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VO_2 and V_2O_3 Films Fabricated on (1000) or $(10\bar{1}0)$ Al_2O_3 by Reactive RF-Magnetron Sputter Deposition and Annealing Processes

Sun Jin Yun,* Jung Wook Lim, Jong-Su Noh, and Hyun-Tak Kim

MIT Devices Team, Electronics and Telecommunications Research Institute
138 Gajeongno, Yuseong-gu, Daejeon, 305-700, Korea
*Phone Number: 82-42-860-5821; Fax Number: 82-42-860-5202; E-mail: sjyun@etri.re.kr

1. Introduction

Vanadium dioxide (VO_2) and vanadium sesquioxide (V_2O_3) are known as Mott-insulators showing abrupt metal-insulator transition (MIT) near 340 and 170K, respectively [1]. These vanadium oxides also show the structural phase transition (SPT) near the MIT temperatures (T_C). It has been reported that the MIT temperature can be varied by applying electric field or by irradiating infrared light [2]. Although it remains controversial as to whether the MIT and the SPT are isochronous, the variability provides a large potential to the MIT materials for programmable thermal or photo sensors.

Vanadium cations can exist in one of several oxidation states, such as V^{3+}, V^{4+}, or V^{5+}, to form several different vanadium oxides. They can also convert from one oxidation state to another, and easily coexist [3]. Therefore, it is very difficult to obtain stoichiometric VO_2 or V_2O_3 films of single chemical state using a simple deposition method without subsequent annealing in a well-controlled environment [4,5]. The VO_2 or V_2O_3 films have been fabricated using the reactivity through which V_2O_5, the oxide of the highest oxidation state (V^{5+}) among the vanadium oxides, can be reduced to VO_2 or V_2O_3 in appropriate environment [4-7]. Especially, earlier works had reported that annealing temperatures higher than 700°C had been required to reduce V_2O_5 to V_2O_3 in an environment flowing reducing agents [6,7]. In a previous work, the authors reported that the annealing in a very low pressure with no reducing agent could reduce sol-gel VO_2 films to V_2O_3 at a temperature much lower than the earlier reported temperatures [5].

In the present work, the preparations of VO_2 and V_2O_3 films were investigated using the oxide film initially deposited by reactive RF-magnetron sputter deposition technique. The difference of the films formed on two different substrates, (1000) and $(10\bar{1}0)$ Al_2O_3, was also briefly discussed.

2. Experiments

The reactive RF sputter deposition of vanadium oxide films was carried out using V-metal target of 4-inch diameter (99.9%, Kojyundo Kagaku) in the atmosphere of O_2 gas mixed with Ar. The O_2 gas fraction was fixed at 12.3 %, and the operating pressure was 5 mTorr. The operating pressure was selected to have the best film quality through the study on the effect of chamber pressure on MIT characteristics of VO_2 [8]. The RF power was 300W. The films were post-annealed to fabricate stoichiometric VO_2 at 490°C with O_2 pressure of 30 mTorr. V_2O_3 films were fabricated by reducing high quality VO_2 films in a very low pressure [5]. Two different kinds of sapphire (Al_2O_3) substrates, with crystalline orientations of (1000) or $(10\bar{1}0)$, were used. The thickness of vanadium oxide films were approximately 110 nm. The resistance was measured by standard four-point probe method.

3. Results and Discussion

First, the composition of as-deposited oxide film and annealed films was measured using Auger electron spectroscopy (AES), as listed in Table 1. Only VO_2 reveals MIT near 340K. Therefore, a reference film showing an abrupt MIT behavior near 340K was considered to be stoichiometric VO_2 film in the sensitivity calibration of vanadium and oxygen.

As shown in Table 1, the composition of an as-deposited oxide film was very similar to that of annealed VO_2 film showing MIT near 336K. Because the as-deposited oxide film did not show any MIT behavior, the film was not in the chemical state of VO_2. XRD measurement (the data not shown here) also indicated that the as-deposited film mostly contained V_2O_5 crystalline phases in spite of its oxygen deficiency.

Table 1 also listed the composition of a V_2O_3 film showing MIT near 172K. The O/V ratio in the film, 1.66, was larger than the expected value, 1.5. The result indicates that the film probably contained some amount of different vanadium oxides with higher oxidation states.

Table 1. The composition of as-deposited vanadium oxide, VO_2, and V_2O_3 films on $(10\bar{1}0)$ Al_2O_3

films	Content Ratio, O/V
as-deposited film	2.04
VO_2	2.08
V_2O_3	1.66

Figure 1 presents the resistance (R) vs. temperature (T) curves of VO_2 films formed on (1000) or $(10\bar{1}0)$ Al_2O_3 substrate. As illustrated in Fig. 1(b), the critical temperature, T_C, is defined as the temperature at which d(-log R)/dT shows the maximum value, and the peak width implicates the abruptness of MIT. The films formed on different substrates showed different T_C values as much as 5.4K. T_C of VO_2 on $(10\bar{1}0)$ Al_2O_3 was 336.0K. In spite of the different MIT temperatures, both films showed abrupt MIT as shown in Fig. 1. The results in Fig. 1(a) and 1(b) also indicate that the VO_2 film on $(10\bar{1}0)$ Al_2O_3 reveals more typical metallic behavior after MIT and underwent a sharper MIT than that on $(1000)Al_2O_3$. The VO_2 film on $(1000)Al_2O_3$ showed that the resistance kept on decreasing even after MIT as indicated by an arrow in Fig. 1(a).

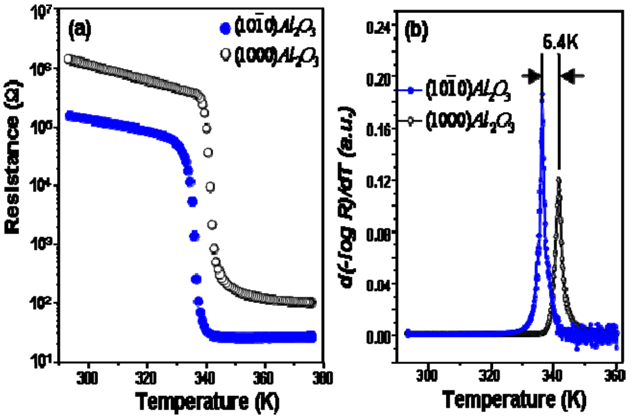

Figure 1. (a) R-T curves of VO_2 films deposited on single crystalline Al_2O_3 substrates and post-annealed at 490°C; (b) d(-log R)/dT vs. T curves showing T_C.

The R-T curves and d(-log R)/dT - T curves of V_2O_3 films on (1000) or $(10\bar{1}0)$ Al_2O_3 substrate are shown in Fig. 2(a) and 2(b), respectively. The films were prepared by reducing VO_2 films shown in Fig. 1. Similarly to our previous work using sol-gel VO_2 films [5], the VO_2 films fabricated in the present work easily lost their MIT characteristics during vacuum-annealing even at a temperature as low as 300°C in the chamber pressure of 2 x 10^{-6} Torr. The vacuum-annealing at a temperature higher than 550°C could fabricate V_2O_3 showing abrupt MIT near 170K.

Figure 2(a) indicates that the VO_2 film on $(10\bar{1}0)$ Al_2O_3 reveals larger resistance change by MIT than that on $(1000)Al_2O_3$. The resistance change of V_2O_3 films is slower than that of VO_2, and the T_C difference of V_2O_3 films deposited on different substrates are only 2.4K. T_C values of V_2O_3 films on $(10\bar{1}0)$ and $(1000)Al_2O_3$ were 172.5 and 174.9K, respectively.

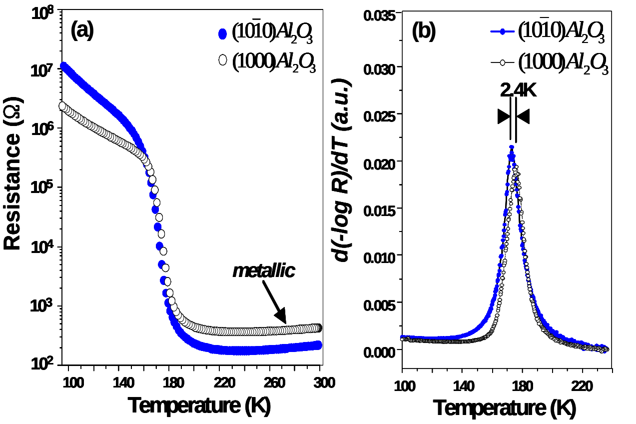

Figure 2. (a) R-T curves of V_2O_3 films formed on single crystalline Al_2O_3 substrates and annealed at 600°C; (b) d(-log R)/dT vs. T curves showing T_C.

4. Conclusion

VO_2 and V_2O_3 films showing abrupt MIT near their typical T_C were successfully fabricated by annealing vanadium oxide films deposited by reactive RF sputter deposition process. The annealing was carried out to prepare VO_2 in a low pressure O_2 ambient. V_2O_3 film was fabricated by further annealing the VO_2 film with no reducing agent at 600°C in 2 x 10^{-6} Torr. The annealing temperature to prepare V_2O_3 film (≥550°C) is much lower than those reported in earlier works.

The dependence of T_C on substrate was also shown for VO_2 and V_2O_3 films. After the transition from insulator to metal, the films on $(10\bar{1}0)$ Al_2O_3 showed lower resistance and more typical metallic behavior than those on $(1000)Al_2O_3$ substrate.

Acknowledgements

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