Kinetics and Diffusing Species of the High-Temperature Selenidization of Molybdenum

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A molybdenum sheet was selenidized at a selenium vapor pressure of 0.40—13.3 kPa at 773—973 K by means of a sealed-tube method. X-Ray diffraction patterns and an electron probe microanalysis of the product films showed that a single layer comprising $MoSe_2$ was formed under all of the selenidization conditions employed. All of the selenidizations obeyed a parabolic rate law and, therefore, the rate-determining step was apparently a diffusion process. The parabolic rate constant (K_p) was expressed as a function of the absolute temperature, and the selenium vapor-pressure dependence of K_p could be clearly recognized. A marker experiment indicated that selenium was the component which diffused.

Metal selenides have become important as fine inorganic materials. Particularly noteworthy is the zinc monoselenide as a blue LED (Light Emitting Diode). Studies of molybdenum selenides have been published concerning their electrical properties,[1,2] thermodynamic quantities,[3,4] and others.

The kinetics[5,6] of the reactions of molybdenum with selenium vapor has been investigated by means of a quartz spring-balance method. The authors have published an article entitled "Kinetics and Diffusing Species in the Reaction between Molybdenum and Selenium Vapor" as a letter.[7] The details concerning its subsequent investigation are described in the present paper.

Experimental

1. Materials. A molybdenum sheet 1 mm thick with a purity of 99.95 wt% was cut into rectangular pieces of 6 mm×20 mm. According to an analysis by the supplier (Nilaco Corporation), the impurity level of this sheet was as follows: Ag<5, Al=10, As<5, Ba<20, C=15, Ca=5, Co=5, Cr<10, Cu=5, Fe=50, H=5, K=5, Mg<5, Mn<5, N=5, Na=5, Ni=5, O=20, P=5, Pb<5, S=5, Si=5, Ti<5, and W=200 ppm. These were vacuum-annealed at 1273 K for 24 h. They were abraded with emery papers (#240, #400, #1000, and #1500), then polished with wet fine chromium(III) oxide powder on a buffing cloth, and rinsed in a refined toluene. Their geometric surface areas and weights were measured.

Selenium shots with a purity of 99.999 wt%, made by Wako Pure Chemical Industries, Ltd., were used as such for this investigation.

2. Preparations and Procedures. The evacuated- and sealed-tube method[8] was employed for the selenidization. A sample sheet and an excess of selenium shots were each placed at ends of the silica tube. This tube was then sealed under vacuum.

The reaction apparatus comprised a porcelain tube maintained in two temperature zones; the first zone was used to heat the sample sheet in a sealed silica tube, and the second zone was used to control the vapor pressure of selenium in this tube. The vapor pressure of selenium was governed by the minimum temperature in the closed system. The selenium vapor pressure (p, in Torr) is given as a function of the Celsius temperature by the following expression:[9]

$$\log(p/\mathrm{Torr}) = 7.6316 - 4213.0/(202.0 + t/^{\circ}\mathrm{C}).$$

The composition of selenium vapor was reported to be a function of the temperature in the literature,[10] in which all molecules from Se_1 to Se_8 are present in equilibrium. The vapor pressure, which was determined from the above equation, gives the selenium total pressure.

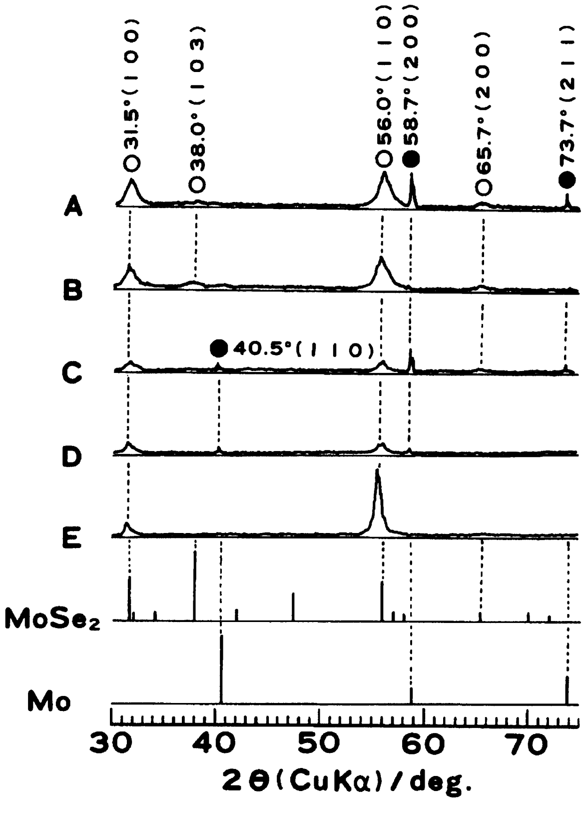

Fig. 1. X-Ray diffraction patterns for the surface side of molybdenum selenides formed at 773—973 K in selenium vapor pressure of 1.33 kPa, compared with patterns reported in the literature.[14] The Miller indices (*hkl*) and numerals of diffraction angles were cited from the reference.[14] Effect of temperature and elapsed time: A: 773 K, 3.6 ks; B: 773 K, 14.4 ks; C: 823 K, 900 s; D: 873 K, 900 s; E: 973 K, 3.6 ks. $MoSe_2$(○), Mo(●).

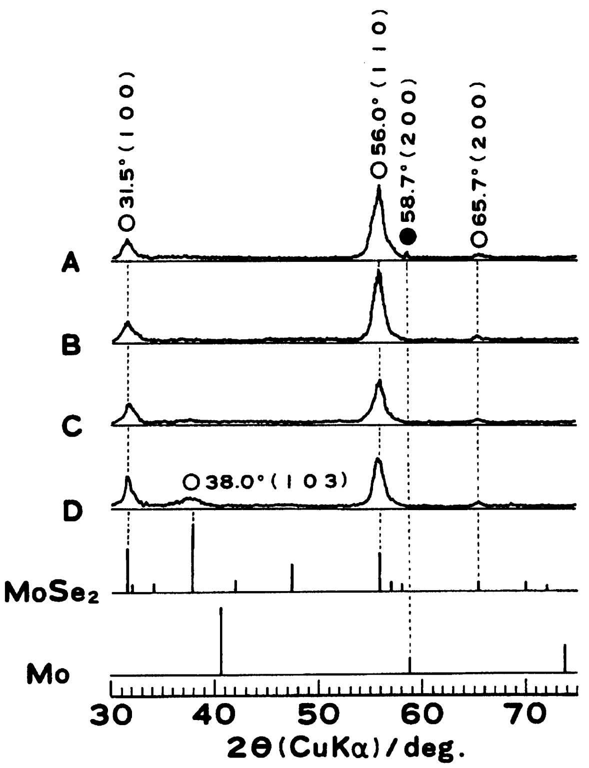

Fig. 2. X-Ray diffraction patterns for the surface side of molybdenum selenides formed at 873 K for 14.4 ks, compared with patterns reported in the literature.14) The Miller indices (*hkl*) and numerals of diffraction angles were cited from the reference.14) Effect of selenium vapor pressure: A: 0.40 kPa (3 Torr); B: 1.33 kPa (10 Torr); C: 4.21 kPa (31.6 Torr); D: 13.3 kPa (100 Torr). MoSe$_2$(○), Mo(●).

The apparatus and experimental methods employed in this study have been described in detail in a previous paper.8)

The experiment was carried out under the following conditions: (i) a selenium vapor pressure of 1.33 kPa (10 Torr) at reaction temperatures of 773, 798, 823, 848, 873, 923, and 973 K and (ii) a temperature of 873 K at 0.40 kPa (3 Torr), 1.33 kPa (10 Torr), 4.21 kPa (31.6 Torr), and 13.3 kPa (100 Torr).

Results and Discussion

1. Composition of Product Films.

The seven molybdenum selenides are known in the literature as: MoSe$_3$,11) Mo$_2$Se$_5$,12) MoSe$_2$,1,13) Mo$_3$Se$_4$,1) Mo$_{15}$Se$_{19}$,14) Mo$_9$Se$_{11}$,14) MoSe.3,15)

X-Ray measurements were performed using a Cu target and a monochromator. Figures 1 and 2 illustrate the X-ray diffraction patterns for the surface side of selenide films. The diffraction patterns shown in Figs. 1 and 2 were drawn in accord with the positions of the diffraction peaks and their heights in the actual diffraction charts. The diffraction peaks were identified by a comparison with the literature values of the diffraction angles of MoSe$_2$14) and Mo.14) All of the peaks of the reaction products belonged to MoSe$_2$ alone, under

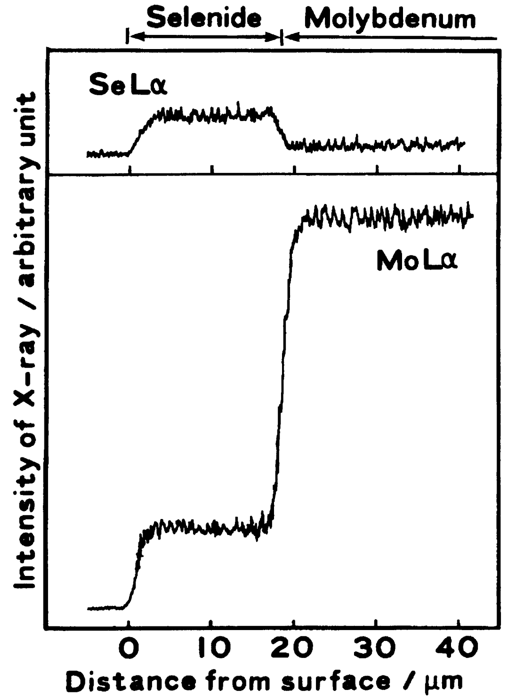

Fig. 3. Distribution profiles of molybdenum and selenium in the selenide film formed at 848 K and 1.33 kPa for 8.1 ks.

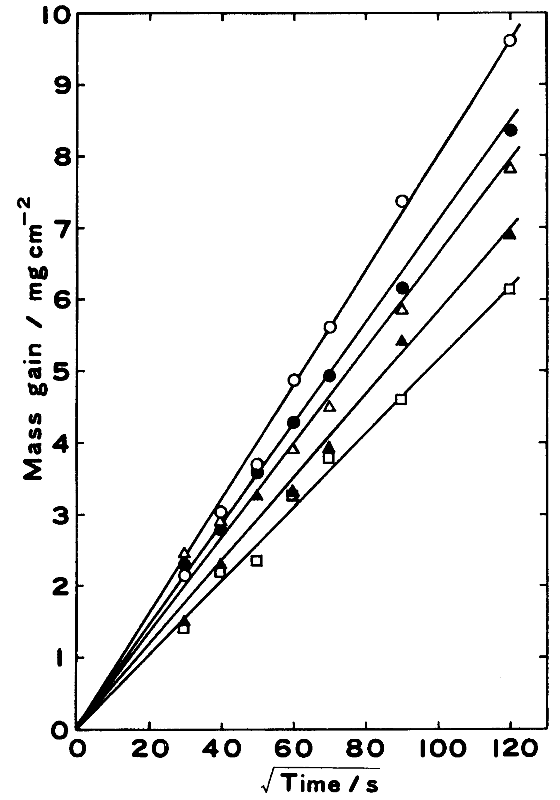

Fig. 4. Selenidization of molybdenum in selenium vapor at 1.33 kPa. 873 K(○), 848 K(●), 823 K(△), 798 K(▲), 773 K(□).

all of the experimental conditions employed. No diffraction peaks belonging to the other molybdenum selenides were observed. Figures 1 and 2 show that the intensities of the diffraction peaks from the (110), (100), and (200) planes are predominantly strong, that is, the molybdenum selenide films have a predominant orientation of their planes parallel to the *c*-axis. The small peaks of $2\theta=38.0°$ from the (103) plane were also partly observed. The diffraction peaks of Mo were also observed during the early stage of exposure; these peaks were due to reflection from the unaltered molybdenum substrate sheets, due to thin product films.

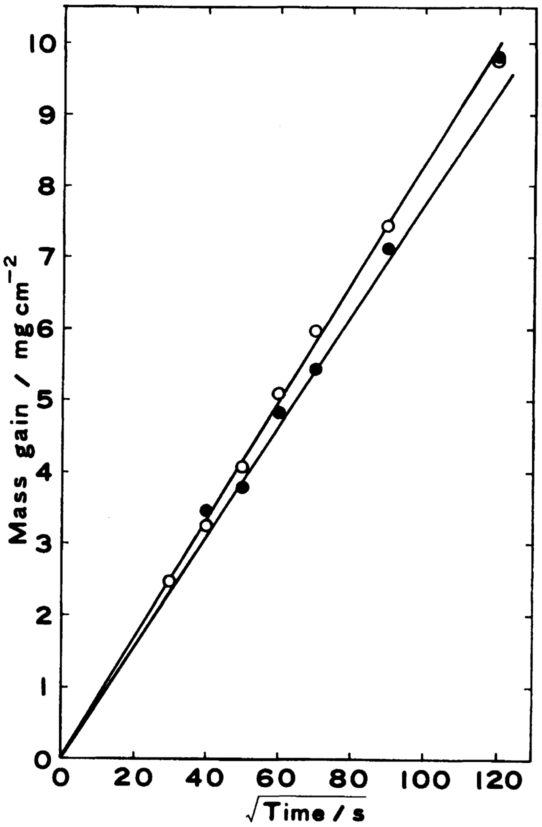

Fig. 5. Selenidization of molybdenum in selenium vapor at 1.33 kPa. 973 K(●), 923 K(○).

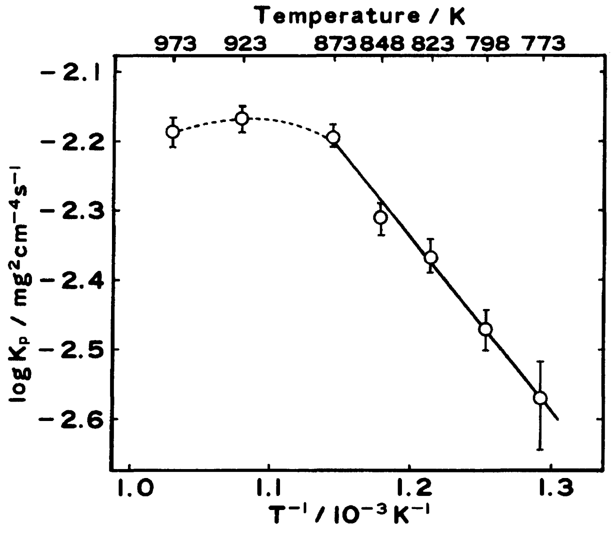

Fig. 6. Temperature dependence of K_p for selenidization of molybdenum in selenium vapor at 1.33 kPa.

The specimen selenidized at 848 K and 1.33 kPa for 8.1 ks was embedded in a methyl methacrylate polymer; its cross section was polished with 3 μm and 0.5 μm diameter diamond pastes. Composition variations through the cross section of the selenide film were examined using an electron probe microanalyzer (EPMA),

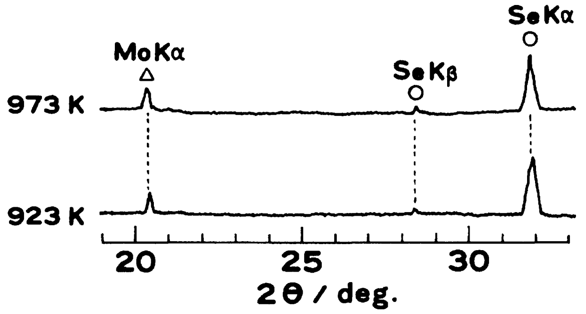

Fig. 7. X-Ray fluorescence spectra taken from the inner wall of the sealed silica tube. Se(○), Mo(△).

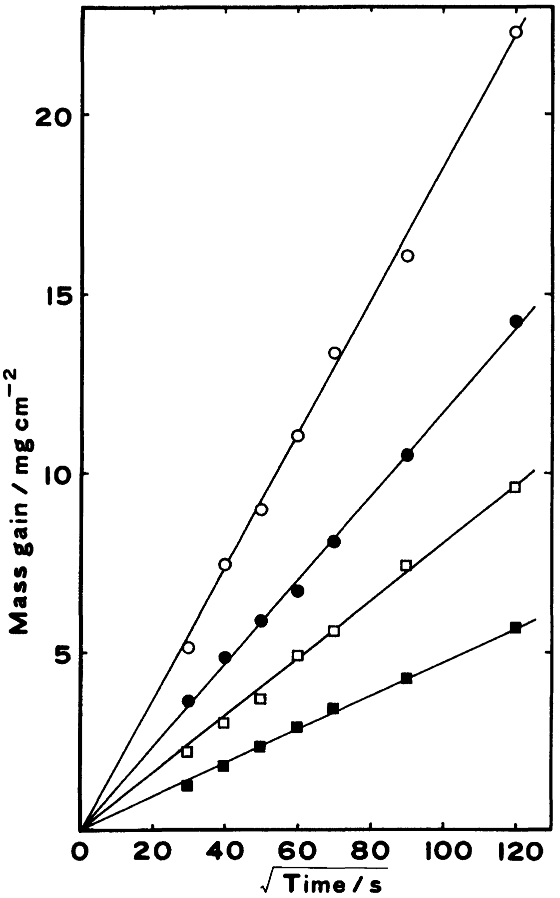

Fig. 8. Selenidization of molybdenum at 873 K under various selenium vapor pressures. 13.3 kPa(○), 4.21 kPa(●), 1.33 kPa(□), 0.40 kPa(■).

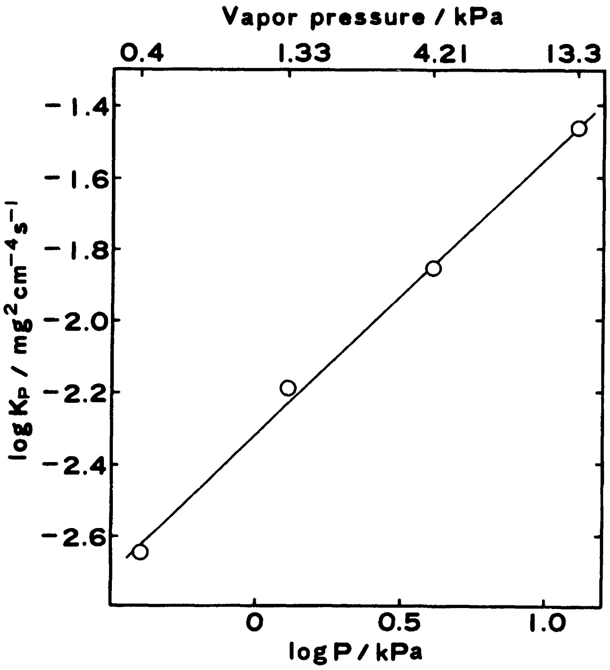

Fig. 9. Selenium vapor pressure dependence of K_p for selenidization of molybdenum at 873 K.

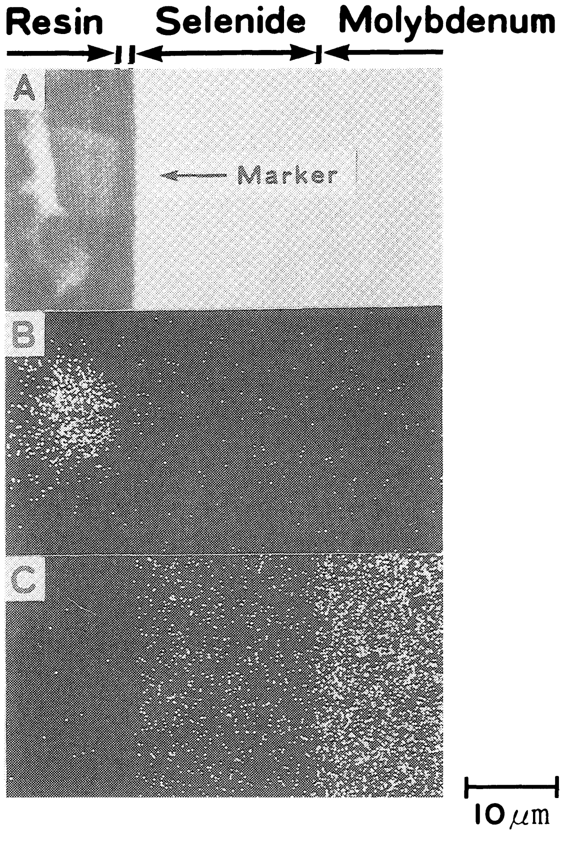

Fig. 10. Cross section of the molybdenum selenide film formed at 848 K for 14.4 ks in selenium vapor at 1.33 kPa and position of a silica fiber marker by EPMA. A : secondary electron image, B : Si $K\alpha$ image, C : Mo $L\alpha$ image.

and are shown in Fig. 3 along with the intensities of Mo $L\alpha$ and Se $L\alpha$ as the ordinate and distance from surface as the abscissa. The intensities of Mo $L\alpha$ and Se $L\alpha$ were nearly constant throughout the entire selenide film. Based on the results of X-ray diffraction and an EPMA measurement, the composition of this selenide film was concluded to be a single layer of $MoSe_2$.

2. Kinetics and Its Temperature Dependence. Although the weight change with time, caused by selenidization, cannot be measured continuously using the sealed-tube method, kinetic results obtained by weighing both before and after exposure to selenium vapor are shown in Figs. 4 and 5. It should be noted that each datum point was obtained from an individual specimen. All of the plots yield straight lines, showing that the weight gains followed a parabolic rate law, which is based on metal or nonmetal diffusion through a plane parallel scaling film. The values of the parabolic rate constants (K_p) obtained from the slopes of these straight lines are summarized in Table 1.

A semilogarithmic plot of K_p vs. the reciprocal of the absolute temperature is shown in Fig. 6. This relationship gives a straight line in the temperature range of 773—873 K, which is approximately expressed as follows:

$$K_p = 4.72\ \exp(-48.1\ \mathrm{kJ\,mol^{-1}}/RT)\ \mathrm{mg^2\,cm^{-4}\,s^{-1}}.$$

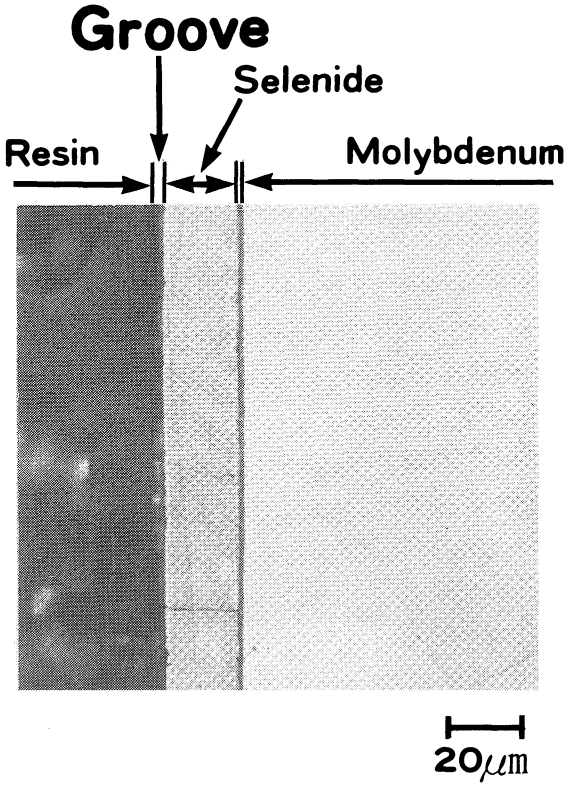

Fig. 11. Optical micrograph of the molybdenum selenide film formed at 848 K for 14.4 ks in selenium vapor at 1.33 kPa.

Table 1. Values of the Parabolic Rate Constants for Selenidization of Molybdenum

Temperature/K	Selenium pressure/kPa	$K_p/10^{-3}$ mg^2 cm^{-4} s^{-1}
773	1.33	2.65±0.39
798	1.33	3.37±0.24
823	1.33	4.28±0.25
848	1.33	4.84±0.25
873	0.40	2.26±0.062
873	1.33	6.47±0.23
873	4.21	13.9 ±0.44
873	13.3	34.4 ±2.13
923	1.33	6.73±0.24
973	1.33	6.51±0.33

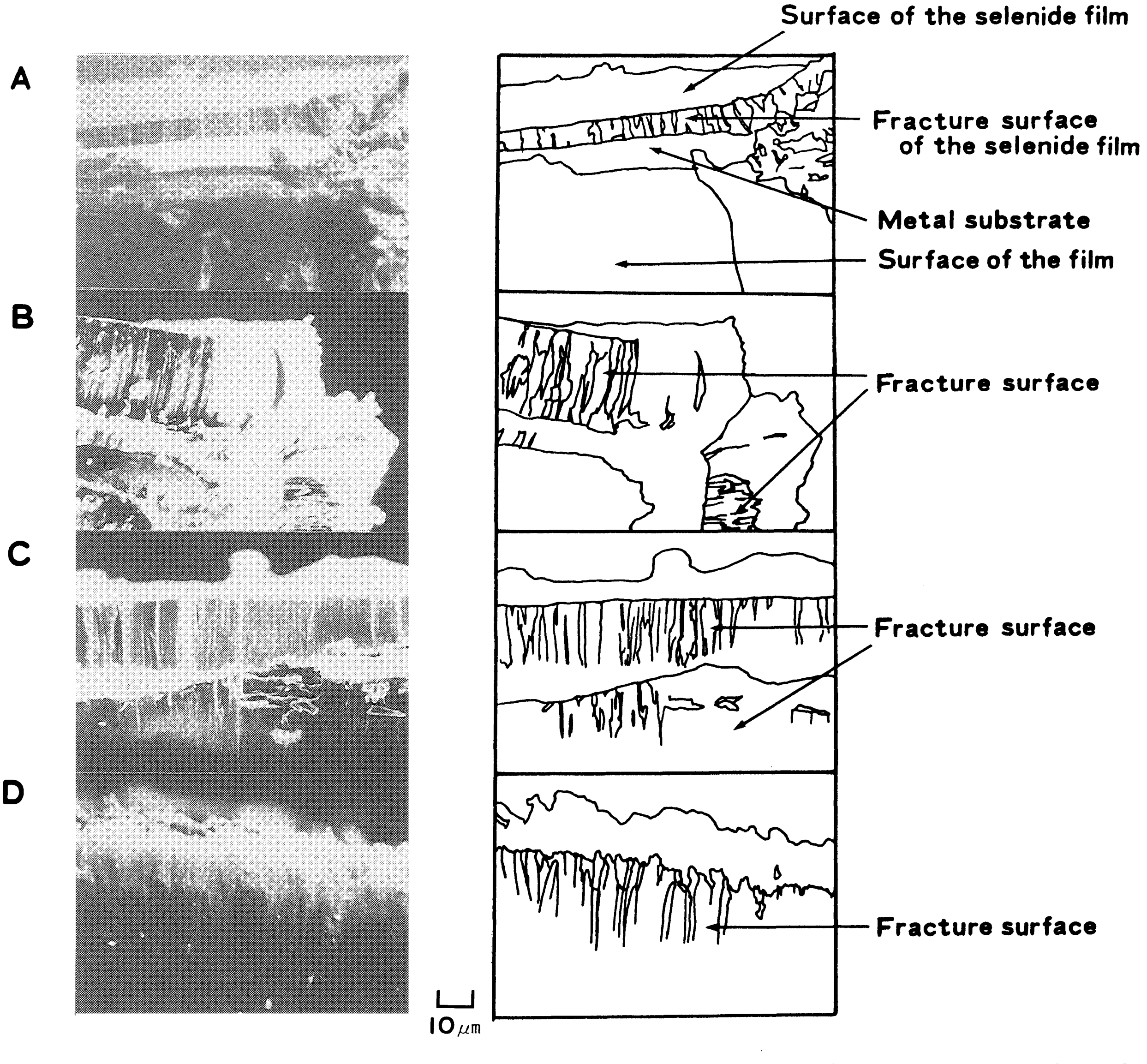

Fig. 12. Secondary electron images of fracture surfaces of the molybdenum selenide films formed at 873 K for 2.5 ks at various vapor pressures and their schematic illustrations. A: 0.40 kPa (3 Torr); B: 1.33 kPa (10 Torr); C: 4.21 kPa (31.6 Torr); D: 13.3 kPa (100 Torr).

The values of K_p at 923 and 973 K have been relatively lowered. The sealed silica tube was divided into pieces, and its inner wall, on which the specimen was placed, was examined using a wavelength dispersive X-ray spectrometer (JSX-60PX, Japan Electron Optics Laboratory, Ltd.) equipped with an analyzing crystal:

LiF(200)$2d$=0.4028 nm. Since Mo and Se spectra were observed (Fig. 7), the deviations at 923 and 973 K from the above relationship (Fig. 6) could be regarded as being caused by a sublimation of the reaction products.

3. Kinetics and Its Pressure Dependence. Figure 8 represents the findings of selenidization of molybdenum at 873 K under selenium vapor pressures of 0.40—13.3 kPa, and shows that all of the selenidizations obeyed a parabolic-type behavior. The rate constants obtained from these slopes are given in Table 1. A log–log plot of K_p vs. the selenium vapor pressure is shown in Fig. 9. This relationship gives a straight line in the selenium vapor pressure range of 0.40—13.3 kPa. K_p obviously increases with an increase in the selenium vapor pressure. The pressure dependence of the K_p is related to the diffusion process of the metal or nonmetal in the selenide film (described later).

4. Diffusing Species. Since in selenide growth the rate-determining step seemed to be a diffusion process, a marker experiment relating to the diffusion process[16) was carried out for the selenidization of molybdenum by using silica fiber as a marker. Figure 10A shows a secondary electron image of the cross section of a specimen selenidized at 848 K for 14.4 ks in selenium vapor at 1.33 kPa, which was examined by EPMA. The portion indicated by an arrow was confirmed to be the silica fiber marker by the Si $K\alpha$ image shown in Fig. 10B. Figure 10C shows the Mo $L\alpha$ image, which corresponds to Figs. 10A and 10B.

Althogh the marker was isolated from the selenide scale (Fig. 10A), this isolation took place due to a thermal contraction of the methacrylate resin. Figure 11 shows an optical micrograph for the wide part of the same specimen shown in Fig. 10, which indicates that the formation of a groove occurred all over the selenide film. Since the marker is situated at the selenide/selenium vapor interface, the reaction can be regarded as being controlled by the diffusion of selenium through the selenide film.

Figure 12 shows secondary electron images of the fracture surfaces of molybdenum selenide films formed at 873 K for 2.5 ks at various vapor pressures, as well as their schematic illustrations. These films have a columnar structure perpendicular to the substrate surfaces, as is shown in Fig. 12. From the X-ray diffraction patterns (Figs. 1 and 2) and Fig. 12, the $MoSe_2$ films clearly have an orientation in which the (00l) plane is perpendicular to the substrate surface at each selenium vapor pressure. $MoSe_2$ has been reported to have a layered structure.[13) K_p is greatly dependent on the selenium vapor pressure, as Fig. 9 shows. This dependence of K_p seems to be due to a rapid diffusion of selenium in the van der Waals gaps[17) parallel to the (00l) planes of the $MoSe_2$ films.

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