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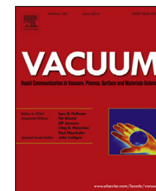

Effects of duty cycle and oxygen flow rate on the formation and properties of vanadium oxide films deposited by pulsed reactive sputtering

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Vanadium oxide (VO*x*) thin films were deposited on glass substrates at room temperature by pulsed DC reactive magnetron sputtering. The effects of the duty cycle of the pulsed power and oxygen flow on the surface morphology, deposition rate, composition and electrical properties of VO*x* films were systematically investigated. Experimental results revealed that decreasing the duty cycle or increasing the oxygen flow leaded to the decrease of the root mean square (RMS) roughness of VO*x* films. Moreover, the deposition rate decreased with the reduction of the duty cycle, and it also became more sensitive to the duty cycle at higher oxygen flow. Electrical measurements indicated that if the oxygen flow was increased from 3.1 sccm to 3.5 sccm, the resistivity and the temperature coefficient of resistivity (TCR) value of VO*x* films varied from 0.005 Ω cm to 0.409 Ω cm and from −0.209%/K to −1.485%/K, respectively. Particularly, by adjusting the duty cycle, the maximum value of the resistivity and TCR of VO*x* films can be achieved as 604.2 Ω cm and −2.864%/K, respectively. X-ray photoemission spectroscopy (XPS) analyses revealed that decrease of the duty cycle or increase of the oxygen flow enhanced the oxidation of vanadium. Therefore, with adjustment of the duty cycle in combination with regulation of the oxygen flow, the thermistor properties of VO*x* films can be well controlled.

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1. Introduction

Vanadium oxides (VO*x*) are important functional materials widely applied in electronic [1], photonic [2] and electrochemical [3] devices in the past few decades. Since VO*x* films with mixture phases can be tailored to meet the demand of reasonable resistivity and relatively high temperature coefficient of resistivity (TCR), these materials have become the mainstream technology in the fast booming uncooled infrared image market. Therefore, research on the preparation techniques of VO*x* thin films, has greatly been stimulated [4–6]. However, the vanadium–oxygen system is a very complex compound system, because vanadium exhibits +2, +3, +4 and +5 valent states, and consequently, a large number of vanadium oxides, such as VO, V_2O_3, VO_2, V_2O_5, $V_{2n}O_{5n-2}$ (Wadsley phase) and V_nO_{2n-1} (Magneli phase) exist in the VO*x* films [7]. Due to these features of the vanadium–oxygen system, how to adjust the optical, electrical and other physical properties of the VO*x* films for particular applications is still a challenge.

Although a lot of physical and chemical film preparation methods have been reported for deposition of vanadium oxide thin films on different substrates [5,8–11], sputtering based process is a preferred choice over other deposition methods. Because the sputtering methods can meet a variety of requirements, such as high deposition rate, large-scale uniformity, low process temperature, compatible with other standard microelectronic process, and better film quality, etc. However, due to that the positive charge will be accumulated on the poor conducting dielectric film formed on the target surface, reactive sputtering of metallic target by a conventional DC power supply may leads to arc. And it is known that sputtering process usually exhibits undesirable hysteresis behaviors with respect to the supply of reactive gas. Due to these unfavorable factors, the reactive sputtering becomes a highly non-linear and unstable process [12–14]. In order to improve the controllability of the reactive sputtering process of VO*x* thin films, a large variety of sputtering methods have been developed, such as pulsed DC reactive magnetron sputtering [4], RF reactive magnetron sputtering [15], inductively coupled plasma-assisted reactive sputtering [16], facing targets DC reactive sputtering [17], ion beam reactive sputtering [18], inverted cylindrical magnetron reactive

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sputtering [19], and reactive-biased target ion beam deposition (RBTIBD) [20] etc.

Among these sputtering methods, pulsed DC reactive magnetron sputtering offers significant advantages over others, including excellent arc suppression, low target poisoning, stable reactive sputtering process, relatively high deposition rate, flexible process control, and simple apparatus. Unlike the RF power supply only works at a fixed frequency, the pulse frequency and duty cycle can be modulated independently, which is the feature of the pulse power supply. The role of the pulsing parameters in changing the properties of plasma and film has become a subject of growing number of studies. It has been demonstrated that the duty cycle is not only the critical parameter to establish an arc-free condition in the Ar–O_2 reactive sputtering process [21,22], but also an important means to change the plasma properties [23,24] and thermal power density delivered to the substrate [25]. Y.H. Cheng et al. found that the crystalline structure, surface morphology, and secondary electron emission properties of MgO thin films deposited by pulsed reactive sputtering were closely related to the duty cycle [26]. W.J. Lee et al. found that by adjusting the ratio of negative pulse-on time/positive pulse-on time (similar to changing the duty cycle) during the pulsed reactive sputtering process, the optical, electrical, and structural properties of ITO films can be optimized [27]. The influence of the duty cycle on the deposition rate and film quality of the Al_2O_3 [28] and AlN [29] has also been observed by A. Belkind and J.S. Cherng et al.

However, to the best of our knowledge, few articles have been reported the effects of duty cycle on the pulsed reactively sputtered VO*x* thin films. Therefore, in order to determine a relationship between the duty cycle and properties of the deposited VO*x* films, a systematic investigation is necessary. In this study, vanadium oxide thin films were prepared by pulsed DC reactive sputtering from a pure vanadium target in the argon–oxygen atmosphere. The main purpose was to investigate the effect of duty cycle and oxygen flow on the deposition process and properties evolution of VO*x* films. Variations in surface morphology, deposition rate, composition and electrical properties with the duty cycle under three different argon–oxygen flow ratio conditions were reported. Correlations between the deposition parameters and properties of VO*x* films were discussed.

2. Experimental

VO*x* thin films were deposited by pulsed DC reactive magnetron sputtering in a custom-built vacuum system. This vacuum system consists of a load-lock chamber, a sample pre-treatment chamber, a deposition chamber and a sample transfer system. With the sample transfer system, samples can be transferred from the load-lock chamber to the deposition chamber without breaking the vacuum. A water cooled rectangle planar vanadium metal target, with a purity level of 99.99%, was used in these experiments. The distance between the sputtering target and substrate holder was fixed at 120 mm. The deposition chamber was evacuated to a base pressure of about 1.0×10^{-4} Pa by combining turbomolecular and rotary vane pumps. An asymmetric bipolar pulsed DC power supply (Pinnacle™ Plus+ 5 KW Advanced Energy Inc) worked in power regulation mode at 200 W was used to generate plasma. The pulse frequency was fixed at 100 kHz. The duty cycle, which was defined as the pulse duration divided by the total pulse period, was varied in the range from 55% to 95%, corresponding to the reverse time varied from 4.5 μs to 0.5 μs.

Glass slides were used as substrates. Before the substrates were mounted on a substrate holder and loaded into the load-lock chamber, they were ultrasonically cleaned in acetone, ethanol and de-ionized water for 20 min sequentially, and then dried by pure nitrogen stream. Argon and oxygen flow were controlled by using independent mass flow controllers, the argon flow was kept constant at 100 sccm and the oxygen flow was varied from 3.1 sccm to 3.5 sccm, the pressure during deposition was about 0.66 ± 0.01 Pa. In order to ensure the same state of the reactive sputtering in every run, the vanadium target was first pre-sputtered by argon plasma for 15 min, and then oxygen injection was kept for 15 min until equilibrium reached in the argon/oxygen mixture. The substrate holder was rotated at 10 rpm to ensure uniformity of film deposition and there were no intentionally heating during experiment.

The compositions of these deposited vanadium oxide thin films were determined by an X-ray photoelectron spectrometer (Kratos XSAM800 system, Al K_α X-ray source without monochromatization, the base pressure of the ultrahigh vacuum chamber was lower than 3×10^{-7} Pa, binding energies (BE) were determined using C1s peak at 284.8 eV as a reference, the pass energy is 50 eV and the resolution is 0.9 eV/104 counts per second.). An Atomic Force Microscope (MFP-3D™-Bio Systems, Asylum Research) worked in tapping mode, was used to probe the film surface morphology. The film thicknesses were measured independently by a profilometer (XP-300, Ambios Technology Inc) and a spectropic ellipsometer (SE850, Sentech GmbH).

The electrical resistivities of the films were measured using four-point probe method, and the TCR measurements were carried out by two probe technique using a Keithley high resistance meter (Model 6517A). A good mechanical and electrical contact to the patterned VO*x* films for TCR measurements was prepared by sputtering 50 nm Vanadium/200 nm Nichrome. A series of stainless steel foil shadow masks were used during deposition to make the VO*x* film pattern's width (w) equals with the coplanar electrode separation (l), and thus the aspect ratio (w/l) of the tested film is one. In order to control the temperature precisely during the TCR measurements, the samples were placed in a temperature chamber (Sigma Systems Corporation, Model M10). Thus, we can freely set the temperature range and temperature ramp rate through a programmable temperature controller (Sigma Systems Corporation, Model C4, temperature accuracy ±0.1 K).

3. Results and discussion

3.1. Surface morphologies

A comparison of the influence of duty cycle on the surface morphology of VO*x* thin films under different oxygen flows is provided in Fig. 1. It is clearly seen that the surface morphology of the deposited films is greatly affected by the plasma excitation mode and oxygen flow. As can be observed in Fig. 1a, the film deposited under an oxygen flow of 3.1 sccm by conventional DC sputtering (duty cycle 100%) possesses a jagged surface microstructure, and its root mean square (RMS) roughness value is about 2.58 nm. When the plasma is excited by pulsing power, the surface roughness of the films will decrease with the duty cycle, which is supported by the RMS values. Generally, smooth and dense films could not be formed without sufficient adatom surface mobility [30]. The evolution of surface microstructure of the films deposited by sputtering is strongly dependent on the substrate temperature and flux and energy of the ions and atoms incident on the substrate [31]. If there are no substrate heating during deposition, relatively low substrate temperature will lead to low adatom mobility, incident atoms adhere where they impinge, so the surface diffusion is kinetically limited and atomic shadowing will become the dominant mechanism for film growth [30]. As a result, a rough and porous microstructure will be formed in the film which looks like the surface morphology shown in Fig. 1a. Besides the substrate

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