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Ion etching of amorphous and semicrystalline fibres

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Ion etching of amorphous and semicrystalline fibres produces structures which can be observed in either the transmission electron microscope or the scanning electron microscope. The structures so produced have previously been identified as resulting from the etching process (artifacts), or as representing characteristics of the material, or both. The artifacts can be eliminated or minimized by rotating the sample during irradiation, using a low angle of incidence, and ensuring that the temperature of the sample surface remains low. When such precautions are used, amorphous fibres and semicrystalline fibres which are *not* oriented remain featureless after ion etching. Oriented semicrystalline fibres, however, develop a striated structure which is oriented perpendicular to the stretch direction. The spacing between the striations is in the range of 500 to 5000 Å, an order of magnitude larger than the characteristic lamellar spacing in the materials. These transverse structural features reflect characteristic features of drawn fibres; but the relation between these features and the lamellar spacing is unclear.

1. Introduction

The technique of ion bombardment (ion milling, ion etching) has been widely used to prepare specimens for examination in the transmission electron microscope (TEM) or the scanning electron microscope (SEM). Ion bombardment can, however, have a significant effect upon the materials being bombarded; and questions have often arisen whether the structures observed after such treatments are representative of the initial structures of the materials (which are generally the subject of interest) or simply reflect artifacts introduced by the process of ion bombardment. These questions are of particular concern in the case of polymeric materials, which are sensitive to many radiation fields and are characterized by low melting points and glass transition temperatures relative to ceramic materials.

Several theories have been advanced to account for the development of surface features in crystalline or amorphous materials during ion bombardment (e.g. [1-5]); and a sizeable number of experimental investigations have been directed to elucidating these effects. It is clear that any structural features observed after ion bombardment must be related to factors such as the erosion rate and the variation in sputtering efficiency with incident angle [2, 3, 5, 6]. To avoid complexities associated with geometrical effects, flat specimens have been most widely investigated, although fibre specimens have received considerable attention as well.

Navez *et al.* [7, 8] bombarded silica glass plates with oxygen and nitrogen ions (ionized air) accelerated by 4 keV in a vacuum of 0.1 Torr. The bombardment was carried out at a variety of incident angles for various times. For ion bombardment times in excess of 60 min, furrow structures were observed. These structures were oriented parallel to the incident beam for grazing angles of incidence, and normal to the incident beam for steeper angles. An example of this furrow surface structure, which evolves during ion bombardment of S-glass fibres, is shown in Fig. 1. The spacing of the striations corresponds closely to the calculated penetration depth [8] of about 0.1 μm. To rationalize

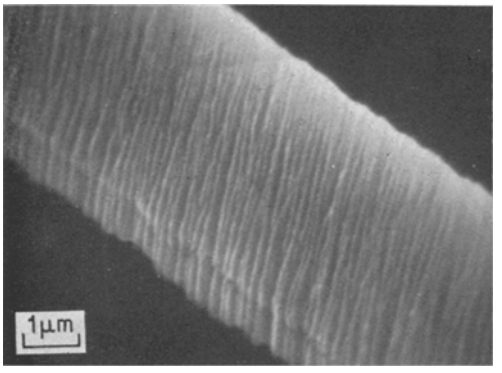

Figure 1 S-glass fibre ion etched at 90° without rotation (7 kV, 2 guns, each 250 μA).

these observations, Nobes *et al.* [11] have presented theoretical arguments for the development of structure in amorphous materials during ion bombardment and concluded that the equilibrium structure which develops should contain only horizontal and vertical planes. When the glass sample was allowed to rotate in its plane during ion bombardment, however, such ledging was not observed [8]; but unoriented structures on the scale of tens of microns were noted. This work has been qualitatively substantiated many times [1, 8-10].

Stewart and Thompson [1] and Auker [12] have noted the occurrence of spiking superimposed on the other structures produced during ion bombardment of polycrystalline materials. The former investigators noted a diminution in the incidence of spiking when the sample surfaces were carefully prepared to avoid contamination, while the latter worker noted that spike formation can be minimized by carrying out the ion bombardment at small angles of incidence.

When carbon fibres derived from polyacrylonitrile (PAN) are ion bombarded, a structure normal to the fibre axis has been observed to develop [13, 14]. Goodhew has proposed that this structure is a consequence of both the cylindrical geometry of the fibre and the initially crenulated surface of the fibre [14], and does not reflect the basic microstructure of the fibre. Fibres of S-glass and smooth-surfaced carbon fibres, pitch-based fibres, subjected to identical etching conditions were observed to maintain their smooth surface [13, 14].

Many investigators have extended the technique of ion bombardment to polymeric materials in order to elucidate their structural characteristics (e.g. [15-22]). Randomly oriented hills have often been observed after ion bombardment of unoriented semi-crystalline polymer sheets. After orientation, in drawn fibres and films, these markings are preferentially oriented normal to the draw axis [15]. Hansel *et al.* [21] have questioned the ability of the method for revealing true characteristics of the materials. They surmize that the observed structures are a product of: (1) heating by the ion beam; (2) primary bond rupture; and (3) loss of chain structure. The observed structures should then change with exposure time and severity of ion bombardment; and evidence was presented for such structural changes. Hansel *et al.* also thermally treated rayon fibres at 400°C and observed structural changes which were similar to those resulting from ion bombardment.

Breedon *et al.* [23], in an attempt to prevent the formation of thermally induced structures as well as to reduce atom collision damage during ion bombardment, have lowered the energy (current and voltage) of the beam. When their technique is applied to melt-crystallized polyethylene, large spherulites are observed. It has not been conclusively shown, however, that the observed structures do not reflect the effects of thermal etching.

In contrast to this behaviour noted with ion bombardment under ambient conditions, Kolbeck [19] has bombarded extruded polyethylene sheets with argon ions using a cryogenic specimen stage to minimize thermally-induced alterations in structure. Subsequent examination in the SEM revealed clearly the anisotropic nature of the material. In the two equivalent directions structures were observed on a scale of several thousand Angstroms. In the third direction, parallel to the extrusion direction, no structures could be discerned.

It is clear from this brief review of recent experience that the question of ion bombardment and its effect on materials is not well resolved. Under some conditions for some materials, it seems to reveal structural characteristics of the materials; under others, it seems to reflect primarily features of the ion bombardment treatment; and in some cases, both material characteristics and treatment features seem to be represented in the microstructures.

The present investigation was undertaken to characterize ion bombardment as a technique for revealing structural features of organic fibres. By varying the parameters of the ion bombard-

ment as well as the material characteristics, it has been possible to separate structural features of the materials from features induced from the bombardment under inappropriate conditions. The results indicate transverse structures on a scale of 500 to 5000 Å as characteristic of drawn semi-crystalline polymers.

2. Experimental procedure

An ion micromilling unit (Commonwealth Scientific, Alexandria, Va.) equipped with a cryogenic specimen stage (Technics Inc, Alexandria, Va.) was employed in the present investigation. The angle of incidence of the ion beam on the specimens was varied from 0 degrees (glancing incidence) to 90 degrees (normal incidence). In general, low angles of incidence were preferred in order to avoid damage induced by recoiling atoms, which is particularly pronounced at normal incidence.

With fibres, due to their geometry, *some* parts of the specimens are effectively bombarded at small angles of incidence, independent of the nominal incident angle. If the fibre is not rotated, it is the *sides* of the fibre which have a low angle of incidence. However, if the fibre is rotated in its own plane at a low angle of incidence, the *top* of the fibre experiences a constant angle of incidence from varying directions while the sides of the fibre experience a varying angle, from 0 to 90°. Our attention is directed only to those parts of the fibre which received a constant low angle of incidence. Fig. 2 shows a schematic diagram of the experimental setup. The figures presented are oriented such that the normal to the specimen plane is normal to the micrographs, offset by the scanning electron microscope tilt angle. For the figures, the specimens were rotated during etching unless otherwise stated.

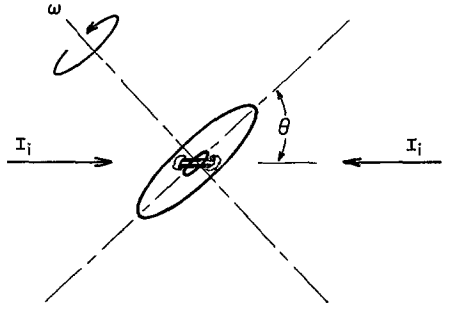

Figure 2 Schematic of ion etching apparatus.

The accelerating potential of the Argon ions was varied between 6 and 7 keV for refractory samples bombarded at room temperature, but was maintained below 3 keV with current of 20 to 30 μA where the liquid nitrogen coolant was used. In accord with previous results [12, 24], the temperatures of the specimen surfaces were in the range of 150° during bombardment at room temperature, and considerably less than 0° when the coolant was employed. The vacuum was as low as 8×10^{-4} Torr for cryogenic etching and as high as 6×10^{-3} Torr for bombardment at room temperature. After ion bombardment for selected periods of time, the samples were gold coated and examined using a Cambridge Stereoscan scanning electron microscope.

The materials studied in the present investigation included a variety of amorphous materials in both sheet and fibre form, as well as a number of semi-crystalline polymers in fibre form and carbon fibres. The materials and their sources are listed in Table I.

TABLE I Materials investigated

Material	Description
Amorphous	
Sheet	
Silica	IR Vitreosil
Epoxy	Shell 828
Polycarbonate (PC)	Lexan
Polyethylene terephthalate (PET)	Du Pont chill roll
Polyester	Clear Cast
Fibre	
Polystyrene (PS)	Dow batting
PS monofil	Fabric Research Lab (FRL)
Polymethylmethacrylate (PMMA)	FRL (monofil)
Stabilized acrylic	Chemstrand Research Triangle (CRT)
Semicrystalline	
Fibre	
Polyacrylonitrile (PAN)	Dralon T
Nylon 6,6	Du Pont
PET	Dacron
PET	Free fall from CRT
Acrylic	CRT Acrilan (6% vinyl acetate)
Acrylic	Free fall from CRT
Carbon fibres	Hercules HT
	Modmor I, II
	Thornel 390
	VYB 1/5 105

3. Results and discussion

3.1. Amorphous materials

Results obtained on fibres of S-glass have indicated that the phenomenon of ledging, such as shown in Fig. 1 above, was eliminated when the fibres were ion bombarded at low angles of incidence (such as 17°) and rotated during the ion bombardment. An example of the relatively featureless microstructure of S-glass fibres observed after ion bombardment at low incidence angles has been presented by Goodhew [13]. In accordance with the results of Auker [12], the occurrence of spiking was eliminated by employing ion bombardment at low angles of incidence coupled with specimen rotation during bombardment.

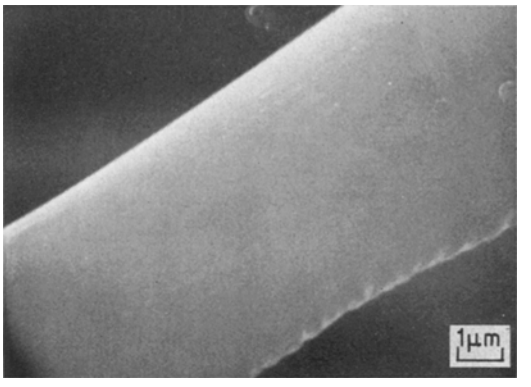

Figure 4 PS batting cryogenically ion etched at 80° (7 kV, 1 gun at 20 μA).

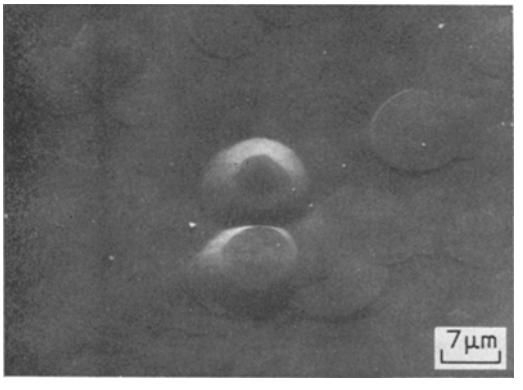

Figure 3 Polycarbonate sheet cryogenically etched at 25° (3 kV, 2 guns at 30 μA).

A representative scanning electron micrograph of a polymer in sheet form that was ion bombarded is shown in Fig. 3. The structures in the sheet materials which have been ion bombarded at cryogenic temperatures for short times occur on a fine scale (in the range of 1000 to 2000 Å). The extent of ion etching during ion bombardment at cryogenic temperatures is significantly less than that which occurs at room temperature, because lower beam currents and accelerating voltages were used with the cryogenic stage. On prolonged bombardment at cryogenic temperatures, structures are developed which are similar to those observed in shorter times during ion bombardment at room temperature, structures on a scale of several microns. Such treatments, involving either modest times at room temperature or long times at cryogenic temperatures, lead to surface topologies which closely resemble those noted in oxide glasses which have been similarly treated. In no case, however, are oriented structures observed.

Turning from sheet form to fibre form, observations have been carried out on amorphous polystyrene and polymethylmethacrylate fibres, which have initially smooth surfaces. As shown in Fig. 4, fibres of polystyrene batting have an essentially featureless microstructure after ion bombardment, which closely resemble the structures of ion bombarded oxide glass fibres. For both polystyrene and polymethylmethacrylate, the ion bombardment was carried out under cryogenic conditions. In the case of polymethylmethacrylate monofil, ion bombardment occasionally leads to fibrillation parallel to the fibre axis, occurring on a scale of a 1000 to 2000 Å. The tendency toward fibrillation in the PMMA fibres is very likely associated with their relatively large diameter (about 500 μm), compared with the much smaller diameter of the polystyrene batting (in the range of 0.25 to 2 μm). In neither of these amorphous polymers is there evidence for structure normal to the fibre axis.

A representative sample of stabilized acrylic fibre (i.e. an acrylic fibre heated to 220 to 290°C in air at constant length generally for 3 to 20 h until it is incapable of combustion), which has been subjected to ion bombardment is shown in Fig. 5. A structure oriented more or less transverse to the fibre axis is apparent on a scale of 1000 to 5000 Å. The precise origin of these transverse structures requires further clarification, since the stabilized fibres display significant orientation, as shown by birefringence

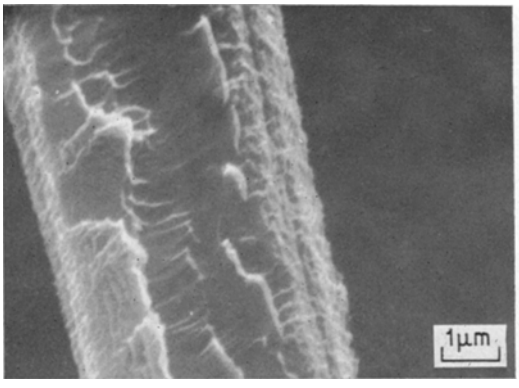

Figure 5 Stabilized acrylic fibre ion etched at 17° (7 kV, 2 guns at 200 μA).

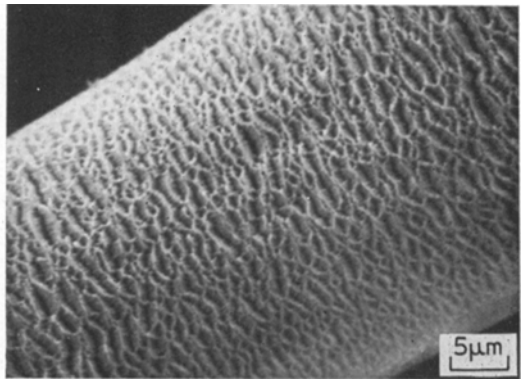

Figure 6 Acrylic cryogenically ion etched at 25° (3 kV, 1 gun at 25 μA).

measurements, but no apparent crystallinity, as determined by X-ray diffraction.

One further observation seems germane here: on prolonged exposure to the electron beam in the scanning electron microscope, extensive cracking of the specimen surfaces and localized melting were observed for the polymer specimens. In cases where mound-like structures were observed, such as in Fig. 3, the cracking was observed to occur between the mounds and around them, but not through them. It was not established whether this cracking occurred simply in the gold coating or whether it went through the specimens; but in any case, an asymmetry between the mound regions and the adjacent plane regions was indicated.

3.2. Semicrystalline fibres

In contrast to the observations on amorphous fibres, both organic and inorganic, scanning electron micrographs of a variety of semicrystalline polymer fibres consistently indicate structures transverse to the fibre axis. A typical example of these structures is shown in Fig. 6 for an acrylic fibre which has been ion bombarded under cryogenic conditions. The spacing of these transverse structures was observed to increase with increasing ion beam dosage, and hence a secondary effect of the ion bombardment is also apparent.

Since there is no evidence for localized melting occurring during ion bombardment of the PMMA fibres, it is suggested that the temperature rise during ion bombardment of the semicrystalline fibres does not exceed 105°C, the glass transition region of the PMMA. The thermal characteristics of the stabilized acrylic fibres would, if anything, be more conducive toward smaller temperature changes than is the case with the PMMA fibres.

In contrast to these observations, scanning electron micrographs of ion bombarded fibres of unoriented (free-fall) polyester and acrylic materials show no structural development similar to those seen in the oriented fibres. A representative microstructure of the unoriented acrylic fibre is shown in Fig. 7, which should be compared with the corresponding micrograph in Fig. 6 for the same material in oriented form. Rather than the well-developed transverse structures, with spacings in the range of several thousand Angstroms, the ion bombarded unoriented fibres show structures similar to those of the amorphous sheet materials which have been ion bombarded under cryogenic conditions.

Since neither the amorphous organic fibres nor the undrawn semicrystalline organic fibres

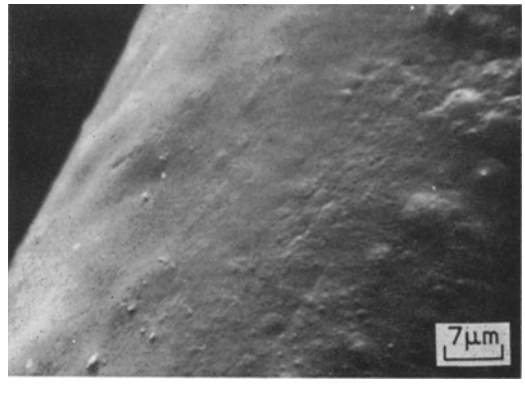

Figure 7 Free fall acrylic fibre cryogenically ion etched at 25° (3 kV, 1 gun at 24 μA).

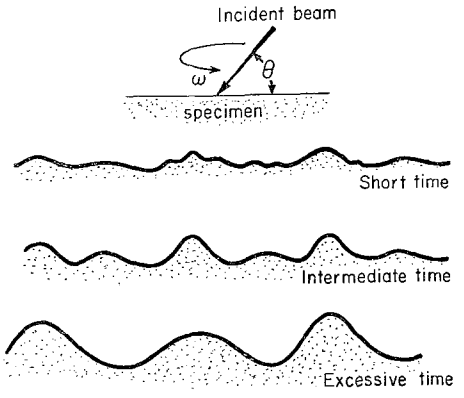

Figure 8 Schematic illustration showing increase of striation wavelength with etching time.

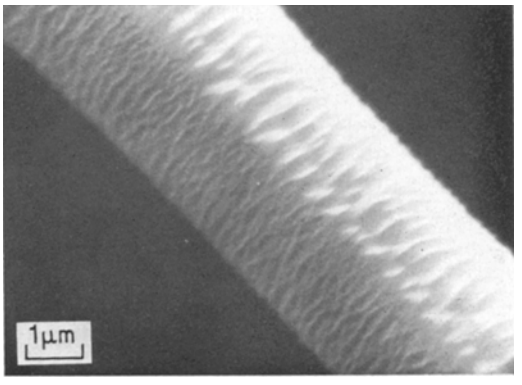

Figure 9 Modmor I ion etched at 17° (7 kV, 2 guns at 250 μA).

display the transverse structural features, their presence in the drawn semicrystalline fibres very likely reflects a characteristic of the drawn materials. It is well established from other work that the underlying crystalline morphology transverse to the fibre axis occurs on a scale of several hundred Angstroms; and the spacing of the structures observed after ion bombardment does depend somewhat upon the conditions of the bombardment. Nevertheless, the appearance of structures transverse to the fibre axis on a scale of several thousand Angstroms seems characteristic of the materials. These apparently reflect inhomogeneities in the fibres on such a scale (about an order of magnitude larger than the characteristic lamellar spacing). The nature of the inhomogeneities cannot be identified with confidence at the present time, but differential etching by the ion beam seems clearly indicated. The change in spacing with time of ion bombardment seems to reflect deeper valleys in the surface overtaking smaller valleys as shown schematically in Fig. 8. The relation between the underlying crystalline structures and the larger suprastructure seems deserving of further investigation, as it should provide useful insight into the formation of fibre textures.

3.3. Carbon fibres

The structures observed after ion bombardment of a number of carbon fibres under various conditions have features represented by Fig. 9. In agreement with the results of Goodhew [13], structural features transverse to the fibre axis are present in all cases, independent of the incident angle and incident direction of the ion beam.

To determine whether the structures observed after ion bombardment are dependent upon the initial fibre geometry, Hercules HT fibres were placed in boiling nitric acid until their surfaces became smooth [25-27]. As with fibres which received no nitric acid treatment, structures transverse to the fibre axis are again observed after a similar ion bombardment. It seems apparent, therefore, that the structures observed after ion etching are independent of the initial surface topology prior to etching. A similar conclusion is drawn by comparing the morphologies noted after ion bombarding organic fibres characterized by different initial surface topologies, namely melt-spun with wet-spun. To determine whether the transverse structure is characteristic of only the surface or the entire cross-section, carbon fibres with an initial diameter of 10 μm were etched to a diameter of 0.1 μm. At all stages of etching, the transverse structures were observed. In further support of the suggestion that the transverse structures are not confined to the surface (skin) of the fibres, PET monofil was peeled following the method of Scott [28], and the split central section was ion bombarded. Again transverse structural features on a similar scale were noted.

In the case of the carbon fibres, the scale of the transverse structures, as characterized by the crest-to-crest distances, is in the range of 0.05 μm for lightly bombarded fibres, but can reach values in the range of 0.5 μm for specimens which have been heavily bombarded. This change in scale seems to take place by the grooves or valleys between the most pronounced ridges overtaking the intervening small ridges. A similar mechanism may be operative as well during the ion bombardment of organic fibres

which are characterized by much smaller thermal stabilities and different absorption characteristics than the carbon fibres.

4. Conclusions

The results presented in the sections above indicate that the technique of ion bombardment can fruitfully be applied to organic fibres, both polymeric and graphitic. It has been demonstrated that ion bombardment of fibres at low angles of incidence, combined with sample rotation, can eliminate many of the problems such as ledging and spiking which have previously been encountered with ion bombardment treatments with such fibres. Thermal effects such as localized melting can be materially reduced by carrying out the ion bombardment using a cryogenic specimen stage.

The observations indicate that fibres of amorphous polymers show no development of structural features transverse to the fibre axis on ion bombardment. A similar absence of structural features transverse to the fibre axis is noted in the case of undrawn fibres containing some crystallinity, such as the undrawn polyester and acrylic.

In contrast, drawn semicrystalline fibres, regardless of their initial surface topology, display a pronounced and consistent microstructural pattern following ion bombardment. This pattern consists of highly oriented features transverse to the fibre axis, which occur on a scale of several thousand Angstroms, with a precise scale depending upon the ion bombardment dosage. These transverse structural features are taken to reflect characteristic features of the drawn fibres; but the relation between these features and the basic crystalline structures on a scale of several hundred Angstroms remains to be satisfactorily elucidated.

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