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# The Electric Properties of $VO_2$ Thin Films Doped with Other Metal Oxides under Water Vapor

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The electric property of a pure $VO_2$ thin films, prepared from a vanadium naphthenate by thermal decomposition, was examined preliminarily under various inorganic gas atmospheres, $H_2O$, $H_2$, $O_2$, $N_2O$, and $NO_2$, at 20—200 °C. Only in the case of the $H_2O$ adsorption, did the conductivity-temperature curve change reversibly; in the other cases it changed irreversibly. With respect to the $VO_2$ films doped with $Na_2O$, $ZrO_2$, $Cr_2O_3$, and $TiO_2$, similarly, the conductivities changed reversibly with the water vapor adsorbed; the extent and the manner of these changes differed rather greatly depending upon the kind of metal oxides doped. In the Zr-$VO_2$ film, which had a large conductivity ($\sigma$) and its gap ($\Delta\sigma$) at the transition point ($T_t$=60 °C) relative to the pure $VO_2$ film, the electric property was almost unaffected by water-vapor adsorption. In the cases of the Cr- and Ti-$VO_2$ films, with quite small $\sigma$ and $\Delta\sigma$ values relative to the pure $VO_2$ film, on the contrary, the ln $\sigma$—$1/T$ curves decreased parallelly to less than about one-half of that under a vacuum throughout the temperature range. With the Na-$VO_2$ film, the $\sigma$—$1/T$ curve measured under water vapor gradually nears that under a vaccum with the elevation of the temperature to 200 °C. From the comparisons of the effects of the electric properties of these doped films on the water vapor adsorbed, the structural features of the films, especially the contact states in the boundary layer, were deduced favorably. Furthermore, a possibility of the application to a switching element working at about 60 °C was suggested for the Zr-$VO_2$ film, and that to a fume sensor working at a temperature less than 200 °C, for the Cr- and Ti-$VO_2$ films.

Many solid-state physisists and chemists have been interested in vanadium oxide compounds because these compounds show a metal-semiconductor transition.[1—9] We have previously proposed a more convenient method for the preparation of a $VO_2$ thin film[10] by improving the Sekiya-Matsushita method.[11] Furthermore, we prepared $VO_2$ thin films doped with various metal oxides and compared their electric properties. The conductivity and also the extent of the conductivity gap, which was observed at the transition point in the pure $VO_2$ film, were largely affected by the metal-oxide additions. Based on the conductivity changes, the structural features, especially in the grain boundary of these $VO_2$ films, were discussed.[10]

In the present paper, the electric properties of the $VO_2$ films doped and undoped with other metal oxides under various atmospheres, especially under water vapor, will be examined in detail in order to obtain further information about the structures and the contact states of the particles in the grain boundary. In fact, the conductivity-temperature curve was considerably affected by the water vapor adsorbed physically, depending upon the kinds of metal oxides doped. The structural features of these doped $VO_2$ films will be discussed favorably based on these findings, and finally a possibility of their application to a solid state sensor will be suggested.

## Experimental

*1) Materials and Procedures.* Vanadium naphthenate (containing *ca.* 3 wt% of 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 ($VO_2$ 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, after which 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 funace during the decomposition.[10]

Upon the preparation of the $VO_2$ thin films containing other metal oxides, such as $Na_2O$, $TiO_2$, $Cr_2O_3$, and $ZrO_2$, these oxides ($NaOCH_3$ in the case of $Na_2O$), weighed exactly, were added to a 10 wt% 1-butanol solution of vanadium naphthenate and then ground well with an agate mortar in order to dissolve them fully. Then, the solution containing the metal oxides was dropped onto the glass plate with the gold electrodes and subsequently decomposed by the procedures used in the case of the pure $VO_2$ thin film. The concentrations of these metal oxides added to vanadium oxide were in the range of 40—60 atom%; $[(M)/(V)]\times100$.

*2) Measurements.* The electric conductivity was measured by the usual two-probe method under various gas atmospheres and under an evacuation below $10^{-3}$ mmHg†. The pressure measurement was carried out by the use of a mercury manometer at a relatively high pressure and by the use of a Pirani gauge, Shimazu Model PM-12, at lower pressures. 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. The relationship between the conductivity and the temperature was determined exactly by means of an automatic measurement system; both the potential difference between the ends of the $VO_2$ thin film and the thermoelectric power generated in the AC-thermocouple attached to the film were amplified simulteneously 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

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† 1 mmHg≈133.322 Pa.

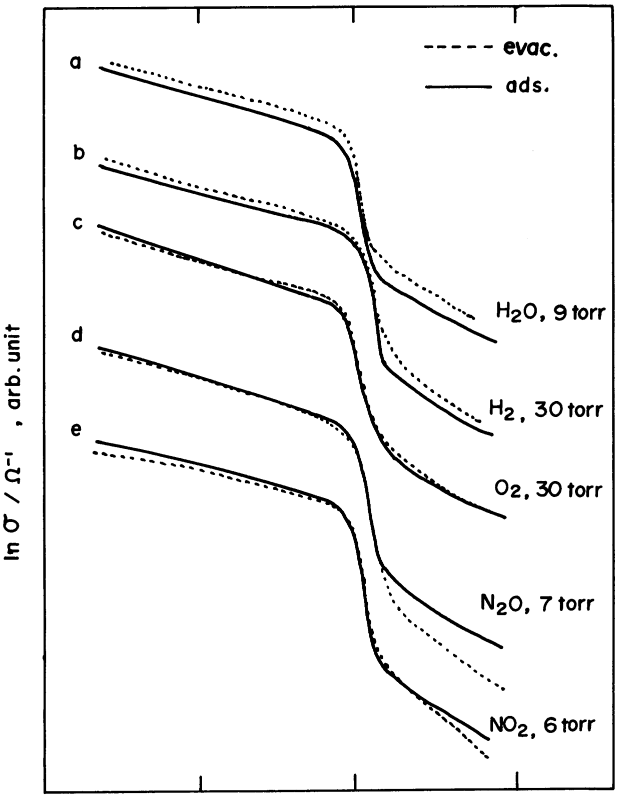

Fig. 1. The $\ln\sigma - 1/T$ curves for the pure-$VO_2$ thin film measured under various inorganic gas atmospheres; the blank curves are given to each curve with dotted lines, which have been measured under the vacuum before the each measurement. The measurements were repeated alternatively by the use of the same film in the sequence of a→e.

Sangiyo Model ADL-1224.

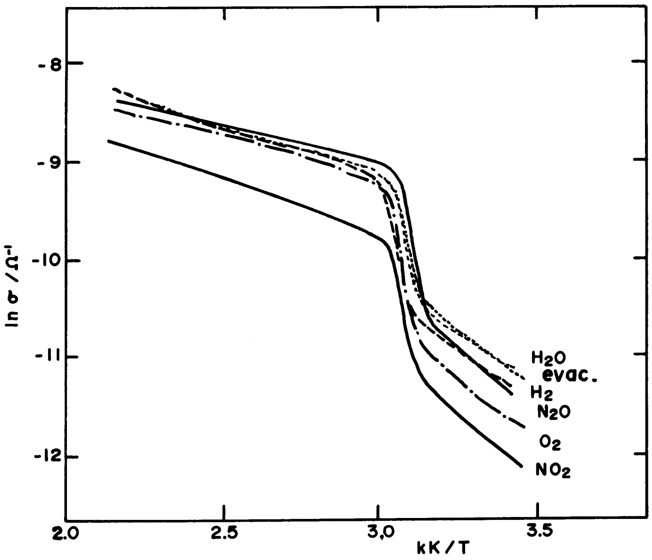

Fig. 2. The comparisons of the blank curves given in Fig. 1: "evac." indicates the curve for the pure-$VO_2$ film measured at the very initial under the vacuum, and "$H_2O$" that measured under the vacuum after the experiment under water vapor. "$O_2$", "$N_2O$", and "$NO_2$" also indicate the same meanings. They were successively measured in the order of "evac.", "$H_2O$", "$O_2$", "$N_2O$", and "$NO_2$", as mentioned in Fig. 1.

TABLE 1. THE CONDUCTIVITIES ($\sigma_h$ AND $\sigma_l$) JUST ABOVE AND BELOW $T_t$ AND THE ACTIVATION ENERGIES ($E_h$ AND $E_l$) AT THE TEMPERATURES ABOVE AND BELOW $T_t$, ESTIMATED FROM THE LN$\sigma$—$1/T$ CURVES UNDER THE VACUUM AFTER THE INORGANIC GAS ADSORPTIONS, *i.e.*, FROM THE Evac. CURVES IN Fig. 2

| Samples | $\sigma_h/10^{-4}\Omega^{-1}$ | $E_h$/eV | $\sigma_l/10^{-4}\Omega^{-1}$ | $E_l$/eV |
|---|---|---|---|---|
| "Evac." | 1.04 | 0.074 | 0.34 | 0.18 |
| "$H_2O$" | 1.04 | 0.082 | 0.31 | 0.21 |
| "$H_2$" | 1.04 | 0.084 | 0.28 | 0.18 |
| "$O_2$" | 0.97 | 0.068 | 0.22 | 0.23 |
| "$N_2O$" | 1.15 | 0.056 | 0.27 | 0.23 |
| "$NO_2$" | 0.54 | 0.084 | 0.15 | 0.24 |

## Results and Discussion

*1) Conductivity Changes of Pure $VO_2$ Thin Film under Various Gas Atmospheres at 20—200°C.* The temperature dependence of the conductivity ($\sigma$) for the pure $VO_2$ thin film measured under various inorganic gas atmospheres in the range of 20—200°C are summarized in Fig. 1, in which the ln $\sigma$ values are plotted against $1/T$. In Curve a, the dotted and full lines denote the curve measured under the vacuum at $10^{-3}$ torr and under water vapor ($p$=9 Torr[††]) respectively. After the measurement of Curve a, the $\sigma$ values for Curve b were measured repeatedly under a $H_2$ atmosphere ($p$=30 Torr). Similarly, the $\sigma$ values under $O_2$ ($p$=30 Torr), $N_2O$ ($p$=7 Torr), and $NO_2$ ($p$=7 Torr) were successively measured, as is shown by Curve c, d, and e respectively. By comparing these $\sigma$ values with the corresponding values under the vacuum, it is known that the $\sigma$ decreases with the water-vapor adsorption at all temperatures. The $\sigma$ decreases just a little under $H_2$ at all temperatures, but, on the contrary, it rather increases under $N_2O$ at temperatures lower than the transition point ($T_t$). Under $O_2$ and $NO_2$, however, the $\sigma$ does not change remarkably.

The $\sigma$—$1/T$ curves, a—e, of Fig. 1 are summarized in Fig. 2, where "Evac." indicates the ln $\sigma$—$1/T$ curve measured first of all under the vacuum and "$H_2$" the curve measured also under the vacuum after measurement under water vapor. Similarly, "$H_2$", "$O_2$", and "$N_2O$" have similar meanings. The curve for "$NO_2$" was measured similarly under the vacuum after the measurement of Curve e in Fig. 1. The electric conductivities just above and below the transition point, $\sigma_h$ and $\sigma_l$, were evaluated approximately by extrapolating linearly the curves above and below $T_t$ in Fig. 2 to the transition point, and the activation energies for the conductions above and below $T_t$, $E_h$, and $E_l$, from the inclination of the corresponding curves. These values are summarized in Table 1. The conduc-

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[†] 1 Torr≈133.322 Pa.

tivity of the pure $VO_2$ thin film is known to be recovered almost to the initial value by evacuation after measurement under water vapor, but not after those under the other gases, $H_2$, $O_2$, $N_2O$, and $NO_2$. Therefore, only in the case of the $H_2O$ molecule, a physical adsorption onto the interface among the $VO_2$ particles (or in the grain boundary) is suggested. Furthermore, the water molecules adsorbed physically could be deduced to affect only the mobility in the grain boundary, because of the parallel change in the $\sigma$—$1/T$.

The $\sigma$ was affected just a little under the atmospheres of $H_2$ and $O_2$, but in both cases it decreased irreversibly after the measurements under these gases, especially rather largely at temperatures lower than $T_t$. A series of vanadium oxides, which are generally shown by the formulae; $V_nO_{2n+1}$ and $V_nO_{2n-1}$, have been reported[12] in which the electric conductivities vary greatly with the $n$.[9] Therefore, the boundary layer of the pure $VO_2$ film is expected to be composed of various vanadium oxide compounds, unlike as in the $n$: *e.g.*, one compound in the grain boundary is mainly affected by the $O_2$ adsorption, and the other compounds in the other part, by the $H_2$ adsorption, so as to make the $\sigma$ values decrease similarly. Under the atmosphere of $N_2O$, which easily releases oxygen atoms near 200 °C, the grain boundary might be oxidized by it so that the $\sigma$ is increased irreversibly. In the case of $NO_2$, we can not explain the irreversible decrease in the $\sigma$.

*2) Dependence upon Water Vapor of the Electric Property of the $VO_2$ Thin Films Doped with Other Metal Oxides.* The electric property of the pure $VO_2$ thin film under water vapor are shown again in Fig. 3 as the ln $\sigma$—$1/T$ curves, a—c. Curve a indicates the curve measured under the vacuum and Curve c, that measured in the air after the film has stood for a long time in a desiccator which had not been kept in a good state. Curve b and c were changed reversibly to Curve a after the evacuation, so their deviation from Curve a can be expected to be caused by water vapor adsorbed physically onto the boundary layer.

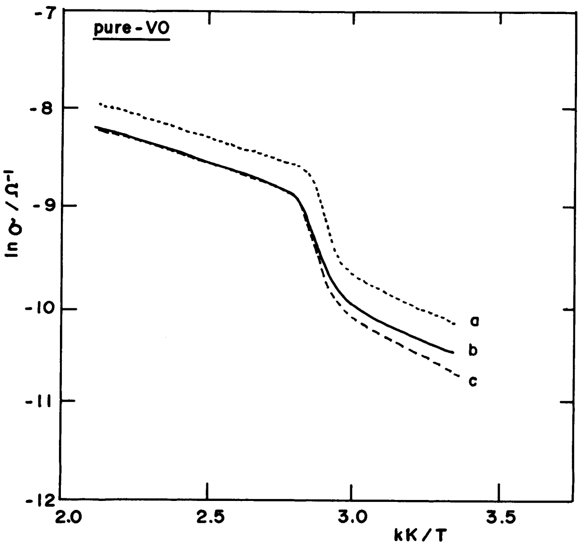

Fig. 3. Changes in the ln $\sigma - 1/T$ curve for the pure-$VO_2$ thin film with water vapor adsorbed physically; a: blank, b: under $H_2O$ (saturated at 20 °C). Curve c indicates the curve measured under the air after keeping it for a long time in a desiccator being not so good in the preservation.

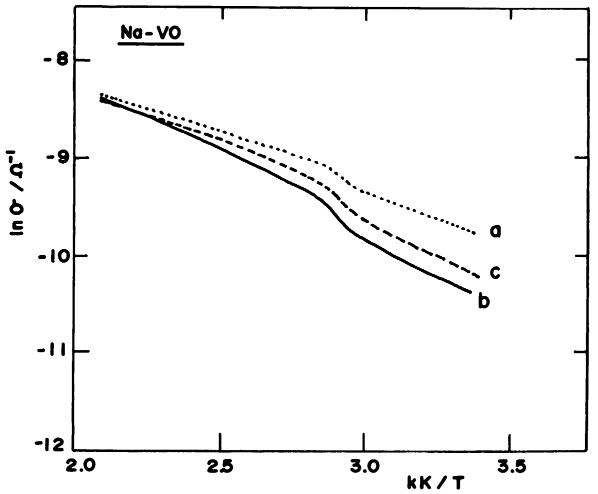

Fig. 4. Changes in the ln $\sigma - 1/T$ curve for the Na-$VO_2$ thin film (Na: 40 atom%) with water vapor adsorbed physically; a: under vacuum, b: under $H_2O$ (saturated at 20 °C). Curve c indicates the curve measured under the air after standing it in the air for 2 d.

With respect to a Na–$VO_2$ thin film (Na: 40 atm%), the conductivity was measured under the vacuum and also under water vapor, as is shown by the ln $\sigma$—$1/T$ curves, a and b respectively, in Fig. 4. Curve c indicates the curve measured in the air after the Na–$VO_2$ film has stood for 2 d in the air. Curves b and c are changed reversibly to Curve a by the evacuation after the measurement. Therefore, the deviations of Curves b and c from Curve a seem to be caused by water vapor adsorbed weakly (or condensed) onto the boundary layer. The extents of the deviations tend to decrease with the elevation of the temperature, nearing zero with the elevation up to near 200 °C in Fig. 4. This finding may suggest that the film is composed of various sizes of particles of the Na–V–O compounds; that the water molecules, which condense into micro-pores formed by the contact of the particles with so many varied types, are desorbed step-by-step with the elevation of the temperature, and, further, that the $\sigma$-difference varies in proportion to the quantity of the water molecules remaining in the layer.

With respect to a Cr–$VO_2$ (Cr: 60 atom%) and a Ti–$VO_2$ (Ti: 40 atm%) thin film, the ln $\sigma$—$1/T$ curves are shown in Figs. 5 and 6 respectively. From a comparison of Curves a and b, it can be seen that both the Cr- and Ti–$VO_2$ films are affected considerably by water vapor adsorbed over all the temperature range, 20—200 °C. Curve c in Figs. 5 and 6 indicates the curves measured under the air after the films have been kept in the desiccator for a long time. In

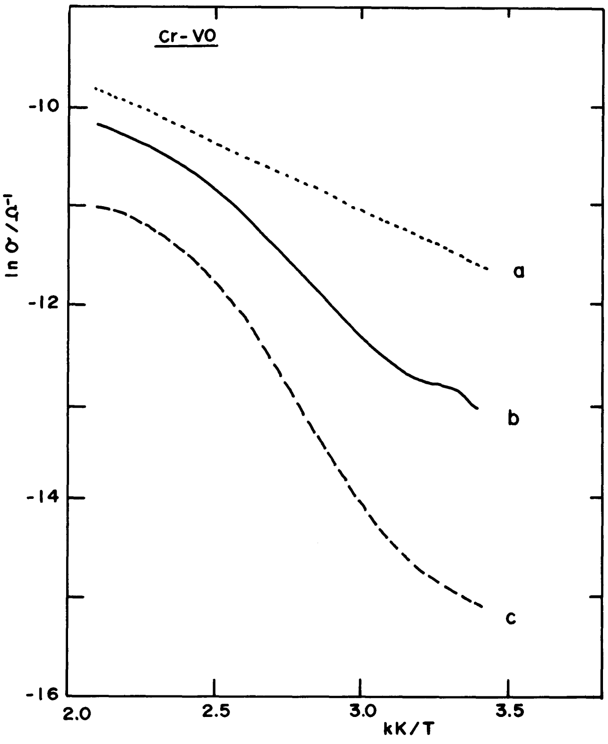

Fig. 5. Change in the ln $\sigma - 1/T$ curve for the Cr-$VO_2$ thin film (Cr: 60 atom%) with water vapor adsorbed physically; a: under vacuum, b: under $H_2O$ vapor (saturated at 20 °C). Curve c indicates the curve measured under the air after keeping it for a long time in a desiccator being not so good in the preservation.

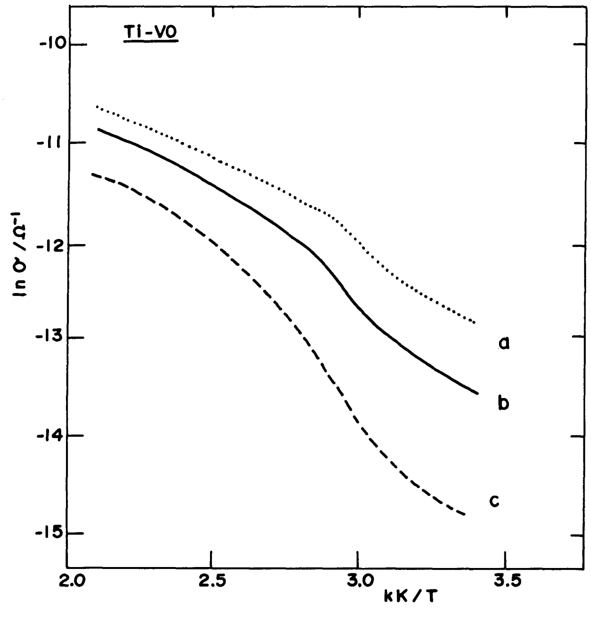

Fig. 6. Changes in the ln $\sigma - 1/T$ curve for the Ti-$VO_2$ thin film (Ti: 40 atom%) with water vapor adsorbed physically; a: under vacuum, b: under $H_2O$ vapor (saturated at 20 °C). Curve c indicates the curve measured under the air after keeping it for a long time in a desiccator being not so good in the preservation.

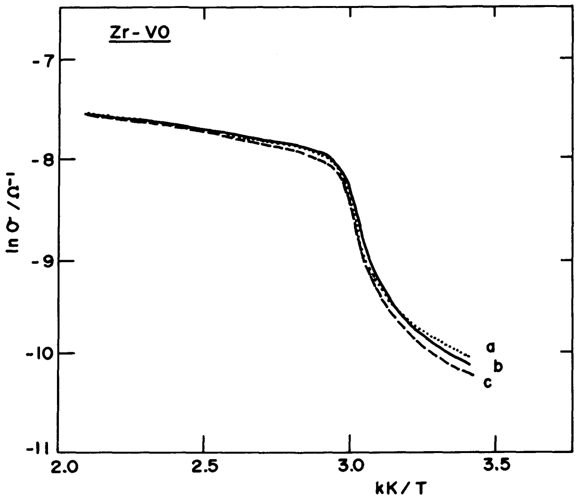

Fig. 7. Change in the ln $\sigma - 1/T$ curve for the Zr-$VO_2$ thin film (Zr: 60 atom%) with water vapor adsorbed physically; a: under vacuum, b: under $H_2O$ vapor (saturated at 20 °C). Curve c indicates the curve measured under the air after keeping it for a long time in the desiccator being not so good in the preservation.

both cases, Curves b and c were also changed reversibly to Curve a by evacuation. In the Cr- and Ti-$VO_2$ it was suggested previously that amorphous (or very small crystalline) $Cr_2O_3$ and $TiO_2$ particles, mixed with some vanadium oxides, were formed at the grain boundary and, further, that the apparent conductivities are controlled by that of the grain parts.[10] We can understand easily from such suggestions that the $\sigma$ values of those films are affected rather greatly by the water vapor adsorbed physically.

With respect to a Zr-$VO_2$ thin film (Zr: 60 atom%), the conductivity was measured under the vacuum and water vapor, as is shown by the ln $\sigma$—$1/T$ curves, a and b, respectively in Fig. 7. In this case, the $\sigma$ value was almost entirely unaffected by water vapor; also, when it was left standing for a long time in the desiccator it was not preserved in a so good state (*cf.* Curve b and c respectively). Curves b and c were also changed reversibly to Curve a. The formation of a grown (or crystallized) $ZrO_2$ particle mixed with vanadium oxide at the grain boundary was shown previously by X-ray diffraction; further, it was suggested that the electric properties of the $VO_2$ particles themselves appeared more strongly, because the conductivity in the grain boundary was high relative to the inner bulk of the $VO_2$ particles.[10] On the basis of the suggestion that the conductivity is mainly controlled by the bulk of the $VO_2$ particles rather than by the grain parts in the Zr-$VO_2$ film, it can be understood why the conductivity is almost unaffected by the water vapor adsorbed.

For these doped $VO_2$ films, the conductivities, $\sigma_h$ and $\sigma_l$ and the apparent activation energies, $E_h$ and $E_l$, were estimated similarly from the ln $\sigma$—$1/T$ curves in Figs. 3—7, as is shown in Table 2. The data for the Cr-

TABLE 2. DEPENDENCE UPON WATER VAPOR OF THE ELECTRIC CONDUCTIVITIES OF THE $VO_2$ THIN FILMS DOPED WITH VARIOUS METAL OXIDES

| Samples | $\sigma_h/10^{-4}\Omega^{-1}$ | $E_h$/eV | $\sigma_l/10^{-4}\Omega^{-1}$ | $E_l$/eV |
|---|---|---|---|---|
| Pure-$VO_2$ | | | | |
| Evac. | 1.57 | 0.089 | 0.66 | 0.113 |
| $H_2O$ | 1.37 | 0.089 | 0.54 | 0.118 |
| Na-$VO_2$ | | | | |
| Evac. | 1.09 | 0.083 | 0.94 | 0.092 |
| $H_2O$ | 0.80 | 0.119 | 0.64 | 0.138 |
| Zr-$VO_2$ | | | | |
| Evac. | 3.42 | 0.036 | 0.79 | 0.152 |
| $H_2O$ | 3.67 | 0.034 | 0.79 | 0.178 |
| Ti-$O_2$ | | | | |
| Evac. | 0.076 | 0.116 | 0.054 | 0.142 |
| $H_2O$ | 0.049 | 0.148 | 0.030 | 0.160 |

$VO_2$ film have been omitted from the table because the transition point could not be seen clearly on the film, but a large effect of adsorbed water vapor can be qualitatively found in Fig. 5. The ratio of the $\sigma(H_2O)$ value to the $\sigma$(Evac.) value is about 0.85 in both $\sigma_h$ and $\sigma_l$ for the pure $VO_2$ film, while the ratios between the values about 1.0 and 0.6 for the Zr- and Ti-$VO_2$ films respectively. Thus, the effect of water-vapor adsorption on the conductivity clearly tends to decrease upon the addition of $ZrO_2$, while, on the contrary, it is considerably extended by the addition of $TiO_2$.

These results may be summarized as follows. The changes in the electric properties with various gases, especially with the water-vapor adsorption, were confirmed to be related not only to the chemical properties of the compounds existing in the grain boundary, but also to the states of the contact between the particles. In other words, the states of the $VO_2$ particles grown and their contact states at the grain boundary, by which the electric property is apparently controlled, could be favorably varied by selecting the kind of metal oxide and its contents.

The Zr-$VO_2$ thin film may be applied to a switching element working near 60 °C, because of its stability in relation to water vapor in the air; on the other hand, the Cr- and Ti-$VO_2$ thin films may be applied to a fume sensor working at temperatures from 20—200 °C because of their showing rather large changes of the water vapor adsorbed reversibly, although further studies will be needed to increase the sensitivity. In the case of the Na-$VO_2$ film, the $\sigma$ value changed delicately with the temperature under water vapor, so we can not make any suggestions about its application, although considering the structural features of the grain boundary of the $VO_2$ thin films gives important information.

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