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Electrical properties of vanadium tungsten oxide thin films

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ABSTRACT

The vanadium tungsten oxide thin films deposited on Pt/Ti/SiO_2/Si substrates by RF sputtering exhibited good TCR and dielectric properties. The dependence of crystallization and electrical properties are related to the grain size of $V_{1.85}W_{0.15}O_5$ thin films with different annealing temperatures. It was found that the dielectric properties and TCR properties of $V_{1.85}W_{0.15}O_5$ thin films were strongly dependent upon the annealing temperature. The dielectric constants of the $V_{1.85}W_{0.15}O_5$ thin films annealed at 400 °C were 44, with a dielectric loss of 0.83%. The TCR values of the $V_{1.85}W_{0.15}O_5$ thin films annealed at 400 °C were about −3.45%/K.

1. Introduction

A technique for detecting and using infrared rays can be importantly applied to various fields of our lives such as medical field as well as for military purpose. Research and development regarding infrared detector devices has been continued for the last several tens of years [1,2]. In spite of high response speed and superior image reproduction, the cooled type infrared detector requires a separate cooling device because of being operated at very low temperature. For this reason, an uncooled type infrared detector device and an infrared image device that does not require a separate cooling device have been developed in various forms. With the recent development of nano-processing technology, research has been actively conducted to manufacture uncooled type infrared sensing device having a number of Focal Plane Arrays (FPAs), and the developed nano-processing technology allows manufacturing of a heating type infrared sensing device that operates at room temperature and has high sensitivity. The heating type infrared ray sensing device can be classified into three types: a bolometer, a thermocouple, and a pyroelectric detector according to a used principle. Among them, the bolometer has been much studied because it can be manufactured using a conventional semiconductor manufacturing process and has a high response feature [3–6]. An infrared sensing layer for the bolometer may be made of various materials such as metal, vanadium oxide, and semiconductor materials such as YBaCuO, SiGe, or the like. Among those materials, vanadium oxide having high temperature coefficient of resistance (TCR) at room temperature is most suitable for the uncooled type infrared ray sensing device. In addition, it is necessary to reduce noise in order to improve the capability of sensing infrared rays of an infrared ray sensing device. A factor that most affects noise is a resistance of the device, which can be reduced by depositing a vanadium oxide thin film having low resistance. Therefore, the deposition of the vanadium oxide thin film having low resistance and high TCR is essential for manufacturing the uncooled type infrared ray sensing device. Vanadium has various oxide forms such as VO_2, V_2O_3, and V_2O_5 and undergoes phase transition from an insulator/semiconductor to metal at a particular temperature. Although the VO_2 form among those forms is most suitable for the bolometer, it is very difficult to manufacture and thus can be manufactured using expensive ion equipment, and has high room temperature resistance. On the other hand, the V_2O_5 form is easy to perform thin film deposition, can be thermally processed at low temperature, and shows superior thermal sensibility in a wide temperature range. For this reason, there has been an attempt to apply the V_2O_5 form for a sensor for detecting radiation energy such as infrared rays by a combination of a radiation energy absorption layer and the V_2O_5 form and the V_2O_5 form has been widely used as a material for manufacturing a chemical sensor, temperature-measuring and heat-sensing image device, or the like [7–10]. A vanadium oxide thin film is manufactured in various ways such as thermal evaporation, thermal oxidation, sol–gel, sputtering, chemical vapor deposition (CVD), and the like. For this purpose, we have

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first prepared the $V_{2-n}W_nO_5$ thin films having an annealing temperature on platinized silicon substrates using the same fabrication conditions by RF sputtering method. The effect of substituting tungsten for vanadium in structure on the dielectric properties, such as the temperature coefficient of resistance has been investigated systematically.

2. Experiment

The vanadium tungsten oxide ceramics target of the RF sputtering system was prepared by the conventional mixed oxide method. The starting materials were V_2O_5, W. Those materials were weighed according to the composition of the $V_{2-n}W_nO_5$, the weight ratio of zirconia ball to powder in the mill was 1:1 and ethyl alcohol was used as a process control agent. The slurry was dried at 100 °C for 24 h. The dried powders were screened by mesh (#325) and the screened powders were then pressed to cylindrical pellets in steel die ($\varphi = 2$ in.) and sintered at 750 °C for 3 h. The sintered ceramic target was lapped and silver paste was fired on the sample faces at 600 °C. The $V_{2-x}W_xO_5$ thin films were grown on $Pt/TiO_2/SiO_2/Si$ substrates by RF sputtering method. The initial vacuum was about 3×10^{-6} [Torr] and the sputtering atmosphere was controlled by the Ar/O_2 ratio at a total pressure of 3×10^{-3} [Torr]. Experimental conditions were Ar/O_2 ratio (50/20), RF power (80W), and the change of $V_{2-n}W_nO_5$ thin films to addition of tungsten at deposition temperature 400 °C. All experiments to fabricate $V_{2-n}W_nO_5$ thin films had been conducted in our laboratory. The thickness of the films was measured using a field emission electron microscope and α step. The crystalline structures of the $V_{1.8}W_{0.2}O_5$ thin films were analyzed by X-ray diffraction (XRD). A Digital Instrument NanoScope IIIa atom force microscope (AFM) was used to investigate the surface morphology of the films. The surface and cross-sectional microstructures of the films were examined by a field emission scanning electron microscope (FESEM). For electrical measurements, an Au thin film was deposited by an evaporator at room temperature on the top electrode with a diameter of 0.1 mm. The dielectric constant and dielectric loss measurements were carried out using an impedance/gain phase analyzer (HP4192A).

3. Results and discussion

Fig. 1 shows the results of Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) to $V_{1.8}W_{0.2}O_5$ powder according to temperature exchange from 30 to 800 °C. Endothermic peak around 500 °C is caused by the impurity of sample itself, the combustion of mixed organic substance during ball mill process, and degradation of CO_2 gas. It has increased in weight comparing to V_2O_5 powder, which was not added tungsten when adding it, and rapid endothermic peak around 660 °C was formed. This indicates lowest temperature of vanadium oxide as about 670 °C of melting point of V_2O_5, and orthorhombic crystal structure is also indicated. Also, for $V_{1.8}W_{0.2}O_5$ powder, it has rapid endothermic response in 657 °C of low endothermic responding temperature, and it is thought that V_2O_5 phase is formed with the composition of low melting point.

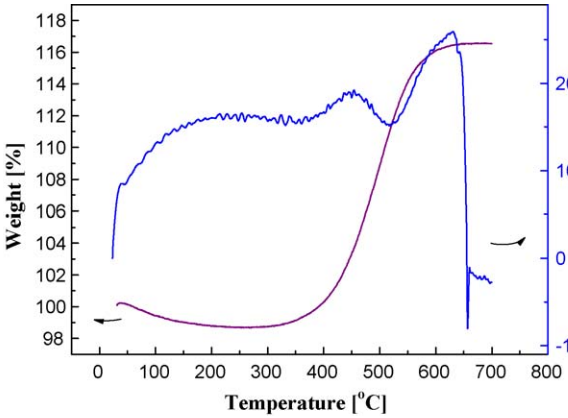

Fig. 1. TG–DTA curve of vanadium tungsten oxide powder.

The XRD patterns for the $V_{2-n}W_nO_5$ thin films deposited as the ratio of W (tungsten) composition ($n = 0$, 0.05, 0.1, 0.15, 0.20) at 400 °C are shown in Fig. 2. As tungsten content increases, the typical peaks of polycrystalline V_2O_5 appear. This peak can be attributed to (0 0 1) tetragonal V_2O_5 lattice plane.

The same crystallographic structure was found for as-prepared V_2O_5 thin films grown by RF sputtering under a gas mixture of argon and oxygen. Also, as tungsten content at lattice structure increases, crystal growth is achieved toward *C* axis and tetragonal structure is shown. The lattice parameters calculated as shown in Fig. 4-2 for the tetragonal cell of vanadium pentoxide are very close to those of the polycrystalline oxide powder: $a = 19.5$ Å, $b = 19.5$ Å, $c = 3.7$ Å. The unusual large value of the interlayer parameter *c* has to be marked. The increase of the tungsten dominated phase results in the decrease of the vanadium oxide phases. AFM images of the thin films with tungsten contents are shown in Fig. 3.

Fig. 3(a) and (b) shows that V_2O_5 and $V_{1.95}W_{0.05}O_5$ thin films have similar average surface roughness value, respectively. Fig. 3(c) and (d) reveals that $V_{1.9}W_{0.1}O_5$ and $V_{1.8}W_{0.2}O_5$ thin films have the roughness values of 38.6 and 40.9 Å, respectively, indicating increased coarseness with increasing tungsten content. In this experiment, high-density thin films were prepared by maintaining the working pressures during the sputtering process.

The composition of the V_2O_5 and $V_{1.85}W_{0.15}O_5$ thin films is also confirmed by FR-IR spectra (Fig. 4). The absorption bands centered

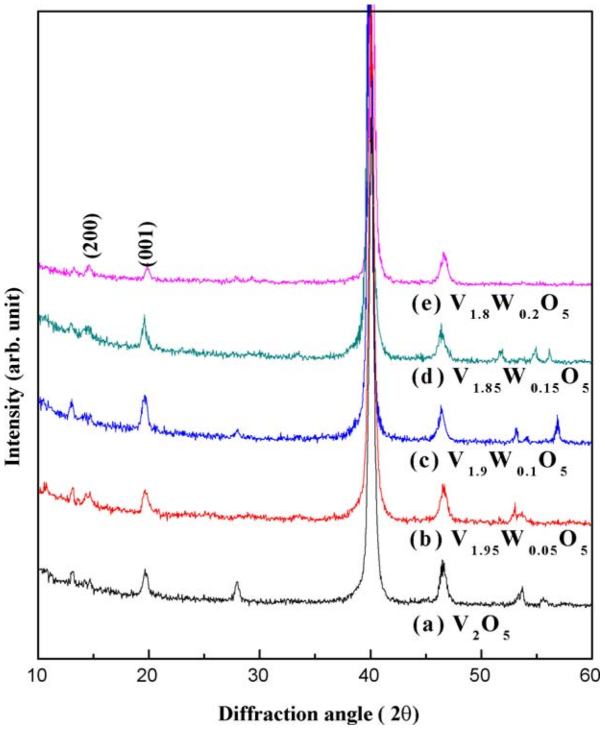

Fig. 2. XRD patterns of the $V_{2-n}W_xO_5$ thin films as a function of W (tungsten) content.