공학석사학위논문

The fabrication and performance analysis of vanadium oxide thin films for microbolometer application

마이크로볼로미터 적용을 위한 바나듐 산화물 박막의 제작 및 성능 분석

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Abstract

The fabrication and performance analysis of vanadium oxide thin films for microbolometer application

Tae-Hyeon Kil

Department of Materials Science and Engineering

The Graduate School

Seoul National University

Research on infrared sensing technology that can detect objects at night can be applied to a variety of fields such as autonomous vehicles, medical devices. There are two kinds of infrared sensor, photon detector and a thermal detector. The photon sensing type detector has relatively high detection performance. However, it is expensive and has low mobility because it requires cryogenic cooling equipment that has a large volume. On the other hand, the thermal sensing type detector has relatively low performance, but it is cheaper and has high mobility than photon detection type device. There are many kinds of thermal sensing type detector, however,

microbolometers with high detectivity are attracting attention, and many new materials are being studied to use for the thermal sensing layer of microbolometer. The most important part of the microbolometer is a thermal sensing layer that absorbs the heat and various materials have been studied as a candidate for thermal sensing material. In general, vanadium oxide and amorphous silicon (a-Si) are being researched as a thermal sensing material.

Vanadium oxide has many advantages over a-Si as a microbolometer material. Therefore, IR cameras using vanadium oxide thin film are being commercially used in many fields. However, although vanadium oxide has been extensively studied, still there are problems such as the stability or operating temperature range of the microbolometer device. Vanadium oxide has various polymorphic phases, which makes it difficult to fabricate the desired phase thin film with high reproducibility. Moreover, the operating temperature range of thin film containing monoclinic VO_2 (VO_2(M)) phase is limited due to the phase transition at 68 ℃.

In this study, we fabricated vanadium oxide thin film for microbolometer which is stable at a high operating temperature and shows high-performance. Thin films containing VO_2(M) phase have limited operating temperature range due to the hysteretic behavior induced by the phase transition. Therefore, single phase VO_2(B) thin film without VO_2(M) was fabricated by sputtering. We have found that the perovskite buffer layer is effective for the production of single phase VO_2(B) thin films and produced stable single

phase VO_2(B) thin films using various perovskite buffers. We also analyzed the electrical properties of VO_2(B) thin films, verifying that buffered VO_2(B) thin film has high TCR & low resistivity simultaneously. Moreover, depending on the type of the buffer layers, the phase of the vanadium oxide and the electrical properties of the thin film could be controlled.

Keywords: Microbolometer, Vanadium oxide, Sputtering, Thin film fabrication

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Contents

1. Introduction

Infrared sensors are devices that detect and transform the radiant energy emitted by an object itself into electrical signals even if no visible light is present. In modern times, the combination of infrared sensor technology with long distance detection has led to successful development of high-performance infrared detectors. The development of infrared sensors has focused on military applications, but more recently, infrared scanning systems are being used not only to measure skin temperature in order to diagnose human diseases but also to detect the night vision for an autonomous driving car system.

Infrared sensors are divided into thermal sensing type detector and photon sensing type detector according to the principle of operation. [1)] In general, photon detector devices have the higher the response rate and the higher detection capability. However, it requires expensive cryogenic cooling device and has high volume, which makes it difficult to use for special purposes such as the automated driving system. [2)] Thermal detector devices typically are operated at room temperature without a cryogenic cooling system, but they have relatively poor detection ability and have a slow response rate. To

overcome the disadvantages of traditional sensing devices, high-performance microbolometer has been actively studied for decades and commercialized microbolometer devices can be seen in the market. As microbolometers can be operated at room temperature, they do not require a cold cooling device, which is suitable for small volume devices. Moreover, because they are also compatible with silicon processes, they can be operated on the CMOS sensor, which is also designed on the ROIC. High-performance microbolometer requires high infrared detection ability and structure that can keep the heat to the sensor part absorbed from the infrared light with less loss. Some of the thermal sensing materials used in the traditional infrared sensor are VO_x, nickel oxide, [3] titanium oxide, [4] amorphous Silicon (a-Si) [5] , etc. Among them, VO_x and a-Si are now the most widely used materials. These two materials are infrared sensitive and have relatively good performance, but they have some physical limitations. For VO_x, it is difficult to secure stability and repeatability because of the different types of oxides that the materials have. [6] Amorphous silicon has a good performance and compatibility with the silicon process of the semiconductor, but they also have high electrical noise limits because of their high resistivity. In the microbolometer system, the most important part is the

thermal sensing material. Therefore, it is vital to research the development of thermal sensing material.

In this work, we fabricated single phase vanadium oxide thin films for microbolometer. To optimize single phase vanadium oxide, we used a buffer layer which can structurally help the formation of a single phase. As a result, we fabricated single phase vanadium oxide thin film with high TCR and low resistivity values at the same time. Moreover, the reproducibility of the thin film was very high, which shows the possibility for an application to microbolometer industry. This result paves the way not only for the high-performance microbolometer but also for the phase control of oxide thin films with proper buffer layers.

2. Background

2-1. Infrared detectors

Distinguishing the object or person in the dark is very important and infrared (IR) cameras help us to see in the dark. Things that cannot be detected by the naked eye or conventional cameras can be distinguished by IR cameras. By the Plank's law, all the objects emit radiation and we can know the temperature of the object by collecting the radiation from the object. Generally, there is a limitation of the visible range with naked eyes. With IR cameras, however, IR radiation (3 – 5 μm and 8 – 14 μm) can be detected and used as an information. [7)]

By an infrared detector device, the incident invisible radiation can be converted into an electrical signal, which can also be used for the image. Infrared detectors can be classified to two types by their operation principle: Photon sensing type and thermal sensing type. [8-9)] In the photon sensing device, the incident radiation is absorbed by the material through direct interaction with the electrons while the thermal sensing device uses the heat from the radiation as an information. Photon sensing type detector shows

high-performance than thermal sensing device but it requires the cryogenic cooling device. On the other hand, the thermal sensing type IR camera has lower detectivity but it has high mobility, which is suitable for light equipment.

2-1.1. Photon detectors

For photon infrared sensor, semiconductors such as InSb and HgCdTe are mainly used. [10] It measures the electrical changes such as changing of the current and voltage induced by the absorption of the infrared rays. There are two types of photon detectors, photoconductive type and photovoltaic type. The ratio of the number of carriers to the number of photons of a given energy of the infrared ray is referred to as the quantum efficiency η, which is a result of absorption, reflection, dispersion and electron recombination in the device.

The basic principle of the photoconductive detectors is the band gap energy of the semiconductor, which is the energy required to move an electron from valence band to conduction band in a semiconductor. If the photons with higher energy than the band gap energy absorbed by the device, excess electron-hole pairs are generated, inducing the change of the electrical characteristics.

Photon type infrared detection, which requires a liquid nitrogen cooling system to reduce the thermal noise, shows a high sensitivity and speed of response. Therefore, photon type detectors are expensive and have a larger volume than other kinds of an infrared detector, so usually photon type detectors are used only for military and special purposes. [11)]

2-1.2. Thermal detectors

The principle of the thermal type detector is simple: when the infrared ray is absorbed into the detector, the temperature of the material is increased. This absorbed energy changes the electrical properties of the device and the real temperature can be known with the calibration. As a matter of fact, the detectivity of thermal detectors is lower than the photon detectors. However, thermal detectors are cheaper than the photon detectors and relatively easy to manufacture. Also, thermal detectors do not require the cooling system, so the volume of the device can be smaller than photon detectors. Moreover, the sensitivity does not dependent on the wavelength, which is highly proper for various purposes.

In general, the thermal detector can be divided into 3 types: pyroelectric, thermopile, and microbolometer. First, the pyroelectric device utilizes the change of the polarization of the material induced by the temperature change. As the suitable materials for the pyroelectric detector, barium strontium titanate (BST) [12] and lead zirconate titanate (PZT) [13] are used in previous researches.

Thermopile device is the infrared detector based on the principle of Seebeck effect. When the heat is induced to the junction of the semiconductor, the voltage can be measured and that voltage is directly proportional to the temperature difference. This voltage is measured to analyze the characteristics and it can be converted to the intensity of the infrared light.

Microbolometer utilizes a resistance change to detect the change of the temperature. Recently, micromachining techniques have been developed, enabling the fabrication of microbolometer. [14] Microbolometer shows better performance than other kinds of thermal detectors. Therefore, microbolometer is currently being studied by many researchers to use for the industrial application. The microbolometer sensor was fabricated with an array size of 240×336 and pixel size of 50×50 μm^2 at Honeywell Company in the 1990s. [15]

2-1.3. Microbolometer

In the 1980s, Honeywell developed a prototype sensor consisting of mechanical bridge-like structures, ~ 100 μm square and 1 μm thick, which is known as the microbolometer. To realize the uncooled IR-camera, several of these microbolometers were fabricated as a two-dimensional focal plane array with many pixels. A single microbolometer is contained in each pixel of the array. Fig. 2-1. shows the basic bridge structure of the microbolometer fabricated by Honeywell. The thermal detection material is encapsulated by the thick Si_3N_4 bridge floated above the underlying silicon substrate to prevent the heat conduction. On the underlying substrate, thin film metal reflector layer is deposited for the reflection of unabsorbed radiation. Moreover, the gap is maintained as a vacuum to produce a quarter wave resonant cavity between the substrate and the bridge for the purpose of maximizing absorption of the incoming infrared radiation. The bridge is supported by two narrow metal legs to electrically connect the device and readout integrated circuit (ROIC), which is encapsulated by Si_3N_4 for the excellent thermal isolation.

Noise equivalent temperature difference, which is the principal figure of merit for an uncooled microbolometer, is given by [1)]

$$\mathrm{NETD} = \frac{4F^2 V_N}{\tau_0 A_D R(\Delta P/\Delta T)_{\lambda 1-\lambda 2}}$$

where F = 1/(2sinθ), θ is the angle which the marginal ray from the optics makes with the optical axis at the focal point of the image, V_N is the total noise voltage over the array readout electrical bandwidth, το is the transmittance of the optics, A_D is the area of the pixel, R is the responsivity, and $(\frac{\Delta P}{\Delta T})_{\lambda 1-\lambda 2}$ is the change with respect to the temperature of the power per unit area emitted by a blackbody at temperature T measured within the spectral bandwidth between λ_1 and λ_2. In these material parameters, responsivity and noise (V_N) can be tailored easily. For high-performance microbolometer, NETD should be as small as possible, which is related with low noise and high responsivity. Responsivity, which is the ratio of the electrical signal output to the incident power, is an important factor for microbolometer. For high responsivity, the high TCR and a high resistivity are required. However, the resistivity should be limited by other parameters of the ROIC such as the power and bias currents. Noise refers to the fluctuations in the output signal that are not caused by the image source. Normally, there are four sources of noise in the microbolometers: Johnson noise, 1/f noise, temperature fluctuation noise, and background fluctuation noise. Johnson noise (V_J) is originated by the random thermal motion of free

electrons in a resistor. On the other hand, 1/f noise ($V_{1/f}$) is due to the trapping and detrapping of the charge carriers in states far off from the Fermi level, and is frequency dependent. The statistical nature of the heat interchange between the detector material and its surroundings gives rise to the temperature fluctuation noise (V_{TF}) and the background fluctuation noise (V_{BF}) is caused by the fluctuations in the absorbed power due to the quasirandom arrival of the photons. Finally, the total noise is given by the square root of the sum of the squares of these uncorrelated four noises. [2)]

$$V_N^2 = V_J^2 + V_{1/f}^2 + V_{TF}^2 + V_{BF}^2$$

Temperature fluctuation noise and background fluctuation noise are inherent properties of the microbolometer and are independent of the sensor material. Therefore, from the point of views of the materials, Johnson noise (V_J) and 1/f noise ($V_{1/f}$) can be controlled. In order to reduce the noise to get better performance of the microbolometer, a material with a high TCR, low resistivity and low 1/f noise is required.

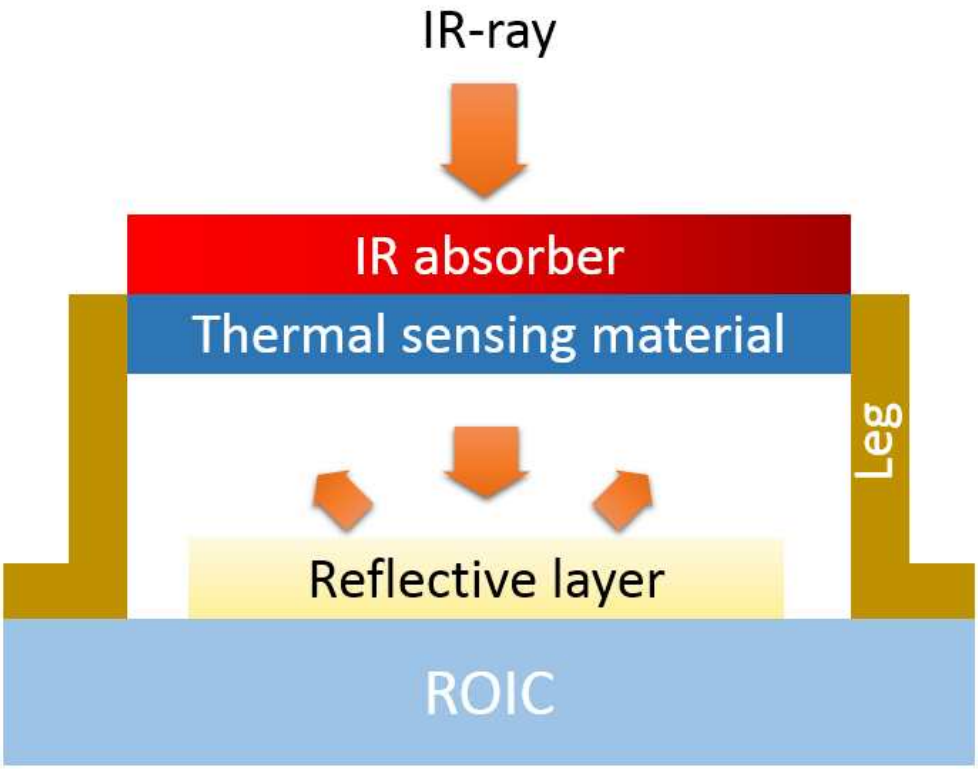

Fig. 2-1. Figure of one pixel in a microbolometer array.

2-2. Materials for microbolometer

Materials that can be used for a microbolometer as a thermal sensing layer should have a high rate of infrared absorption basically, so the thickness range of the thin film should be controlled. For example, a thin film with higher thickness will show low resistance. However, the thermal capacity of the thin film will be increased and the increment of the temperature of the thin film will be decreased, which will lead to the performance degradation.

Among the figure-of-merit, the TCR and 1/f noise (related to the resistivity) are the most important and difficult factor to control because of their ambiguous properties in the materials. [2)] Therefore, many researchers are studying various kinds of materials that have relatively high TCR and low resistivity simultaneously, and also for the origin of such properties.

2-2.1. Amorphous silicon

Amorphous silicon (a-Si), which is a familiar material with semiconductor technology, can be used for the microbolometer application. [16) 17)] As a thermal sensing material of microbolometer, a-Si shows lower performance than other materials but a-Si is compatible with the CMOS process. Also, this fabrication process can be done under 400 ℃. However, because of the high resistivity of a-Si material, Enhancement of the detectivity is hard to achieve.

Therefore, due to the demand for the high-performance microbolometer, many researchers are studying other kinds of materials with low resistivity and high TCR values at the same time.

2-2.2. Nickel oxide

Nickel oxide, which is a stable material, can be applied to microbolometer application. [18) 19)] For microbolometer application, high TCR and low resistivity are required. However, the TCR of the nickel oxide thin films is slightly lower than other microbolometer materials. Therefore, in order to

achieve the similar detection ability, more bias power is required, which means an inefficiency in terms of power consumption.

2-2.3. Vanadium oxide

As mentioned above, the promising materials currently used for the thermal sensing material of the microbolometer are vanadium oxide, amorphous silicon and nickel oxide. Among these, the industry favorable material is vanadium oxide (VO_x with $x \sim 1.8$) which has a relatively high TCR and a reasonably low resistivity at the same time. [20] Vanadium oxide shows other advantages such as the low-temperature processing and the compatibility with current CMOS fabrication technology. Although VO_x films satisfy most of the necessary conditions for the microbolometer application, the origin of the properties, such as conduction mechanisms and role of oxygen vacancy, are little understood. In spite of this lack of fundamental understanding of the origin, the entire microbolometer device with better performance can be fabricated. With a better understanding of the underlying conductions, we can control the electrical properties of the VO_x thin films, and thus greatly enhance the impact on society.

Vanadium oxide has many advantages than a-Si and vanadium oxide thin films were fabricated through several techniques such as ion beam sputtering [21-23], RF or DC magnetron sputtering [20,24,25,26], e-beam evaporation [27], pulsed laser deposition [28], and molecular beam epitaxy [29]. However, although vanadium oxide has been extensively studied, there is a problem such as the stability or operating temperature range. Vanadium oxide has various phases, which makes it difficult to fabricate a thin film with high reproducibility. Moreover, the operating temperature range of thin film containing monoclinic VO_2 (VO_2(M)) phase is limited due to hysteresis. [30] Therefore, for high temperature and reliable operation of microbolometer, it should be possible to make vanadium oxide thin films that are easy to fabricate and have no hysteresis loop.

3. Experiments

3-1. Fabrication process

In this experiments, we fabricated thin films with RF sputtering, e-beam evaporation and thermal evaporation. To deposit the proper VO_x thin film for microbolometer application, we tried to find the deposition conditions for a thin film that shows high TCR and low resistivity values at the same time.

Vanadium oxide thin films were fabricated by sputtering. We used the monoclinic VO_2 target and focused on making the thin film suitable for microbolometer application by controlling the gas ratio, sputtering power, temperature, deposition partial pressure and so on.

As mentioned earlier, vanadium oxide has numerous polymorphic phases and is very sensitive to the deposition conditions. Therefore, for the reproducibility of the experiment, a mixing gas of argon and oxygen was used to precisely control the oxygen in the chamber and a buffer layer was deposited in advance to deposit the desired phase.

The phase of the deposited thin film was confirmed by XRD. In order to verify the electrical characteristics, Au/Ti metal layers, which can form an

ohmic contact with n-type VO_x material, were deposited by e-beam and thermal evaporation methods and then the hall measurement was performed. In order to measure the TCR value, the sample was placed on the thermoelectric module, and the I-V was measured while changing the temperature, and the resistance value according to the temperature change was measured. All of these process steps are shown in Fig. 3-1.

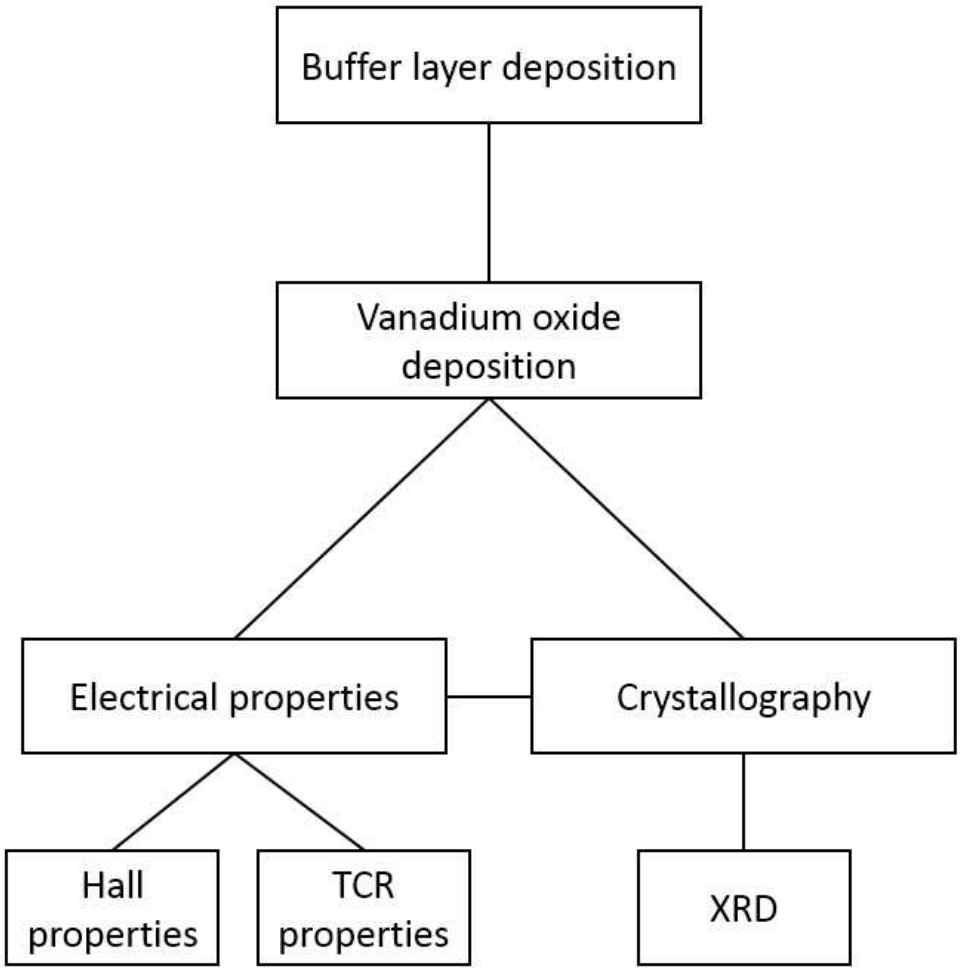

Fig. 3-1. Flowchart of the experiment process.

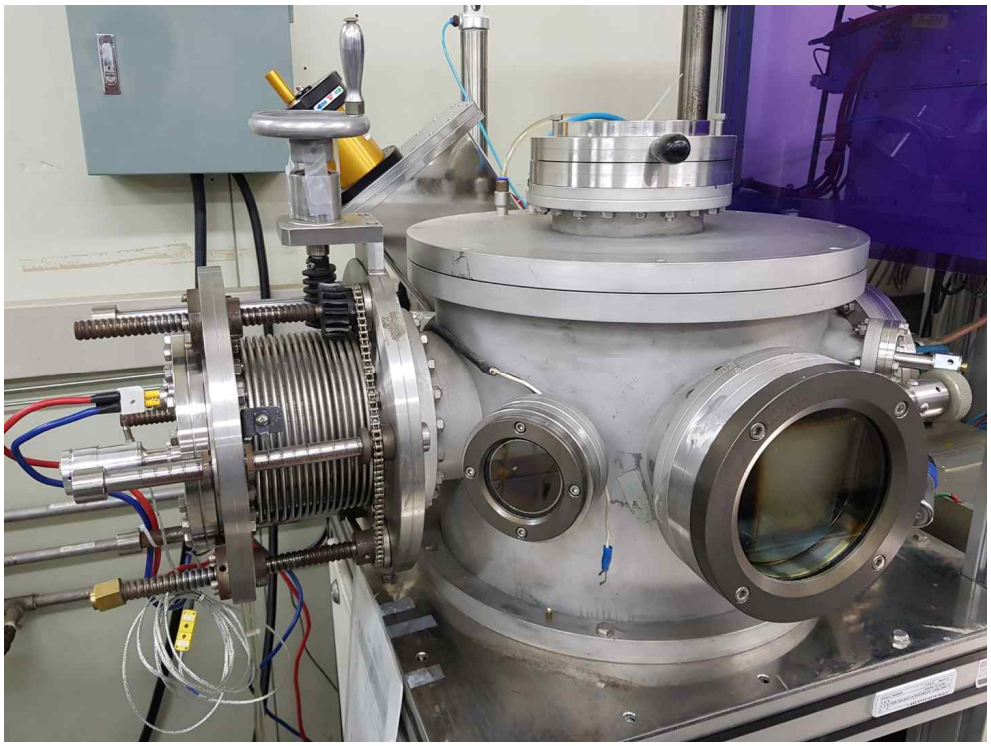

Fig. 3-2. Sputtering chamber for VO_x thin film deposition.

3-2. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) utilizes the signals that occur by impinging X-rays on the surface of the sample. Diffraction occurs in all directions when the X-ray impinges on the surface of the sample, but diffraction patterns cause interference and produce a uniform pattern. If the sample is periodically arranged in a valence, we have a deterministic pattern in XRD pattern, and there is also significantly regularity, so it is possible to know the crystal structure of the sample. With further analysis, it is also possible to confirm the preferred orientation and crystallinity of sample.

When we compare the XRD method to other kinds of analysis method, there are several advantages of the XRD method. First, XRD is non-destructive and no special sample preparation step is needed. Also, from XRD method, we can obtain various kinds of data about the average structure from the large area of the sample.

However, there is a difference between bulk analysis and thin films analysis with XRD. Normally, θ-2θ measurement is used for crystal structure analysis for a bulk sample but other kinds of analysis methods are required for thin film sample. The thin film is a thin layer on a bulk substrate so the thickness of thin films is very lower than the substrate, so if we use the normal θ-2θ

measurement for thin film sample, we get the intense signal of the substrate and weak signal of the thin film, which is not a favorable result.

Therefore, Grazing Incidence X-ray Diffraction (GIXRD) technique is used for thin films material. With using the GIXRD technique, we can get the strong signal from the thin film, avoiding the intense signal from the substrate at the same time.

In this study, we used ATX-G of RIGAKU, Japan, equipped with Cu target for the phase analysis of VO_x thin film with GIXRD technique. The X-ray generation condition was 40 KV, 300 mA, and the 2θ section between 10 and 75 ° was scanned at a rate of 10 ° per minute.

Fig. 3-3. XRD system for thin films analysis.

3-3. Electrical properties analysis

3-3.1. TCR measurement

The most important characteristic to apply the vanadium oxide thin film to the microbolometer is the TCR value and the resistivity of the thin film. The TCR value indicates the degree of resistance change with temperature change. To know the TCR value, the resistance should be measured while changing the temperature. [1)]

$$\mathrm{TCR}(\%/\mathrm{K}) = \frac{1}{R}\frac{dR}{dT} \times 100$$

First, Au/Ti electrodes were deposited using an e-beam and thermal evaporation system to accurately measure the resistance of the sample. Because vanadium oxide is an n-type material, Au and Ti are used to make ohmic contacts. The thickness of the deposited Au and Ti thin films was 30 nm, respectively.

We used a thermoelectric module to raise the temperature of the sample accurately. When electricity is applied to the thermoelectric module, the

temperature increases on one side and the temperature decreases on the other depending on the direction of the electricity.

To increase the temperature of the vanadium oxide thin film, the thin film was placed on the heating side and the temperature of the thin film was measured using a thermocouple.

A Keithley instrument was used to accurately record the change in resistance of the sample with temperature. We used a Keithley-2182A instrument for temperature measurements and a Keithley-2400 instrument for I-V measurements. We also measured the change of temperature and resistance at the same time using the LabVIEW program.

Finally, to analyze the performance of the microbolometer, the TCR value at room temperature was calculated according to the principle.

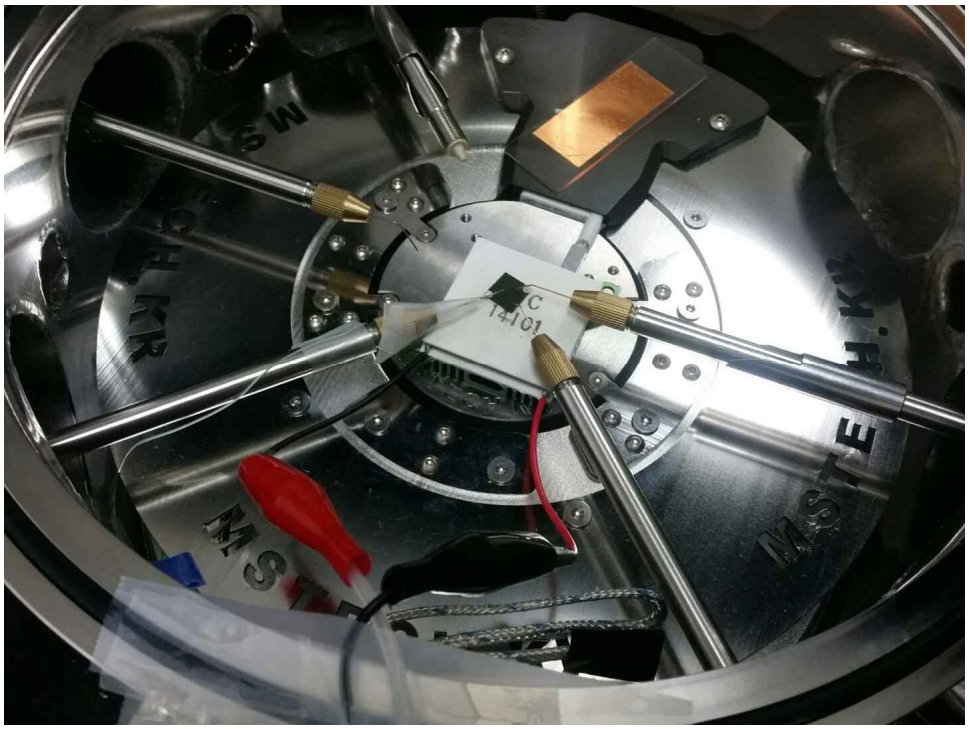

Fig. 3-4. The stage for TCR measurement.

3-3.2. Hall measurement

First, a solid such as a metal or a semiconductor is placed in a magnetic field. When the current flows perpendicularly to the direction, an electric field is formed in the solid at right angles to each of the two directions, and Hall voltage is generated at this time. This phenomenon of Hall voltage is called the Hall Effect.

Using these effects, electrical characteristics such as carrier concentration, mobility, and resistivity can be analyzed. In order to determine the applicability of the vanadium oxide thin film as a microbolometer, the resistivity value was obtained through Hall measurement.

4. Discussion

4-1. VO_x thin films on SiO_2

4-1.1. Phase analysis by XRD results

First, the phase of the vanadium oxide thin film prepared by the sputtering was analyzed. Thin films were deposited at 350 ℃ and the sputtering power was decreased from 100 W to 30 W. The ratio of argon to oxygen was decreased from 30% to 2%. As a result, the V_2O_5 phase thin films were deposited. It was also confirmed that the sample deposited at 150 W and the oxygen ratio of 10% also exhibited the V_2O_5 phase (PDF # 04-007-0398).

Generally, V_2O_5 single-phase thin film is not used in a microbolometer. V_2O_5 is reported to be the most stable phase among the vanadium oxide polymorphic phases, but the resistance is very high, which causes noise in the microbolometer. Therefore, a VO_x thin film with less oxygen than V_2O_5 should be deposited.

Fig. 4-1. shows that all the thin films were a polycrystalline V_2O_5 phase, but a simple measuring of the resistance of the thin film revealed the differences

in these samples. The thin film of V_2O_5 phase deposited with 2% argon and oxygen ratio showed a resistance value of 1.8 MΩ when measured with a multimeter at room temperature. However, when the rate of oxygen increased, the resistance of the deposited samples was also increased so it was not measurable by the multimeter. These thin films are not suitable for the microbolometer because of the high resistance.

In other words, it is necessary to lower the resistance value of the thin film by conducting the experiment in the direction of lowering the oxygen in the chamber to make a thin film which can be used as a microbolometer. We also tried to lower the oxygen content in the thin film by lowering the sputtering power.

Deposition of the thin film by lowering the sputtering power and lowering the oxygen ratio induced the change in the phase and the resistance of the thin film. Fig. 4-2. shows that the V_2O_3 phase (PDF # 04-008-7634) is produced by sputtering with a gas of only argon. Since the monoclinic VO_2 phase was used as a sputtering target, it can be seen that oxygen is lost during the deposition process. Then, the ratio of oxygen to argon is set to 1% and sputtering is performed. That sample had the V_2O_5 phase, which is the same with sample deposited at 2% oxygen ratio (Fig. 4-1.).

It can be seen that when the ratio of oxygen to argon is adjusted to 0.2%, another phase is generated. A thin film with a VO_2(B) phase (PDF # 00-081-2392) is deposited. The resistance of the thin film was about 100 kΩ. By measuring the resistance after making a solid metal contact, it shows a lower value (~40 kΩ), which indicates the possibility of application for microbolometer.

However, as mentioned above, the most important factor in the microbolometer is the high TCR and the low resistivity, that is, the electrical characteristics. Phase control is essential to obtain the desired electrical properties of the thin film, but in order to apply it to the microbolometer, the electrical properties of the thin film must be confirmed.

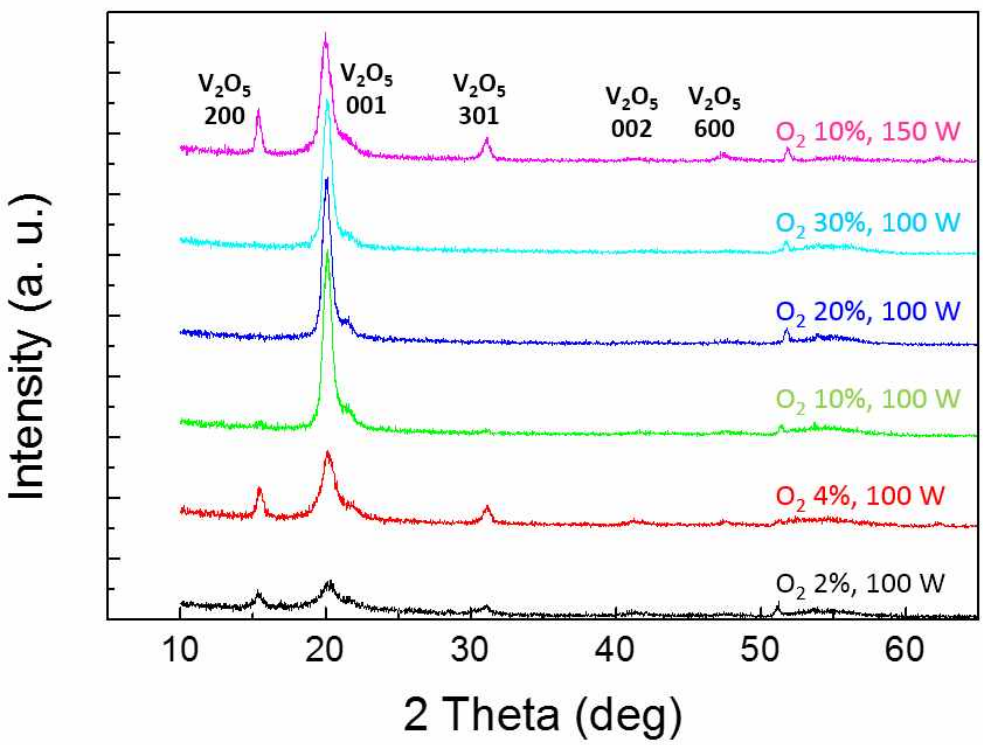

Fig. 4-1. X-ray diffraction patterns of sputtered V_2O_5 thin films.

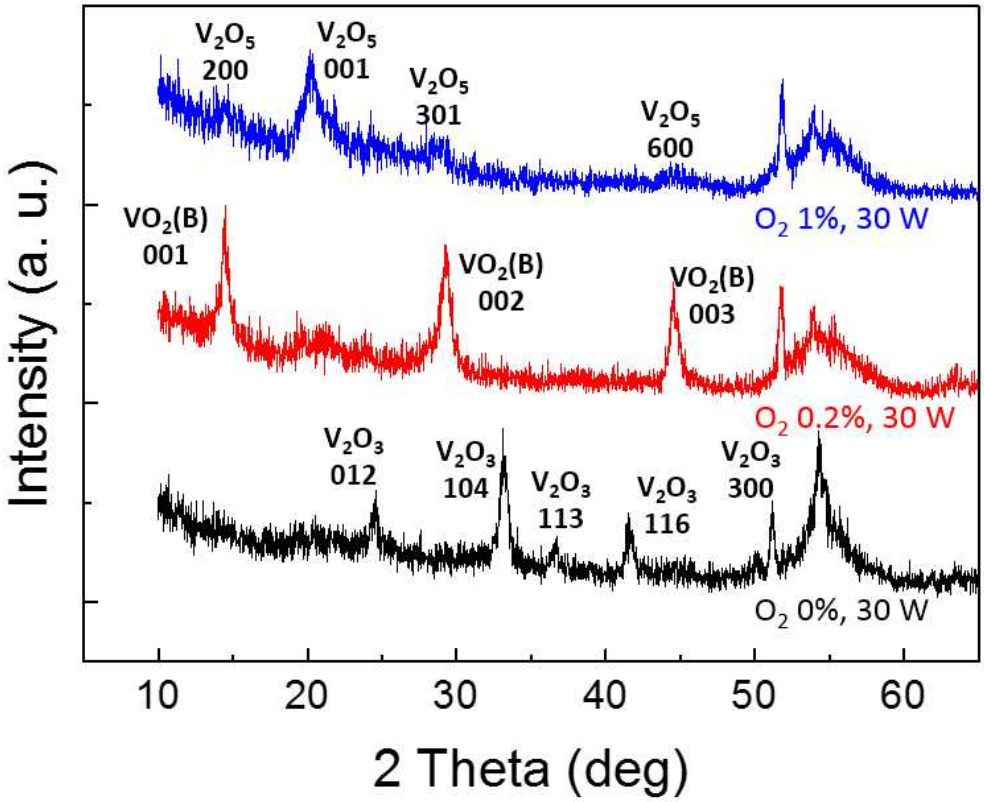

Fig. 4-2. X-ray diffraction patterns of sputtered VO_x thin films with the varying gas ratio.

4-1.2. Electrical properties analysis

Fig. 4-3 shows the graph of resistance change of V_2O_5 thin film with temperature change. Thin films deposited at 10% of oxygen partial pressure and 2% of oxygen partial pressure show little difference in XRD analysis results, however, the electrical characteristics are completely different.

It can be seen that the thin film sputtered at an oxygen ratio of 10% has a very high resistance at room temperature. The TCR value at room temperature is very large, and the resistance is very high.

The thin film deposited at an oxygen ratio of 2% has a much lower resistance than the sample deposited at 10%. The XRD results indicate the same V_2O_5 phase, but the electrical characteristics are very different. This is because the vanadium oxide thin film is an n-type semiconductor and oxygen vacancy produces electrons. The thin film deposited at low oxygen ratios had relatively more oxygen vacancies within the V_2O_5 crystalline, resulting in the more electrons in the thin film.

However, since V_2O_5 is basically a highly resistive material, it is not easy to lower the resistance enough for the microbolometer application. Therefore, it is necessary to analyze the electrical characteristics of thin films having different phases other than a V_2O_5 phase.

Fig. 4-4. is a graph comparing and analyzing the electrical characteristics of thin films having V_2O_5 and other phases. First, the thin film deposited at 1% oxygen ratio shows the V_2O_5 phase and thus the resistance is the highest. The TCR value is large, but the resistance is too high to be suitable for the microbolometer application.

The thin film deposited with only argon without oxygen shows the V_2O_3 phase, but the V_2O_3 phase has already been reported to show metallic characteristics at room temperature. In this work, we also showed that V_2O_3 phase shows very low resistance and low TCR values. The V_2O_3 phase is also difficult to apply to a microbolometer as a single phase due to its low TCR value.

Finally, it can be seen that the thin film deposited with 0.2% oxygen has a VO_2(B) phase and exhibits a very good electrical characteristic. The VO_2(B) phase is an unfavorable phase, but it has a large TCR value and a very low resistance value at the same time. Therefore, VO_2(B) phase thin film is suitable for microbolometer application. [31-32)]

However, the VO_2(B) phase has a problem in the reproducibility. Fig. 4-5. shows the electrical properties of five thin films deposited under the same conditions to form a thin film having a VO_2(B) phase. As can be seen from

the graph, the electrical characteristics are all not the same. Some thin films show hysteresis in the temperature-resistance graph, which is a metal-insulator transition (MIT) phenomenon of the widely known monoclinic VO_2 (VO_2(M)).

Vanadium oxides have many polymorphic phases and thus different phases are deposited even when the deposition conditions did not change. Therefore, very fine control is required to obtain a thin film having a desired phase.

It has been confirmed that the thin film having a VO_2(B) phase has a high TCR value and a low resistance value simultaneously, so it is important to deposit a VO_2(B) phase thin film with high stability and reproducibility.

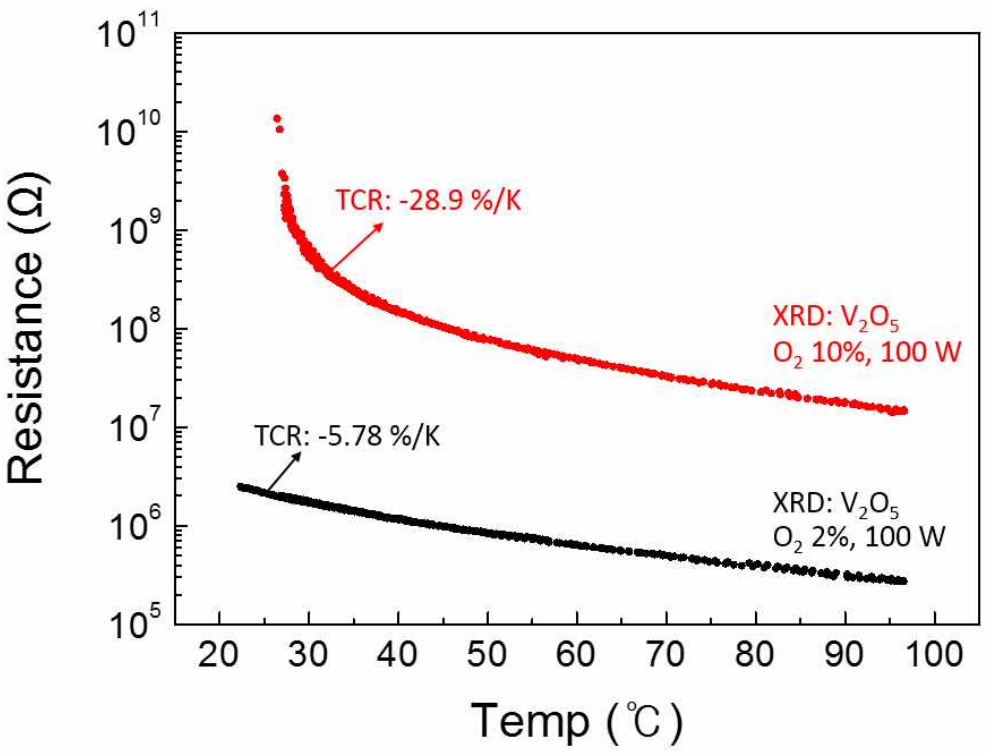

Fig. 4-3. Temperature-Resistance graph of V_2O_5 thin films.

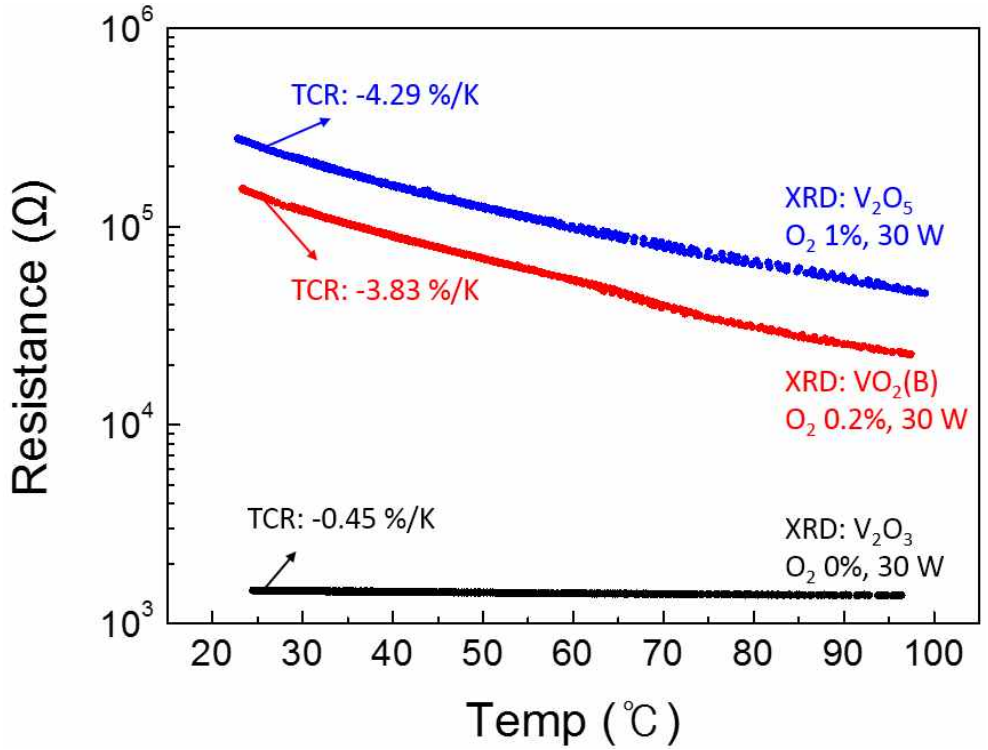

Fig. 4-4. Temperature-Resistance graph of V_2O_3, VO_2(B) and V_2O_5 thin films.

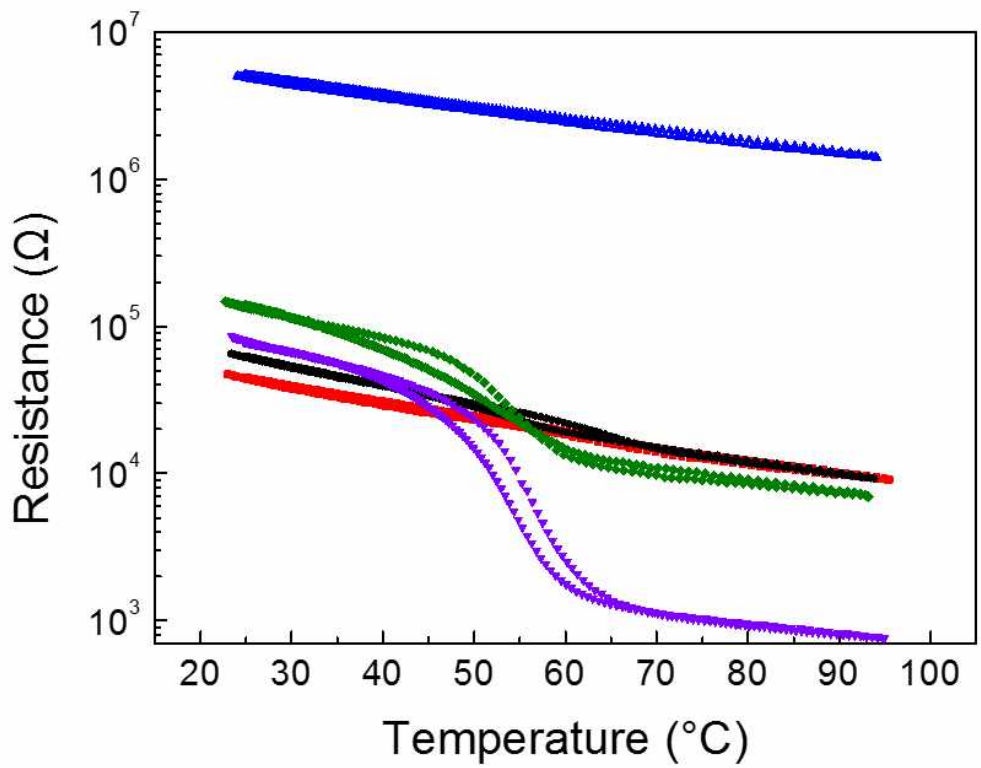

Fig. 4-5. Temperature-Resistance graph of VO_x thin films deposited at the same condition for 5 times.

4-2. VO_2(B) thin films for microbolometer application

4-2.1. Buffer layers for selective VO_2(B) deposition

As mentioned in Fig. 4-5., vanadium oxide has a very large number of phases, which makes it difficult to reproduce a specific phase with reproducibility. Therefore, an additional method is required to obtain the desired phase, and a method widely used is to use a buffer layer. There are three major conditions that the buffer layer must have. First, the crystal structure must fit well. The crystal structure of the buffer layer should match the crystal structure of the desired phase so that the thin film of the desired phase will be deposited. And the buffer layer should be easy to fabricate. The overall reproducibility of the experiment will decrease if the buffer layer is not deposited easily. Finally, the buffer layer must be an insulator. This condition is important because this thin film structure will be applied to the microbolometer. If the conductivity of the buffer layer is high, current will flow to the buffer layer, making it difficult to use the electrical characteristics of the vanadium oxide thin film.

The $SrTiO_3$ (STO) material was selected as a buffer layer satisfying all of the above conditions. As we can see in Fig. 4-6., the crystal structure of STO is suitable for the deposition of VO_2(B). It has also been reported that VO_2(B) can be epitaxially deposited on the STO (100) and STO (110) substrates.[33-34] In addition, STO can be deposited easily and reliably and is a good insulator. Therefore, in this experiment, STO with perovskite structure was selected as the buffer layer.

The STO thin film was deposited by sputtering and the STO crystal structure was analyzed before deposition of the VO_x thin film.

4-2.1.1. XRD analysis of $SrTiO_3$ buffer layer

On the SiO_2 substrate, the STO thin film was deposited by a sputtering method like the VO_x thin film. We used home-made STO target for sputtering. The sputtering power was 30 W and the deposition working pressure in the chamber was 5 mTorr. The distance between the target and the substrate was 7 cm. We compared the two types of buffer layers, amorphous STO and crystallized STO thin films. In order to confirm the XRD results, a thickness of deposited STO thin films was 40 nm or more. Fig. 4-7 and Fig. 4-8 show that STO is amorphous when grown at room temperature and crystallized when STO is deposited at 600 °C (PDF # 04-007-0044).

Fig. 4-7 shows the result of sputtering with the ratio of oxygen to argon adjusted to 50%. Fig. 4-8. shows the result of sputtering with the ratio of oxygen to argon adjusted to 20%. Comparing the two XRD results, we can check that the oxygen partial pressure has not much impact on STO buffer layers.

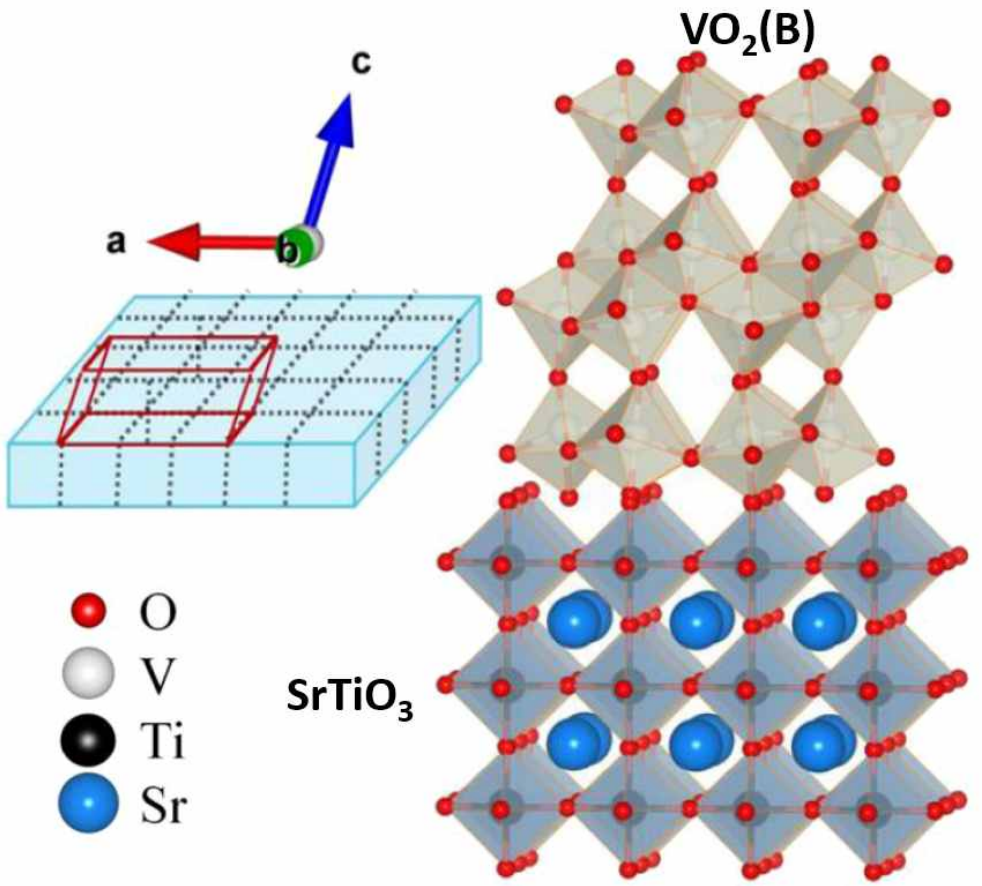

Fig. 4-6. Crystal structure of epitaxial VO_2(B) thin film on the $SrTiO_3$ substrate. [33)]

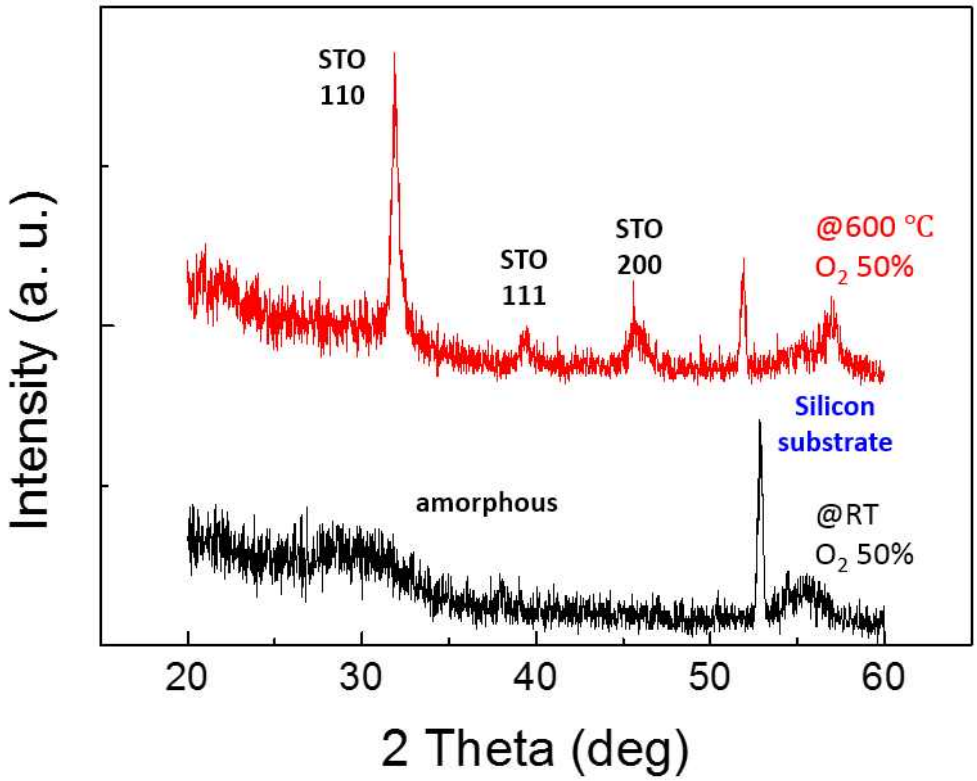

Fig. 4-7. XRD results of the $SrTiO_3$ buffer layer on SiO_2 substrate

(Ar: 15 sccm, O_2: 15 sccm).

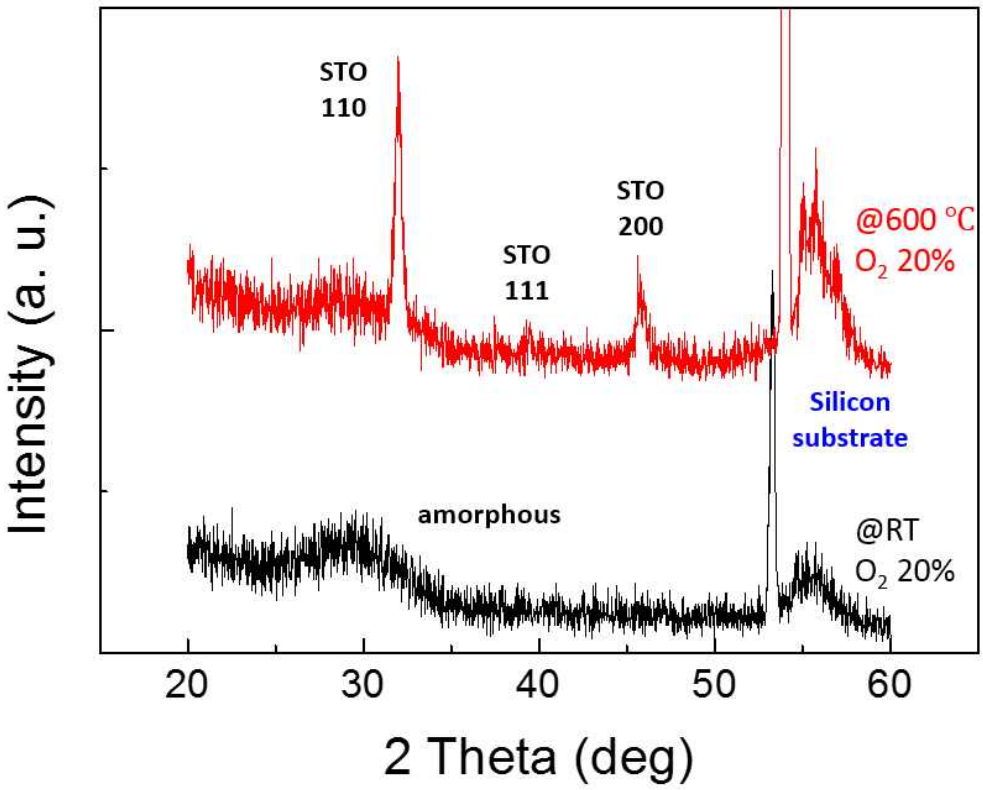

Fig. 4-8. XRD results of the $SrTiO_3$ buffer layer on SiO_2 substrate

(Ar: 20 sccm, O_2: 5 sccm).

4-2.2. VO_2(B) on the $SrTiO_3$ buffer layer

The deposition of a VO_2(B) thin film on a $SrTiO_3$ single crystal substrate has already been reported. At room temperature, VO_2(B) crystal shows a monoclinic unit cell [a = 12.03 Å, b = 3.69 Å, c = 6.42 Å and β = 106.6°] with a space group C2/m (12)). VO_2(B) can sit on the STO unit cell with the following relation: $a_{VO_2(A)}(= 12.03\text{Å}) \cong 3a_{STO}\,(= 11.715\text{Å})$, $b_{VO_2(A)}(= 3.69\text{Å}) \cong a_{STO}\,(3.905\text{Å})$. [34] However, it is necessary to investigate whether the STO layer can act as a buffer layer for the selective deposition of VO_2(B) when we deposit polycrystalline vanadium oxide on the non-epitaxial STO buffer layer.

4-2.2.1. XRD analysis

A control sample is needed to determine if the VO_2(B) phase thin film can be selectively deposited on the buffer layer. In this experiment, a SiO_2 substrate was selected as a control sample. We used the SiO_2 substrate which 1 μm of SiO_2 was grown through wet oxidation of the silicon substrate. Since the electrical characteristics of the thin film itself must be measured, the thickness of the SiO_2 layer is increased to prevent the current flowing to the substrate.

Vanadium oxide was deposited on a SiO_2 substrate and a substrate on which an STO buffer layer was deposited on a SiO_2 substrate. The sputtering power was 30 W and the deposition working pressure was 5 mTorr. The distance between the substrate and the target was 10 cm and the deposition temperature was 350 °C. The ratio of oxygen to argon was 0.1%. The thickness of the vanadium oxide was 50 nm and the thickness of the STO buffer layer was 10 nm. Fig. 4-9, it can be seen that when the vanadium oxide is deposited on the SiO_2 without a buffer layer, various phases can be mixed. However, it can be seen that the VO_2(B) single phase appears when the STO buffer layer is pre-deposited and the vanadium oxide is deposited thereon. These results show that the STO buffer layer helps to make a VO_2(B) single-

phase thin film.

To compare the reproducibility, we deposited VO_x on a SiO_2 substrate for 5 times. As we can show in Fig. 4-10., that five samples had other kinds of crystal structures. We tried to control and fix the sputtering condition, however, due to the slightly different oxygen amount in the chamber, results were not similar. When the crystal structure of the thin film is changed every time it is deposited, there is a large problem in commercialization and it is difficult to apply to the microbolometer. We have succeeded in making a single phase of VO_2(B) using the STO buffer layer, but we also need to check its reproducibility.

The same experiment was repeated 5 times to demonstrate that the deposition of vanadium oxide on the STO buffer layer is not a coincidence that a single phase of VO_2(B) appears. As we can show in Fig. 4-11., the same result is repeated. All these thin films showed single phase VO_2(B).

However, to completely solve the reproducibility problem using the STO buffer layer, we have to check the electrical characteristics. Even though we checked the same phase of thin films with XRD analysis, the oxide thin films may show different electrical characteristics depending on the amount of an oxygen vacancy.

4-2.2.2. Electrical properties analysis

As mentioned above, phase control of the vanadium oxide is also important, but electric characteristic control is essential for application to the microbolometer. In other words, the difference in electrical characteristics according to the presence or absence of the buffer should be examined. The electrical properties vary depending on the type of vanadium oxide phase and the oxygen vacancy content.

In Fig. 4-12., we can compare the electrical properties of the VO2(B) thin film with the STO buffer and the VO_x thin film on the SiO_2 substrate without a buffer layer. First, when the VO_x is deposited on a SiO_2 substrate, the TCR value is large but the resistivity is high. Moreover, the vanadium oxide thin film directly deposited on SiO_2 is difficult to control the phase and resistivity value, which makes it hard to apply for microbolometer application.

However, VO_2(B) single-phase thin films can be obtained by pre-deposition of STO buffer and deposition of vanadium oxide thereon. The VO_2(B) thin film has a high TCT value and a very low resistivity value at the same time. Thin films with such a high-performance have considerable potential as TCR materials for the microbolometer.

As shown in the XRD results, the VO_2(B) single-phase thin film can be stably

deposited repeatedly by several same experiments. Because the process is stable, mass production is possible by sputtering, and it can be industrialized immediately.

In order to investigate the degradation of thin films, we repeated heating and cooling 10 times as we can show in Fig. 4-13. The reason for making vanadium oxide in this experiment is for application to the microbolometer and it is necessary to confirm that there is no change in performance even if this thin film is used repeatedly for the microbolometer. As a result of the experiment, it was confirmed that the resistance and the TCR value were not changed even after 10 repetitions of heating and cooling to 95 °C. Therefore, it can be seen that the sample prepared in this experiment is free from the degradation problem. Moreover, with VO_2(B) phase thin film with no hysteresis, we can fabricate microbolometer that can be operated at the more higher temperature.

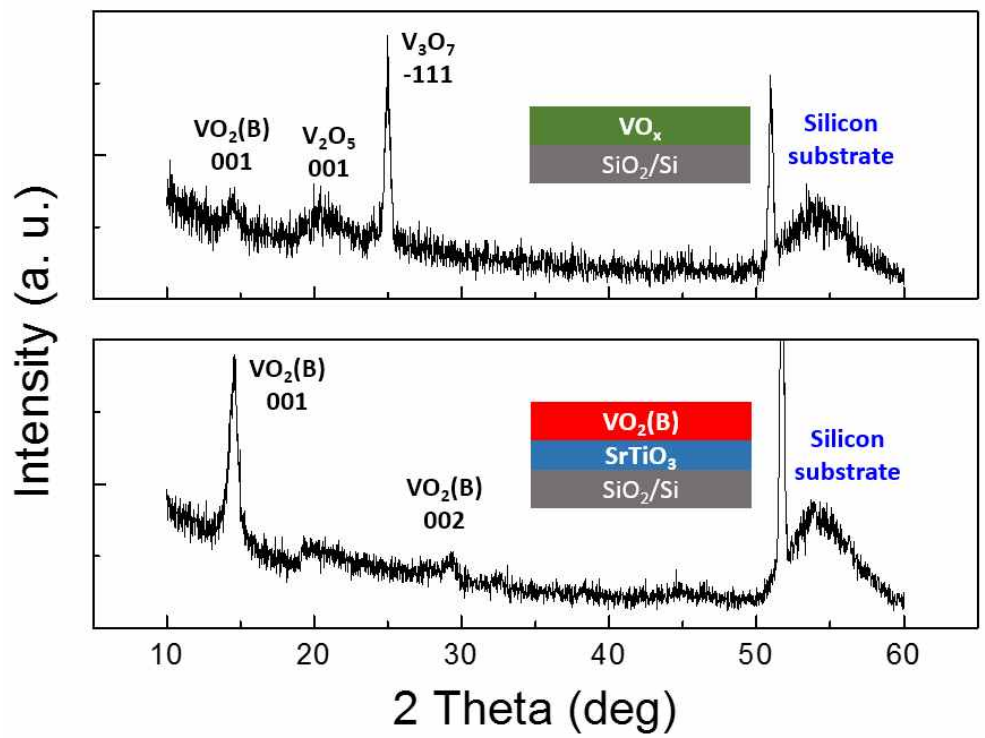

Fig. 4-9. Comparison of XRD results of VO_x on SiO_2 and VO_2(B) on STO buffer layer.

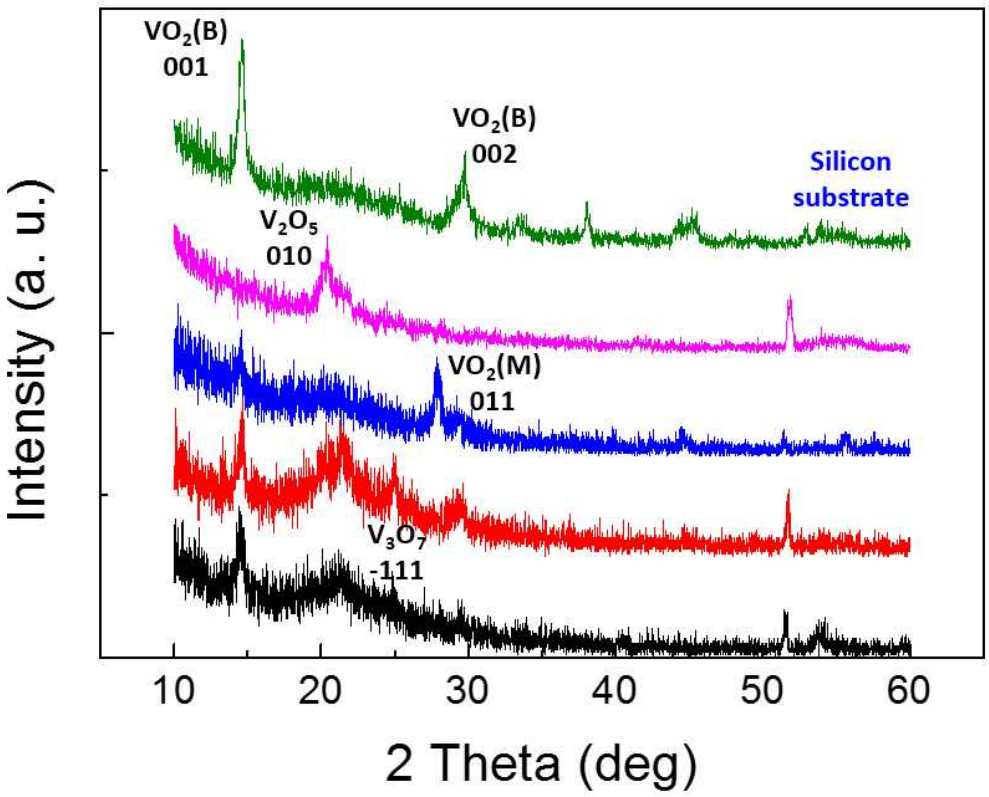

Fig. 4-10. XRD results of 5 samples of VO_x on SiO_2 deposited under the same condition for reproducibility test.

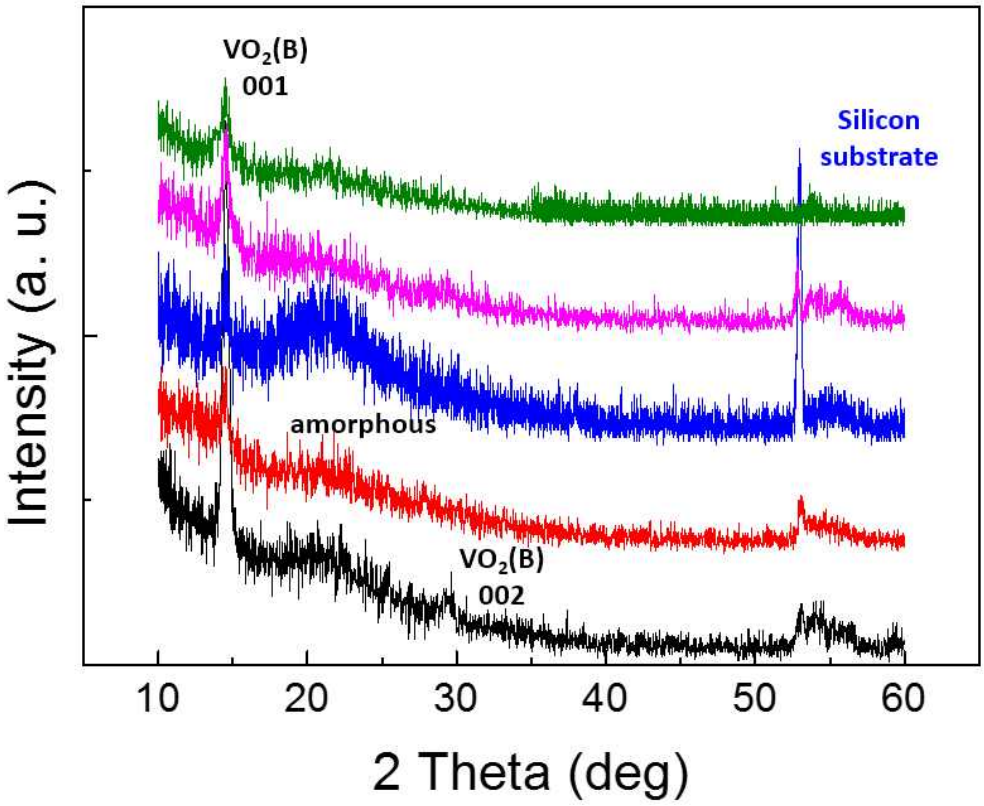

Fig. 4-11. XRD results of 5 samples of VO_2(B) on STO buffer layer deposited under the same condition for reproducibility test.

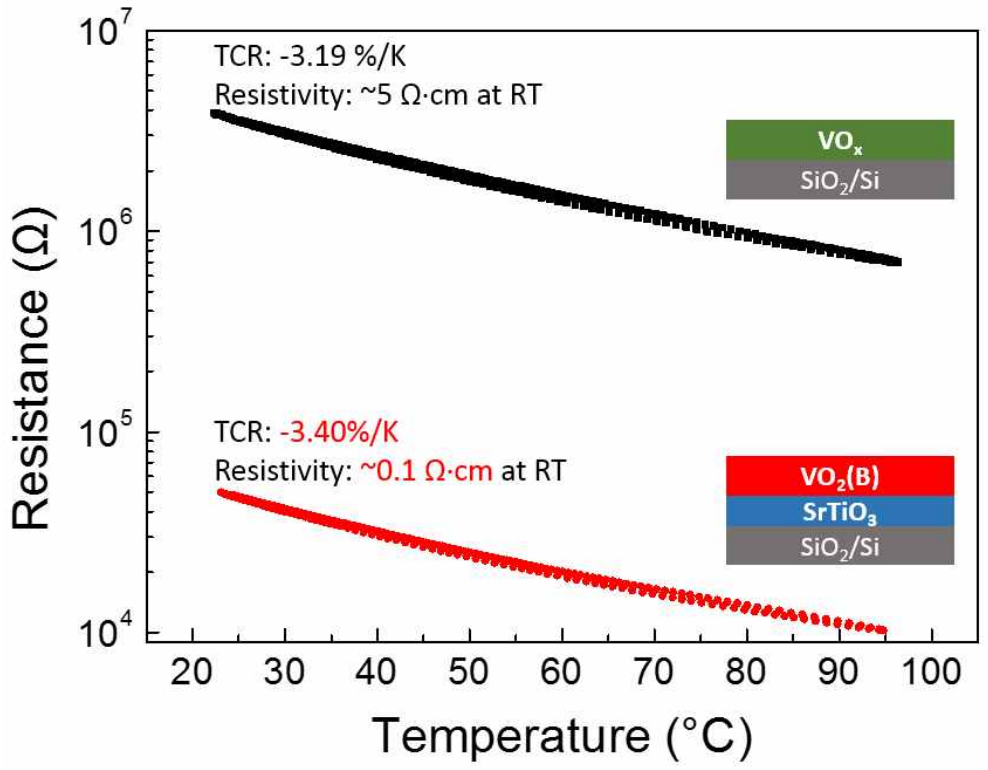

Fig. 4-12. Comparison of electrical properties of VO_x thin films and VO_2(B) thin film on STO buffer layer.

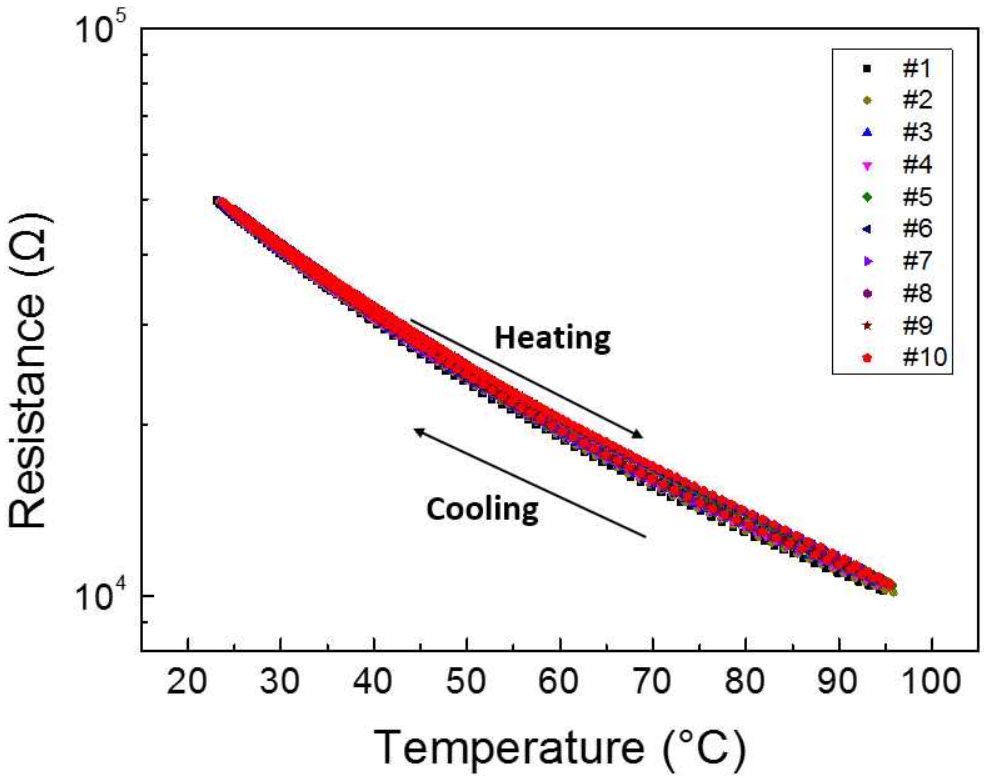

Fig. 4-13. Stability test of VO_2(B) thin films on STO buffer layer.

4-2.3. VO_2(B) on the perovskite buffer layer

The STO buffer was previously selected to selectively deposit VO_2(B). STO has a perovskite structure and therefore materials similar in structure to STO can help to selectively deposit VO_2(B). In this experiment, $LaAlO_3$ (LAO) and $SrRuO_3$ (SRO) were selected as a perovskite buffer materials other than STO. The STO has a cubic structure with a lattice constant of 3.905 Å. The lattice constants of LAO and SRO are 3.787 Å and 3.91 Å, respectively, similar to STO.

4-2.3.1. XRD analysis

In order to check whether the LAO and SRO buffer layers play a role similar to the STO buffer layer, we first checked the XRD results. As a result, as we can see in Fig. 4-14., VO_2(B) single-phase thin film can be obtained by depositing a vanadium oxide thin film on LAO and SRO buffer. LAO and SRO have a perovskite structure similar to that of STO, thus confirming that it plays a role of a buffer layer to support single-phase production of VO_2(B) similarly

to STO. We have analyzed the electrical properties to see if thin films of these phases can be applied to the microbolometer.

4-2.3.2. Electrical properties analysis

VO_2(B) thin films were deposited on various kinds of perovskite buffers and their electrical characteristics were analyzed. As we can see in Fig. 4-15., The VO_2(B) thin films deposited on the STO, LAO and SRO buffer layers have large TCR values and low resistivity values at the same time. All of these films are capable of being used for the microbolometer.

Though the thin film deposited on STO and the thin film deposited on LAO have similar performance, the VO_2(B) thin film deposited on SRO buffer has a lower TCR value but a lower resistivity value. That is, as we select the type of perovskite buffer, we can choose whether to concentrate on the high TCR value or on the low resistivity value, which means the control the electrical characteristics.

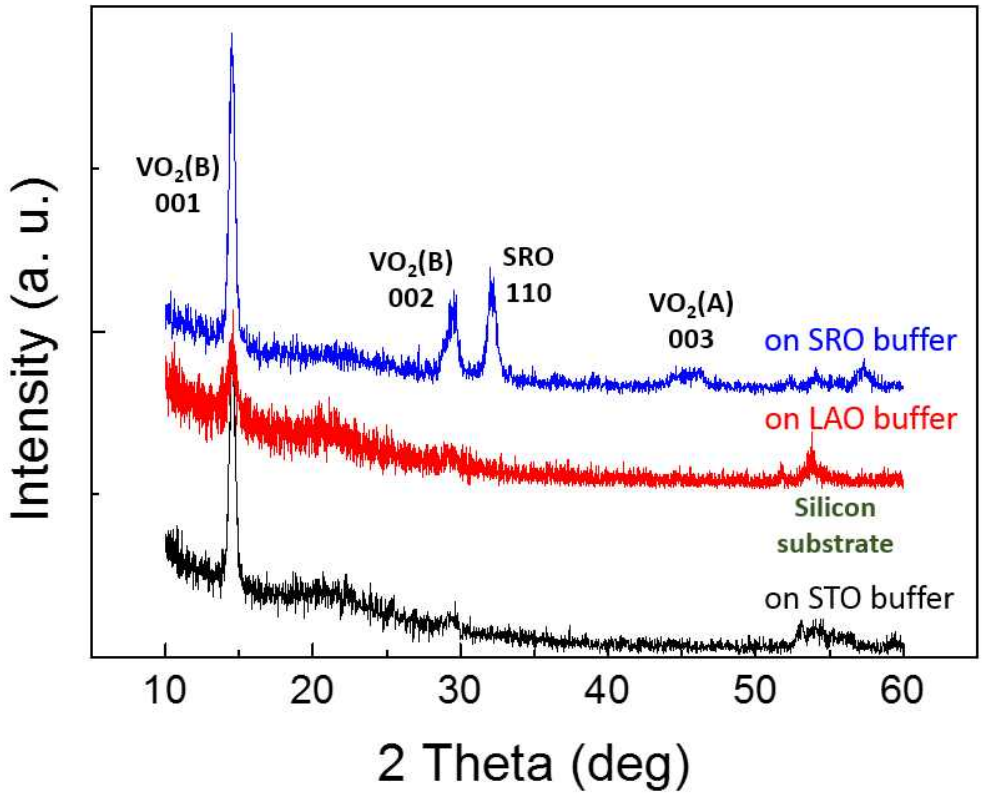

Fig. 4-14. XRD patterns of VO_2(B) thin films on STO, LAO and SRO perovskite buffer layers.

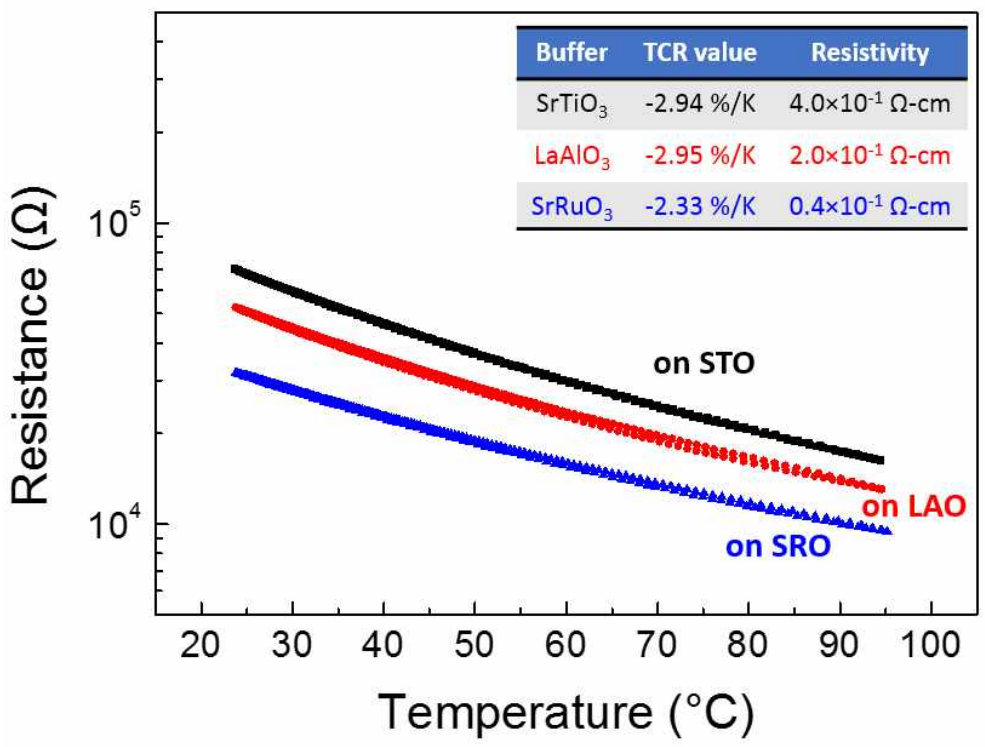

Fig. 4-15. Electrical properties of VO_2(B) thin films on STO, LAO and SRO perovskite buffer layers.

5. Summary

The vanadium oxide thin film has a higher TCR value and lower resistivity than other oxide and metal thin films, and thus is widely applied to uncooled microbolometer. However, since there are many phases of vanadium oxide, it is very hard to control the phase and it is also difficult to control electric characteristics. Therefore, there is a need for a technique which is capable of controlling the vanadium oxide thin film stably. In this study, we tried to control the phase of the vanadium oxide thin film with the high-performance that can be used for the microbolometer.

V_2O_3, VO_2, and V_2O_5 are the most commonly studied vanadium oxide phases. The V_2O_3 phase has very low resistivity, but the TCR value is too small to be applied as a microbolometer. The V_2O_5 phase has a large TCR value, but the resistivity is too large to be used for the microbolometer. Monoclinic VO_2 has low resistivity and high TCR value at the same time, however, due to the metal-insulator transition (MIT) phenomenon, hysteresis occurs in the temperature-resistance graph and stable operation is difficult in microbolometer. Therefore, it is currently being studied to use mixed phase

thin films of vanadium oxides or to mix vanadium metal and V_2O_5 phase into a sandwich structure. However, these methods have a problem of poor reproducibility. Also, there can be a problem of oxidation when the vanadium metal layer is used.

Therefore, in order to secure the stability of the TCR material used in the microbolometer, it is necessary to use different methods or types for thin films. In this study, VO_2(B) phase thin film, which has not been studied much previously, was fabricated and its electrical characteristics were analyzed. The VO_2(B) phase showed suitable electrical properties for the microbolometer, however, the reproducibility of the thin film was also the problem like other kinds of vanadium oxides.

In order to solve this problem, a buffer layer was used. Heteroepitaxial deposition of VO_2(B) on a $SrTiO_3$ (STO) single crystal substrate with a perovskite structure has been reported. Moreover, since STO is easy to make and STO is a good insulator, we used STO material as a buffer layer. As expected, the STO served as a good buffer layer to assist in the single-phase production of VO_2(B), and the VO_2(B) phase thin film on the STO had a high TCR value and a low resistivity value simultaneously. The

reproducibility problem was solved by pre-deposition of STO buffer. VO_2(B) thin film showed no change in performance even after heating and cooling more than 10 times.

In addition to STO, $LaAlO_3$ (LAO) and $SrRuO_3$ (SRO) materials which have the same perovskite structure were also used as buffer layers. When vanadium oxide was deposited on the STO, LAO, and SRO buffers, a single phase of VO_2(B) was obtained. The electrical properties of VO_2(B) deposited on STO and LAO were similar. VO_2 (A) deposited on SRO, however, the TCR value was slightly lower and the resistivity was lower than VO_2(B) on STO or LAO. In other words, depending on which perovskite buffer is selected, TCR value or resistivity value could be further controlled.

This result paves the way not only for the high-performance microbolometer but also for the phase control of oxide thin films with proper buffer layers.

6. References

1. A. G. Unil Perera, “BOLOMETERS”, Intech (2012).

2. Torrence M. Walcott, “BOLOMETERS: Theory, Types and Applications”, Nova Science Publishers (2011).

3. Yao O. Jin et al., Optical Engineering 54, 037101 (2015).

4. Akio Tanaka et al., Proc. Of SPIE, 3061, p198-210 (1997).

5. Frank Niklaus et al., Proc. Of SPIE, 6836, 68360D (2007).

6. Youn-Bae Kang, J. of the Eur. Ceram. Soc. 32, 3187-3198 (2012).

7. A. Rogalski, Prog. in Quantum. Elec., 27, 59 (2003).

8. P. W. Kruse, “Uncooled Thermal Imaging – Arrays, Systems and Applications,”SPIE, (2001).

9. A. Rogalski, Infrared Phys. Technol., 43, 187 (2002).

10. O. Nesher et al., Proc of SPIE, 7298, 72983K (2009).

11. R. Hornsey et al., IEEE Trans. on Electron. Devices. 47, 12 (2000).

12. Hong Zhu et al., Sens. and Actuator A: Phys., 110, 371-377 (2003).

13. C. C. Chang et al., Sens. and Actuators A: Phys., 65, 171-174 (1998).

14. R. A. Wood, Semiconductors and Semimetals, 47, 43 (1997).

15. W. Radford et al., Proc. SPIE 2746, 82 (1996).

16. Eric Mottin et al., Proc. SPIE 4369, 250-257 (2001).

17. M. Garcia et al, J. of Non-Cryst. Solids, 338-340, 744-748 (2004).

18. D. S. Kim et al., Proc of SPIE, 7660, 76601B (2010).

19. Y. S. Lee et al., Proc of SPIE, 8012, 80121P (2011).

20. Nicholas Fieldhouse et al., J. Phys. D: Appl. Phys., 42, 055408 (2009).

21. E. E. Chain, J. Vac. Sci. Technol. A, 4, 432 (1986).

22. E. E. Chain, J. Vac. Sci. Technol. A, 5, 1836 (1987).

23. S. B. Wang et al., Vacuum, 75, 85 (2004).

24. B. D. Gauntt et al, Proc of SPIE, 8012, 80123T (2011)

25. Y. Y. Su et al., Appl. Surf. Sci., 357, 887-891 (2015).

26. P. Deepak Raj et al., J Mater Sci: Mater Electron, 27, 7494-7500 (2016).

27. C. V. Ramana et al., Thin Solid Films, 305, 219 (1997).

28. R. T. Rajendra Kumar et al., Sens. and Actuators A 107, 62-67 (2003).

29. A. D. Rata et al., Surface Sci., 532, 341 (2003).

30. L. A. L. de Almeida et al., Appl. Phys. Lett., 85, 16 (2004).

31. N. Emond et al., Appl. Phys. Lett., 107, 143507 (2015).

32. Z. Ding et al., RSC Adv., 7, 29496 (2017).

33. A. Srivastava et al., APL Mater, 3, 026101 (2015).

34. S. Lee et al., Sci. Reports, 6, 19621 (2016).

국문 초록

야간에 물체를 감지 할 수 있는 적외선 감지 기술에 대한 연구는 자율 차량, 의료 기기 등 현대 사회의 다양한 분야에 적용될 수 있다. 적외선 센서에는 크게 광자 검출기 와 열 감지 센서의 두 종류가 있다. 광자 감지형 검출기는 비교적 높은 검출 성능을 갖는다. 그러나, 이것은 부피가 큰 극저온 냉각 장치를 필요로 하기 때문에 고가이며 이동도가 낮다. 한편, 열 감지형 검출기는 성능이 비교적 낮지만, 광자 검출 형 디바이스보다 저렴하고 이동도가 높다. 열 감지 형 소자 중 고성능을 지닌 마이크로 볼로미터가 주목 받고 있으며, 볼로미터에 사용하기 위해 많은 재료가 연구되고 있다. 마이크로 볼로미터에서 가장 중요한 부분은 열에 반응하는 열 감지 층이며 열 감지 층의 재료의 후보로 다양한 재료가 연구되고 있다. 일반적으로 산화 바나듐과 비정질 실리콘이 열 감지 소재로 연구되고 있다.

산화 바나듐은 마이크로 볼로미터 물질로서 비정질 실리콘보다 많은 장점을 가지고 있다. 따라서 바나듐 산화물 박막을 이용한 적외선 감지 카메라가 등장하고 있다. 그러나, 산화 바나듐이 광범위하게 연구되고 있지만, 여전히 마이크로 볼로미터 장치의 안정성 또는 작동 온도 범위와 같은 문제점이 있다. 먼저, 바나듐 산화물은 다양한 상을 가지고 있으므로 재현성있게 박막을 제조하는 것이 어렵다. 또한 널리 알려진 바나듐 산화물의 상 중 하나인 단사정계 VO_2 (VO_2(M)) 상을 함유 한

박막의 볼로미터 동작 온도 범위는 약 68℃에서의 상변화로 인해 제한된다.

본 연구에서는 마이크로 볼로미터에서 안정적으로, 특히 고온에서 사용할 수 있도록 재현성있는 산화 바나듐 박막을 제작하였다. VO_2(M) 상을 함유 한 박막은 상 변화에 따른 열적 이력현상으로 인해 작동 온도 범위가 제한된다. 따라서 본 연구에서는 스퍼터링을 이용하여 VO_2(M)가 포함되지 않은 단일상 VO_2(B) 박막을 제작 하였다. 본 연구에서는 페로브스카이트 버퍼층이 단일상 VO_2(B) 박막의 제조에 효과적이며 다양한 페로브스카이트 버퍼를 사용하여 안정한 단일상 VO_2(B) 박막을 제작할 수 있다는 것을 발견했다. 또한 VO_2(B) 박막의 전기적 특성을 분석한 결과 마이크로볼로미터에 적용할 수 있을 만큼의 높은 TCR 과 낮은 비저항값을 갖는 것을 확인하였다. 게다가, 버퍼층의 유형에 따라서 바나듐 산화물의 상 및 박막의 전기적 특성을 제어 할 수 있었다.

키워드: 마이크로 볼로미터, 산화 바나듐, 스퍼터링, 박막 제작
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