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The Electrical and Structural Features of Vanadium-oxide Films as Formed by the Thermal Decomposition of Vanadium Naphthenate

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Vanadium-oxide thin film, which was amorphous, brownish, and transparent, was prepared more conveniently by improving Sekiya-Matsushita's method by, for instance, decomposing vanadium naphthenate thermally; that is, 10 wt% of a 1-butanol solution of vanadium naphthenate was dropped on slide glass, dried in air, decomposed at 600 °C for 20 min under 0.5 l/min of a N_2 stream which was equilibrated with water at 21.5 °C, and then taken out rapidly into the air for cooling. The VO thin film thus prepared usually showed an abrupt change in electric conductivity from 2×10^{-5} to 1×10^{-4} Ω^{-1} at about 60 °C. The electrical feature was greatly affected by the addition of other metal oxides, such as Na_2O, TiO_2, Cr_2O_3, MoO_3, and ZrO_2. Both the conductivity and the gap tended to decrease in the cases of TiO_2, Cr_2O_3, and MoO_3, and to increase in ZrO_2. On the addition of Na_2O, however, the conductivity increased only at temperatures lower than the transition point; thus, the gap decreased greatly, almost disappearing. It was concluded from these facts that the electrical feature of the vanadium-oxide film must be controlled to a great extent by the addition of some compounds of vanadium oxide with the other metal oxides formed at the grain boundary of the VO_2 amorphous particles. That is, the larger the conductivity of the compound in the boundary layer, the more clearly the intrinsic feature of the VO_2 particles appears, and *vice versa.*

Many vanadium-oxide compounds show a metal insulator or semiconductor transition, accompanied by a small change in the crystal structure.[1] Because big changes in not only the electrical property, but also the magnetic and optical properties, occur at the transition point, many solid-state physicists and chemists have worked on these subjects.[2—9] In order to investigate in detail such solid-state properties, the single crystal[10,11] and the thin film of the compounds have been prepared. With respect to the preparation of those thin films, the methods of the chemical deposition of the compounds from the vapor phase and the oxidation of the metal particles sputtered on substrates have mainly been applied,[12—16] but the procedures seem to be too complicated and it seems to be difficult to obtain a good film constantly. Recently, Sekiya and Matsushita[17] have reported a convenient method for the preparation of a vanadium-oxide thin film with a conductivity gap of one order of magnitude at about 60 °C. We have taken notice of the Sekiya-Matsushita method because the film may be used for studying the catalytic property of vanadium-oxide compounds in connection with their solid-state properties. In the present experiment, the method of preparing the vanadium-oxide thin film (VO thin film) was re-examined in order to make the procedure of Sekiya-Matsushita more convenient; further, the method of preparing VO thin films containing other metal oxides, such as Na_2O, TiO_2, Cr_2O_3, MoO_3, and ZrO_2, was examined. The electrical and structural features of the VO thin films thus prepared were discussed.

Experimental

1) Materials and Procedures. Vanadium naphthenate (containing *ca.* 3 wt% of the vanadium(IV) ion, Harima Kasei Co., Ltd.) was dissolved in 1-butanol to prepare 10 wt% of the solution. A thin film of vanadium oxide (VO thin film) was formed on a Pyrex glass plate by the following procedures. The glass plate was cut in the size of 11×24 mm²; on both ends there had previously been deposited gold film (7 mm in width) as an electrode in order to keep a good ohmic contact during the conductivity measurements. Three droplets of the vanadium–naphthenate solution were placed on the plate, and it was dried at 20 °C in air for 1 h. The plate was then inserted into a furnace kept at 600 °C for 20 min to decompose the vanadium naphthenate and then rapidly taken out into the air for cooling. A nitrogen gas stream, bubbled in water kept exactly at 21.5 °C, was introduced into the furnace during the decomposition.

Upon the preparation of the VO thin films containing other metal oxides, such as Na_2O, TiO_2, Cr_2O_3, MoO_3, and ZrO_2, these oxides (CH_3ONa in the case of Na_2O) were weighed exactly and were then ground well with 10 wt% of a 1-butanol solution of vanadium naphthenate in an agate mortar in order to dissolve them fully. Then, the solution containing the metal oxides was dropped on the glass plate with the gold electrodes and subsequently decomposed by the procedures used in the case of the pure VO thin film. The concentrations of these metal oxides added to vanadium oxide were changed in the range of 10—60 atom%; (M)/(V).

2) Measurements. The electric conductivity was measured by the usual two-probe method. In the measurements of the conductivity, the temperature was elevated from 20 to 200 °C at the constant speed of 4.5 °C/min by the use of a programable controller, Yokogawa Model PC-182. In order to determine exactly the relationship between the conductivity and the temperature, an automatic-measurement system was constructed; both the potential difference between the ends of the VO thin film and the thermoelectric power generated in the CA-thermocouple attached to the film were amplified simultaneously by means of microvoltmeters, Ookura Denki Model AM-2002, and then introduced, at intervals of 1 °C into a microcomputer, Sharp Model MZ-80K2E, *via* a 12-bit A/D-convertor, Hoowa Sangiyo Model ADL-1224. The X-ray analyses of the thin films were done in the range of $2\theta=4$—60° by setting the glass plate with the VO thin film deposited directly in the sample holder. The diffractometer used was Rigaku Denki Model GF-Rad-γA. Cu $K\alpha$ radiation and nickel filter were used.

Results

1) Preparation Conditions of Vanadium-oxide Thin

Film. The VO thin films were prepared by decomposing the vanadium naphthenate for 10—20 min at 600 °C in a nitrogen stream equilibrated with water kept exactly at 21.5 °C. As a result, the VO thin film, transparent, was found to be formed only by decomposition for 20 min; its conductivity and the conductivity gap at the transition point were similar in extent with those shown in Fig. 1. In the VO thin films formed by decomposition for 10 and 15 min, however, both the conductivity and the gap were quite small. The VO thin films were also prepared by decomposing the vanadium naphthenate in a nitrogen stream equilibrated with water kept at 20—25 °C at 600 °C for 20 min. In the VO thin films formed in the N_2 stream equilibrated with water kept at 21 and 22 °C, an electrical feature similar to that shown in Fig. 1 was found. However, in the films formed in the stream equilibrated with water kept at 20 °C, both the conductivity and the gap became very small, and in those formed at 23—25 °C the transparency disappeared completely. Therefore, it was make clear that the VO thin film, which is transparent and which, further, shows the conductivity change of one order of magnitude accompanied by a phase transition at about 60 °C, could easily be prepared under the following conditions: vanadium-naphthenate film formed by dropping 10 wt% of the 1-butanol solution on a Pyrex glass plate and then by drying should be decomposed at 600 °C for 20 min in a nitrogen stream equilibrated with water kept at exactly at 21.5 °C.

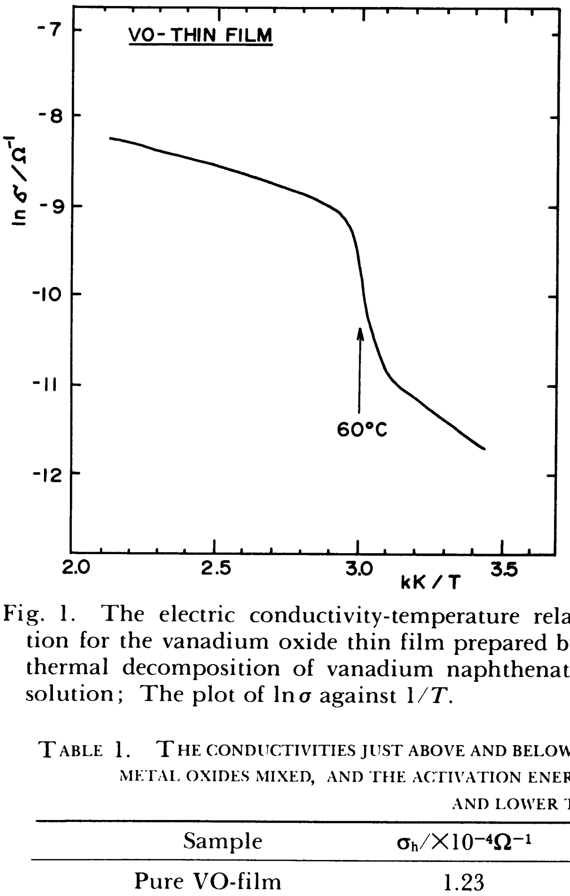

Fig. 1. The electric conductivity-temperature relation for the vanadium oxide thin film prepared by thermal decomposition of vanadium naphthenate solution; The plot of $\ln\sigma$ against $1/T$.

The thickness of the VO thin film thus prepared was evaluated roughly as 1—2 μm from the amounts of the vanadiun-naphthenate solution dropped on the substrate. The activation energies for the conductivity were estimated as 0.08 and 0.21 eV for above and below the transition temperature respectively, as shown in Table 1. Furthermore, the larger the conductivity, the smaller the activation energy tended generally to become, especially at temperatures above the transition point.

2) The Lnσ-1/T Curves of the VO Thin Films Containing Other Metal Oxides. With respect to the VO thin films formed from the vanadium-naphthenate solution, in which 10 and 40 atom% of sodium to vanadium were mixed, the conductivity-temperature curves ($\ln\sigma-1/T$) are shown in Figs. 2-a and b respectively. The conductivity of the film at 10 atom% was kept at the same level with that of the pure VO thin film above the transition temperature, but it became much higher than the pure VO film below that temperature. Thus, the conductivity gap at the transition point apparently decreased; further, in the film at 40 atom%, the conductivity gap almost disappeared. With respect to the VO thin films containing TiO_2, at 10 atom%, the $\ln\sigma-1/T$ curve was sim-

TABLE 1. THE CONDUCTIVITIES JUST ABOVE AND BELOW THE TRANSITION POINT FOR THE VO-THIN FILM WITHOUT AND WITH OTHER METAL OXIDES MIXED, AND THE ACTIVATION ENERGIES FOR THE ELECTRIC CONDUCTION AT TEMPERATURES HIGHER AND LOWER THAN THE TRANSITION POINT

Sample	$\sigma_h/\times10^{-4}\Omega^{-1}$	$E_a(h)/eV$	$\sigma_l/10^{-4}\Omega^{-1}$	$E_a(l)/eV$
Pure VO-film	1.23	0.08	0.22	0.21
$NaOCH_3$				
10 atom%	1.19	0.05	0.89	0.13
40 atom%	0.84	0.07	0.64	0.15
TiO_2				
10 atom%	1.28	0.09	0.26	0.24
20 atom%	0.42	0.08	0.29	0.20
30 atom%	0.14	0.13	0.12	0.31
Cr_2O_3				
10 atom%	0.32	0.12	0.15	0.23
40 atom%	0.21	0.12	0.17	0.21
MoO_3				
20 atom%	1.15	0.13	0.31	0.15
40 atom%	0.29	0.16	0.13	0.21
ZrO_2				
30 atom%	0.79	0.11	0.21	0.28
60 atom%	3.08	0.03	0.85	0.33

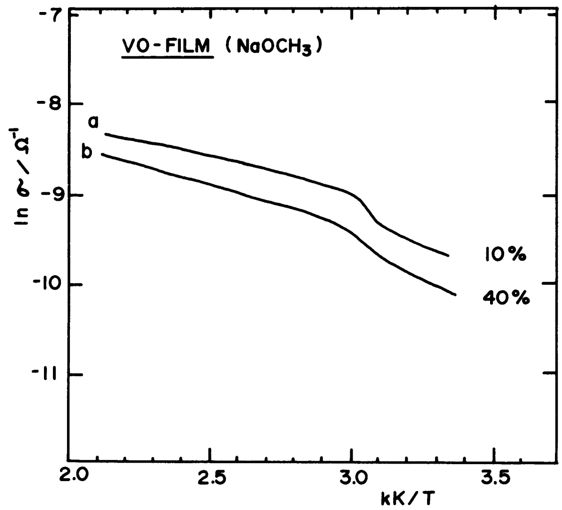

Fig. 2. The lnσ-1/T curves for the VO thin films containing 10 and 40 atom% of Na_2O.

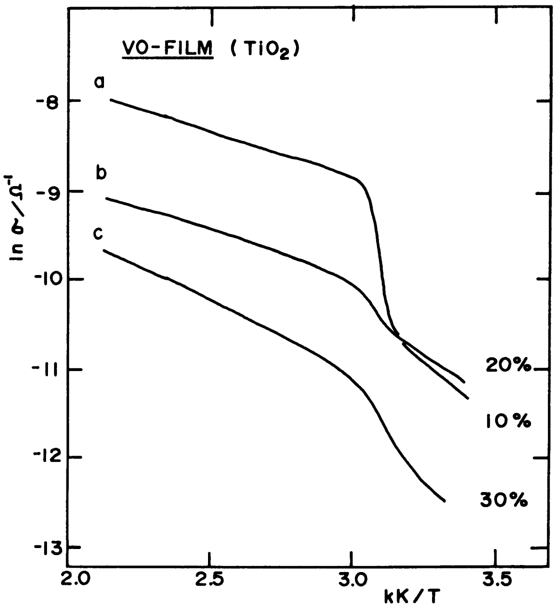

Fig. 3. The lnσ-1/T curves for the VO thin films containing 10, 20, and 30 atom% of TiO_2.

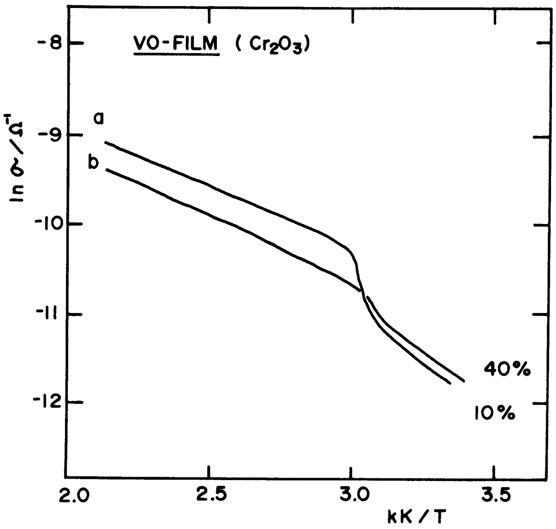

Fig. 4. The lnσ-1/T curves for the VO thin films containing 10 and 40 atom% of Cr_2O_3.

ilar to that of the pure VO thin film, as can be seen by comparing Fig. 3-a with Fig. 1, but at 20 atom% the σ-values considerably decreased only above the transition temperature, and thus the conductivity gap almost disappeared, as can be seen in Fig. 3-b. At 30 atom%, however, the conductivity decreased throughout the temperature region, as is shown in Fig. 3-c. With the VO thin films containing Cr_2O_3, both the conductivity and the gap considerably decreased at 10 atom%, and the gap almost disappeared at 40 atom%, as Fig. 4 shows. With the VO thin films containing MoO_3, the feature of the lnσ-1/T curve did not change, even at 20 atom%, but both the conductivity and the gap decreased considerably at 40 atom%,

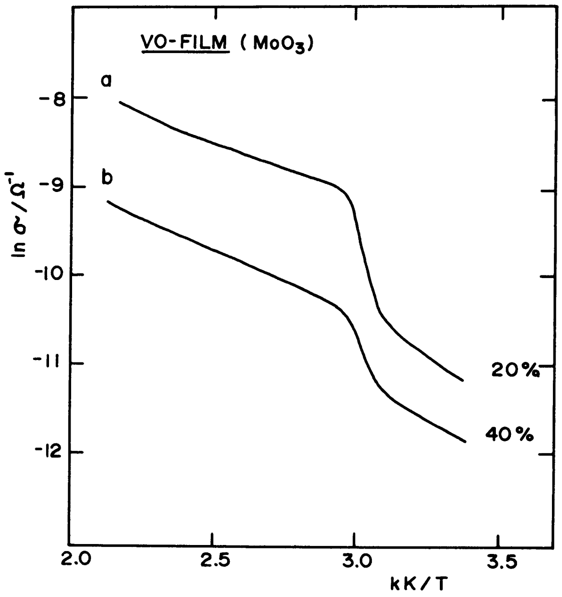

Fig. 5. The lnσ-1/T curves for the VO thin films containing 20 and 40 atom% of MoO_3.

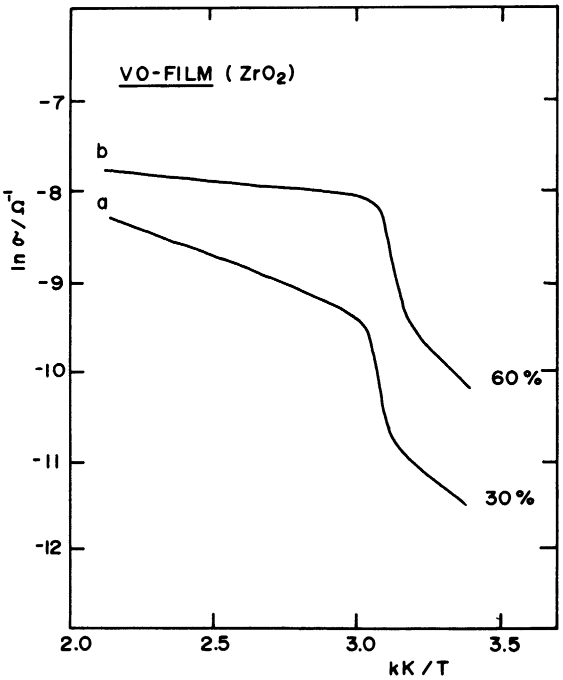

Fig. 6. The lnσ-1/T curves for the VO thin films containing 30 and 60 atom% of ZrO_2.

as Fig. 5 shows. With respect to the VO thin film containing ZrO_2, however, the conductivity and the gap tend to increase with an increase in the content of ZrO_2, especially at 60 atom%. Furthermore, it is known form Fig. 6-b and Fig. 1 and in Table 1 that the inclination of the $\ln \sigma - 1/T$ curve increases greatly above the transition temperature, while it decreases below that temperature.

3) X-Ray Analyses of the VO Thin Films. The X-ray diffraction patterns of the pure VO thin film are shown in Fig. 7-a, where the strong lines at $2\theta = 38.65$ and 44.95° are those caused by the gold electrodes deposited on both ends of the glass plate. Only rather weak peaks are seen at $2\theta = 12.2$, 19.3, 28.0, and 29.2° in Fig. 7-a, except for a very broad unsplit line. These data suggest that the pure VO thin film is composed of very small crystalline particles or amorphous particles. X-Ray diffraction patterns similar to those of the pure VO thin film were also found in all the VO thin films containing TiO_2, Cr_2O_3, and MoO_3 except for the very weak peaks which appeared at angles differing a little from sample to sample, as Figs. 7-b—f show. However, no compounds corresponding to those weak peaks were found in any ASTM card. On the other hand, many sharp peaks were found in the X-ray diffraction patterns for the VO thin film containing ZrO_2, as Fig. 7-f shows; they are summarized in Fig. 8. Thus, it has to be emphasized that, only in ZrO_2 is the VO thin film composed of rather large crystalline particles. However, no compounds corresponding to those peaks were found in the ASTM cards.

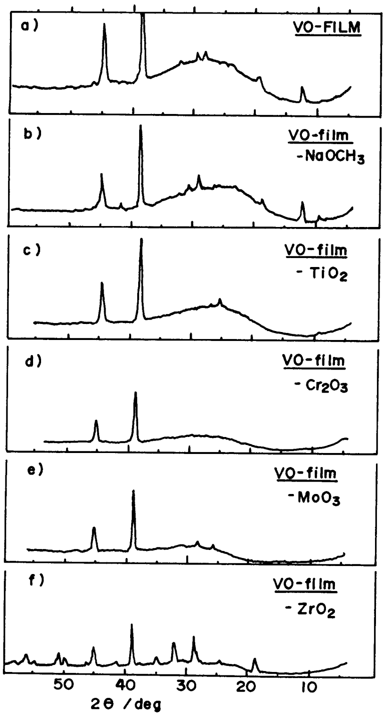

Fig. 7. X-Ray powder diffraction spectra for the vanadium oxide films: a) The pure VO-film, b) the VO-film containing 40 atom% of Na_2O, c) 30 atom% of TiO_2, d) 40 atom% of Cr_2O_3, e) 40 atom% of MoO_3, and f) 60 atom% of ZrO_2.

Discussion

1) Preparation Conditions of the Vanadium-oxide Thin Film. Sekiya and Matsushita successfully prepared a vanadium-oxide thin film by the thermal decomposition of vanadium naphthenate on a slide glass and a quartz plate.[17] The VO thin film showed a crystalline state and a conductivity change of about one order of magnitude at about 60 °C. To obtain a conductivity gap of such an extent, a thermal decomposition procedure must be repeated four times while the temperature is elevated at the speed of 5 °C/min from 25 up to 600 °C. The present paper proposes a more convenient procedure for the preparation of a VO thin film which showed a conductivity and a gap almost identical in extent with those of Sekiya and Matsushita; that is, the vanadium-naphthenate film formed by drying 10 wt% of the 1-butanol solution on a Pyrex glass plate needs to be decomposed thermally only once at 600 °C for 20 min under 0.5 l/min of a nitrogen stream equilibrated with water kept

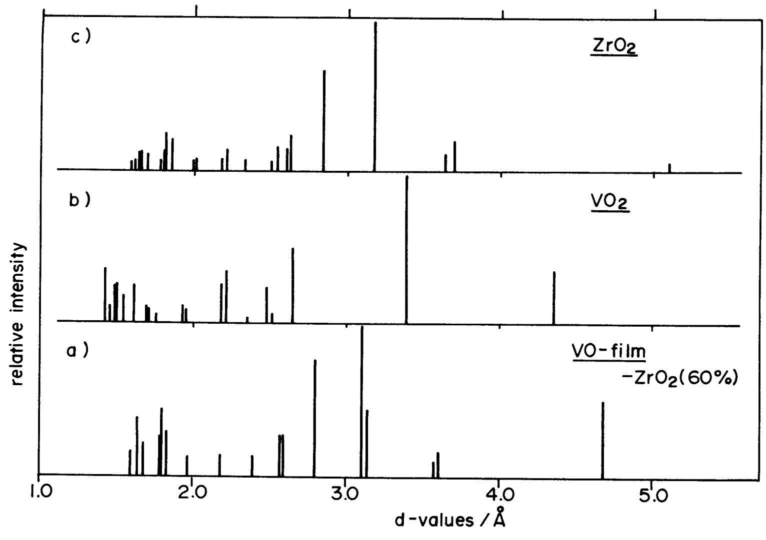

Fig. 8. X-Ray powder diffraction patterns for a) the VO-film, containing 60 atom% of ZrO_2, b) VO_2 crystalline powder,[19] and c) the original ZrO_2 powder.

at 21.5 °C and then to be rapidly taken out into the air. Sekiya and Matsushita suggested that the water vapor contained in the N_2 stream might affect the hydrolysis process of the vanadium naphthenate during the decomposition and might thus be an important factor in the formation of the VO thin film.[17] In the present study, the water vapor was confirmed to play a very important role in the formation process of the VO thin film; that is, under saturated water vapor at 21.0 and 22.0 °C, a favorable conductivity was obtained, but under that at 20.0 °C, both the conductivity and the gap became quite small, and under that at 23—25 °C, the transparency disappeared completely and the color changed to dark blue, as has been mentioned above. These results suggest that, under a rather high vapor pressure, the rates of the decomposition and the growth of the vanadium-oxide particles are accelerated to a great extent, and that thus, the VO_2 particles grown become so large as to block the transmission of visible light, while, on the contrary, under a lower vapor pressure, the decomposition and the growth of the particles cannot occur rapidly, so that both the conductivity and the gap become small.

2) *The Conductivity Changes in the VO Thin Films Containing Other Metal Oxides.* The VO_2 single crystal showed a metal semiconductor phase transition at 340 ± 2 K (67 ± 2 °C), and the specific conductivity changed abruptly from 10^{-3} to 10^{1} $\Omega^{-1}\text{cm}^{-1}$ at the transition point.[1,18] In fact, the inclination of the $\ln \sigma$-$1/T$ curve changed from a positive to a negative value in the VO_2 single crystal. The conductivities, σ_l and σ_h, which were estimated by extrapolating the $\ln \sigma$-$1/T$ curves from the temperatures below and above the transition point to the transition temperature in Fig. 1, were 2.2×10^{-5} and 1.2×10^{-4} Ω^{-1} respectively, as Table 1 shows. In the vanadium-oxide film of Sekiya and Matsushita,[17] 6.7×10^{-5} and 1×10^{-3} Ω^{-1} have been obtained as the values corresponding to σ_l and σ_h respectively. The conductivities of the thin films prepared by Sekiya *et al.* and by us at the transition point are very small relative to those of the VO_2 single crystal. Such a large difference in the conductivity is probably caused by the difference in dimensions. The difference might also arise from the difference in the extent of the contribution of the grain boundary to the conductivity; the conductivity is affected by the boundary layer to a much greater extent in the polycrystalline and amorphous films than in the single crystal. The VO thin film of Sekiya *et al.* is probably thicker than the present film because the former has been prepared repeatedly and is composed of rather large crystalline particles, while the present film is composed of amorphous or polycrystalline particles too small to be detected by X-ray diffraction analysis. In fact, both the conductivity and the gap are larger in Sekiya and Matsushita's film rather than in the present one. It can be expected, therefore, that the properties would be affected by those in the boundary layer to a much lesser extent in the former film than in the latter. Based on such an understanding with regard to the the apparent conductivity of the VO thin film, the electrical and structural features of the VO thin films containing the other metal oxides will be discussed below.

The conductivity gap at the transition point almost disappeared in the $\ln \sigma$-$1/T$ curves of the VO thin films, containing 10 and 40 atom% of Na, as shown in Figs. 2-a and b. These films, brown and transparent, are composed of amorphous particles, as is known from the X-ray diffraction paterns in Fig. 7-b, although several minor peaks are seen in the patterns. By comparing the $\ln \sigma$-$1/T$ curves of the VO thin film containing Na_2O with that of the pure VO thin film, the conductivity gap can apparently be seen to decrease because the conductivity increases considerably below the transition temperature upon the addition of Na_2O. Such changes may be caused by some sodium vanadium oxides formed in the grain boundary of the vanadiun-oxide particles. Upon the addition of TiO_2, the $\ln \sigma$-$1/T$ curve was not affected at such rather low contents as 10 atom%, but at a high content, such as 20 or 30 atom%, it decreases as a whole, and also the conductivity gap becomes small, as shown in Figs. 3-a—c and in Table 1. These result might also be caused by the change in the conductivity of the grain boundary, accompanied by the formation of some titanium vanadium oxides. The additions of Cr_2O_3 and MoO_3 similarly affected the $\ln \sigma$-$1/T$ curves, as shown in Figs. 4-a and b Figs. 5-a and b, and also in Table 1, although the effects seem to be relatively small upon the addition of MoO_3.

On the other hand, the conductivities of the VO thin films containing ZrO_2, especially at 60 atom%, generally increase relative to the pure VO thin film. Furthermore, the conductivity gap becomes large, and the inclination of the $\ln \sigma$-$1/T$ curve tends to decrease above the transition point, while, on the contrary, it increases below the transition. That is, the activation energies for the electron conduction were estimated from the inclinations as 0.03 eV above the transition and as 0.33 eV below the transition, while the corresponding values for the pure VO thin film were similarly estimated as 0.08 and 0.21 eV respectively, as shown in Table 1. By comparing these corresponding values, therefore, we can make it clear that the activation energies decrease about 1/3 times at higher temperatures, while, on the contrary, they increase about 1.6 times at lower temperatures, upon the addition of ZrO_2. The change in the electrical property is probably connected with the facts that only in the addition of ZrO_2 did the transparency disappear completely, that the color changed dark blue from brown, and, further, that the crystalline part increased considerably relative to the amorphous part, as is shown by the X-ray powder patterns in Fig. 7-f.

3) *The Electrical and Structural Features of the VO Thin Films.* The X-ray diffraction patterns of the VO thin film containing 60 atom% of Zr are given in Fig. 8-a, while those of the pure VO_2 crystalline powder[19] and of the original ZrO_2 powder are shown in Figs. 8-b and c respectively for the sake of comparison. Since no peaks in Fig. 8-a are consistent with those in Fig. 8-b, the VO thin film containing ZrO_2 may not be composed of VO_2 crystalline particles, but of amorphous particles. On the other hand, the main peaks in Fig. 8-a, for instance, d=3.100, 2.797, 1.800, and 1.791 A, correspond well to those in Fig.

8-c: d=3.165, 2.842, 1.848, and 1.818 A respectively, although the d-values always shift a little relative to one another. Therefore, the diffraction peaks may be ascribed to some ZrO_2 crystallines, dissolving a little of the vanadium oxide, which are growing at the grain boundary. Thus, a large increase in the conductivity gap and a large decrease in the activation energy above the transition temperature can be understood if this Zr–V–O coumpound formed at the boundary layer has a large conductivity relative to the grain boundary of the pure VO thin film. The findings that the conductivities of the VO thin films containing TiO_2, Cr_2O_3, and MoO_3 became apparently smaller than that of the pure VO thin film, could similarly be understood if some compounds of vanadium oxide with the metal oxides were formed in the boundary layer and if, further, their conductivities were quite small. In the addition of Na_2O, the conductivity increased to a great extent below the transition temperature, while it changed almost not at all above the transition point, as has been mentioned above. This would suggest that the conductivities of some compounds of sodium vanadium oxide formed at the boundary layer are quite large.

Only in the addition of ZrO_2, did both the conductivity and the gap increase greatly; that is, the electrical feature of the VO_2 particle itself appeared more clearly, because the compounds of the vanadium oxide with ZrO_2 formed at the boundary showed quite a high conductivity. Upon the addition of Na_2O and ZrO_2, the corresponding compounds formed at the grain boundary of the vanadium-oxide particles showed a high conductivity relative to the boundary of the pure vanadium oxide itself, but the conductivity gap decreased greatly in the former and increased in the latter. Therefore, it can be expected that, upon the addition of Na_2O, almost no pure VO_2 particles are formed, but, rather, some sodium oxide particles are, while, on the contrary, almost all the pure VO_2 particles remain, without mixing with ZrO_2, on the addition of ZrO_2, except the boundary layer.

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