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Synthesis and characterization of vanadium oxide thin films on different substrates

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Abstract In this study, the V_8O_{15} derivative of vanadium oxide was produced on plain glass, indium tin oxide and silicon wafer substrate layers by taking advantage of wet chemical synthesis which is an easy and economical method. The structural properties of the produced films were examined by XRD and SEM analyses. Besides, Al/VO_x/p-Si metal-oxide-semiconductor (MOS) structure was obtained by the same synthesis method. Doping densities of these MOS structures were calculated from frequency dependent capacitance–voltage measurements. It was determined that the interface states which were assigned with the help of these parameters vary according to frequency.

1 Introduction

In daily life, technological devices based on semi-conductor transparent metal oxides provide many advantages to us. Titanium, tungsten, zinc and tin oxides are the most important of these [1–10]. Vanadium oxides which are transient metal oxides play important role in scientific research and applications due to their interesting physical phenomena [11]. Vanadium oxides are able to form many oxide compounds. Some of their types demonstrate phase transition under certain conditions such as temperature, pressure and electric field. Therefore, they have various optical and electronic properties [12], Vanadium oxides are unique materials which have various potential usage areas such as optic keys [13], super capacitors [14], batteries and non-cooling infrared detectors [15, 16].

Since semiconductor to metal phase transition in VO_2 discovered by F. Morin in 1959, there has been an intensive interest in VO_x thin films [17]. In the paper of Morin, the phase transition and conductivity of VO, VO_2, V_2O_3 and some different metal oxides were examined. He also observed drastically changes in conductivities of VO and V_2O_3 compared to VO_2 during the transition from insulator to the metallic phase. However, the most important advantage of VO_2 is that it demonstrates this transition property in temperatures close to room temperature. Therefore, many characterization techniques can be easily applied this structure.

2 Experiment

VO_2 which has the closest stoichiometry to VO_x is not easily manufactured due to the possibility of formation of many different oxides during and after production. Up to date, several methods have been tried in the subject. In this study, we tried to produce the V_8O_{15} derivative of vanadium oxide (which has not been produced in literature so far) on bare glass, indium tin oxide (ITO) and silicon wafer substrate. Moreover, without the need of any special devices, wet chemical synthesis was used as production process which is a simple and economical method.

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Therefore, we fabricated oxide films in lower temperatures, unlike conventional methods.

In this study, three different base materials were employed. These are amorphous glass, ITO and Si-wafer. The base materials were initially subject to the cleaning process. After that, commercial amorphous glass material was washed with water and soap, it was immersed in ethanol and then was left to dry in open air.

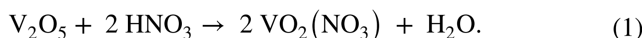
A lot of metal-oxide-semiconductor (Al/VO_x/p-Si) structures were fabricated on the 1-inch diameter float zone (100) p-type (boron-doped) single crystal silicon wafer with a thickness of 280 µm and a resistivity of 1–10 Ω cm. For the fabrication process, Si-wafer was degreased through RCA cleaning procedure [18]. Technical details can be found in the previous studies for RCA process [19, 20].

The beaker including 1.8188 g of V_2O_5 was left on a magnetic stirrer and 25 mL of nitric acid was added to it slowly. Meanwhile, the solution was kept at 50 °C. After stirring the solution for 2 h, totally 1 mL of H_2O_2 was added. The stirred solution was mixed with dense ethylene glycol liquid at a ratio of 1:1 and kept on the magnetic stirrer. The obtained solution was left on the magnetic stirrer for 2 h. Next, the plain glass, ITO and Si wafers were immersed in the stirred solution. The only ohmic side of Si wafer among base materials was cleaned by cotton with ethyl alcohol. The base materials were taken out and were post-annealed at the temperature of 300 °C for 1 h. In order to obtain a rectifying contact on the front p-Si surface with VO_x high-purity aluminum was coated in vacuum under the pressure of 10^{-6}Torr.

The crystalline structure of ZrO_2 was confirmed by X-ray diffraction (XRD) with a CuK$_{\alpha1}$ radiation source (Rikagu-RadB model, λ = 1.5406 Å) over the range $10 < 2\theta < 90°$ at a speed of ° min^{-1} with a step size of 0.02°. The surface properties of the films were examined by using EVO40-LEO (Carl Zeiss, UK) computer controlled digital scanning electron microscope (SEM). The capacitance–voltage (*C–V*) measurements were performed by using a Keithley 4200 SCS (Semiconductor Characterization System). All measurements were carried out in a dark environment at room temperature.

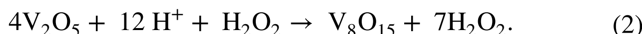
3 Results and discussion

Initially, the reaction that we aimed to apply in our study was like below:



$$V_2O_5 + 2\,HNO_3 \rightarrow 2\,VO_2(NO_3) + H_2O. \quad (1)$$

However we failed to obtain the oxidation of vanadium derivative compounds in an environment where there is lack of hydrogen peroxide (H_2O_2). Vanadium oxide can be dissolved in H_2O_2, if the reaction is like below:



$$4V_2O_5 + 12\,H^+ + H_2O_2 \rightarrow V_8O_{15} + 7H_2O_2. \quad (2)$$

The XRD results of the thin films obtained on glass, ITO and Si-wafer substrate can be seen in Fig. 1. While amorphous structure among these base materials was observed

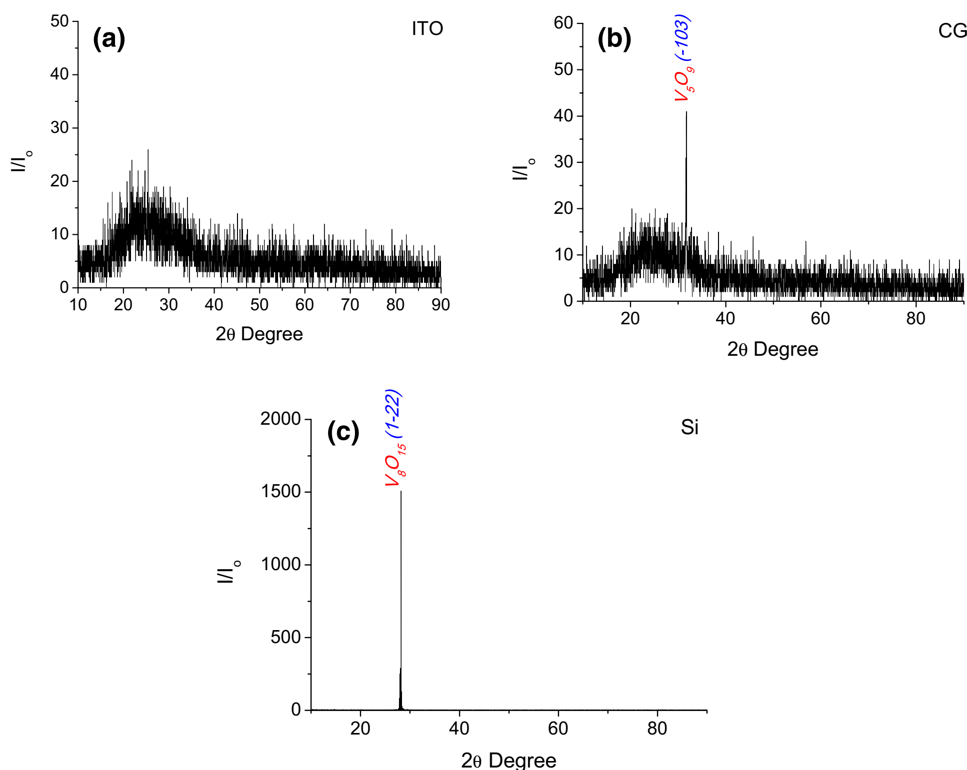


Fig. 1 XRD patterns of V_xO_y thin films on different substrates: **a** ITO, **b** CG, **c** Si-wafer

at ITO, crystal peaks in pronounced magnitudes were determined on the others. The peak observed in glass substrate was V_5O_9 (PDF: 18-1450) with triclinic structure at peak 31.22° with an orientation of (−103). On the other hand, the peaks in Si wafer substrate at 27.83°, 28.08°, and 28.67° (PDF number was almost same as 18-1448 and is the V_8O_{15} structure) in which a peak with three serial magnitudes were observed although a little deviation occurred in angles. The highest peak in this structure is the triclinic structure with an orientation of (1–22). Park and Moon, could only produce thin films in V_2O_5 form instead of vanadium oxide which they managed to produce in different forms with the purpose of IR detector [11]. Manning and Parkin, managed to produce VOCl films by chemical vapor storage method [2]. Wang et al. also could only produceV_2O_5 films by RF magnetic sputtering method [4]. On the other hand, Lee et al. could only produce vanadium oxide thin films with amorphous structure [6]. According to the mentioned above studies, vanadium oxide films at V_5O_9 and V_8O_{15} which can be properly crystallized could not be produced by our method.

SEM images of the produced films are given in Fig. 2. The formation of large cracks or separation can be seen in the structure coated on ITO surface for which there are no peaks observed in the XRD pattern (Fig. 2a). Tiny crystal particles at nano dimension could be observed on the structure coated on the glass surface (Fig. 2b). The gaps between particles were too large and separated from each other. The fairly big crystal structure can be seen in Fig. 2c.

In the study, while the substrates are different, the coating method is the same. The V_5O_9 and V_8O_{15} oxide layers which are different forms of vanadium oxide on glass and Si wafer substrate are obtained. The different structural results may be the reason why vanadium oxide is physically coated on the amorphous glass, while attaching chemically on silicone at the oxygen part as seen in Fig. 3.

The capacitance–voltage–frequency (*C–V–f*) characteristics of the Al/VO_x/p-Si/Al (MOS) structure were measured in the frequency range of 10 kHz–2 MHz and are given in Fig. 4, respectively. The measured *C* is strongly dependent on bias voltage and frequency. The accumulation capacitance decreases with increasing frequency. Such behavior of *C* is attributed to the particular distribution of interface states (N_{ss}) at VO_x/p-Si interfaces [21]. At low frequencies, N_{ss} can easily follow the ac signal and yield an excess capacitance, which depends on the frequency and time constant of interface states [22, 23]. However, in a sufficiently high frequency limit (f ≥ 500 kHz), the N_{ss} can hardly follow the ac signal and contribution of the interface states capacitance to

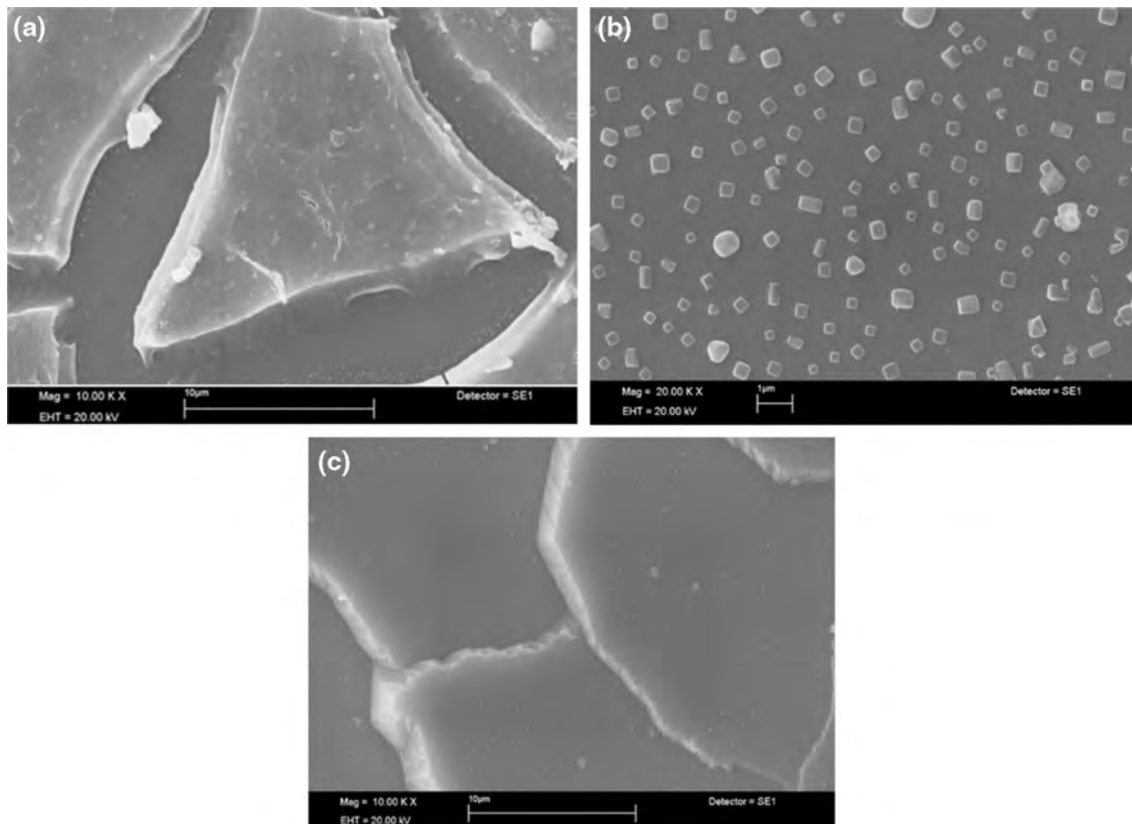


Fig. 2 SEM images of VO_x thin films at different substrates **a** ITO, **b** CG, **c** Si-wafer

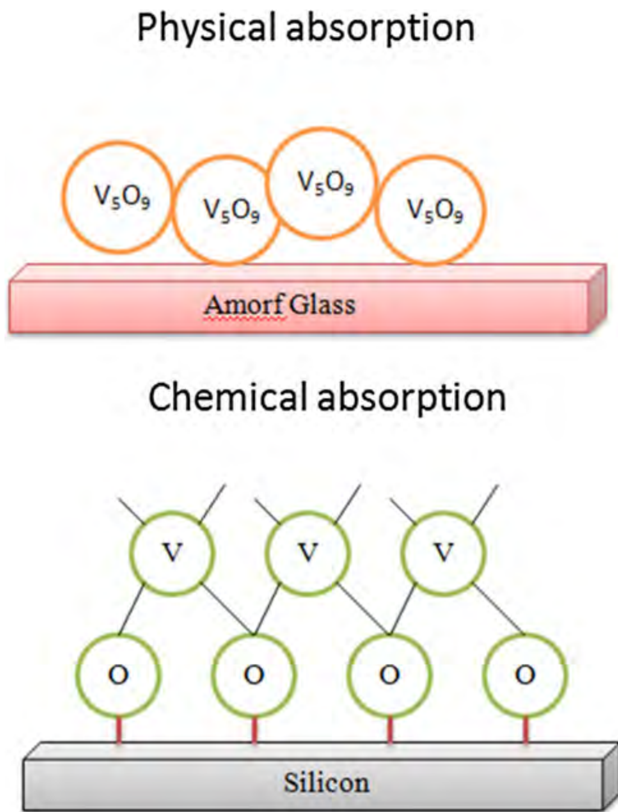


Fig. 3 Coating mechanisms of VO_x thin films

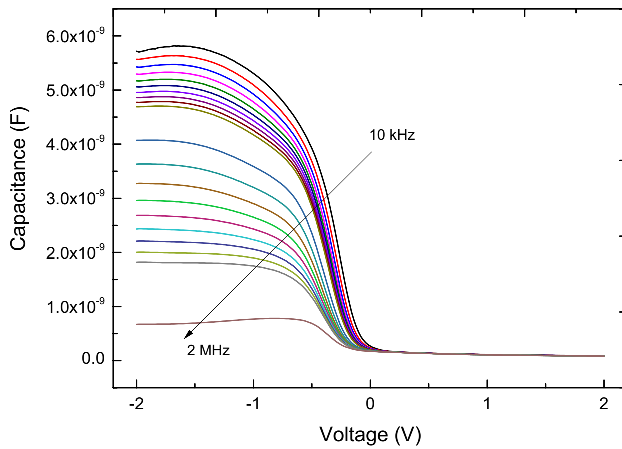


Fig. 4 The capacitance–voltage–frequency (*C–V–f*) characteristics of the Al/VO_x/p-Si/Al (MOS) structure

the total capacitance may be neglected. The N_{ss} obtained from the slope of C^{-2}–V plot as function frequency at room temperature. As observed in Fig. 5 the values of N_{ss} decrease with increasing frequency and they become almost constant at a high frequency. The high values of capacitance at low frequencies are attributed to the excess capacitance resulting from the N_{ss}, which is in

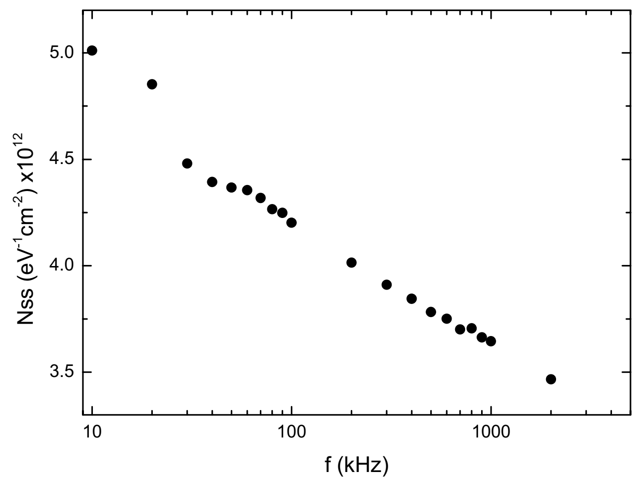


Fig. 5 Density of interface states (N_{ss}) as a function of frequency

Table 1 The values of various parameters for Al/VO_x/p-Si (MOS) structure determined from *C–V* characteristics in the frequency range 10 kHz–2 MHz

f (kHz)	N_A (10^{15}cm^{-3})	V_d (eV)	W_D (10^{-5} cm)	N_{SS} ($10^{12}\times$eV^{-1} cm^{-2})
10	4.13	0.605	4.25	5.010
20	4.09	0.603	4.27	4.852
30	3.99	0.601	4.31	4.480
40	3.96	0.599	4.32	4.393
50	3.96	0.595	4.31	4.367
60	3.95	0.592	4.30	4.355
70	3.94	0.588	4.29	4.318
80	3.93	0.585	4.29	4.265
90	3.92	0.582	4.28	4.248
100	3.91	0.577	4.27	4.202
200	3.86	0.575	4.29	4.014
300	3.83	0.572	4.29	3.910
400	3.81	0.569	4.29	3.845
500	3.80	0.565	4.29	3.783
600	3.79	0.557	4.26	3.751
700	3.78	0.552	4.25	3.701
800	3.78	0.546	4.23	3.706
900	3.77	0.541	4.21	3.663
1000	3.76	0.533	4.18	3.645
2000	3.71	0.495	4.06	3.466

equilibrium with the semiconductor that follows the ac signal. As could be seen in Fig. 5 and Table 1, the values of N_{ss} are sufficiently low and promote the formation of a low defect density interface. The obtained magnitudes of interface states of Al/VO_x/p-Si (MOS) structure are sufficiently lower than Al/SnO_2/p-Si and Al/SiO_2/p-Si (MIS) structures [15, 16].

4 Conclusion

In this study, we managed to produce the V_8O_{15} derivative of vanadium oxide, on glass, ITO and Si wafer substrates by wet chemical synthesis which is a simple and economical method. While the structure of the film on ITO surface was observed to be amorphous from the XRD measurement results, the observed structure on glass sub-layer is V_5O_9 (PDF: 18-1450) in triclinic structure and the structure on Si substrate is V_8O_{15} with three serial peaks with high magnitude despite slight deviation in angles. According to literature researches, it was observed that vanadium oxide thin films in V_5O_9 and V_8O_{15} forms have not yet been produced. In addition, Al/VO_x/p-Si (MOS) electronic device structure was obtained from V_8O_{15} structure. The interface states of this structure were determined from the capacitance–voltage measurements depending on the frequency at room temperature. It was observed that the interface states values were dependent on the applied frequency. Besides, it was observed that the N_{ss} values of Al/VO_x/p-Si were lower than those of MOS structures with SiO_2 and SnO_2. As a result, the electronic devices with V_8O_{15} structure can be considered as an alternative to many oxidized MOS devices.

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References

1. G. Wu, J. Li, K. Wang, Y. Wang, C. Phan, A. Feng, J. Mater. Sci. doi:10.1007/s10854-017-6343-6
2. T.D. Manning, I.P. Parkini, Polyhedron **23**, 3087 (2004)
3. G. Wu, Y. Cheng, Q. Xie, Z. Jia, F. Xiang, H. Wu, Mater. Lett. **144**, 157 (2015)
4. X.J. Wang, H.D. Li, Y.J. Fei, X. Wang, Y.Y. Xiong, Y.X. Nieand, K.A. Feng, Appl. Surf. Sci. **177**, 8 (2001)
5. G. Wu, Y. Ren, X. Li, L. Wang, Chemistry A **22**(26), 8864 (2016)
6. S.H. Lee, H.M. Cheong, M.J. Seong, P. Liu, C.E. Tracy, A. Mascarenhas, J.R. Pittsand, S.K. Deb, Solid State Ionics **165**, 111 (2003)
7. G. Wu, Y. Cheng, F. Xiang, Z. Jia, Q. Xie, G. Wu, H. Wu, Mater. Sci. Semicond. Process. 41, 6 (2016)
8. G. Wu, Y. Cheng, Z. Wang, K. Wang, A. Feng, J. Mater. Sci. **28**(1), 576 (2017)
9. G. Wu, Y. Wang, K. Wang, A. Feng, RSC Adv. **6**(104), 102542 (2016)
10. G. Wang, H. Wu, K. Wang, C. Zheng, Y. Wang, A. Feng, RSC Adv. **6**(63), 58069 (2016)
11. C.W. Park, S. Moon, H.B. Chung, J. Korean Phys. Soc. **39**, 138 (2001)
12. G. Golan, A. Axelevitch, B. Sigalov, B. Gorenstein, Microelectron. J. **34**, 255 (2003)
13. S. Chen, H. Ma, X. Yi, H. Wang, X. Tao, M. Chen, X. Liand C. Ke, Infrared Phys. Technol. **45**, 239 (2004)
14. Z. Huang, H. Zeng, L. Xuea, X. Zhou, Y. Zhaoand, Q. Lai, J. Alloys Compd. **509**, 10080 (2011)
15. K.J. Takeuchi, A.C. Marschilok, S.M. Davis, R.A. Leisingand E, S. Takeuchi, Coord. Chem. Rev. **219**, 283 (2001)
16. R. T. R. Kumar, B. Karunagaran, D. Mangalaraj, S. K. Narayandass, P. Manoravi, M. Joseph, V. Gopal, Sens. Actuat. **107**, 62 (2003)
17. F.J. Morin, Phys. Rev. Lett. **3**, 34 (1959)
18. A. Tataroglu, Ş. Altındal, Microelectron. Eng. **83**, 582 (2006)
19. O. Pakma, C. Tozlu, N. Kavasoglu, A.S. Kavasoglu, S. Özden, J. Sol-Gel. Sci. Technol. **58**, 244 (2011)
20. O. Pakma, N. Serin, T. Serin, J. Mater. Sci. **44**, 401 (2009)
21. E.H. Nicollianand, J.R. Brews, *Metal-oxide semiconductor (MOS) physics and technology*. (Wiley, New York, 1982)
22. S. Altındal, S. Karadeniz, N. Tugluoglu, A. Tataroglu, Solid State Electron. **47**, 1847 (2003)
23. M. M. Bülbül, S. Zeyrek, Microelecron. Eng. 83, 2522 (2006)