

Preparation of polycrystalline VO₂ films on glass and TiO₂/glass substrates by means of excimer laser assisted metal organic deposition

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An excimer laser assisted metal organic deposition process for the preparation of vanadium dioxide (VO₂) films is described. When a precursor film grown on a silica glass substrate by preheating at 300°C was irradiated with a KrF laser at room temperature in air, the film was crystallized into polycrystalline VO₂ phases. Generally, the preparation of VO₂ films requires strict atmosphere control, but in this process, the polycrystalline VO₂ films were successfully prepared without it. Moreover, it was revealed that crystallization into the VO₂ phases was promoted by a TiO₂ buffer layer placed on the glass substrate. This means that the photochemical reaction induced by the TiO₂ absorbing the laser participates in the crystallization. The electrical resistivity of the film grown on the TiO₂/glass substrate was lowered compared to that of the film grown on the glass substrate due to improvement of the film uniformity. The crystallinity of the obtained film was dependent on the irradiation time. With the improved crystallinity of the film, the resistivity drop through the metal-insulator transition became large.

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Key-words : VO₂, Film, Laser, KrF, MOD

[Received March 23, 2010; Accepted May 20, 2010]

1. Introduction

Vanadium dioxide (VO₂) undergoes a metal-to-insulator (MI) transition at 341 K.^{1,2)} Significant variations in the electrical and optical properties accompanied by the MI transition are very attractive for thermal sensors^{3,4)} and optical switching devices.⁵⁾ VO₂ films have been prepared by various processes, e.g., sputtering, chemical vapor deposition, pulsed laser deposition and chemical solution deposition (CSD).⁶⁻¹⁰⁾ Among them, the CSD would be advantageous in process and cost. So far, by means of the CSD such as sol-gel and metal organic deposition (MOD), VO₂ films have been often prepared.⁸⁻¹⁰⁾ However, in these processes, VO₂ films have been prepared at around 500°C in reducing atmosphere or at strictly controlled oxygen partial pressure. Considering that VO₂ films are put to practical uses, it is desirable that the processing temperature is 300°C or less in order to be compatible with device fabrication technologies.¹¹⁾ Additionally, for a simpler and lower-cost process, it is necessary that VO₂ films are prepared in air without controlled ambient atmosphere.

For this purpose, we employed the excimer laser assisted metal organic deposition (ELAMOD). In the ELAMOD process, crystallization of a film is induced by irradiation using the excimer laser instead of by heat treatment used in typical MOD processes. The excimer laser is a pulsed laser with narrow pulse width of 26 nanoseconds and with high photon energy. Hence, a precursor film can be annealed on the nanosecond time scale during the laser irradiation with no heat-damage to the substrate. So far, various oxide films, such as manganese perovskites, SnO₂, TiO₂ and PZT, have been successfully prepared at low temperature.¹²⁻¹⁵⁾

In this study, we prepared polycrystalline VO₂ films on silica glass substrates by means of the ELAMOD at 300°C or less in air without strict atmosphere control. The VO₂ films were first directly prepared on the glass substrates by laser irradiation and then a crystallization process of the films were discussed based on the thermal simulation results. Secondly, we examined the effect of the TiO₂ buffer layers deposited on the glass substrates on crystallization of the VO₂ films.

2. Experimental

A vanadium carboxylate solution was spin-coated onto a silica glass substrate at 3000 rpm for 10 sec, then preheated in air at 300°C for 10 min to eliminate the solvent and part of the organic components. The preheated film was irradiated with a KrF excimer laser ($\lambda = 248$ nm; Lambda Physik Compex110) at room temperature in air. The laser fluence was in the range of 20–80 mJ/cm², and the repetition rate was fixed at 10 Hz. This procedure produced a 25-nm-thick film. Thicker films were obtained by repeating this procedure. The preparation procedure for the TiO₂ buffer layers was as follows. A titanium carboxylate solution was spin-coated onto the silica glass substrate and preheated at 300°C for 10 min to eliminate the organic components. The obtained films were heated at 900°C to convert them to the rutile structure. The thickness of the TiO₂ layer was estimated to be about 100 nm. The preparation procedure of the VO₂ films on the TiO₂/silica glass substrates was the same as already described.

The structure of the obtained film was evaluated by X-ray diffraction (XRD) of a Rigaku SmartLab diffractometer and by a Hitachi S-800 field emission-scanning electron microscope (SEM). The electrical resistivity of the film was measured by using a Toyo Corp. RET8300. The temperature distribution in the films during laser irradiation was calculated with a one-dimen-

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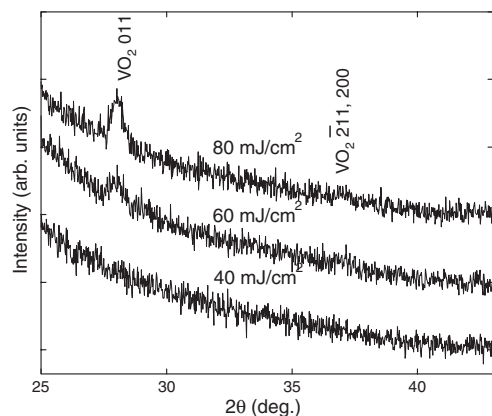


Fig. 1. XRD patterns of the films grown on the silica glass substrates by irradiation with the KrF laser.

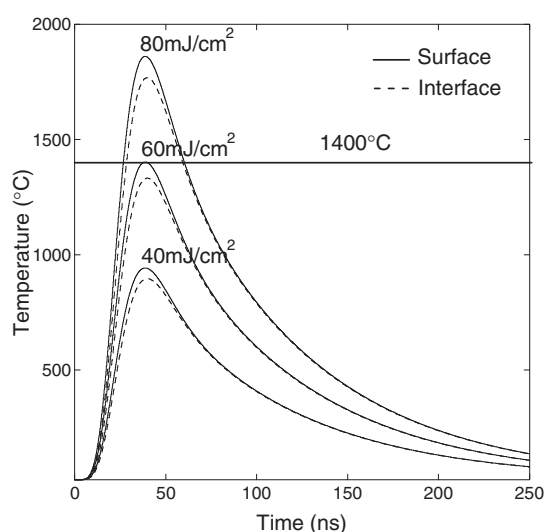


Fig. 2. Calculated temperature of films as a function of time after laser irradiation in the silica glass substrate case.

sional heat conduction equation, as described in detail in Ref. 13). This thermal simulation was carried out under the assumption that the film was a V_2O_5 phase.

3. Results and discussion

The precursor films preheated at 300°C on the silica glass substrates were irradiated with the KrF laser at 40, 60 or 80 mJ/cm² for 10 min at room temperature in air. **Figure 1** shows XRD patterns of the 75-nm-thick films obtained by repeating this procedures three times. As seen in the figure, no diffraction peak was observed in the film irradiated at 40 mJ/cm². In contrast, the films irradiated at 60 or 80 mJ/cm² were crystallized into the polycrystalline VO_2 phases. **Figure 2** shows the calculated temperature of the films as a function of time after one pulse shot of the laser. The temperature of the film rapidly increases for about 40 ns after the one pulse shot, owing to the film absorbing the laser. The maximum surface temperatures of the films irradiated at 40, 60 and 80 mJ/cm² are about 940, 1400 and 1860°C, respectively. Based on an Ellingham diagram for a V–O system,¹⁰⁾ V_2O_5 is reduced to VO_2 at about 1400°C in air. Hence, the film crystallization by laser irradiation at 60 and 80 mJ/cm² is attributed to the film temperature. This means that the crystallization was mainly induced by this photothermal reaction. During the irradiation at 60 mJ/cm², the maximum surface tem-

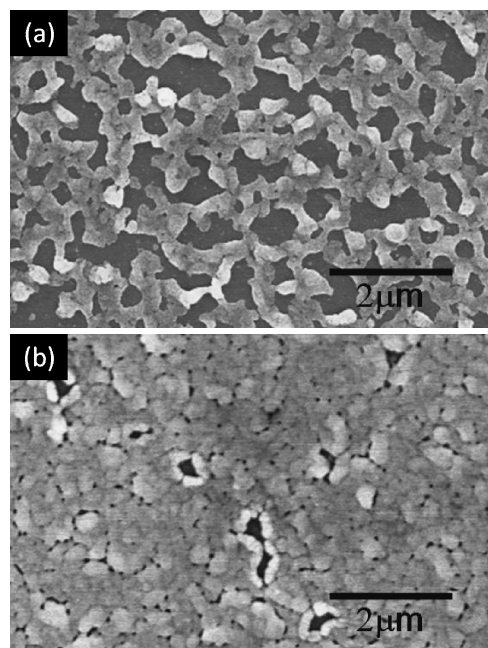


Fig. 3. SEM images of the films grown on the silica glass substrates (a) by laser irradiation at 80 mJ/cm² for 10 min (b) by laser irradiation at 80 mJ/cm² for 60 min for first and second layers and 60 mJ/cm² for 10 min for upper layers.

perature reaches 1400°C, but the temperature rapidly decreases on a nanosecond scale. Therefore, the film was not sufficiently crystallized compared to the film irradiated at 80 mJ/cm².

Figure 3(a) shows the SEM image of the film irradiated at 80 mJ/cm². As seen in the figure, the crystallized grains of the film aggregated due to the low adhesion to the substrate. This indicated that the interface between the film and the substrate remained amorphous phases because the crystallization occurred from the film surface due to the higher temperature than the substrate interface by about 100°C (Fig. 2). Also, when the amorphous phase is remained, the film temperature becomes higher due to the low heat conductivity of the amorphous phase. This promotes the aggregation of the grains since a part of the film would melt.

To make homogeneous dense films, the first and second layers were irradiated at 80 mJ/cm² for 60 min. The upper layers were then irradiated at 60 mJ/cm² for 10 min. The total film thickness was about 200 nm. **Figure 3(b)** shows the SEM image of the obtained film. The film became dense, but aggregations were partly observed. Therefore, the adhesion was improved by prolonging the irradiation time, but in part of the interfacial area, the crystallization did not sufficiently progress. **Figure 4** shows the temperature dependence of electrical resistivity of the film. The MI transition was observed at around 340 K in the film. Based on these results, it was revealed that the VO_2 films were prepared at 300°C in air without ambient atmosphere control using the ELAMOD process.

In order to prevent the aggregation, we examined the effect of the TiO_2 buffer layers on the crystallization. **Figure 5** shows XRD patterns of 200-nm-thick films grown on the TiO_2 /silica glass substrates by laser irradiation at 20–80 mJ/cm² for 10 min for each layer. At 20 mJ/cm², no diffraction peak was observed. When the films were irradiated at higher than 40 mJ/cm², the films were crystallized into the VO_2 phase. The calculated temperature distributions in the films during the laser irradiation were shown in **Fig. 6**. The temperature of the film on the TiO_2 /

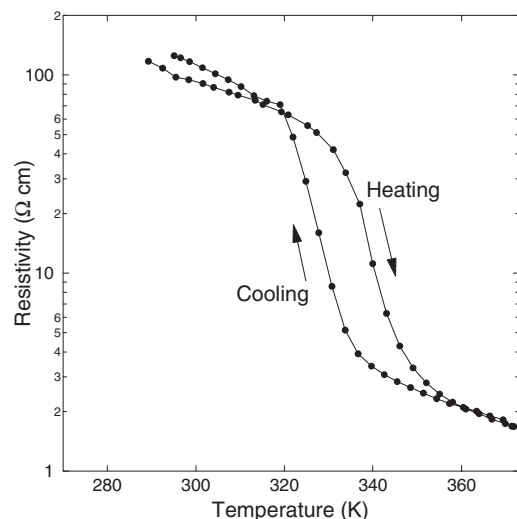


Fig. 4. Temperature dependence of electrical resistivity of the film on the silica glass substrate.

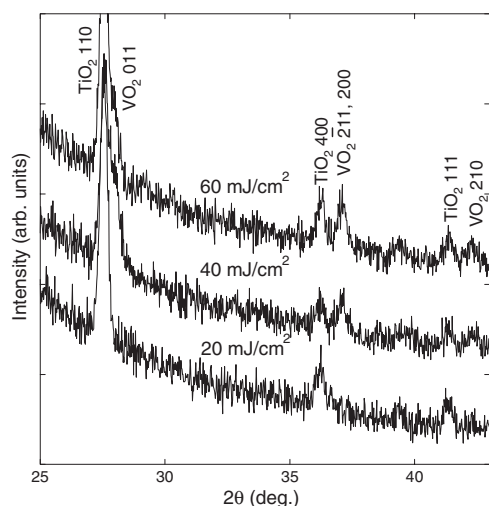


Fig. 5. XRD patterns of the films grown on the TiO₂/silica glass substrates by laser irradiation.

glass substrate is low compared to that of the film on the glass substrate during laser irradiation at the same fluence, due to higher heat conductivity of the TiO₂ layer than that of the silica glass. It is worth noting that the maximum surface temperature of the films irradiated at 40 mJ/cm² is about 800°C, which is much lower than the reduction temperature of 1400°C from V₂O₅ to VO₂. This indicates that the crystallization into the VO₂ phase was not mainly induced by the photothermal effect unlike the case without the TiO₂ layer. The TiO₂ layer can absorb the KrF laser since the band-gap energy of TiO₂ (3.2 eV) is lower than the photon energy of the KrF laser (5.4 eV). In addition, the lattice mismatch between VO₂ and TiO₂ is very small (tetragonal VO₂: $a = 0.4554$ nm, $c = 0.2856$ nm, rutile TiO₂: $a = 0.4593$ nm, $c = 0.2959$ nm, lattice mismatch; $a = 0.863\%$, $c = 3.62\%$).^{16),17)} Therefore, it is considered that the photo-activated dangling bond on the TiO₂ interface, induced by absorbing the laser, plays an important role in the crystal nucleation. Such photochemical reaction would result in decreasing the laser energy for the crystallization. In our previous work, it was revealed that the crystallization of the film is enhanced when a substrate with small lattice mismatch to a film absorbed the laser.^{13),15)}

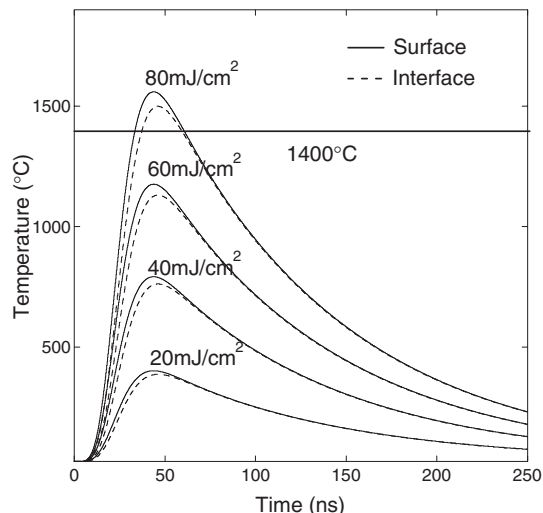


Fig. 6. Calculated temperature of the films as a function of time after laser irradiation in the TiO₂/silica glass substrate case.

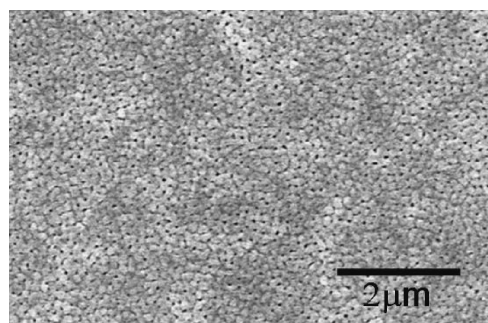


Fig. 7. SEM image of the film grown on the TiO₂/silica glass substrate by laser irradiation at 40 mJ/cm².

Figure 7 shows an SEM image of the film grown on the TiO₂/glass substrate. There was no aggregation of the grains in the film. This indicates that the adhesion between the film and the substrate was significantly improved. It is considered that the film was selectively crystallized from the substrate interface, due to the photochemical reaction that occurred at the interface. In addition, the crystal nucleus was not generated in other parts of the film, due to a temperature lower than 1400°C. **Figure 8** shows the temperature dependences of electrical resistivity of the films. The film irradiated at 20 mJ/cm² was semiconductor since it was not crystallized based on the XRD result. The films irradiated at higher than 40 mJ/cm² exhibited MI transitions at around 340 K due to the VO₂ phase. The resistivity of these films grown on the TiO₂/glass was reduced to about one-fifth over the temperature compared to the film grown on the glass as shown in Fig. 4. **Figure 9** shows the intensity of 011 Bragg diffraction for the VO₂ and full width at half maximum (FWHM) of the peaks; each peak was evaluated by Gaussian fitting. In the TiO₂/glass substrate case, the intensity and FWHM were almost the same in the range of 40–80 mJ/cm². For the glass substrate case, the intensity is much higher than that of the films grown on the TiO₂/glass substrates, and the FWHM slightly increased compared to the films grown on the TiO₂/glass substrates. This indicates that the crystallization in the film grown on the glass substrate sufficiently progressed compared to the films grown on the TiO₂/glass substrates. Therefore, the difference in the resistivity between the film on the glass and the films on the

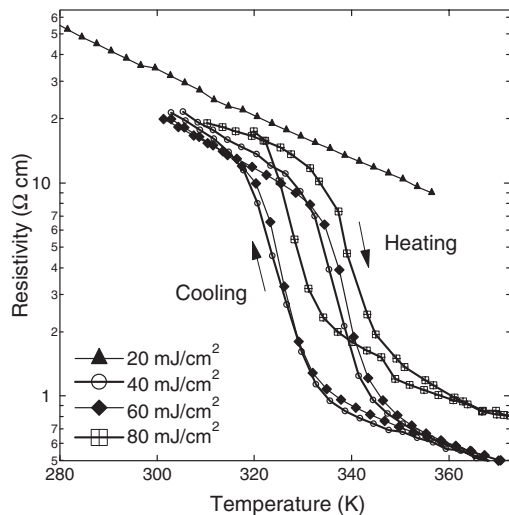


Fig. 8. Temperature dependence of electrical resistivity of the films on the TiO_2 /silica glass substrates by laser irradiation at different fluences for 10 min.

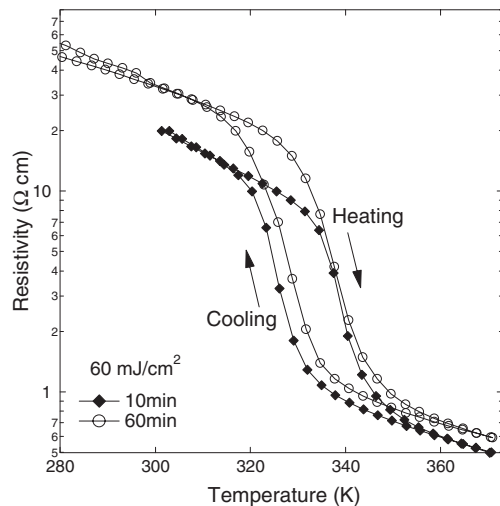


Fig. 10. Temperature dependences of electrical resistivity of the films on the TiO_2 /silica glass substrates by laser irradiation at 60 mJ/cm^2 for 10 or 60 min.

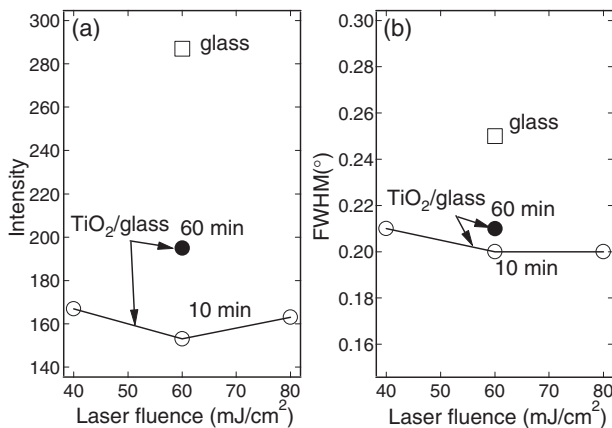


Fig. 9. (a) VO_2 011 Bragg diffraction intensity and (b) full width at half maximum (FWHM) of the peaks. The film on the glass substrate was prepared by laser irradiation at 80 mJ/cm^2 for 60 min for first and second layers and 60 mJ/cm^2 for 10 min for upper layers.

TiO_2 /glass would be due to the degree of the density. Namely, the film grown on the TiO_2 /glass was homogeneous and dense with no aggregation of the film, resulting in the low resistivity.

For the crystallization in the film on the TiO_2 /glass substrate to proceed, the laser irradiation time was prolonged to 60 min at 60 mJ/cm^2 . The 011 peak intensity of the XRD pattern for the VO_2 increased as shown in Fig. 9(a). The temperature dependence of electrical resistivity of the film was shown in Fig. 10. The resistivity drop of the film irradiated for 60 min became larger than that of the film irradiated for 10 min because the crystallinity was improved by prolonging the irradiation time. Based on these results, it was found that the laser-absorbing TiO_2 buffer layer was effective for the preparation of uniform and well crystallized VO_2 films on the glass substrate without aggregation.

4. Conclusions

We prepared the polycrystalline VO_2 films on the silica glass substrates at 300°C in air by the ELAMOD process. When the film was directly prepared on the glass substrate, the adhesion between the film and the substrate was low because the crystallization would progress from the film surface. Accord-

ingly, the grains making up the film were partially aggregated. To prevent the aggregation, we revealed that putting the TiO_2 buffer layer on the glass substrate was a very effective solution since the film crystallization was strongly enhanced by photochemical reaction induced by the TiO_2 absorbing the laser energy. Due to this effect, the film was selectively crystallized from the substrate interface. This resulted in preventing of the aggregation. The resistivity of the film grown on the TiO_2 /glass substrate was lower than the film grown on the glass substrate.

The crystallinity of the obtained films was dependent on the irradiation time. By improving the crystallinity of the film, the resistivity drop through the MI transition became large.

References

- 1) F. J. Morin, *Phys. Rev. Lett.*, **3**, 34–36 (1959).
- 2) A. Zylbersztejn and N. F. Mott, *Phys. Rev. B*, **11**, 4383–4395 (1975).
- 3) M. Nagashima and H. Wada, *J. Mater. Res.*, **12**, 416–422 (1997).
- 4) J. Li and N. Yuan, *Appl. Surf. Sci.*, **233**, 252–257 (2004).
- 5) H. Wang, X. Yi and Y. Li, *Opt. Commun.*, **256**, 305–309 (2005).
- 6) Y. Muraoka and Z. Hiroi, *Appl. Phys. Lett.*, **80**, 583–585 (2002).
- 7) D. Brassard, S. Fourmaux, M. Jean-Jacques, J. C. Kieffer and M. A. El Khakani, *Appl. Phys. Lett.*, **87**, 051910 (2005).
- 8) G. Guzman, R. Morineau and J. Livage, *Mater. Res. Bull.*, **29**, 509–515 (1994).
- 9) F. B  teille, L. Mazerolles and J. Livage, *Mater. Res. Bull.*, **34**, 2177–2184 (1999).
- 10) I. Yamaguchi, T. Manabe, T. Tsuchiya, T. Nakajima, M. Sohma and T. Kumagai, *Jpn. J. Appl. Phys.*, **47**, 1022–1027 (2008).
- 11) J. Dai, X. Wang, S. He, Y. Huang and X. Yi, *Infrared Phys. Technol.*, **51**, 287–291 (2008).
- 12) T. Tsuchiya, A. Watanabe, Y. Imai, H. Niino, I. Yamaguchi, T. Manabe, T. Kumagai and S. Mizuta, *Jpn. J. Appl. Phys.*, **38**, L823–L825 (1999).
- 13) T. Nakajima, T. Tsuchiya, M. Ichihara, H. Nagai and T. Kumagai, *Chem. Mater.*, **20**, 7344–7351 (2008).
- 14) T. Tsuchiya, F. Kato, T. Nakajima, K. Igarashi and T. Kumagai, *Appl. Surf. Sci.*, **255**, 9808–9812 (2009).
- 15) T. Tsuchiya, I. Yamaguchi, T. Manabe, T. Kumagai and S. Mizuta, *Mater. Sci. Semicond. Process.*, **5**, 207–210 (2003).
- 16) K. D. Rogers, *Powder Diffraction*, **8**, 240–244 (1993).
- 17) S. C. Abrahams and J. L. Bernstein, *J. Chem. Phys.*, **55**, 3206–3211 (1971).