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Terahertz and Metal-insulator Transition Properties of VO_2 Film Grown on Sapphire Substrate with MBE

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Abstract: High quality stoichiometric VO_2 films were grown on single crystal sapphire substrates by molecular beam epitaxy (MBE), the film thicknesses were precisely controlled on the nanoscale ranging from 15 nm to 60 nm. For the optimized sample, a distinct reversible metal-insulator transition (MIT) with abrupt resistance change more than four orders of magnitude was observed, which was comparable to the ever reported result for high quality single crystal VO_2. Especially, the optical properties in the terahertz (THz) frequency range were characterized with THz time-domain spectroscopy (THz-TDs) measurements for samples with various thicknesses, and the results indicate that the THz properties of VO_2 film was significantly affected by the thickness. Therefore, the thickness should to be precisely controlled to obtain reproducible and reliable performance. The THz devices based on VO_2 film may benefit significantly from these achievements.

Key words: vanadium dioxide film; terahertz time-domain spectroscopy (THz-TDs); molecular beam epitaxy (MBE); metal-insulator transition

THz radiation (0.1–10 THz, 1 THz = 10^{12} Hz) falls in between the infrared and microwave region of the electromagnetic spectrum, and it shares some properties with each of these. Many common materials and living tissues are semi-transparent and have ‘THz fingerprints’, permitting them to be imaged, identified, and analyzed. Meanwhile, the non-ionizing properties of THz radiation and the relatively low power levels used indicate that it is safer than commonly used X-ray radiation. Therefore, the THz region is of particular scientific importance due to its remarkable and unique characteristics[1]. While this spectral region has been historically difficult because of low power sources and inefficient detectors, technological advances in recent decades have allowed new applications. Especially, the recently demonstration of THz field induced insulator to metal transition (IMT) in vanadium dioxide (VO_2) metamaterial has greatly intensified the interest in THz properties of VO_2 film[2]. VO_2 have been proved as a unique and outstanding archetypal correlated oxide materials, because it undergoes an abrupt reversible phase transition at a critical temperature (T_c) of 341 K, known as metal-to-insulator transition (MIT) or semiconductor-to-metal (SMT) first-order transition[3-5]. At temperatures below T_c, VO_2 is in semiconducting state with monoclinic structure, in which the V atoms pair open an energy gap of 0.6 eV. At temperatures above T_c, VO_2 is in metallic state with tetragonal structure, in which overlap between the Fermi level and the V3d band eliminates the band gap[6-8]. This allotropic transition in crystal symmetry and electronic band structure, which can be triggered by some specific external stimuli such as temperature or voltage, is usually accompanied by an abrupt and ultra-fast change in its resistance and optical transmittance especially in infrared region. While the structure-driven MIT properties of VO_2 have inspired a wide range of applications for energy, sensors, and optoelectronics[3-8]. There has been very little research on the THz properties of VO_2 film. Since the THz frequency falls below the optical phonon resonances of VO_2, the optical properties of the insulating and metallic phases of VO_2 are expected to be significantly different at THz frequency[9]. More insight into the THz properties of VO_2 films and its modulation method are absolutely desirable for the utilization of VO_2 films in this new field.

In our recent report, high quality VO_2 films with precisely controlled thickness were grown on sapphire substrates by MBE technique, the results indicated that the MIT transition behaviors can be modulated by the variation of film thickness through internal stress relaxation,

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and the small distortion of the V-V chain length along the c axis triggered by internal stresses was supposed to be responsible for the occurrence[8]. For the thin film samples grown on substrate, the subtle variation in film thickness would generally result in a dramatic change in internal stress in the as-grown film. Recently, there has been a growing interest in modulating film properties through internal stress since it predicted inherent advantages for its practical applications[9-11]. THz-TDs has been demonstrated to be a powerful technique for semiconductor materials due to the features of non-contact, coherent and transient. Some valuable physical and chemical information can be identified through in-depth analysis of the optical parameters of the THz-TDs[12-13]. Unfortunately, less attention has been paid to the thickness dependent THz properties of VO_2 films. Understanding such effects is essential to achieve reliable THz device performance.

In this study, high quality VO_2 films with precisely controlled thickness were grown on sapphire substrates by MBE technique. For the optimized sample, a distinct reversible MIT with abrupt resistance change more than four orders of magnitude was observed. Especially, the optical properties in the THz frequency range were characterized with THz-TDs measurements, and the results indicated the THz properties of VO_2 film was significantly affected by the thickness. The underlying reasons for the observation were also tentatively discussed. It was believed that the experimental results obtained here will provide valuable information for the future design and development of high-performance VO_2 based THz devices.

1 Experimental

VO_2 films were grown on single crystal c-axis (0001) sapphire substrates by a radio frequency (RF)-plasma assisted MBE with a base pressure better than 3×10^{-9} Torr. A stander RF plasma source was used to provide reactive oxygen radicals with 6N O_2 as gas source controlled by a mass flow controller with a precision of 0.1 sccm (stander cubic centimeter per minute). The pure metallic vanadium powder was evaporated by a customized e-beam evaporator system where the vanadium flux was controlled by a crystal oscillator (MAXTEKTM-350). For high quality pure phase VO_2 films deposition, all the parameters, such as the substrate temperature, the chamber pressure, and the metallic vanadium evaporation rate as well as the O_2 flux rate, were kept at the optimized values according to our recent reports[8,14-15]. To investigate the influence of film thickness on THz properties, four samples with precisely controlled thickness were grown by adjusting the deposition duration time while keeping other parameters constant. The growth time was varied from 10 min to 40 min with the time interval of 10 min, and the corresponding film thicknesses were determined to be around 15, 30, 45 and 60 nm, respectively. For convenience, the samples were labeled as S1 to S4 with increasing growth time.

The crystalline quality was evaluated by X-ray diffraction (XRD) in regular θ-2θ scanning mode with LabXRD-6000 (CuKa1: λ = 0.154056 nm) at room temperature. The diffraction photons were collected by the diffractometer from 10° to 80° with a 0.02° step size. The surface morphology was examined by MI PicoScan 2500 atomic force microscope (AFM) with tapping mode at room temperature. The temperature-driven phase transition behavior was investigated by measuring the electrical resistivity in the heating and cooling process by Keithley 2635A source meter using the conventional 2-probe method[8]. To evaluate the suitability of as-grown VO_2 films for THz application, the THz-TDs measurement was carried out by measuring the THz transmission at normal incidence in the 0–4.0 THz range with the system illustrated in Fig.1. As shown in Fig.1, the system was consisted of a femtosecond laser, a THz emitter, a THz wave detector and a time delay system. The laser beam of 40 fs, 800 nm at 80 MHz from a Ti:sapphire oscillator (KMLabs Inc.) was split into two arms. One arm was used to generate the THz pulse by exciting a biased photoconductive antenna, while the other one was used as gate for the photoconductive detector[16]. The generated THz pulse was focused on the sample position by a polymethylpentene (TPX) lens (focal length f = 5 cm). When the sample was excited, the THz pulse was detected. The transmitted THz radiation was then focused onto the photoconductive detector by another TPX lens of same focal length. Therefore, the THz-TDs was formed based on the difference of the detected signal, some parameters of the sample such as the complex refractive index, the extinction coefficient, and the dispersion characteristics would be obtained. In order to minimize the THz absorption by the air humidity, all THz measurements were carried out under purged conditions in the super- clean laboratory.

2 Results and discussion

2.1 Structural and morphological analysis

Figure 2 shows the typical θ-2θ XRD patterns of the high quality VO_2 films grown on sapphire substrate by MBE under optimized conditions. For comparison, the XRD patterns of the c-axis sapphire substrate were also presented in the bottom of Fig. 2. As can be seen from Fig. 2, in addition to the dominant diffraction peaks from sapphire substrate corresponding to Al_2O_3 (0006), the well-defined sharp XRD pattern narrow width at half

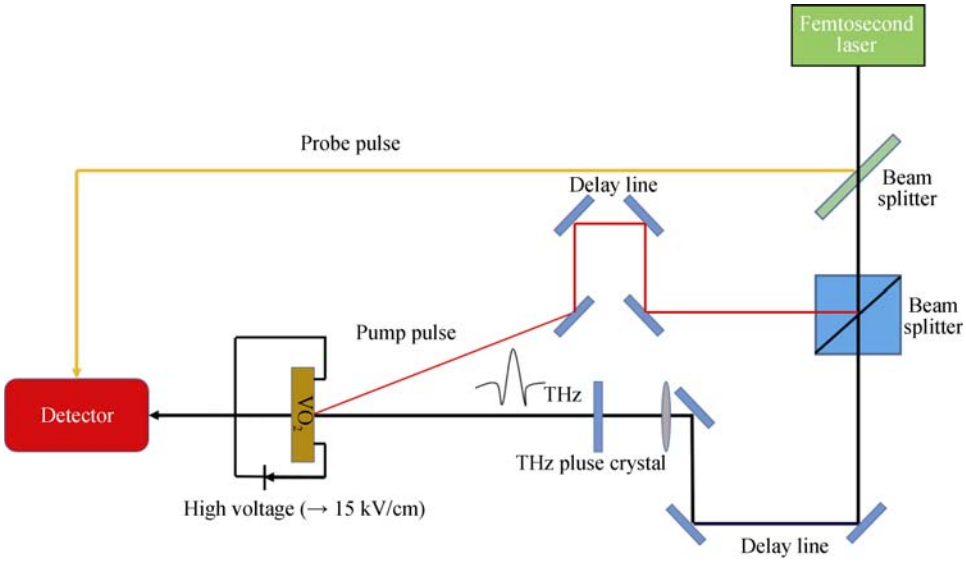

Fig. 1 Schematic diagram of THz-TDs measurement system

maximum (FWHM) was observed at 39.96°, which can be indexed to the monoclinic VO_2 (020). No additional peaks due to other vanadium oxide phases are observed from the patterns. The broad peaks appear from sapphire substrate just because of its extremely high intensity, which was more than 100 times stronger than that from VO_2 (020). Therefore, the XRD results demonstrat that the high quality pure monoclinic phase VO_2 films with (020) preferred orientation have been obtained on sapphire substrate by MBE.

Figure 3 shows the surface morphology of the VO_2 films with preciously controlled thickness ranging from 15 nm to 60 nm characterized by AFM images, and the scanning area was 4 μm×4 μm. From these images, the VO_2 films exhibit a rather smooth surface with the root mean square (RMS) on the nanometer scale, and the RMS for sample S1 to S4 was determined to be 3.6, 1.9, 8.7 and 1.8 nm, respectively. In addition, the samples were composed of uniform and dense grains with spherical granular crystallites as long as the thickness is over 30 nm (shown inFig. 3(b) to (d)). While for the sample S1, we can see fuzzy

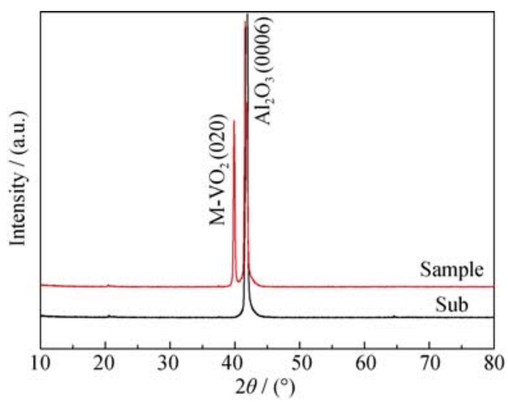

Fig. 2 Typical XRD patterns of VO_2 films grown on sapphire substrates by MBE

surface morphology with irregular grains and nanoscale crack line (Fig. 3(a)). In that case, we supposed that this nanoscale crack would be attributed to the presence of tensile stress within VO_2 film due to the mismatch in thermal expansion coefficient between VO_2 and sapphire substrate, as confirmed Raman spectra in our previous studies[8].

2.2 Phase transition characterization

A study on the performance of MIT properties was made through measuring resistance in the process of heating and cooling. The thermal hysteresis loops of sheet resistance was recorded as a function of temperature, and the result for the optimized sample was shown in Fig. 4. The smooth transition profile revealed a distinct MIT phase transition behavior in both heating and cooling process, showing the evidence of first-order phase transition. The inset of Fig. 4 shows the differential $d(R)/d(T)$ *versus* temperature curves for heating and cooling branches to determine the phase transition critical temperature (T_c), which was defined as peak temperature for both heating and cooling runs. When the temperature decreased from high temperature, the resistance-temperature curve was not exactly coincident with that in increasing temperature. Nevertheless the transition is found to be reversible, and it takes a very short time to accomplish this transition[17]. The MIT properties can be characterized by the following parameters: T_c (the MIT critical temperature), the hysteresis width (ΔH, defined as the difference of T_c for heating and cooling branch), the transition sharpness (ΔT, characterized by the FWHM of the derivative curve of dR/dT-T plot), as well as the transition magnitude (Amplitude, defined as ratio of resistivity in insulator phase at 25℃ to that in metallic phase at 85℃

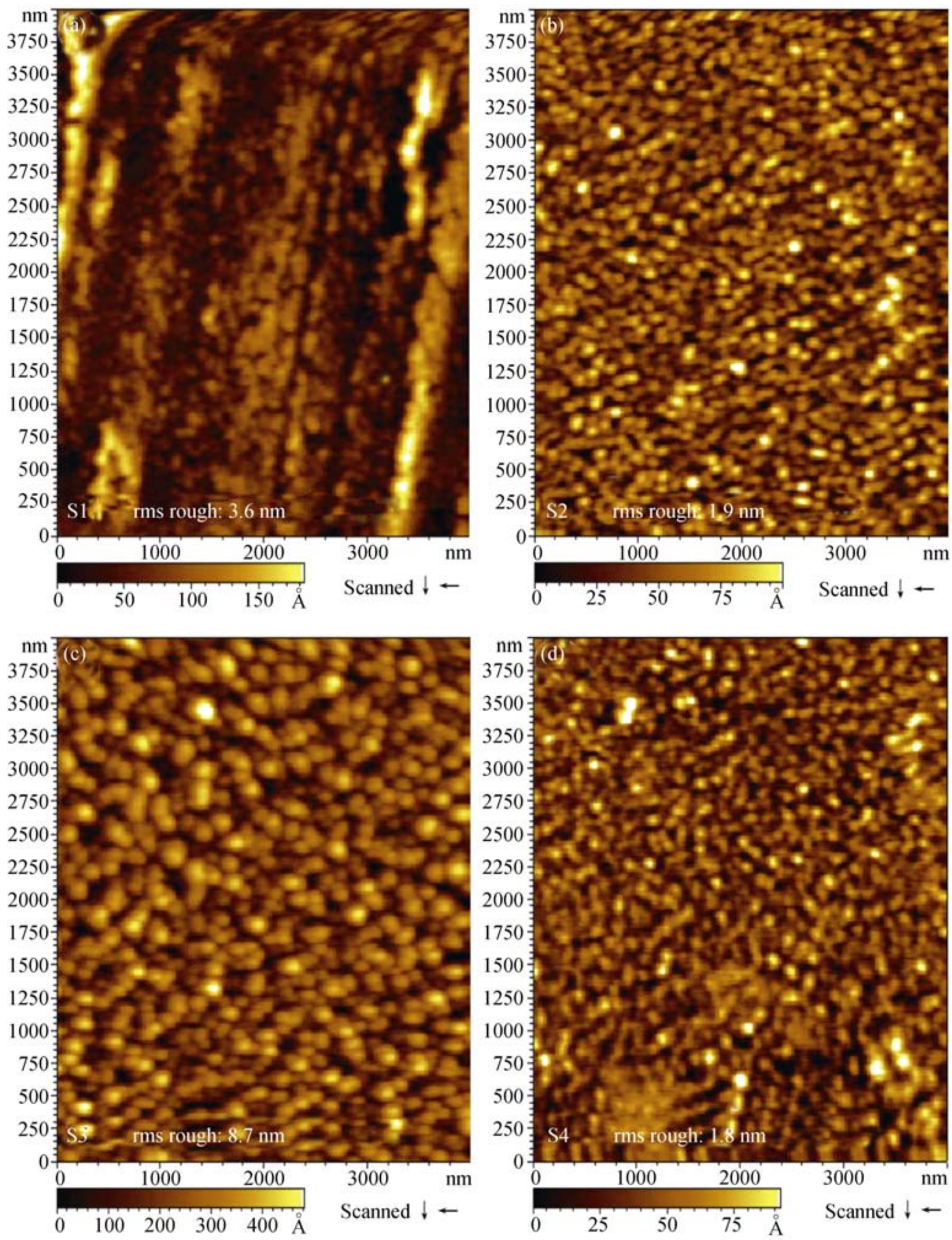

Fig. 3 AFM images with scanning area of 4 μm×4 μm for surface morphology of VO_2 films grown on sapphire substrates by MBE with various thicknesses

(a) S1; (b) S2; (c) S3; (d) S4

in the heating process). Herein, the detailed MIT parameters were summarized in Table 1. A distinct MIT phase transition behavior with the transition amplitude more than four orders of magnitude was achieved for our optimized sample, and the value of T_c (63.5℃ on average), ΔT (10.5℃ on average) and ΔH (5℃) was in reasonable agreement with the best ever reported value for high quality stoichiometric VO_2 films grown on sapphire substrate, indicating the high quality and phase purity of the current VO_2 film[10,14]. The thermal hysteresis (ΔH) might originate from the latent heat of the first order phase transition, which was closely related to the crystalline microstructure, residual stress due to the lattice and/or thermal mismatch between the film and the substrate[18]. The excellent MIT characteristic of current VO_2 films will be especially imperative for switching-type

Table 1 Detailed MIT parameters of the optimized VO_2 thin film grown by MBE

Parameters	T_c /℃	ΔH/℃	ΔT/℃	Amplitude
VO_2	66 (Heating) 61 (Cooling)	5	9 (Heating) 12 (Cooling)	1.01×10^4

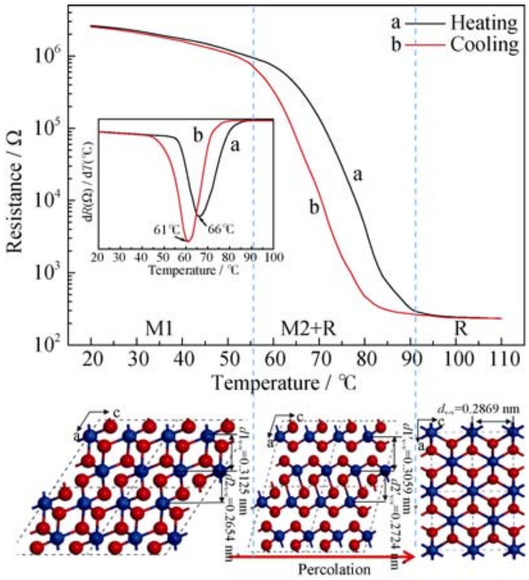

Fig. 4　Thermal hysteresis loops of sheet resistance of the optimized VO_2 sample grown on sapphire substrates by MBE

Inset shows the differential d(*R*)/d(*T*) *versus* temperature curves for heating and cooling branches to determine the phase transition T_c from the Gaussian fit of the peaks. The lower plan exhibits the schematic diagram of microstructure evolution with the infinite linear V–V chains in different temperature range

applications to acquire larger response and higher efficiency. In essence, the temperature-driven MIT process was strongly dominated by the V–V chains in different temperature range, the microstructure evolution with the infinite linear V–V chains concomitant with the MIT process was illustrated in the lower plan of Fig. 4. For low temperature insulator phase with monoclinic structure (M_1, Monoclinic, P21/c), the lattice constant along the *c*-axis of equal atomic V-V distance was $d1_{\text{v-v}}$=0.3125 nm, and $d2_{\text{v-v}}$=0.2654 nm, while for high temperature metal phase with the tetragonal rutile structure(R, Rutile, P42/mnm), the lattice constant along the c-axis of equal atomic V-V distance was $d_{\text{v-v}}$=0.2869 nm, and between them is another monoclinic structure of VO_2, M_2 phase[19]. As VO_2 film changed from low temperature to high temperature, it was found that the V-V distance changed slowly, passing a transition zone: M_2+R, lattice constant $d1'_{\text{v-v}}$ =0.3059 nm, and $d2'_{\text{v-v}}$ =0.2724 nm, which is closed to the tetragonal rutile structure's lattice constant. In the M_2+R structure, only half of the vanadium atoms dimerized, while the other half form zigzag chains.

2.3　Optical properties in the THz range

The optical properties in the THz frequency range were investigated by measuring the THz-TDs at room temperature. Fig. 5(a) shows the THz-TDs for the VO_2 films as the thickness increasing from 15 nm to 60 nm. The spectra shapes of THz-TDs were similar for all the samples, suggesting high transmittance in THz range. It can be noticed from Fig. 5(a) that the maximum THz amplitudes were observed at the time range of 7 ps to 9 ps for all samples, indicating that the thickness had little effect on the refractive index in THz range. Moreover, the narrow FWHM of THz amplitudes peak suggested that the VO_2 thin films grown on a sapphire substrate has better chromatic dispersion properties in THz range[20]. Fig. 5(b) shows the normalized THz transmission amplitudes as a function of VO_2 film thickness. As the increasing of VO_2 film thickness from 15 nm, the THz amplitude increased initially, and reached the highest value for sample S3 with 45 nm thickness, further increasing thickness lead to the decrease of THz transmission amplitude. Since the maximum value of THz transmission amplitude reflects the sample's extinction coefficient, the result suggested that the sample S3 (the blue one in Fig. 5(a)) have a better extinction property than others in THz wave, which demonstrated that the sample S3 has high quality with well crystallinity at room temperature[12-13]. This was in well accordance with above AFM analysis where the maximum grain size was achieved for sample S3. The similar behavior of the thicknesses dependent THz transmission has been observed by Walther and coauthors, the same mechanism should be valid for the current case[21]. Taken together, the results indicated that the optical properties

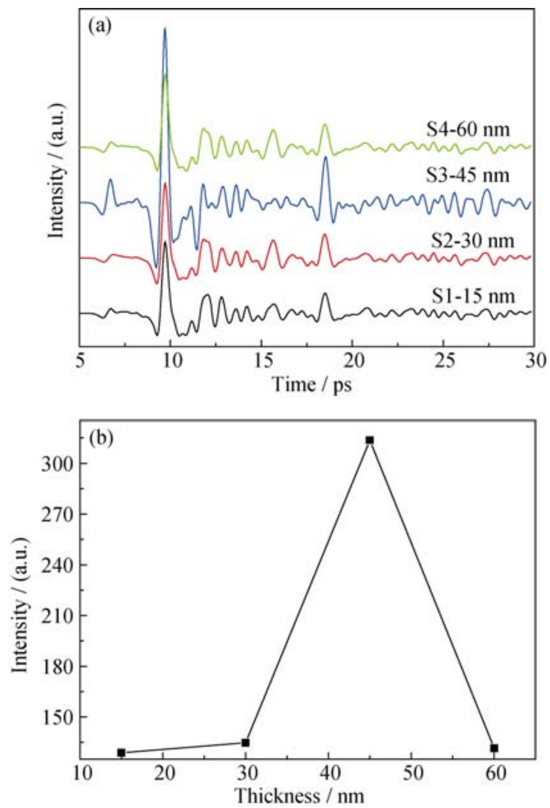

Fig. 5　(a) The time-domain THz transmission of VO_2 films grown on sapphire substrates by MBE with preciously controlled thickness ranging from 15 nm to 60 nm and (b) the THz transmitted amplitude as a function of film thickness

of VO_2 film was significantly affected by the thickness in

THz range. Hence, the thickness must be precisely controlled to obtain reproducible and reliable performance THz devices based on VO_2. More detailed discussion on the temperature-dependent THz properties will be presented in a separate publication.

3 Conclusion

High quality VO_2 films with precisely controlled thickness were grown on sapphire substrates by MBE technique. For the optimized sample, a distinct reversible MIT with abrupt resistance change up to nearly four orders of magnitude was observed. Especially, the optical properties in the THz frequency range were characterized with THz transmission measurements, and the results indicated the optical properties of VO_2 film was significantly affected by the thickness in THz range. The current achievements will facilitate the realization of VO_2 based devices for specific THz applications.

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MBE 技术蓝宝石衬底上生长 VO_2 薄膜及其太赫兹和金属–绝缘体相变特性研究

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摘 要: 采用分子束外延(MBE)技术在单晶蓝宝石衬底上生长了高质量化学计量比二氧化钒(VO_2)薄膜, 通过该技术实现薄膜厚度 15~60 nm 精确控制。对于优化条件下 VO_2 薄膜, 实现了电阻率变化超过 4 个数量级的优异金属–绝缘体相变, 近似于之前报道高质量单晶 VO_2 相变特性。特别是通过太赫兹时域光谱分析了不同厚度的 VO_2 薄膜在太赫兹波段的光学特性。结果表明: VO_2 薄膜的厚度对其在太赫兹波段的光学特性有很大影响。因此, 为了获得更优的可靠性和重复性能, VO_2 薄膜的厚度必须得到精确控制。本研究结果对于下一步 VO_2 基太赫兹器件研究具有重要意义。

关 键 词: 二氧化钒薄膜; 太赫兹时域光谱; 分子束外延; 金属–绝缘体相变

中图分类号: TB34　　**文献标识码:** A