JOURNAL OF MATERIALS SCIENCE 20 (1985) 46–52

Soft X-ray contact microscopy of polyethylene microstructures

W. M. LEUNG*, D. M. SHINOZAKI, J. Wm. McGOWAN‡
Faculty of Engineering Science, The University of Western Ontario, London, Ontario, Canada N6A 5B9

A new technique of high resolution soft X-ray contact microscopy has been used to produce images of polyethylene microstructures. Both single crystals and spherulitic cast films have been imaged using this method which has previously been used in the examination of biological materials. A soft X-ray sensitive thin film of polymethylmethacrylate (PMMA) has been used to record the image of the polyethylene specimens. The exposed PMMA was then developed in a solvent and the resultant topographic image was examined in an electron microscope. It was found that direct observation of the lightly coated PMMA surface in the scanning electron microscope resulted in significant loss of resolution due to radiation damage. A method of obtaining a transmission electron microscope replica specimen is described, and the images so obtained are presented.

1. Introduction

The microstructure of partially crystalline polymers consists of structure at various scales from molecular dimensions to optically visible spherulites. Attempts to observe the finer details using transmission electron microscopy have been restricted by the rapid rates of radiation damage which occur in the electron beam during observation and image recording [1, 2]. Recent progress in using soft X-rays to produce contact images of biological materials has led to a new method of examining microstructures in synthetic polymers which is discussed here. As pointed out by Sayre *et al.* [3], soft X-rays have some inherent advantages over electrons in microscopy of biological materials. Suitably chosen wave lengths of X-rays can give high resolution images at lower doses than can be obtained with electrons. The purpose of this work is to show that images of polyethylene (PE) microstructures can be made using this technique.

The technique has been described elsewhere in the biological literature [4, 5], but the salient points are outlined here, and some modifications to the existing methods are discussed. The usefulness of the technique, which is essentially contact radiography [4], has become apparent with recent advances in the field of microelectronics. The attempts to fabricate smaller circuits have led to increased interest in the use of soft X-rays together with extremely high resolution polymer resists (for example polymethylmethacrylate (PMMA)). The same systems have recently been used to image biological materials with possible theoretical resolutions of close to 10 nm [4]. The procedure is shown in Fig. 1. A thin film (~ 1.5 μm thick) of PMMA is deposited on a polished surface of silicon or glass. The material to be examined is held in contact with the surface of the PMMA and the combination is exposed to soft X-rays. The X-rays are absorbed by different amounts in different parts of the specimen, depending on the local chemistry, density and thickness. The underlying PMMA undergoes chain scission at low doses. The specimen is removed and the irradiated PMMA is immersed in a solvent which preferentially dissolves the lower molecular weight material. Using scanning electron microscopy, the coated PMMA surface may be examined and the topography of the etched surface is a replica of the specimen

*Present address: Energy, Mines and Resources, Edmonton, Alberta, Canada.
‡Present address: The Director of the National Museum of Science and Technology, Ottawa, Ontario, Canada.

 0022–2461/85 $03.00 + .12 © *1985 Chapman and Hall Ltd.*

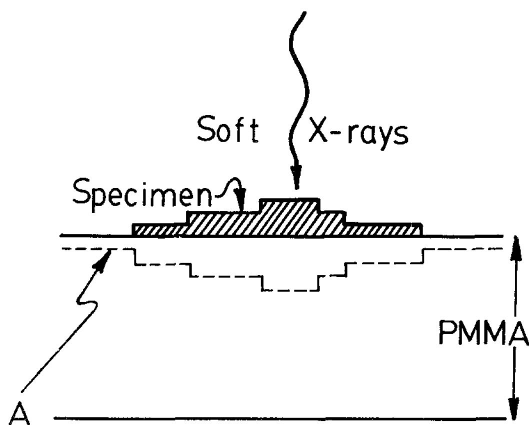

Figure 1 Schematic diagram of the exposure technique. The profile of the PMMA after development is shown as (A).

microstructure [4, 5]. Higher resolution images may be obtained by examining the developed PMMA film directly in the transmission electron microscope (TEM) [5]. However, as shown in the present work, these examination techniques damage the polymer resist and thus distort the image. Modifications to the existing methods are thus made and discussed here.

2. Experimental procedure

Linear polyethylene (PE) used for the preparation of crystals was polymerized and characterized at the Research Centre of SNPA at Lacq, France. The weight average molecular weight ($\bar{M}_w$) was 8.4×10^3 g mol^{-1}, and the polydispersity ($\bar{M}_w/\bar{M}_n$) was 1.11. A suspension of PE in *p*-xylene was heated in an oil bath at 100° C for 20 min until completely dissolved. An aliquot of the solution was transferred to a thermostat held at the crystallization temperature of 60° C, and an appropriate amount of pure solvent previously heated to the same temperature was added to the solution (the concentration of solution from which the crystals precipitated was 0.05% (w/w)). This minimized the time to reach the crystallization temperature and a uniform lamellar thickness was achieved. The lamellar thickness thus produced was measured from the PE crystals which were filtered from the suspension at 60° C, washed in acetone and dried in vacuo at room temperature. Small angle X-ray scattering was used to measure the lamellar thickness of the mat so produced and a value of 9.7 ± 0.4 nm was found.

Spherulitic polyethylene thin films were prepared in the following manner. High density polyethylene pellets from Dupont (Canada) Research Laboratories (provided by Dr D. Axelson) were dissolved in *p*-xylene, and a precipitated suspension of PE in the xylene was produced by cooling to room temperature. This suspension (nominally 0.5% (w/w)) was heated until the PE was dissolved completely. One or two drops of this solution were then applied on a glass slide which was covered by a thin film of phosphoric acid (preheated to 130° C). The heater was turned off and the glass slide was allowed to cool at room temperature. The thin PE film was floated off on distilled water, washed several times in water, then examined in an optical microscope. The average thickness of the polymer film was measured by light interference microscopy and was estimated to be about 1.5 μm. Appropriate areas for X-ray replication were selected.

3. Soft X-ray replication

Solution of polymethylemethacrylate (PMMA) (obtained from R. Feder at Thomas J. Watson Research Laboratories of IBM) in chlorobenzene (6% w/v) was used to prepare the thin resist film on glass cover slips. The measured molecular weight was 350 000. It was spin coated and baked in an oven in the standard way (appropriate to fabrication of integrated circuits). The thickness of the resist was measured by light interference microscopy to be approximately 1 μm.

The PE crystal specimens were prepared by applying a few drops of the crystal suspension to a transmission electron microscope (TEM) grid which had been covered with a 10 nm thick carbon film (prepared by vacuum evaporation). After the crystals were dried the TEM grids were placed on the PMMA resist in a manner so that the PE crystals were in intimate contact with the resist. The resist–specimen combination was then mounted in a holder for the soft X-ray machine.

The spherulitic films were cut to TEM grid size, then floated on water and picked upon on a TEM grid. After being dried, the specimens were placed in contact with the resist, mounted in a holder and placed in the X-ray machine.

The soft X-ray generator used for the exposures was a laboratory built apparatus, incorporating a water-cooled flat faced solid target (which could be changed to use a variety of materials), surrounded by a heated filament. The operating conditions for these experiments were: aluminium target, accelerating voltage 1.8 keV, tube current

8×10^{-9} A. The PE crystals were irradiated for 30 h and the spherulitic films for 60 h. The exposure times were estimated in the following way. The development rates (rate of dissolution as a function of X-ray energy deposited) of PMMA exposed to the laboratory source were measured using the given solvents, at the given temperature. The dose incident on the PMMA film through the polyethylene specimen was estimated using the absorption coefficient calculated assuming pure carbon. This is, of course, an approximation, since other experiments performed at the Canadian Synchrotron Radiation Facility using monochromatic radiation show significant differences from carbon in the absorption coefficient for polymers (this is to be published).

After exposing the X-rays, the PMMA resist on its glass substrate was developed by immersing it in a stirred solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) (1 : 3 by volume) which was held at 25° C. To minimize solvent swelling each development step involved immersion in the developer of no longer than 20 sec, followed by washing in isopropyl alcohol and air drying. The image was checked optically at each step until the best contrast was achieved. With the given specimens, and under the exposure conditions used, the optimum development times were about 8 min for PE crystals and about 20 min for the spherulitic films. The entire development and optical microscopy procedures were performed in a class 100 clean room.

4. Recording high resolution images

With thin specimens and correct exposure conditions, it was expected that structure down to a scale as small as perhaps 10 nm could be resolved. The standard technique for examining the etched surface of the exposed PMMA has been either direct observation of a lightly metal coated surface using scanning electron microscopy [4], or by direct observation in the transmission electron microscope [5]. In the latter case, the PMMA film was initially spun onto a very thin silicon nitride window (approximately 100 nm thick), the image recorded and developed in the manner described earlier, and the PMMA–silicon nitride combination was placed directly in the TEM. The resultant image was due to differential thickness contrast, which could be enhanced by shadowing. The problem which arises in both cases, and which has not yet been addressed in the literature, is that the examination of the PMMA film in the electron beam results in radiation damage in the PMMA itself. Studies of electron microscope images of surfaces and thin films of polymers have shown that the radiation damage distorts the topography of the polymer [7], so a simple set of tests was performed to determine if SEM techniques were suitable for the examination of the images on such an electron sensitive material as PMMA.

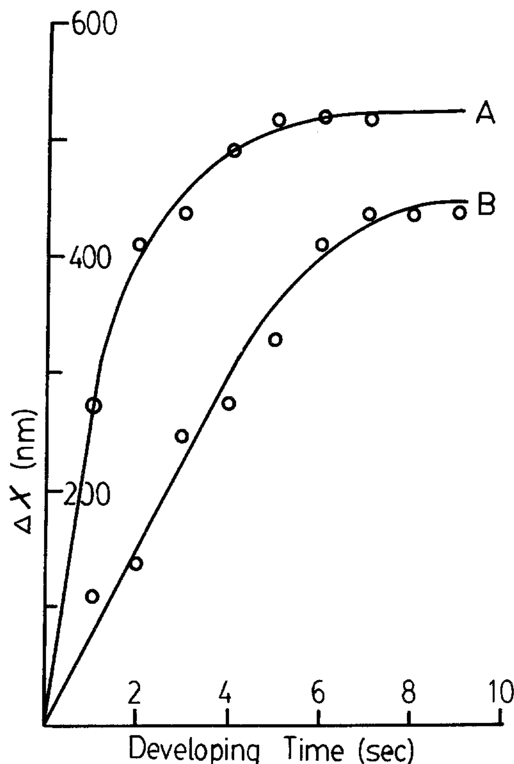

Figure 2 Development curves (developed relief height ΔX against development time in 1 : 3 MIBK to IPA). (A) has been exposed to soft X-rays (30 min) and an SEM electron beam (2 min). (B) has been exposed to soft X-rays only.

Copper TEM grids were placed on top of a PMMA coated silicon wafer and exposed to soft X-rays for a short time (1/2 h). The aluminium target was used. Subsequently, the grid was removed, and the X-ray exposed PMMA (with the grid pattern as a latent image) was irradiated with the electron beam over half its area in a scanning electron microscope (SEM) (Stereoscan 600 at 25 keV). A large spot size was used to facilitate damage observations. The relative development curves of the PMMA (a) irradiated with soft X-rays only and (b) irradiated with soft X-rays and electrons were compared in Fig. 2. In this example, the images were examined in the SEM for 2 min.

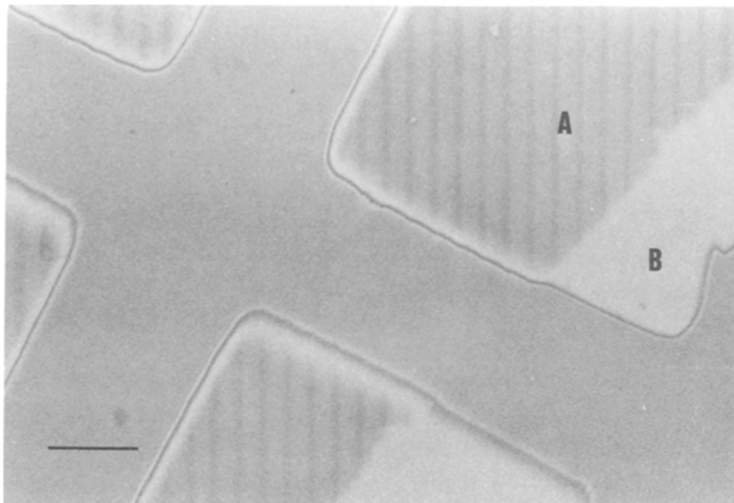

Figure 3 Optical micrograph of the PMMA image of a TEM grid developed for 5 sec. The area (A) was irradiated for 30 min to soft X-rays plus 2 min to an SEM electron beam. The area (B) was irradiated to 30 min of soft X-rays only. The scale marker is 20 μm. Compare Figs. 4 and 5.

The PMMA was developed in a solution of 1 : 3 (v/v) MIBK to IPA. The observed images after development for varying times are shown in Figs. 3, 4 and 5. The regions irradiated in the SEM are clearly distinguished from the regions irradiated only by the soft X-rays (the scan lines from the rastered electron beam are visible). Indeed, the width of the grid bar image is measurably reduced after exposure to the electron beam. This observation should be considered in attempting to optimize the image quality by repeated steps of dissolution/SEM examination, as has been reported elsewhere [8]. The radiation enhanced dissolution of the PMMA results from a significant decrease in the molecular weight as a result of chain scission at these doses [9, 10]. The differences in the development rates, and in the images (Figs. 2 to 5) are a reflection of a large decrease in molecular weight in the PMMA during the examination in the SEM for typical observation times. Further examination of image quality, even at low beam current, also reveals significant damage. The obvious conclusion is that direct observation of the PMMA film in a electron microscope will result in a loss of resolution, and in significant change in the image as a consequence of the observation itself.

To circumvent this problem, a secondary replication process was used to record a stable image. A carbon replica of the etched PMMA film was taken in the following manner. The lightly etched PMMA surface (the image of the PE specimen)

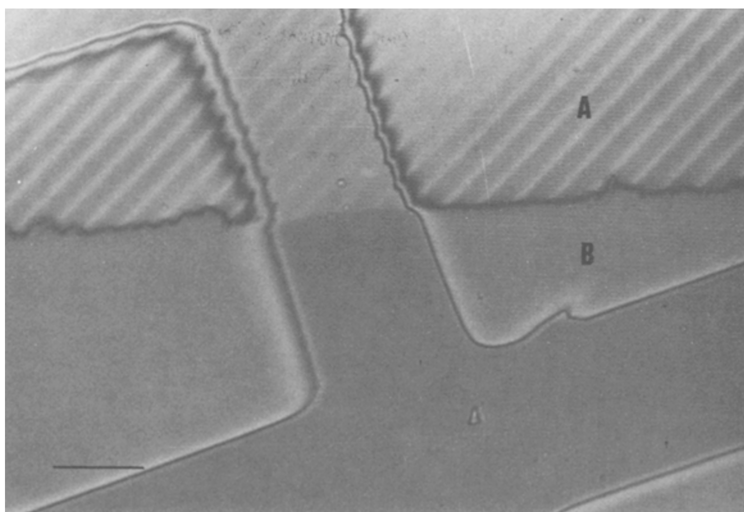

Figure 4 Optical micrograph of the same area as Fig. 3, developed for 30 sec.

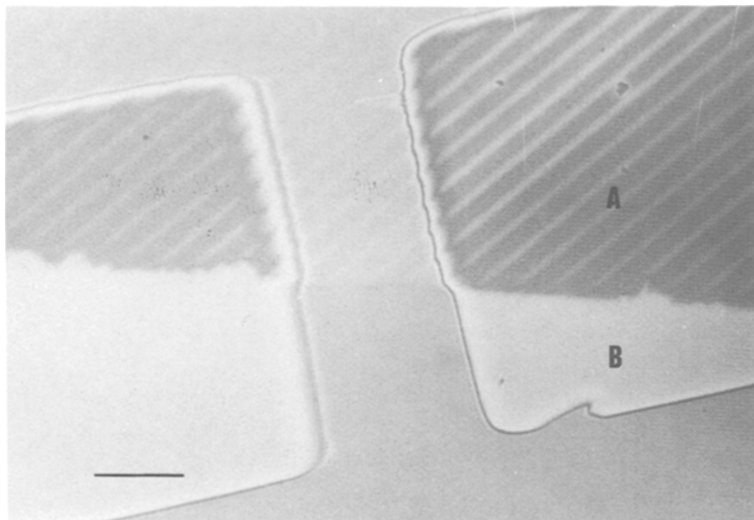

Figure 5 Optical micrograph of the same area as Fig. 3, developed for 120 sec.

was shadowed with platinum at a shallow angle of 5° to 8° using vacuum evaporation. At this point the PMMA was still supported on a glass cover slip. A 12 nm thick carbon film (measured by a film thickness monitor) was deposited on top of this shadowed surface by vacuum evaporation. The surface of the area of interest on the replica was scored into squares about 2 mm on a side. The glass cover slip was floated on a 2% HF solution with the carbon film on top, until the glass was dissolved. The floating carbon replicas, still on the PMMA film, were repeatedly washed in distilled water, and picked up with TEM grids. The PMMA was then dissolved in acetone, leaving the shadowed carbon replica on a TEM grid.

A major additional advantage to using carbon replicas of the PMMA surface is that for ultrahigh resolution the depth of etching of the PMMA must be small. In resolving the low contrast microstructures such as those in crystalline polymers, lateral dissolution rates may be significant and fine structure may be seen only in the top layers of the PMMA. Feder and Sayre also point out that diffraction effects will become important at larger distances from the specimen–PMMA interface (deeper into the resist) [5]. Hence, there is definite advantage in using only a very light etch (for which a carbon replica technique is ideal).

5. Results and discussion

The TEM micrographs of the carbon replicas of the PE multilayer crystals are shown in Figs. 6 and 7. The first shows a multilayered lozenge-shaped crystal and the second shows a dendritic growth pattern. These crystals are typically formed at low crystallization temperatures and consist of several superposed chain-folded layers which are all of equal thickness. In Fig. 7, the 10 nm thick lamellar layer can be clearly distinguished up to the sixth layer. The number of layers which can be distinguished is determined by these factors, namely, the transmitted X-ray intensity, the sensitivity and the resolution of the resist. The first two factors govern the rate at which the PMMA undergoes radiation damage, which in turn determines the dissolution rate in the developer. As the number of superposed layers increases, the transmitted X-ray intensity will decrease accordingly. When the specimen becomes very thick, the transmitted intensity is too small to cause significant molecular weight changes in the PMMA, and the lamellar layers beyond this limit are not separately resolvable.

In examining the microstructures of Figs. 6 and 7, superposed layers of approximately 60 nm edge to edge distance can be observed. Fig. 8 shows the carbon replica image of a PE thin film crystallized from melt. Two spherulities are visible with centres at the top left and at the lower right corners, respectively. The spherulite boundary is clearly visible, and microstructure within each spherulite is identifiable down to a scale of about 60 nm. The arrangement and shapes of these microstructural elements are consistent with arrays of lamellae. On a large scale, the radial fibrils are clearly part of the accepted spherulitic morphology. The contrast and the resolution of the images should become significantly better with

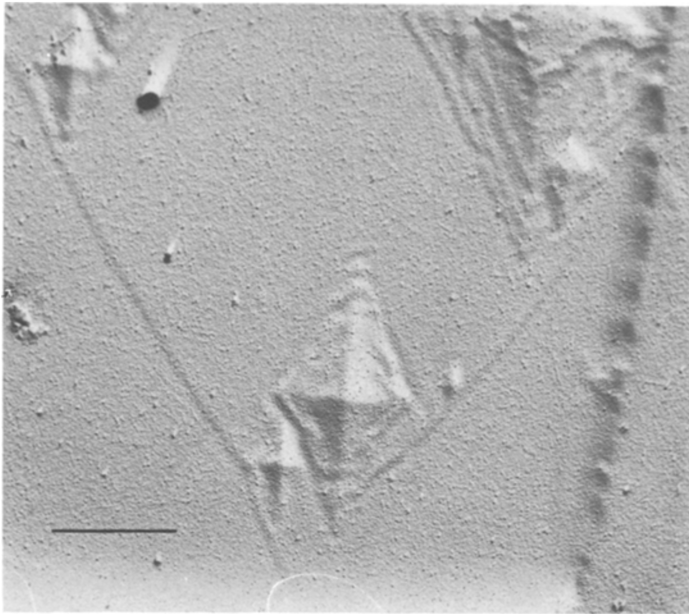

Figure 6 Soft X-ray micrograph of PE crystals on a carbon substrate. The scale marker is 500 nm.

thinner films of PE (of the order of 50 to 100 nm). An approximate calculation of the expected contrast between crystalline and amorphous regions has been made by comparing the densities of the two phases. The result suggests that, in thin PE specimens, the lamellar structure should be resolvable, if the PMMA resist can record such small structures. Experiments with these materials and other kinds of fine scale structures are proceeding to investigate the possibility of this. The achievement of this kind of resolution obviously has important implications for the examination of lamellar microstructures in polymers.

In addition to revealing the standard microstructures, the technique can be extended to reveal distributions of chemical elements on this microscopic scale [12], as has been demonstrated in biological materials. Using images of one area of the specimen above and below X-ray absorption edges of the relevant element, digitizing and subtracting the images, a map of the distribution of the element may be obtained. Work also continues in this area.

6. Conclusions

The first images of crystalline polymers using a

Figure 7 Soft X-ray micrograph of PE crystals on a carbon substrate. The scale marker is 500 nm.

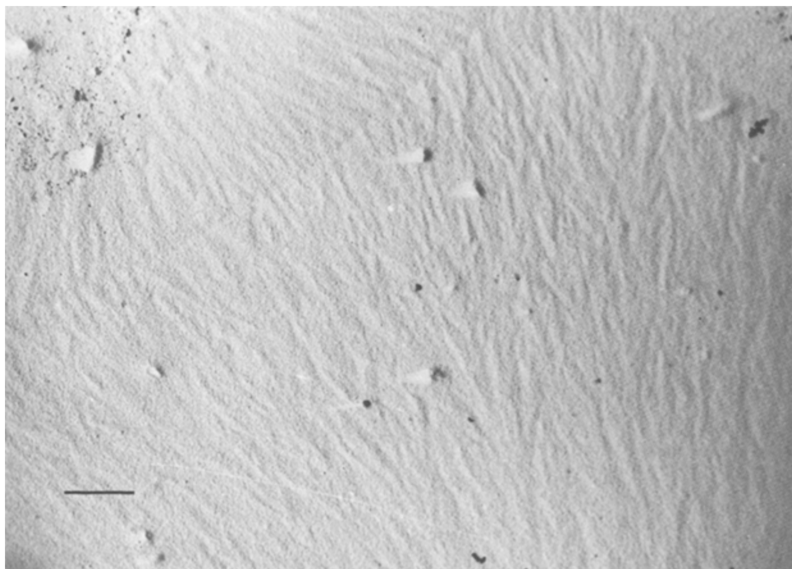

Figure 8 Soft X-ray micrograph of spherultic PE (thin cast film). The scale marker is 500 nm.

high resolution soft X-ray contact replication have been presented. Multilayer PE crystals grown from solution, and melt crystallized spherulitic PE have been shown. The theoretical resolution of this technique using PMMA resist is of the order of 10 nm or smaller. The work follows that of recent attempts in the study of biological structures, but incorporates the additional improvement that a shadowed carbon replica of the etched PMMA surface is taken to examine in the TEM. This step produces a stable, high resolution image, whereas the previous direct observations of the PMMA surface in the SEM or in the TEM were subject to radiation induced image distortion. More detailed experiments involving monochromatic radiation from a synchrotron source are underway, and this will produce more exact quantitative methods for optimizing the images.

Acknowledgements
The authors wish to acknowledge the financial support of the National Science and Engineering Research Council (Strategic Grant). Technical support was obtained from R. Pandey and P. Perquin.

References

1. A. KELLER and D. C. BASSETT, *Proc. Roy Microscop. Soc.* 79 (1960) 243.
2. P. GEIL, "Polymer Single Crystals" (Wiley Interscience, New York, 1963).
3. D. SAYRE, J. KIRZ, R. FEDER, D. M. KIM and E. SPILLER, *Ultramicroscopy* **2** (1977) 337.
4. J. Wm. McGOWAN and M. J. MALACHOWSKI, *Ann. New York Acad. Sci.* **342** (1980) 288.
5. R. FEDER and D. SAYRE, *ibid.* 213.
6. J. Wm. McGOWAN, B. BORWEIN, J. A. MEDEIROS, T. BEVERIDGE, J. D. BROWN, E. SPILLER, R. FEDER, J. TOPALIAN and W. GUDAT, *J. Cell Biology* **80** (1979) 732.
7. J. DLUGOSZ and A. KELLER, *J. Appl. Phys.* **39** (1968) 5776.
8. B. J. PANESSA, R. A. McCORKLE, P. HOFFMAN, J. B. WARREN and G. COLEMAN, *Ultramicroscopy* **6** (1981) 139.
9. W. S. DeFOREST, "Photoresists, Materials and Processes" (McGraw-Hill, New York, 1975).
10. H. H. G. JELLINEK (ed.), "Aspects of Degradation and Stabilization of Polymers" (Elsevier Publishing, Amsterdam, 1978).
11. E. SPILLER and R. FEDER, "Topics in Applied Physics", Vol. 22, "X-ray Optics and Applications to Solids", edited by H. J. Queisser (Springer-Verlag, Berlin, 1977) p. 35.
12. P. C. CHENG, K. H. TAN, J. Wm. McGOWAN, R. FEDER, H. B. PENG and D. M. SHINOZAKI, X-ray Microscopy, edited by G. Schmal and D. Rudolf (Springer-Verlag, Berlin, 1983).

Received 16 January and accepted 24 February 1984