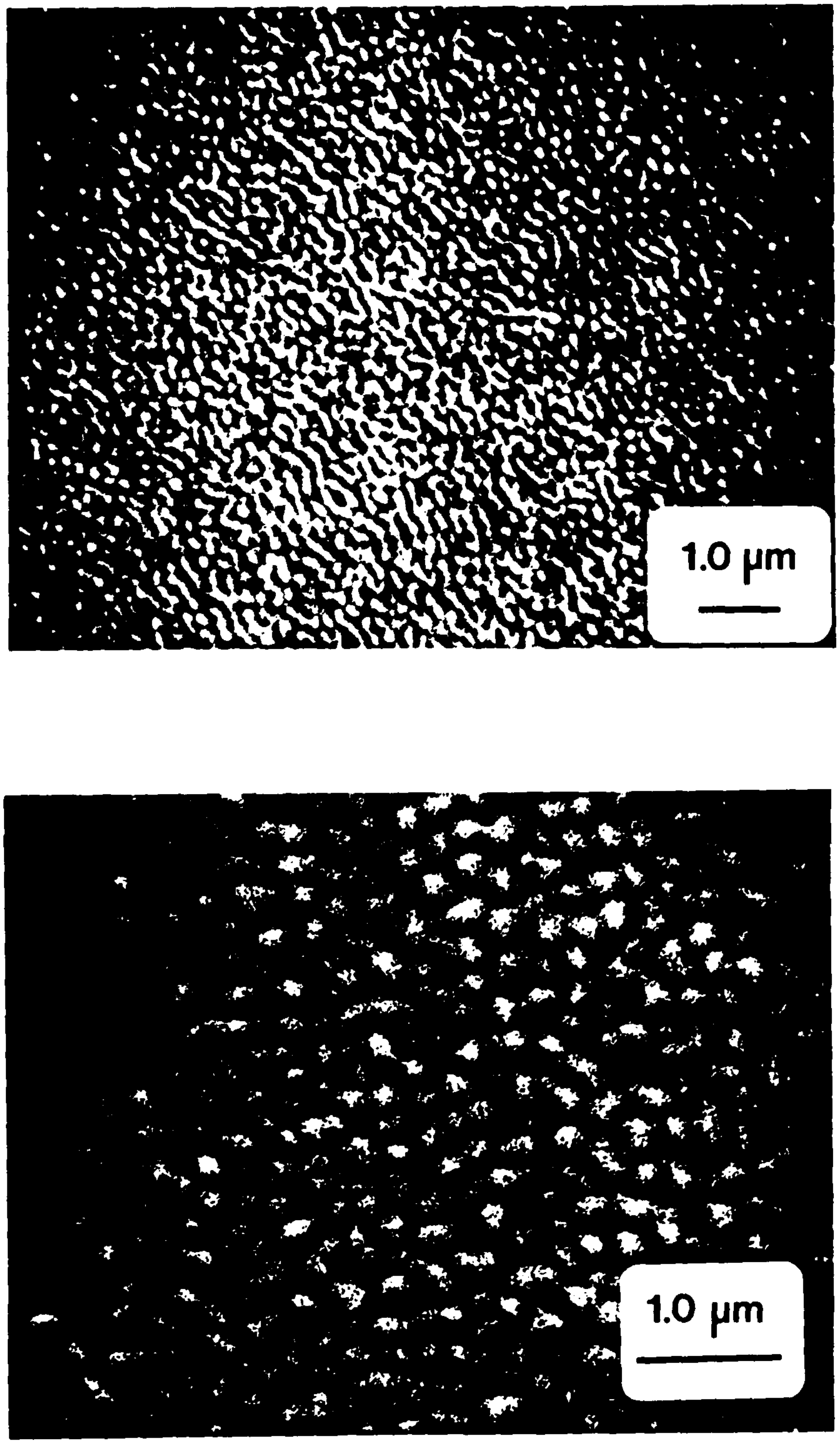


Figure 8. Scanning electron micrograph of RTI film. Note the rounded, "hillock" features.

600 grit silicon carbide paper. The substrate was then dimpled using a steel ball coated with 1 micron diamond paste. After mounting the sample on a molybdenum support ring, the substrate was ion milled to a thickness of less than 1000 angstroms using a 6kV beam of Ar^+ ions.

Figures 9 (a) and (b) are plan-view TEM micrographs of a diamond grain in Kobe Sample #1 viewed at different tilt conditions. As the tilt angle is altered, the variation in contrast in certain regions indicate the presence of twins (see arrows on micrographs). In addition, dislocation lines can also be seen in these micrographs as indicated by the * on micrograph 9(b).

Figure 10 is a plan-view TEM of a single diamond grain observed with the e^- beam parallel to the [110] direction in sample 84. Numerous twins are present on the {111} planes which are in the diffracting condition. Figure 11 is the electron diffraction pattern from this grain. Twinning is found on the $(11\bar{1})$ and $(1\bar{1}1)$ planes, as evidenced by the twin spots which are indicated on the diffraction pattern. These twins have probably occurred in [112] directions which are characteristic of diamond. The streaking in the diffraction pattern is believed to be due to the presence of coherent twin boundaries of thickness less than 100 angstroms (B. V. Derjaguin et al., J. Crystal Growth, 31 (1975). Another interesting feature of this bright field examination is that under higher magnification, no particulates or other impurities were observed in the films. Furthermore, the grain boundaries appeared to be very sharp within the resolution limits of the current study.

The spacings of different planes in the diamond grain were calculated and the results of these calculations are shown in Table 3. In addition, the spacings for natural diamond are included in the table for comparison and show excellent agreement. It is also important to note that no graphite or amorphous component was observed during the electron diffraction research of the Kobe films.

Plan view TEM of the RTI film showed a very different structure. Small crystals were embedded in what appeared to be an amorphous matrix. Selected area electron

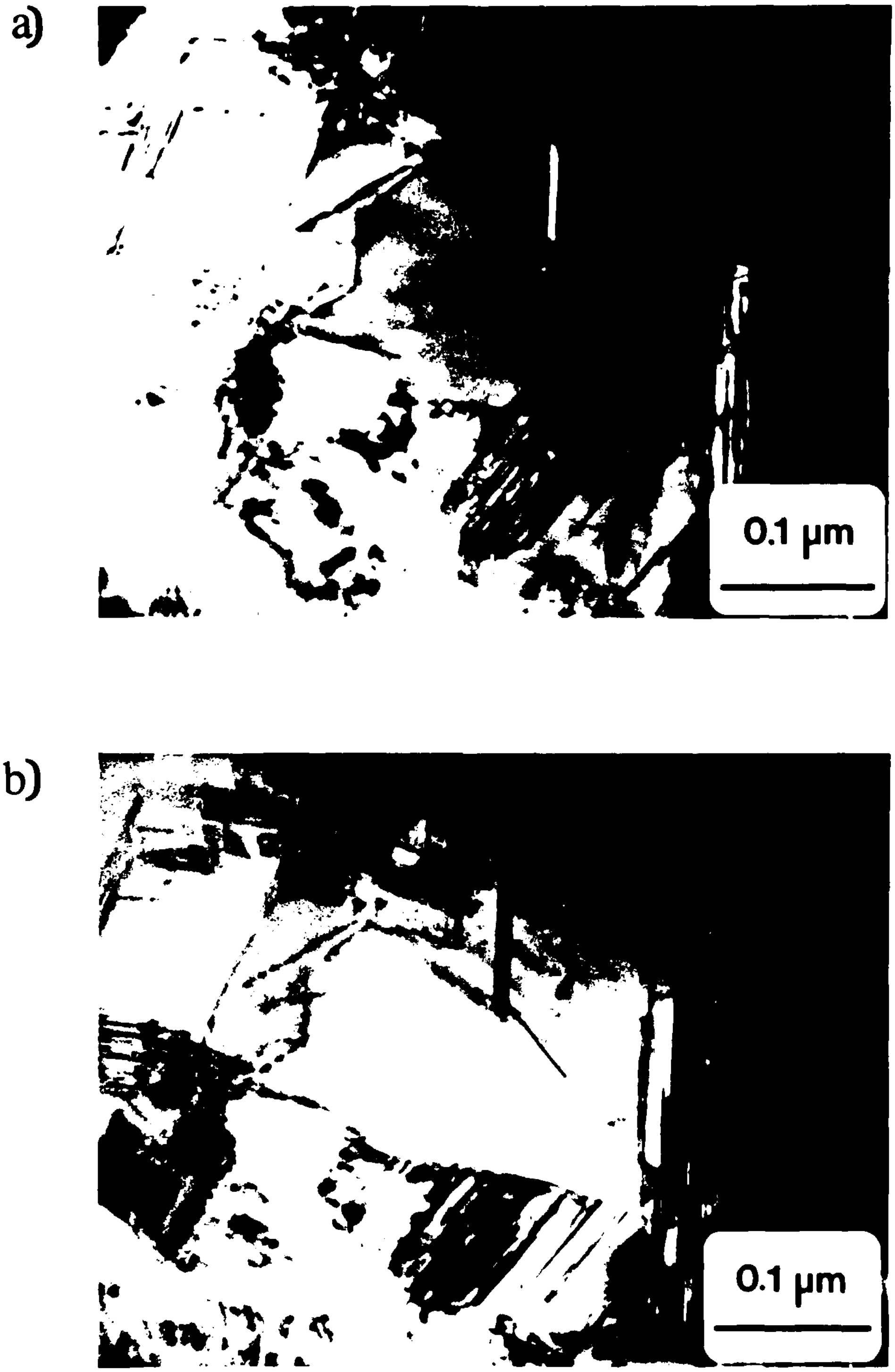
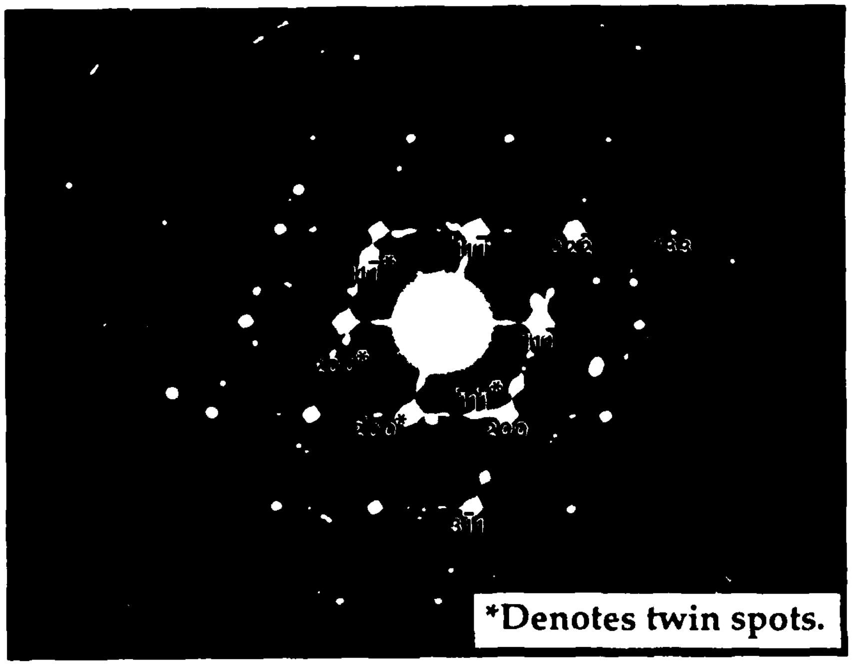


Figure 9. Plan view TEM of Kobe sample #1 at two different tilt conditions. Arrow indicates twinned region and star indicates dislocations.

Figure 10. Plan view TEM of Kobe sample #1 illustrating twinning along two sets of (111) planes. Electron beam is parallel to the [110] direction.



*Denotes twin spots.

Figure 11. Electron diffraction pattern of diamond grain shown in Figure 10. Pattern was taken along [110] direction.

hkl	Observed d(Å)	Reported (ASTM 6- 675) d(Å)
111	2.060	2.060
220	1.265	1.261
311	1.073	1.0754
400	0.896	0.8916
331	0.814	0.8182

Table 3. Electron diffraction data for diamond film and reported values of natural diamonds.

diffraction of these crystals indicated the presence of polysilicon as opposed to diamond. However, RHEED analysis at RTI indicated some polycrystalline diamond was present. This suggests that there is possibly a mixture of the two. It should be noted that this was a film grown very early in the RTI program and is not believed to be indicative of current growth. Therefore, no more work has been attempted on this "first generation" plan view TEM sample. Also, no further techniques have been accomplished because the piece of this sample received from RTI has been entirely consumed by the TEM and SIMS analyses.

Cross-sectional TEM (XTEM) is a particularly useful technique because it allows detailed study of the interface between the film and substrate. The procedure for preparing XTEM samples of SiC thin films has been well established at NCSU and involves using epoxy to glue together a "sandwich" of the film/substrate pieces and silicon support layers to provide rigidity. This "sandwich" is then thinned in much the same manner as the plan-view TEM samples. However, XTEM of the diamond films has been very difficult because of the poor adherence of the diamond film to the substrate which causes the "sandwich" to fall apart. Evidence of this lack of adherence was observed in SEM research of an area where a Kobe diamond film was fractured away from the surface. The extremely clean appearance of the silicon substrate also suggested that there was no bonding between the film and substrate. Despite this lack of adherence, some success was achieved with the Kobe sample and is discussed below. In fact, recent modifications to sample preparation appear to consistently, yield acceptable TEM samples. However, a thorough analysis of these samples has not yet been completed. Due to the small size of the RTI samples, coupled with the sample preparation problems, no XTEM specimen was successfully prepared.

Figure 12 is a low magnification micrograph of the XTEM sample successfully prepared from the Kobe sample #2 and several interesting features can be noted. First, a gap is observed at the interface which is possibly due to sample preparation coupled with a high stress at the interface. This observation further illustrates the non-

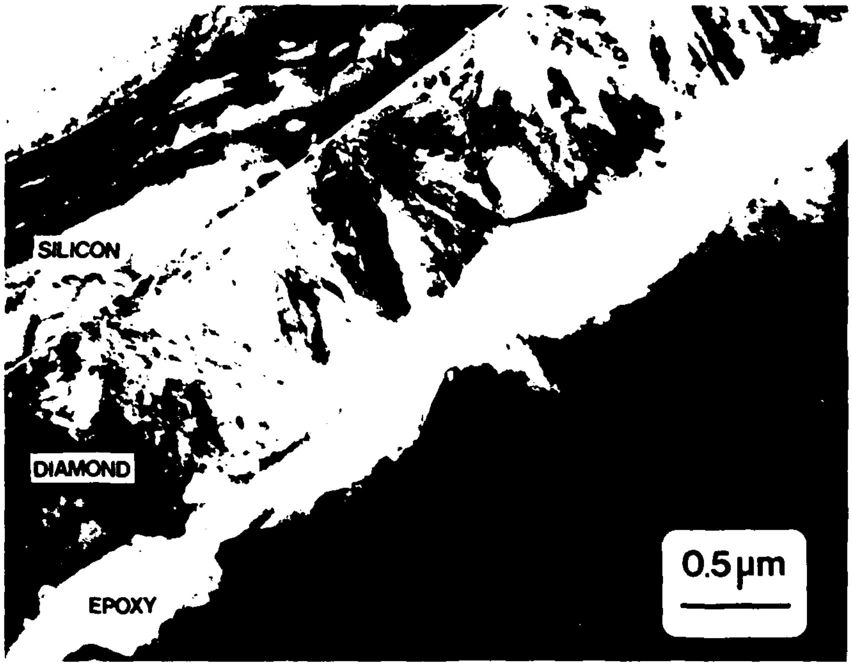


Figure 12. Cross-sectional transmission electron micrograph of Kobe sample #2.

adherent nature of the film. Furthermore, to date, no buffer layer has been observed in the films although more research is necessary to confirm this. Regions of stress concentration at the interface are also evident (see as dark areas in the silicon), but further work is necessary to determine the cause of this stress. Furthermore, high concentrations of defects are present in most grains as illustrated by the numerous dark streaks in the micrograph. It is interesting to note that the defects appear to "fan out" from the interface, perhaps indicating defect sites at the base of the grains.

Figure 13 is a higher magnification micrograph of the same XTEM sample. Note the dislocation lines which are prominent in the grain which has a lower defect concentration than the surrounding grains. A diffraction pattern from this relatively clean grain is inset in the micrograph.

D. X-ray Photoelectron Spectroscopy (XPS)

XPS was conducted by Dr. D. Vitkavage at the Research Triangle Institute on a Kobe film utilizing a Leybold-Heraeus Hemispherical Electron Energy Analyzer and twin anode x-ray source. Mg radiation at 300 W and an analyzed area of 2 x 10 mm was utilized. Figure 14 is a wide energy range scan of Kobe sample #3 containing x-ray excited KLL Auger and 1s peaks for C and O as well as Si 2s and 2p peaks. The relatively high concentrations of Si and O may be due to x-ray excitation of exposed areas of the Si substrate where diamond was not deposited as well as Si and O surface contamination. In the XPS system employed, no method of localizing the x-ray source was possible. This broad energy scan indicates elements which are present but does not yield any information concerning the bonding of the C.

The more significant data is obtained by analyzing the C1s peak using a small energy window as shown in Figure 15. This curve indicates that carbon is in an sp^3 (or σ) bonding configuration (characteristic of diamond). If sp^2 (or π) graphitic bonds were present, a secondary peak would be observed as shown in Figure 16. This is

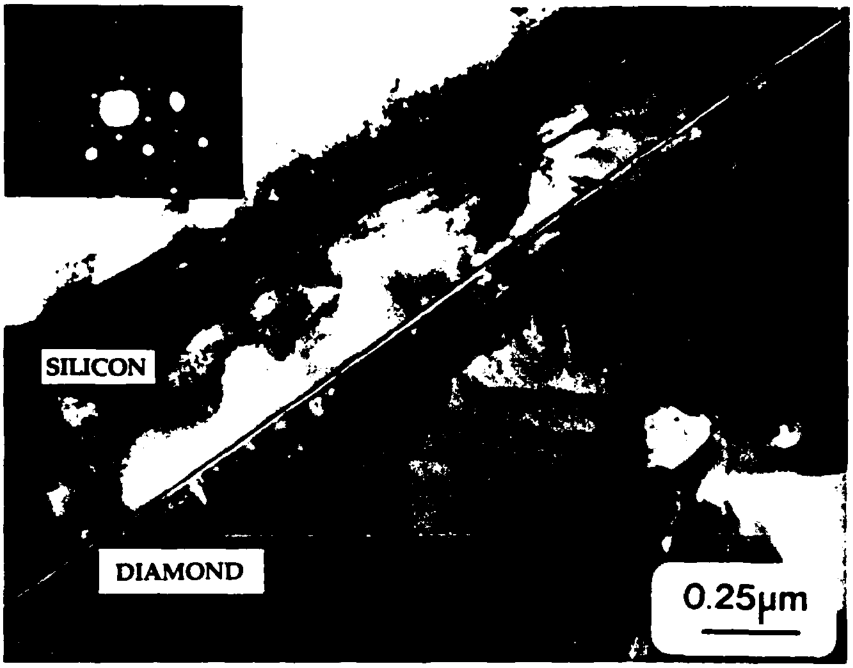


Figure 13. Cross-sectional transmission electron micrograph and electron diffraction pattern from Kobe sample #2.

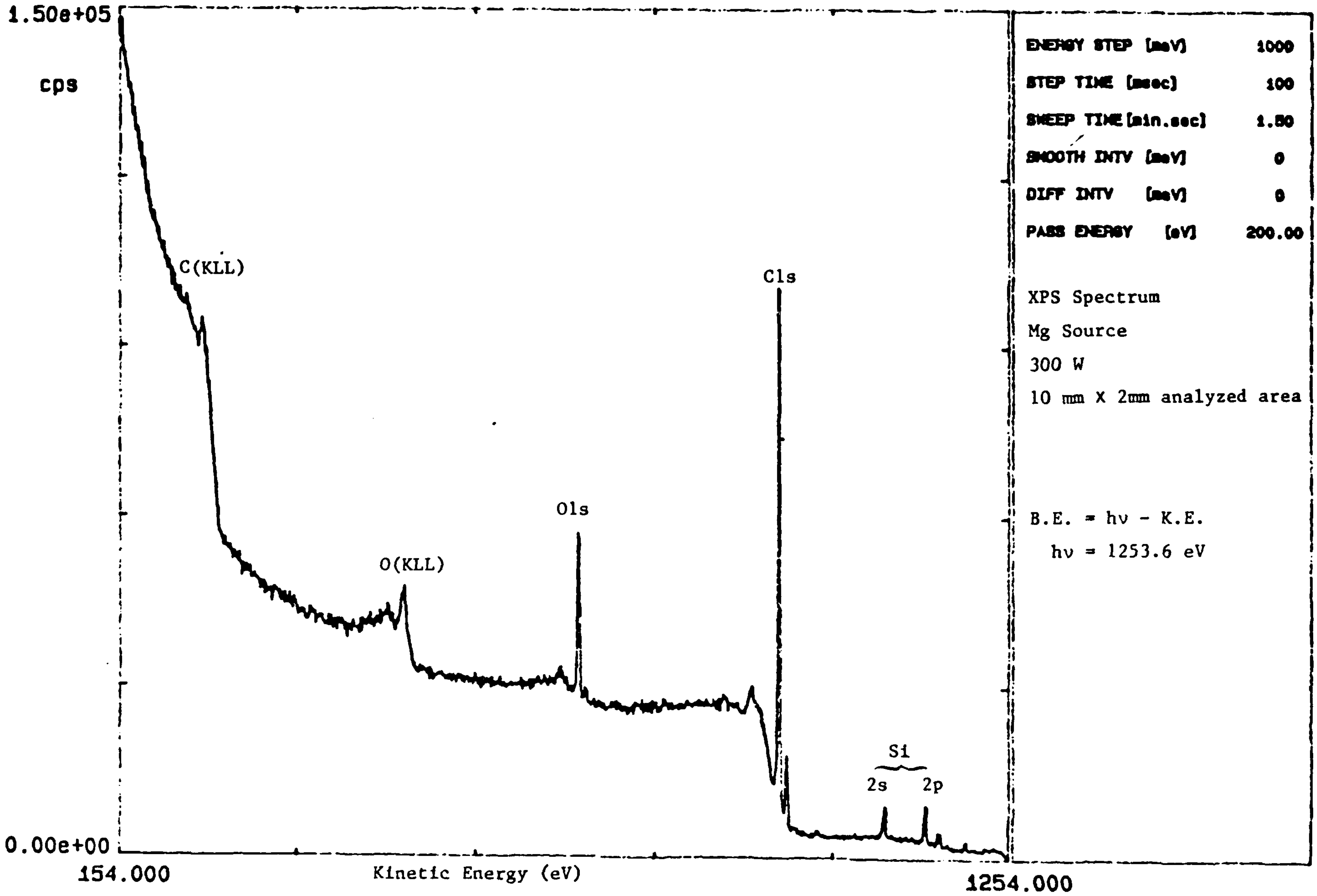


Figure 14. Broad energy window XPS spectrum from Kobe sample #3 indicating the presence of Si, 0 and C.

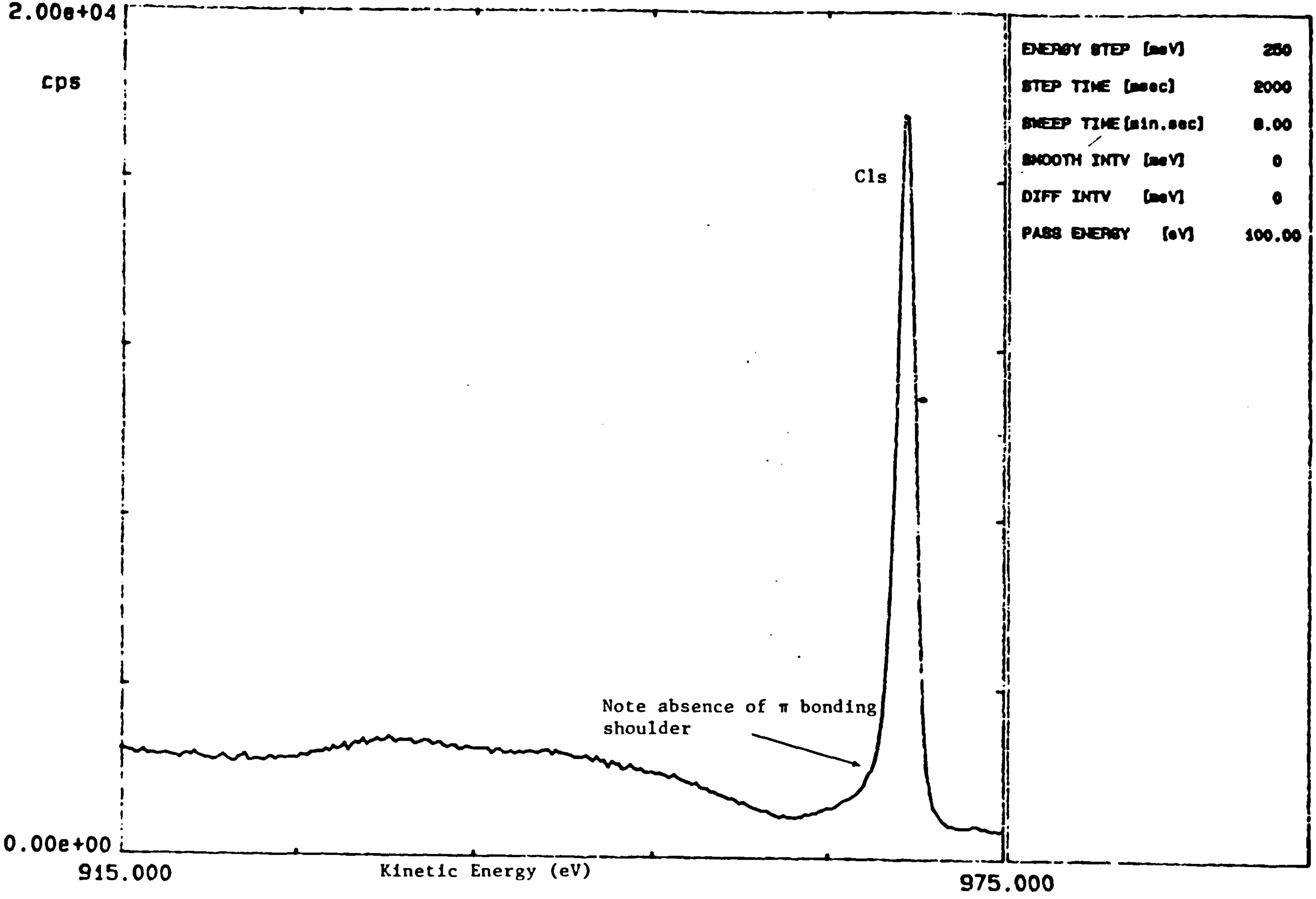


Figure 15. XPS spectrum of C1s peak from Kobe sample #3 illustrating absence of π bonding shoulder.

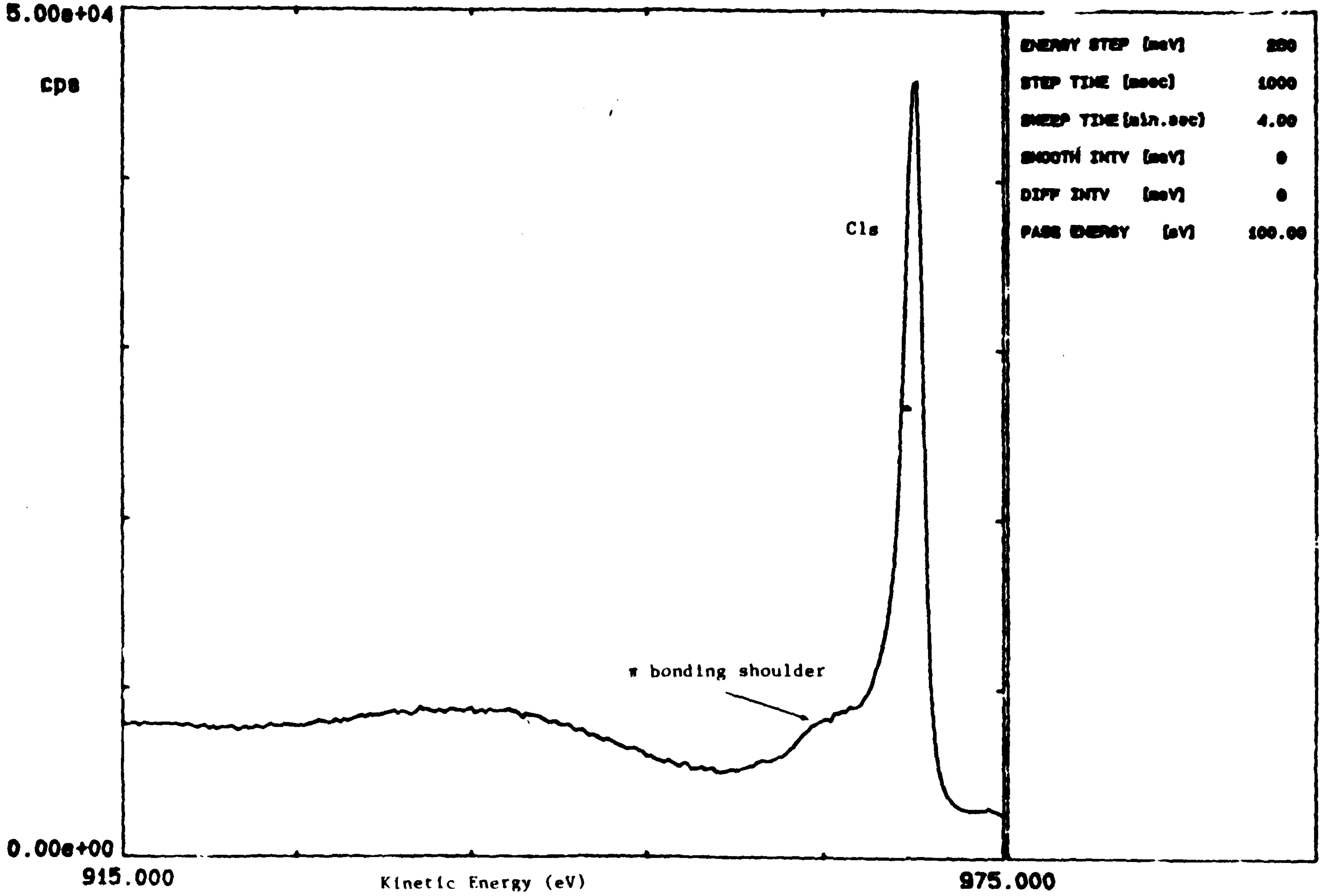


Figure 16 XPS spectrum from an amorphous C film illustrating a π bonding shoulder on C1s peak.

confirmed when the intensity axis of the data from the Kobe film is expanded such that the electron energy loss fine structure to the left (i.e., lower energy) of the C1s peak can be examined (Figure 17). It is found that this fine structure coincides with data obtained from natural diamond as shown in Figure 18 (from McFeeley et. al., Phys. Rev. B, 9, No. 12, June (1974)). Comparison of the peaks labelled P_1, P_2 and P_3 illustrates this similarity. Graphite is also shown in this figure and can be seen to yield a significantly different energy loss spectrum from the C1s peak

In summary, this XPS data indicates that true diamond bonding is present at the surface* of these samples without any evidence of a graphitic component. It should be noted that the sample was not pretreated prior to this analysis. Thus, the surface consists of diamond bonding even after long exposure to the atmosphere and significant "handling".

E. Auger Electron Spectroscopy (AES)

This section describes preliminary AES results obtained on Kobe sample #3 using a Perkin-Elmer Physical Electronics Electron Gun and Double Pass Cylindrical Mirror Analyzer (CMA). Although these results were obtained very recently and thus have not been fully analyzed, certain conclusions are readily apparent and will be discussed in this report. Any further insights obtained after a more thorough analysis of the data will be included in future communications or progress reports.

A broad energy window scan is shown in Figure 19 where the differentiated electron intensity is plotted vs. electron kinetic energy. The beam voltage was 1.5 keV, beam current was .50 mA and the sample was not pretreated in any way. In this spectrum, the carbon KLL peak as well as silicon LMM and oxygen KLL impurity peaks are observed. If one compares the Si peak to published spectra+, it is apparent that the the Si is almost entirely in the form of SiO_2. In fact, no free Si shoulder at ~92 eV is

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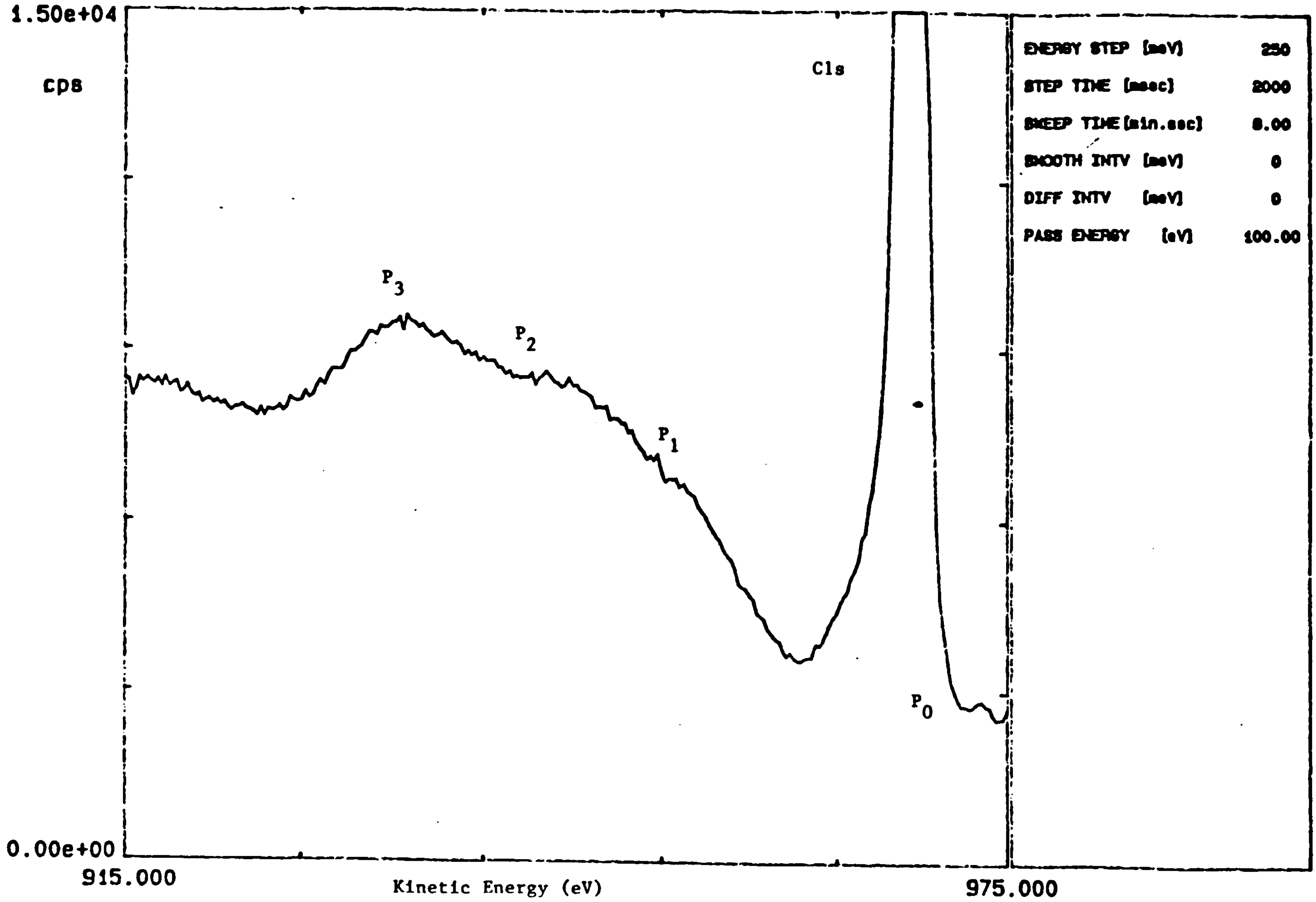
* The XPS data is very surface sensitive, examining less than the first 30 Å of the film.

+See for example, "Handbook of Auger Spectroscopy", Physical Electronics Industry.



ENERGY STEP [meV] 250
STEP TIME [msec] 2000
SWEEP TIME [min.sec] 8.00
SMOOTH INTV [meV] 0
DIFF INTV [meV] 0
PASS ENERGY [eV] 100.00

Figure 17. Expanded XPS spectrum of C1s peak and the associated energy loss structure.

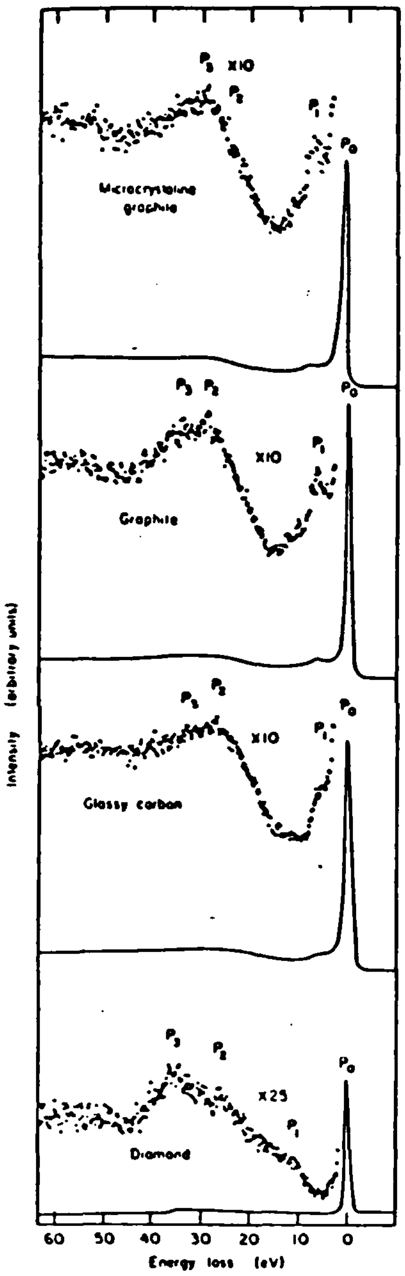


Figure 18. XPS spectra of Cls peak and associated fine structure from several forms of Carbon (from F. R. McFeeley et. al., Physical Review B, Vol. 9, No. 12, June (1974)). Note the excellent agreement of the natural diamond spectrum shown here with the Kobe diamond spectrum in Figure 17.

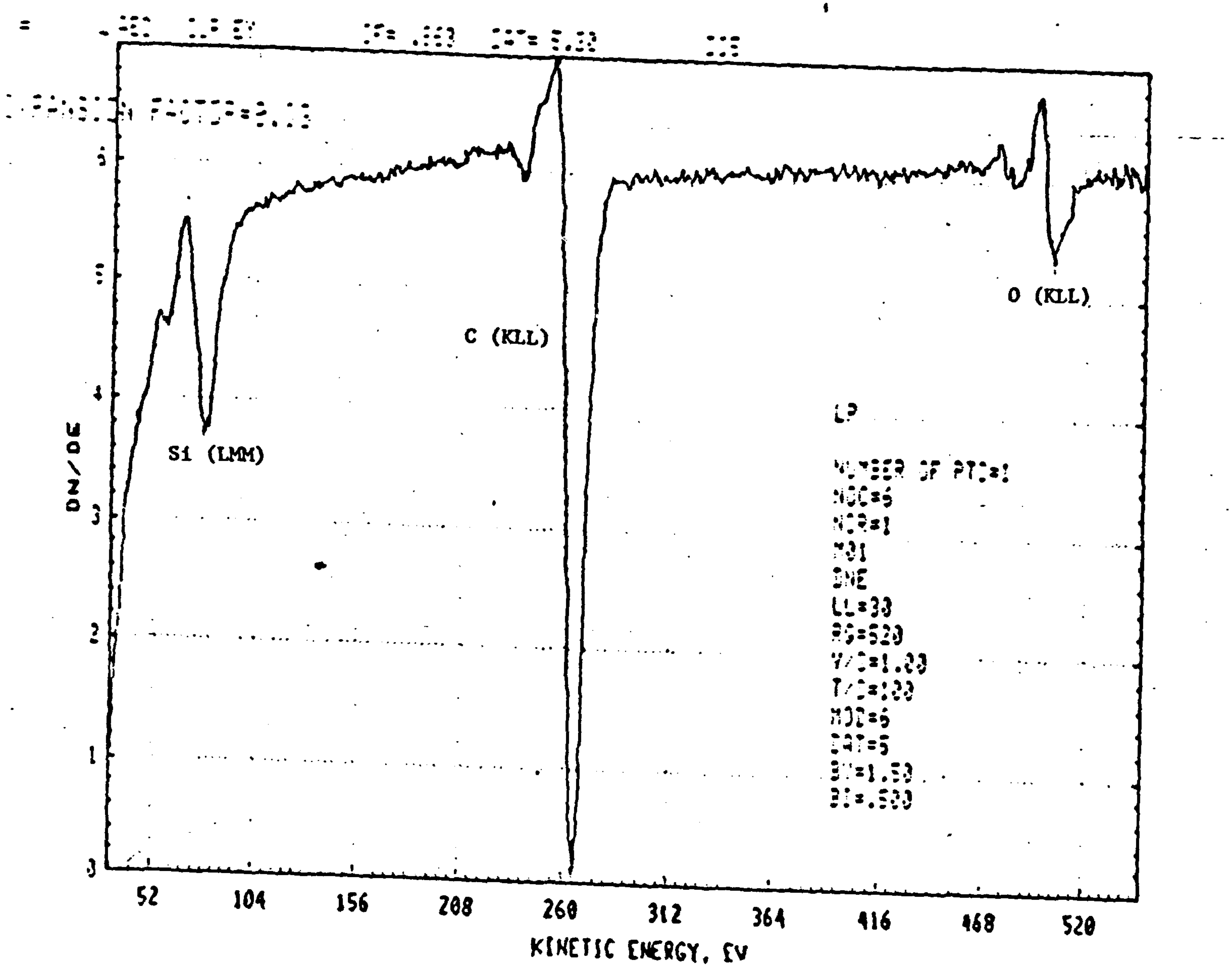


Figure 19. Differentiated Auger spectrum from Kobe sample #3 indicating Si and 0 impurities in diamond matrix. Si peak indicates SiO_2 rather than free Si.

observed in the fine structure of this peak whereas in many oxide films on Si samples free Si is apparent. The origin of this SiO_2 is unknown but it is not believed to be due the substrate since, unlike the XPS data, the AES utilizes a 10 mm x 10 mm spot size and this should be free of any edge effects. The detectability of this SiO_2 with AES indicates that it is located at the surface but it is not known if it is in the form of a thin layer of contamination or finely dispersed islands. No other impurities are observed in this spectra. However, it should be noted that impurities less than approximately 1% (greater for certain elements) would be undetectable and H and He are, in general, entirely undetectable.

A narrow energy window scan spectrum around the C(KLL) peak is shown in Figure 20. The fine structure to the left (i.e., lower energies) of the major peak is of greatest interest because it can be used to "fingerprint" the diamond structure similar to the XPS data discussed in section D. This fine structure can be compared to Auger spectra from natural diamond shown in the inset in Figure 20 (from P. G. Lurie and J. M. Wilson, Surface Science, 65, p. 476–498 (1977). Thus, the Kobe film is seen to yield an Auger fine structure qualitatively very similar to natural diamond as opposed to graphite. That is, the fine structure peak closest to the major peak is largest in the diamond with a smaller peak of lower energy observed immediately to its left. In the graphite, the lower energy peak intensity is much greater than the peak closest to the major C peak, thus yielding an excellent method of distinguishing between the graphite and the diamond. This is verified by the Auger analysis of graphite in the present research as shown in Figure 21. An Auger spectrum similar to previously reported results is observed. Therefore, it can be seen that the Kobe film does not appear to contain any graphitic component.

Another interesting feature of the data collected thus far is illustrated in Figure 22. Spectrum A was obtained with a beam voltage of 1.5 KeV and current of .5 mA whereas Spectrum B utilized a 3 keV and 3 mA electron beam. Literature reports indicate that positive charging and thus a shift to lower energies is found on natural

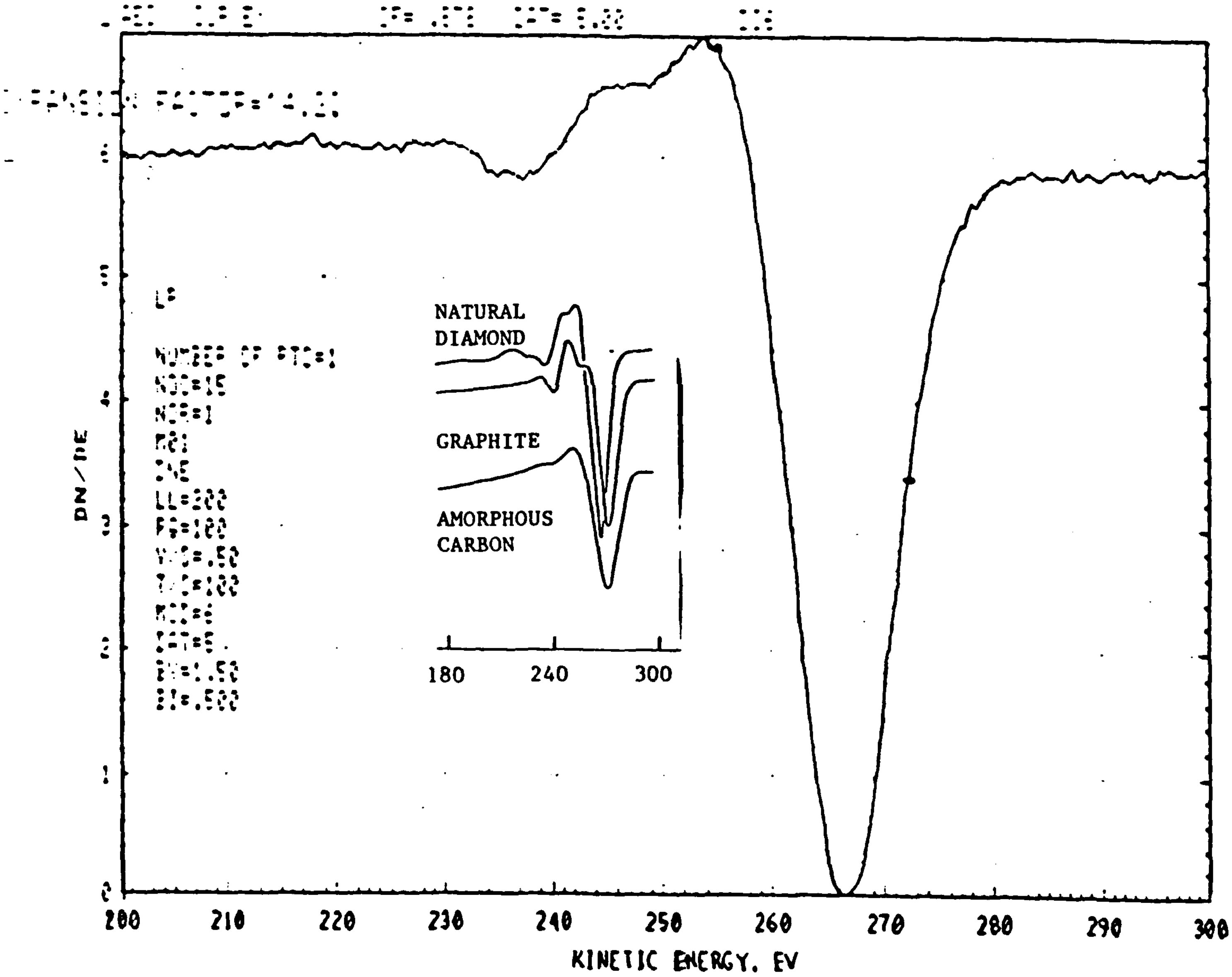


Figure 20. Differentiated Auger spectrum of C KLL peak from Kobe sample #3 with inset of spectra from literature (Surface Science, 65, p. 476 (1977)).

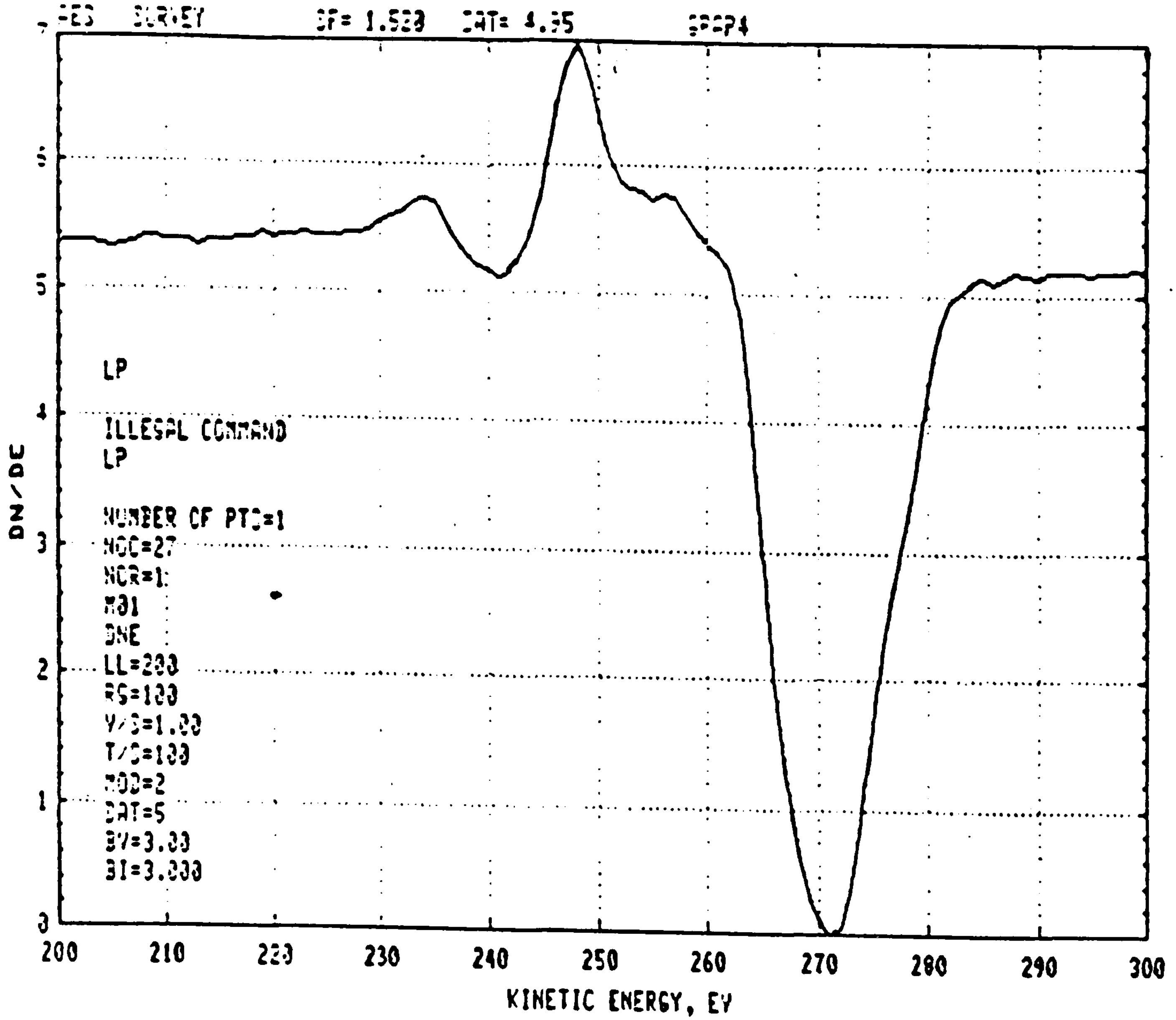


Figure 21. Differentiated Auger spectrum of C KLL peak for high purity graphite.

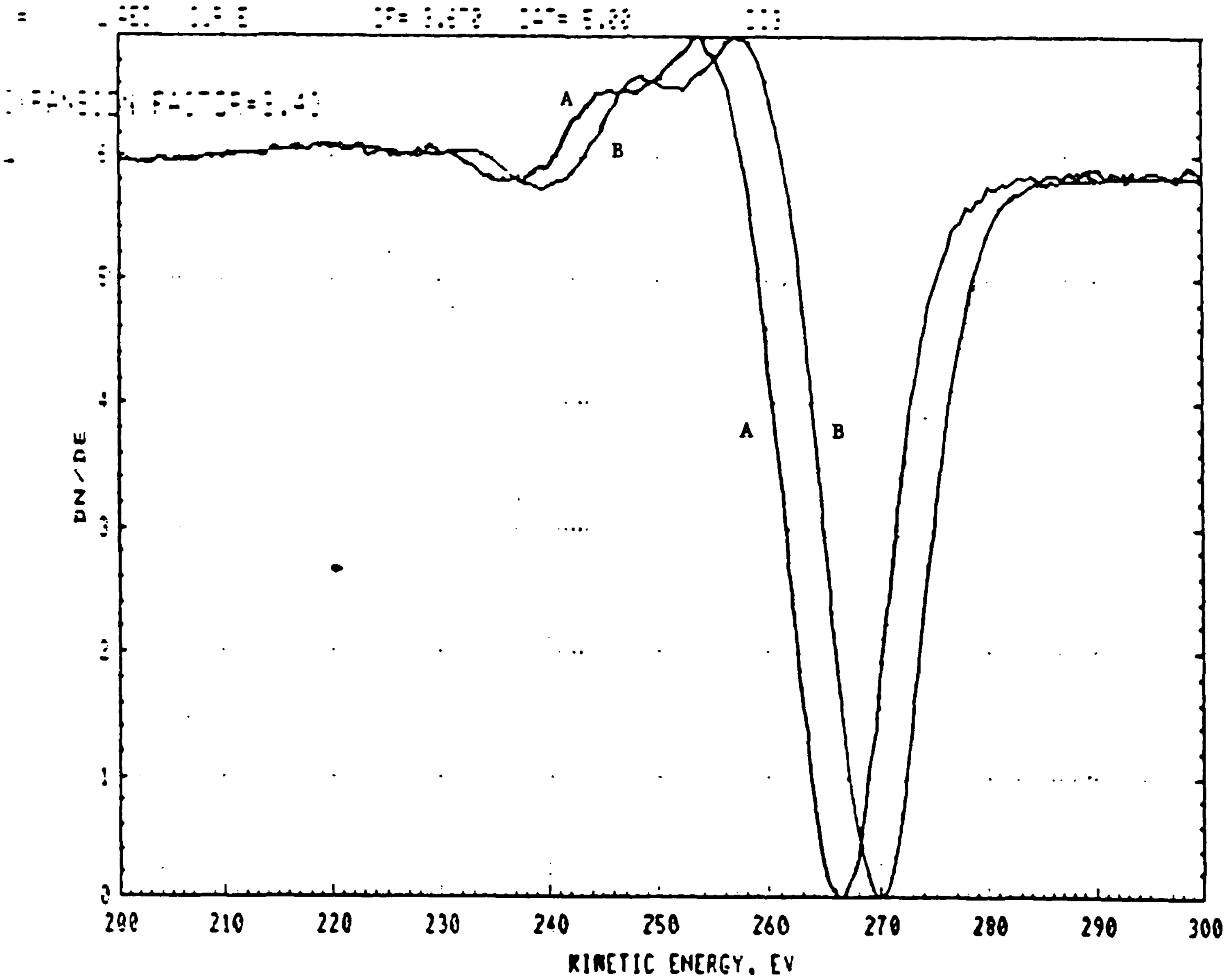


Figure 22. Effect of beam voltage and current on differential Auger spectra;
A. $V_b = 1.5$ keV, $I_b = .5 \mu A$, B. $V_b = 3$ keV, $I_b = 3 \mu A$.

diamond bombarded with electrons. However, the thin, polycrystalline nature of the CVD film and the presence of the Si substrate may cause significant differences from the natural diamond case.

A final result from the Auger work presented here involves the effect of Ar^+ bombardment — a typical method of sample pretreatment. A broad window energy scan is shown in Figure 23. A new peak due to Ar is observed immediately to the left of the C(KLL) peak. The Si peak is shifted to ~95 eV indicating it is no longer in the form of $Si0_2$, however, O is still present as seen by the O(KLL) peak in the spectrum. More significant are the changes observed in the C(KLL) fine structure. This is illustrated more clearly in Figure 24. When compared to the previous spectra it is obvious that the Ar^+ bombardment graphitized the surface bonds in the diamond film. Obviously, this indicates that this type of pretreatment is not recommended for diamond. It should be noted that the Argon sputtering was rastered (9 x 9 mm^2) and was of relatively low energy (V = 1.5 KeV, I = 2.5 mA) in order to minimize surface damage, yet still caused this graphitization. A future experiment is planned to attempt to return this surface to its diamond bonding state via a high temperature H_2 treatment.

F. Summary of Diamond Film Analysis

Kobe thin diamond films have been evaluated utilizing several materials analysis techniques. Grain structure, crystallography, defects, impurities and bonding have been examined. In general, a diamond structure and bonding has been identified without any evidence of a graphitic phase. However, the films are polycrystalline with apparently random grain orientations. Furthermore, most grains contain high concentrations of twins and/or dislocations. A very abrupt, non-adherent interface has also been observed. Impurities have been examined and appear to be segregated although in general their concentrations are relatively small. However, if these impurities are electrically active, they will be prohibitive for electronic applications and will need to be eliminated. In summary, the capabilities of SIMS, XPS, Auger

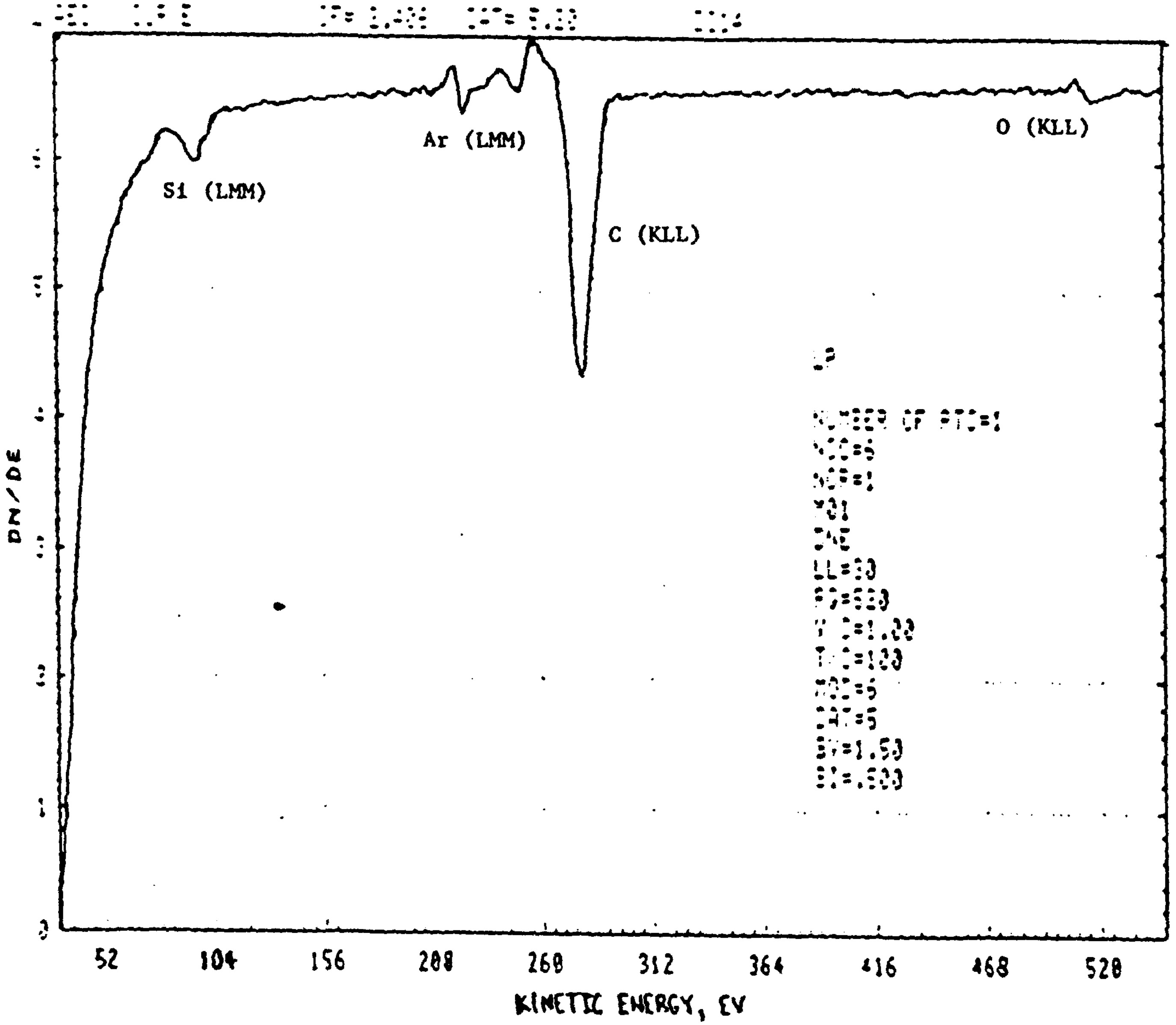


Figure 23. Differential Auger spectrum of C KLL peak from Kobe sample #3 after Ar+ bombardment.

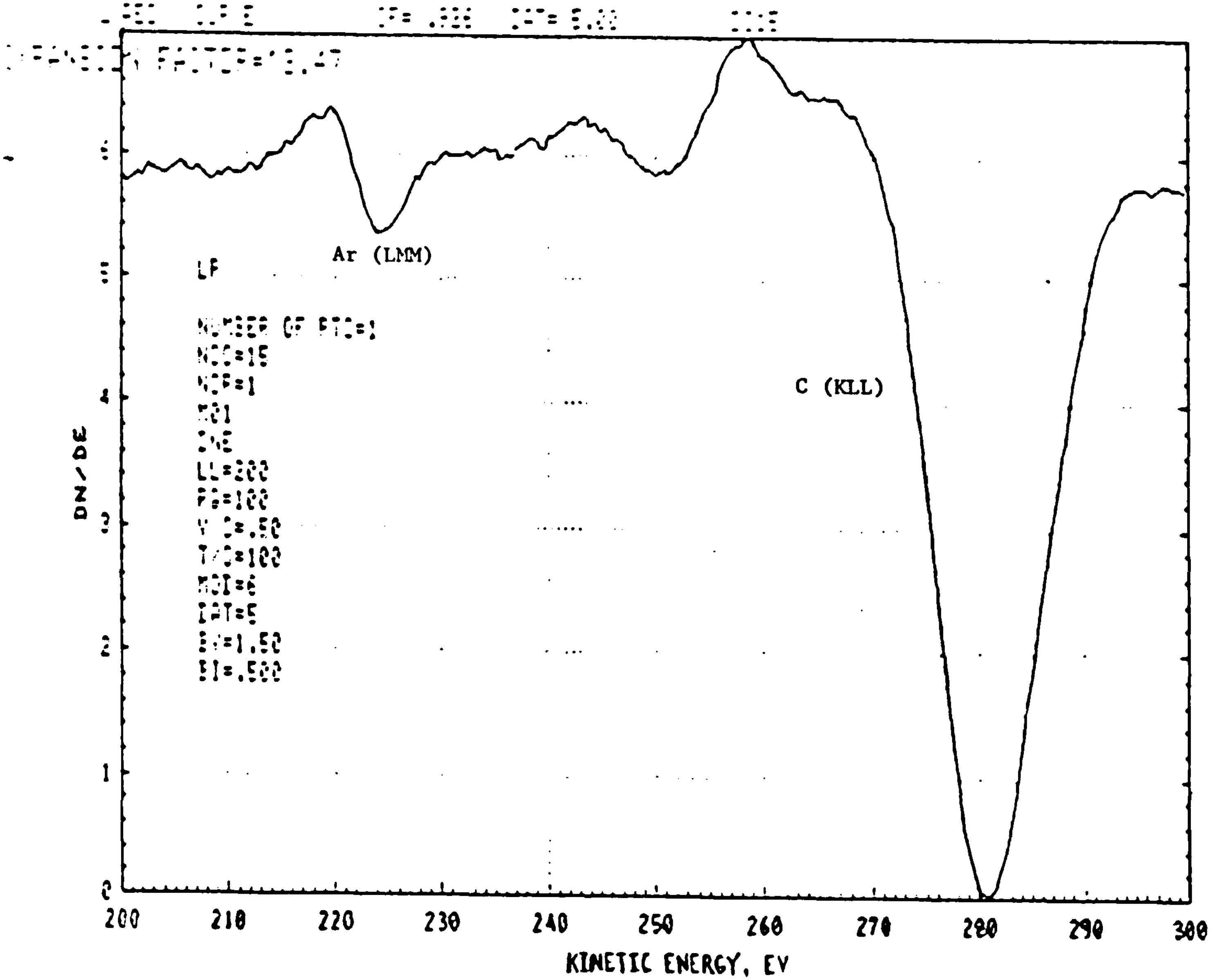


Figure 24. Differential Auger spectrum of C KLL peak from Kobe sample #3 after Ar+ bombardment. Fine structure of C KLL peak indicates a graphitized surface.

Spectroscopy, Optical Microscopy, SEM, EDX, Plan-View TEM, XTEM and SAD have been examined with respect to the evaluation of Kobe diamond films.

A sample from RTI's preliminary growth experiments was also examined. However, a thorough analysis was not possible due to the small size and thin nature of the film. The surface morphology was of a rounded hillock nature and small crystals embedded in an amorphous matrix appears to be the most likely explanation. The small crystals may be a mixture of both diamond and polysilicon since TEM indicated Si but RHEED analysis at RTI indicated diamond was present.

VI. Deposition of Dielectric Films on Diamond Surfaces (Lucovsky)

There are two main objectives for this phase of the project: (1) The characterization of the surfaces of diamond films by XPS, AES and ELS and (2) The deposition of dielectric films on diamond surfaces. This second objective encompasses the characterization of dielectric materials (SiO_2 and Si_3N_4) as well as the characterization of interfaces between diamond and the dielectric materials.

The research during this reporting period involving the XPS, AES and EELS System focused on three issues: (1) The characterization of diamond films obtained from NCSU and outside sources as discussed earlier in this report, (2) an upgrade of the system for use with a heated sample probe; and (3) an upgrade of the system to deal with the problem of residual water vapor. A heater and control unit for the heated sample probe has been ordered. This will enable measurements with samples heated to temperatures as high as 600°C. It has been observed that certain types of samples; Si, Al, *etc.*, display a build-up of surface oxygen and carbon immediately after surface sputtering with Ar. A series of measurements involving Si, Al, Au and Cu has demonstrated that these contaminants only occur on highly reactive surfaces, namely Al and Si, but not on Cu and Au. It is believed that the O and C are chemisorbed to these surfaces and derive respectively from residual water vapor and hydrocarbons. Furthermore, the source of water vapor is believed to be the Ar sputtering gas. An in-line gas purifier has been ordered and received and a series of experiments will be conducted to determine its effectiveness in reducing O surface contamination.

Regarding the deposition of dielectrics on diamond, the five chamber system to be used in the fabrication of diamond/dielectric insulator interfaces has just been completed. The system has two load locks, a sample preparation chamber, a dielectric deposition chamber and an analysis chamber. The first tests of the system indicated that it was free of any vacuum leaks. It has also been verified that the RHEED system in the analysis chamber worked using a Si substrate. The discharge spectra in the excitation region of the plasma tube have been studied using an optical multi-channel analyzer and the appropriate ports have been incorporated into this system design for on-line monitoring of gas discharges. Plans have been made to purchase an in-situ AES system to complement the RHEED system in obtaining information relative to surface composition and structure. This is an important aspect of the formation of electronic quality semiconductor dielectric interfaces.

VII. Substrate Growth (Bachmann)

The major goal of this part of the diamond program is to grow metal single crystal for use as substrates for the diamond CVD growth. Two of the most promising candidates are Nickel and Copper as well as their alloys. Initial tests have been successful in the growth of an apparently single crystalline boule of Cu as shown in Fig. 25. Note the cellular region at the top of the boule, probably due to impurity transport. A surface grain is also visible in this region, illustrating the single crystallinity of the majority of the boule. Verification of this single crystallinity as well as its preparation for use as a substrate is underway. After refining this Cu growth, Ni crystal growth experiments will begin.

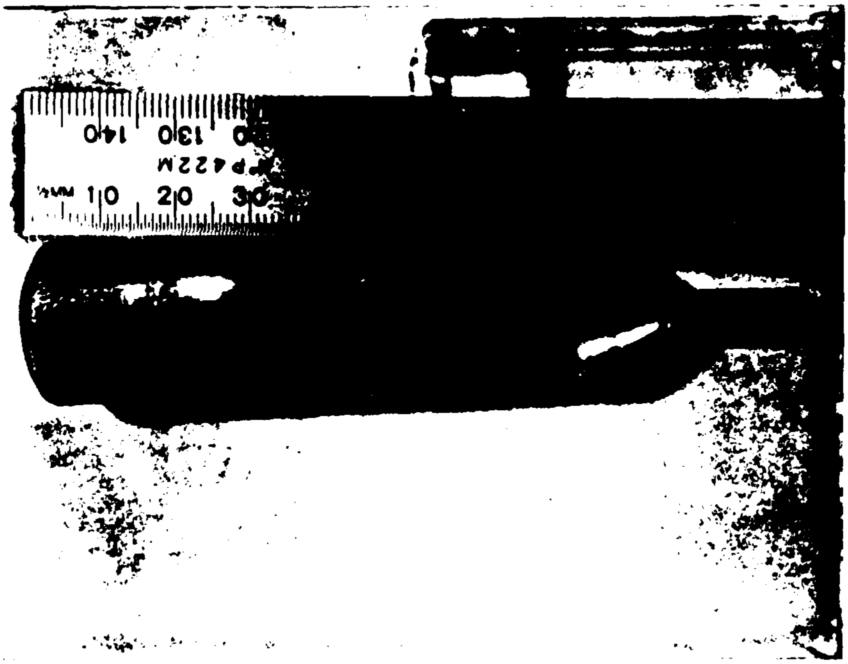


Figure 25. Copper single crystal boule grown at NCSU. Cellular region at top of boule is probably due to impurity transport.

VIII. Diamond Research In Japan (Glass)

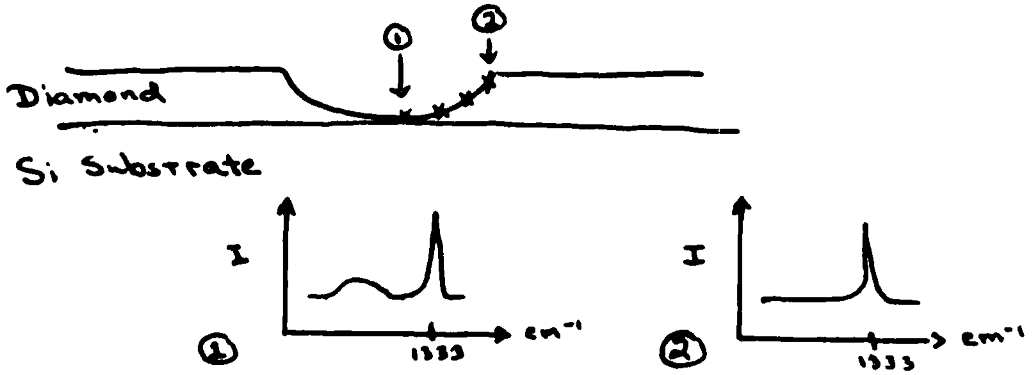
One of the co-principal investigators for the NCSU diamond project, Dr. Jeffrey T. Glass, recently returned from a two-week trip to Japan. Through Professor Davis' contacts and contacts made through Kobe Steel, Ltd., Dr. Glass was able to visit certain labs conducting diamond and SiC research. He also attended a diamond session of the Japan Applied Physics Meeting. His trip report concerning diamond is given below. Unless otherwise stated, these notes refer to growth by Microwave Plasma Enhanced Chemical Vapor Deposition.

- Grains contain (111) facets when $[CH_4] \leq .4\%$ in H_2. However, (100) facets are observed from .4 to 1.2% CH_4/H_2. Greater concentrations of CH_4 give graphitic or amorphous components.
- After > 30 hours growth samples become covered with small secondary crystals, then at 44.8 hours, the surface becomes very crystallographic again (small particles are consumed). This oscillation occurs again if longer growth runs are made.
- Many step and ledge features have been observed on large grains.
- If a high CH_4 concentration microcrystalline region is first grown on the sample a smaller grain structure is observed in the film and at $[CH_4] = .8\%$ the film changes from (111) to (100) facets at $[CH_4] \geq .8\%$ in H_2 rather than .4% when this interface layer is not grown. Also the (220) XRD peak reaches a maximum at $[CH_4] = .6\%$ and the [111] peak simply rises continuously.
- In 1.2% CH_4 growth runs, the (220) XRD peak grows with deposition time even though the (100) planes appear to be parallel to the surface according to SEM results.
- Growth rate levels off with time (generally 0.3 to 0.5µm/hr).

- Best growth occurs at 330 W and 30 Torr, Substrate Temperature ~ 900°C. Parameters are not very sensitive.
- At lower microwave power, (~ 250 W) can extend [CH_4] concentration range which gives diamond.
- 100 W ⇒ Amorphous, Hydrogenated Films
  300 W ⇒ Best Diamond
  500 W ⇒ Mostly Diamond
- To obtain constant substrate temperature the microwave power is decreased slightly (10–20W) after first half hour.
- Rounded particles contain graphitic component according to Raman.
- SiO_2 substrates give somewhat better crystals. Si substrates yield good crystals at first but they eventually become rounded.
- Higher growth rates appear to give larger particles without secondary nucleation.
- Films are generally 30–50% thicker at edges of substrate with larger grains also.
- Sample prep — Obtain polished wafer, scratch with 1/4 mm diamond paste on napped cloth (with H_2O) for 1 hour. Ultrasonic bath in H_2O, Alcohol and Acetone for 5–10 minutes. Growth is not very sensitive to the specifics of the treatment.
- Chamber is cleaned approximately once a week to remove amorphous C deposits. This is done by allowing air into chamber at 10 Torr and 200 W microwave power for 3 hours to etch chamber. The lower pressure is necessary to increase mean free paths in order to allow plasma to interact with walls. Must avoid this during deposition.
- No special precautions are necessary concerning microwave leakage but the system is monitored frequently to assure that it meets Federal regulations. Can use Faraday cage if needed.

- Use SiO_2 reaction chamber. Cannot use Al_2O_3 because it damps the microwave power too much.
- The microwaves do not couple with Si substrates. It is the plasma which actually causes heating.
- Believe that higher pressure (hundreds of Torr) would be better but in their system this would cause temperature to be too high.
- At lower pressures (down to 1 Torr) get increasing sp^2 peak in Raman.
- Some work in mTorr range has been attempted but with very little success in film deposition. Possibly due to sputtering effect (caused by higher mean free paths) or different gas species.
- Future work will start to concentrate on gas phase analysis.
- Diamond has been successfully deposited on diamond (111) but films contain microcracks along (111) planes if they are > 10μms thick.
- Usually films are non-adherent, however, occasionally the films stick very well and fracture occurs in the Si, not at the Si/Diamond interface. It is believed this may be more probable with films grown at higher temperatures (> 900°C).
- Seiko has developed a Thermal Conductivity test for films 5mm x 5mm x 10mms using microheater probes and a infrared emission detection system. The thermal conductivity decreases as CH_4 concentration in H_2 increases. The best thermal conductivity was from .1% CH_4 in H_2 mixture for this growth system. This correlated with best Raman spectrum. Reference for this is Japanese J. Appl. Phys. Vol. 25, No. 10, pp. L808–L810, Oct. (1986).
- Have found that Raman spectrum shifts to graphite as CH_4/H_2 increases.
- They have tried numerous sample preparation procedures but "scratches" are the only way that has yielded diamond films.
- Both (111) and (100) Si substrates yield similar deposits.

- RF plasma has worked but microwave is cheaper, easy and gives higher e^-densities.
- The W filament approach is attractive because of its simplicity. However, sagging and embrittlement of the filament causing nonuniformity and nonreproducible results is a problem. Also, the results are very flow rate sensitive whereas with PECVD there is little difference from 40–400 ml/min. Generally want lower flow rates than with plasma.
- Some people have utilized low energy (20–400 eV) ion beams but so far no temperature and E_B variation can produce true diamond.
- Many different substrates have been examined;
  - Cu, Au, Mo, Ta, W, SiC, Ge, Ti, Zr oxides, SiO_2, Al_2O_3 (sintered and saphire), AlN, c-BN, h-BN -All are similar to Si substrates
  - Ni, Fe, Co - First get a well crystallized graphitic layer, and then get diamond particles. Note that these are catalysts for hydrocarbons possibly causing high reaction rates on initial surface.
- Raman features change with film thickness;



Film is dimpled and Raman data is taken from different points in crater. Graphitic type bonding feature is observed in spectra near the interface.

- H_2O vapor has been added to the growth systems which causes a decrease in growth rate but extends the CH_4/H_2 ratio at which diamond rather than graphite is formed. This is possibly due to the fact that O_2 "etches" both graphite and diamond at higher rates than H_2 and still etches graphite faster than diamond.
- Initial results of laser (excimer) CVD using SiC substrates indicate a single crystal diamond film may have been obtained (< 1µm). (Only analyzed using RHEED; thus, a significant amorphous component may be present).
- Microwave PECVD, Arc discharge, Tungsten Filament, and DC Plasma have all been shown to give good diamond films.
- Ultrasonic polishing (i.e., "scratching") gives more nucleation.
- Up to 300µm particles have been fabricated at 20µm/hr. with a DC plasma method.
- Some films have been shown to have good adherence to non-diamond substrates but appears they always have significant amorphous components.
- Continued theoretical work showed that both CH_3^+ and CH_3^* give similar results of good epitaxial film growth.
- Apparently, more than 100 companies in Japan are working on diamond growth in some manner.

IX. Miscellaneous

Several miscellaneous items are worthy for inclusion in this report. First, two presentations regarding diamond have been given during the past year; Professor Davis spoke at the first diamond seminar in July, 1986 and a poster, was presented at the February, 1987 diamond workshop. This poster was entitled "Characterization of Diamond Films, Growth of Substrates and PECVD System Design" and was co-authored by Williams, Glass, Davis, Schell and Bachmann. A presentation will be made by J. T. Glass (co-authored by B. E. Williams and R. F.Davis) at the July, 1987 diamond seminar and the abstract for this presentation is enclosed. An abstract is also attached which has been submitted jointly with Kobe Steel, Ltd. researchers, to the November, 1987 AVS meeting regarding the analysis of Kobe films. An abstract concerning the NCSU diamond CVD system is currently being written for the January, 1988 SPIE meeting. It will be submitted to the diamond session of the Innovative Science and Technology Symposium.

Finally, various company representatives have visited NCSU in the last year to discuss diamond research. Most were considering starting a research program involving diamond and were seeking background information regarding the state-of-the-art of this field. Many documents, reference lists and discussions were provided. They have been encouraged to collaborate with the diamond research effort at NCSU whenever possible. A partial list of these companies is given below:

- Eastman Kodak Company—Rochester, NY.
- E.I. DuPont de Nemours and Company—Wilmington, DE.
- Norton Christensen, Inc.—Salt Lake City, UT.
- Hercules, Inc.—Wilmington, DE.
- Westinghouse Corp.—Orlando, FL.
- Technology Unlimited/Souder Associates—Raleigh, NC.
- Charles River Ventures—Boston, MA.

The Characterization of Diamond Thin Films Grown by PECVD*.

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ABSTRACT

The North Carolina State University Diamond effort couples investigators from four departments to achieve; (1) the growth of monocrystalline diamond films, (2) the characterization of these films regarding bonding, structural and electrical character, (3) the modeling and fabrication of simple device structures utilizing these films, and (4) collaboration with the personnel at the Research Triangle Institute and other groups involved in diamond research. Efforts during the first year are concentrating on the design and construction of a diamond Plasma Enhanced Chemical Vapor Deposition (PECVD) apparatus and the growth of suitable substrates. However, in conjunction with these efforts, diamond films from outside sources are being characterized. This characterization research will be the main topic of this presentation.

The objective during the initial phases of characterization has been to determine the suitability of several materials analysis techniques for examining diamond thin films. These techniques have included Optical Microscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X- ray Analysis (EDX), Transmission Electron Microscopy (TEM) - both plan-view and cross-sectional, Selected Area Electron Diffraction (SAD), X-ray Diffraction (XRD), Secondary Ion Mass Spectroscopy (SIMS), X-ray Photo-electron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). Raman Spectroscopy is also expected to be conducted in the near future. Most of the films analyzed were grown by Kobe Steel, Ltd. of Japan utilizing Microwave Plasma Enhanced Chemical Vapor Deposition. Films are polycrystalline diamond with preferred growth facets which are determined by the deposition conditions. Films do not adhere well to the Si substrates and grains contain high densities of defects. However, no evidence of sp^2 (i.e., graphitic) type bonding has, thus far, been observed. Current efforts are concentrating on high magnification TEM observations of the interface region in order to learn more about the nucleation of the films.

Progress regarding other areas of the N.C.S.U. diamond program such as CVD system design and construction and substrate growth will also be discussed.

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*Plasma Enhanced Chemical Vapor Deposition (PECVD)

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STRUCTURAL AND CHEMICAL CHARACTERIZATION OF DIAMOND FILMS AND DIAMOND-SUBSTRATE INTERFACES, B. E. Williams, J. T. Glass and R. F. Davis, Materials Science and Engineering Department, North Carolina State University, Raleigh, N.C. 27695-7907. K. Kobashi and T. Horiuchi, Asada Research Laboratories, Kobe Steel, Ltd., Kobe, Japan.

Diamond and thin films grown by microwave plasma enhanced chemical vapor deposition (PECVD) were characterized by a variety of materials analysis techniques. Optical and scanning electron microscopy were used to characterize the as-grown film surfaces which consist of multi-faceted grains up to one micron across a single facet. Orientation of the grains relative to the substrate appeared to be random, however, individual facets have symmetry characteristics of certain crystallographic planes. Secondary nucleation of diamond on diamond was also observed. Transmission electron microscopy (both plan view and cross-sectional) was employed to study the defect structures in the films and examine the diamond-substrate interface. Dislocations and twins were identified in the grains which, in general, contained high densities of these defects. Electron diffraction was utilized to identify both the diamond structure and the twin planes. X-ray photoelectron spectroscopy and Auger electron spectroscopy confirmed that diamond bonding (i.e., sp^3) was present in the films by "fingerprinting" the films and comparing this to data obtained from natural diamond and graphite. No evidence of sp^2 bonding was observed. Finally, secondary ion mass spectrometry was utilized to examine impurity contents and segregation in the film.

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APPENDIX

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