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Kinetics and Mechanism of the High-Temperature Selenidization of Titanium

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A titanium sheet was selenidized in selenium vapor of 1.33—13.33 kPa at 823—973 K by means of a sealed-tube method. X-Ray diffraction patterns and an electron-probe microanalysis of the product films showed the layer to comprise only $TiSe_2$. Since the selenidization obeyed a parabolic rate law under all of the conditions employed, the rate-determining step was a diffusion process. The parabolic rate constant (K_p) could be expressed as a function of the absolute temperature, and was approximately proportional to the partial pressure of Se_2. A marker experiment indicated that selenium was the component which diffused in the product film.

Metal dichalcogenides have been intensively investigated concerning their crystal structures, non-stoichiometry, and physical properties. There have been several papers concerning the reaction of metals or metal oxides with selenium vapor. The selenidization of molybdenum sheet in selenium vapor gave a highly oriented $MoSe_2$ film having a columnar structure perpendicular to the metal surface.[1,2] On the other hand, fine particles of MX_2 (M=Mo, W; X=S, Se), having fullerene-like structures, were discovered in the products obtained by the reaction of molybdenum or tungsten oxide film with H_2S or selenium vapor.[3] These examples suggest that the reactions between solids and selenium vapor give selenides comprising crystallites which possessed unusual structures, which are not seen in selenides prepared by the solid–solid reaction or by the chemical-vapor transport technique.[4,5]

It is of significance to study the formation kinetics, composition, and orientation of the selenide film formed in the reaction of titanium sheet with selenium vapor, because little has been known about them. The kinetics have been researched only for 673—823 K under selenium pressures of 0.01—4.3 kPa by means of a silica-spring thermogravimetric method.[6] Two of the present authors have reported on the kinetics and diffusing species of selenidization at temperatures of 823—973 K in a selenium vapor at 4.53 kPa by means of a sealed-tube method.[7] The details of its subsequent and further investigation are described in the present paper.

Experimental

Materials. A 1 mm thick titanium sheet with a purity of 99.5 wt% was cut into rectangular pieces of approximately 6×25 mm. According to an analysis by the supplier (Nilaco Corporation), the impurity level of this metal was Fe=460, H=7, N=120, and O=780 ppm. These were vacuum-annealed at 1073 K for 4 h. They were abraded with emery paper (#80, #120, #240, #400, and #1000), then polished with wet fine chromium(III) oxide powder on a buffing cloth, and rinsed in toluene. Their geometric surface areas and weights were measured.

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

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

The tube was inserted into a furnace with two temperature zones, the first zone being used to heat the sample sheet in a sealed silica tube, and the second zone being used to control the vapor pressure of selenium in this tube. The vapor pressure of selenium was governed by the lowest temperature in the closed system. It has been reported that all molecules from Se_1 to Se_8 are present in the selenium vapor.[9] The total selenium pressure (P_{total}) is given as a function of the Celsius temperature by the following expression:[10]

$$\log(P_{\mathrm{total}}/\mathrm{Torr}) = 7.6316 - 4213.0/(202.0 + t/\mathrm{C}) \quad (1)$$
$$(1\ \mathrm{Torr} = 133.322\ \mathrm{Pa}).$$

The apparatus and experimental methods were described in greater detail in a previous paper.[8]

The experiment was carried out under the following conditions: (i) a total selenium pressure of 4.53 kPa (34 Torr) at reaction temperatures of 823, 873, 923, and 973 K and (ii) a temperature of 923 K at 1.33 kPa (10 Torr), 2.67 kPa (20 Torr), and 13.33 kPa (100 Torr).

Experimental Results

Composition of Product Film. For most of the selenidized samples exfoliation of the product films from the metal substrates took place when they were cooled to room temperature. The X-ray diffraction (XRD) patterns of the exfoliated films ((a) and (b) in Fig. 1) and powdered samples of the exfoliated films ((c), (d), (e), and (f) in Fig. 1) were obtained. All of the diffraction angles in these patterns were in agreement with the literature values of the powder data of TiSe$_2$ (hexagonal, a=3.540, c=6.008 Å),[11] shown in Fig. 1(g). In Fig. 1(a) and Fig. 1(b), the intensities of the diffraction peak from the (002) plane relative to the peaks from the (100) and (110) planes were very weak, compared with those in (c), (d), (e), and (f), indicating that the selenide films have a predominant orientation of their planes parallel to the c-axis of TiSe$_2$. This orientation is observed for the films formed under all selenium vapor pressures.

Figure 2 shows the secondary electron images of the fracture surfaces of the exfoliated films formed at 923 K for 3 h at various vapor pressures. These films have a columnar structure perpendicular to the substrate surfaces. This columnar structure was probably formed as the result of predominant growth of crystalline grains parallel to the (00l) plane.

The composition variations through the cross section of a selenide film were examined using an electron-probe microanalyzer (EPMA). An exfoliated film formed at 823 K and a total selenium pressure of 4.53 kPa for 4 h was embedded in a methyl methacrylate polymer; its cross section was polished with fine chromium(III) oxide powder, and the intensities of Ti $K\alpha$ and Se $L\alpha$ radiation were measured. The results are shown in Fig. 3. As Fig. 3 shows, the concentration of titanium is nearly constant throughout the selenide film, and that of selenium slightly decreases along with an increase in the distance from the surface. In combination with the result of an XRD analysis, the composition of this selenide film was concluded to be a single layer of TiSe$_2$.

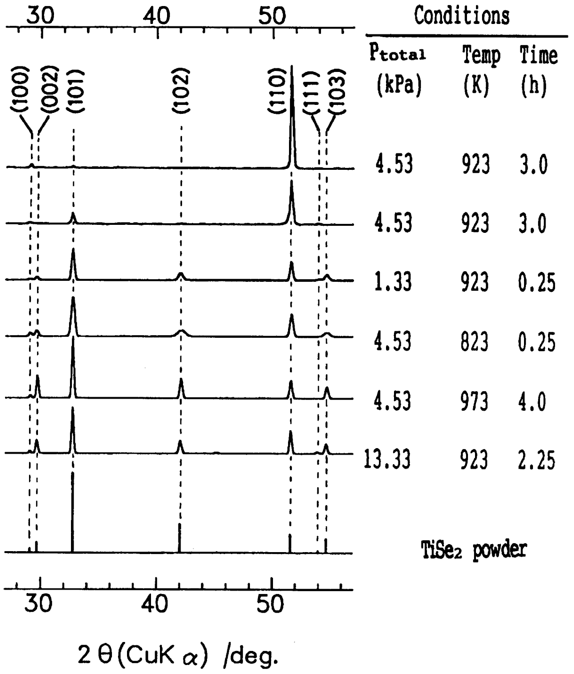

Fig. 1. X-Ray diffraction patterns of the titanium selenide formed under various conditions. (a): gas side of the exfoliated film; (b): metal side of the exfoliated film; (c), (d), (e), (f): powdered sample of the exfoliated films; (g): the powder pattern of TiSe$_2$.[11]

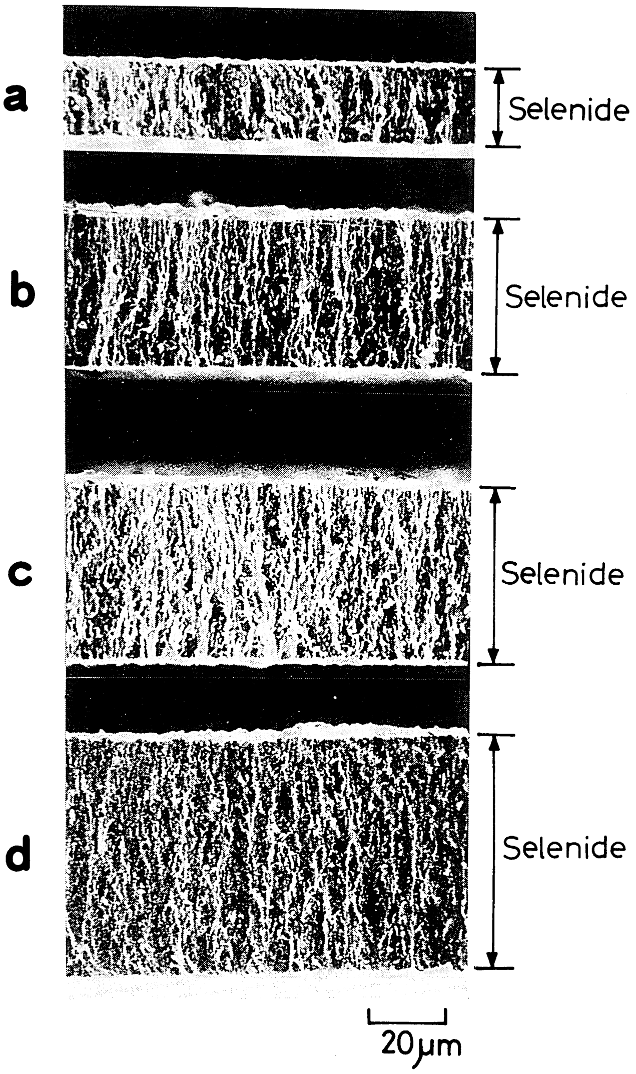

Fig. 2. Secondary electron images of fracture surface of the exfoliated titanium selenide films formed at 923 K for 3 h at total selenium pressures of 1.33 (a), 2.67 (b), 4.53 (c), and 13.33 kPa (d). The upper side of each film corresponds to the gas/selenide interface.

Kinetics and Diffusing Species. Mass gains of the specimens were observed by weighing both before and after selenidization. Figure 4 shows plots of the mass gain per unit area against (time)$^{1/2}$. It should be noted that each datum point was obtained from a separated specimen. The plots exhibit a linear relation for all of the temperatures and pressures employed in this study, showing that the selenidization proceeds according to a parabolic rate law. Selenidization is controlled by the diffusion process of selenium or titanium through the product film. The values of the parabolic rate con-

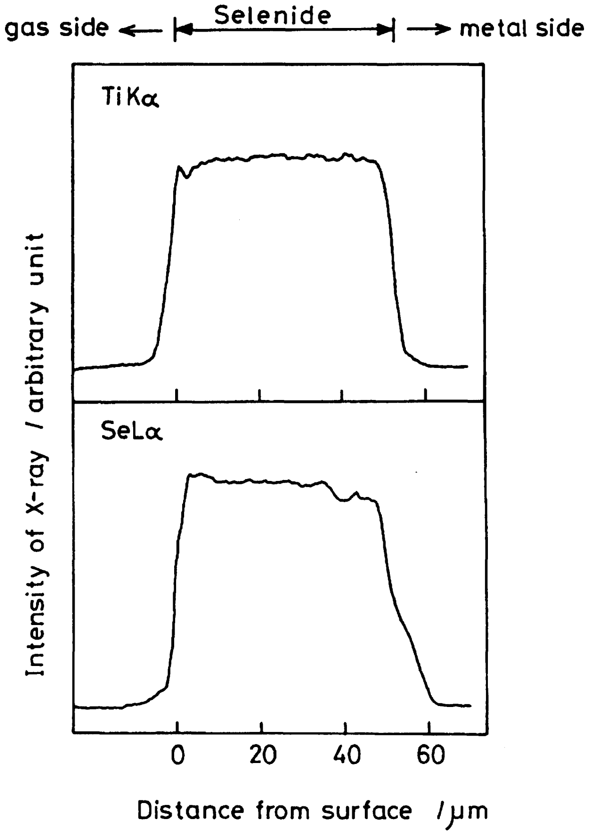

Fig. 3. Distribution profiles of titanium and selenium in the exfoliated titanium selenide film formed at 823 K and total selenium pressure of 4.53 kPa for 4 h.

stants (K_p) obtained from the slopes of these straight lines are summarized in Table 1.

A marker experiment was carried out by using a silica fiber as a marker. The cross section of a sample sheet selenidized at 923 K and a total selenium pressure of 4.53 kPa for 4 h was examined by EPMA. Figure 5A represents the secondary electron image of the cross section. In Fig. 5A the circle existing at the gas/selenide interface (indicated by an arrow) is the silica marker. This was confirmed by X-ray radiation of Si $K\alpha$, as shown in Fig. 5B. From this result it was concluded that selenidization proceeds by the inward diffusion of selenium through the selenide film.

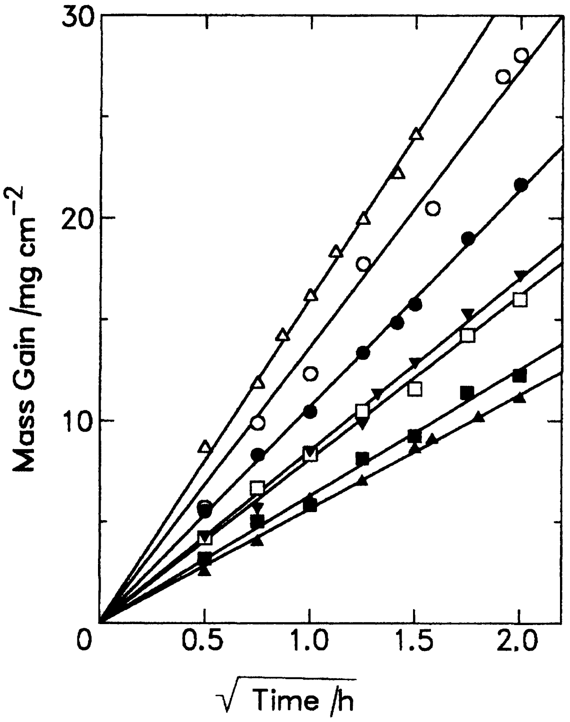

Fig. 4. Selenidization of titanium in selenium vapor. 973 K, 4.53 kPa (○); 923 K, 4.53 kPa (●); 873 K, 4.53 kPa (□); 823 K, 4.53 kPa (■); 923 K, 13.33 kPa (△); 923 K, 2.67 kPa (▼); 923 K, 1.33 kPa (▲).

Temperature and Pressure Dependence of Kinetics. A semilogarithmic plot of K_p vs. the reciprocal of the absolute temperature at P_{total} of 4.53 kPa gave a linear relation (not shown); then, K_p was approximately expressed as a function of temperature,

$$K_p=1.05\times10^6\exp(-69.9\ \text{kJ mol}^{-1}/RT)\quad[\text{mg}^2\,\text{cm}^{-4}\,\text{h}^{-1}]\quad(823\text{—}973\ \text{K},\ P_{\text{total}}=4.53\ \text{kPa}).\quad(2)$$

In Table 1, K_p at 923 K obviously increases along with an increase of P_{total}. A log–log plot of K_p vs. P_{total} at 923 K is shown by open circles in Fig. 6, exhibiting not a straight line, but a curved one. The partial pressures of Se_2 (P_{Se_2}), calculated by using the equilibrium constants given by Illarionov and Lapina,[12] are also listed in Table 1. A log–log plot of K_p vs. P_{Se_2} is shown by closed circles in Fig. 6. This gives a straight line. From the slope of this line, the following relation is obtained:

$$K_p \propto {P_{Se_2}}^{1.05}\quad(923\ \text{K},\ P_{Se_2}=1.30\text{—}9.51\ \text{kPa}).\quad(3)$$

Table 1. Parabolic Rate Constants for Selenidization of Titanium

Temperature /K	$P_{\text{total}}$$^{a)}$ /kPa	$P_{Se_2}$$^{b)}$ /kPa	K_p /10^{-2} mg^2 cm^{-4} h^{-1}
823	4.53	2.08	0.39 ±0.04
873	4.53	3.29	0.66 ±0.05
923	4.53	4.08	1.15 ±0.09
973	4.53	4.37	1.87 ±0.19
923	1.33	1.30	0.31 ±0.02
923	2.67	2.51	0.69 ±0.07
923	13.33	9.51	2.58 ±0.10

a) Selenium total pressure. b) Partial pressure of Se_2.

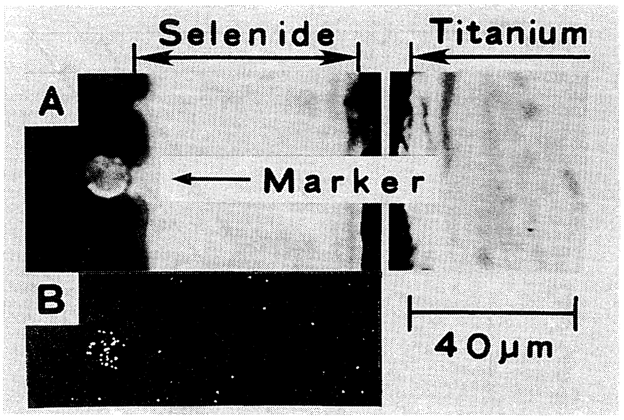

Fig. 5. A: Secondary electron images of cross section of exfoliated titanium selenide film formed at 923 K for 4 h at total selenium pressure of 4.53 kPa. The position of the silica marker is indicated by an arrow. B: Si *Kα* image.

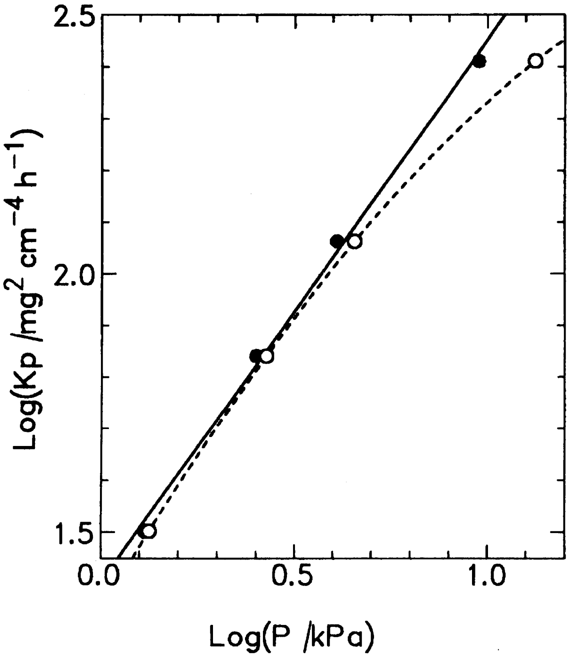

Fig. 6. Selenium vapor pressure dependence of K_p for selenidization of titanium at 923 K. ○: total selenium pressure (P_{total}), ●: partial pressure of Se_2 (P_{Se_2}).

Thus, K_p is approximately proportional to P_{Se_2}.

Discussion

$TiSe_2$ has a layered structure comprising van der Waals gaps parallel to the (00*l*) plane.[13)] The results of an XRD analysis show that the (00*l*) plane of the $TiSe_2$ film has a predominant orientation that is perpendicular to the metal substrate. A similar orientation has been reported for $MoSe_2$ films formed in the selenidization of a molybdenum sheet.[1,2)] This reaction was also controlled by the inward diffusion of selenium through the product film.[2)] $MoSe_2$ also shows a layered structure having van der Waals gaps. It has been reported[1)] that the orientation of the $MoSe_2$ film is due to the rapid diffusion of selenium in the gaps. The P_{Se_2} dependence of K_p for the selenidization of molybdenum sheet was examined using published data.[2)] Then, an approximately proportional relationship, $K_p \propto P_{Se_2}^{0.96}$ (873 K, P_{Se_2}=0.39—6.27 kPa), was obtained. This fact shows that the behavior of the selenidization of titanium is similar to that of molybdenum.

Based on the assumption that Se_2 molecules diffuse in the van der Waals gaps which are perpendicular to the metal substrate, the P_{Se_2} dependence of the kinetics is discussed below. The following equilibrium is provided:

$$Se_2(gas) \rightleftharpoons Se_2(gas/selenide), \tag{4}$$

where Se_2(gas) and Se_2(gas/selenide) are Se_2 molecules in the gas phase and in the van der Waals gaps near to the gas side surface of the $TiSe_2$ film, respectively. Its equilibrium constant (K) is expressed as $K = [Se_2(gas/selenide)]/P_{Se_2}$. Since the rate-determining step is the diffusion of selenium, the parabolic rate constant should be proportional to a difference in the selenium concentrations at the gas side ([Se_2(gas/selenide)]) and the metal side ([Se_2(selenide/metal)]) of the $TiSe_2$ film,

$$K_p \propto [Se_2(gas/selenide)] - [Se_2(selenide/metal)]. \tag{5}$$

The concentration variation of selenium through the $TiSe_2$ film (Fig. 3) shows evidence of this difference. Since an equilibrium dissociation pressure of selenium at the selenide/metal interface is usually much lower than P_{Se_2}, an approximate relation,

$$K_p \propto KP_{Se_2}, \tag{6}$$

is given by using $[Se_2(gas/selenide)] = KP_{Se_2}$. This relation is consistent with the observed P_{Se_2} dependence, viz., Eq. 3. Only the Se_2 species in the gas phase is considered to contribute to selenidization, because (i) the partial pressures of Se_1 are much lower than those of Se_2 at temperatures below 1277 K[14)] and (ii) the diffusion of Se_n (n=3—8) molecules in the van der Waals gap seems to be difficult due to their large sizes.

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