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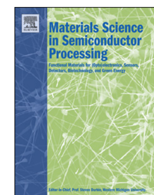

Effect of oxygen content on the electrical properties of sputter deposited vanadium oxide thin-films

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ABSTRACT

In this article, different oxidation states of vanadium in vanadium oxide (VO) thin-films, deposited on Si(100) at room temperature by reactive rf-sputtering of a pure metallic vanadium target at different Ar/O_2 ratios, have been identified. A qualitative assessment of the XPS spectra reveals that vanadium exists in the V^{5+} and V^{4+} oxidation states in the oxide thin-films. The highest content of V^{5+} oxidation state is present in the oxide film deposited at highest O_2 ratio (Ar:O_2 = 1:4). Vanadium oxide deposited at highest O_2 ratio shows insulator-to-metal (IM) transition whereas the devices, deposited at other oxygen ratios do not show any appreciable change. This transition has been ascribed to a voltage-induced joule heating effect which in turn results in formation of metallic conduction channel across the device. Thus, the ratios of Ar and O_2 in the reactive plasma play a critical role in determining the IM transition properties of vanadium oxide thin-films.

1. Introduction

Vanadium Oxides(VO) exhibit different stoichiometry owing to the multivalent character of the vanadium cation. In the various known oxide phases, the oxidation state of vanadium ranges from + 2 (as in VO) to + 5 (as in V_2O_5), with V_2O_5 being the most stable phase [1]. These oxide phases have garnered significant interest due to their widespread applications in memory [2,3], photonics [4] and optoelectronic devices [5]. Some of these devices mainly hinge on the phase-change material characteristics of vanadium oxide [6,7] undergoing a metal-to-insulator (MI) phase transition [8,9]. The temperature for insulator-to-metal (IM) transition is the highest in V_3O_5 at about 150 °C [10]. Deposition methods of vanadium oxide thin-films involve sputtering [11,12], atomic layer deposition [13], pulsed laser deposition [14,15] and electron-beam evaporation [1,15]. Chemical Vapor deposition (CVD) technique has also been tried to grow VO at elevated temperatures wherein it was revealed that oxide phases of vanadium depend only on growth temperatures [16]. An attempt was also made to grow VO on SnO_2 pre-coated glass substrates by atmospheric pressure chemical vapor deposition at higher temperatures at various N_2 flow rates in the absence of oxygen wherein the film was found to be amorphous in nature. However a short-range crystalline ordering was revealed due to the presence of monoclinic VO_2 for N_2 flow rates at 4 L/min [17]. Extensive works have been done using sputtering where a subtle interplay of the different growth/deposition conditions, results in a variety of vanadium oxide films which differ in their stoichiometry, phase and the oxidation state of vanadium. Further, modulation of the ratios of Ar and O_2 in reactive sputtering results in oxide films with variable oxidation states and stoichiometry [11,18]. Therefore, in order to use the phase change and metal-insulator-transition(MIT) property of vanadium oxide in any electronic devices, a knowledge of the oxidation states of vanadium in the oxide film is required beforehand.

With a motivation to gain the apriori knowledge, this work deals with characterization of reactively sputtered vanadium oxide thin-films, deposited at different Ar/O_2 ratios on silicon substrate at room temperature, by x-ray photoelectron spectroscopy(XPS). Further, metal-VO-semiconductor (MOS) structure, fabricated with aluminum as gate electrode, was used to study its IM transition properties. The results are presented and discussed here.

2. Experimental

n-type Si(100) substrates having 1 cm × 1 cm area and resistivity 1–10 Ω − cm were used for VO thin-film deposition. The substrates were cleaned by standard technique of Radio Corporation of America (RCA) followed by a 1 min-dip in 1% HF acid for native oxide removal. Vanadium oxide films were then deposited at room temperature on these substrates by reactive rf-sputtering of 99.9% pure vanadium metal target at various Ar:O_2 ratios. The deposition was carried out for 30 min at a constant pressure of 5 mTorr and 70 W rf-power. The ratios of

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Argon and oxygen were controlled by modulating their respective flow rates using mass flow controllers and a constant pressure was maintained by programmable throttle valve. The partial pressure of oxygen in the plasma was varied from 20% to 80%. A rotation of 30 rpm was given to the substrate in order to ensure the film uniformity. X-ray reflectivity measurements revealed that the thickness of the deposited films was in 5–7 nm range.

The films were then probed using x-ray photoelectron spectroscopy (XPS) technique to identify the oxidation states of vanadium in the samples. The XPS measurements were taken with a Omicron Multiprobe Electron Spectroscopy System (Omicron Nanotechnology, UK) equipped with a monochromated Al K (1486.7 eV) (Model: XM 500) source. The base pressure of the Omicron system was 2.5×10^{-10} mbar. The binding energy of V 2p and O 1s were measured in a single energy window and a pass energy of 30 eV. Usually, the C 1s is used as the reference for binding energy calibration in XPS spectra. But for vanadium oxide, the O 1s signal is a far better reference than C 1s for the V 2p binding energies [19,20]. The signals for O 1s and V 2p were measured together in one energy window. The XPS data were analyzed using CasaXPS processing software. The background of the spectra was subtracted using a Shirley background function. Apart from the V signal, the O 1s signal needs to be taken into consideration for extracting the Shirley background [19]. The overall XPS spectra was deconvoluted into various peaks corresponding to different oxidation states of vanadium. A convolution of Gaussian-Lorentzian functions was used for fitting the peaks and the overall spectra. Si spectra were also deconvoluted in a similar manner and Si 2p, SiO_2 and SiO_x peaks were identified. A 200 nm-thick aluminum metal was then deposited on the top of VO using electron beam deposition system. The metal was then patterned to gate electrodes of 100 µm diameter using UV-photolithography. The separation between two gate electrodes is 25 µm. The I-V characteristics of the devices were then measured in a Signatone (1160 series) probe station using keithley 4200-SCS equipped with keithley-made 4200-PA preamplifiers. All the measurements were carried out at room temperature and under light tight and electrically shielded conditions.

3. Results and discussions

3.1. Analysis of XPS data for vanadium and oxygen

The XPS spectra of vanadium oxide film deposited at 4:1 Ar:O_2 ratio is illustrated in Fig. 1(a). The deconvolution of the spectra reveals five major peaks. A peak at 530 eV denotes the O 1s level and corresponds to the O–V bonds [1,19]. The peak for O 1s level does not show any significant shift for the VOs deposited at increasing oxygen partial pressures but a growing asymmetry on the higher binding energy (BE) side of O 1s level is quite evident from Fig. 1(b)–(d). The O 1s level serves as a reference for fitting the V 2p spectrum. Fig. 1(a) shows a narrow and sharp feature, deconvoluted into two peaks at 516.93 eV and 515.71 eV, representing the $V^{5+}2p_{3/2}$ and $V^{4+}2p_{3/2}$ levels, respectively. The deconvoluted peaks at 524.54 eV and 523.25 eV corresponds to $V^{5+}2p_{1/2}$ and $V^{4+}2p_{1/2}$ peaks [19,21,22]. Besides these major energy levels, a number of less intense satellite peaks are also present. These V 2p satellite peaks are a result of strong hybridization between the V 3d and O 2p energy levels and are necessary for appropriate fitting of the XPS spectra [23,24]. Since the peaks corresponding to the various oxidation states of vanadium might undergo a shift, the difference in BE between the O 1s and V $2p_{3/2}$ level is an appropriate measure of determining the oxidation state of vanadium [19,20]. In the different XPS spectra (Fig. 1), the BE for O 1s and $V^{5+}2p_{3/2}$ differ by 12.8 eV. This difference for $V^{4+}2p_{3/2}$ comes out to be 14 eV. Both these values match with literature data for vanadium oxides [19,21]. Due to spin-orbit coupling, the V 2p spectrum is split into V $2p_{3/2}$ and V $2p_{1/2}$ levels, differing by 7–8 eV [22,24]. Taking this difference into account, the $V^{5+}2p_{1/2}$ and $V^{4+}2p_{1/2}$ levels have been correctly represented by the peaks at 524.54 eV and 523.25 eV. Thus, all the major peaks representing the various oxidation states of vanadium have been accurately denoted.

The XPS spectra for the VO samples, deposited at increasing oxygen partial pressure, are shown in Fig. 1(b)–(d). It can be seen that the $V^{5+}2p_{3/2}$ peak gradually shifts to higher BE values with increasing oxygen partial pressure. The BE of V 2p level is known to increase with the increasing oxidation state of vanadium cation [19]. Thus the above shift with increasing oxygen partial pressure, signifies that the amount of V_2O_5 in the film is gradually increasing. On the other hand, $V^{5+}2p_{1/2}$ shift does not show a continuously increasing trend however there is an overall shift to higher BE values from 524.54 eV to 524.83 eV for the samples deposited at 4:1 and 1:4 Ar:O_2 ratios, respectively. The V^{4+} peak shifts show a discontinuous trend.

However, the evolution of the feature at 531 eV contributing to the asymmetry of O 1s level is quite interesting. At lowest oxygen partial pressure, this feature is not so significant. But with increasing oxygen partial pressure, its intensity becomes prominent and finally renders a doublet structure to the O 1s level as shown in Fig. 1(c) and (d). The peak at 530.76 eV has been associated with V^{5+} as mentioned above.

A more quantitative assessment of film content is presented in Table 1. The highest amount of V_2O_5 is present in the film reactively sputtered in 10 sccm of Ar and 40 sccm of O_2 along with the presence of VO_2. The VO_2 is maximum in the film deposited under 20 sccm of Ar and 30 sccm of O_2. Thus a proper choice of the ratios of Ar to O_2 can significantly alter the film content.

The various component peaks of the V 2p spectrum has a corresponding satellite peak on the higher BE side in the vicinity of the O 1s level. The satellite peak for the $V^{4+}2p_{3/2}$ level occurs in between the O 1s and V $2p_{1/2}$ level. This is represented by the very less intense peak at 527 eV as evident from Fig. 1(a). The $V^{5+}2p_{1/2}$ has a satellite peak at 540 eV (not shown in the spectra). The $V^{5+}2p_{3/2}$ and $V^{4+}2p_{1/2}$ levels have their satellite peaks on the higher BE side of the O 1s level [19,24]. This can render an explanation for the peak at around 531 eV which makes the O 1s level asymmetric. This asymmetric feature becomes more prominent with increasing oxygen partial pressure and eventually attains a doublet structure. A doublet structure in the O 1s spectrum, shown in Fig. 1(c) and (d), is usually associated with the presence of V_2O_5 (V^{5+} in the sample) [25]. $V^{5+}2p_{3/2}$ is separated from its satellite peak, appearing on the higher BE side of O 1s, by 14–15 eV as reported earlier [24]. In Fig. 1, this separation comes out to be ~ 14 eV. Thus the growing asymmetry with increasing partial pressure is a signature of increasing amount of V^{5+} in the sample. Besides these, three small peaks lying adjacent to one another in the 518–521 eV range are added [26] for rendering a proper fit to the entire spectra.

3.2. Analysis of Si 2p XPS peak

The Si 2p XPS spectra for all the samples, deconvoluted into various peaks, are revealed in Fig. 2 (a)–(d). A major component peak of this spectra is the Si $2p_{3/2}$ peak occurring at around 99 eV for all the films deposited at various Ar: O_2 ratios. Apart from this peak, several less intense peaks occurring in the range of 100–102 eV in each of the spectra denote the SiO_x structure. An additional peak occurring at around 103.60 eV as evident from Fig. 2(d) for the film deposited in Ar: O_2 = 1: 4 corresponds to the BE of SiO_2 [27]. Thus the appearance of SiO_2 in the XPS spectra signifies the onset of complete oxidation of SiO_2 in the presence of highest oxygen partial pressure. Further the SiO_x peak for the sample, deposited at highest oxygen partial pressure located at a higher binding energy, ~ 0.5 eV more than the one at lowest oxygen ratio indicates SiO_2 structure [28].

3.3. Electrical characterization

The I-V characteristics of all the devices are shown in Fig. 3. It is evident from the figure that the VO, deposited at higher O_2 partial pressure (Ar: O_2 = 2:3 and 1:4) show an insulator to metal transition as

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