Electron Diffraction Study on the Structure of Amorphous Films Prepared by Low Temperature Condensation : I. Apparatus and Preliminary Results

Electron Diffraction Study on the Structure of Amorphous Films Prepared by Low Temperature Condensation

I. Apparatus and Preliminary Results*

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(Received March 22, 1973)

Synopsis

An electron diffraction camera equipped with a sector has been constructed which enables one to observe diffracted intensities at sufficiently large scattering angles in order to improve the radial distribution analysis of electron diffraction patterns. Values of the structure-sensitive intensity $I_m(s)$ have been obtained in the range from $s=1.2$ to 22.0 Å^{-1} for an amorphous tellurium film condensed onto substrate at the liquid helium temperature by use of a sector of s^2-type. The radial distribution function of the film is also calculated from the obtained $I_m(s)$.

I. Introduction

Several studies on the structure of amorphous films prepared by low temperature condensation[1~3] were previously carried out by means of the radial distribution analysis of electron diffraction patterns. Patterns of many of films prepared at very low temperature showed diffuse halos which are characteristic of highly disordered structure. The radial distribution functions (*RDF*) determined from such patterns differ from those calculated from models of minute crystallites, which suggests that such films do not consist of minute crystals, but are certainly in an amorphous state. However, little has so far been known on a detailed local arrangement of atoms in such films. It is a very interesting problem to make clear this point.

RDF with well resolved peaks is required to know the nature of atomic aggregates in amorphous films because exact positions and co-ordination numbers of the peaks are important keys in the structural analysis. Such a *RDF* is obtained by Fourier transformation of the structure-sensitive intensity $I_m(s)$ over a sufficiently wide range of s ($=4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ the wave length of electrons). However, the range of s where $I_m(s)$ is obtained is limited by experimental conditions. The damping factor, i.e. the so-called artificial temperature factor, is often introduced to reduce the termination effect

* The **1576th** report of the Research Institute for Iron, Steel and Other Metals.

(1) S. Fujime, Japan. J. appl. Phys., **5** (1966), 764.
(2) S. Fujime, Japan. J. appl. Phys., **5** (1966) 778.
(3) T. Ichikawa, Japan. J. appl. Phys., **9** (1970) 748.

caused by the limitation. The damping factor B is usually chosen so that $exp\ (-Bs^2_{max})=0.1$, where s_{max} is the maximum value of s below which $I_m(s)$ is obtained. In the previous works, values of s_{max} were at most about 12.0Å^{-1}, and so, large damping factors had to be used. Peaks in the *RDF* were consequently much broadened and overlapped, resulting in less resolved ones because *RDF* experimentally determined is the folding of a true *RDF* with a Gaussian broadening function $exp\ (-r^2/4B)/\sqrt{2B}$ [4], the reduced termination effect being neglected. Such peaks made it very difficult to know accurately the nature of the local arrangement. Therefore, it is indispensable to extend the range of s for which $I_m(s)$ is obtained, into a much larger value.

The scattered intensity in electron diffraction rapidly decreases with increasing s, and so, only a fraction of a diffraction pattern recorded on a photographic film enters the range where the darkness of the diffraction pattern is proportional to the scattered intensity. Therefore, in order to record the diffracted intensity over a sufficiently wide range of s, the rotating sector method has often been used in electron diffraction studies of gases[5] and amorphous substances.[6,7] In the present work, an apparatus equipped with a rotating sector, besides a low temperature specimen stage has been constructed in order to obtain *RDF* with well-resolved peaks. Rotation of the sector enables a part of a diffraction pattern at large scattering angles to get a more effective time of exposure. In this report, construction and characteristics of the apparatus are described together with some preliminary results of the radial distribution analysis on amorphous tellurium films prepared by condensation onto substrate at the liquid helium temperature.

II. Design and construction of the apparatus

In the present work specimens were prepared by condensation onto cold substrate in a specimen chamber of the diffraction camera, and diffraction patterns of the specimens were *in situ* observed to study their structure at low temperature and also to detect structural changes on heating up to room temperature. Two points were particularly considered in the design of a sector and its attachment. One was to design them lest the degree of vacuum in the specimen chamber should drop by rotating a sector, because a slight contamination due to condensation of residual gases onto the specimen films would markedly affect diffraction patterns. The other was to design them so that the sector might be at will removed from the path of diffracted electrons not so as to disturb visual observation of diffraction patterns on a fluorescent screen.

The sector and its attachment are shown in Fig. 1. Three kinds, i.e. s–, s^2– and s^3–type, of sector were made of brass plates 1 mm in thickness and 70 mm in

(4) J. Waser and V. Schomaker, Rev. mod. Phys., **25** (1953), 671.
(5) I. Karle and J. Karle: J. chem. Phys., **17** (1949), 1052.
(6) T. Ino, J. Phys. Soc. Japan **8** (1953), 92.
(7) J. Kakinoki, K. Katada, T. Hanawa and T. Ino, Acta Cryst., **13** (1960), 171.

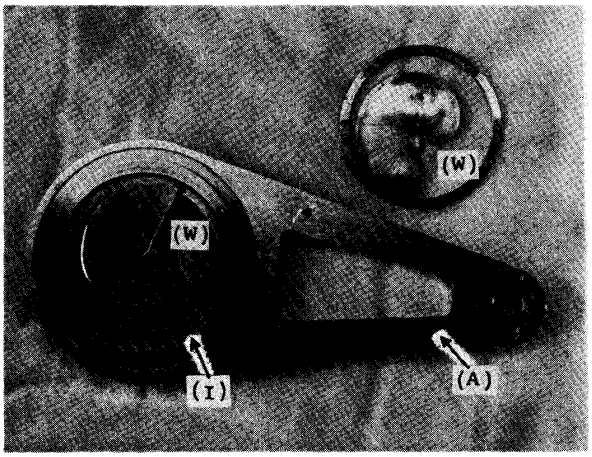


Fig. 1. Sector and its attachment. The sector of s^2-type is attached to an inner race of ball-bearing. A: arm, I: inner race of ball-bearing, W: window of sector.

diameter. Open angles θ of windows (W in Fig. 1) of sectors at the distance r from the center were cut to be proportional to r, r^2 and r^3, respectively, so that the effective time of exposure for diffracted electrons at the distance r may be proportional to r, r^2 and r^3 by rotating the sectors. The region from $r=1.8$ mm to 30.0 mm in the sectors works as a sector. The open angle at $r=30.0$ mm is 300°. Cutting was carefully carried out by handicraft so that the curves of sectors might coincide with those in plans. Values of θ for r were measured, the sectors being magnified by five or twenty times by a projector. The values for the sector of s^2-type are shown in Fig. 2. The open angles take very small values in the region of

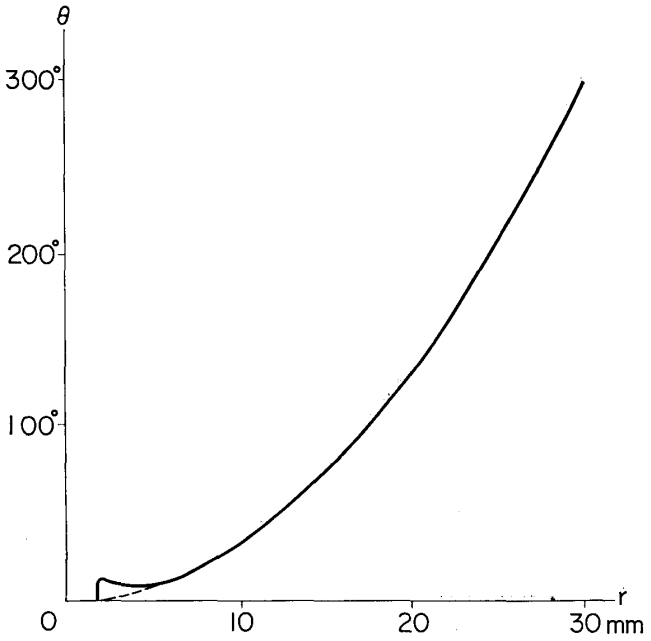
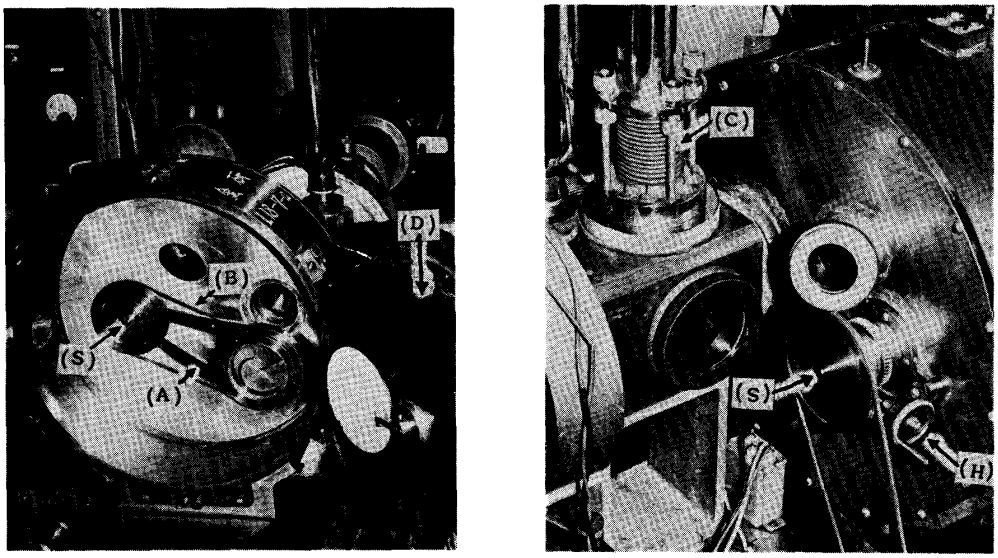


Fig. 2. Values of open angle of window for s^2-type sector. Full line and dotted one show the measured values and designed ones, respectively.

small r owing to the relations $\theta \propto r^n$ ($n=1$, 2 and 3). Therefore, the deviation of the open angles from the designed values was caused by manufactural difficulties in the neighborhood of the center of sectors. Except this region, the deviation, even if it exists, is small and changes smoothly and gradually with r. It was possible, therefore, to correct the influence of the deviation of $I_m(s)$, as the measured values of θ for r were used in the derivation of $I_m(s)$. $I_m(s)$ in the range of small s was derived from patterns recorded without using a sector. The distances from the specimen position to the sector position and from the former to the photographic film position are about 13 cm and 21 cm, respectively, in the present camera. The maximum s value of diffracted electrons passing through the sector is about 25 $Å^{-1}$ under the accelerating voltage 42 KV.

The sector was mounted on an inner race (I in Fig. 1) of a ball-bearing made of non-magnetic stainless steel. The inner race is connected to a shaft (S in Fig. 3 (a) and (b)) by a spring belt (B in Fig. 3 (a)). The shaft projects from the vacuum through a Wilson seal and is rotated by a synchronous motor. The sector is rotated at a speed of about 800 cycles per minute. The accuracy of the exposure time is limited by vibration due to the rotation and by disagreement of the center of the sectors with the direct beam position. Error due to the latter is almost corrected by photometry, the photographic film being rotated with high speed, so long as the darkness of a diffraction pattern lies in the range where the darkness is proportional to the diffracted intensity. In order to attain an accuracy of 2–3%, the radial amplitude of the vibration should be less than 0.04 mm for the sector of s^2–type. This requirement is fully achieved in the present camera.

A hole 1.2 mm in diameter was bored in the center of the sectors, and the direct beam was adjusted so as to pass through the center of this hole. A holder



(a) (b)

Fig. 3. View of the apparatus. S: shaft, B: spring belt, A: arm, H: handle, C: cryostat, D: disc case.

of the ball-bearing was fixed to an arm (A in Fig. 1 and Fig. 3 (a)). The foot of the arm was attached to the bearing of the shaft. The rotation of the handle (H in Fig. 3 (b)) is converted to that of the bearing by gears and turns the arm and the holder about the shaft. Thus, the sector is removed from the path of diffracted electrons when unnecessary.

Double vacuum seals composed of two pieces of Wilson seal were designed for the shaft, in order to decrease the leak during rotation of the sector. A diffusion pump with high speed of evacuation was located at a position near the vacuum seal lest the leaking gas should enter the specimen chamber. In practice, a single Wilson seal was enough for use. The degree of vacuum in the chamber dropped little by rotating the sector so long as the Wilson seal was elaborately made of Neoplane rubber.

III. Experimental

In this chapter experimental conditions and procedures are described. Details about a cryostat having a substrate holder were reported in a previous paper.[8] Specimen material was evaporated from a tungsten helical filament and condensed onto a thin Poly-vinyl Formvar film. The filament was located at a distance about 16.5 cm from the substrate. This distance was sufficient to prevent the substrate from temperature rise due to the radiation from the filament. The substrate film was supported on a thin platinum plate 0.05 mm in thickness with two holes $\sim 30\,\mu$ in diameter. A silver film was in advance condensed onto one of the holes in order to use its diffraction rings as a standard of s values.

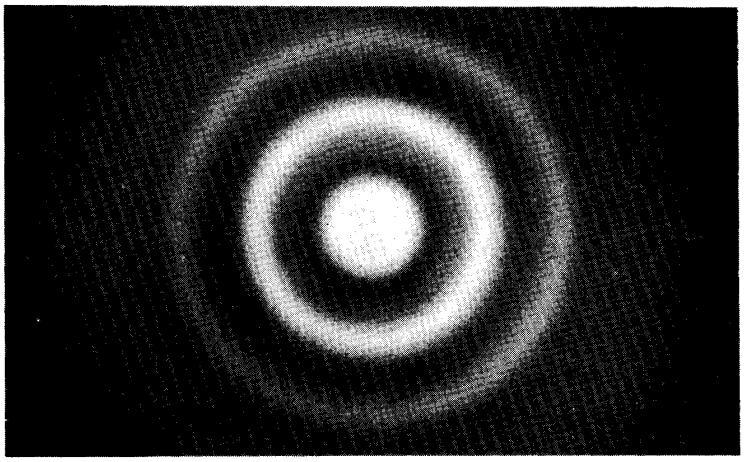
The diffraction camera was evacuated for 24 hours by two oil-diffusion pumps, and then two traps cooled by liquid nitrogen were worked. By this procedure the degree of vacuum in the camera attained $\sim 5\times 10^{-7}$ Torr. When liquid helium was poured into the cryostat, the pressure decreased to $\sim 3\times 10^{-7}$ Torr. The pressure increased to 5×10^{-7}–2×10^{-6} Torr during evaporation. After condensation, the sector was set and diffraction patterns were recorded on photographic films for electron microscope use. Three sheets of photographic films 12 cm × 10 cm in size were set on a disc on the back side of a door (D in Fig. 3 (a)). The films were brought to a fixed position in turn on photographing by rotating the disc from the outside. After a diffraction pattern of specimen was recorded on the area 10 cm × 10 cm, the disc was rotated by about 40° and a ring pattern of the silver film was recorded on the rest 2 cm × 10 cm of the same film. Photometry was made using a self-balanced type densitometer, the film being rotated with high speed, and densities were converted into the intensity of electrons by the Karle-Karle method.[5] S values of diffraction patterns of specimens, determined from the ring pattern of the silver film, involve errors due to the bending of photographic film on photographing, its stretching and shrinkage due to develop-

(8) S. Fujime, Japan. J. appl. Phys., **5** (1966), 59.

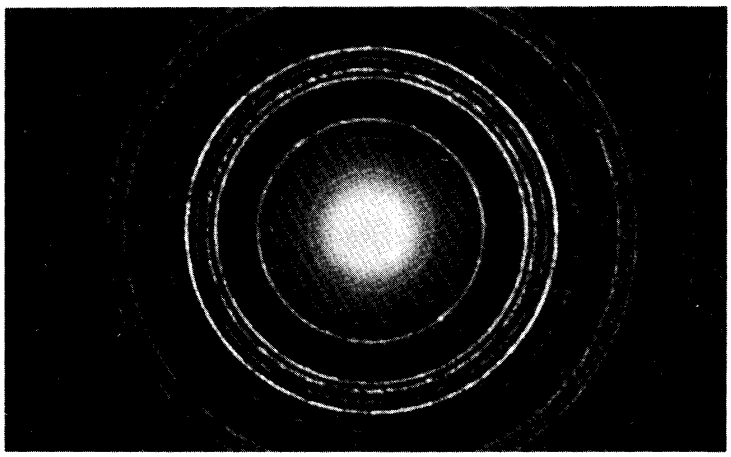
ment, and change of the camera length due to the rotation of the disc, but a total of the errors was less than 0.3%. The method of derivation of $I_m(s)$ from the intensity curve was described previously.[2,3]

IV. Preliminary results of the radial distribution analysis on a tellurium film

A tellurium film about 100–150 Å in thickness which was prepared by condensation onto substrate at the liquid helium temperature in high vacuum gave a very diffuse halo pattern as shown in Fig. 4 (a). The pattern abruptly changed to a ring pattern of trigonal tellurium as shown in Fig. 4 (b) at about 23°C on heating. A curve in Fig. 5 shows the structure-sensitive intensity $I_m(s)$ derived from the diffuse halo pattern of the tellurium film at the liquid helium temperature. Values of $I_m(s)$ were obtained in the range from $s=1.2$ to 22.0 Å^{-1}. Those in the range from $s=0$ to 1.2 were reasonably extrapolated to −1.0 at $s=0$, because an appreciably diffracted intensity in the neighborhood of $s=0$ due to long-ranged density fluctuation in the



(a)



(b)

Fig. 4. Diffraction pattern of tellurium film. (a); immediately after condensation. (b); after crystallization.

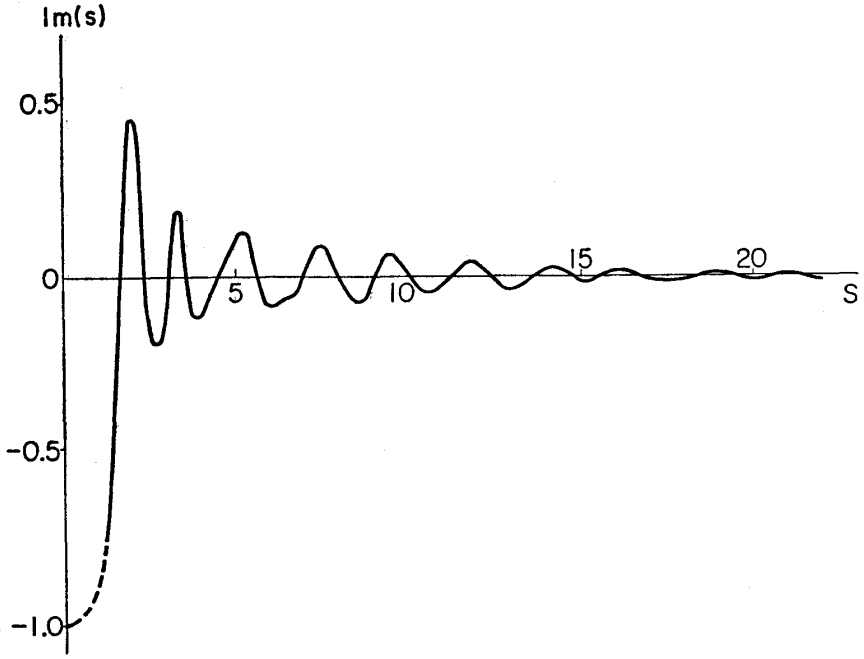


Fig. 5. $I_m(s)$ of tellurium film condensed at the liquid helium temperature.

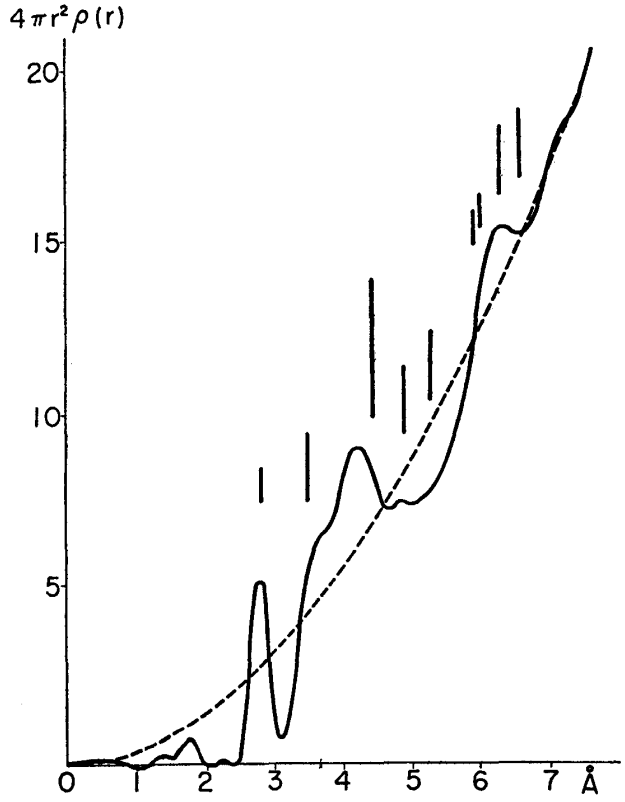


Fig. 6. *RDF* curve for tellurium film condensed at the liquid helium temperature. Bars show the interatomic distances in trigonal tellurium. Dotted curve shows $4\pi r^2\rho_0$.

film was not found by visible observation. Ten maxima in the curve are observed at $s=2.0_2$, 3.3_4, 5.2_3, 7.4_4, 9.4_2, 11.8, 14.2, 16.1, 19.9, and 21.1Å^{-1}. If the sector is not used, maxima observed are at most the first five ones. The range of s where $I_m(s)$ is obtained has thus been extended much farther by use of the rotating sector method.

The *RDF* in Fig. 6 was determined by the Fourier transformation of $I_m(s)$ with $\rho_0=0.0280$ Å^{-3}[9] as the mean density and $B=0.0048$ Å^2 as the damping factor. Interatomic distances in trigonal tellurium are shown by those bars entered into Fig. 6 whose length is proportional to the number of neighbors having the respective distance.

If atoms are arranged so as to form minute trigonal crystals, peaks in *RDF* should occur at the positions marked by those bars. However, most of the peaks, especially the second and third ones, in the present *RDF* do not coincide with the bars, which suggests that the film does not consist of very minute trigonal crystals. However, since the position 2.79 Å of the first peak in the *RDF* is closer to the covalent bond distance 2.835 Å[10] in the chain in trigonal tellurium than to any bond distances in other phases of tellurium, atoms in the films are considered to be arranged in chains. The average number of the first neighbor should be two in a chain of infinite length, but is less than two in a finite chain. The average number of atoms composing a chain in the films is estimated from the first co-ordination number 1.70 to be 6.7 because the average number $C_N(1)$ of the first neighbor is connected with the average number N of atoms composing a chain by a formula $C_N(1)=(2N-2)/N$. A detailed local arrangement in the amorphous tellurium film will be discussed elsewhere.

Acknowledgement

One of the present authors (T.I) would like to thank Dr. T. Ino of Osaka City University for his kind advice on the design of the sector.

(9) Gmelin, *Handbuch der anorgan. Chemie*, 8. Aufl. Nr. 11, Verlag Chemie, Berlin 1940. (s. 173)

(10) P. Cherin and P. Unger, Acta Cryst., **23** (1967), 670.