Highly oriented VO$_2$ thin films prepared by sol-gel deposition method

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Abstract

Highly oriented VO$_2$ thin films were grown on sapphire substrates by the sol-gel method that includes a low pressure annealing in an oxygen atmosphere. This reduction process effectively promotes the formation of the VO$_2$ phase over a relatively wide range of pressures below 100 mTorr and temperatures above 400°C. X-ray diffraction analysis showed that as-deposited films crystallize directly to the VO$_2$ phase without passing through intermediate phases. VO$_2$ films have been found to be with [100]- and [010]-preferred orientations on Al$_2$O$_3$(1012) and Al$_2$O$_3$(1010) substrates, respectively. Both films undergo a metal-insulator transition with an abrupt change in resistance, with different transition behaviors observed for the differently oriented films. For the [010]-oriented VO$_2$ films a larger change in resistance of 1.2×10$^4$ and a lower transition temperature are found compared to the values obtained for the [100]-oriented films.
Vanadium dioxide (VO$_2$) has been known to undergo the metal-insulator transition (MIT) near 68°C accompanied by abrupt changes in electrical resistivity and infrared transmission.$^{1-4}$ These transition properties make VO$_2$ films suitable for technological applications such as electrical switches and electro-optical modulators.$^{3,5}$ VO$_2$ films have shown reproducible switching characteristics without sample degradation, while bulk materials did not endure repeated transitions due to stress. Although films with transition characteristics comparable to single crystal have been grown, there have not yet been any representative devices realized using this system. One of the reasons may be the stabilization of VO$_2$ phase. The formation of VO$_2$ phase is complicated due to the fact that there are several phases in vanadium oxide system with oxygen stoichiometry. Establishing a process for the fabrication of VO$_2$ film that possesses stable transition characteristics is crucial for the realization of devices.

Up to now, VO$_2$ films have been fabricated by various methods such as pulsed laser deposition,$^{6-9}$ sputtering,$^{10-12}$ and chemical vapor deposition.$^{13,14}$ Among these methods, researchers have focused on the sol-gel method for depositing VO$_2$ films because it has many advantages such as low cost, large area deposition, and the feasibility of metal-doping.$^{15-17}$ Fabrication of films with a variety of transition properties is needed in order to satisfy particular device specifications. The switching behavior of the MIT strongly depends on the crystallinity and the stoichiometry of the films. The sol-gel method can easily make films with various stoichiometries and metal dopants, thus permitting the growth of numerous films with a specific transition behavior. Therefore, this method is suitable for fabricating films for switching devices. However, the formation of the pure phase is not easy even when employing the sol-gel technique due to the difficulty in controlling the annealing condition. The annealing regime of the films has been known to be crucial for forming the VO$_2$ phase. It has been reported that a reducing gas atmosphere at a low pressure is required for successful phase formation. Moreover, vanadium oxide system undergoes successive reduction with increasing annealing temperature.$^{15,17}$ This means that the films pass through numerous intermediate phases during the annealing process, thus resulting in a narrower fabrication
In this research, we have successfully fabricated VO$_2$ films by the sol-gel method with a more simplified annealing process. The formation of the VO$_2$ phase was affected by annealing in oxygen only without a reducing gas. The films have highly preferred orientations related to the sapphire substrates. We investigate the different characteristics of the transition behavior with respect to the film orientation.

VO$_2$ films were grown on sapphire substrates by a sol-gel method. This method consists of spin-coating and a subsequent annealing process under low pressure. The coating solutions were prepared by synthesizing the vanadium tri-isopropoxide, VO(OC$_3$H$_7$)$_3$ (Stream Ltd. USA), in isopropanol using a catalyst of acetic acid. The final 0.12 M solution concentration was thus prepared. The solution was spin-coated onto sapphire substrates with a spin rate of 2000 rpm for 20 s. The coated films were dried at 250°C for 3 min on a hot plate to remove the excess alcohol. The procedure was performed in air to partially hydrolyze the alkoxide film with ambient moisture and repeated three times in the same manner. The thickness per cycle was approximately 32 nm. The final heat treatment was carried out at 410°C for 30 min in air, which made the films turn orange-yellow in color. In order to form the VO$_2$ phase through a reduction process, subsequent annealing of the films was done in a low pressure of oxygen.

An X-ray diffractometer (XRD) using Cu K$_\alpha$ was used to determine the film orientation. The surface morphology and the grain structure of the films were investigated by scanning electron microscopy (SEM). The electrical resistance of the films was measured by using the four-probe method.

Figure 1 shows X-ray diffraction patterns of the films annealed at various temperatures. The films were annealed at each temperature for 10 min at a pressure of 32 mTorr. The XRD $\theta$-2$\theta$ scans indicate that both films have a strong orientation relation to the sapphire substrate. The films on Al$_2$O$_3$(1012) are grown with a [100]-preferred direction, as shown in Fig. 1(a). As-deposited film without an annealing has V$_2$O$_5$(001) peak, but its intensity is very weak compared to the completely crystallized films on sapphire. This indicates that the
degree of the film crystallization to the $V_2O_5$ phase is low. For the films annealed over and at 400°C, the strong XRD peak related to the crystallization appears at a $2\theta$ value of 37°, which corresponds to the $VO_2$(200) reflection of the monoclinic phase. Although the small peak with other direction exists, we can confirm that the films have a strong orientation from the comparative analysis of the peaks. The crystallization behavior of the films grown on $Al_2O_3$(1010) is also similar to that on (1012) except that the [010]-preferred orientation is obtained, as shown in Fig. 1(b). The films have a strong (040) peak of the monoclinic $VO_2$ phase. We also found that the phase formation of the films during the annealing process depends largely on the annealing temperature rather than the pressure. A stable $VO_2$ phase is formed in the range from a few mTorr to near 100 mTorr.

The fact that no other peak expected for $VO_2$ phase is observed in all films annealed at various temperatures is of particular interest. As-deposited films have been known to undergo a reduction process to the final $VO_2$ phase passing through intermediate phases such as $V_3O_7$ and $V_6O_{13}$ during the annealing process.\textsuperscript{15,17} That is, the reduction of vanadium oxide successively occurs as the annealing temperature increases. However, our results show that the annealing process does not follow the successive reduction of the vanadium oxide and thus no intermediate phases appear at the various annealing temperatures. Generally, the annealing process was carried out under reducing gas mixture as like $H_2$ and CO, whereas our process was performed in oxygen only without reducing gases. Although the further study is required to understand completely the phase formation, our simplified reducing process can be the origin of this phenomenon. Our fabrication process of $VO_2$ films has considerable advantages over those in previous reports.\textsuperscript{15,17} Since various intermediate phases are not generated during the fabrication process, there is a large process window for the production of high quality film.

Figure 2 shows SEM images of the films. Optically, the color of the $VO_2$ films is golden-brown. The change of surface morphology of both films grown on (1012) and (1010) with annealing temperature is similar. As shown in Fig. 2, as-deposited films without a subsequent annealing process show well-formed grains although the crystallinity is very weak in
the X-ray patterns of Fig. 1. Small grains are generated in the interior of initial grains, as illustrated in films annealed at 400°C. This image may be related to the formation of the VO$_2$ phase. Well crystallized films of the VO$_2$ phase at 470°C have grains which are roundish in shape and the average grain size is estimated to be about 100 nm.

Figure 3 shows the temperature dependence of the electrical resistance for both films. The characteristics of the resistance of the films can be another indicator of the film quality. The measurement was performed through sweep-up and -down processes. Both films undergo a metal-insulator transition with temperature. The film resistance decreases exponentially with increasing temperature and then an abrupt drop occurs at the critical temperature. It has been reported that the increasing hole density leads to the breakdown of the sub-gap and thus the transition into the metallic state.$^{3,18}$ As shown in Fig. 3, the change in resistance gets to as large as $8.7 \times 10^3$ and $1.2 \times 10^4$ for the VO$_2$/Al$_2$O$_3$(I012) and the VO$_2$/Al$_2$O$_3$(10I0) films, respectively. These values are comparable to those of the single crystal, which means that the films are highly oriented and possesses good stoichiometry.$^{10}$ Hysteresis in the resistance also occurs during the sweep-up and -down processes of temperature.

The inset of Fig. 3 displays the change in resistance curves for the different annealing temperatures. The films reveal different MIT behaviors with respect to the crystallinity. The onset and sharpness of the transition are characterized by the plot of $dR/dT$ for [100]-oriented films as shown in Fig. 4(a). The transition width defined as the full width at half maximum of this peak is as low as 0.6°C. The sharpness of the transition has been known to be related to the degree of misorientation between adjacent grains.$^{10}$ Well-matched grains permit an effective propagation of the metallic regions in the films without additional energy loss. The VO$_2$ films grown on (I012) have a lower transition width than 3.1°C for the films on (10I0), which indicates that the former films have higher in-plane alignment of grains.

Figure 4(b) shows the change in the transition temperature ($T_c$) and the magnitude of the resistance change ($\Delta R$) for both of the films annealed at various temperatures. $T_c$ is defined as the peak value of the $dR/dT$ curve. The resistance of the films annealed at 400°C decreases slowly with little change at a critical temperature. This indicates that the films
are not totally crystallized although the crystallinity of VO$_2$ phase is confirmed from the XRD patterns. Both of the films annealed above 430°C display good transition behaviors as evidenced by change in resistance but exhibit different transition characteristics. As shown in Fig. 4(b), for the VO$_2$/Al$_2$O$_3$($\bar{1}012$) films, the transition temperature of 65°C almost doesn’t change with annealing temperature above 430°C, while the resistance change slightly increases from $4.8\times10^3$ to $8.7\times10^3$. For the VO$_2$/Al$_2$O$_3$(10$\bar{1}$0) films, the transition temperature slightly changes from 63°C to 60°C, while the magnitude of the resistance change remains of order of $1.2\times10^4$ with increasing annealing temperature.

[010]-oriented VO$_2$ films show relatively higher $\Delta R$ and lower $T_c$ than [100]-oriented films. This is consistent with previously reported results. The direction in which the resistance was measured with respect to the film orientation could influence the transition characteristics. A further study is necessary to understand the different transition properties of both films in detail.

In conclusion, VO$_2$ phase was well-formed on sapphire substrates by using a simplified annealing process. The VO$_2$ films were grown in a wide range of pressures from several mTorr up to 100mTorr of oxygen atmosphere and at temperatures above 400°C, without passing through any intermediate phases. The VO$_2$ films had a highly preferred orientation, and showed resistance changes as large as $1.2\times10^4$ which is the comparable property of the single crystal. Different transition properties were obtained depending on the film orientation. Our method with a simplified annealing process leads to the effective growth of high quality VO$_2$ films.
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FIG. 1. X-ray diffraction patterns of vanadium oxide films grown on (a) Al$_2$O$_3$(1012) and (b) Al$_2$O$_3$(1010) substrates. The films were annealed at various temperatures in 32 mTorr of oxygen atmosphere.
FIG. 2. SEM images of vanadium oxide films grown on (a) Al$_2$O$_3$(1012) and (b) Al$_2$O$_3$(1010) substrates.
FIG. 3. Changes in resistance for (a) the VO$_2$/Al$_2$O$_3$(1012) and (b) the VO$_2$/Al$_2$O$_3$(1010) films. The inset displays the changes in resistance with annealing temperature with the curves normalized for convenience.
FIG. 4. (a) Derivative of the change in the resistance with respect to temperature for the film on Al₂O₃(1012). (b) Changes in the magnitude of the resistance change and transition temperature as a function of annealing temperature for the films on Al₂O₃(1012) and Al₂O₃(1010).