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# ELECTRON-BEAM CRYSTALLIZATION OF SILICON, GERMANIUM, AND CADMIUM SULFIDE

by John C. Evans, Jr.

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Cleveland, Ohio

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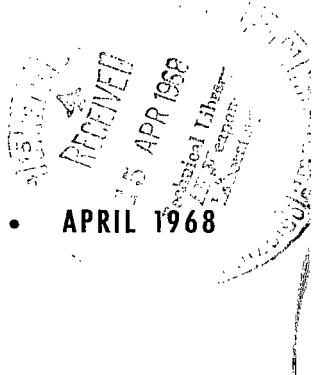
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SUMMARY

Amorphous semiconductor films were electron-beam irradiated, and the effects were observed in the electron microscope. This study shows that oriented polycrystalline films of silicon, germanium, and cadmium sulfide may be made by electron bombardment of their amorphous films deposited on glass and plastic substrates. This transition was shown to occur without deleterious effects upon the substrates.

The film bombardment was conducted both in the electron microscope and in a separate vacuum crystallizer capable of electron-beam raster scanning. Electron micrographs and electron diffraction patterns were used to record the results of the film treatments. Both silicon and germanium films underwent amorphous-to-crystalline changes at substrate temperatures well below the melting points of the semiconductors. Nucleation and crystal growth by coalescence were observed. The compound semiconductor, cadmium sulfide, crystallized by passing through a quasi-liquid state without subliming in the vacuum environment. The thickness of the untreated films was such as to allow transmission electron microscopic studies.

INTRODUCTION

Semiconductor films are readily formed on an amorphous substrate such as glass or plastic by evaporation or sputtering. The resulting films, however, do not have the crystallinity required for electronic or photovoltaic device applications. In practice, the desired crystallinity can be obtained by maintaining the substrate at an elevated temperature during the semiconductor deposition. One example of this approach is the deposition of cadmium sulfide onto a silver-zinc-coated polyimide sheet during the preparation of thin-film solar cells (ref. 1). A similar accomplishment with higher melting semiconductors such as silicon or germanium has not been achieved because of the temper-

ature limitations of available plastic substrates.

It is known that for certain solid films the change from the amorphous condition to the crystalline involves a reduction in the total energy content of the material (ref. 2). Part of this energy increment is thought to be the release of strain energy (ref. 3). The ultimate state for such a solid film (i.e., the lowest energy condition) is a single crystal. One method of releasing strain energy, and thereby inducing crystallization, is by electron bombardment (ref. 4). The impinging electrons supply the small amount of activation energy necessary to initiate the release of the strain energy. With electron bombardment techniques, the temperature rise experienced in the film during the onset of crystallization is a fraction of that required to produce melting or sublimation (ref. 3).

In this study the nucleation and growth of crystalline films of silicon, germanium, and cadmium sulfide on substrates of plastic and glass were investigated. An electron-beam, raster-scanning technique was used in addition to the technique of general electron bombardment employed in previous investigations. It was believed that more controllable results could be achieved with the beam scanning technique than with the general bombardment technique. It was also anticipated that the electron-beam scanning technique would allow the formation of crystalline regions within an amorphous material of a predetermined pattern. This feature would have application to the programming of microcircuits and the development of photovoltaic devices.

PROCEDURE

For this study, amorphous semiconductor films were formed by evaporation and sputtering in vacuum. The films were deposited on factory precleaned glass microscope slides. Some predeposition ion-bombardment cleaning was employed. In order to ensure amorphous deposits the films were deposited on substrates held at room temperature. Some of the slides were coated on half the area of the deposit side with a plastic parting layer to facilitate removal of the semiconductor films for study in the electron microscope. The thickness of film varied from approximately 800 angstroms $(8\times10^{-2} \mu m)$ at the center of the slide to approximately 300 angstroms $(3\times10^{-2} \mu m)$ at the ends, as shown in figure 1.

In some of the experiments crystallization was brought about by electron bombardment within the electron microscope and in other cases by treatment of the amorphous films in the electron-beam scanning crystallizer shown in figure 2. A raster scan pattern was employed to move the crystallization front over the film area, as shown in figure 3.

Those films which were bombarded within the electron microscope were studied visually during the transformation process, and transmission electron micrographs, as

well as selective- and general-area electron diffraction patterns, were taken. Those films treated in the crystallizer were studied by surface replication and by removal to the electron microscope for transmission studies by the dissolution of the plastic parting layer shown in figure 1.

The electron-beam crystallizer shown in figure 2 consisted of a vacuum chamber capable of being exhausted to a pressure of approximately 10^{-7} torr (1.33×10^{-5} N/m^2). A Pyrex "double-tough" 2- by 6-inch (5.08- by 15.24-cm) cross was used. On the top flange was mounted an electron gun containing focusing and X-Y deflection coils. The transverse beam sweep across the 1-inch (2.54-cm) width of the slide was accomplished by a 60-hertz supply of variable potential. The longitudinal beam movement along the 3-inch (7.62-cm) length of the slide to advance the crystallizing front was accomplished manually as this allowed a fairly long dwell time during the experiments.

The lower 6-inch (15.24-cm) opening of the chamber was mounted on the base plate of a conventional vacuum pumping system containing cryogenic trapping provisions. Just above this port in the lower portion of the Pyrex cross was a furnace used for some of the film depositions. Around this furnace were placed thermal-radiation shields and shutters so that the substrate was not exposed to excessive heating during the furnace preheat before the opening of the shutter.

One of the 2-inch (5.08-cm) openings of the Pyrex cross was used for vacuum gaging. The other opening allowed for insertion of the slide holder. In order to allow for visible focusing of the otherwise invisible electron beam, a second microscope slide coated on one side with a phosphor was placed back-to-back with the slide containing the film to be treated or on which the film was to be deposited if made in the crystallizer. An arrangement with a rotary seal was used to allow the slide to be turned 180° from the downward facing position for coating to the upward facing position for beam-scanning treatment. While the furnace for deposition was preheating, it was possible to focus and adjust the sweep parameters of the beam on the phosphor screen. For some of the work involving resistance measurements of the deposited films, connections were made to contacts on the slide surface from feedthroughs set in the same flange with the rotary seal. These items are shown in figure 2.

Studies of the amorphous untreated films were accomplished within the electron microscope by keeping the beam intensity as low as possible. Transmission electron micrographs were taken at magnifications up to 38 800. Electron diffraction patterns were taken to show the structural changes as they occurred during treatment. The procedure for those films which were treated within the electron microscope by generalized electron bombardment over the total viewing area of approximately 20 microns in diameter was to increase the beam intensity gradually with a diffuse illumination while recording the changes photographically.

The crystallizer apparatus shown in figure 2 used an electron gun capable of being

focused to a spot size of approximately 1 millimeter. The beam current was controllable up to a maximum of 50 microamperes with an accelerating potential of 7 kilovolts. Only a very small part of the available power was required for the film treatment. Control of the beam power was very important since the system could evaporate a 100-micron-thick film in less than a second. The dwell time of the swept beam was an additional control method used. In practice, a strip approximately 3 by 20 millimeters was affected by the sweeping focused spot. A fringing effect occurred in which the transition of the film was noted beyond the visible limits of the beam as seen on the phosphor screen. At the beam intensities used for film treatment of the three subject materials the spot was not visible on the film surface to be treated. However, beam intensities approaching closely those which produced sublimation of the cadmium sulfide did produce a characteristic orange light in the film.

RESULTS

Germanium

The first material studied was amorphous germanium deposited in film form approximately as shown in figure 1. Prior to any electron-beam treatment a portion of the film was removed from the slide by dissolution of the parting plastic and was floated on to a specimen examination screen for transmission electron microscopy. Loosely packed material resembling snow was seen.

For the first experiment it was desired to treat two spots on the film with intensified beam energy within the electron microscope. With the magnification of the microscope set at 5000 the beam was slowly focused and the illumination intensified. In the center of the beam the material migrated rapidly to nucleation sites, and discernible crystals grew. From time to time the beam intensity was turned down, and the action was arrested for observation and photography at different magnifications. The specimen screen was traversed, and another spot was so treated. The results are shown in figure 4, with electron diffraction patterns of the amorphous untreated region and the crystallized region inset. In this figure may be seen the circular pits on the glass slide from the cleaning procedure. These were not present on every brand of slide used.

After completion of treatment of the two spots on the germanium film, the entire specimen was treated by defocusing the electron beam and gradually increasing the overall intensity. The result of this treatment is shown in figures 5 and 6. These electron micrographs and the electron diffraction patterns indicate that generalized electron-

beam bombardment converted the entire film from the amorphous condition to polycrystallinity.

Silicon

Amorphous silicon films were prepared by vacuum evaporation of semiconductor-grade material. Attempts were made to produce thicknesses of the order shown in figure 1 so that examination by transmission electron microscopy could be used. The first treatment with the electron beam was performed in the crystallizer by scanning one of the thinner regions over the parting plastic layer and then by scanning a central portion of the film over both the parting layer and the glass substrate. Portions of the treated region overlying the plastic film were removed for study in the electron microscope.

During the scanning the film was observed by light reflected at a shallow angle from the silicon film surface. A subtle change was noted in the treated area; subsequent light microscopic viewing showed this to be an area of dendritelike growth. The film adjacent to the treated zone which was floated off for examination remained amorphous and served as comparison material in the electron microscopic examinations. Figure 7 shows the transmission view of the effect on the film of the edge of the electron beam. The right side of this micrograph shows the unaffected amorphous region and the left side has been crystallized with microcrystals in rows. Figure 8 is a transmission electron micrograph of both the amorphous and the crystallized films (from the thinner portion of the film) with their respective electron diffraction patterns inset. Figure 9 shows the arrangement of the microcrystals in the dendritelike arms of the crystallized region. Figure 10 is an electron micrograph of some of the individual silicon crystals with an inset showing an electron-diffraction pattern in a selected area of one crystal.

Since the total thickness of film was of the order of a few hundred angstroms, the available material for crystal formation was limited, and this is suggested as the reason for the formation of many crystals of essentially the same size as shown in figure 9 instead of the true dendrites observed by those working with much thicker films (ref. 3).

Additional experiments were performed with the silicon films in which resistance measurements of the newly deposited films were attemped. The films were deposited in the crystallizer apparatus onto slides having indium alloy conductivity tabs which connected through the vacuum feedthroughs to external measuring equipment. An estimated thickness of 500 angstroms of silicon was evaporated onto the slide and the resistance between the tabs was measured. The tabs were approximately 1 centimeter long and spaced 1 centimeter apart. The resistance of the untreated films measured at approximately 10^9 ohms.

After approximately 15 minutes of scanning treatment at relatively low beam intensities, as judged by the illumination level of the focusing phosphor, the resistance was measured again. Of three films so run the average resistance after treatment was 10^5 ohms. A decrease of four orders of magnitude was thus seen in the relatively thin films.

Cadmium Sulfide

Since cadmium sulfide does not exhibit a liquid phase at pressures less than several dozens of atmospheres and since it sublines when heated in a vacuum, the possibility of crystallizing amorphous films of this material by electron bombardment in vacuum is uncertain.

The first tests with this material were performed within the electron microscope so that trends could be observed and recorded. A cathodically sputtered film was deposited in the pattern shown in figure 1. Some of the film was removed by dissolving the plastic parting layer and was caught on a specimen screen. Since the film was so thin, as it was caught on the screen some of it folded upon itself in stretching across the screen grid openings. In these fold regions, as shown in the electron micrograph in figure 11, the effective thickness of film material exposed to the electron beam was doubled. This extra material proved of advantage in some of the results which followed.

The film as caught was placed in the electron microscope and examined to ascertain the amorphous nature of the deposit. In figure 11 (a transmission micrograph) may be seen the fairly uniform fluffy structure. Inset in this figure is the electron diffraction pattern obtained.

The film was treated by a gradual increase in the electron microscope beam intensity over the entire viewing area. Rapid motion of the material was observed with a liquid-like appearance of the coalescing particles. The process was arrested during its evolution at several points, and electron micrographs and electron diffraction patterns were made. Figure 12 shows a fold region viewed at a magnification of 2000 with fairly large clusters adjacent to the thicker folded regions. Upon increasing the magnification to that shown in figure 13, the individual crystals formed by the bombardment could be seen. The electron diffraction pattern of the larger hexagonal crystal shown in the center of figure 13 is inset. It was observed that most of the crystals so formed were oriented with the hexagonal face presented to the beam or with the C-axis alined with the beam.

Further studies of this material were made in the crystallizer. In figure 14 may be seen a surface replication of the amorphous cadmium sulfide film at a magnification of approximately 15 000. After beam sweeping, a shrinking of the film was observed, as shown in figure 15 at a magnification of about 5000. Some of this film was placed in the

electron microscope and was reduced in thickness by intensive electron bombardment which revealed the chainlike arrangement of crystals shown in figure 16. The electron diffraction pattern of this overall area is shown inset.

SUMMARY OF RESULTS

Amorphous films 800 to 300 angstroms (8×10^{-2} to 3×10^{-2} μm) thick of germanium, silicon, and cadmium sulfide on amorphous substrates of glass and plastic were converted to the crystalline condition by electron bombardment. Two methods of electron bombardment were employed, namely, electron-beam raster scanning and general surface bombardment. The use of the electron-beam scanning technique to produce a predetermined pattern of crystalline regions in films of the semiconductor material deposited on the amorphous substrates was demonstrated.

At electron-beam intensities which produce crystallization of the films no damage was noted to the plastic material immediately below the treated region. In separate tests, the vacuum decomposition temperature of the plastic material was found to be 250° C.

Observations of the crystallization of the amorphous semiconductor films have been presented in the forms of electron micrographs and electron diffraction patterns.

Order-of-magnitude electrical-resistance measurements were made on 500-angstrom- (5×10^{-2}-μm-) thick silicon films before and after crystallization. A resistance decrease of four orders of magnitude was found.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 8, 1968,
120-33-01-02-22.

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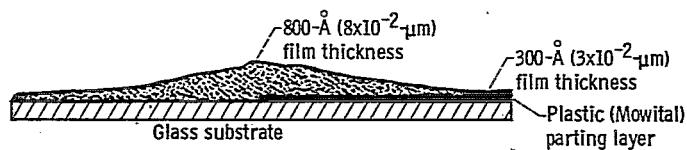
Figure 1. – Deposition cross section of amorphous films.
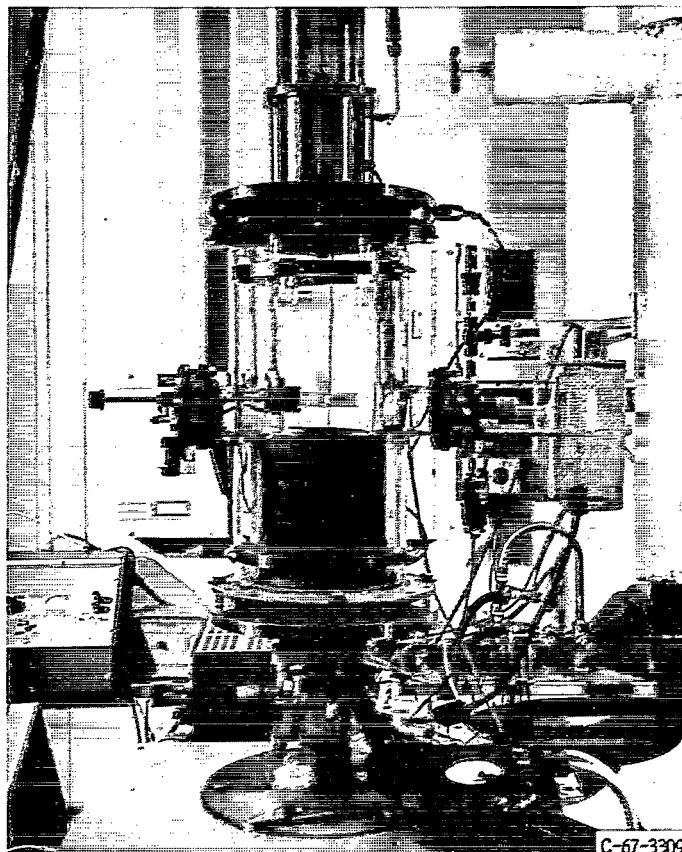
Figure 2. – Electron-beam scanning crystallizer.
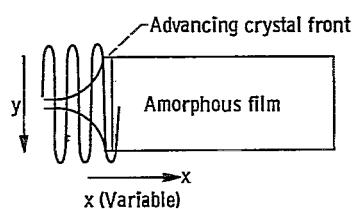
Figure 3. – Raster scan pattern. Scan
frequency, 60 hertz.

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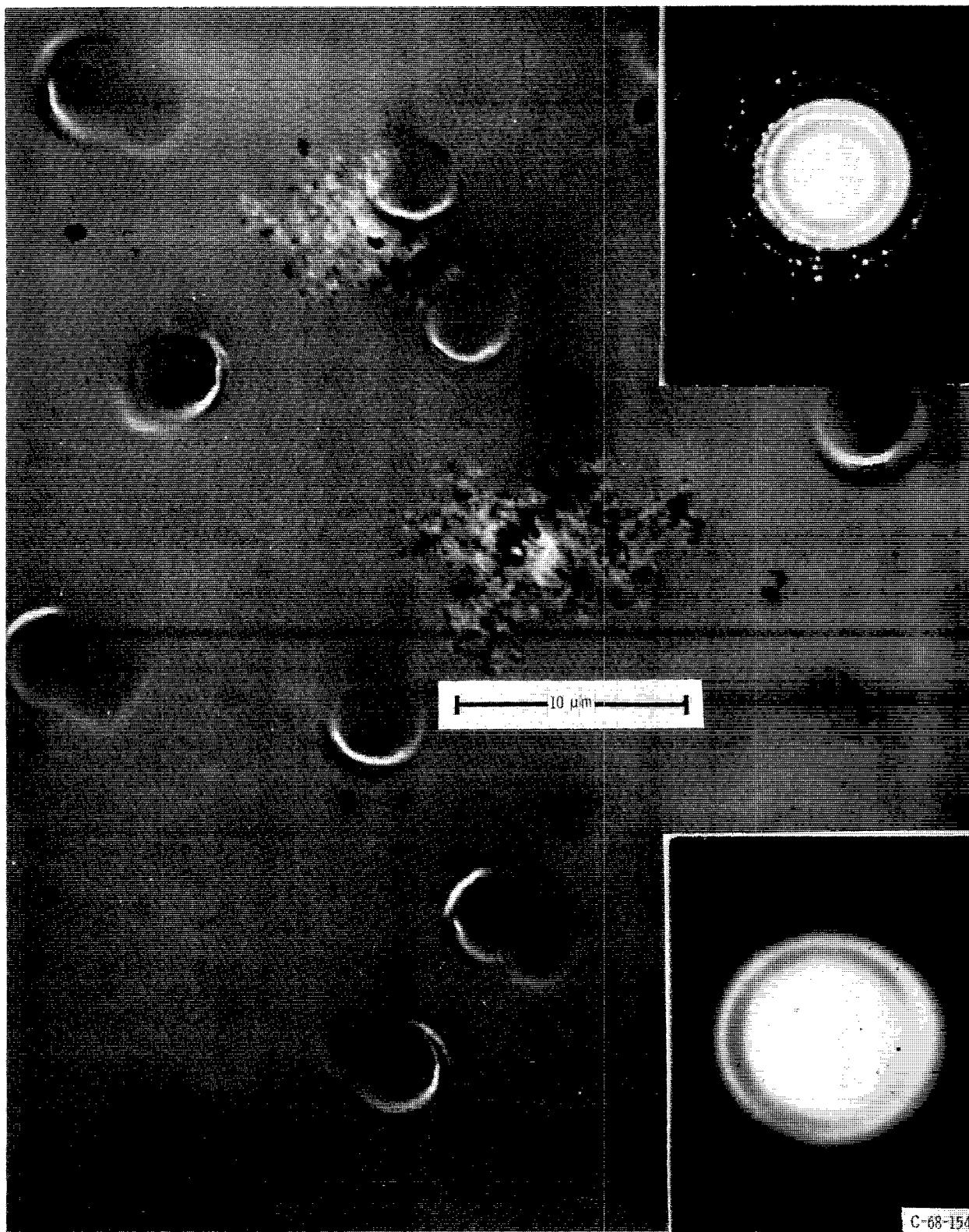
Figure 4. - Germanium film showing two treated regions.   Electron diffraction patterns inset.

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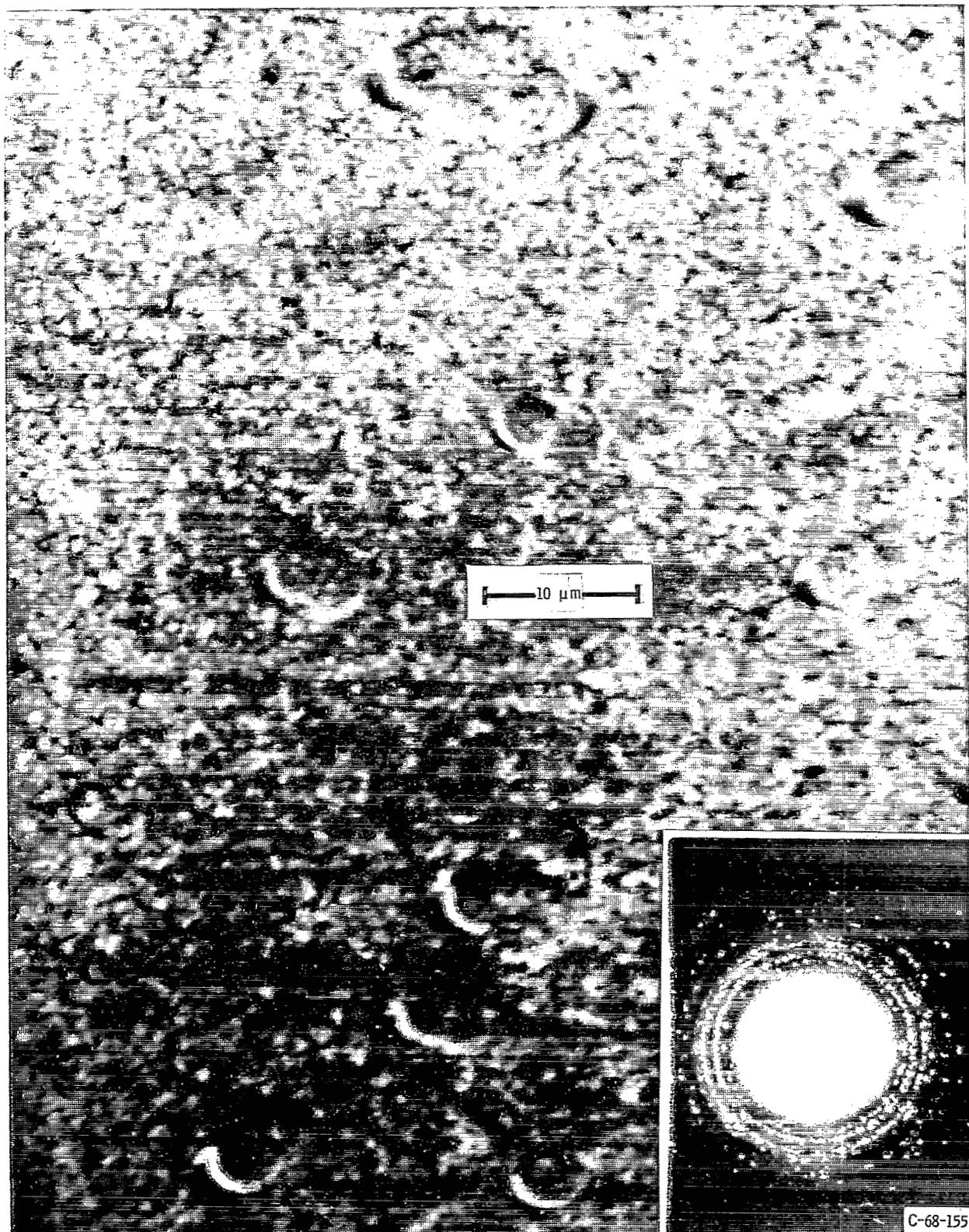
Figure 5. - Germanium film completely crystallized.   Electron diffraction pattern inset.

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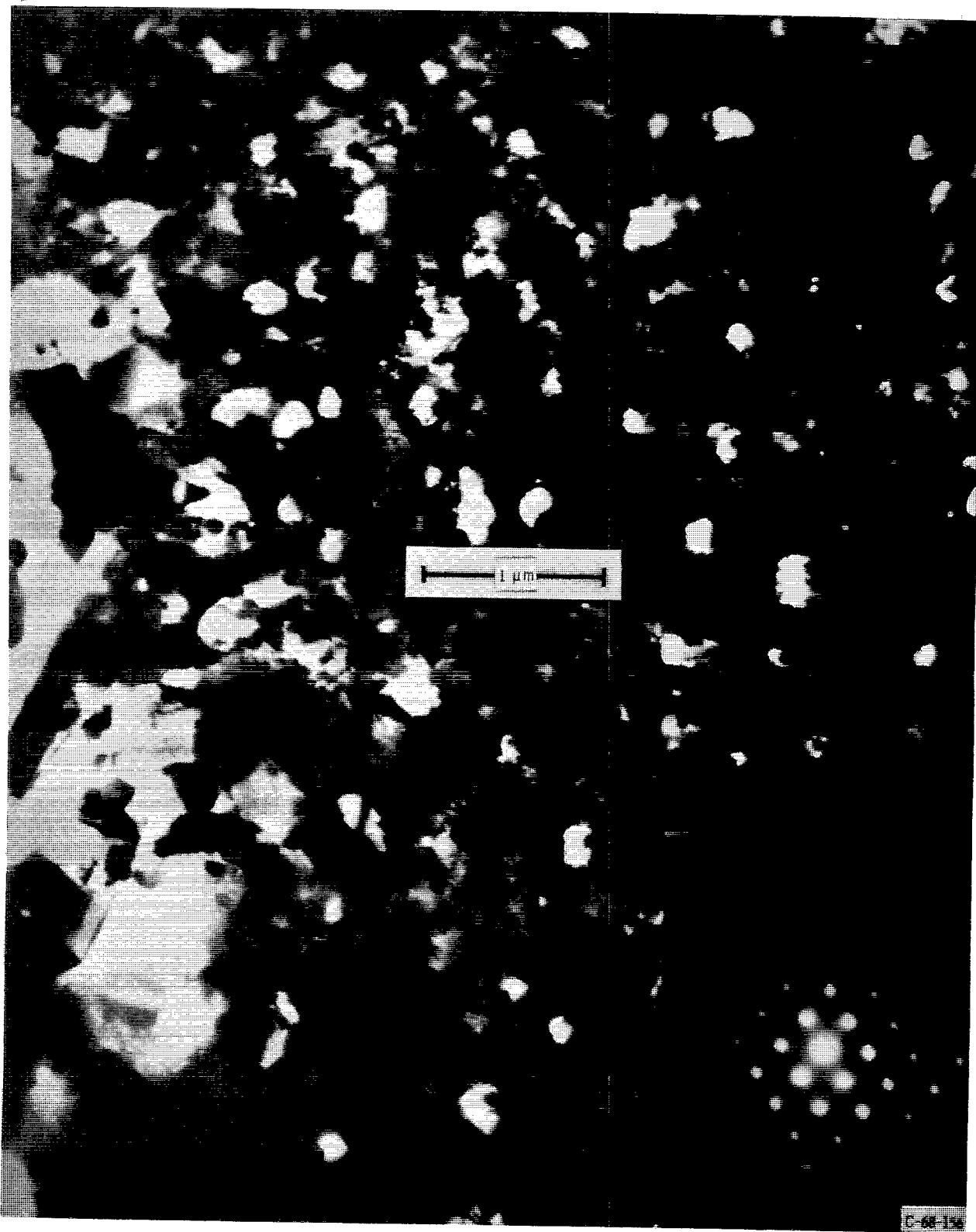
Figure 6. - Enlarged view of germanium crystallized film. Selected-area electron diffraction pattern inset.
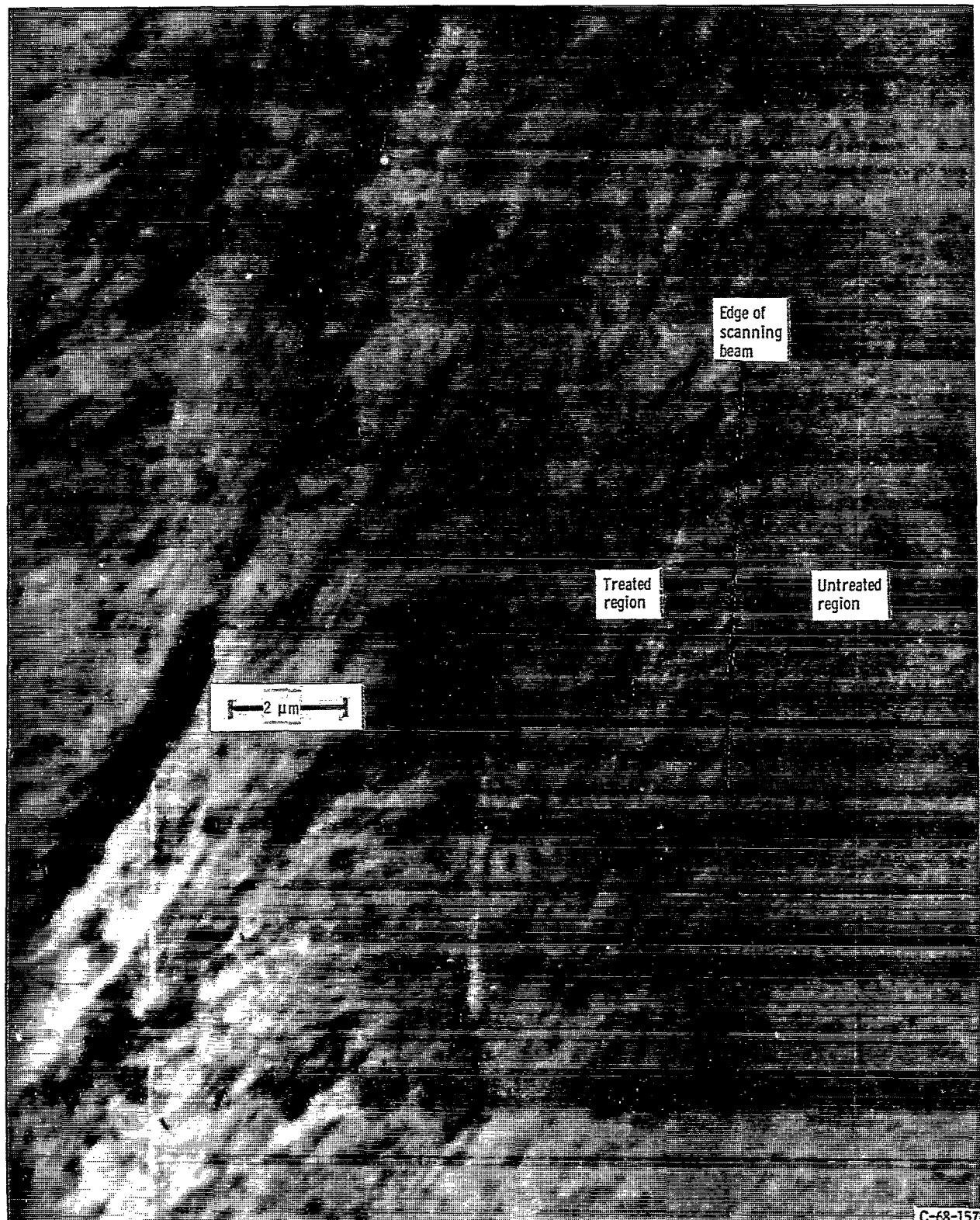
Figure 7. – Transmission electron micrograph showing edge of treated region in silicon film.
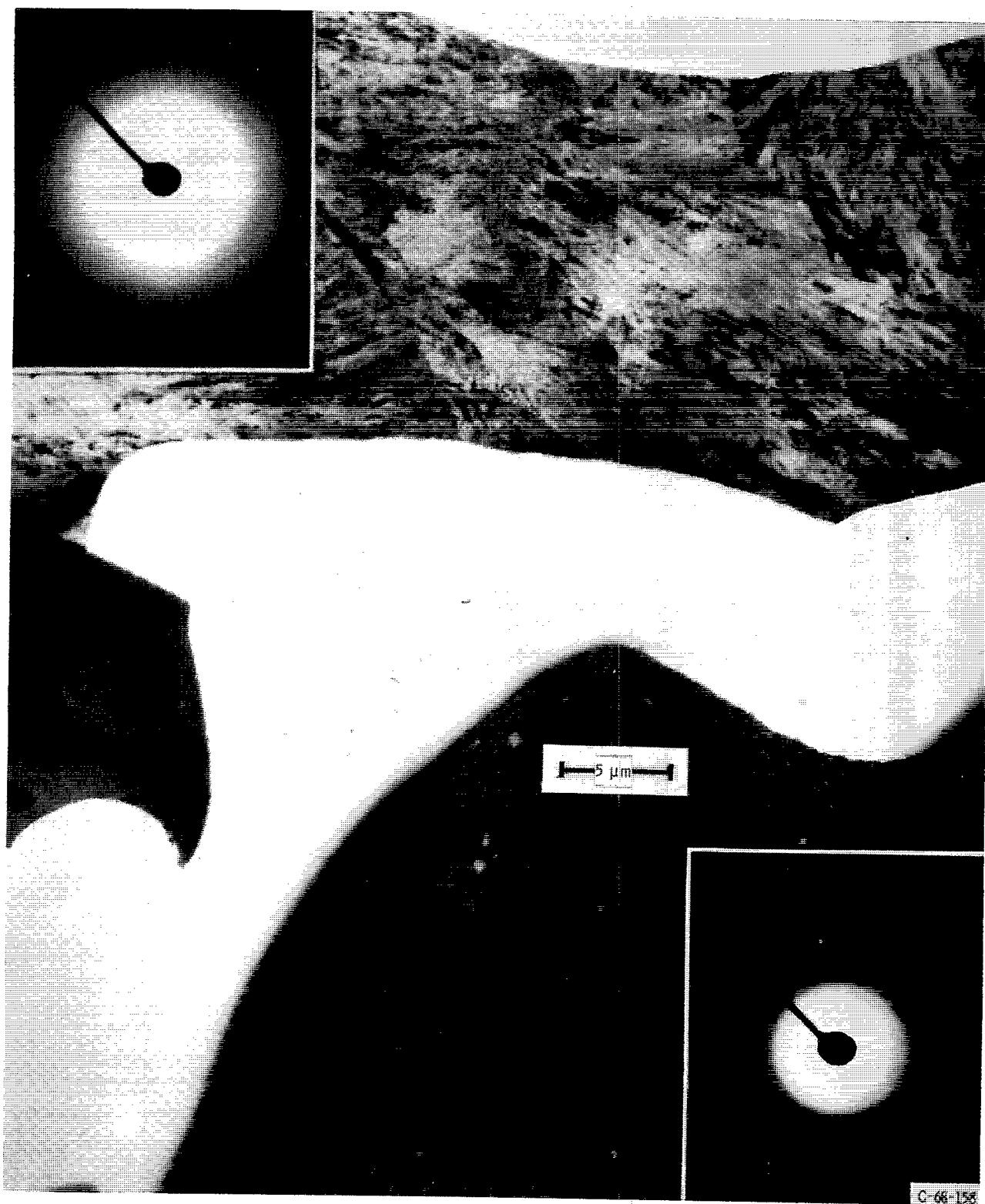
Figure 8. - Transmission electron micrograph of silicon film removed from substrate. Beam-scanned film (crystallized) at top with electron diffraction pattern inset; untreated film region (amorphous) at bottom.

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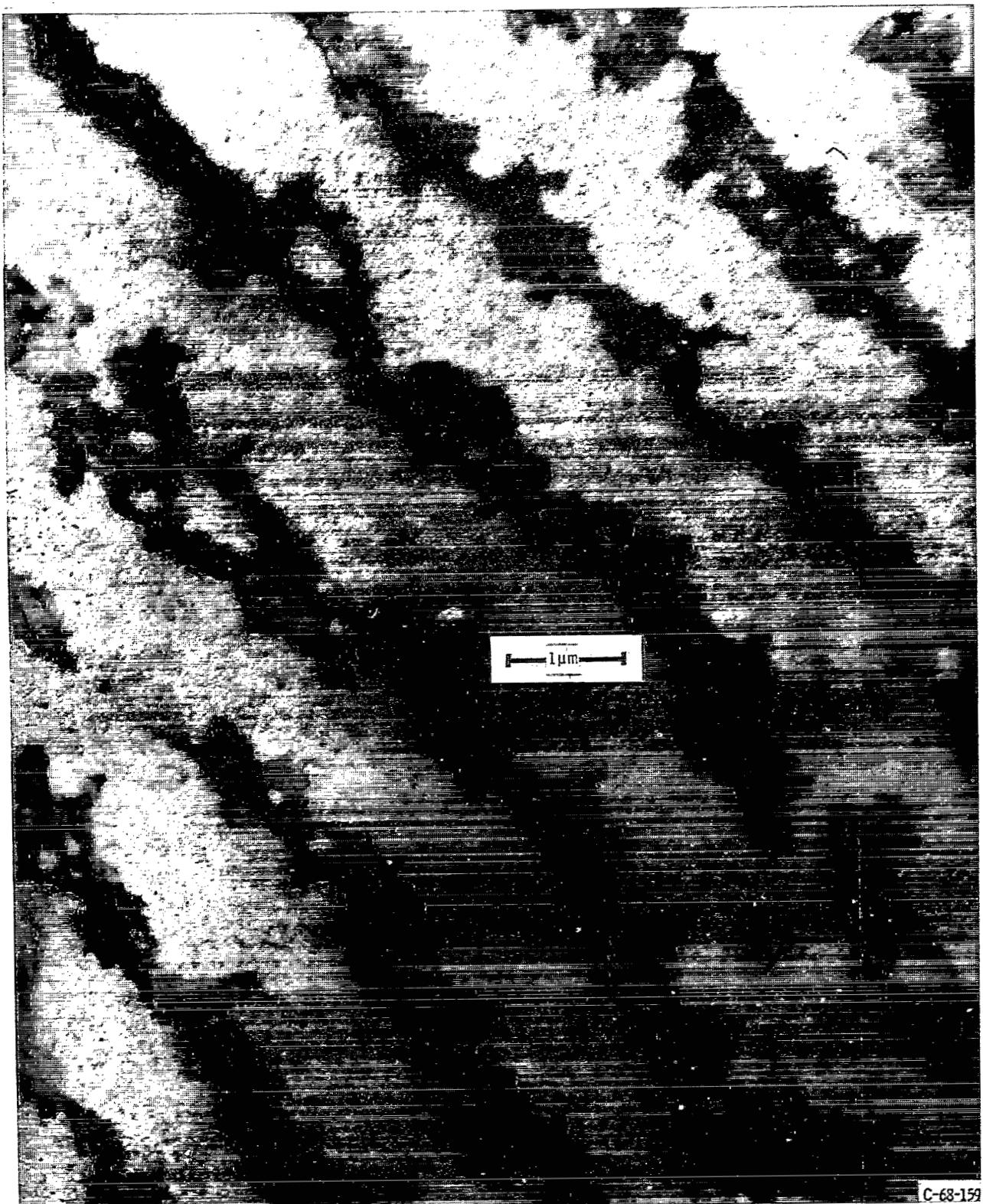
Figure 9. – Silicon polycrystalline dendrite arms.

Figure 10. - Individual silicon crystals in treated film. Electron diffraction pattern inset.
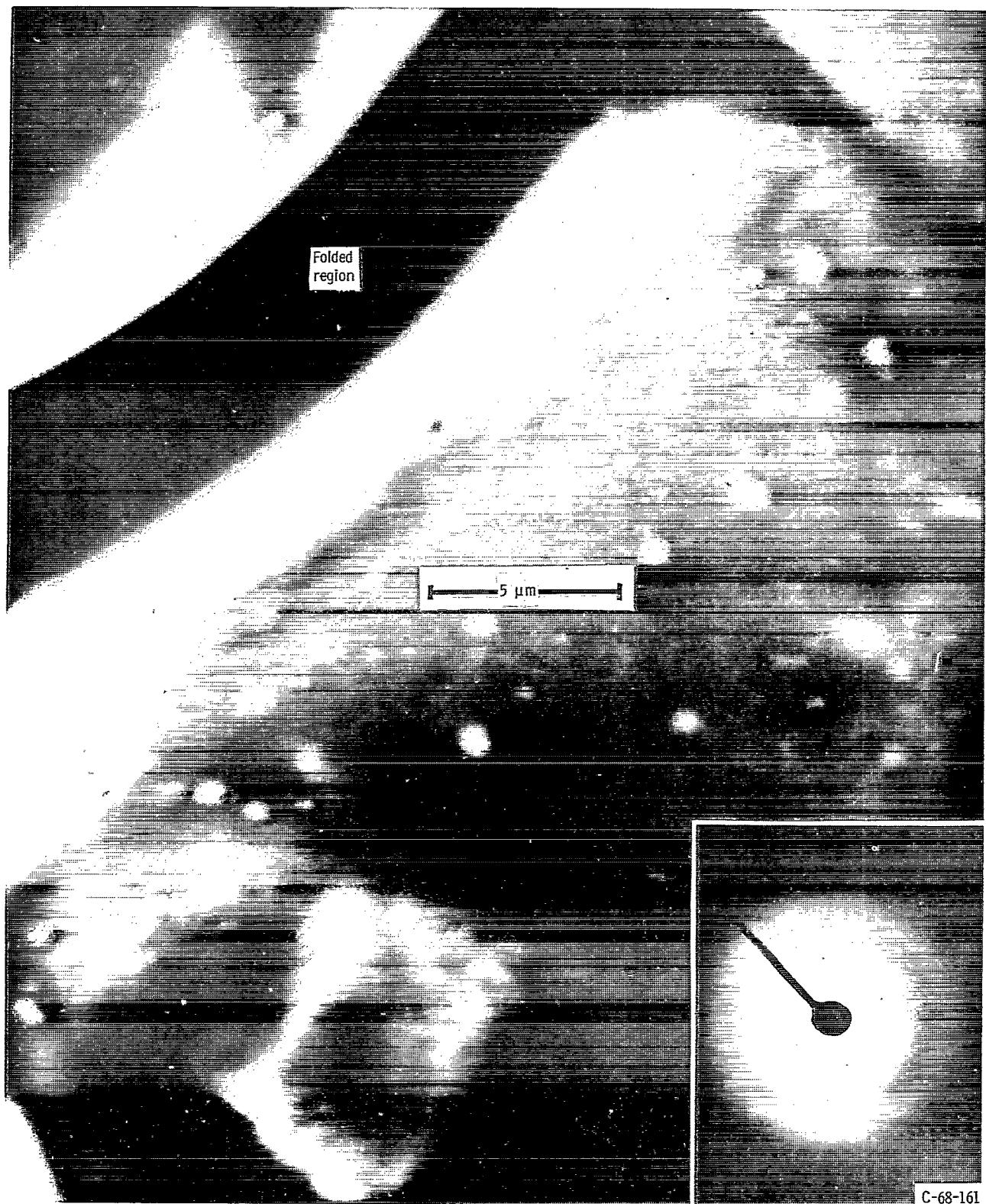
Figure 11. – Cadmium sulfide amorphous film showing folded region.   Electron diffraction pattern inset.

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Figure 12. - Cadmium sulfide film showing fold region after electron-beam crystallization.
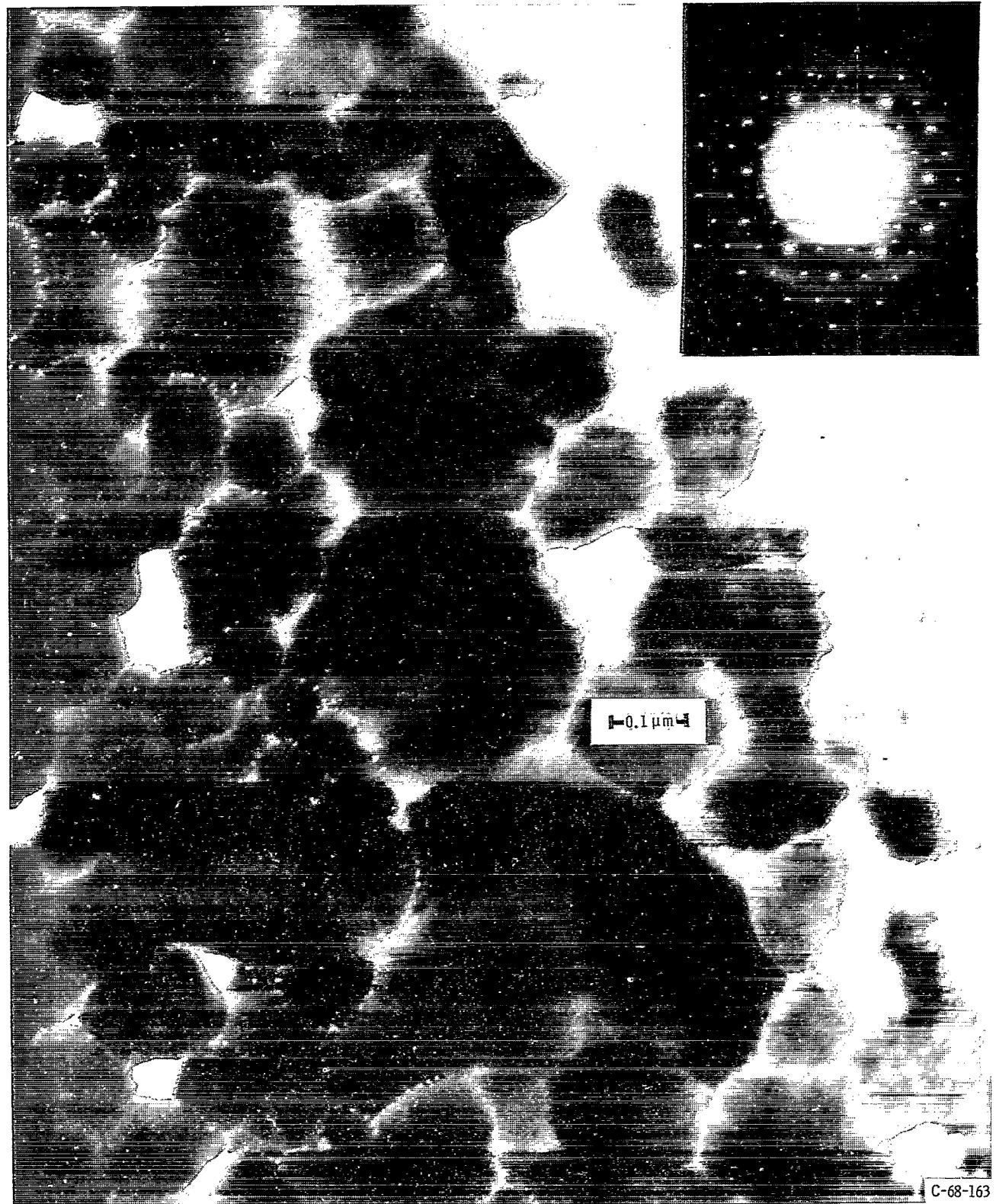
Figure 13. – Cadmium sulfide crystals in region of fold. Electron diffraction pattern of central crystal inset.

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Figure 14. - Replica of surface of untreated area of cadmium sulfide film.
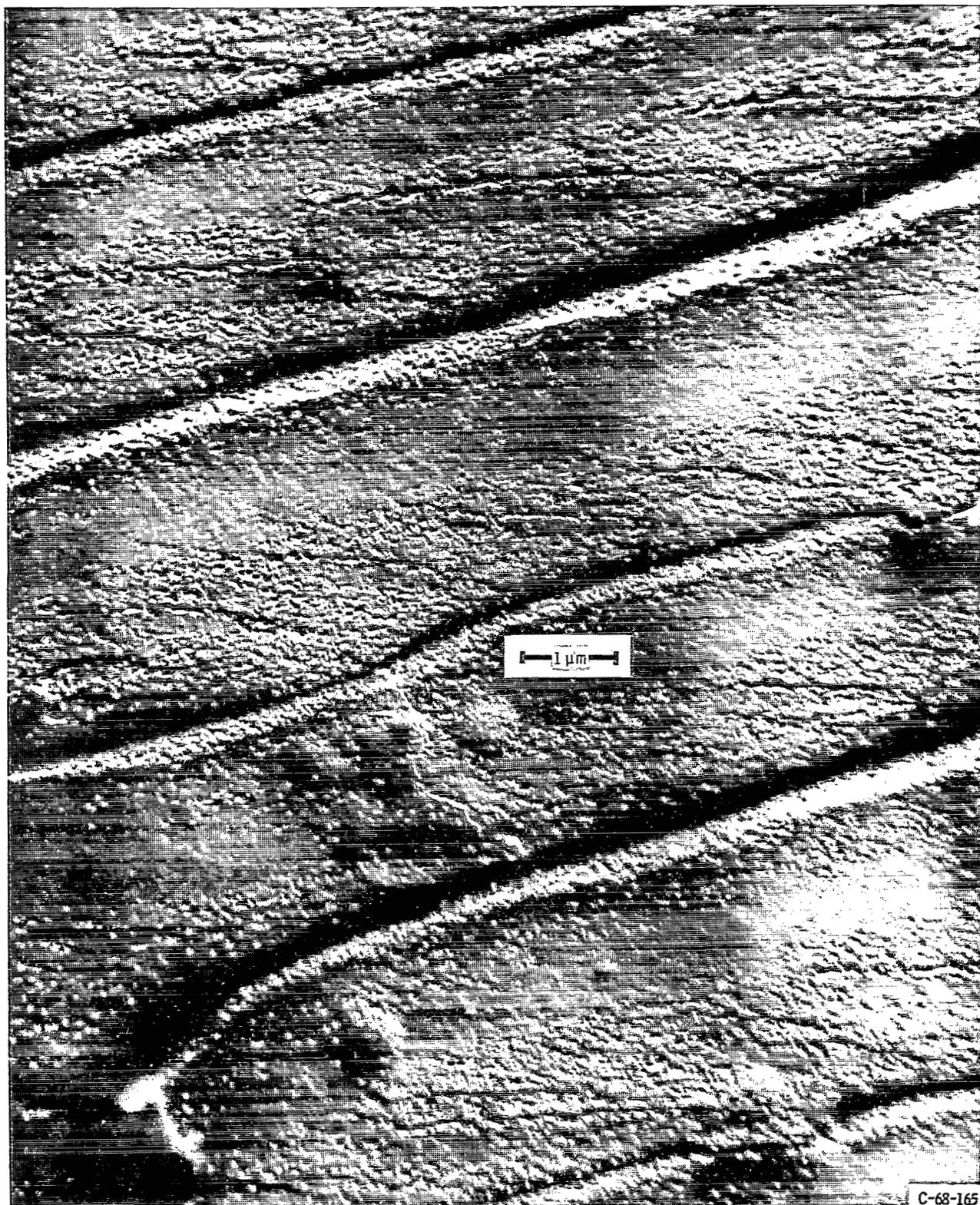
Figure 15. – Cadmium sulfide film region showing shrinkage after scanning with electron beam.

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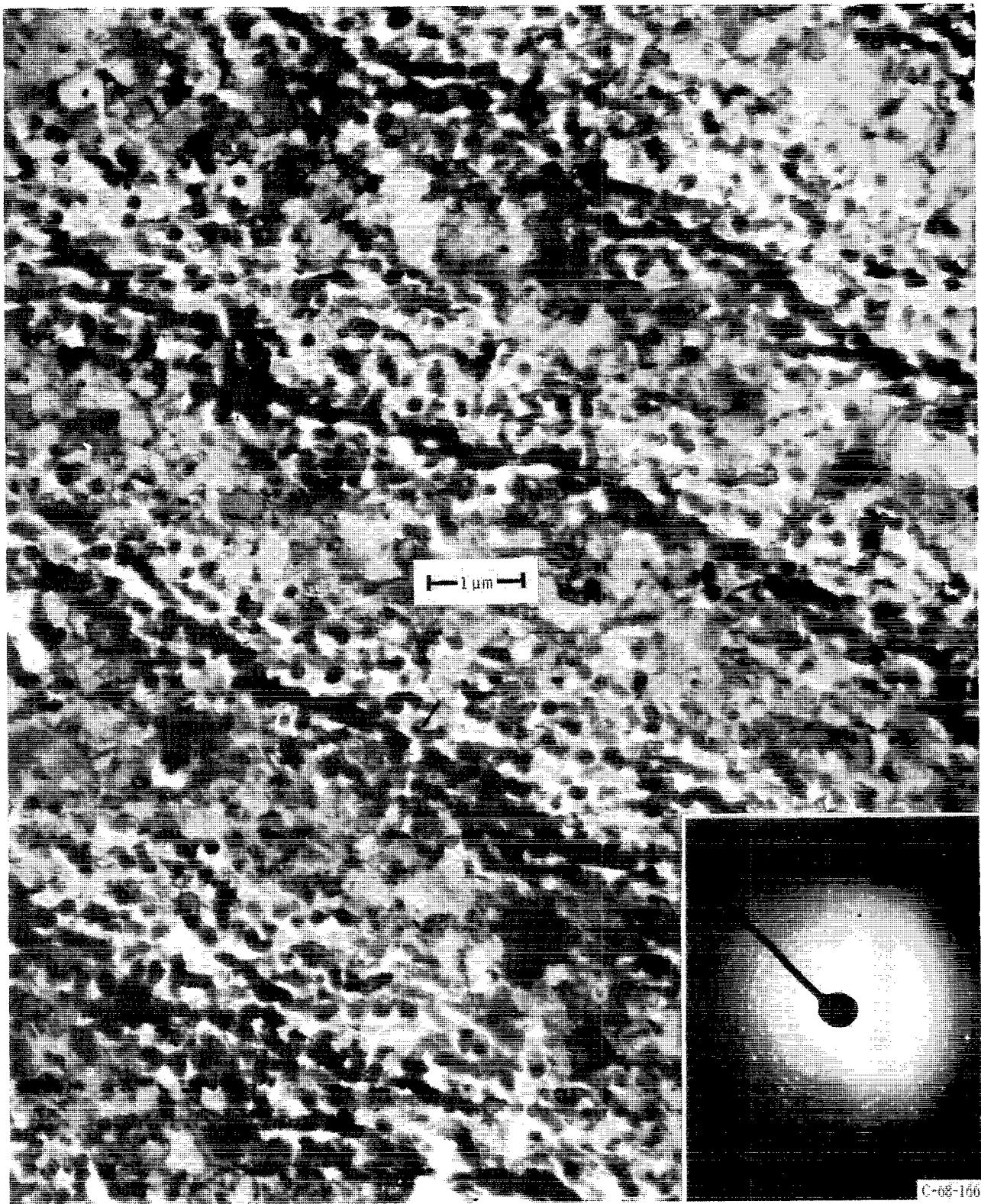
Figure 16. - Electron transmission micrograph of cadmium sulfide film showing chain arrangement of crystals. Electron diffraction pattern inset.

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