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Structural and electrical properties of vanadium tungsten oxide thin films Grown on $Pt/TiO_2/SiO_2/Si$ substrates

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$V_{1.9}W_{0.1}O_5$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrates by an RF sputtering method exhibited fairly good and dielectric properties. It was found that film crystallinity, dielectric properties, and TCR properties were strongly dependent upon the annealing temperature. The dielectric constant of the $V_{1.9}W_{0.1}O_5$ thin film annealed at 300 °C was 37.7, with a dielectric loss of 2.535, respectively. Also, the TCR values of the $V_{1.9}W_{0.1}O_5$ thin films annealed at 300 °C were about -3.6 %/K

Key words: Vanadium, Tungsten, Thin film, TCR, Dielectric property.

Introduction

A technique for detecting and using infrared rays can be of importance when applied to various fields of our lives such as a medical field as well as for a military purpose. Research and development regarding infrared detector devices have continued for the past several tens of year. [1] Research using PbS, PbSe, PbTe, or the like was actively conducted at an early stage, and a cooled-type infrared detector using HgCdTe that is a II-VI group compound semiconductor and InSb that belongs to a III-V group has come into common use recently. In spite of the high response speed and superior image reproduction, the cooled-type infrared detector requires a separate cooling device because of operating at very low temperature. For the separate cooling device, a vacuum container capable of maintaining a vacuum state of more than about 133×10^{-5} [Pa] is required, which is very expensive due to its short life span of about 5000 hours. For this reason, an uncooled type infrared detector device and an infrared image device that do not require a separate cooling device have been developed in various forms. A representative example of them is a night vision device commonly used for a military purposes. The night vision device performs imaging of near infrared rays reflected from the surface of an object using a light amplification principle and can be manufactured at low cost. However, the night vision device consumes substantial amount of power, has low temperature resolution, and cannot effectively function in a dark room where light is blocked or in a cloudy night. With the recent development of nano-processing technology, research has been actively conducted to manufacture au uncooled type infrared sensing device having a number of Focal Plane Arrays (FPAs), and the nano-processing technology developed allows the manufacture 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 as a bolometer, a thermocouple, and as a pyroelectric detector according to the principle used. Among them, the bolometer approach has been extensively studied because it can be manufactured using a conventional semiconductor manufacturing process and has a high response feature [2-4]. An infrared sensing layer for the bolometer may be made of various materials such as a metal, vanadium oxide, and semiconductor materials such as YBaCuO, SiGe, etc. Among these materials, vanadium oxide which has a 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 for an infrared ray sensing device. A factor that most affects noise is the resistance of the device, which can be reduced by depositing a vanadium oxide thin film which has a low resistance. Therefore, the deposition of a vanadium oxide thin film which has a low resistance and high TCR is essential for to manufacture an uncooled type infrared sensing device. Vanadium has various oxide forms such as VO_2, V_2O_3, and V_2O_5 and then undergo phase transitions from an insulator/semiconductor to a metal at a particular temperature. Although the VO_2 form among these forms is most suitable for a bolometer, it is very difficult to manufacture requiring expensive ion equipment, and has a high room temperature resistance. The V_2O_3 form has a low formation energy, undergoes a semiconductor-metal phase transition at −123 °C, and has a very low specific resistance at room temperature. On the other hand, the V_2O_5 form is easy to thin film deposit, can be thermally processed at a low temperature, and

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shows superior thermal sensitivity are a wide temperature range. For this reason, there has been an attempt to apply the V_2O_5 form as 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. Also the V_2O_5 form has been widely used as a material for manufacturing a chemical sensor, for temperature-measuring and as a heat-sensing image device, etc [5-8]. A vanadium oxide thin film is manufactured in various ways such as by thermal evaporation, thermal oxidation, sol-gel, sputtering, chemical vapor deposition (CVD), etc. For this purpose, we have first prepared $V_{1.9}W_{0.1}O_5$ thin films by annealing on platinized silicon substrates using the same fabrication conditions by an RF sputtering method. The effect of substituting tungsten for vanadium in the structure on the dielectric properties, such as the temperature coefficient of resistance has been investigated systematically.

Experimental

The vanadium tungsten oxide ceramic targets of the RF sputtering system were prepared by a conventional mixed oxide method. The starting materials were V_2O_5, W. These materials were weighed according to the composition of $V_{1.9}W_{0.1}O_5$, the weight ratio of zirconia balls-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 (φ = 50 mm) 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 $V_{1.9}W_{0.1}O_5$ thin films were grown on Pt/TiO$_2$/SiO$_2$/Si substrates by a RF sputtering method. The initial vacuum was about 400 [μPa] and the sputtering atmosphere was controlled by the Ar/O$_2$ ratio at a total pressure of 400×10^3 [μPa]. The RF power for the $V_{1.9}W_{0.1}O_5$ targets was 100 W and the target-substrate distance was about 7 mm. The thickness of the films was measured using a field emission electron microscope and an α step profilometer. The crystalline structures of the $V_{1.9}W_{0.1}O_5$ 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). The compositional depth profile and interdiffusion between the films and substrate were investigated by Auger electron spectroscopy (AES). For electrical measurements, an Au thin film was deposited by an evaporator at room temperature as 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).

Results and Discussion

The X-ray diffraction (XRD) patterns of the $V_{1.9}W_{0.1}O_5$ thin films are presented in Fig. 1, after being annealed for 30 minutes in an oxygen atmosphere at temperatures ranging from 150 °C to 350 °C. As the annealing temperature increased to 200 °C, the vanadium tungsten oxide thin film began to crystallize. This fact indicates that the beginning of crystallization to a layer of perovskite is below 200 °C. All the films consisted of a single phase of a vanadium-layered tetragonal structure without any preferred orientation. The microbolometer resistance and corresponding resistivity as a function of temperature are shown in Fig. 2. The temperature dependence resistance data are best fitted to the Arrhenius relation $R = R_o\exp(-Ea/kT)$ (k, Boltzmann constant; T, temperature in K; E_a carrier activation energy), which clearly indicates that the conduction is a thermally-activated process. From the curves, representing the dependence of TCR on the temperature we could obtain a high TCR close to -3.6%/K. In these experiments, we have found an inversion of the TCR with an increase of the annealing temperature that may be related to variations in the grain size. Fig. 3 shows the dielectric constant and the dielectric loss at 1 kHz of $V_{1.9}W_{0.1}O_5$ thin films annealed at different temperatures. These curves were obtained using amplitude of 0.1V and measured at 1 kHz. The dielectric constant gradually increased with an increase in the annealing temperature. Also, the dielectric loss decreases with an increase in the annealing temperature. It is

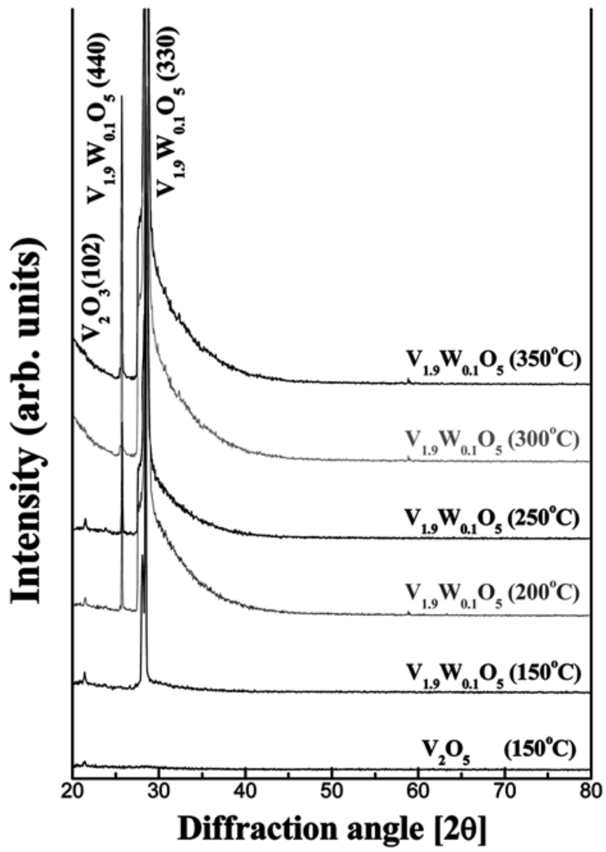

Fig. 1. XRD patterns of $V_{1.9}W_{0.1}O_5$ thin films on Pt/Ti/SiO$_2$/Si substrates annealed at different temperatures.

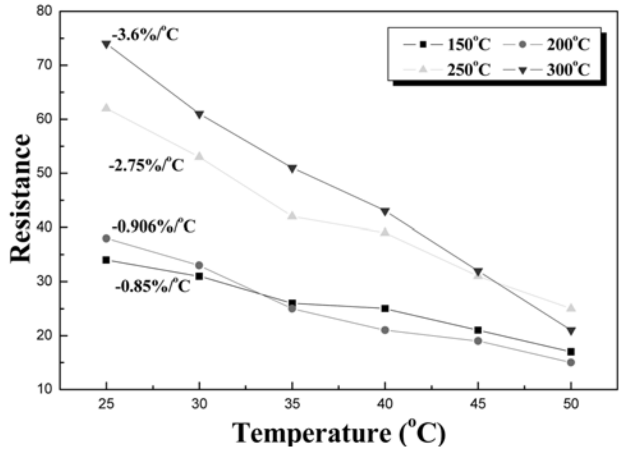

Fig. 2. Dependence of bolometer resistance and resistivity on temperature.

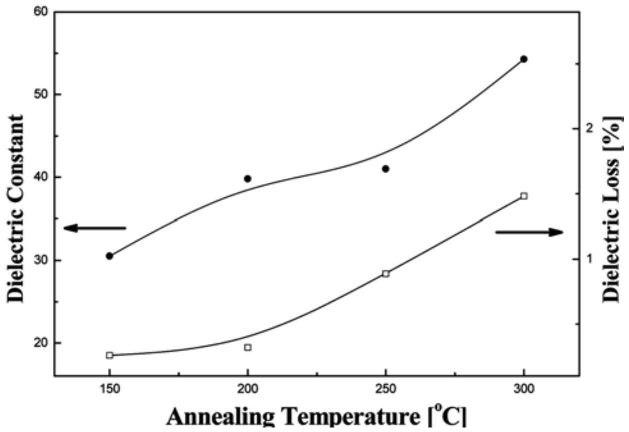

Fig. 3. Dielectric constant and dielectric loss of the $V_{1.9}W_{0.1}O_5$ thin films on $Pt/Ti/SiO_2/Si$ substrates annealed at different temperatures.

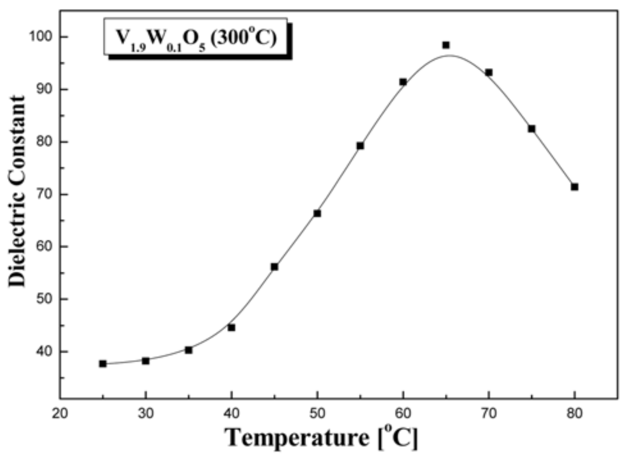

Fig. 4. Dielectric constant of the $V_{1.9}W_{0.1}O_5$ thin films on $Pt/Ti/SiO_2/Si$ substrates annealed at 300 °C, as a function of temperature.

well known that the dielectric loss in vanadium and tungsten materials is affected by various factors such as space charge polarization, crystallinity, domain wall pinning, secondary phase, and interfacial diffusion. The dielectric constant-temperature characteristics of the $V_{1.9}W_{0.1}O_5$ thin films annealed at 300 °C measured at different temperatures are shown in Fig. 4. There was no appreciable increase in the dielectric constant in the temperature range 25-65 °C. This lack of change could be attributed to the grain orientation and the internal residual stress between grains and between the films and the underlying substrate.

Conclusions

The $V_{1.9}W_{0.1}O_5$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrates by an RF sputtering method exhibited fairly good TCR and dielectric properties. It was found that film crystallinity, dielectric properties, and TCR properties were strongly dependent upon the annealing temperature. The dielectric constants of the $V_{1.9}W_{0.1}O_5$ thin films annealed at 300 °C were 37.7, with a dielectric loss of 2.535. Also, the TCR values of the $V_{1.9}W_{0.1}O_5$ thin films annealed at 300 °C were about −3.6 %/K.

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