Photoelectrochemical Properties of the Sol–Gel Derived $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ Thin Film Electrodes

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ゾル–ゲル法により作製した $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ 薄膜電極の光電気化学的挙動

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The origin of the photoresponse in the visible region observed for the sol-gel derived $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin films has been studied in relation to the doping level, x , which is ranging from 0.03 to 0.12. Effects of the post-heating atmosphere and the substrate nature on the crystallization behavior and photoelectrochemical properties of the films were examined. X-ray diffraction analysis revealed that thin films with $x \leq 0.06$ consisted only of anatase type TiO_2 phase regardless of the post-heating atmosphere and substrate nature, whereas for the samples with $x \geq 0.07$, VO_2 or V_2O_5 phases have been detected in addition to anatase phase depending on the post-heating atmosphere. Differences in photoelectrochemical characteristics between the thin film electrodes with $x \leq 0.06$ and $x \geq 0.07$ and the origin of the visible photoresponse are discussed on the basis of the difference in crystallization behavior of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrodes.

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1. Introduction

The discovery of photo-assisted water decomposition on the TiO_2 electrode,¹⁾ utilizing significantly lower electrical energy than thermodynamically demanded, has revealed potential promise for the practical application of semiconductor electrodes in the field of solar energy conversion and its storage as chemical energy. Since then researches on TiO_2 -based photoelectrochemical cells have attracted much attention and much work has been done to realize this system.

As an alternative attempt to prepare an efficient electrode in photoelectrochemical cell, researches on the bandgap graded $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ system consisting of thin films with compositional gradient^{2),3)} have been conducted on the basis of the facts that the bandgap of a mixed crystal semiconductor takes a value between those of the two end members^{4)–6)} and also the bandgap energy of a solid solution of two similar semiconductors is changed with the composition.⁷⁾

The bandgap energy of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrode is then supposed to lie between the bandgap energies of VO_2 and TiO_2 . VO_2 has been chosen as a dopant to TiO_2 matrix mainly on the basis of its narrow bandgap energy⁸⁾ and the ionic radius of V^{4+} ion⁹⁾ that is similar to that of Ti^{4+} so that the formation of a uniform solid solution will be realized. In fact, the formation of rutile- or anatase-type solid solution of composition $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ prepared by the solid state reaction,^{10),11)} sol-gel,^{12),13)} and co-precipitation¹⁴⁾ techniques were reported. If the vanadium content in the solid solution, x , is changed continuously throughout the thickness of the thin film, the bandgap gradient can be achieved. Thus, it can be assumed that when such an electrode is illuminated by a white light, photons with different energies will be absorbed at the point where the photon energy is equal to the bandgap. Therefore, such an electrode is expected to possess (i) photoresponse over a wide wavelength range, (ii) photoelectrochemical stability, (iii) high charge carrier mobility due to the lack of an energy barrier within the film and so on.

Here we have laid an emphasis on preparing an anatase type solid solution rather than rutile type, since anatase was found to possess better photoelectrochemical properties due to the shallow donor level and high mobility.^{15),16)} Gautron et al. studied the photoelectrochemical properties of rutile type $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ ($x = 0, 0.4, 0.45, 0.6$ and 1.0) sintered ceramics and came to the conclusion that this material was not suitable for the photoanode to decompose H_2O under illumination.¹¹⁾

It was found²⁾ that the anatase type $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ solid solution thin film electrodes with x ranging from 0.025 to 0.15, which were prepared by the conventional sol-gel method, possess a conspicuous photoresponse in the region from 300 up to 540 nm. Furthermore, by controlling the vanadium amount, x , in $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ it was possible to obtain a composition gradient to a certain extent.³⁾ However, there are some drawbacks in this $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrode system. Firstly, the photocurrent onset potential of these electrode samples was found to be more positive than that of TiO_2 . Secondly, the photocurrent was largely dependent on the external bias potential, in other words, it did not exhibit a saturation current. Moreover, significant differences in photoelectrochemical characteristics such as photocurrent onset potential and photocurrent at higher applied potentials have been observed between the thin film electrode samples doped with $x \geq 0.05$ and $x \leq 0.10$. This fact may suggest different mechanisms of the charge recombination and charge transfer processes between the thin film electrodes containing different amounts of VO_2 . Thus, in this paper we study the effects of the vanadium concentration and post-heating atmosphere on the crystallization behavior and photoelectrochemical properties of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin films in detail and discuss the origin of the visible photoresponse observed for the present thin film samples.

2. Experimental

2.1 Thin film electrode preparation and characterization

$\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin films were deposited on plain and nesa ($\text{SnO}_2\text{:Sb}$)-coated silica glass substrates by adopting the sol-gel dip-coating technique. Samples deposited on plain silica glass substrates were used to examine the effect of the nesa substrate on the crystallization behavior.

Reagent grade titanium isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, and vanadium (IV) oxyacetylacetonate, $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, were used as sources for TiO_2 and VO_2 , respectively. Composition of the coating solution was as follows, $\text{Ti}(\text{OC}_3\text{H}_7)_4$: $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$: H_2O : HNO_3 : $\text{C}_2\text{H}_5\text{OH}$ = $1-x$: x : 1 : 0.2 : 25 , where x is ranging from 0.03 to 0.12.

To attain adequate film thickness multiple dipping was employed. After each dipping gel films were heated at 500°C in air for 10 min. Finally, samples were subjected to post-heat treatment either in N_2 or in air for 30 min. The thickness of all the electrode samples used for the present study was about 90 nm as measured by Kosaka Laboratory SE-30D Surfcode.

Crystal phases precipitated in the samples were examined by the step-scan thin film X-ray diffraction analysis using Rigaku RINT 1200-S X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Incidence angle was fixed at 0.1° and step-scanning speed was 10 s/step at intervals of 0.005° .

2.2 Cell design and apparatus

Photoelectrochemical (PEC) measurements were performed in a three-electrode cell composed of sample (working), platinized Pt (counter) and SCE (reference) electrodes. The buffer solution of pH 7 composed of 0.2 M $\text{Na}_2\text{B}_4\text{O}_7$, 0.14 M H_2SO_4 and 0.3 M Na_2SO_4 was used as an

electrolyte. A potentiostat equipped with a frequency response analyzer, Hokuto Denko HZ-3000, was employed to evaluate the PEC properties. The photocurrent-potential (I - V) curves were measured under an illumination of 500 W Xe lamp. I - V curves were also recorded under a visible light illumination. For this propose sharp-cut optical filters which can transmit the light portion of wavelengths longer than 420, 440 and 460 nm were placed between the Xe lamp and electrode cell. The Xe lamp light was monochromatized by a Shimadzu SPG-100ST monochromator when action spectra were measured. Capacitance measurements were performed in the dark.

3. Results

3.1 XRD analysis

Results of X-ray diffraction analysis of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin films studied in the course of the present experiment are displayed in Fig. 1 and Table 1. Figures 1A and 1B show a part of the XRD patterns of the samples post-heated in N_2 and air, respectively. Though their XRD patterns are not presented, the as-prepared samples consisted solely of anatase phase indifferently to the doping level and substrate nature.

Samples with $x \leq 0.06$: When the dopant concentration is between 3 and 6 mol% ($x = 0.03$ – 0.06), only anatase TiO_2 phase was detected for all the samples regardless of the post-heating atmosphere and substrate nature.

Samples with $x \geq 0.07$: For the thin films of $x \geq 0.07$, either V_2O_5 or VO_2 phase precipitated and anatase-to-rutile phase transformation was observed. Owing to the same heat-treatment conditions the observed differences in crystallization behavior are considered to be caused by the

Fig. 1. XRD patterns of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin films post-heated (A) in N_2 and (B) in air.

Table 1. XRD Phase Detected in the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ Thin Films

x	As-prepared		Post-heated in N_2		Post-heated in air	
	Glass	Nesa	Glass	Nesa	Glass	Nesa
TiO_2	A	A	A			A
0.03	A	A	A			A
0.05	A	A	A			A
0.06	A	A	A			A
0.07	A	A	A		A + V_2O_5	A + V_2O_5
0.08	A	A	A		A + V_2O_5	A + V_2O_5
0.10	A	A	A + VO_2	A	A + V_2O_5	A + V_2O_5 + R
0.12	A	A	A + VO_2	A	A + V_2O_5	A + V_2O_5 + R

A – anatase; R – rutile

post-heating atmosphere, substrate nature and dopant concentration.

3.1.1 Effect of the post-heating atmosphere

In case of the post-heating in N_2 , no other phases than anatase were detected for the samples with $x=0.07$ and 0.08 . When the doping level increased to $x=0.10$, a weak peak at 26.3° was detected in the samples deposited on plain silica glass substrate and assigned to VO_2 phase in its orthorhombic structure. Crystallization of the same VO_2 phase, especially in the presence of TiO_2 has been reported.¹⁷⁾ This peak was not detectable for the samples deposited on "nesa" substrate since the peak position coincides with that of SnO_2 phase. In the samples post-heated in air, V_2O_5 phase started to be precipitated from $x=0.07$ and at the same time rutile phase formation was observed. The intensity of either V_2O_5 or rutile phases went on increasing with increasing dopant concentration.

3.1.2 Effect of the substrate nature

It has been well known that the presence of V_2O_5 on the surface of anatase TiO_2 enhances the anatase-to-rutile phase transformation with a consequent reduction of V^{5+} to V^{4+} and the formation of $Ti_{1-x}V_xO_2$ solid solution in rutile structure.^{14),18)-21)} However, the formation of TiO_2 rutile phase observed for the samples is thought to be partly due to an effect of the "nesa" substrate because rutile phase was not detected at all for the samples deposited on plain silica glass substrate. In fact it has been reported that the precipitation of TiO_2 in the presence of SnO_2 can be considered as a useful way to obtain single phase rutile crystal²²⁾ and in 3 mol% SnO_2 doped TiO_2 no anatase phase forms above 473 K.²³⁾

The cell parameters of anatase lattice were determined. There was seen significant increase in c axis with increasing V^{4+} concentration, while a axis was left almost unaffected with doping. For example, c axis of undoped TiO_2 film was found to be 0.9499 nm and it increased gradually to 0.9516 nm when doping level reached 8 mol%. Beyond 8 mol% no increase in c lattice parameter was observed. No significant difference in cell parameters was found between post-heating atmospheres.

3.2 Photoelectrochemical properties

3.2.1 Current-potential characteristics

Figure 2 shows the photocurrent of the $Ti_{1-x}V_xO_2$ thin film electrodes measured as a function of applied bias potential in the range of -0.5 to 2.0 V vs. SCE under an illumination of 500 W Xe lamp. $I-V$ curves of undoped TiO_2 film prepared by the same procedure is shown in Fig. 2B for comparison.

As shown in Fig. 2A, photocurrent onset potential of the electrodes $x \leq 0.06$ reveals small positive shifts and photocurrent at bias potentials beyond ca. 1 V vs. SCE increases slightly with dopant concentration. Moreover, post-heating in air resulted in a small positive shift in onset potential and lower photocurrent throughout the bias potential range compared to that in N_2 . Figure 2B shows the $I-V$ characteristics of the electrodes with $x \geq 0.07$. An obvious difference between the $I-V$ curves of the electrodes with $x \leq 0.06$ and $x \geq 0.07$ can be seen from the inset of Fig. 2A, revealing a significant positive shift in the photocurrent onset potential and almost double increase in photocurrent beyond 1 V vs. SCE. It should be noted that in the samples with $x \geq 0.07$ post-heating in N_2 resulted in further positive shift in onset potential compared to post-heating in air (Fig. 2B). With increasing x , the onset potential of the electrode samples post-heated in air remains almost unchanged.

The photocurrent in the visible region as a function of applied bias potential was recorded for $Ti_{0.95}V_{0.05}O_2$ and $Ti_{0.90}V_{0.10}O_2$ thin film electrodes post-heated in N_2 and is presented in Fig. 3. A quick rise in photocurrent at applied bias

Fig. 2. Photocurrent-voltage ($I-V$) characteristics of the $Ti_{1-x}V_xO_2$ thin film electrodes with (A) $x \leq 0.06$ and (B) $x \geq 0.07$, under an illumination of 500 W Xe lamp (solid and dotted lines represent samples post-heated in N_2 and air, respectively; at a sweep rate of 20 mV/s).

Fig. 3. Photocurrent-voltage ($I-V$) characteristics of the $Ti_{1-x}V_xO_2$ thin film electrodes with $x=0.05$ and 0.10 under an illumination of the visible light (at a sweep rate of 20 mV/s).

potentials beyond 1.0 V vs. SCE found for $Ti_{0.90}V_{0.10}O_2$ remained almost unchanged even under the visible light illumination. Another important feature to be noted is as follows. That is, with increasing cut-wavelength of the optical

filter a clear shift in photocurrent onset potential is found for $\text{Ti}_{0.90}\text{V}_{0.10}\text{O}_2$, while the onset potential of $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ is not affected when the photon energy of incident light is changed.

3.2.2 Capacitance measurements

Capacitance vs. bias potential curves of the thin film electrodes measured under frequency modulation of 1 Hz are shown in Fig. 4, where solid and dotted lines represent the samples post-heated in N_2 and air, respectively. It can be seen from this figure that the samples post-heated in N_2 with $x \geq 0.07$ possess an extremely large capacitance. A drastic decrease in capacitance was observed when the samples were post-heated in air, implying the largely reduced density of surface states in the electrode sample post-heated in air. On the contrary, post-heating the samples with $x \leq 0.06$ in air gave larger capacitance compared to post-heating in N_2 as shown in the inset of Fig. 4.

3.2.3 Photocurrent action spectra

In Fig. 5, photocurrent action spectra of the electrodes post-heated in N_2 at a bias potential of 1.5 V vs. SCE are shown. There was basically no difference in action spectra between the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrode samples post-heated in air and N_2 . Short-circuit photocurrents (J_{sc}) were measured in the excitation wavelength (λ) region from 300 to 600 nm at intervals of 10 nm, and incident photon (I_{inc}) to current conversion efficiency (IPCE) was calculated using the following equation:²⁴⁾

$$\text{IPCE}(\%) = \frac{I_{\text{sc}} (A/\text{cm}^2)}{I_{\text{inc}} (W/\text{cm}^2)} \times \frac{1240}{\lambda (\text{nm})} \times 100$$

At a bias potential of 1.5 V vs. SCE $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes did show a photoresponse in the visible region up to 560 nm the degree of which depended on the dopant concentration. For example, the photoresponse in the visible region was extended from 510 to 560 nm, when the V^{4+} content was increased from $x = 0.03$ to 0.06. However, no extension was observed with further addition of V^{4+} .

4. Discussion

Photoelectrochemical (PEC) characterizations of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes reveal an obvious difference between electrode samples with $x \leq 0.06$ and $x \geq 0.07$. An abrupt change in PEC properties of the $\text{Ti}_{0.93}\text{V}_{0.07}\text{O}_2$ electrode compared to $\text{Ti}_{0.94}\text{V}_{0.06}\text{O}_2$ electrode and a close resemblance of the former to the electrodes with $x \geq 0.10$, in which VO_2 phase has been detected, lead us with a reasonable intuition to the assumption that the precipitated VO_2 species are also present in $\text{Ti}_{0.93}\text{V}_{0.07}\text{O}_2$ and $\text{Ti}_{0.92}\text{V}_{0.08}\text{O}_2$ electrode samples. The presence of VO_2 species unsolubilized into anatase lattice is considered mainly to cause the differences in PEC properties as mentioned above.

Based on this assumption we propose a band model as shown in Fig. 6. However, it is evident that the incorporation of VO_2 into an anatase matrix even within the solubility limit produces a lot of surface states, which results in positive onset potential shift and lower photocurrent at even higher applied potentials. Moreover, the precipitation of the VO_2 species should raise the density of energy levels within the bandgap. This can be seen from the observed large capacitance of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrodes with $x \geq 0.07$ especially at lower applied potentials, e.g., at 0–1.0 V vs. SCE. At a lower bias potential, where the band bending is smaller as shown in Fig. 6 by the solid line, such VO_2 -derived surface states trap the photogenerated charge carriers serving as an extensive recombination center. This is thought to be the reason why the photocurrent onset potential of the thin film electrodes with $x \geq 0.07$ is more positive than that of the electrodes with $x \leq 0.06$. On the contrary, at a higher applied potential (≈ 1.0 V vs. SCE), where an adequate band bend-

Fig. 4. Capacitance of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes as a function of applied bias potential (solid and dotted lines represent samples post-heated in N_2 and air, respectively; measured at 1 Hz).

Fig. 5. Photocurrent action spectra of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes post-heated in N_2 (at an applied bias potential of 1.5 V vs. SCE).

Fig. 6. Band model of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes with $x \geq 0.07$.

ing is attained, it is supposed that electron transfer from the precipitated VO_2 phase to the conduction band of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrodes possibly due to a tunnel effect may take place.

This results in the continuous increase in the photocurrent with increasing bias potential. Such a tunnel effect would not be expected at a lower applied potential due to small band bending.

I - V characteristics of the $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ and $\text{Ti}_{0.90}\text{V}_{0.10}\text{O}_2$ electrodes measured under the illumination of the visible part of the 500 W Xe lamp (Fig. 3) support the above model. A large photocurrent of the $\text{Ti}_{0.90}\text{V}_{0.10}\text{O}_2$ electrode beyond 1.0 V vs. SCE still remained even under the illumination of the visible light compared to $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ electrode. Considering that the bandgap energy of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes did not decrease further beyond $x=0.06$ as it can be seen from Fig. 5, the above results unambiguously suggest different origins of visible photoresponse between the $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ and $\text{Ti}_{0.90}\text{V}_{0.10}\text{O}_2$ electrodes. If we assume that the origin of the visible photoresponse of $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ is intrinsic or due to the decrease in the bandgap energy, there must be other extrinsic source of the visible photoresponse for $\text{Ti}_{0.90}\text{V}_{0.10}\text{O}_2$ electrode beyond 1.0 V vs. SCE, which may possibly be the precipitated VO_2 phase. The positive shift in photocurrent onset potential with cut-wavelength of optical filter is then explained as follows. With decreasing energy of the excitation light the tunnel effect via VO_2 species takes place at more positive bias potential. In other words, much deeper band bending is required for the more efficient electron transfer via the tunnel effect.

With an intention to suppress the precipitation of VO_2 , the samples were subjected to post-heating treatment in air. As a result, V_2O_5 phase instead of VO_2 was detected and less positive shift in photocurrent onset potential was observed. Contrary to our expectation, however, photocurrent at a higher applied potential did not decrease. Therefore, we consider that in case of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ samples with $x \geq 0.07$, VO_2 species are still present even when the sample is post-heated in air, though it has not been detected by an XRD analysis. By post-heating in air, a part of VO_2 species mainly located at the surface is oxidized to V_2O_5 , which is soluble in aqueous electrolyte. Since this V_2O_5 phase is dissolved when the electrode is immersed in aqueous solution, the number of the recombination sites might appreciably decrease resulting in less positive shift of the onset potential. In fact, the capacitance of the films post-heated in air was found to be much smaller than that post-heated in N_2 (Fig. 4) and almost no V_2O_5 phases has been detected in the samples after PEC measurements.

5. Conclusion

The solubility limit of VO_2 in TiO_2 is about 6 mol% under the present sample preparation conditions. When the doping level exceeds this limit, excess VO_2 species is oxidized into V_2O_5 or crystallized in its orthorhombic structure depending on the post-heat treatment atmosphere. Such VO_2 species unsolubilized into anatase lattice is thought to affect the photoelectrochemical properties of the thin film electrodes in two different ways depending on the applied bias potential. It introduces additional energy levels within the bandgap of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ electrode. At a lower applied potential, such

energy levels trap the photogenerated charge carriers serving as an extensive recombination site. As a result the photocurrent onset potential of the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ thin film electrodes with $x \geq 0.07$ shifts to more positive values. On the other hand, when an adequate band bending is achieved at more positive bias potentials, such VO_2 sites contribute to the photocurrent possibly due to a tunnel effect resulting in the continuous increase in the photocurrent.

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References

- 1) Fujishima, A. and Honda, K., *Nature*, **238**, 37-38 (1972).
- 2) Zhao, G., Kozuka, H., Lin, H. and Yoko, T., *Thin Solid Films*, **339**, 123-28 (1999).
- 3) Zhao, G., Kozuka, H., Lin, H., Takahashi, M. and Yoko, T., *Thin Solid Films*, **340**, 125-31 (1999).
- 4) Indradev, Van Ruyven, L. J. and Williams, F. D., *J. Appl. Phys.*, **39**, 3344-48 (1968).
- 5) Thompson, A. G. and Woolley, J. C., *Can. J. Phys.*, **45**, 255-61 (1967).
- 6) Richardson, D., *J. Phys.*, **C4**, L289-92 (1971).
- 7) Emtage, P. R., *J. Appl. Phys.*, **33**, 1950-60 (1962).
- 8) Nikolaev, A. V., Kostrubov, Yu. N. and Andreev, B. V., *Sov. Phys. Solid State*, **34**, 1614-17 (1992).
- 9) Shanon, R. D., *Acta Crystallogr.*, **A32**, 751-67 (1976).
- 10) Kristenson, I. K., *J. Appl. Phys.*, **39**, 5341-43 (1968).
- 11) Gautron, J., Lemasson, P., Poumellec, B. and Marucco, J.-F., *Sol. Energy Mater.*, **9**, 101-11 (1983).
- 12) Davidson, A. and Che, M., *J. Phys. Chem.*, **96**, 9909-15 (1992).
- 13) Busca, G., Tittarelli, P., Tronconi, E. and Forzatti, P., *J. Solid State Chem.*, **67**, 91-97 (1987).
- 14) Bond, G. C., Sarkany, J. and Parfitt, G. D., *J. Catal.*, **57**, 476-93 (1979).
- 15) Forro, L., Chauvet, O., Emin, D., Zuppiroli, L., Berger, H. and Levy, F., *J. Appl. Phys.*, **75**, 633-35 (1994).
- 16) Tang, H., Prasad, K., Sanjines, R., Schmid, P. E. and Levy, F., *J. Appl. Phys.*, **75**, 2042-47 (1994).
- 17) Marinder, B.-O. and Magneli, A., *Acta Chem. Scand.*, **16**, 1345-47 (1958).
- 18) Rooseboom, F. and Gellings, P. J., *J. Phys. Chem.*, **84**, 2783-91 (1980).
- 19) Saleh, R. Y., Wachs, I. E., Chan, S. S. and Chersich, C. E., *J. Catal.*, **98**, 102-14 (1986).
- 20) Kozłowski, R., Pettifer, R. F. and Thomas, J. M., *J. Phys. Chem.*, **87**, 5176-81 (1983).
- 21) Vejux, A. and Courtine, P., *J. Solid State Chem.*, **23**, 93-103 (1978).
- 22) Kumar, K. P., Keizer, K., Burggraaf, A. J., Okubo, T. and Nagamoto, H., *J. Mater. Chem.*, **3**, 923-29 (1993).
- 23) Ding, X. Z., Qi, Z. A. and He, Y. Z., *Nanostructured Materials*, **4**, 663-68 (1994).
- 24) Hotchandani, S. and Kamat, P. V., *J. Phys. Chem.*, **96**, 6834-39 (1992).