7

UCRL-84043
PREPRINT
CONF-7905140--1

MASTER

X-RAY ZONE PLATES FABRICATED USING ELECTRON-BEAM AND X-RAY LITHOGRAPHY

D. C. SHAVER, D. C. FLANDERS,
N. M. CEGLIO, H. I. SMITH

PREPARED FOR PRESENTATION AT THE FIFTEENTH
SYMPOSIUM ON ELECTRON, ION AND PHOTON BEAM
TECHNOLOGY, BOSTON, MA. May, 1979

MAY, 1979

Lawrence
Livermore
Laboratory

X-Ray Zone Plates Fabricated Using Electron-Beam and X-Ray Lithography(a)

by

D. C. Shaver,(b) and D. C. Flanders
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, Massachusetts *02173*

N. M. Ceglio
Lawrence Livermore *Laboratory*
Livermore, California 94550

Henry I. Smith(c)
Dept. of Electrical Engineering and Computer Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Prepared for presentation at the Fifteenth Symposium
on Electron, Ion and Photon Beam Technology - (Boston, Mass.)

Abstract

Fresnel zone plate patterns, free of spherical abberation, with diameters of up to 0.63 mm and linewidths as small as 1000 Å were fabricated on polyimide-membrane X-ray masks using scanning electron beam lithography Distortion of the electron beam scan raster was reduced to <2500 Å over a 2 mm x 2 mm field by applying deflection corrections, while viewing the distortion using a moiré method. C_k X-ray lithography was used to replicate the zone plate pattern in thick PMMA over a 100 Å thick plating base on a glass substrate. Zones plates in 1.3 μm thick gold were fabricated by plating, and made free-standing by removal of the plating base and the supporting glass substrate. Zone plates were tested as imaging elements with visible light and soft X-rays.

(a) This work was sponsored by the Department of the Air Force and under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48. (b) Also, Dept. of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. (c) Also, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173.

Fresnel zone plates are focusing elements that operate using diffraction rather than refraction or reflection. Zone plates are of particular interest for focusing soft X-rays since refractive index values of materials in this portion of the spectrum make conventional refractive or reflective optics impractical. (Generally $\eta \equiv k/\delta \approx (.1 - 1)$ and $\delta \sim (10^{-3} - 10^{-6})$ at x-ray wavelengths; notation: refractive index $N = 1 - \delta + i K$) make . Pinhole cameras, grazing-incidence reflection optics, multilayer mirrors [1,2], and zone plates show promise as soft X-ray optical elements. Zone plates may be used in X-ray microscopes or telescopes, or their highly dispersive character may be used to build focusing X-ray monochromators [3].

Our goal has been to fabricate zone plates suitable for imaging X-ray emission from laser-produced plasmas. A typical application is to image the helium-like Ar_K line emission (0.395 nm) from a laser-compressed target containing a few percent argon. A spatial resolution of <1 μm is desirable to allow observation of the smallest structures of interest. Since the theoretical resolution of a zone plate, when used with monochromatic radiation, is of the order of the minimum zone width, we chose a 0.3 μm minimum zone width. The opaque zones are made of gold with a thickness >1 μm to keep transmitted power below 1% at a wavelength of 0.4 nm. The bandwidth of the argon line is of the order of a few eV, centered at 3.14 keV, so the zone plate should be limited to a few hundred zones to minimize chromatic abberation.

Holographic lithography, electron-projection lithography, and diamond-turning techniques have been used to generate zone plate patterns. Minimum zone widths near 1000 Å have been achieved [3,4]. However, the zone plates produced by these methods were limited to gold thicknesses of the order of 1000 Å, which has restricted their use to very soft X-ray wavelengths (e.g. 4.5 nm).

We have developed a process which allows zone plates with submicrometer linewidths to be fabricated in thick gold. The zone plate pattern is first generated on an X-ray mask using scanning electron beam lithography (SEBL) and the pattern on the X-ray mask is then replicated using C_K soft X-ray lithography. Though the original mask absorber pattern is fabricated in gold less than 1000 Å thick, the X-ray lithography produces very high aspect ratio resist profiles which can serve as a 'mold' during a subsequent electroplating step, to produce the final thick gold structure.

In principle, any of the previously mentioned methods for fabricating zone plates in thin gold could be used to form the X-ray mask absorber pattern. However, scanning electron beam lithography has several advantages:

(1) It is possible to extend the SEBL technique to linewidths of 1000 Å or less. At the present time, other methods have not demonstrated comparable resolution.

(2) Changes in zone plate parameters, such as focal length or minimum zonewidth, are simply entered from a keyboard. Time-consuming modifications to the optical setup would be required if the zone plates were generated holographically.

(3) Free-standing zone plates require support structures. Using SEBL the support structure is written at the same time as the zone plate pattern. Complex support structures are easily generated and modified through software changes.

(4) Good linewidth control can be achieved. The exposure can easily be varied across the zone plate to compensate for cooperative exposure effects due to changes in periodicity. The resist profile can be uniform across the zone plate.

(5) Spherical abberation can easily be avoided. With holographic lithography, the zone plate is used at a different wavelength than the exposure wavelength, resulting in spherical abberation unless special correcting optics are used during exposure of the zone plates [3].

(6) As described below, it is possible to insure that the electron beam scan raster is free of distortion which would impair the optical performance of the zone plates.

In order to produce accurate zone plate patterns, we require the distortion of the electron beam scan raster to be less than the minimum zonewidth (e.g. 3160 Å) over the zone plate diameter (0.532 mm), or about 5 parts in 10^4. Using a moiré technique [5], we have reduced scan distortion to <2.5 parts in 10^4. Our ETEC LEBES-D SEBL system has a distortion correction module which allows small correction terms to be added to the deflection signals to compensate for the predominant distortions (e.g. pincushion, trapezoidal). By observing on the display CRT a moiré pattern produced by rastering the electron beam over a distortion-free gold reference grating, any distortion in the scan raster is easily visualized and can be corrected using the distortion correction controls. Our reference gratings were holographically generated, and consisted of 5000 Å period etched gold lines on a silicon substrate. The grating lines could be oriented parallel to either the X or Y deflection axis, to allow distortion checking in both axes. Grids of gold dots, formed by holographic double exposure of orthogonally oriented grating lines, were also used. Figure 1a shows a moiré pattern indicating that there is some pincushion distortion in the scan raster. In Fig. 1b, the pincushion distortion has been corrected and only straight, equally spaced fringes are visible. The distortion is corrected, but the fringes appear because the spacing between the raster lines does not match the grating period exactly. In Figs. 1c and 1d, the scan line spacing has been adjusted to match the grating period exactly; by translating the scan raster one half period (2500 Å) with respect to the reference grating, the entire pattern can be made dark (Fig. 1c) or bright (Fig. 1d) as the scan raster falls exactly between or on the gold lines, respectively. A similar result is obtained by scanning with an orthogonally oriented raster/grating combination. These data were obtained with scans over 1 mm square field, and indicate that our LEBES machine has a distortion of less than 2500 Å over 1 mm, or <2.5 parts in 10^4. Raster distortion could also be reduced to approximately 2500 Å over a 2 mm square field.

The moiré distortion correction technique brings the X and Y deflection axes into precise registration with the lines of the X and Y oriented reference gratings. For our zone plates, we require that the scan axes be orthogonal to within 7 minutes of arc and that the X and Y axis gains match to 1 part in 10^3. The orthogonality of our X and Y reference gratings is within 1 degree, but is not precisely controlled. Slight adjustments were performed to reference the scan axes to the X and Y axes of our laser interferometer which measures X and Y sample stage motion. The interferometer axes are orthogonal to < 1 minute of arc.

Beam position drift during writing is another potential source of pattern distortion. Beam drift in our system was measured by observing shifts in moiré fringe patterns, and is typically less than 5000 Å per hour. Large zone plates with 3000 Å minimum zone width take about one hour to write, and may be affected slightly by drift.

The zone plate patterns were written in a 1500-3000 Å thick layer of PMMA over a 9000 Å thick layer of polyimide on a 76 mm diameter silicon substrate. The 76 mm diameter silicon substrate is used because it is conveniently handled in our SEBL system. The polyimide layer will serve as the support membrane of the X-ray mask. Our SEBL system was operated with a tungsten filament, and a beam current of 0.2 nA was used for all writing to insure a beam diameter of <1000 Å. Patterns were written in 950,000 molecular weight PMMA at a dose of 1.8×10^{-4} C/cm^2. A one minute development in 2:3 methyl isobutyl ketone (MIBK):isopropanol was used. The resist profile in Fig. 2 shows 2000 Å wide lines with vertical sidewalls which were produced by SEBL. Lines as narrow as 1000 Å have also been exposed in 3000 Å thick PMMA, with vertical sidewalls which are suitable for liftoff.

The zone plate pattern is written by drawing concentric circles, with the system's minicomputer functioning as a point-plotting circle generator. Since the circles are generated on-line, the entire zone plate, including the struts, can be represented algorithmically, providing data compaction and allowing exposure to be varied radially to improve linewidth control. A zone plate of 0.63 mm diameter is composed of about 3×10^7 discrete points, and takes about 1 hour to write.

After the PMMA has been developed, a 500 Å thick gold absorber pattern is formed on the polyimide layer by liftoff. Figure 3 shows scanning electron micrographs of some gold absorber patterns. Linewidths as small as 1000 Å have been fabricated as shown in Fig. 3d.

The polyimide layer with the absorber pattern was then transformed into a polyimide membrane X-ray mask. A procedure similar to that used with glass substrates [6] was used. Briefly, the entire top side and most of the underside of the silicon wafer, except for about a 30 mm diameter region under the zone plate patterns, is protected while the wafer is immersed in a solution of 4% concentrated nitric acid: 96% concentrated HF. This etches a hole through the silicon to form a polyimide membrane supported by the surrounding unetched silicon. A flat plastic ring is then epoxy bonded to the polyimide on the absorber pattern side. Finally, the polyimide membrane surrounding the plastic ring is cut away, leaving a polyimide membrane mask on a plastic ring. A 400 Å thick layer of aluminum is then evaporated onto the polyimide on the absorber side. This aluminum layer serves as an electrode to hold the mask electrostatically in intimate contact with the substrate during X-ray exposure, while the polyimide membrane serves as a dielectric.

Using this X-ray mask, the zone plate pattern was exposed onto 225 μm thick Corning 0211 glass substrates which had been coated, in order, with 50 Å Cr, 50 Å Au, 2 μm PMMA, and 100 Å of chromium. The chromium on top of the PMMA serves as the second electrode for electrostatic holdown of the X-ray mask; the chromium is etched away before development of the PMMA. The thin gold under the PMMA serves as a plating base. We used the C_K wavelength (4.5 nm) to expose the resist. A 9 hour exposure was required at a 60 mm source to substrate distance. The C_K X-ray was used in order to obtain high contrast with our thin (500 Å) gold absorber patterns, and to minimize problems with photoelectrons generated by X-ray absorption at the plating base. With harder X-rays, and with a higher bremsstrahlung background, the partial exposure produced by these photoelectrons results in rapid undercutting of resist profiles at the plating base surface during development, causing adhesion loss for small structures. All X-ray exposures were developed in 2:3 MIBK:isopropanol, with typical development times of 5-10 minutes.

After development, patterned slots are present in the resist extending down to the plating base. After a 10 second exposure to a 3% oxygen plasma to remove a thin resist scum which covers the plating base, gold was electroplated to a height of 1.3 μm. Plating was performed using BDT-510 plating solution maintained at 40°C, witn a plating current of 1 ma/cm^2 or less. Using this plating solution we have been able to produce bright gold films, with no graininess observable in the scanning electron microscope. Our plated films are under considerable compressive stress, which can lead to deformation of the completed free-standing zone plates. Figure 4 shows 1600 Å wide gold lines plated to a height of 7200 Å, using a 3200 Å period grating exposed in PMMA as the 'mold' for the plating.

After electroplating, the PMMA was dissolved away. A copper support tube (1.5 mm bore) was epoxy bonded to the continuous gold film surrounding the zone plate. The glass substrate was then etched away in concentrated HF, to produce a free-standing gold zone plate supported on a copper tube. In some cases, the thin chromium and gold of the plating base, which have little effect on the zone plate performance, were also removed by chemical etching. Figure 5 shows a free-standing, 1.3 μm thick gold zone plate, with 3000 Å minimum zone width.

Preliminary X-ray testing of the zone plates has been performed at Lawrence Livermore Laboratory using a proton bombardment source of Al_K X-rays. A resolution of better than 1 μm has been demonstrated to date [7], and further tests are in progress. In parallel with the X-ray imaging tests, we have conducted imaging tests using visible light. For these tests, zone plates having 5000 Å minimum zone-width were exposed using SEBL on chromium photomasks, and were chemically etched. A 400X microscope was constructed using the zone plate as the objective lens, and a He-Ne laser (632.8 nm) as the source of illumination. The lens pattern was free of spherical abberation at 632.8 nm, and the zone plate had a focal length of 316 μm. Figures 6a and 6b show an interdigital electrode pattern, imaged with a conventional optical microscope using white light and He-Ne laser light, respectively. In Fig. 6c, the same pattern is imaged using the zone plate microscope. Lines and spaces of 0.8 μm can be resolved, indicating that the SEBL pattern generation method will enable zone plates with submicrometer resolution to be fabricated.

We would like to thank A. Hawryluk for holographic exposure of the moire reference gratings, C. Smith for scanning electron microscopy and assistance with the SEBL, P. DeGraff for scanning electron microscopy, N. Efrenow for performing plating experiments, and R. Hartford, who has assisted in many phases of mask and sample preparation.

References

1. R. Haelbich, A. Segmuller, and E. Spiller, Appl. Phys. Lett. 34, 184 (1979).

2. T. W. Barbee, Jr. and D. C. Keith, Proceeding of the Workshop on Instrumentation for Synchrotron Radiation, (SSRL Report No. 78/04, April, 1978), p. III-26.

3. D. Rudolph and G. Schmahl, "High power zone plates for soft X-rays". Presented at the Conference on Ultrasoft X-ray Microscopy: Its Application to Biological and Physical Sciences, June 13-15, 1979, New York City. To be published in the Annals, The New York Academy of Sciences. Also, B. Niemann, D. Rudolph, and G. Schmahl, Optics Comm. 12, 160 (1974).

4. H. Brauninger, P. Predehl, and K. P. Beuermann, Appl. Opt. 18, 368 (1979).

5. H. I. Smith, S. R. Chinn, and P. D. De Graff, J. Vac. Sci. Technol. 12, 1262 (1975).

6. D. C. Flanders and H. I. Smith, J. Vac. Sci. Technol. 15, 995 (1978).

7. N. M. Ceglio, "Micro-Fresnel structures for microscopy of laser generated bright X-ray sources". Presented at the Conference on Ultrasoft X-ray Microscopy: Its Application to Biological and Physical Sciences, June 13-15, 1979, New York City. To be published in the Annals, The New York Academy of Sciences.

Figure Captions

Fig. 1. Moiré patterns formed by scanning the electron beam in a raster over a 5000 Å period gold reference grating while viewing the secondary electron image. The field of view is 1 mm x 1 mm. In (a) pincushion distortion is visible. In (b) the moiré fringes are straight and equally spaced, indicating freedom from scan raster distortion, though the scan raster period is not identical to the grating period. By matching the scan raster and grating periods, a completely dark (c) or bright (d) pattern can be obtained, demonstrating less than 2500 Å of distortion over the entire 1 mm field.

Fig. 2. A 4000 Å period grating exposed in PMMA using scanning electron beam lithography.

Fig. 3 SEM micrographs of zone plate gold absorber patterns on an X-ray mask. The patterns were written by SEBL, followed by a liftoff of 500 Å of gold. The inner (a) and outer (b) zones of a zone plate with 2000 Å minimum zonewidth are shown. In (c) and (d), sections of a 1000 Å minimum zonewidth zone plate are shown.

Fig. 4 Gold lines electroplated between very high aspect-ratio PMMA lines exposed by X-ray lithography. The slight bending of the tops of the PMMA lines occurred during SEM observation.

Fig. 5 A completed zone plate in 1.3 μm thick gold. Minimum zonewidth is 3000 Å.

Fig. 6. (a) and (b) show an interdigital electrode pattern imaged with an optical microscope using white light and He-Ne laser light, respectively. (c) shows the same electrode pattern imaged with a zone plate. The 8000 Å lines and spaces are clearly resolved. The bright spot is due to unfocused light passing through the zone plate in the zero order.

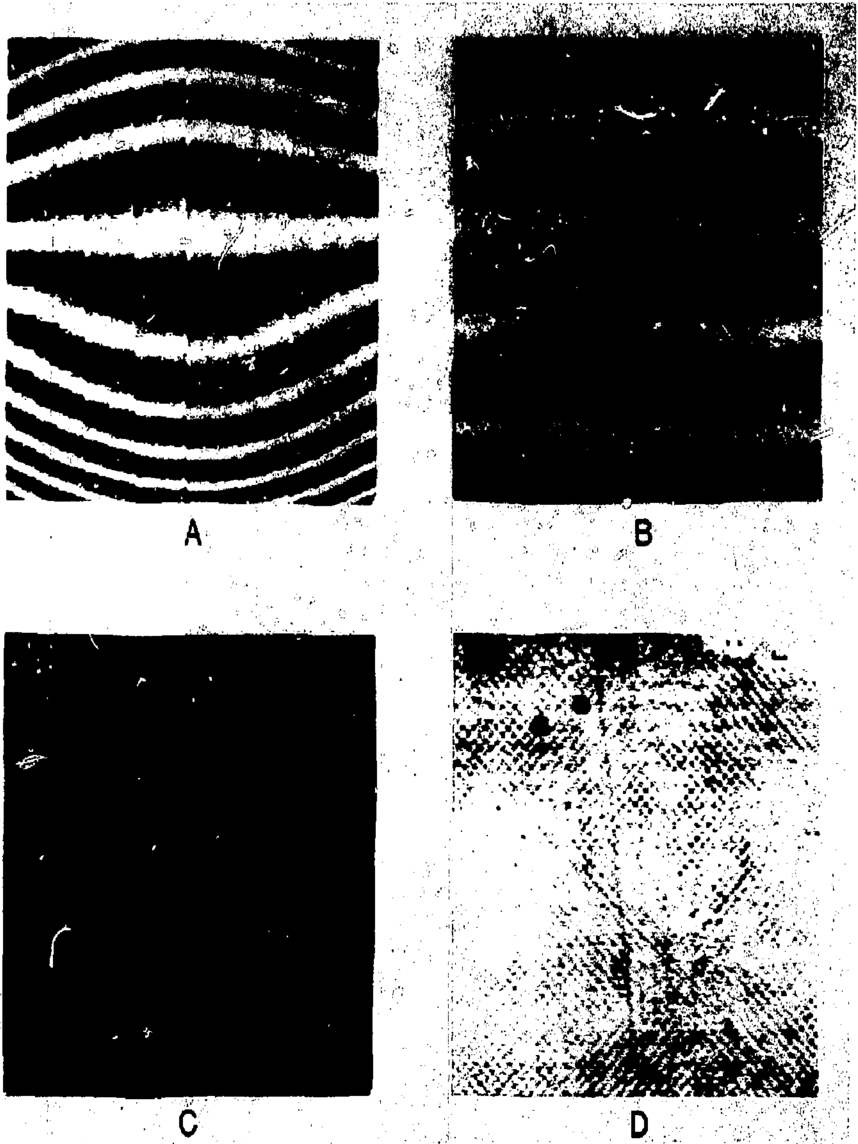

Fig. 1

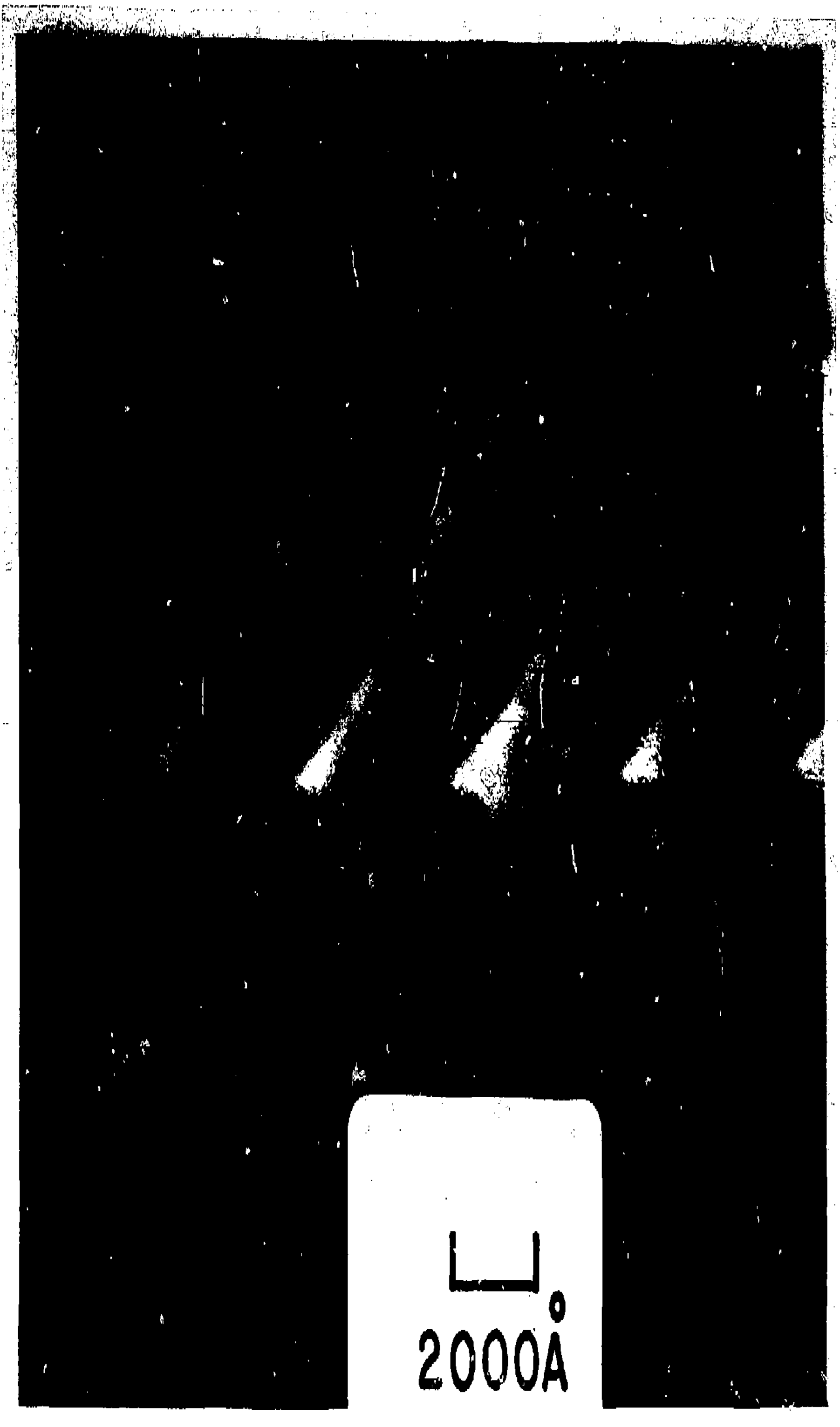

Fig. 2

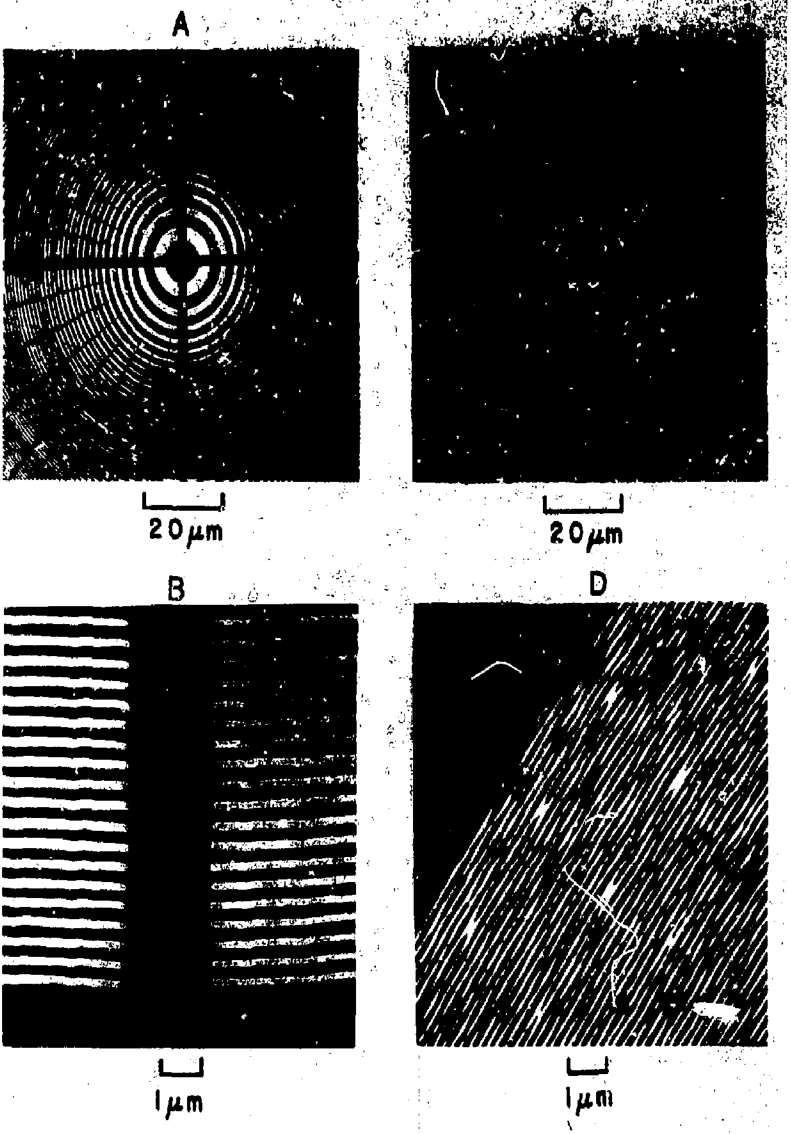

Fig. 3

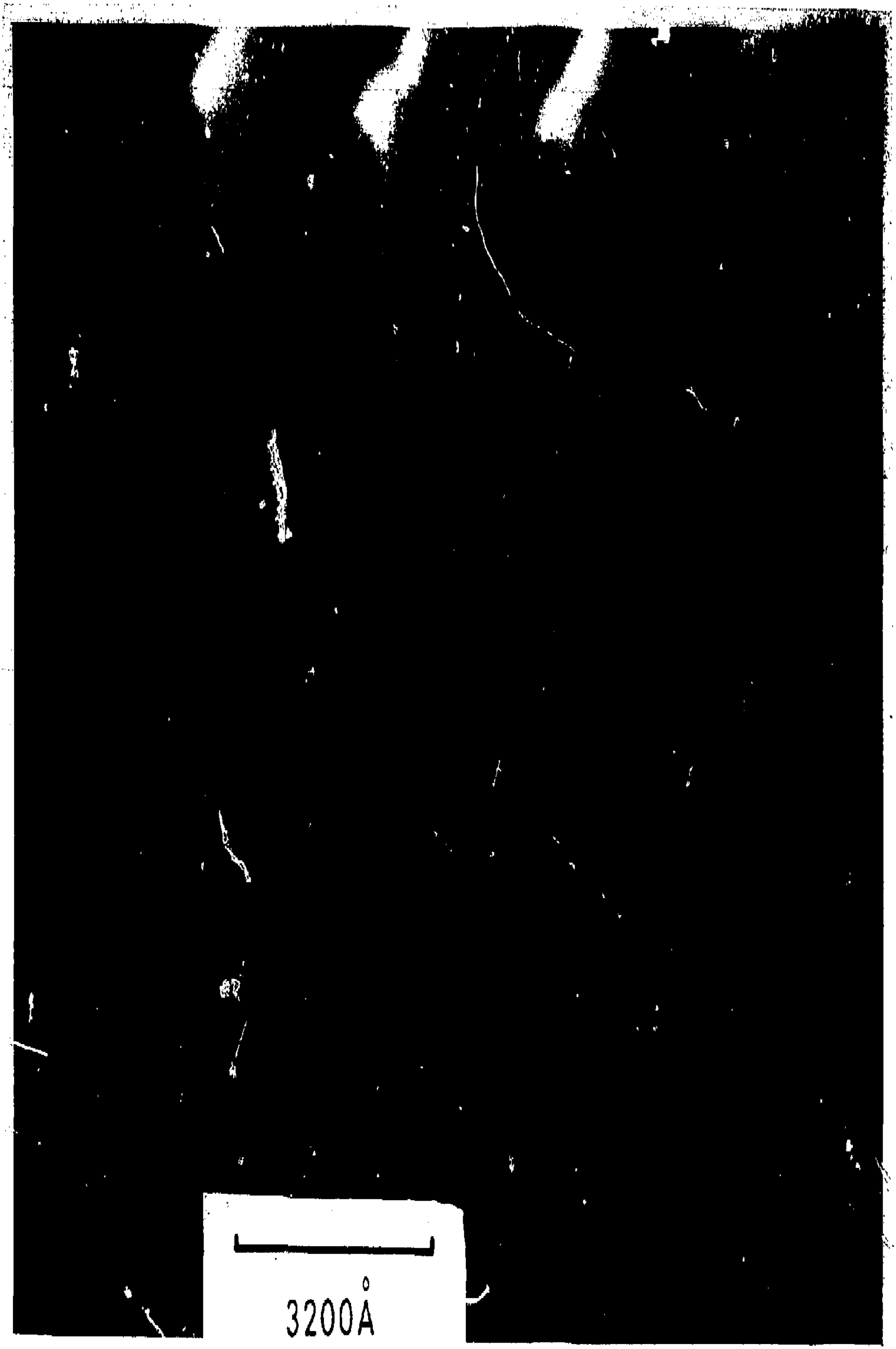

Fig. 4

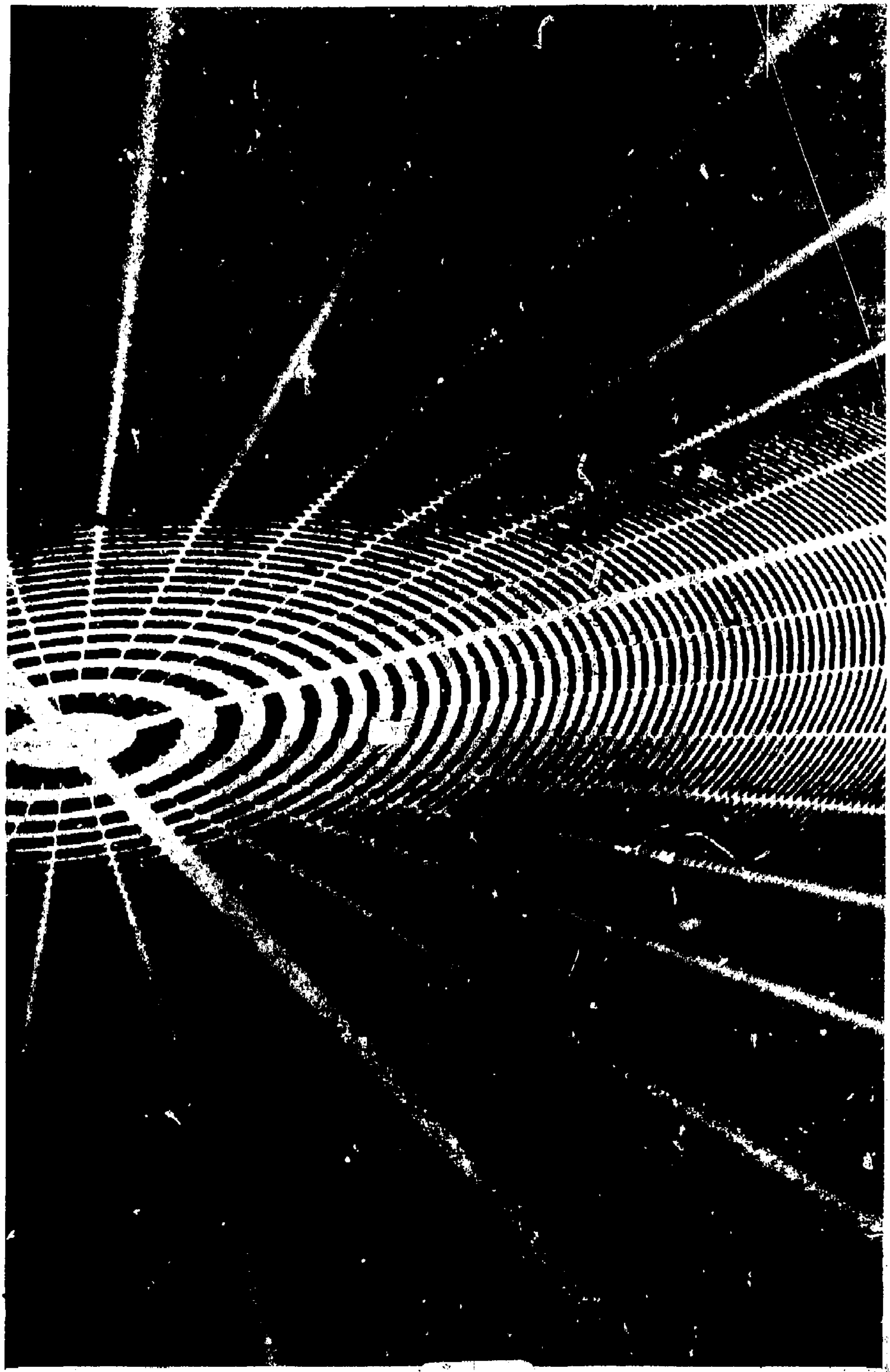

Fig. 5

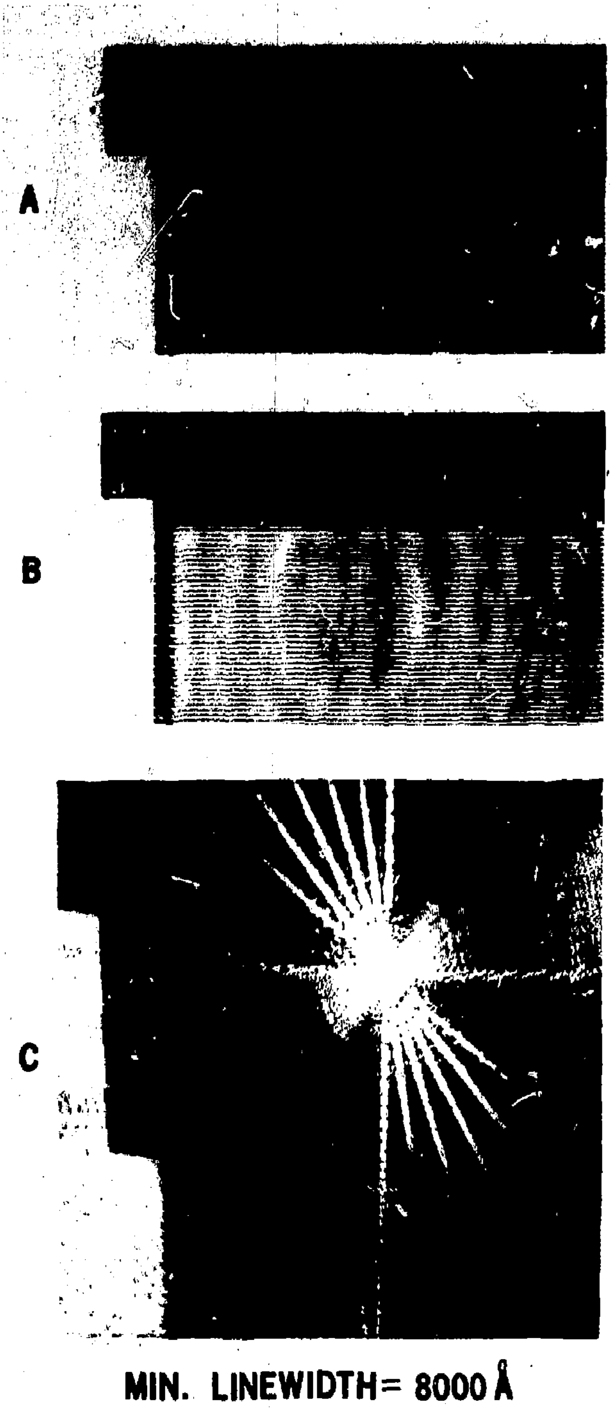

Fig. 6