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Preparation of VO_2 films by organometallic chemical vapour deposition and dip-coating

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Low-pressure organometallic chemical vapour deposition (OMCVD) and dip-coating of VO_2 films using vanadyl tri(isobutoxide) as the starting material were investigated. In OMCVD, discontinuous VO_2 films, which were composed of fine needle crystals, formed under very limited conditions, around 600° C with a flow rate of oxygen gas of 0.2 to 0.5 $cm^3 sec^{-1}$. However, very uniform and tightly packed VO_2 films were grown by deposition at 300 to 700° C in the absence of oxygen gas and subsequent annealing in nitrogen at 500° C for 2 h. The films exhibited a sharp semiconductor to metal transition at 60 to 70° C, accompanied by a change in the resistivity by four to five orders of magnitude. In dip-coating with two-step heat-treatments (300° C for 1 h in nitrogen and subsequently 500° C for 2 h in nitrogen), of the gel films formed from $VO(O\text{-}i\text{-}Bu)_3\text{–}H_2O\text{–}i\text{-}PrOH$ system, uniform (0 1 1) oriented VO_2 films were formed. A transition in the electrical conductivity by two to two and a half orders of the magnitude was found to occur around 60° C. Before and after the transition, no distinct variation in the XRD pattern was observed.

1. Introduction

VO_2 is well known to have metal to semiconductor transition at 60 to 70° C, where a very abrupt change in electrical conductivities and optical properties can be found [1, 2]. Therefore, it has received attention because of its potential as a useful material for temperature sensing devices. In order to avoid the deterioration by volume change during the transition, the use of VO_2 in the form of film rather than the bulk is proposed [3], and the film preparation methods, including chemical vapour deposition (CVD) [3–6], sputtering process [7–9], decomposition of organo-vanadium compound [10] and sol–gel method [3], are reported. Doping with some ions has been found to change the transition temperature [3, 9]. As far as film preparation is concerned, the CVD method is very common, especially OMCVD, where organometallic compounds are used as the starting compounds for the CVD, which is frequently used in the preparation of electronic devices, because the corrosive atmospheres present in the halide process can be avoided. Some OMCVDs have been reported [3, 5], but the relationship between the deposition conditions and the deposits were very ambiguous. Normal pressure alkoxide-based OMCVD tends to accompany homogeneous vapour decomposition to result in the deposition of discontinuous films; the deposition is diffusion controlled [11, 12]. In the present work, therefore, it was our intention to perform low-pressure OMCVD in which deposition could be surface reaction controlled, and to clarify the effect of the deposition conditions on the deposits, in particular, those of VO_2 films in the alkoxide-based OMCVD.

On the other hand, the sol–gel method is an interesting processes which forms a uniform film on a large pane of substrate [13]. The sol–gel process reported so far [3] incorporates the dip-coated V_2O_5 films being reduced by a hydrocarbon vapour. In the present paper, a simple heat-treatment process in nitrogen is used for the preparation of uniform VO_2 films.

2. Experimental procedure

2.1. OMCVD method

The vanadyl tri(isobutoxide) $VO(O\text{-}i\text{-}Bu)_3$ was purchased from Stauffer Chemical Co., (Westport, Connecticut) and was used as the starting compound for OMCVD of VO_2 films after purification by vacuum distillation. The furnace for the OMCVD was composed of a vertical-type quartz glass (40 cm total length, 24 mm i.d.) which was connected to the alkoxide glass reservoir through a glass pipe. The pipe was heated to 100 to 120° C in order to avoid condensation of the alkoxide vapour. The length of the hot furnace zone was about 7 cm. The fundamental CVD system was very similar to that reported previously [14].

The substrate (Corning Co. no. 7059 glass), which was mounted on a supporter with magnetically rotating facilities, was heated from the outside by a Nichrome heater. It was cleaned before use by successively washing with distilled water and acetone.

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After the furnace was evacuated at a given temperature, a given flow rate of gas mixture which contains nitrogen, vanadium alkoxide vapour and oxygen gas, if necessary, was introduced at a given pressure. Transport of the alkoxide vapour to the furnace was achieved by bubbling the nitrogen gas at a reduced pressure to the reservoir which was heated at a given temperature. After deposition the furnace was allowed to cool down to near room temperature under the flowing nitrogen gas. The nitrogen and oxygen gases used in this experiment were deoxygenated and/or dehydrated by passing through a titanium sponge or phosphorous pentoxide bed, respectively. The deposition conditions investigated in the present work are summarized in Table I. The effect of a post-deposition annealing (in nitrogen gas at 500° C for 2 h) was examined.

2.2. Sol–gel method

Vanadyl tri(isobutoxide) was used in a similar manner to in OMCVD. It is soluble in isopropanol, but after the addition of water to the isopropanol solution, greenish precipitates separated out from the solution especially when the alkoxide concentration was higher than 0.4 M. In this study, the homogeneous solution containing 0.2 M alkoxide and water was used as the dipping solution. The precipitation was accelerated by light in the room, and therefore, the solution should be kept in the dark. The modifiers, such as glycols and ethanolamines, which effectively stabilized the solutions of zirconium [15], titanium [16], and magnesium aluminium alkoxides [17] in alcohol in the presence of water were found to be ineffective in this case.

The substrate pulling-up rate was fixed at 18 cm sec^{-1} in this study. After coating by dipping, the gel films were dried at room temperature for 1 h and subsequently heated in a horizontal furnace at a given temperature under flowing nitrogen gas or in air for 1 to 2 h. The optimum heat-treatment conditions for VO_2 film preparations were the first heating at 300° C in nitrogen for 1 h and a subsequent second heating at 500° C in nitrogen for 2 h.

2.3. Measurement of the physical properties of films

The electrical conductivity was measured using a common four-probe method. Transition behaviour was followed by a conventional two-probe method. In both measurements, point contacts with copper metal wires were used. The sample was located on a heater plate, and heated at a rate of 9° C min^{-1} in a heating cycle. In a cooling cycle a spontaneous decrease in the temperature was adopted. A resistor (2.0 kΩ) and the direct-current power source (10 V) were connected in series to the test sample, and the voltage induced across the resistor and the e.m.f. of the CA (chromel-alumel) thermocouple attached to the sample were recorded on an 8-bit personal computer (NEC, PC-8801) through a AD-convertor (Micro Science Co., Tokyo, DAS-1280BPC). The transition temperature is defined in this paper as the temperature at which the conductivity equals the mean value of the conductivities before and after the transition.

TABLE I Conditions of OMCVD used in this study

Parameter	Condition
Deposition temperature	260–700° C
Saturation temperature of vanadyl tri(isobutoxide)	80° C
Flow rate of the carrier (N_2) gas	0.2 $cm^3 sec^{-1}$
Flow rate of O_2 gas	0–1.1 $cm^3 sec^{-1}$
Total gas flow rate	2.2 $cm^3 sec^{-1}$
Pressure of the system	4.0–4.2 torr
Linear velocity	160–300 cm sec^{-1}

2.4. SEM observation, identification, etc.

The morphologies and the crystal modifications of the films were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). For SEM observation an Akashi-Horiba EMAX-8000S system (with tungsten filament, beam energy 30 kV) was used. XRD patterns were measured using a Rigaku RU-300, equipped with rotating anode (Cu$K\alpha$, 50 kV, 300 mA) and 2θ scan unit (scan speed 4° min^{-1}). The composition of the films was estimated partly using the relationship between the temperature of the transition and the composition [18], and partly by electron spectroscopy for chemical analysis (ESCA) measurement and crystal modifications determined from XRD. ESCA spectra were obtained on a Shimazu ESCA-750 spectrometer with an Al$K\alpha$ X-ray source. All spectra were referenced to the C_{1s} peak for hydrocarbon species, which was assigned to the value of 284.6 eV. Argon-ion sputter-etching was used to remove surface contaminants.

3. Results and discussion

3.1. Film growth by OMCVD

The temperature dependence of the deposition rate on the oxygen gas flow rate is shown in Fig. 1. The optimum deposition temperature was about 400° C irrespective of oxygen concentration. Above 700 and below 300° C no deposition on the substrate was found. The quantity of the deposit was linearly proportional to the deposition time as shown in Fig. 2. The deposition rate under the conditions shown in Fig. 2 (450° C) is about 14.5 $\mu g\, cm^{-2} min^{-1}$, corresponding to about 30 nm min^{-1} when the density of the film was assumed to be 4.4 (the density of VO_2).

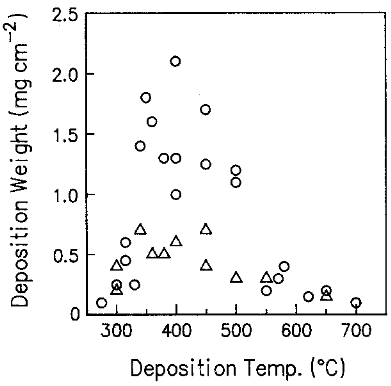

Figure 1 Effect of the deposition temperature on the deposition weight for deposition time of 30 min at different oxygen gas flow rates: (○) 0.1, (△) 1.1 $cm^3 sec^{-1}$.

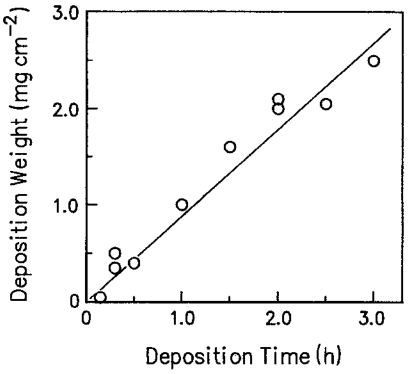

Figure 2 Time dependence of deposition weight under an oxygen gas flow rate of $0.5\,cm^3\,sec^{-1}$ at 450° C.

The deposits were green, brown, dark yellow, or sometimes purple, depending on the deposition conditions, especially temperature and oxygen concentration. In the absence of oxygen gas, the deposits were amorphous, except for those obtained around 300° C. On the other hand, crystalline films were obtained at 300 to 700° C in the presence of oxygen gas. Examples of XRD patterns of these films are shown in Fig. 3. XRD patterns of the as-deposited films at lower temperatures (Figs 3, 300 to 400° C) were not consistent with those of any vanadium oxide reported, while those of the higher temperature deposits (Figs 3, 600 to 700° C) indicated the presence of VO_2 and V_2O_5.

The films obtained in this study generally had only a few XRD peaks, partly due to the partial orientation and partly due to the small thickness itself of the films. Sometimes several crystal modifications may exist in the same stoichiometric compound. Moreover, it is rare for one compound to be formed purely under a given condition. Therefore, it was difficult to identify the deposits only from their XRDs. On the other hand, the electrical properties can be used as a guide for the identification of the deposits, because different vanadium oxides may have different electrical properties, particularly conductivity or the transition temperature [18]. Therefore, identification of the deposits was made using both XRD patterns and the electrical properties of the deposits obtained. The variation of the deposits with CVD parameters were therefore investigated, and the results are shown in Fig. 4.

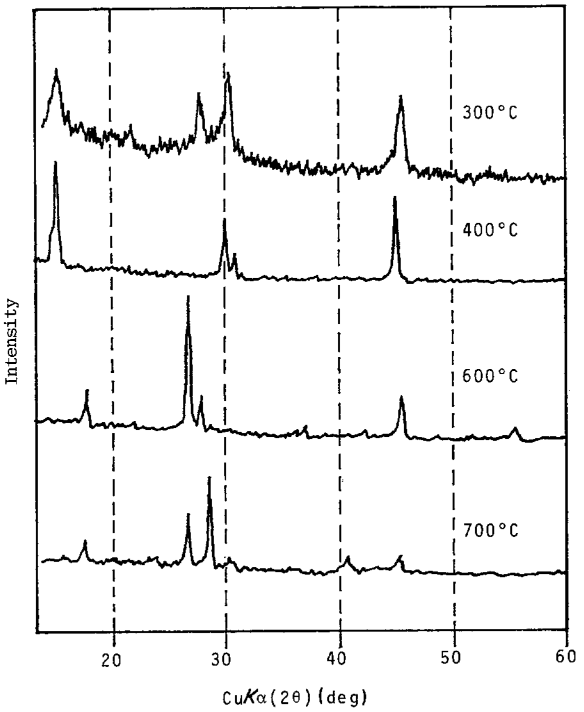

Figure 3 X-ray diffraction patterns of the deposits obtained at different temperatures under an oxygen gas flow rate $0.5\,cm^3\,sec^{-1}$.

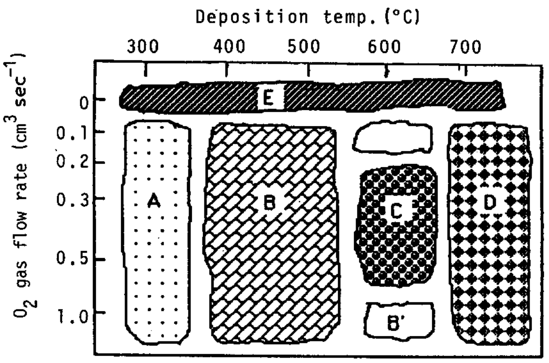

Figure 4 Variation of the as-deposited films with the CVD parameters.

In the absence of oxygen gas, blackish films with a low resistivity were formed, independent of the deposition temperature (Region E). Only around 300° C, did crystalline films form. However, the XRD pattern was not consistent with that of any vanadium oxide. So, in order to evaluate the atomic ratio O/V in the crystalline and amorphous films formed in the absence of oxygen gas, ESCA spectra were measured. Intense peaks due to O_{1s} (binding energy 530.6 to 530.8 eV), $V_{2p(1/2)}$ (about 521 eV), $V_{2p(3/2)}$ (515.2 to 515.7 eV), and V_{3p} (42.0 eV) were observed after argon-ion etching for 10 min. The peak area ratios of O_{1s} to V_{3p} were used for the composition determination because the both peaks are independent of other signals. It was found that the ratio after correction with the sensitivities was in the range 2.0 to 2.2 at all deposition temperatures, indicating that the compounds corresponded to VO_2, V_6O_{13}, etc. The binding energies of $V_{2p(3/2)}$ (515.2 to 515.5 eV) strongly suggest a valency of 4 for the vanadium atom.

The resistivities of the film obtained at different temperatures are shown in Fig. 5. Around 400 to

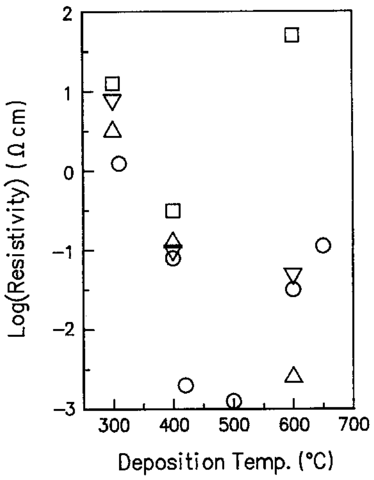

Figure 5 Relationship between the resistivity and the deposition temperature of the films at different oxygen gas flow rates: (○) 0; (△) 0.1; (□) 0.5; (▽) $1.0\,cm^3\,sec^{-1}$.

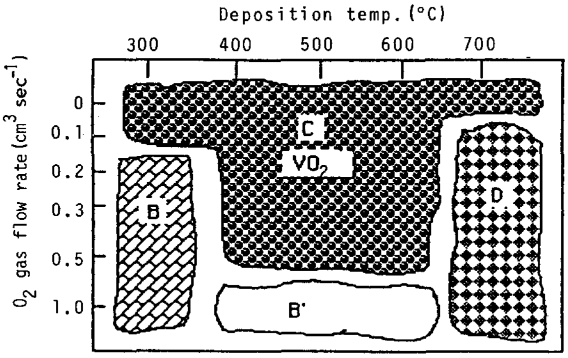

Figure 6 Variation of the films annealed at 500° C in nitrogen gas for 2 h with the CVD parameters.

500° C, the lowest resistive films ($10^{-3}\,\Omega$cm) were formed, which correspond to that of the Magnéli phase V_nO_{2n-1}. The resistivities of the films formed under other deposition conditions suggest the formation of VO_2-like oxides.

In the presence of oxygen gas (when the flow rate of oxygen gas was higher than 0.1 cm^3 sec^{-1}), the deposits changed depending merely on the deposition temperatures and irrespective of the oxygen gas flow rate. At 300 to 500° C (Region A or B in Fig. 4), greenish films with a low resistivity were found. The films in Regions A and B had different XRD patterns and also different temperature dependences of the resistivity. Around 600° C (Region C) the films which can be identified as VO_2 were obtained at an oxygen flow rate of 0.2 to 0.5 cm^3 sec^{-1}, above or below which (i.e. Region B′ or B″) oxides other than VO_2 formed. The films in Region C consisted of the fine VO_2 needle crystals ($> 3\,\mu$m long and 0.1 to 0.2 μm diameter: see later section), and had a sharp transition in the electrical conductivity at about 60° C. The VO_2 composition was also confirmed by the XRD pattern corresponding to monoclinic dioxide phase (Fig. 3, 600° C). At about 700° C (Region D) almost insulating and yellow crystals, which may be identified as V_2O_5, were formed. Thus, it is found that the VO_2 films of interest can be grown directly but over very narrow deposition conditions. Moreover, the films have poor uniformity and adherence to the substrates, probably due to the fact that the films are composed of needle crystals. It can be concluded, therefore, that the OMCVD process is not suitable for the direct deposition of VO_2 films.

Post-deposition annealing (at 500° C in flowing nitrogen for 2 h) of the as-grown films drastically converted the properties of the films. The film properties after annealing compared to the CVD parameters are shown in Fig. 6 using the classifications which were used in Fig. 4 (as-deposited films). It can be clearly seen that the region of VO_2 formation is expanded extensively. The deposits at Regions B and E in Fig. 4 were converted to Region C, i.e. VO_2 formation region, after annealing. Generally, the annealing corresponds to raising the deposition temperatures by 100 to 200° C. After annealing, the deposits at 300° C, for example, have the properties of deposits at 400 to 500° C. The VO_2 films thus obtained after annealing are well condensed and have a good adherence to the substrate. No variation of V–O composition after annealing was detected by ESCA measurement, suggesting that only a slight composition deviation around O/V = 2 took place during the annealing process, but not drastic oxidation or reduction. A typical SEM image of the VO_2 film obtained by post-deposition annealing is shown in Fig. 7, along with that of as-grown VO_2 film for comparison.

3.2. Films by the sol–gel method

A very uniform VO_2 film coating was obtained by OMCVD, but as described in the previous section, it requires subsequent annealing after deposition. The composition of the as-deposited vanadium oxide films obtained by OMCVD in nitrogen was very close to VO_2, but not VO_2 itself. It is very natural to suppose that the VO_2-like films were formed in the OMCVD process through an intermediate with a V–O network including organic moieties. In the sol–gel method, on the other hand, a gel film is formed by the hydrolysis and subsequent polycondensation. Thus, the film may contain organic fragments including the solvent itself along with V–O framework. This structure seems to be very much like the intermediate one supposed in the OMCVD. Therefore, it can be assumed that thermal decomposition of the gel films in nitrogen can lead to deposits similar to those in OMCVD, and hence VO_2 films can be prepared by the sol–gel methods including the heat-treatment in nitrogen. If the heat-treatment is performed in air, vanadium pentoxide films will be formed. With this in mind, we investigated the sol–gel coatings of vanadium oxides using vanadyl

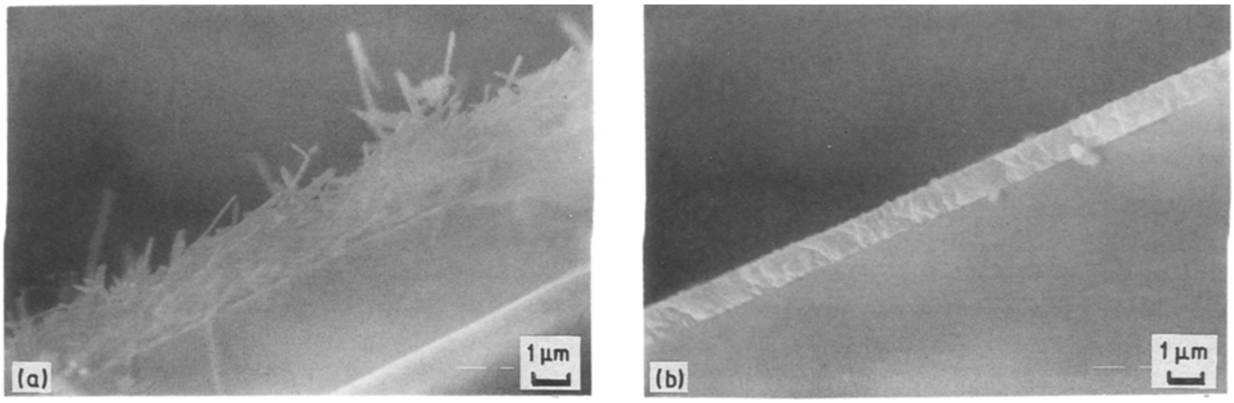

Figure 7 Scanning electron micrographs of the cross-sections of VO_2 films: (a) as-deposited at 600° C; (b) obtained by deposition at 400° C and subsequent post-deposition annealing at 500° C in nitrogen for 2 h.

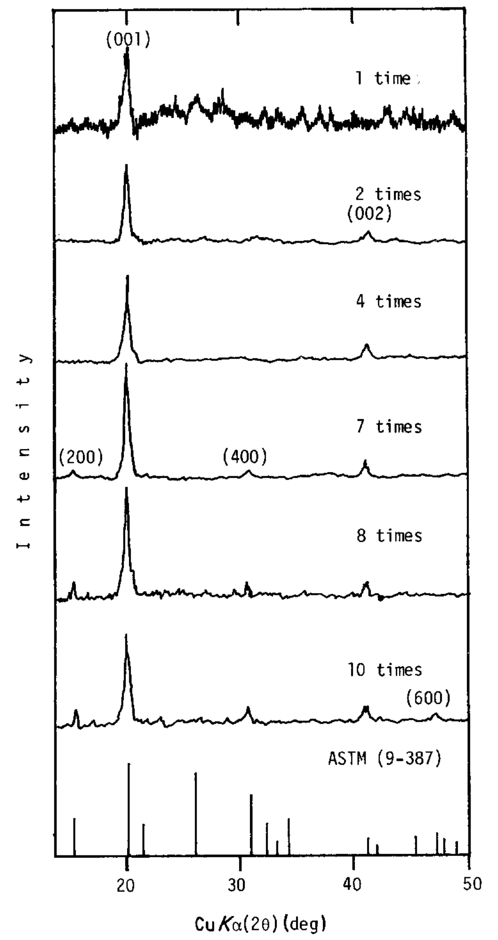

Figure 8 XRD patterns of highly c-axis oriented V_2O_5 films formed at 400° C. The numbers on the spectra represents the number of applications.

tri(isobutoxide). In the following section the results on this sol–gel process are described.

3.2.1. Coating of vanadium pentoxide

When the gel films on the glass substrates were heated in air, orange–yellow V_2O_5 films were formed. Below 350° C, the films were amorphous, and crystallized to V_2O_5 around 400° C. Above 450° C they again became amorphous, probably due to the reaction with the substrate. The XRDs shown in Fig. 8 indicate that they were highly oriented to the $\langle 0\,0\,1 \rangle$ direction, although the orientation degree somewhat decreased with increasing film thickness: another diffractions assignable to $(h\,0\,0)$ appeared after seven-time coating.

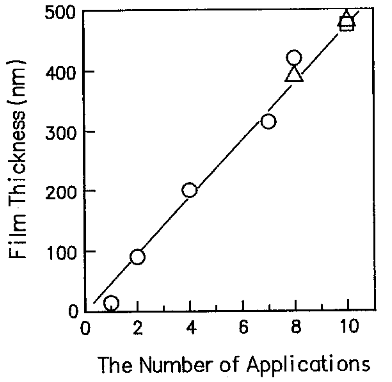

Figure 9 Relationship between the number of applications and the thickness of the V_2O_5 films. The thickness was evaluated by (○) weight gain, (△) SEM, (□) visible spectra.

The dependence of film thickness on the number of applications is shown in Fig. 9. In this figure the film thickness data are plotted, which were obtained by three different methods including evaluation from the film weight, visible spectra and direct observation by SEM. It can be seen that the data in good agreement, suggesting that the density of the film is close to that of V_2O_5. The thickness is proportional to the number of applications, in agreement with the tendency in common dip-coating, and the thickness in one coating process was evaluated to be 45 nm in the present system.

The refractive indices of the films, evaluated from the visible spectra and the film thickness [16], are in the range 2.11 to 2.15, being consistent with reported values [19].

3.2.2. VO_2 films

When the gel films were heated in nitrogen, greenish films were obtained. The XRD patterns of the films which were obtained by treatment at different temperatures in nitrogen for 2 h are shown in Fig. 10. Only at 400 to 500° C were crystalline films formed in a similar manner to the case of V_2O_5 films. The XRD patterns observed were not consistent with those of known vanadium oxides. The XRD patterns of films at 500° C suggest that they were composed of at least two different substances, because they had diffraction peaks with different half-widths. One of them is assignable to VO_2. It was impossible to prepare pure VO_2 by a simple one-step heat-treatment, but it is very interesting to note that the XRD pattern of the film obtained by heat treatment at 400° C is very similar to that of low-temperature deposits obtained by OMCVD (Fig. 3, 300° C), which had been converted effectively to VO_2 film by further heat-treatment in nitrogen at 500° C. Therefore, it is easy to presume that the films which were also obtained by a low-

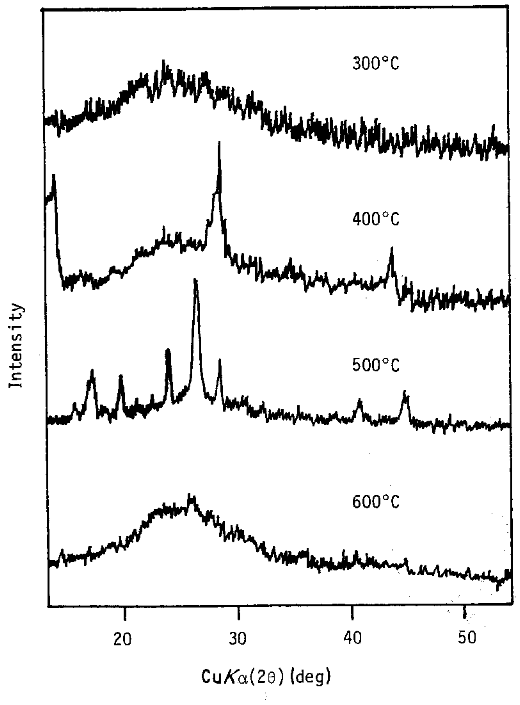

Figure 10 XRD patterns of VO_x films obtained by heating the gel films at various temperatures in nitrogen gas.

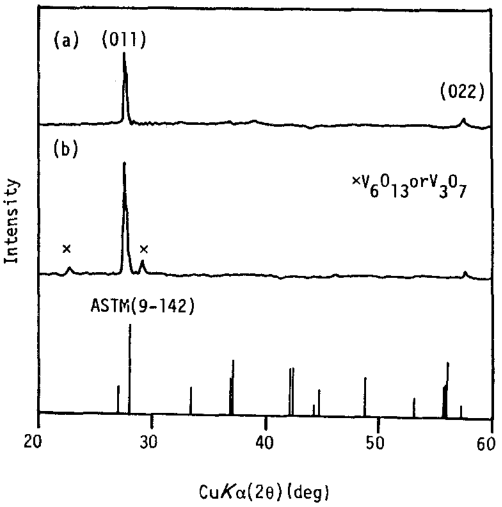

Figure 11 XRD patterns of the oriented VO_2 films: (a) obtained directly from the gel films; (b) obtained by heating V_2O_5 films at 600° C in a nitrogen atmosphere for 5 h.

temperature heat-treatment at 300 to 400° C can be converted to VO_2 films analogously by further heat-treatment at a higher temperature. This was found to be true. So, VO_2 films can be obtained with the sol–gel process using the two-step heat-treatment method. A pre-VO_2 film is obtained in the first heat treatment. The pre-VO_2 film has a conductivity larger than $10\,S\,cm^{-1}$, and can be converted to VO_2 film by further heat-treatment at a higher temperature, 500° C, in nitrogen. When heated at a higher temperature, say at or above 500° C, at the first heat-treatment, the films might be heavily reduced by the organic contaminants to give the Magnéli phase or similar, which could not be restored to VO_2 by heating in nitrogen.

The XRD pattern of the VO_2 films thus obtained is shown in Fig. 11a, in which only [0 1 1] diffraction is found. The VO_2 films can also be obtained from the V_2O_5 films (⟨0 0 1⟩ oriented as described above) by heating them at 600° C in nitrogen for 6 h, and the XRD pattern shown in Fig. 11b suggests the orientation to be in the ⟨0 1 1⟩ direction. Therefore, the (0 0 1) plane in V_2O_5 must be common with (0 1 1) plane in VO_2.

The effect of the number of applications on the film thickness is shown in Fig. 12. One dip-coating corresponds to a 25 nm thickness. This is about half the thickness of V_2O_5 (45 nm) despite use of the same solution. This difference can be explained by the effect of viscosity of the solution. Depending on the time elapsed after the preparation of the solution, the degree of hydrolysis and polycondensation may be different, leading to the different viscosity of the solution. The V_2O_5 films were prepared about one month later.

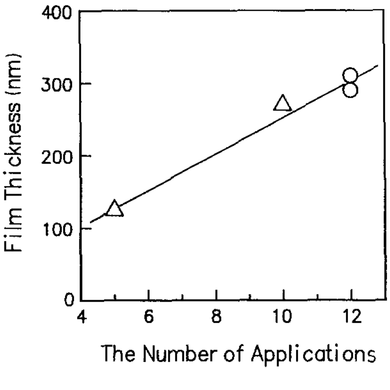

Figure 12 Relationship between the number of applications and VO_2 film thickness evaluated by: (○) weight gain, (△) SEM.

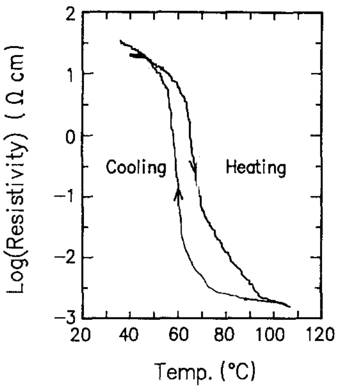

Figure 13 Typical transition behaviour in electrical resistivity of a VO_2 film obtained by OMCVD (post-deposition annealing).

3.3. Transition behaviour of VO_2 films

3.3.1. *OMCVD VO_2 films*

A typical example of temperature variation in the electrical resistivity of a VO_2 film obtained by annealing is shown in Fig. 13. Around 60° C, an abrupt jump in the resistivity is clearly observed, characteristic of the VO_2 modification. The resistivity change amounts to four or five orders of magnitude, comparable to that of single crystals [1, 2]. The VO_2 transition temperature depends slightly on the deposition conditions of the films before annealing as shown in Fig. 14. The case of VO_2 films which were obtained by deposition in the absence of oxygen gas and subsequent annealing is presented, and the electrical conductivities, before annealing, of the films at different deposition temperatures are also shown in Fig. 14. It is found that the conductivity strongly depended on the deposition temperatures, and maximum conductivity was obtained at about 500° C. In this connection, the minimum transition temperature 57° C (at the heating cycle) or 49° C (at the cooling cycle) is observed for a sample deposited at 500° C, below and above which the transition temperatures are apt to increase. However, we have no clear idea as to the explanation of the relationship between both behaviours.

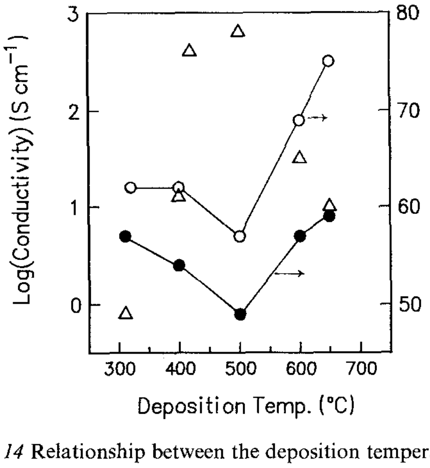

Figure 14 Relationship between the deposition temperatures of the VO_2 films (obtained by post-deposition annealing) and the film conductivity (△), and the transition temperatures: (○) heating cycle; (●) cooling cycle.

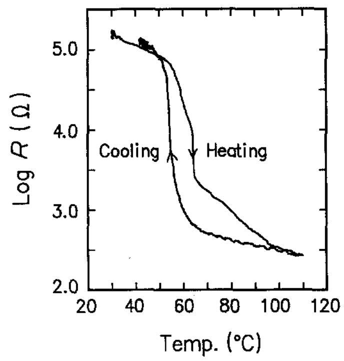

Figure 15 Typical transition behaviour in electrical resistivity of a VO_2 film obtained by the sol-gel method.

The XRDs of all VO_2 films showed one to four peaks assignable to the monoclinic VO_2 (e.g. ASTM Card No. 9-142). In order to confirm the identification, the transition during the heating was followed by XRD. However, appreciable variation in the XRD pattern was not observed before or after the transition, except that the peaks became slightly sharper and shifted by 0.2 to 0.3 to the lower angle side with temperature increase, in spite of the occurrence of a resistivity decrease of three orders of magnitude. Many investigations have been made into the transformation of VO_2, and the transformation from monoclinic form at room temperature to the tetragonal form at a temperature above 100° C is generally accepted. However, in the present case the corresponding variation of XRD pattern was not observed. In the Raman spectra, the intensity of scattering at $149\,cm^{-1}$ increased with increasing temperature. We are not sure whether this behaviour is attributable to a property of the thin film. Discontinuous variation in the electrical conductivity may be explained by a mechanism other than the transformation of the modification, for example electron correlation [20].

3.3.2. Sol-gel films

A typical example of transition behaviour in the electrical conductivity of the dip-coated VO_2 films is shown in Fig. 15. The film was coated 15 times: thickness was about 400 nm. At about 60° C a sharp transition is observed. The variation in the conductivity amounts to two to two and a half orders of magnitude, which seems to be smaller than that found for OMCVD VO_2 films. The transition temperature is comparable to that of OMCVD films, especially for films which were formed by deposition in nitrogen at 450 to 500° C and subsequently annealed at 500° C for 2 h in nitrogen.

4. Conclusions

1. By OMCVD from vanadyl tri(isobutoxide), VO_2 films were grown directly on glass substrates under very limited conditions, namely at a deposition temperature of 600° C and a flow rate of oxygen gas of 0.2 to $0.5\,cm^3\,sec^{-1}$. However, the films were discontinuous and were composed of fine needle VO_2 crystals.

2. On the other hand, very uniform and tightly packed VO_2 films were grown on glass substrates by a deposition at 300 to 700° C in the absence of oxygen gas and subsequent annealing in nitrogen at 500° C for 2 h.

3. The films exhibited sharp semiconductor–metal transition at 60 to 70° C, accompanied by a change in resistivity by four or five orders of magnitude.

4. The transition temperature was varied depending on the deposition conditions at which the original films were formed before annealing. The as-grown films which had highest conductivity showed the lowest transition temperature after annealing.

5. In the sol–gel method, using two-step heat-treatments (300° C for 1 h in nitrogen and subsequently 500° C for 2 h in nitrogen), from the gel films formed from $VO(O\text{-}i\text{-}Bu)_3\text{-}H_2O\text{-}i\text{-}PrOH$ system, uniform VO_2 films were formed. A transition in the electrical conductivity by two to two and a half orders of magnitude was found to occur around 60° C.

6. During the transition no distinct variations in the XRD pattern were observed. In the Raman spectra, the intensity of the scattering at $149\,cm^{-1}$ increased with increasing temperature.

References

1. F. J. MORIN, *Phys. Rev. Lett.* **3** (1959) 34.
2. A. S. BARKER Jr, H. W. VERLEUR and H. J. GUGGENHEIM, *ibid.* **17** (1966) 1286.
3. C. B. GREENBERG, *Thin Solid Films* **110** (1983) 73.
4. J. B. MacCHESNEY, J. F. PORTER and H. J. GUGGENHEIM, *J. Electrochem. Soc.* **115** (1968) 52.
5. L. A. RYABOBA, I. A. SERINOV and A. S. DAREVSKY, *ibid.* **119** (1972) 427.
6. J. P. DISMUKES, J. KANE, B. BINGGELI and H. P. SCHWEIZER, Proceedings of VIth International Conference on CVD (The Electrochem. Soc. Inc., Princeton, New Jersey, 1973) p. 275.
7. G. A. ROZGONYI and W. J. POLITO, *J. Electrochem. Soc.* **115** (1968) 56.
8. E. N. FULS, D. H. HENSLER and A. R. ROSS, *Appl. Phys. Lett.* **10** (1967) 199.
9. M. FUKUMA, S. ZEMBUTSU and S. MIYAZAWA, *Appl. Opt.* **22** (1983) 265.
10. Y. KERA, H. IMORI, S. KIDA and K. DEGAWA, *Bull. Chem. Soc. Jpn* **57** (1984) 2069.
11. Y. TAKAHASHI and T. SHIMONO, Proceedings of 16th Annual Meetings of Union of Chubu-Area Chemistry-Related Societies Association, October, 1985, Toyohashi, Japan (1985) p. 182.
12. H. KOMIYAMA, *Ceramics* **21** (Ceramic Society of Japan, Tokyo, 1986) 305 (in Japanese).
13. H. DISLICH and E. HUSSMANN, *Thin Solid Films* **77** (1981) 129.
14. Y. TAKAHASHI, K. TSUDA, K. SUGIYAMA, H. MINOURA, D. MAKINO and M. TSUIKI, *J. Chem. Soc. Faraday Trans. I.* **77** (1981) 1051.
15. Y. TAKAHASHI, K. NIWA, K. KOBAYASHI and M. MATSUKI, *Yogyo-Kyokai-Shi* **95** (1987) 942 (in Japanese).
16. Y. TAKAHASHI and Y. MATSUOKA, *J. Mater. Sci.* **23** (1988) 2289.
17. Y. TAKAHASHI and H. NAGANAWA, *Yogyo-Kyokai-Shi* **95** (1987) 1107 (in Japanese).
18. "Kagaku-Binran (Handbook for Chemistry)", edited by The Chemical Society of Japan (Maruzen, Tokyo, 1985) II-497.
19. B. W. KING and L. L. SUBER, *J. Amer. Ceram. Soc.* **38** (1955) 306.
20. N. TSUDA, A. YANASE and K. SHIRATORI, "Denki-Dendosei-Sankabutu (Electronic Conduction in Oxides)" (Syokabo, Tokyo, 1983).

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