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Preliminary work was carried out on the preparation of filaments prepared by ion bombardment of carbon surfaces. The effects of ion energy, ion dose (time), substrate temperature, type of substrate carbon, and the presence of Fe catalyst were investigated. This work was continued at IBM by the research assistant, William Solberg, and the results are presented in the IBM report. Models for growth were developed at both CSU and IBM.

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Report on Theoretical Portion of Work on Carbon Whiskers
Conducted under AFOSR Contract No. F49620-84-K-0006
at IBM Thomas J. Watson Research Center

Kink Site Saturation Mechanism for Whisker Growth Under
Sputtering Conditions

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Abstract

We consider what should happen when surface adsorbed atoms
are created at a rate faster than they can be accommodated at
kink sites on a surface, such as graphite, for which the
nucleation of new grow steps and kinks is difficult. We
suppose that this is the condition of common ion beam
sputtering systems when the beam current exceeds a critical
value. We conclude that, following the nucleation of a
second phase as a basal structure, whiskers should grow in
the direction of the ion beam, whatever its orientation to
the surface normal. Provided that possible attachment sites
on the sides of the whiskers are bound, as by termination of
dangling bonds by the hydrogen generally present in
sputtering systems, the whiskers should grow in length at a
constant rate with little or no increase in their diameter.
This is because the tips of the whiskers would provide the
only nonsaturable source of attachment sites for the
surface adsorbed atoms produced by subsequent sputtering.
We suggest that this mechanism is responsible for the growth
of carbon whiskers with diameters of order 15 nm and
remarkably high aspect ratios on graphite surfaces in 1 kev
sputtering systems. Such whiskers have been grown to a
length in excess of 20 um and have been demonstrated to be
clearly different from the scrolled-graphite structure
whiskers obtained by catalytic pyrolysis of hydrocarbons.

The growth of whiskers from graphite surfaces under ion sputtering conditions has been reported[1-3] for several years, but without any determination of the crystal structure of the whiskers nor of the mechanism of their nucleation and growth. In a separate publication[4] we give a detailed report of an investigation of the chemical purity, bonding, and crystal structure of these whiskers that has been made by the method of electron energy loss spectroscopy (EELS) done in a high resolution transmission electron microscope (TEM). The TEM allows us to distinguish the whiskers from adjacent material and to interrogate various sections of an individual whisker. This EELS investigation shows the structure of some of these whiskers, those of the smallest diameters observed, which is characteristically about 15 nm, definitely to be different from either diamond or the scrolled-graphite structure found[5] in C fibers grown by catalytic pyrolysis of hydrocarbons.

Larger whiskers are also observed[2,3] to grow in sputtering systems under some conditions. These have diameters ranging from 30 to 100 nm. They definitely appear to grow thicker as they grow longer, whereas the smaller diameter whiskers are reported[1] to grow only in length. It appears that some of these thicker whiskers have the scrolled-graphite structure at least on the outer portions. While fibers grown by catalytic pyrolysis are generally hollow, these thicker sputter-grown whiskers appear to have a solid core that may be different from the outer core. It would seem that there should be a minimum diameter to which the graphitic structure could be scrolled and it may be that the inner structure of the thicker sputter-grown whiskers is similar to that of the thinner sputter-grown whiskers; we have no firm evidence of this.

Here we propose an explanation of the nucleation and growth mechanisms of the thinner sputter-grown whiskers. It is offered in the form of a theory rather than as an explanation of an exhaustive set of firmly established experimental facts. This is because the theory has implications which are consistent with the report of Ref. 1 and related work, but which were unconfirmed in Refs. 2 and 3 and some of our subsequent work. We believe that the reason for the variable results observed, particularly as to the diameters of the whiskers and as to whether or not they grow thicker as they grow longer, is the presence of a hidden and uncontrolled variable. We suspect that this uncontrolled variable is the background hydrogen partial pressure in the sputtering apparatus. It is also true that the configuration of the sputtering apparatus used in Ref. 1 was quite different from the so-called Kaufman ion sources[6] that were used in Refs. 2 and 3, and in our subsequent work and this may have affected the whiskers. However, we believe that the most significant difference is that the older sputtering systems had much more hydrogen in their chambers than do the modern Kaufman sources. (The older systems have been discarded and were not available for our recent study.)

Our theory is based upon the phenomenon of kink-site saturation,[7] that has sufficed to explain the kinetic segregation of AlGaAs alloys[7-9] grown by molecular beam epitaxy, MBE, on <110> oriented substrates at sufficiently high growth rates. We suppose that a time t is required after the attachment of a surface-adsorbed atom to a kink site for the energy released thereby, which is almost a great as the cohesive energy, to be dissipated before another atom can attach to that kink on that growth step. For the case of the AlGaAs alloy, the empirical value of t was found[7] to be of order 10^{-7} s. It is remarkable that we here find a value of the same order of magnitude is

required to account for what we believe is a critical ion beam current, about 0.1 mA/cm^2.

The following is a list of the consequences of our theory. We believe that each of these is truly a characteristic of those runs that produce C whiskers that: a) do not grow significantly thicker as they grow longer; b) have a diameter of about 15 nm along their entire length; and c) have no scrolled-graphite structure even on the walls of the whisker.

a) there is a critical value for the ion beam current density, about 0.1 mA/cm^2, below which the no whiskers grow;

b) there is an initial time, or flux, before the whiskers begin to grow during which there is no alteration of the graphite surface evident in a high resolution, scanning electron microscopy (SEM) inspection. This critical flux is 0.06 C/cm^2 or 1 minute at 1 mA/cm^2 ion current density;

c) after the critical flux, SEM shows major portions of the surface to be covered by basal structures of order 3 μm in height. The whiskers subsequently grow from the top of the bases (Fig. 1). (Inspection of some of the broken bases in Fig. 1 seems to imply that the bases are three-sided, like pyramids. In other views they seem to be more like cones. This question is outside our theory.)

d) once nucleated, the rate of growth of the whiskers is linear in ion beam flux (or in time at constant current);

e) the whiskers always grow in the direction of the ion beam, and need not be perpendicular to the surface;

f)   while the diameter of sputter-grown whiskers may vary from run

     to run between 15 and 100 µm, they are generally quite

     constant from one to another whisker in a given run. Those

     with 15 nm diameter are constant in diameter along the length

     of the whisker, while the larger ones may have a slight taper;

          The following points have been established as generally

     valid for sputter-grown C whiskers in our recent work and will

     be elaborated upon in Ref. 4 and elsewhere.

g)   the process is insensitive to the choice of sputtering ion--

     the effect of Ar^+ sensibly the same as that of Ne^+ or of a

     mixture of 30% O^+ with either Ar^+ or Ne^+;

h)   no evidence has been found for the presence of any impurity in

     the body or at the tip of the whiskers although this has been

     looked for using the SEM, X-ray back scattering and EELS.

     (EELS has found evidence of H in benzene ring-type bonding on

     the surfaces of the whiskers.[4])

i)   .nere is evidence of H termination of bonds on the side walls

     of the whiskers, as just noted;

j)   the effect of deliberately contaminating the graphite surface

     with Ta, Al, Au, Fe or stainless steel impurities, some of

     which would catalyze growth of graphitic fibers under

     pyrolytic conditions,[5] is to suppress whisker growth. When

     surface impurity coverage exceeds 1%, there is no growth;

k)   the whiskers will grow at substrate temperatures as low as

     -150 C and at least as high as 600 C, but the areal density of

     whiskers is a generally increasing function of substrate

temperature (Fig. 2). There is some tentative evidence of a
region from room temperature to about 100 C in which the
aerial density decreases with increasing temperature;

1) the volume of the whiskers approximately accounts for all the
C atoms that should have been knocked out of their normal
lattice sites by the incident ions. That is, the sputter rate
of graphite is much too small to account for growth of the
whiskers out of the vacuum, but there should be enough sur-
face-adsorbed atoms to supply the requisite number of fast
diffusing C atoms.

We have not thoroughly determined the relation between ion energy
and whisker properties but voltages in the range 700 to 1000 V seem to
work best.

In our theory, the critical ion current density and flux, points a)
and b) above, should occur when C atoms are displaced from the graphite
substrate's lattice faster than they can reattach in the graphite struc-
ture. They then build up a critical density of such surface-adsorbed,
mobile C atoms so that the basal structures must be nucleated. Thus,
the array of bases consume the supersaturation of surface-adsorbed C
atoms. The critical current density, 0.1 mA/cm^2, corresponds to an ion
impingement rate of $6.5 \times 10^{14}/cm^2$ s. Because the minimum energy that
must be transferred to a C atom on a lattice site to displace it and
create a vacancy-interstitial pair is[10,11] 50 eV and because the average
energy lost from the irradiating particles per pair created is usually
about twice the minimum, we expect one C atom to be displaced per 100 eV
of incident ion energy. Some fraction, perhaps 25%, of these

interstitials will reach the surface; a majority should be retained between the layers of graphite until they annihilate the vacancies left behind. Thus, we estimate the rate of production of surface-adsorbed C atoms to be of order $0.65x7^4 = 1x10^{15}/cm^2$ s. We also estimate the density of kink sites on the graphite surface to be of order $10^8/cm^2$. Thus, as noted above, the same value $t = 10^{-7}$ s for the time required to dissipate the energy of attachment from the kink site, that was determined empirically for the case of AlGaAs, also fits this situation.

If the critical rate of production of surface-adsorbed C atoms is $1x10^{15}/cm^2$ s at 0.1 mA/cm^2 then the rate of increase of the density of such atoms at 1 mA/cm^2 is $4x10^{15}/cm^2$ s and in 1 minute, the critical time at this current density (recall b) above), their density reaches $2.4x10^{17}/cm^2$. As the density of atoms in diamond is $1.76x10^{23}/cm^3$, this would suffice to produce $1.4x10^{-6}/cm^3$ of nucleated basal phase per cm^2 of surface if the bases have the same density as diamond. As the density of graphite is 64% that of diamond, $2.2x10^{-6}/cm^3$ of the nucleated basal phase could be formed at that density. If there are 10^6 pyramids/cm^2 (see Fig. 2) nucleated and if they are 3 μm high with a base 1 μm square (see Fig. 1), then the volume of the bases is $1x10^{-6}$ cm^3/cm^2, in rough agreement with estimate of 1.4 to $2.2x10^{-6}$ cm^3/cm^2 that could be nucleated.

Our theory that bases should be nucleated from a supersaturation of surface atoms that develops when the kink sites are saturated is also in accord with point j) above because the effect of contaminating the surface with metal impurities should be to introduce more sites for the attachment of adsorbed C atoms than would be present on the clean

graphite surface. It is further supported by observation of the broad pattern of whiskers, Fig. 3. We see that they occur in forests separated by thin boundaries containing no whiskers. We believe these are large angle grain boundaries or cracks, which would also supply a much larger density of attachment sites than could be found on the ideal thermally roughened surface.

After the bases have been nucleated we suppose that whatever density of attachment sites their surfaces might present for surface adsorbed C atoms is reduced by the bonding of hydrogen from the chamber onto the dangling bonds. As long as the sputtering continues at a rate which produces surface adsorbed C atoms faster than they can be reattached at the available sites on the sides of the bases or on the graphite substrate, there will continue to be a super saturated population of such C atoms migrating across the surface looking for attachment sites. We posit the existence of a screw dislocation a the peak of the basal structure from which the whisker grows as it absorbs surface adsorbed C atoms from this population. To the extent that there is any partial pressure of H in the chamber, attachment sites on the sides of the whiskers will tend to be terminated by hydrogen bonding to produce the benzene ring structure, that we have observed with EELS. Whereas the sides of a whisker that points into the direction of the ion beam, which need not be perpendicular to the surface, is shielded from the beam by the rest of the whisker, the tip of the whisker will receive the full flux of the beam. We suppose that this sputtering action of the beam roughens the surface and breaks up hydrogen bonds that begin to form the benzene ring structure there. Thus a good supply of attachment

sites is to be found only at the tips of whiskers that point into the ion beam. If the partial pressure of H is high, as we are confident was the case with the older style sputtering system used in Ref. 1, the whiskers should grow longer at a linear rate and not grow thicker at any measurable rate, as was reported. For lower H partial pressures, as generally present in the new Kaufman systems, the whiskers should grow longer at a linear rate but also grow thicker with a linear rate, as reported in Refs. 2 and 3. We ascribe the run-to-run variation in the thickness of the whiskers to variations in the H partial pressure, which is neither controlled nor measured. This is consistent with the observation of uniform diameter within any particular run.

We suppose that the general increase in the density of bases with increasing temperature occurs because thermal roughening of the surface[12] increases the density of sites at which the bases may nucleate. If the decrease in base density with increasing temperature between 0 and 100 C is real, we would ascribe it to the effect of thermal activation of the migration of surface adsorbed C atoms; with increasing temperature the adsorbed atoms can migrate further to find better site to nucleate the bases. It is evident that the rate of production of surface adsorbed C atoms should not be much dependent on temperature and there is probably a significant nonthermal contribution to their migration that results from the irradiation.

It should be noted that there is a significant electric field (>10 V/cm) at the graphite surface due to the sputtering current. The effect of this field on whisker growth is not clear. Whereas the field would be particularly intense at the end of the whisker, it is always normal
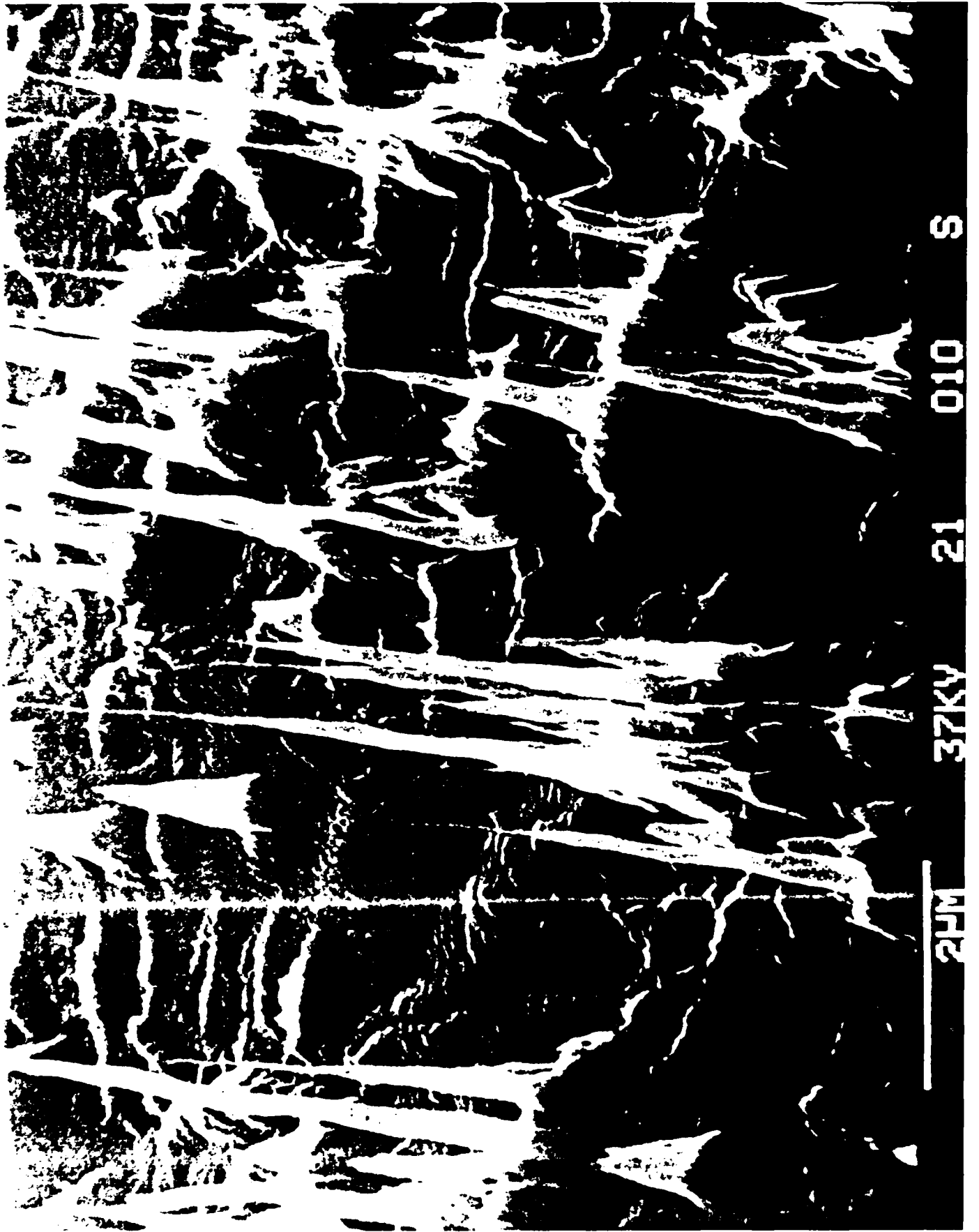
to the (metallic) graphite surface, rather than in the direction of the

ion beam. Recall that the whiskers always grow in the direction of the

beam--a fact that we attribute to the availability of attachment

sites. It is also difficult to believe that a major fraction of the

displaced C atoms could remain ionized through the growth process.
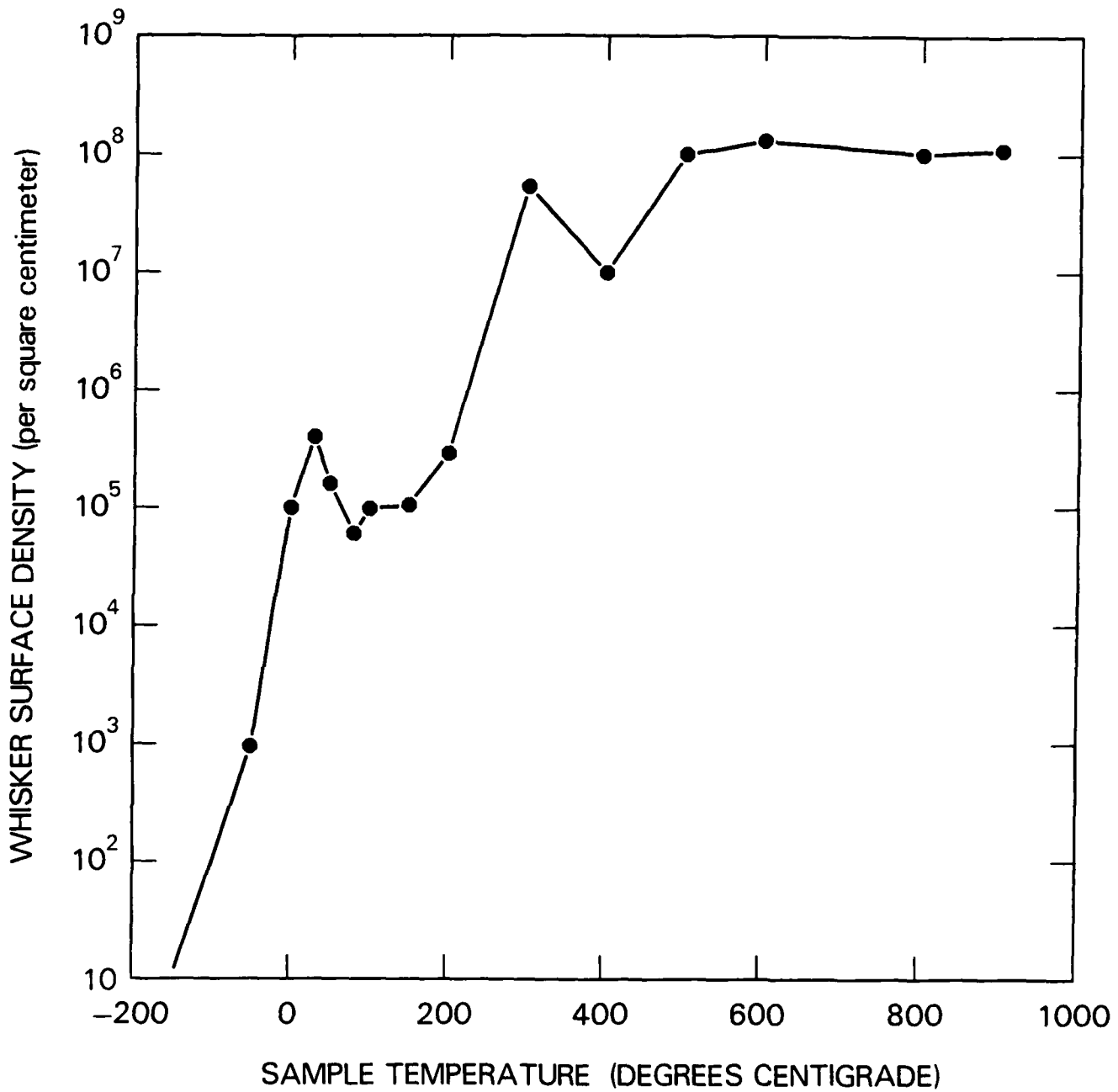
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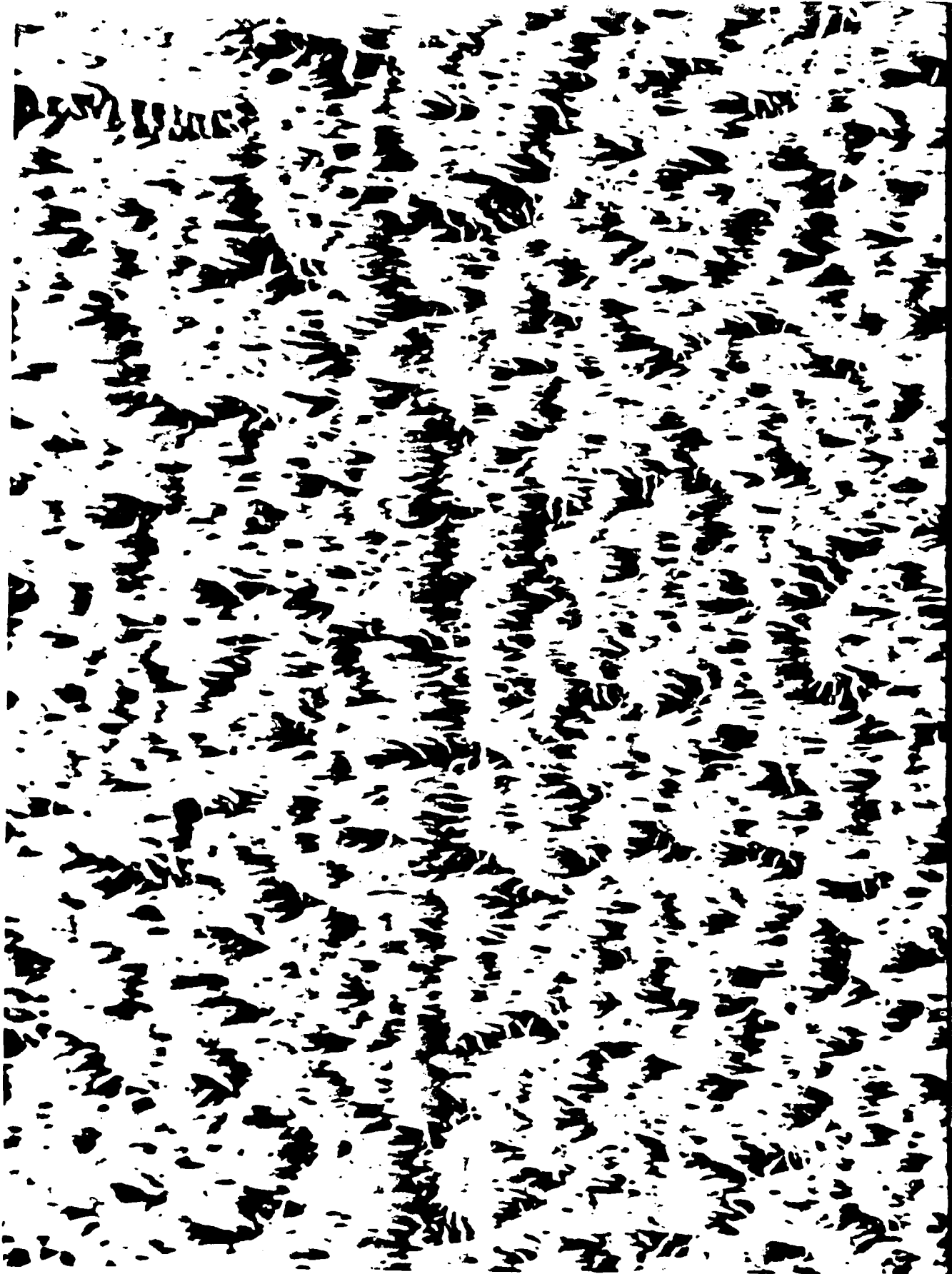
FIGURE CAPTIONS

Fig. 1   SEM photograph of carbon basal structures with whiskers grow-
         ing from their peaks.

Fig. 2   Variation of density of bases and whiskers with substrate
         temperature.

Fig. 3   Broad area view of two whisker forests showing denuded
         boundary, which is believed to be a large angle grain boundary
         of the graphite substrate.

ION BOMBARDMENT-INDUCED CARBON
WHISKER FORMATION

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This work is intended as a final report of work performed at IBM Research on the Carbon Whisker Joint Study Project with Colorado State University, funded by the Air Force Office of Scientific Research. The work at IBM Yorktown Heights focussed on the formation of long thin whiskers on graphite substrates produced during high intensity, relatively low energy ion bombardment of graphite. The overall goal of the work at IBM was to develop a basic understanding of the fundamental phenomena involved in the whisker growth process. The eventual goal of the project as a whole was pointed toward the controllable formation of fine carbon filaments, their eventual harvesting and collection, and their use possibly as absorbers of incident electromagnetic radiation.

The work at IBM centered on experimental, analytical and theoretical studies of the whiskers formed by ion bombardment on graphite and the parameters which effect whisker properties. Experimentally, this includes systematic work with the sputtering process, examining the effects of such variables as ion bombardment rate, energy, direction, substrate orientation and crystallinity, bombarding dose and im-

purity levels. The general result of variations of these and other parameters was to vary the dimensions, density and structure of the whiskers. Analytical measurements were aimed at observing whisker sizes and densities, chemical effects such as impurities and bond states, and structural characteristics such as crystalline orientation and degree of order. The theoretical work centered on developing a general theory that might be applicable in explaining the whisker growth phenomena. This theoretical work, as might be expected, is based on experimental results of both this work and related work in the semiconductor field.

The structure of this report will have three parts, describing in turn the experimental, analytical and theoretical work undertaken during the course of this grant. This work describes the efforts of several additional collaborators here at IBM, and each contribution will be identified when appropriate.

Experimental Studies of Ion-Bombardment-Induced Carbon Whisker Growth

These experiments consisted primarily of directing an intense inert gas ion beam onto a graphite substrate. Under suitable operating conditions, whiskers were observed on the substrate growing into the ion beam. Whiskers of this general type were first observed by Cuomo and Harper in 1977.[1] Subsequent work by Rossnagel and Robinson at Colorado State University in 1980-1982 focused on the related phenomena of ion bombardment-enhanced surface diffusion, and the parallels between the formation of whiskers on graphite during sputtering and the formation of

sputter cones on various metal surfaces also during sputtering with and without the presence of dilute impurities.[2-6] A more complete study of only the carbon whisker formation process was carried out by Floro, Rossnagel and Robinson in 1983,[7] in which a phenomenological description of the whisker growth process was presented.

The experimental details have varied slightly in each of these earlier works and in the present project. In the first case, Harper and Cuomo observed whisker formation on graphite cathodes in DC plasma discharge. The bombardment of the cathode served to raise its temperature to some unknown level, and the exact intensity and energy of the ion bombardment was not well known. The next two previous studies[2,7] as well as the present work, utilized directed broad beam ion bombardment of graphite samples whose temperature was controlled externally. In this way, the ion bombardment energy, flux, dose and species can be easily controlled and adjusted, and the sample temperature, which is critical for any diffusion-based process, can be well characterized. These two studies, as well as the present one, used ion sources of the Kaufman type, originally developed for use as thrusters for spacecraft. Sources of this type operate typically in the 200-2000 eV ion energy range, produce beams of predominantly singly ionized inert gas species, and can cover broad areas, up to several hundreds of square inches. The intensity of the ion beam resulting form this source is capable of sputtering simple metals, such as Cu or Au, at several thousand angstroms per minute. In the case of carbon whisker growth, whiskers could be observed in as little as 30 seconds on samples at elevated temperatures.

Before proceeding farther into the experimental process, it should be noted that there is a significant difference between the formation of carbon whiskers and most other surface topographies induced by sputtering. The formation of carbon whiskers during sputtering is clearly a GROWTH process. This contrasts to other ion bombardment effects, in which sputtering always leads to an EROSION of the surface. The incident ions generally have many hundreds of electron volts of energy when they strike the sample surface. This energy usually results in the breaking of bonds and the ejection, or sputtering, of surface atoms. Thus, topography which is formed is indicative of the removal of material, and the observed structures are what remains. In the case of graphite sputtering, structures are observed which are many times higher than the maximum amount of material which could have been removed by the sputtering. Thus, they are indicative of an actual growth of the whisker into the ion beam.

As indicated above, the principle experimental procedure was to bombard graphite substrates with an energetic ion beam. Typically one parameter of the bombardment was varied from run to run, and the subsequent surface structures were observed by Scanning Electron Microscopy (SEM) and other analytical techniques. See Figure 1 for a schematic representation of the experiment.

One of the most straightforward methods to examine whisker growth phenomena is to vary the length of time the ion beam is on, and observe the different structures as a function of the total ion dose. This is not the most ideal case in which to observe

the time development of the whisker growth: that case would be to monitor a single whisker site during the ion bombardment process in real time. However, while individual whiskers can not be monitored directly in the present case, the average behavior of large groups of structures can be examined as a function of ion bombardment dose (time). Experiments of this type showed that there are three different time periods in which different phenomena dominate the growth process.[7] The first period might be called an incubation period. At short sputtering times, no whisker growth was observed to a resolution of less than 10 nm. This incubation period was followed by a rapid growth period, in which the whiskers grew very rapidly to lengths of several thousand angstroms to a few microns. The whiskers observed in this rapid growth period were very thin, generally under a thousand angstroms in diameter. The third period is one of slow, steady growth, in which the whiskers slowly increase both their length and diameter with increased bombardment dose.

A related phenomena was the apparent smoothing of the graphite surface.[7] This smoothing was observed on pyrolytic and poco graphite surfaces, but not significantly on HOPG samples. During the incubation and early growth periods, the initially rough substrate was rapidly becoming much smoother. In the last growth stage, the surfaces at the base of the whisker appeared relatively flat, with few edges or structures other than the whiskers. This smoothing phenomena is supportive of the high levels of carbon atom surface mobility indicated by the whisker growth. This

is in contrast to vapor-growth whiskers in which the growth is based on the arrival of carbon atoms to the whisker tip.

A second, and more involved study, examined the sample temperature dependence of the whisker formation. This study was carried out with the assistance of Wm. Solberg, a graduate student on loan from Colorado State University. In this experiment, samples were bombarded under controlled conditions with sample temperatures ranging from $-150°C$ to $900°C$. The goal of this work was to determine whether activation energy-like processes were important in the whisker formation. The results are somewhat ambiguous and can be described in terms of a graph (Figure 2).

This graph charts the spatial density of the whiskers as a function of substrate temperature. The spatial density was measured by counting the number of whiskers over several large areas and averaging. The temperatures were measured by means of a thermocouple attached to the substrate platform on which the samples rested. Both of these measurements have errors associated with the technique. For example, the temperature measurements assume good thermal conductivity from the sample to the backing plate. This is easy to achieve at low temperature by the use of a thermal grease between the sample and the backing plate. At high temperatures, the use of the grease is not possible. Also, the effects of radiative cooling are not included. This will cause the surface temperature of the sample to be cooler or hotter than the measured substrate temperature depending on the ion beam power flux.

These uncertainties result in error bars on Figure 2 which vary in length depending on the temperature. The spatial whisker density measurements are also difficult. The whiskers in many cases are complicated structures with large bases. Occasionally the bases had multiple whisker structures.

The spatial density of whisker-like structures shows an overall increase with increasing temperature. This feature is unlike other activation energy based processes in which there is reported a strong decreasing feature density with increasing sample temperature. The decrease is correlated with increasing diffusion path lengths for surface diffusion due to the increased surface atom mobility at higher temperature.

The chart of Figure 2 has three areas of interest. The lowest temperature region is characterized by increasing whisker density with temperature. At temperatures below about −50°C, almost no structures similar to whiskers are ever observed. However, as the sample temperature increases towards room temperature, the density of whisker-like structures rises rapidly several orders of magnitude.

The intermediate region, from about 0°C to 150°C is characterized by a mild decrease in the whisker density with increasing temperature. Decreases of this type have been generally associated with activation-energy-based surface mobility processes.[2,4,5,6] In an activation energy process, such as the formation of sputter cones on surfaces undergoing sputtering in the presence of trace impurities, the density of surface structures can be plotted in van't Hoff form (the natural log of the density

vs 1/temperature.) While the mobility of the surface adatoms increases strongly with temperature in this sort of activation energy process, so does the spacing between clustering sites. This phenomena is based on the random walk path length of an individual surface adatom as a function of temperature. Increasing the random walk path length allows the nucleation sites to be farther apart and yet still retain stability.[2] Thus, at high temperatures the clustering sites are much larger, but also significantly farther apart than at low temperature. Increasing adatom mobility leads to a decrease in the number of surface clusters, even though there may be significantly larger numbers of moving surface adatoms at high temperature. The present data, which consisted on only 3-4 points in this region, does not really support this type of analysis to any great accuracy. However, the observation remains that the decreasing surface density of carbon whiskers in this temperature range follows the general direction of an activation energy based-surface mobility mechanism. The third region of the figure at the high temperature end suggests a saturation effect in whisker density. At these higher temperatures the whiskers became larger with increasing temperature rather than increased in spatial density. Again, this region is not characteristic of an activation energy process. However, it is indicative of an increase in the number of mobile carbon atoms on the surface, which would be expected to increase with rising temperature. It should be noted that recent experimental work by Solberg at Colorado State University indicates an overestimate of the sample temperature at the highest ranges. This would result in a compression of the high temperature data points to lower temperature.

The general shape of this curve suggests that some other process than surface diffusion-based nucleation is dominating for most of the temperature range. At present, that mechanism is not known, although it may be related to thermal, or bombardment enhanced thermal roughening of the surface, increasing the number of defect sites and hence the number of formation locations for the whiskers. On the other hand, the general increase in whisker density, and hence the amount of mobile carbon atoms available for whisker growth, appears to be increasing strongly with temperature, as might be expected from an activation-energy-based process. As will be shown below, the whiskers have three structural modes. The formation of each of these modes is suggestive of different processes. However, at least for the purpose of describing the spatial density of the whisker growths over most of the temperature range, surface diffusion is not the rate limiting step.

A third variable, that of the intensity of the ion bombardment, was also examined to determine the effect on whisker growth and structure. In this work, the total ion fluence and energy was kept constant, as was the sample temperature. The bombardment rate was varied inversely with sputtering time to produce a constant dose. In general, the higher intensity ion bombardment lead to finer, higher density whiskers. No systematic measurements of length were undertaken. There did appear to be a general minimum in the ion current density needed to form whiskers, of about 0.1 mA/cm^2. This should be regarded as tentative because extensive experiments below this ion current density were not attempted.

Other techniques of whisker growth and sputter cone formation depend critically on the presence of impurities or other species. For example, in the case of vapor deposited carbon fibers or tubes, a fine impurity particle of iron or iron oxide is required at the tip of the whisker. This process is a vapor-condensation process, however, and is only related to the present study by the similarity in material. Other studies of ion bombardment induced sputter cones have shown the critical role of impurities.[2-6] In those cases, impurities were used to form dynamically stable nucleation sites on the surface undergoing ion bombardment. The nucleation sites collected diffusing surface impurity atoms as well as dislodged bulk atoms into stable clusters. With continued sputtering, these clusters were shaped into erosional structures known as sputter cones.[2-6] The impurity was shown to be critical in experiments which removed the source of impurities after the initial surface structures had been formed. In that case, the surface sputter cones quickly eroded to a relatively flat, featureless surface.[3]

Extensive measures were undertaken to observe whether impurities were present in the whiskers, or at the tip. These will be described in more detail in the Analytical Results section below. The primary result is that impurities do not seem to be sufficient to be the driving force in whisker formation. A convincing experiment is to specifically add impurities, such as Fe, W or Ta, to the graphite surface during the ion bombardment process. In that case, the formation of whiskers is reduced, often by 2-3 orders of magnitude, and the whiskers that form are thick and short in comparison the the no-impurity case.

The whisker diameter was observed to be constant over a large percentage of its length. In the related analytical work, individual whiskers were "followed" in the electron microscope for several microns. The whiskers were not perfectly smooth, right cylinders, but their overall diameter did not vary more than 20% over most of its length away from the base. At the whisker tips, the whisker often tapered gently to a point. The whisker bases were often conical in shape, depending on the temperature. At high temperatures, the degree of cone formation was limited, in comparison to low temperatures 300°C, where the cones were quite evident and could be relatively short. Often complicated base structures were observed at the whisker/substrate interface. These structures appears amorphous, and often had several whiskers growing out of each structure. The whisker diameters ranged from as low as 10 nm to several microns, depending on the sample temperature, the intensity of the ion bombardment, and the length of time (or dose) of the ion bombardment. In general, high temperatures, or high intensity bombardment lead to the thinnest whiskers: low temperature or low intensity bombardment to the thickest whiskers. The effect of time, as described above, was to cause increases in both the length and diameter of the structures.

Several measurements have been made with different ion species bombarding the surface. For example, Ne and Kr also form whisker structures on graphite during ion bombardment. The addition of oxygen to the Ar gas during the sputtering to levels of 30-40% caused a reduction in the whisker density, and an increase in the whisker

diameter. It did not, however, suppress whisker formation as might be expected in the very reactive chemical environment of oxygen ions and clean carbon surfaces.

Other types of carbon surfaces were sputtered under similar conditions to determine the effects of crystal structure. Most of the work described here was done with pyrolytic graphite sheets, formed by chemical vapor deposition. Other substrates used were Highly Oriented Pyrolytic Graphite (HOPG), POCO graphite (a reactor grade, pressed structure), vitreous carbon, and diamond. Each of the graphites formed whiskers under ion bombardment to varying degrees. The POCO formed the lowest levels of whiskers, possibly due to the very rough surface structure. The other two graphites were roughly comparable. The vitreous carbon showed no evidence of whisker formation. The diamond experiments were fine diamond particles (1-3 microns) scattered on graphite. Whiskers were observed to form from the diamond surfaces, but no visual evidence of facetting was observed by SEM. Bulk diamond was not used as a substrate by itself.

Analytical Studies

The whisker-covered substrates were examined with a number of diagnostics to help discern the effects of structure and purity on whisker growth. A number of samples were examined with Auger Electron Spectroscopy (AES), which is a surface sensitive diagnostic. Sample traces from the AES analysis are shown in Figure 3a and b for the case of an as-is whisker covered sample, and for a sample lightly

sputter-cleaned in the analysis chamber. In each case, aside from a small level of surface oxygen, no other impurities were detected to the sensitivity (0.2% atomic) of the technique. The oxygen is likely to be due to atmospheric contamination, and was easily removed in the AES device with light sputtering. The second diagnostic used was Microprobe, or Energy Dispersive Analysis with X-Rays (EDAX). The results here were similar to the AES case. The substrates were found to be essentially pure carbon. A third technique, Rutherford Backscattering, was also used. This technique can be less surface sensitive and can probe down into the sample with sputtering. In this case, traces of Ar and W were observed, along with possibly some iron. The technique suffered from the roughness of the samples. The whiskered substrates are effectively rough to the scale of several microns, which tends to spread out the signal. The Ar impurities were in the $10^{13}/cm^2$ range when integrated through the first few microns on the sample. The W level was an order of magnitude lower. The W was likely to be due to the filaments in the ion source, and is below the levels commonly used to induce surface topography in other materials under sputtering. The Ar is implanted gas from the sputtering process. It should be noted that it was not possible to measure Hydrogen concentrations with any of these techniques. Possible ways to measure H levels are Nuclear Resonance reactions, Secondary Ion Mass Spectroscopy, possibly thermal desorption measurements and Ion Surface Scattering with light ions. None of these techniques has sufficient spatial resolution to look at individual whiskers, or to easily discern the whiskers from the substrate.

Aside from the routine Scanning Electron Microscopy (SEM) analysis of the whiskers, several samples were examined with Transmission Electron Microscopy (TEM) and with Electron Energy Loss Spectroscopy (EELS). The TEM work was done in collaboration with George Walker, of IBM Research. The TEM samples were made by imbedding a field of whiskers in an epoxy medium, and cleaving laterally through the sample. The whiskers are then effectively cross-sectioned. With this analysis, the whiskers in cross-section appeared as circles. Within those circles, a spiral line structure was observed around the outer perimeter of the sample. This appears to be consistent with a scroll-like graphitic growth, with the c-axis perpendicular to the axis of the whisker. This work would initially suggest that the whiskers are graphitic scrolls, which is a similar structure to the vapor deposition whiskers grown with the small Fe or Fe/Ox seed particle.

The EELS work was performed by Dr. Phil Batson, of IBM Research, and represents an extremely sensitive diagnostic technique that may not be duplicated in more than a few laboratories in the world. The technique is to direct a colimated beam of electrons onto the surface of a sample in a high resolution SEM/TEM. The energy spread of the incident electrons must be very small, a few tenths of an eV. The energy spectrum of the electrons reflected from the surface is then analyzed in a high resolution spectrometer. Depending on the chemical bonding state of the surface atoms, it is often possible to discern the crystallographic orientation of the sample surface. For example, the device has sufficient resolution to discern between graphite, amorphous carbon and diamond. The results of this work are somewhat

ambiguous, but later data has helped clear up the structure. Looking at rather thin whiskers, the structure observed was of predominantly graphitic carbon, but with a range of orientations. The general orientation was that the c-axis of the graphite was not radial on the side of the whisker, but more closely aligned with the axis of the whisker. This suggests that the scroll-like structure is not appropriate. On the conical base of the whisker, the carbon appeared to be amorphous. The suggestion from this work with very thin whiskers is that the central core of the whisker is approximately a step-like spiral formation or varying degree of crystallinity. The base of the whiskers is amorphous, possible sputter deposited from the near-by flat areas between whiskers. On more mature whiskers, as measured by the cross-sectional TEM, a scroll-like coating has apparently formed over the internal core. This was not specifically observed with the EELS, but that work only looked at relatively young, early stage whiskers.

The scroll-like structures would be expected to have a minimum radius, at which the scroll could not energetically be rolled any tighter.[7] Thus the fine central core, which is only 10 nm or so in diameter, could probably not be of the scroll structure. After the whisker has enlarged slowly over time by addition of atoms to the outer perimeter of the spiral form, it may then be more energetically favorable to form the scroll-like structure observed on the mature whiskers.

Later work by Sharon Fortner, also of IBM Research, using very high resolution SEM/TEM has shown clear evidence of bands in the whisker which are perpendic-

ular to the axis of the whisker. These bands cross the width of the whisker (5-7 nm) and are spaced at 1.2-1.5 nm intervals. The bands persist for many hundreds of layers from the whisker tip, as far as could be observed with the SEM/TEM. This work is at the moment preliminary, and has not been reported elsewhere. A paper describing this work is in preparation, but a pre-print has not been attached.[9]

The EELS work by Batson has been collected into a short paper, a pre-print of which is included as Appendix A.

Theoretical Aspects of Carbon Whisker Formation

The growth aspect of the formation whisker formation during ion beam sputtering fails to be simply explained in terms of the sputtering process and related phenomena such as reflection of incident ions from the sides of whiskers and the redeposition of sputtered material back onto the whisker or neighboring whiskers. Growth is clearly taking place directly into the ion beam. Earlier work,[7] described the removal by sputtering of whiskers not aligned within 5-7 degrees of the ion beam direction. However, this was a cross-section effect, where the whisker presented too large of a target to the ion beam. The removal rate by sputtering then exceeded the supply rate of atoms, by whatever means, and the whisker was destroyed. The supply of atoms to form the whiskers can either come from the substrate surface, or from recapture of nearby sputtered atoms by the whisker. As the whiskers are often quite small in

diameter, and appear to increase uniformly in length and diameter with time, the recapture aspect is less likely to be the primary supply mechanism. The redeposition would be expected to be significant near the base of the whisker, but decrease rapidly at levels above the surface. Redeposition may help produce the tall conical bases often observed at the bases of the whiskers, which are found to be predominantly amorphous in structure. That leaves the primary source of C atoms to the whisker to be the sample surface. Surface diffusion is a well known phenomena, and is generally characterized by an activation energy, which can be envisioned as a barrier height for te surface-adsorbed atom to cross on its random walk form one site to the next. Activation energy based processes have a characteristic temperature dependence, which has been explored to a large degree by one of the authors.[2-6] The general result of an activation-energy based process on the formation of surface topography is that the density of this structures decreases with increasing temperature. The reason for this is that at higher temperatures, the surface atoms are much more mobile: they can get over the activation energy barrier much more readily, and the nucleation sites for those diffusing atoms can then be much farther apart than at colder sample temperature.

The basic result, then, of an activation energy-based surface process is that the surface density of structures decreases with increasing temperature. Unfortunately, the results of the present study do not support this trend. The surface density of structures strongly increases with sample temperature, and thus indicated that another process may be important.

Λ related phenomena is the topic of kink-site saturation, which has been used successfully to describe work in the semiconductor field.[10] The phenomena is based on the oversupply of mobile surface atoms, in this case on the graphite surface or on the sides of a whisker structure. The oversupply is caused by the formation of large numbers of displaced atoms caused by the incident ion. These atoms are displaced from their lattice site at a rate faster than they can dissipate the energy of attachment to a kink or adsorption site. If, for example, the rate of production of surface-mobile atoms was approximately 1-2 per incident ion, then 10^{15} or so surface atoms would be formed per square centimeter per second. Since there can be as many as 10^8 surface adsorption sites (corresponding to the number of observed whiskers), the energy absorption time then is on the order of 10^{-7} seconds or longer, similar to the magnitude of the empirically determined semiconductor case.[10] Λ more complete description of this work has been written in the form of a paper to be published. The paper, in pre-publication form, is appended to this work as Appendix B.

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FIGURE CAPTIONS

1. Schematic of the experimental configuration

2. Plot of the Average Whisker Density vs. Sample Temperature for pyrolytic graphite substrates in a 1 mA/cm^2 ion beam of Ar at 1000eV.

3. a) Auger Electron Spectra of an as formed carbon whisker sample of pyrolytic graphite. b) the same sample after light sputtering.

GRAPHITE

HEATER

CARBON WHISKERS

ION SOURCE

ION BEAM
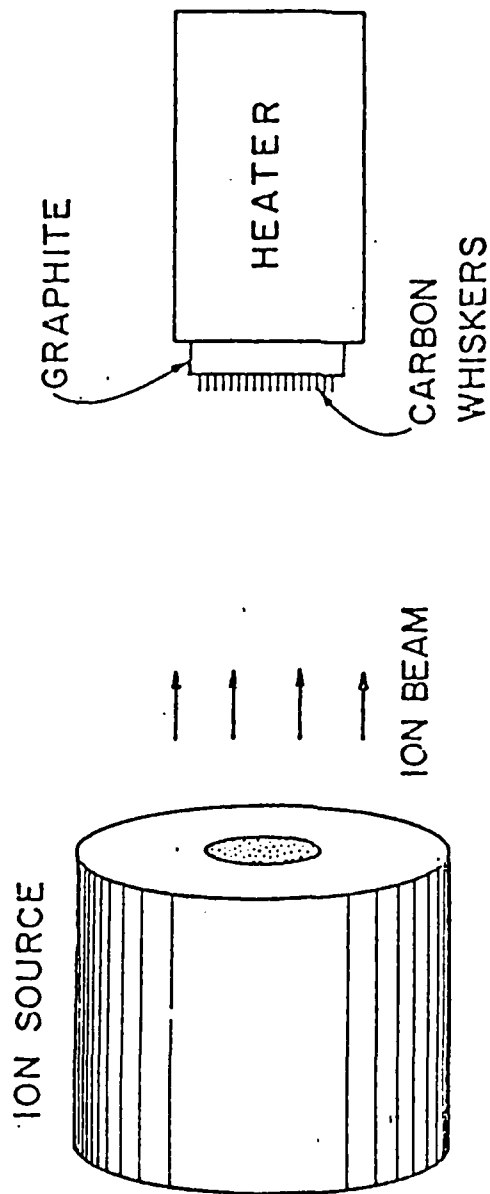
SCHEMATIC OF THE METHOD USED TO PREPARE CARBON WHISKERS BY BOMBARDING A CARBON SURFACE WITH ~ 1000V Ar^+ IONS.
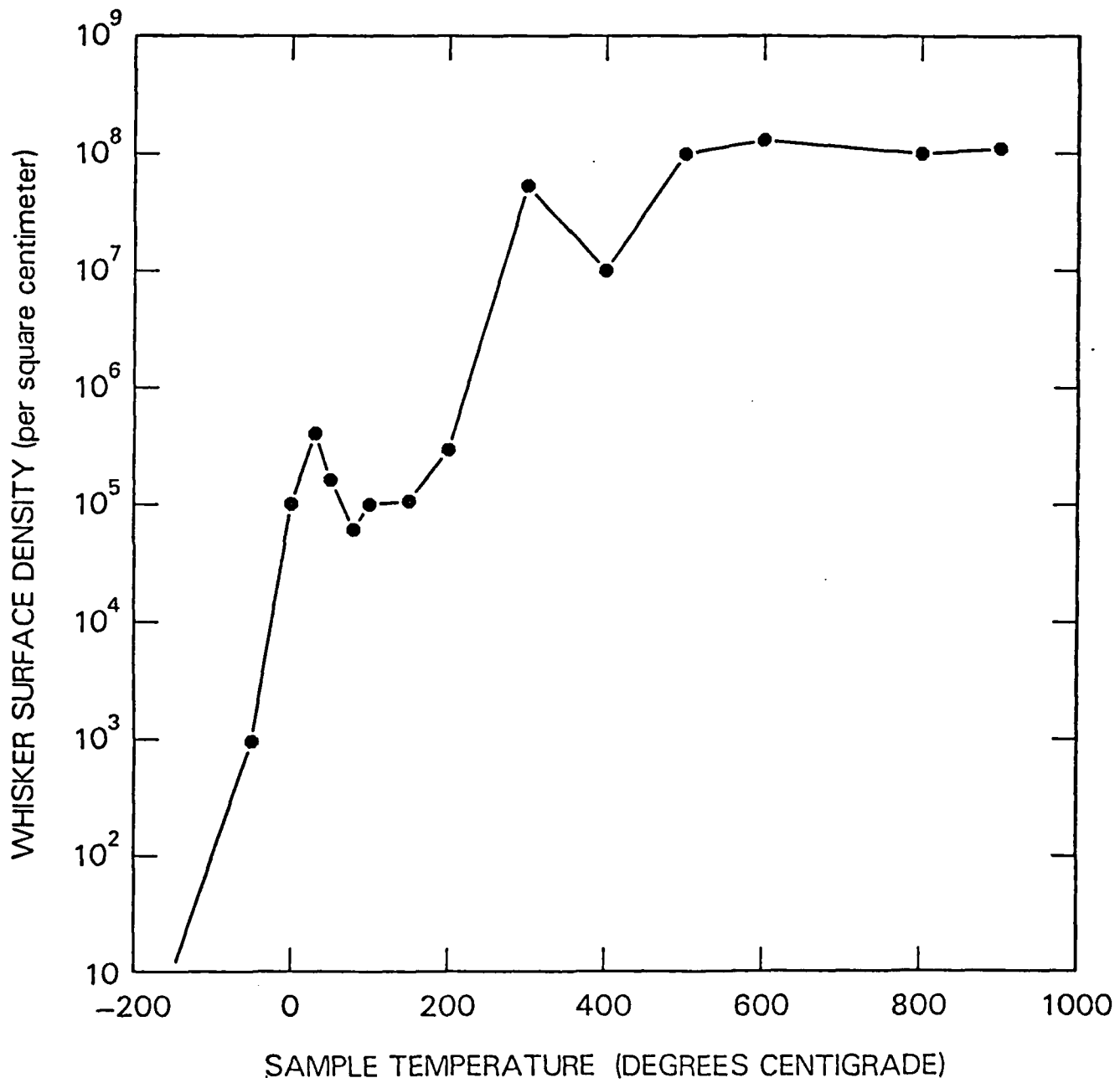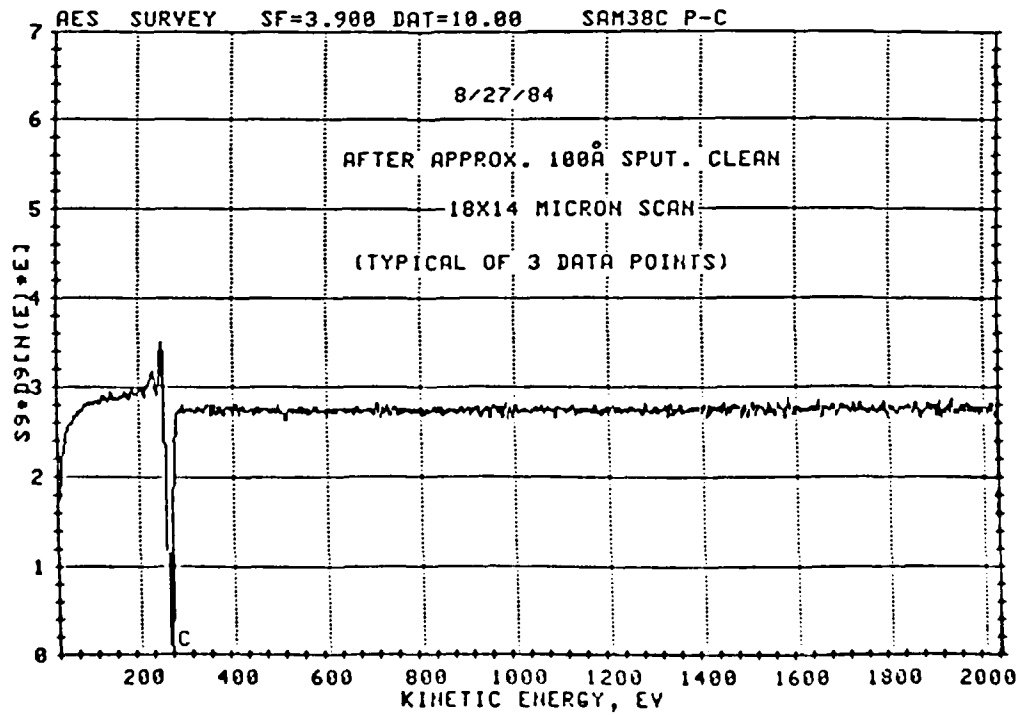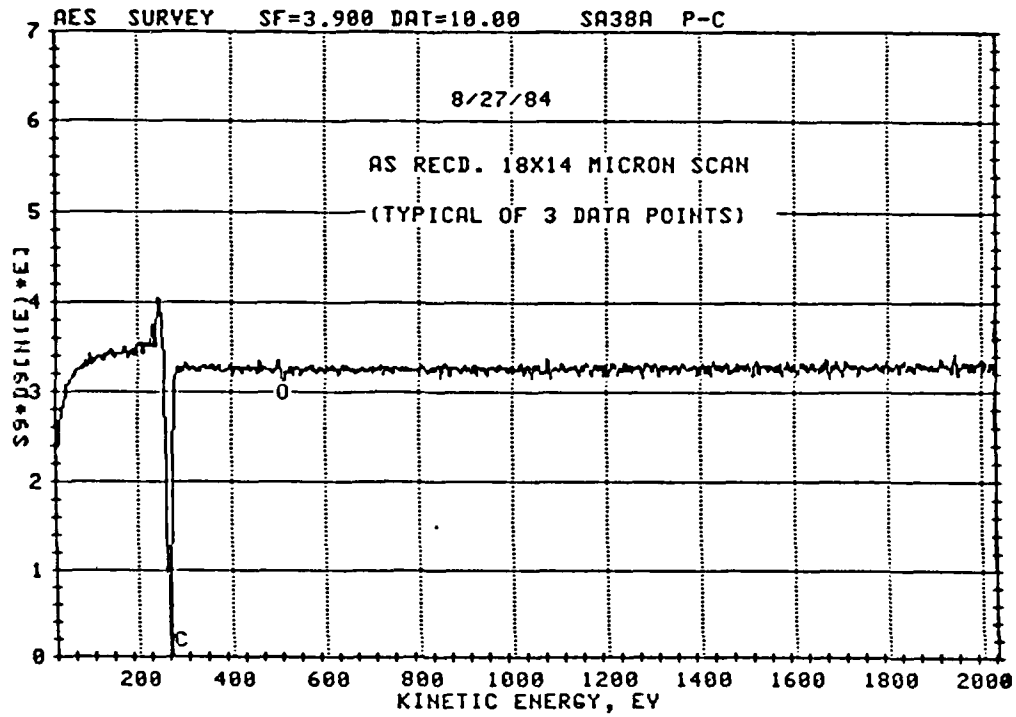
Fig. 1

Fig. 2

Fig. 3

KINK SITE SATURATION MECHANISM FOR WHISKER GROWTH UNDER SPUTTERING CONDITIONS

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ABSTRACT: We consider what should happen when surface adsorbed atoms are created at a rate faster than they can be accommodated at kink sites on a surface, such as graphite, for which the nucleation of new grow steps and kinks is difficult. We suppose that this is the condition of common ion beam sputtering systems when the beam current exceeds a critical value. We conclude that, following the nucleation of a second phase as a basal structure, whiskers should grow in the direction of the ion beam, whatever its orientation to the surface normal. Provided that possible attachment sites on the sides of the whiskers are bound, as by termination of dangling bonds by the hydrogen generally present in sputtering systems, the whiskers should grow in length at a constant rate with little or no in-

crease in their diameter,. This is because the tips of the whiskers should provide the only nonsaturable source of attachment sites for the surface adsorbed atoms produced by subsequent sputtering. We suggest that this mechanism is responsible for the growth of carbon whiskers with diameters of order 15 nm and remarkably high aspect ratios on graphite surfaces in 1 keV sputtering systems. Such whiskers have been grown to a length in excess of 20 μm and have been demonstrated to be clearly different from the scrolled-graphite structure whiskers obtained by catalytic pyrolysis of hydrocarbons.

The growth of whiskers from graphite surfaces under ion sputtering conditions has been reported[1-3] for several years, but without any determination of the crystal structure of the whiskers nor of the mechanism of their nucleation and growth. In a separate publication[4] we give a detailed report of an investigation of the chemical purity, bonding and crystal structure of these whiskers that has been made by the method of electron energy loss spectroscopy (EELS) done in a high resolution transmission electron microscope (TEM). The TEM allows us to distinguish the whiskers from adjacent material and to interrogate various sections of an individual whisker. This EELS investigation shows the structure of some of these whiskers, those of the smallest diameters observed, which is characteristically about 15 nm, definitely to be different from either diamond or the scrolled-graphite structure found[5] in C fibers grown by catalytic pyrolysis of hydrocarbons.

Larger whiskers are also observed[2,3] to grow in sputtering systems under some conditions. These have diameters ranging from 30 to 100 nm. They definitely appear to grow thicker

as they grow longer whereas the smaller diameter whiskers are reported[1] to grow only in length. It appears that some of these thicker whiskers have the scrolled-graphite structure at least on the outer portions. While fibers grown by catalytic pyrolysis are generally hollow, these thicker sputter grown whiskers appear to have a solid core that may be different from the outer core. It would seem that there should be a minimum diameter to which the graphitic structure could be scrolled and it may be that the inner structure of the thicker sputter-grown whiskers is similar to that of the thinner sputter grown whiskers; we have no firm evidence of this.

Here we propose an explanation of the nucleation and growth mechanisms of the thinner sputter-grown whiskers. It is offered in the form of a theory rather than as an explanation of an exhaustive set of firmly established experimental facts. This is because the theory has implications which are consistent with the report of Ref. 1 and related work, but which were unconfirmed in Refs. 2 and 3 and some of our subsequent work. We believe that the reason for the variable results observed, particularly as to the diameters of the whiskers and as to whether or not they grow thicker as they grow longer, is the presence of a hidden and uncontrolled variable. We suspect that this uncontrolled variable is the background hydrogen partial pressure in the sputtering apparatus. It is also true that the configuration of the sputtering apparatus used in Ref. 1 was quite different from the so-called Kaufman ion sources[6] that were used in Refs. 2 and 3, and in our subsequent work and this may have affected the whiskers. However, we believe that the most significant difference is that the older sputtering systems had much more hydrogen in their chambers than do the modern

Kaufman sources. (The older systems have been discarded and were not available for our recent study.)

Our theory is based upon the phenomenon of kink-site saturation[7], that has sufficed to explain the kinetic segregation of AlGaAs alloys[7-9] grown by molecular beam epitaxy, MBE, on <110> oriented substrates at sufficiently high growth rates. We suppose that a time is required after the attachment of a surface-adsorbed atom to a kink site for the energy released thereby, which is almost as great as the cohesive energy, to be dissipated before another atom can attach to that kink on that growth step. For the case of the AlGaAs alloy, the empirical value of t was found[7] to be of order 10^{-7} s. It is remarkable that we here find a value of the same order of magnitude is required to account for what we believe is a critical ion beam current, about 0.1 mA/cm².

The following is a list of the consequences of our theory. We believe that each of these is truly a characteristic of those runs that produce C whiskers that: a) do not grow significantly thicker as they grow longer; b) have a diameter of about 15 nm along their entire length; and c) have no scrolled-graphite structure even on the walls of the whisker.

a) there is a critical value for the ion beam current density, about 0.1 mA/cm², below which the no whiskers grow;

b) there is an initial time, or flux, before the whiskers begin to grow during which there is not alteration of the graphite surface evident in a high resolution, scanning electron microscopy (SEM) inspection. This critical flux is 0.06 C/cm^2 or 1 minute at 1 mA/cm^2 ion current density;

c) after the critical flux, SEM shows major portions of the surface to be covered by basal structures of order $3\mu m$ in height. The whiskers subsequently grow from the top of the bases (Fig. 1). (Inspection of some of the broken bases in Fig. 1 seems to imply that the bases are three-sided, like pyramids. In other views they seem to be more like cones. This question is outside our theory.);

d) once nucleated, the rate of growth of the whiskers is linear in ion beam flux (or in time at constant current);

c) the whiskers always grow in the direction of the ion beam, and need not be perpendicular to the surface;

f) while the diameter of sputter-grown whiskers may vary from run to run between 15 and $100\mu m$, they are generally quite constant from one to another whisker in a given run. Those with 15 nm diameter are constant in diameter along the length of the whisker, while the larger ones may have a slight taper;

The following points have been established as generally valid for sputter-grown C whiskers in our recent work and will be elaborated upon in Ref. 4 and elsewhere.

g) the process is insensitive to the choice of sputtering ion - the effect of Ar^+ sensibly the same as that of $Ne+$ or of a mixture of 30% O^+ with either Ar^+ or $Ne+$.

h) no evidence has been found for the presence of any impurity in the body or at the tip of the whiskers although this has been looked for using the SEM, X-ray backscattering and EELS. (EELS has found evidence of H in benzene ring type bonding on the surfaces of the whiskers[4].;

i) there is evidence of H termination of bonds on the side walls of the whiskers, as just noted;

j) the effect of deliberately contaminating the graphite surface with Ta, Al, Au, Fe or stainless steel impurities, some of which would catalyze growth of graphitic fibers under pyrolytic conditions[5], is to suppress whisker growth. When surface impurity coverage exceeds 1%, there is no growth.

k) the whiskers will grow at substrate temperatures as low as $-150°C$ and at least as high as $600°C$, but the aerial density of whiskers is a generally increasing function of substrate

temperature (Fig. 2). There is some tentative evidence of a region from room temperature to about 100°C in which the aerial density decreases with increasing temperature;

l) the volume of the whiskers approximately accounts for all the C atoms that should have been knocked out of their normal lattice sites by the incident ions. That is, the sputter rate of graphite is much too small to account for growth of the whiskers out of the vacuum, but there should be enough surface-adsorbed atoms to supply the requisite number of fast diffusing C atoms.

We have not thoroughly determined the relation between ion energy and whisker properties but energies in the range 700 to 1000 eV seem to work best.

In our theory, the critical ion current density and flux, points a) and b) above, should occur when C atoms are displaced from the graphite substrate's lattice faster than they can reattach in the graphite structure. They then build up a critical density of such surface-adsorbed, mobile C atoms so that the basal structures must be nucleated. Thus, the array of bases consume the supersaturation of surface-adsorbed C atoms. The critical current density, 0.1 mA/cm^2, corresponds to an ion impingement rate of 6.5×10^{14}/cm^{2}s. Because the minimum energy that must be transferred to a C atom on a lattice site to displace it and creates a vacancy-interstitial pair is[10,11] 50 eV and and because the average energy lost from the irradiating particles per pair created is usually about twice the minimum, we expect one C atom to be displaced per 100 eV of incident ion energy. Some fraction, perhaps 25%,

of these interstitials will reach the surface; a majority should be retained between the layers of graphite until they annihilate the vacancies left behind. Thus, we estimate the rate of production of surface-adsorbed C atoms to be of order $1 \times 10^{15}/cm^2s$. We also estimate the density of kink sites on the graphite surface to be of order $10^8/cm^2$. Thus, as noted above, the same value $t = 10^{-7}s$ for the time required to dissipate the energy of attachment from the kink site, that was determined empirically for the case of AlGaAs, also fits this situation.

If the critical rate of production of surface-adsorbed C atoms is $1 \times 10^{15}/cm^2s$ at 0.1 mA/cm^2, then the rate of increase of the density of such atoms at 1 mA/cm^2 is current density (recall b) above), their density reaches $2.4 \times 10^{17}cm^2$. As the density of atoms in diamond is $1.76 \times 10^{23}/cm^3$, this would suffice to produce $1.4 \times 10^{-6}/cm^3$ of nucleated basal phase per cm^2 of surface if the bases have the same density as diamond. As the density of graphite is 64% that of diamond, $2.2 \times 10^{-6}/cm^3$ of the nucleated basal phase could be formed at that density. If there are 10^6 pyramids/cm^2 (see Fig. 2) nucleated and if they are $3\mu m$ high with a base $1\mu m$ square (see Fig. 1), then the volume of the bases is $1 \times 10^{-6}cm^3/cm^2$, in rough agreement with estimate of 1.4 to $2.2 \times 10^{-6}cm^3/cm^2$ that could be nucleated.

Our theory that bases should t nucleated from a supersaturation of surface atoms that develops when the kink sites are saturated is also in accord with point j) above because the effect of contaminating the surface with metal impurities should be to introduce more sites for the attachment of adsorbed C atoms than would be present on the clean graphite sur-

face. It is further supported by observation of the broad pattern of whiskers, Fig. 3. We see that they occur in forests separated by thin boundaries containing no whiskers. We believe these are large angle grain boundaries or cracks, which would also supply a much larger density of attachment sites than could be found on the ideal thermally roughened surface.

After the bases have been nucleated we suppose that whatever density of attachment sites their surfaces might present for surface adsorbed C atoms is reduced by the bonding of hydrogen from the chamber onto the dangling bonds. As long as the sputtering continues at a rate which produces surface adsorbed C atoms faster than they can be reattached at the available sites on the sides of the bases or on the graphite substrate, there will continue to be a super saturated population of such C atoms migrating across the surface looking for attachment sites. We posit the existence of a screw dislocation at the peak of the basal structure from which the whisker grows as it adsorbs surface adsorbed C atoms from this population. To the extent that there is any partial pressure of H in the chamber, attachment sites on the sides of the whiskers will tend to be terminated by hydrogen bonding to produce the benzene ring structure, that we have observed with EELS. Whereas the sides of a whisker that points into the direction of the ion beam, which need not be perpendicular to the surface, is shielded from the beam by the rest of the whisker, the tip of the whisker will receive the full flux of the beam. We suppose that this sputtering action of the beam roughens the surface and breaks up hydrogen bonds that begin to form the benzene ring structure there. Thus a good supply of attachment sites is to be found only at the tips of

whiskers that point into the ion beam. If the partial pressure of H is high, as we are confident was the case with the older style sputtering system used in Ref. 1, the whiskers should grow longer at a linear rate and not grow thicker at any measurable rate, as was reported. For lower H partial pressures, as generally present in the new Kaufman systems, the whiskers should grow longer at a linear rate but also grow thicker with a linear rate, as reported in Ref. 2 and 3. We ascribe the run-to-run variation in the thickness of the whiskers to variations in the H partial pressure, which is neither controlled nor measured. This is consistent with the observation of uniform diameter within any particular run.

We suppose that the general increase in the density of bases with increasing temperature occurs because thermal roughening of the surface[12] increases the density of sites at which the bases may nucleate. If the decrease in base density with increasing temperature between 0 and 100 degree C is real, we would ascribe it to the effect of thermal activation of the migration of surface adsorbed C atoms; with increasing temperature the adsorbed atoms can migrate further to find better site to nucleate the bases. It is evident that the rate of production of surface adsorbed C atoms should not be much dependent on temperature and there is probably a significant non-thermal contribution to their migration that results from the irradiation.

It should be noted that there is a significant electric field (>10 V/cm) at the graphite surface due to the sputtering current. The effect of this field on whisker growth is not clear. Whereas the field would be particularly intense at the end of the whisker, it is always normal

to the (metallic) graphite surface, rather than in the direction of the ion beam. Recall that the whiskers always grow in the direction of the beam - a fact that we attribute to the availability of attachment sites. It is also difficult to believe that a major fraction of the displaced C atoms could remain ionized through the growth process.

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Figure Captions

Fig. 1   SEM photograph of carbon basal structures with whiskers growing from their peaks.

Fig. 2   Variation of density of bases and whiskers with substrate temperature.

Fig. 3   Broad area view of two whisker forests showing denuded boundary, which is believed to be a large angle grain boundary of the graphite substrate.
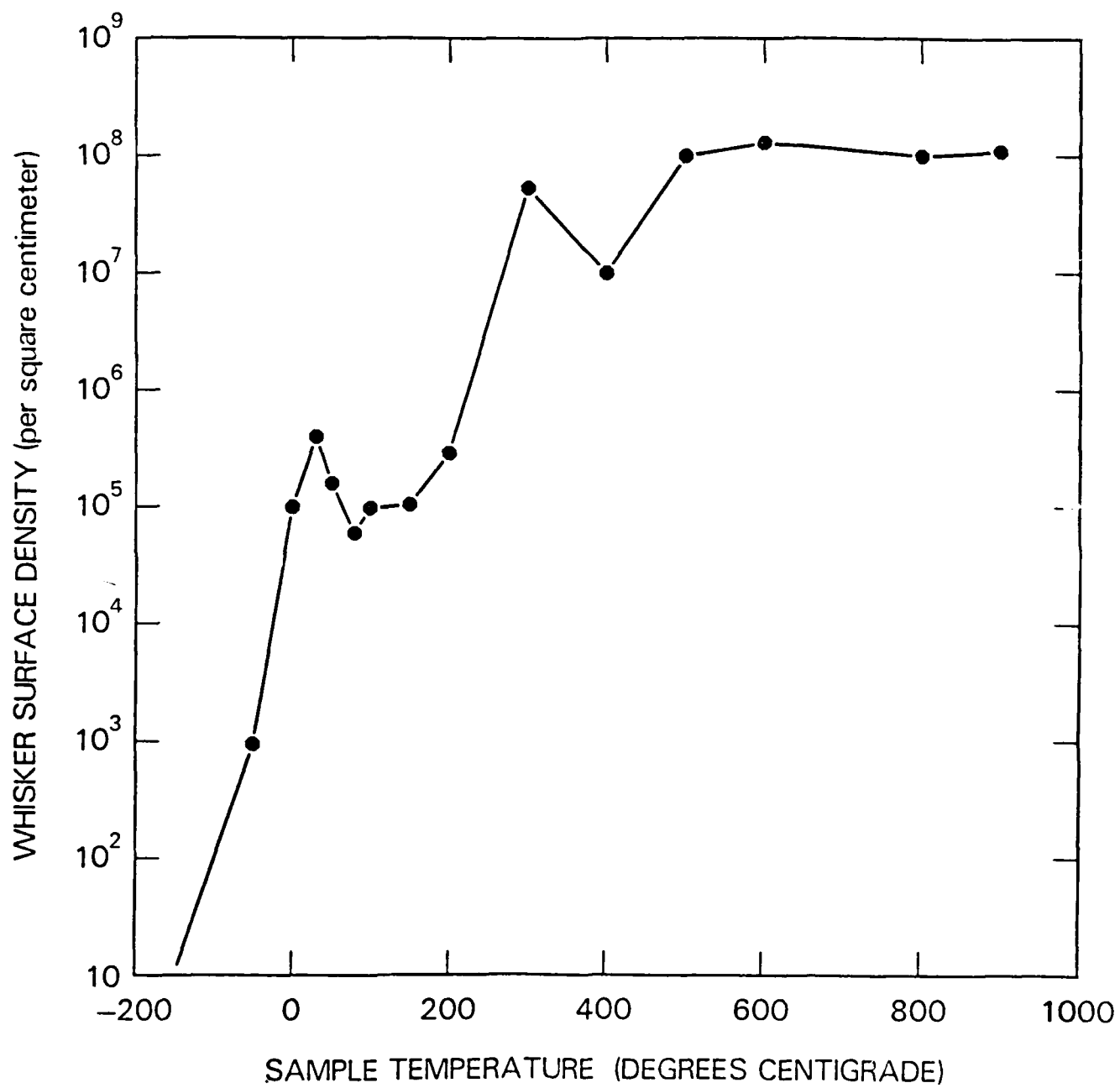
Study of the s-Core to Conduction Band Absorption Edge in Small Filaments Formed on Graphite During Ion Beam Bombardment

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Abstact:

Preliminary studies of the carbon K edge excitation near 285eV have been made for small filamentary structures grown on graphite under ion beam bombardment. Inelastic scattering from 1nm sized areas of single filaments shows similarities to that obtained for amorphous hydrogenated carbon films.

Core to conduction band excitations in many materials have been observed using high energy inelastic electron scattering. In the case of the carbon s-core to conduction band edge near 285eV, the scattering intensity for 100KeV energy incident electrons is reasonably large, leading to recording times of as short as 10min for a 1nA incident beam current. The three main forms of carbon -- amorphous, graphitic, diamond -- also have grossly different near edge structure. The main reason for this is the disparity of 5eV between the s-π excitation and the s-σ excitation at 290eV. The relative intensity of these two peaks is then a reflection of the relative amount of π bonding and σ bonding. Since the scattering matrix element for these two excitations can be different, however, a comparison does not readily yield this ratio. Fink, et. al.[1] have used the low energy loss (0-30eV) region with an appropriate electron sum rule to deduce the percentage of π and σ bonding for various hydrogenated amorphous carbon films. Since these films were formed in glow discharge environments, is seems not unreasonable that some similarity may exist between those experiments and the present experiments. Therefore, the following development relies heavily on the Fink, et. al. work for interpretation.

Since the filamentary structures of interest here may be as small as 10nm in diameter, a large beam instrument cannot obtain energy loss structure from morphalogically well defined areas. This study has used a Scanning Transmission Electron Microscope to produce a 1nm diameter probe of 100KeV electrons. This probe may be easily positioned onto precise areas of single carbon fibers -- viewed from the side. The electron energy loss spectrometer is a Wien Filter type with an energy resolution of 0.15eV at a collection semi-angle of 12mR. Since the microscope uses a cold field emission electron source with an energy width of about 0.25eV, the spectral resolution for the combination was about 0.3eV for these studies.

Figure 1. (solid lines) shows representative spectra for the three major forms of carbon -- diamond, evaporated amorphous carbon, and graphite. The gross differences in qualitative structure suggest that it should be easy to distinguish amoung the vari-

ous forms. At the outset, the intention of this work was to find if the small filamentary structures gave spectra which resembled any of those curves in the figure. Data points in Figure 1 show the structure which was found to be typical in regions of well developed filamentary structure well away from the graphite substrate.

The results for the whisker clearly resemble the results from the evaporated amorphous carbon. Further, similar measurements were made on larger, apparently tubular whisker structures which were located closer to the graphite substrate. Those measurements closely resembled the results for graphite. In addition, comparison of the relative strengths of the π and σ peaks as a function of tube orientation confirmed the "scroll" structure. The results described here were done far away from the graphite substrate, on whiskers that showed very large aspect ratios, almost filamentary in nature. These structures clearly do not exhibit the "scroll" structure.

A major difference between the amorphous case and the whisker result is highlighted by the vertical line through the graphite π peak at 285.2eV. Apparently there is some graphitic bonding in the whisker giving rise to π intensity which is shifted from the amorphous carbon position. Reference to Fink et. al.[1] shows that a similar shift was found in hydrogenated films heat treated at moderately high temperatures (650°C). Figure 2 shows the low energy loss structure for the whiskers. This shows a strong π plasmon near 6eV, and a strong $\pi + \sigma$ plasmon near 21eV. These resemble closely the low loss data in Fink, et. al. for the same 650°C annealed material as above. Their interpretation indicates a composition of $\simeq 2/3$ sp^2 bonding and $\simeq 1/3$ sp^3 bonding.

These preliminary studies suggest that the structures are mainly disordered, but have some graphitic nature in the form of excess sp^2 bonding. They definitely do not have the commonly seen scroll structure seen for larger fibers. Preliminary work with high resoluiton electron microscopy is consistent with this result.

References:
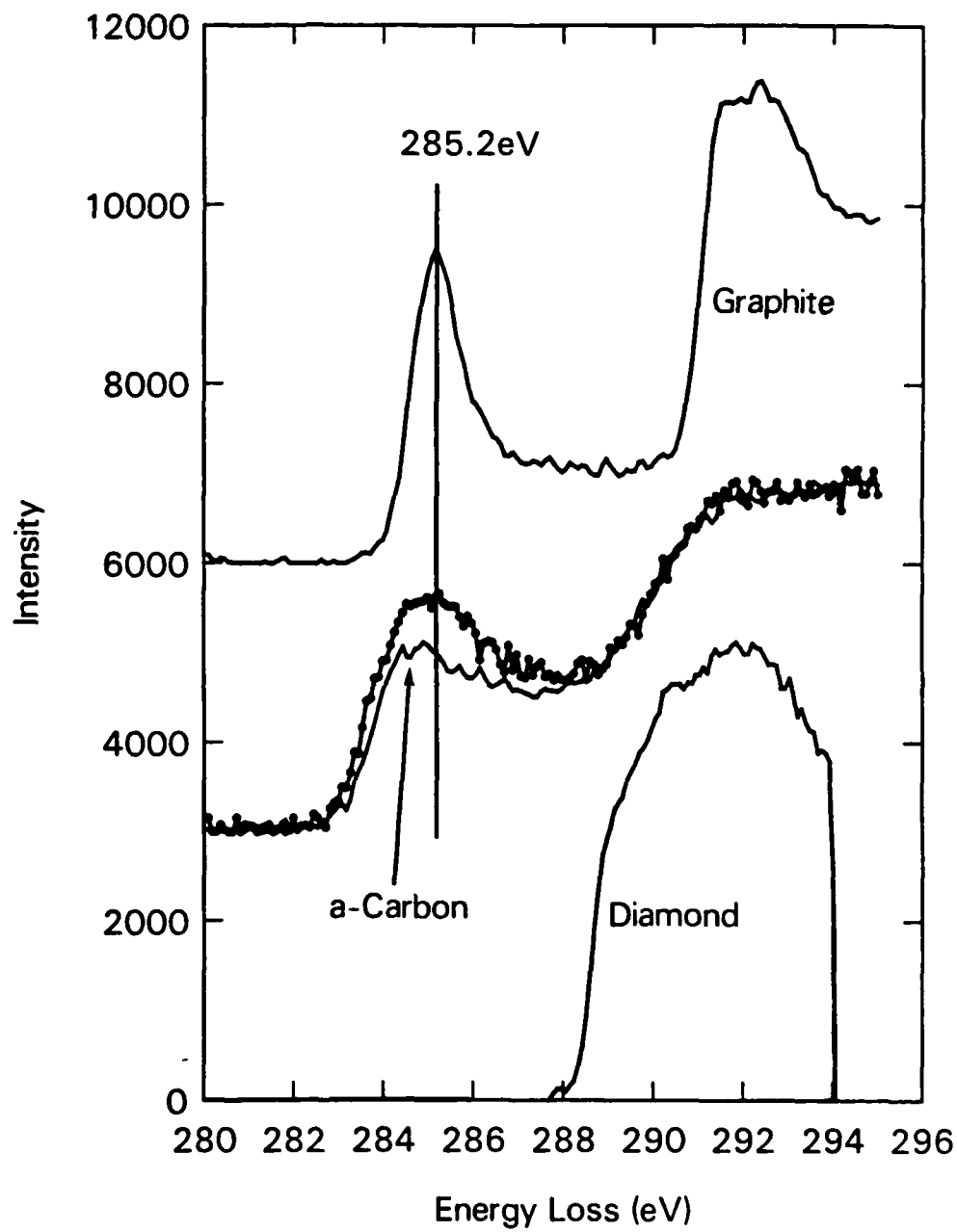1. J. Fink, T. Muller-Heinzerling, J. Pfluger, A Bubenzer, P. Koidl and G. Crecelius, S.S. Comm. 47, 687 (1983).
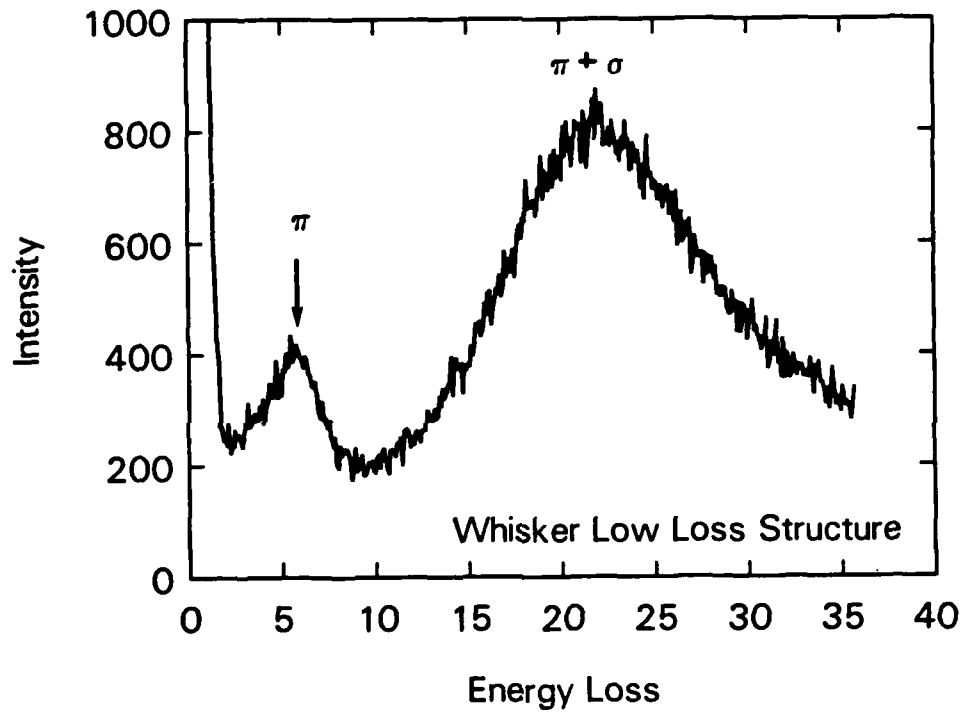
Figure 1 Batson

Figure 2 Batson

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